Studies of organonitrogen groups in metal carbonyl systems

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STUDIES OF ORGANONITROGEN GROUPS IN METAL CARBONYL SYSTEMS

by

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September 1969 and August 1970. It has not been submitted for any other degree and is the original work of the author except where acknowledge by reference.

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J.N. Pinkney
Durham 1970.

SUMMARY

The nature of the product formed in the reaction of methyleneamine derivatives with transition metal complexes depends upon the nature of the methyleneamino-substituents. Complexes of the type π-$C_5H_5M(CO)_2N{=}CR_2$, $[\pi$-$C_5H_5M(CO)N{=}CR_2]_2$ and π-$C_5H_5M(CO)_2(R_2CNCR_2)$ are formed with phenyl substituents but the bulkiness of t-butyl groups leads to only complexes of the first type. The complexes formed using a mixed phenyl-t-butyl derivative should not be restricted solely by steric factors to complexes of the first type. The study is concerned with the syntheses of carbonyl complexes of molybdenum and tungsten containing the phenyl-t-butylmethyleneamino-ligand, and the influence of the substituent groups on the nature and reactions of the complexes produced.

The dicarbonyl complexes π-$C_5H_5M(CO)_2N{=}CPhBu^t$ are produced by a metathetical reaction between π-$C_5H_5M(CO)_3Cl$ and (i) $PhBu^tC{=}NLi$ [M = Mo,W] (ii) $PhBu^tC{=}NSiMe_3$ [M = W]. The complexes show no tendency to form dinuclear complexes and closely resemble the corresponding di-t-butylmethyleneamino-complexes. Reaction with iodine produces the monocarbonyl complexes π-$C_5H_5M(CO)I_2(N{=}CPhBu^t)$; the monocarbonyl molybdenum complex shows ^1H n.m.r. spectral changes with temperature which indicate structural changes in the complex and various possible explanations of these changes are discussed. Reaction of the dicarbonyl molybdenum complex with triphenylphosphine produces the monocarbonyl complex π-$C_5H_5Mo(CO)Ph_3P(N{=}CPhBu^t)$ by substitution of CO by Ph_3P, this reaction being unique in the dicarbonyl methyleneamino-complexes so far studied. The corresponding reaction is not observed with the dicarbonyl tungsten complex.

Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $PhBu^tC{=}NSiMe_3$ results in hydrogen abstraction, possibly from the solvent, and the formation of the dicarbonyl complex π-$C_5H_5Mo(CO)_2(HN{=}CPhBu^t)Cl$, containing the methyleneamino-group as a two electron donor.

Exploratory investigations into the formation of carbonyl complexes of molybdenum and tungsten containing the di-(trifluoromethyl) methyleneamino-group are also described. Some mass spectroscopic evidence for the formation of such complexes is discussed but the reaction conditions so far employed do not lead to isolation of pure samples of the complexes.

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CHAPTER I

INTRODUCTION

1. General Considerations

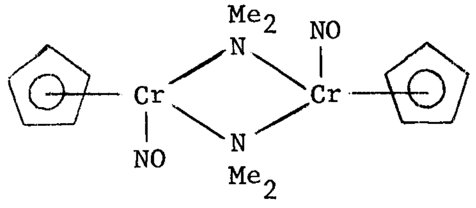
The ability of carbon monoxide to bond to transition metals in low oxidation states relies on the simultaneous donation of the lone pair of electrons from the weakly donating carbon monoxide and back donation from non-bonding metal d-orbitals to the antibonding π-orbitals of the carbon monoxide molecule. This 'synergic' effect prevents excessive build-up of electron density on the metal and results in a metal-carbon bond order greater than one. Replacement of a carbonyl group by another ligand results in competition between the new and remaining ligands for the bonding potentialities of the metal. Thus the stability to disproportionation of the complex will depend upon the relative σ- and π-bonding capabilities of the ligands concerned.

Replacement of carbon monoxide from a binary metal carbonyl by a stronger Lewis base with a lower π-bonding capacity has the effect of increasing the electronic charge build-up on the metal and reducing the competition to dissipate the charge. Consequently the metal-carbon bonds are strengthened. Organic amines, R_3N (including ammonia), are strong Lewis bases having no π-bonding capacity, and consequently their introduction into a carbonyl complex strengthens the metal-carbonyl bonding to the remaining carbonyl groups, through the increase in $d\pi$-π^* bonding. Successive replacement of carbonyl by R_3N groups results in a corresponding increase in the M-C bond order of the remaining groups but there is invariably a stage reached when the remaining groups are unable to dissipate further charge build-up e.g.[1]

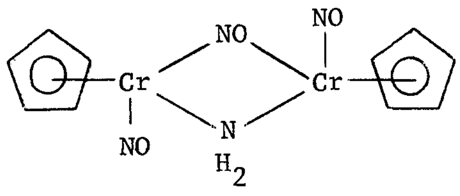
$$Cr(CO)_6 + liq.NH_3 \xrightarrow{120^o} Cr(CO)_3(NH_3)_3 + 3CO$$

When the organonitrogen ligand has a π^* electron system available for bonding, the charge build-up at the metal is somewhat reduced. Consequently complexes of the type $M(CO)_3L_3$ readily form, and further carbonyl groups may be replaced before the limit for replacement is achieved.[2]

The bonding of the amido-group in a transition metal complex is more complex because of the availability of two nitrogen orbitals for bonding. If nitrogen is sp^2 hybridised and the lone pair accommodated in a p-orbital, then the amido-group may act as a three electron donor to one metal through σ- and p_π-d_π-bonding. If the nitrogen orbitals correspond to sp^3 hybridisation, then only σ-bonding to the metal will be possible. The lone pair will be directed away from the metal and available for bonding to a second metal atom. Thus the amido-group may act as a bridge between two metals, and act again as a three electron donor. The dialkylamido-compounds $(R_2N)_nM$ of the Ti (n = 4) and V (n = 5) group metals have been investigated and spectroscopic evidence indicates a considerable degree of nitrogen ⟶ metal π-bonding.[3] Thus the hybridisation of the nitrogen orbitals corresponds to sp^2. Such a charge build-up on the metal is apparently only possible for transition metals with few d-electrons. The ability of the amido-group to form bridges between metal atoms is illustrated by the chromium compounds I[4] and II.[5]

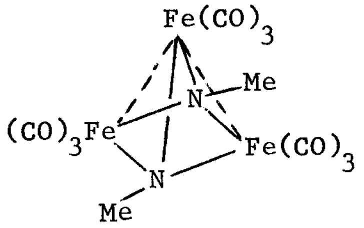


I

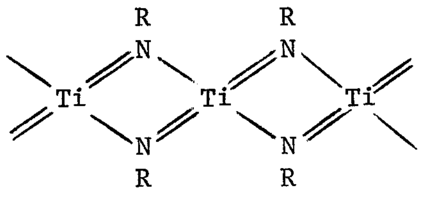


II

The RN< group has even greater bridging potential and in complex III is found to bridge three iron atoms.[6]



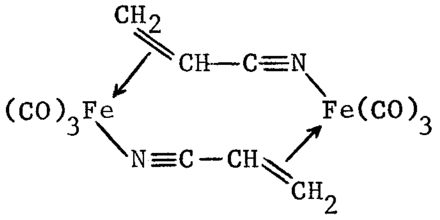
III



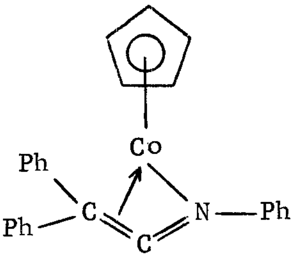
IV

Bridging between two metal atoms and using the third available orbital for additional π-bonding to the metal is also seen in a series of polymeric titanium complexes IV.[7]

In none of the examples so far cited has the nitrogen containing ligand been able to reduce electron density on the metal atom. Interest has therefore recently focused on unsaturated organonitrogen ligands where the possibility of a 'synergic' effect similar to that operating in metal carbonyls might be applicable. The possibility also occurs of such ligands σ-bonding to the metal through the π-system as well as, or in place of, σ-donation from the nitrogen. For acrylonitrile the various types of bonding are possible and with the chromium group of metal carbonyls up to three carbonyl groups have been replaced.[8] For comparable complexes with acetonitrile[8] the bonding is via the nitrogen lone pair for all complexes, and the same bonding mode is adopted for $M(CO)_{6-n}(CH_2{=}CH\text{-}CN)_n$ (n = 1,2). However for the complex $M(CO)_3(CH_2{=}CH\text{-}CN)_3$, bonding is via the olefinic π-system. The ability of both types of bonding to occur simultaneously occurs in the compound V where acrylonitrile bridges two iron atoms.[9] Ketenimines $R_2C{=}C{=}NR$ bond in a similar way through nitrogen and the olefinic π-system in VI.[10]

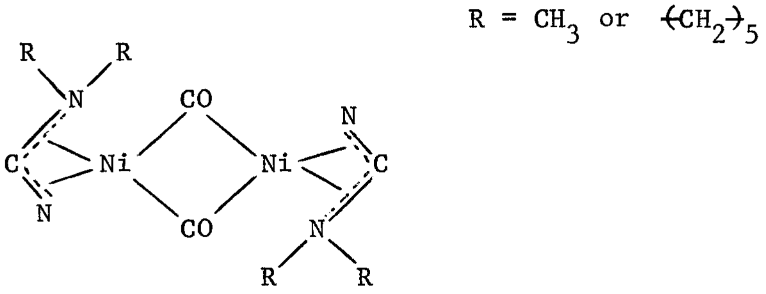


V



VI

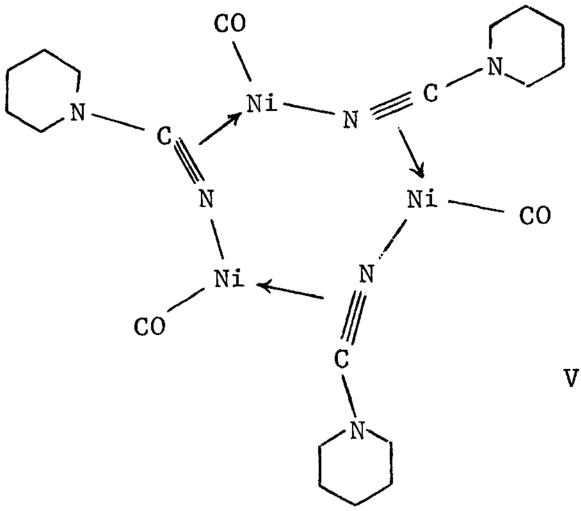
Dialkylcyanamides, R_2NCN, form a series of complexes by replacement of carbonyl groups from $Cr(CO)_6$ and $Mo(CO)_6$ of the type $(R_2NCN)_nM(CO)_{6-n}$ (n = 1,2,3) in which σ-bonding to the metal from the lone pair on the nitrile was inferred from i.r. data.[11] Tetracarbonyl nickel gave a series of dinuclear complexes $[(R_2NCN)Ni(CO)]_2$. In a preliminary note the structure assigned involved π-bonding from a delocalised N-C-N structure VII.[12]



R = CH_3 or $-(CH_2)_5-$

VII

Later work indicated a localised system was present involving two σ M-N bonds.[13] However a crystal structure of the piperidine-N-carbonitrile complex revealed that neither was correct and that the structure contained trimers of nickel atoms σ-bonded to CO and cyanonitrogen groups, the trimer VIII being formed from the monomer using the nitrile π-bonds.[14]



VIII

2. The methyleneamino-group as a ligand in metal carbonyl systems

The methyleneamino-group has a number of potential ways of bonding to transition metals and is thus a very versatile ligand. As the neutral ligand, $R_2C{=}NH$, σ-bonding to the metal occurs via the nitrogen lone pair, and as the nitrogen is part of an unsaturated system, back-bonding from filled metal d-orbitals to the antibonding π-orbitals of the $>C{=}N$ bond is also possible. The most likely geometrical arrangement of the relevant atoms is shown in Fig.I.1(a).

As an anionic ligand further bonding modes are possible. In one extreme the bonding to the metal will involve an sp^2 hybrid orbital of nitrogen, and the lone pair will occupy a similar hybrid orbital. The lone pair may still contribute to L-M π-bonding in such an arrangement - Fig.I.1(b). Ebsworth[15] calculated overlap integrals for nitrogen bonded to silicon and concluded that substantial (p-d)π-bonding from a nitrogen lone pair to vacant silicon d-orbitals is possible in a non-linear system. Similar multiple bonding may occur for non-linear C-N-M skeletons, where M is a transition metal, but there is the additional possibility that the lone pair

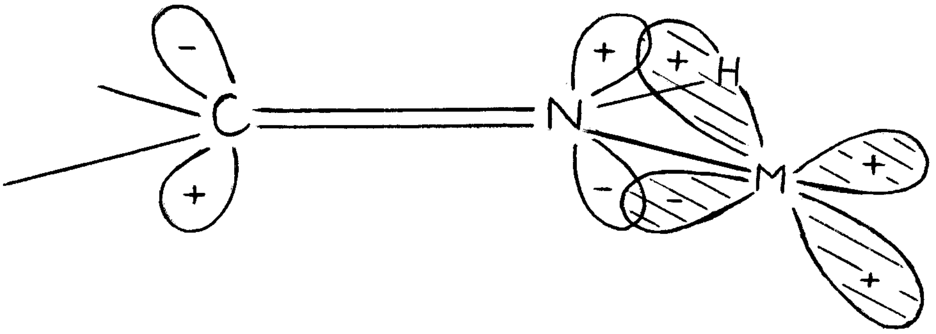


Fig.I.1(a) dπ-π* bonding involving a neutral methyleneamino-ligand

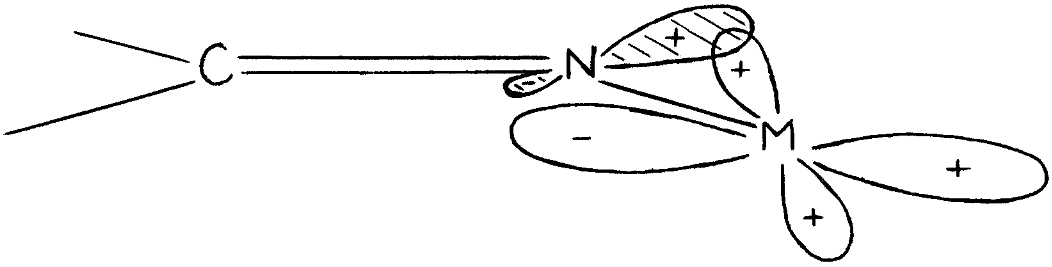


Fig.I.1(b) π-bonding involving a bent C=N-M skeleton

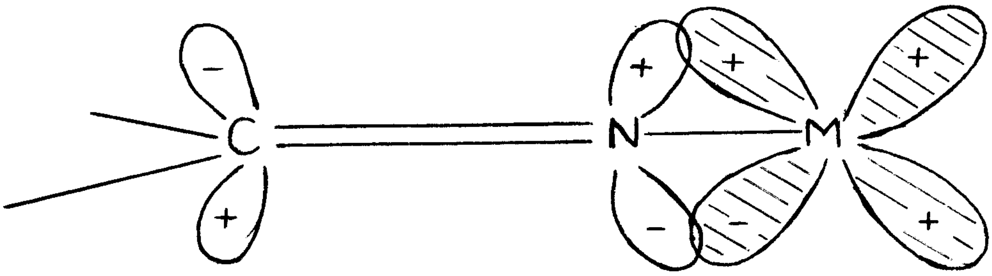


Fig.I.2(a) dπ-π* bonding involving linear C=N-M skeleton

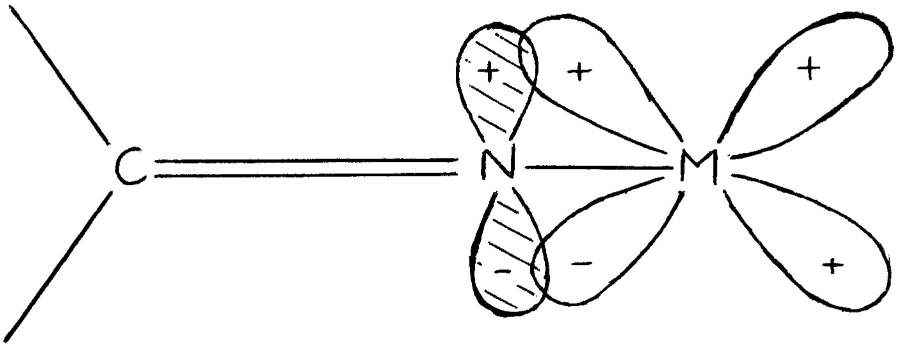


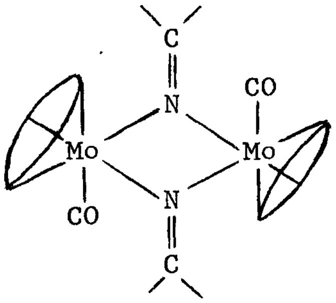
Fig.I.2(b) pπ-dπ bonding involving a linear C=N-M skeleton will donate to a second metal atom. Thus in a ligand bridged dinuclear complex, overlap of the d-orbitals of both metal atoms with the π^*-orbitals of the $>$C=N bond could occur, resulting in a weakening of the $>$C=N bond which would be reflected in the vibrational frequency of the bond. In this way the bridging $>C{=}N^{\ominus}$ unit would closely resemble the bridging carbonyl unit with which it is isoelectronic.

Alternatively the C-N-M skeleton may be linear and not bent. The nitrogen atom would be sp hybridised, one hybrid orbital being used to σ-bond to the metal. A pure p-orbital would be used for the C-N π-system, and the lone pair accommodated in a p-orbital lying in the plane of the $R_2C{=}N$-group. Maximum overlap of the metal d-orbitals with both the lone pair and π^*-orbitals would then be achieved as shown in Fig.I.2. The bonding would then involve electron donation via σ- and p_π-d_π-bonding, and back donation via d_π-π^* bonding.

Finally there is the added possibility, as with all unsaturated ligands, of lateral co-ordination of the $>$C=N group to form a π-complex analogous to olefin complexes.

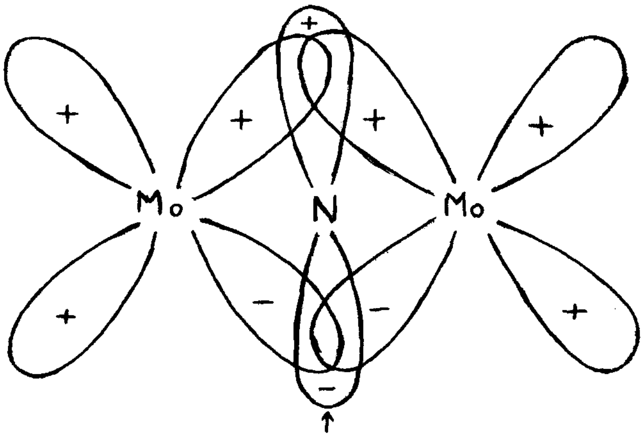
Methyleneamines are quite strong Lewis bases[16] and a number of complexes are known in which they act as neutral ligands in metal carbonyl systems e.g. $Mn(CO)_3(Ph_2C{=}NH)_2X$,[17] $Cr(CO)_5(RR'C{=}NH)$.[18] In these cases the ligand is a two electron donor. A series of complexes of molybdenum and tungsten have been obtained in these laboratories in which methyleneamino-groups act as three electron donors. Di-t-butylmethyleneamine derivatives form complexes of the type π-$C_5H_5M(CO)_2N{=}CBu^t{}_2$.[19] The relatively low frequencies of the carbonyl absorptions in the complexes and their failure to add a further neutral donor molecule such as pyridine, Ph_3P or CO even under forcing conditions are indicative of the methyleneamino-ligand acting as a three electron donor. X-ray structural data[20] on the molybdenum complex also reveal a Mo-N-C unit which is approximately linear and a short Mo-N bond distance of 1•87Å which indicates considerable multiple bonding between the metal and nitrogen. These observations are in agreement with the previous bonding considerations (Fig.I.2). The reactions of the complex are summarised in Fig.I.4. Substitution of CO could not be achieved but oxidation with iodine gave complexes of the type $\pi\text{-}C_5H_5M(CO)I_2.N{=}CBu^t{}_2$.

Reaction of $Ph_2C{=}NSiMe_3$ with $\pi\text{-}C_5H_5M(CO)_3Cl$ also gave rise to similar complexes by replacement of a carbonyl group by the diphenylmethyleneamino-group.[21] However, these complexes readily lost a further molecule of carbon monoxide with the formation of the dinuclear complexes $[\pi\text{-}C_5H_5M(CO)N{=}CPh_2]_2$ in which it is believed the methyleneamino-group acts as a bridging ligand between two metal atoms, the bridging group donating a total of three electrons. The metal atoms appear to be two electrons short of a noble gas configuration and the formation of M-M bonds is implied. The molybdenum complex showed only one strong and one weak C-O stretching absorption indicating a structure IX in which the two carbonyl groups are on opposite sides of the planar Mo_2N_2 ring and the proposed structure is based on an octahedral arrangement of groups about the metal atoms.



IX

This structure allows the d_{xy} and d_{yz} orbitals of one Mo atom to overlap with equivalent orbitals of the other metal atom. The Mo-Mo bonding molecular orbital thus formed would have π-symmetry and be bent towards the nitrogen, thus being able to overlap with >C=N π^*-orbitals in the formation of a stabilising extended π-system as in Fig.I.3.



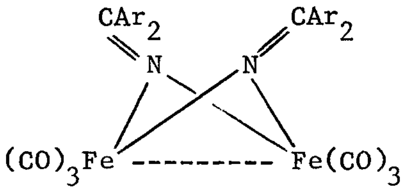
π-bonding involving one of the bridging >C=N groups

Fig.I.3

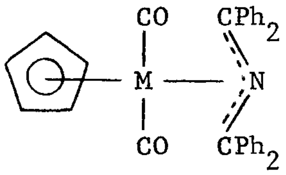
The tungsten complex shows two strong C-O stretching vibrations indicating a cis-arrangement of the carbonyl groups relative to the Mo_2N_2 ring.

An analogous complex in which bridging methyleneamino-groups are present is formed from pentacarbonyl iron and the azine Me.C_6H_4C=N-N=C.C_6H_4.Me.[22] Its crystal structure X is entirely consistent with sp^2 hybridised nitrogen, as indicated for bridging methyleneamino-ligands, and also the very short Fe-N bond length indicates substantial double bonding.

Reaction of $Ph_2C{=}NLi$ with π-$C_5H_5M(CO)_3Cl$ resulted in the formation of an entirely new type of complex [π-$C_5H_5M(CO)_2Ph_2CNCPh_2$] in which the ligand Ph_2CNCPh_2 acts as a three electron donor, and the mode of bonding to the metal is believed to involve the π-system of the pseudo-allylic group[23] as in XI.



X



XI

The reactions of diphenylmethyleneamino-complexes are summarised in Fig.I.5. Again substitution reactions could not be achieved with these complexes.

The apparent effect of the groups attached to the $>C=N$ on determining the bonding mode of the methyleneamino-ligand prompted the work described here with phenyl-t-butylmethyleneamine. The extreme bulkiness of the t-butyl groups appears to favour the linear M-N-C unit, which results in maximum overlap of metal d-orbitals with ligand π-orbitals, and hence the formation of only mononuclear complexes. The effect of only one such bulky t-butyl group on the course of the reactions and upon the properties of the resultant complexes was therefore of considerable interest.

The "aza-allyl" ligand Ph_2CNCPh_2 will be stabilised by the presence of four phenyl groups through the considerable delocalisation of the π-system, whereas the corresponding ligand $Bu^t_2CNCBu^t_2$ will lack this stability. Also the bulky t-butyl groups on such a ligand may well sterically hinder its approach to the metal atom sufficiently to prevent strong bonding. The $PhBu^tCNCPhBu^t$ ligand will have the stabilising influence of two phenyl groups and may be less sterically hindered for binding purposes, especially if the M-N-C skeleton is non-linear.

The synthesis, reactions and general features of the chemistry of methyleneamines are relevant to the research concerned with their introduction into metal complexes, and will first be reviewed.

Di-t-butylmethyleneamino-complexes of Mo and W[19]

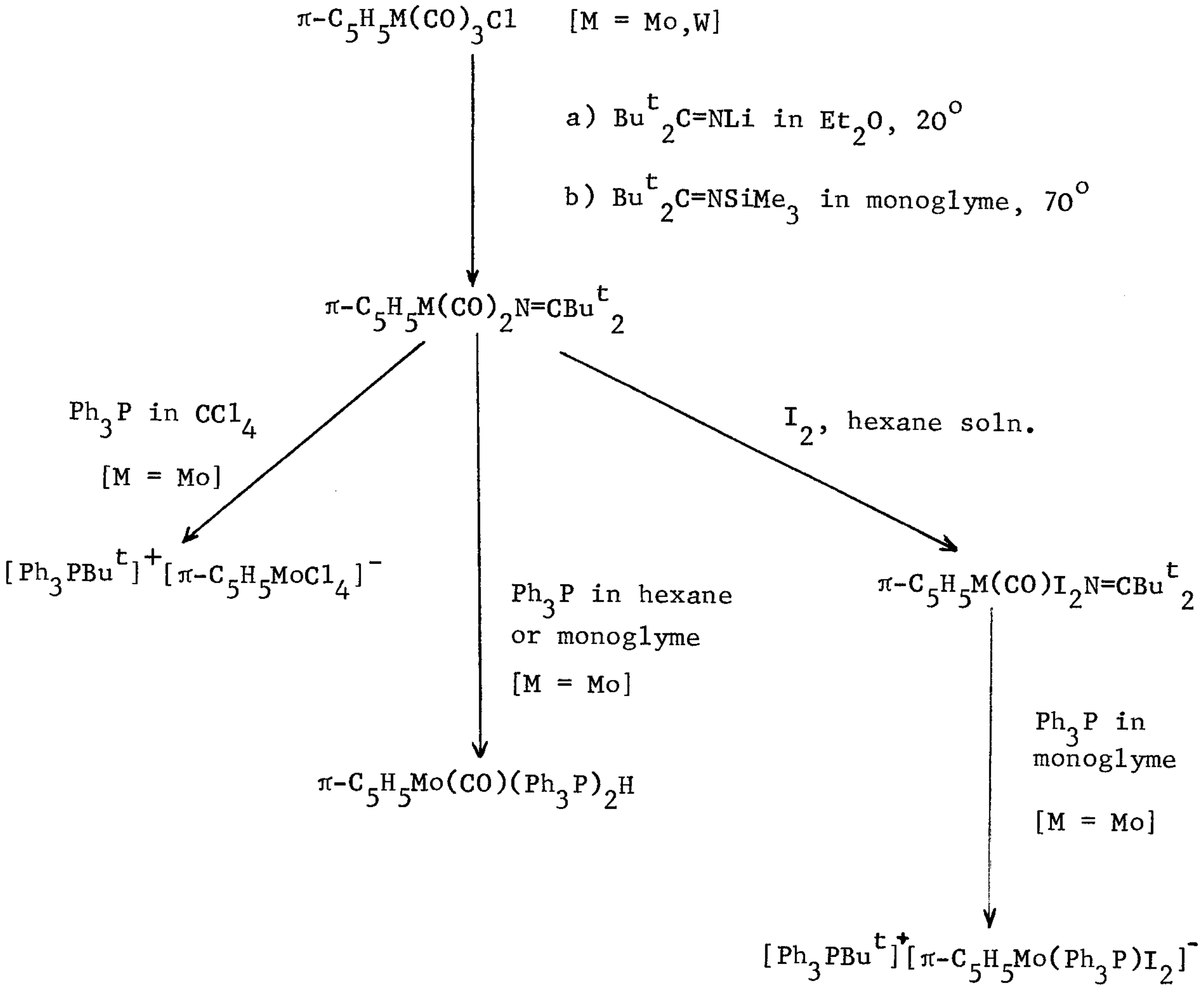


Fig.I.4.

Diphenylmethyleneamino-complexes of Mo and W[21]

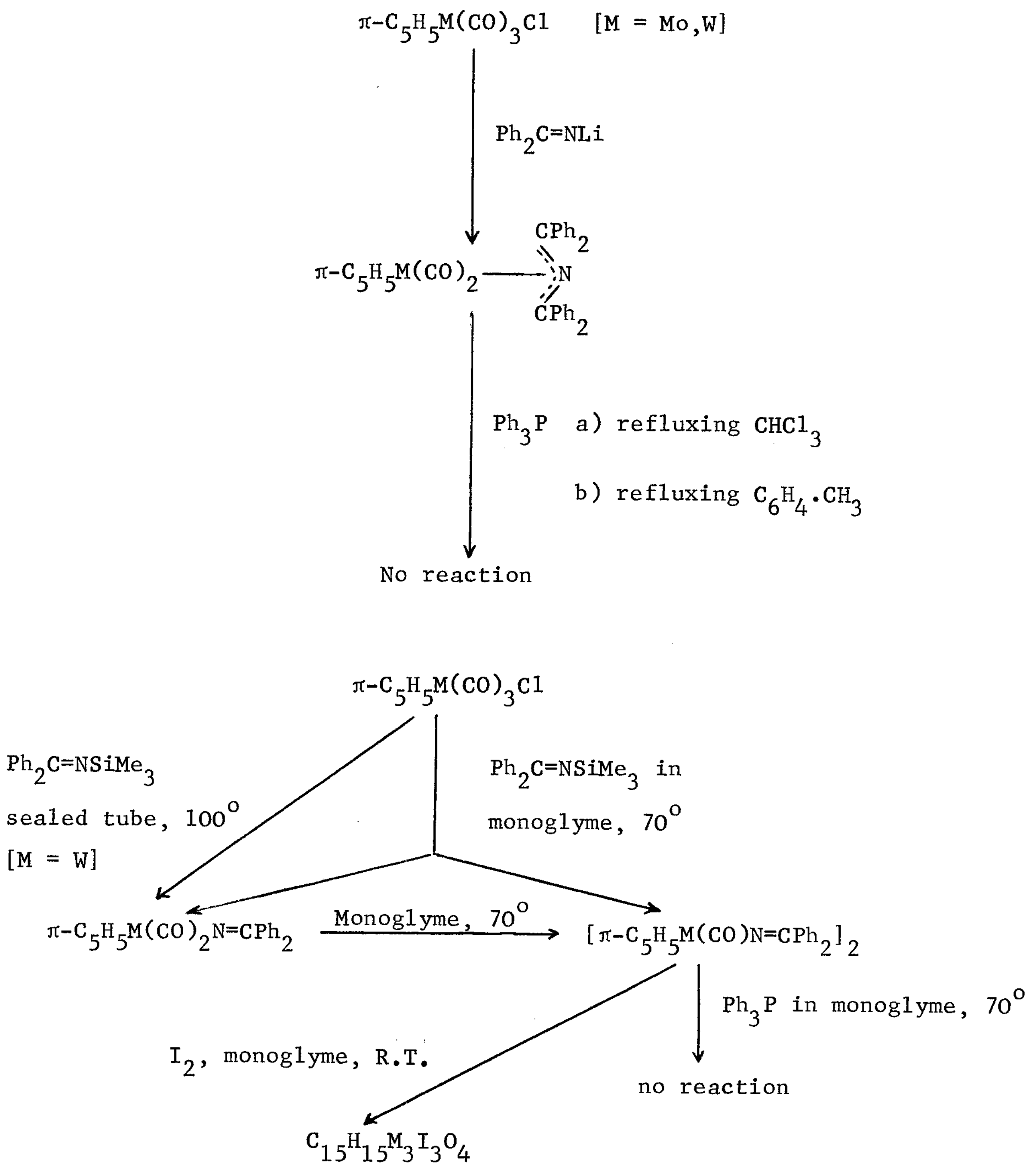


Fig.I.5.

CHAPTER II

THE SYNTHESIS, PROPERTIES AND REACTIONS OF METHYLENEAMINES

1. Introduction

The chemistry of methyleneamines and N-substituted methyleneamines has been reviewed[24] and a comprehensive survey of the chemistry of compounds containing the $>$C=N-group has been published recently.[25]

Methyleneamines RR'C=NH are a group of quite reactive organic compounds. Most are high boiling liquids but where R and/or R' are substituted aromatic groups the compounds are often solids; a few compounds e.g. $(CF_3)_2C=NH$ are gases at normal temperatures. The nitrogen atom is quite basic, the compounds readily forming salts RR'C=NH.HX. All the compounds on hydrolysis yield the corresponding ketone but the ease of hydrolysis varies considerably, dialkyl- and alkylaryl-methyleneamines being most reactive particularly where enamine tautomerism is possible. Care must be taken to use anhydrous conditions during their synthesis and to avoid contact with even moist air after isolation. The diarylmethyleneamines are much less susceptible to hydrolysis and a few have been found to be extremely resistant.

The N-H proton is readily substituted to give a variety of N-substituted methyleneamines. The $>$C=N being polar in a similar way to the carbonyl group of ketones shows several reactions analogous to those of ketones e.g. electrophilic addition reactions with HCN, condensation reactions with NH_2OH, $PhNHNH_2$, etc. Reaction with CS_2 results in the formation of the corresponding thio-ketone and the thiocyanate salt of the methyleneamine. Reduction of methyleneamines to primary amines is readily achieved by catalytic hydrogenation.

2. Synthesis of methyleneamines

Various organic compounds may be used as starting materials for the synthesis of methyleneamines and it will be convenient to consider each type of compound in turn and consider the various reactions by which they produce methyleneamines. The main types of compounds used are nitriles, amines and oximes and a brief review of their use in syntheses is given below.

(a) Nitriles: The polar nature of the -C≡N group renders the carbon atom susceptible to nucleophilic attack by organometallic compounds such as Grignard reagents and organolithium compounds, in a similar way to the ketonic >C=O group. Cautious hydrolysis of the complex formed yields the methyleneamine. Alternatively the nitrile can behave as an electrophilic reagent and reaction with a suitably activated aromatic compound, usually poly-hydroxy or -alkoxy substituted, results in formation of the corresponding methyleneamine (Houben-Hoesch synthesis). Aldol-type condensations of nitriles with H atoms in the α-position to the nitrile group occurs to form cyanomethyleneamines.

(b) Amines or ammonia: Ammonolysis of ketones is only of limited application as a method of synthesis, although good yields for a few methyleneamines have been achieved using a catalytic reaction. Dehydrogenation of amines is only of limited use also, largely due to side reactions such as deammination. Good yields of a limited number of methyleneamines have been achieved by reaction of amines with potassium amide in liquid ammonia.

(c) Oximes: Catalytic reduction of oximes forms a potentially good method of synthesis but has not yet received much attention. Electrolytic reduction likewise has only been used in the successful synthesis of very few methyleneamines. The action of nitrous acid on oximes, although being the first method used to obtain methyleneamines, has not been further studied.

2A. From nitriles

(i) Addition of Grignard reagents

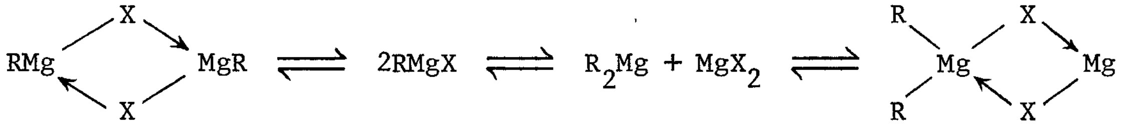
$$RC{\equiv}N + R'MgX \longrightarrow RR'C{=}NMgX \xrightarrow{\text{hydrolysis}} RR'C{=}NH$$

This is the most widely used method for synthesising methyleneamines. The reaction was first used by Blaise[26] for the synthesis of ketones previously unattainable by traditional methods. Although the nature of the methyleneamino-intermediate was realised, subsequent acid hydrolysis gave the required ketone. Cautious hydrolysis of the Grignard/nitrile complex to liberate the free methyleneamine was achieved[27] using ammonium chloride solution at -15° for diarylmethyleneamines which are fairly stable to hydrolysis, or anhydrous hydrogen chloride for the less stable alkylarylmethyleneamines. Anhydrous ammonia was also used[28] and the use of solvents other than ether for the reaction led to increased yields.[29-35] The extremely hydrolysable dialkylmethyleneamines tended to decompose even in such mild anhydrous conditions but the use of anhydrous methanol[36] was found to give good yields and enabled the first isolation of $Et_2C{=}NH$ and $Pr^nPr^iC{=}NH$.

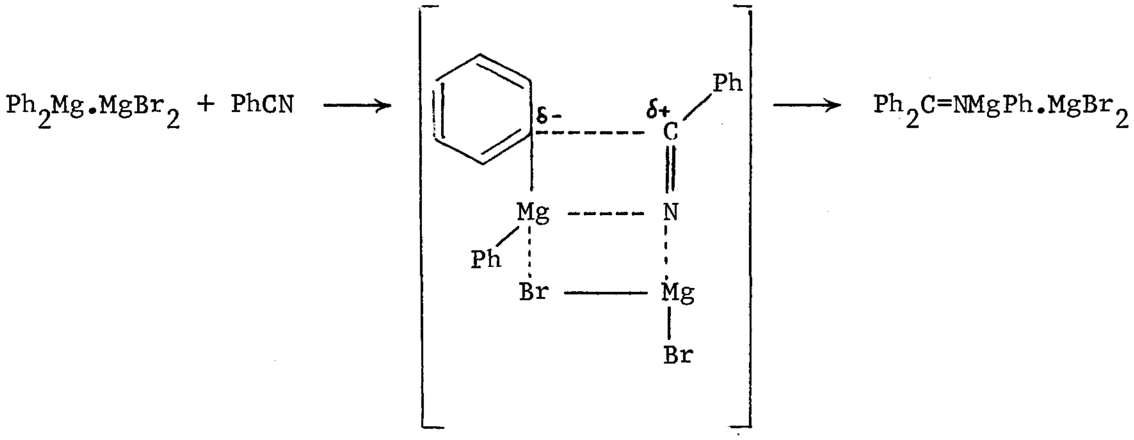
Where the methyleneamine was more stable to hydrolysis aqueous acid[37] or aqueous alkali[38,39] have been used to decompose the complex. Anhydrous oxalic acid has also been used.[40] Decomposition of the complex with acyl chlorides[41] or primary amines[42] led to the formation of N-acyl- and N-alkyl- or N-aryl-methyleneamines respectively.

Hydroxyphenylnitriles reacted with Grignards to form the corresponding hydroxydiphenylmethyleneamines,[43] but two moles of Grignard are required due to the presence of hydroxy groups.

The kinetics of the Grignard nitrile reaction are complex, largely due to continued speculation upon the nature of the Grignard reagent in solution. In general, solutions of Grignard reagents could be regarded as mixtures involving the following equilibria together with small proportions of ionised species and species more associated than dimeric.[44] The nature of the equilibrium would depend upon R, the halogen X, the solvent,



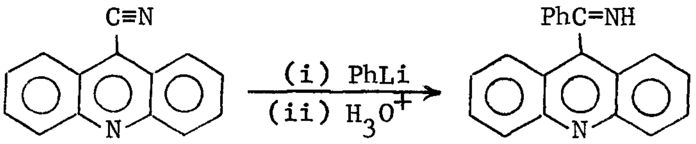
concentration and temperature. Storfer and Becker,[45] assuming the reactive agent to be R_2Mg, studied the kinetics of the reaction of Et_2Mg with benzonitrile. They found the kinetics followed no simple rate law and that the reactive ethyl groups were consumed at two different rates. They suggested the presence of a dimer of Et_2Mg to fit this data and proposed a mechanism for the reaction based upon this supposition. The data from the reaction of EtMgBr with benzonitrile also failed to fit a simple rate law but tended to confirm that Et_2Mg was the reactive species in the mixture. Edelstein and Becker,[46] who investigated the reaction of PhMgBr with benzonitrile, found the reaction to be first order in each for the first 25% of the reaction and also suggested that Ph_2Mg was the reactive species. The reaction was also found to be strongly dependent on the $[MgPh_2]/[MgBr_2]$ ratio and they suggested that the role of the $MgBr_2$ was to increase the polarity and hence decrease the order of the transition state complex.



(ii) Addition of organolithium and organoaluminium compounds

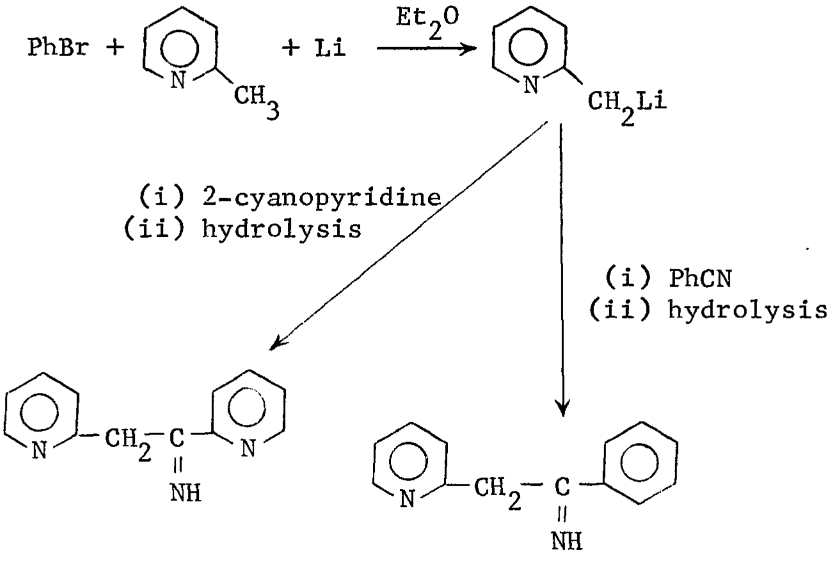
$$RC{\equiv}N + R'Li \longrightarrow RR'C{=}NLi \xrightarrow{\text{hydrolysis}} RR'C{=}NH$$

The action of these compounds on nitriles very closely resembles the addition of Grignards. Gilman and Marple[47] obtained phenyl-p-tolylketone in 17% yield on hydrolysis of the reaction product from benzonitrile and tri-p-tolylaluminium, and also the same product in 22% yield from benzonitrile and di-p-tolylzinc at 135-40°. The intermediate methyleneamine was not isolated. The first free methyleneamine obtained by use of organolithium compounds was from the reaction of 9-cyanoacridine with phenyllithium in the presence of a trace of hydrochloric acid,[48] excess acid resulted in hydrolysis to the ketone.



The reaction of alkyl- and aryl-lithium with excess benzonitrile at room temperature led to the formation of 1,3,5-triazine derivatives;[49] a similar reaction was observed with benzonitrile and diethylzinc.[50]

2-picolyllithium was used to synthesise the corresponding 2-pyridyl- and phenyl-methyleneamines.[51]

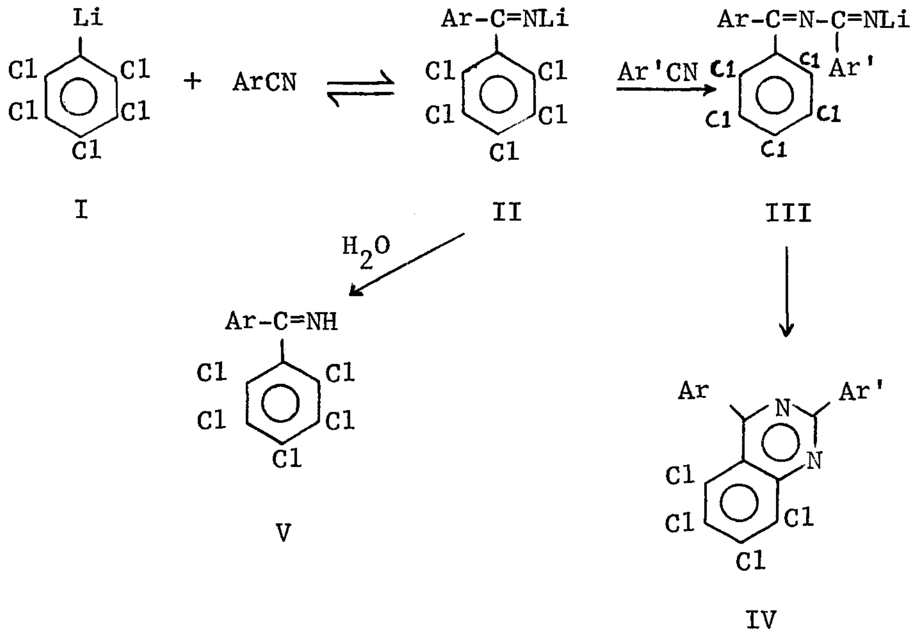


Di-t-butylmethyleneamine was obtained by reacting t-butyllithium with t-butylcyanide and prolonged refluxing of the intermediate lithium derivative with anhydrous methanol.[52]

$$\mathrm{Bu^tLi + Bu^tC{\equiv}N \longrightarrow Bu^t{}_2C{=}NLi \xrightarrow{MeOH} Bu^t{}_2C{=}NH}$$

Although very few free methyleneamines have been prepared by this reaction, the method has proved a very convenient way of preparing in situ the N-lithium derivative which has been used in the synthesis of methylene-amino-derivatives of main group elements[53,54] and of transition metal carbonyls.[17,19,21]

Recently evidence has been produced that this reaction, in at least one case, may be reversible.[55] The reaction of pentachlorophenyllithium I with benzonitrile and p-toluinitrile gave good yields of the corresponding methyleneamines V, but attempts to react the lithium derivative III [Ar=Ph] with a further mole of p-toluinitrile to obtain the quinazoline IV [Ar=Ph; Ar'=p-Me.C_6H_4] led to a mixture of products IV(a) and IV(b). It was suggested that this was due to the reaction forming the lithium derivative II being reversible, and this was shown to be the case by refluxing ether solutions of II [Ar=p-tolyl]. On hydrolysis p-toluinitrile and pentachlorobenzene were detected. The reverse reaction was carried to completion by heating the solution of II [Ar=p-tolyl] with mesitylene which trapped the benzyne derivative formed by loss of LiCl from I.

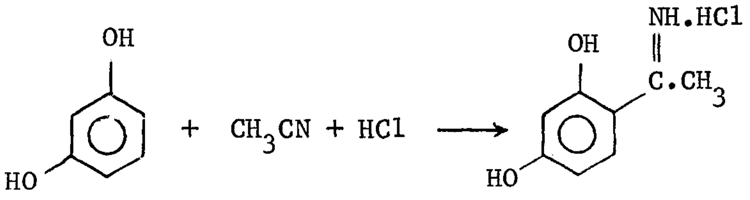


(a) Ar=Ph; Ar'=p-tolyl

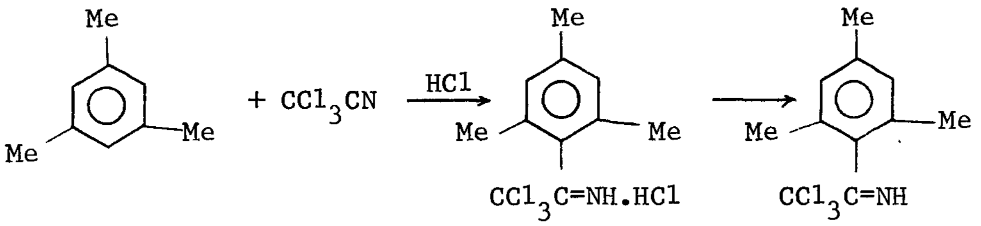
(b) Ar=Ar'=p-tolyl

(iii) Substitution reactions involving nitriles as electrophiles (Houben-Hoesch reaction)

The Gattermann synthesis of aromatic hydroxyaldehydes by reaction of aromatic hydroxy-compounds with HCN in the presence of HCl and a Lewis acid catalyst proceeds via an intermediate arylmethyleneamine. Hoesch extended the scope of this reaction by using nitriles instead of HCN to synthesise a number of aromatic hydroxyketones.[56] Houben[57] used the reaction to prepare a number of methyleneamines and their salts by isolation of the intermediate.

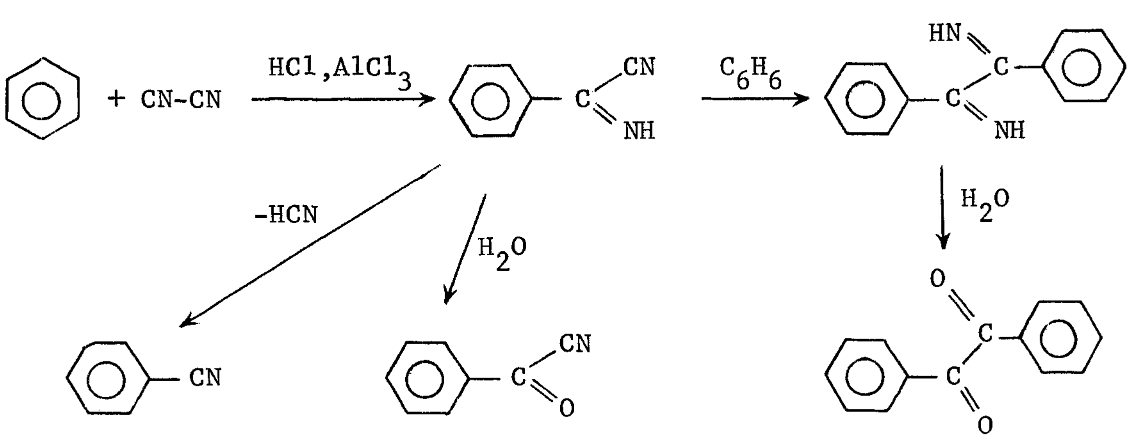


He found the reaction proceeded as above for di- and poly-hydroxy and -alkoxy compounds, the monohydroxy compounds such as phenol produced the "imino phenyl ester" PhOC(R)=NH.HCl. It was also found[58] that by the use of the very reactive trichloroacetonitrile the reaction could be extended to reactive aromatic hydrocarbons such as mesitylene and m-xylene.

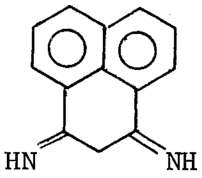


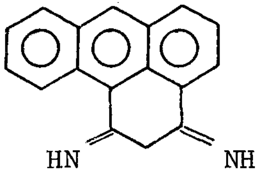
This methyleneamine proved of interest in that hydrolysis with aqueous alkali did not yield the ketone but chloroform and the nitrile. Benzene itself was found to react with dichloroacetonitrile[59] to give the phenyldichloromethylmethyleneamine in 41•5% yield and this compound proved to be surprisingly stable to hydrolysis.

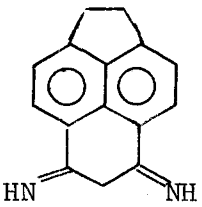
The use of dinitriles such as cyanogen or malononitrile in the reaction resulted in the formation of dimethyleneamines[60] in the reaction products. The various products of the reaction of benzene and cyanogen are explained in the scheme below.



With suitable aromatic hydrocarbons e.g. naphthalene, anthracene and perinaphthane and using malononitrile, a double reaction occurred with the formation of a new ring,[61] i.e.





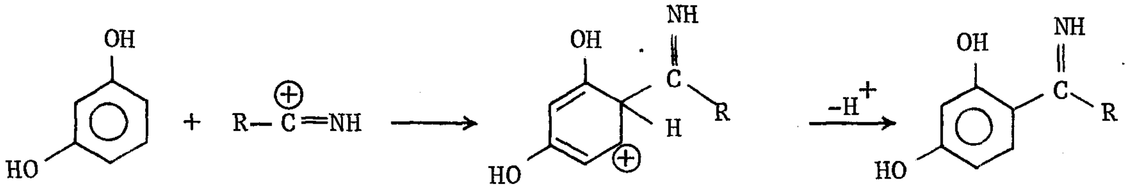


The extensive literature of the Houben-Hoesch reaction has been reviewed.[62,63]

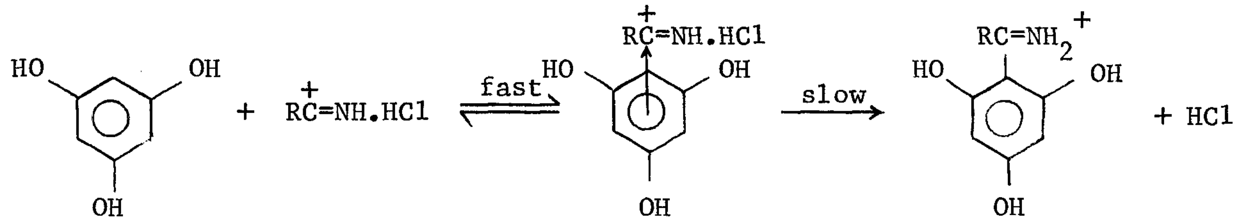
Reaction Conditions and Mechanisms

The majority of examples of the reaction have been carried out with equimolar quantities of nitrile and aromatic compound in anhydrous ether, the solution saturated with dry hydrogen chloride and kept at 0°. The reaction usually requires a catalyst, zinc chloride being most often used, and this generally gives higher yields. The presence of a catalyst has occasionally caused complications e.g. its use in the reaction of quinol with benzonitrile[64] led to formation of a complex of the methyleneamine and zinc chloride but reaction proceeded smoothly in the absence of catalyst.

The reaction mechanism has been the subject of some speculation. Hoesch[56a] assumed initial reaction of the nitrile and HCl to form the methyleneamine salt which then substituted in the aromatic ring with elimination of HCl. The fact that phenol does not react to form the methyleneamine but the "imino ester" led Houben[57,58] to investigate the possibility that this might be the first step in the reaction, the methyleneamine being formed by rearrangement, but he was unable to substantiate his theory. Ruske[63] suggested a simple electrophilic aromatic substitution involving a carbonium ion formed by protonation of the nitrile.



A recent kinetic study[65] of the reaction between phloroglucinol and acetonitrile or benzonitrile in the presence of dry HCl and zinc chloride showed the reaction to be first order in phloroglucinol and nitrile and also first order in hydrogen chloride ($[HCl] > 1{\cdot}0M$). Below 1·0M concentration it was suggested that appreciable amounts of HCl were engaged in association with the product methyleneamine as $>C=NH.HCl$ or $>C=\overset{\oplus}{N}H_2.\overset{\ominus}{HCl_2}$ species. The initial formation in the Houben-Hoesch reaction of a solid which contains nitrile, substrate and hydrogen chloride was explained as being a charge-transfer complex which is slowly transformed into the substitution product.

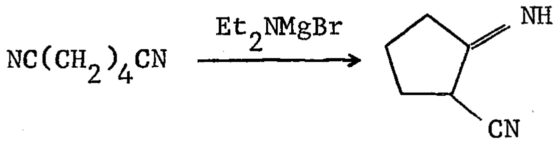


The effect of the catalyst appeared to greatly increase the acidity of the hydrogen chloride solutions.

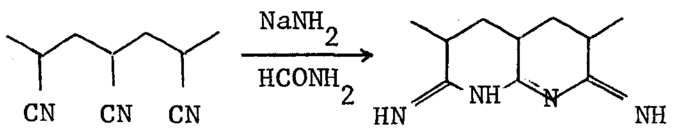
(iv) Aldol-type condensations of nitriles

The strong polarity of the -C≡N bond of nitriles renders the hydrogen atoms on carbon atoms α- to the nitrile group slightly acidic making feasible aldol-type condensations similar to those in carbonyl compounds. In the presence of strong bases, nitriles have been found to react in this way forming cyanomethyleneamines. The long chain nitriles, $NC(CH_2)_nCN$, may be converted into cyclic cyanomethyleneamines by use of condensing agents RR'NM

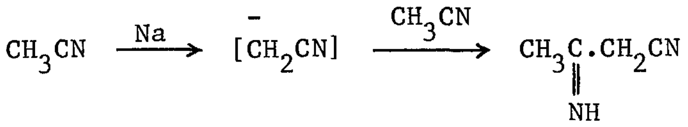
(M = alkali metals, alkaline earth metal, Al) e.g. adiponitrile reacts with Et_2NMgBr below $0^{o}C$ to form 2-cyanocyclopentylideneamine.[66]



Other long chain nitriles with cyano-groups at every alternate carbon atom were found to react with sodamide in formamide solution to give cyclic products.[67]

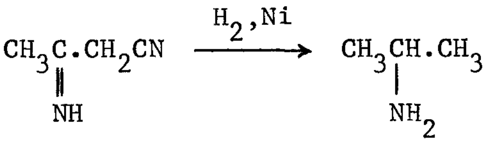


Alkyl nitriles and benzyl cyanide on reaction with metallic sodium formed simple cyanomethyleneamines.[68]



$$CH_3CN \xrightarrow{Na} [\overset{-}{CH_2}CN] \xrightarrow{CH_3CN} CH_3\underset{\overset{\|}{NH}}{C}.CH_2CN$$

The behaviour of these compounds towards catalytic hydrogenation, when cleavage of the nitrile group often occurred, indicated the possibility that they existed in the enamine form $RC(NH_2)=CHCN$.

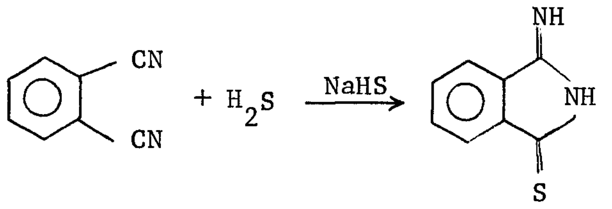


$$CH_3\underset{\overset{\|}{NH}}{C}.CH_2CN \xrightarrow{H_2,Ni} CH_3\underset{\overset{|}{NH_2}}{CH}.CH_3$$

The synthesis of mixed methyleneamines was achieved using acetonitrile and an arylnitrile in the presence of sodium, or better, sodamide.[69]

(v) Miscellaneous reactions of nitriles

Phthalonitrile on reaction with hydrogen sulphide in the presence of sodium bisulphide in an ethanol/water solvent produced 3-thioisoindolylideneamine.[70]



Free radical attack at the carbon atom of the nitrile group has been shown to produce methyleneamines.[71] Cyclohexyl radicals, formed by photolysis of di-t-butyl peroxide in cyclohexane solution, reacted with benzonitrile to give trace amounts of phenylcyclohexylmethyleneamine, the main product being cyclohexylbenzonitriles by ring substitution. The yield of the methyleneamine was increased by thermal production of the radicals. Heating benzoyl peroxide in benzonitrile similarly produced diphenylmethyleneamine.[71]

$$(PhCO_2)_2 \xrightarrow{\Delta} 2PhCO_2^{\bullet} \longrightarrow 2Ph^{\bullet} + 2CO_2$$

$$PhC{\equiv}N + Ph^{\bullet} \longrightarrow Ph_2C{=}N^{\bullet} \xrightarrow{\text{solvent}} Ph_2C{=}NH$$

Treatment of t-butylcyanide in petroleum ether solution with metallic sodium produced di-t-butylmethyleneamine.[72]

Reactions of perfluoroalkyl nitriles with chlorine in the presence of metal fluorides resulted in the formation of some N-chloro-perfluoroalkylmethyleneamines.[73]

e.g. $$CF_3CF_2CF_2CN + Cl_2 \xrightarrow{PbF_2} CF_3CF_2CF_2CF{=}NCl$$

2B. From amines, imides or ammonia

(i) Condensation of ketones with ammonia

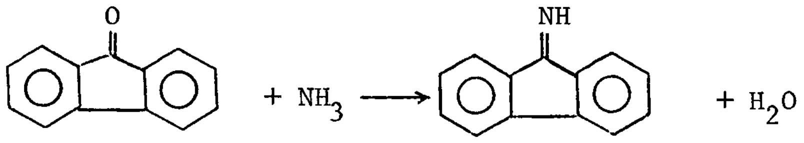
$$>C=O + NH_3 \longrightarrow >C=NH + H_2O$$

The condensation of carbonyl compounds with derivatives of ammonia is a well-known method by which various N-substituted methyleneamines are prepared.

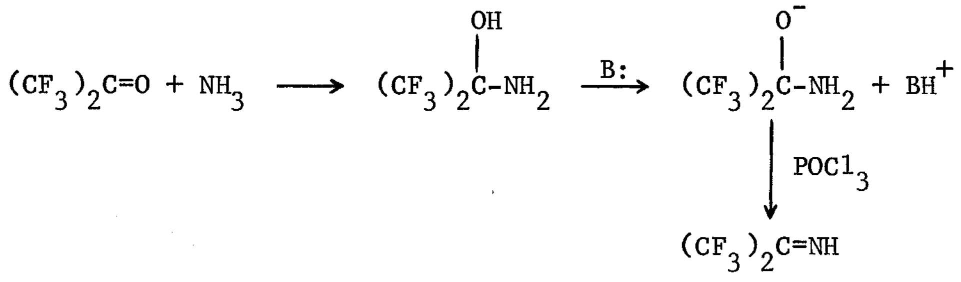
$$>C=O + RNH_2 \longrightarrow >C=NR$$

[R = alkyl,aryl,-OH,-NHPh, etc.]

However, the reaction with ammonia itself is more difficult and has led to the successful preparation of only a few methyleneamines. Generally, non-aqueous and fairly drastic conditions are required. Thomae[74] claimed the successful synthesis of diphenylmethyleneamine by prolonged heating of benzophenone with alcoholic ammonia in a sealed tube. Liquid ammonia and an aluminium chloride/ammonia compound, to remove the water formed in the reaction, were used with various ketones and proved reasonably successful.[75] Whereas molten fluorenone at 165° on reaction with anhydrous ammonia yielded 66% of the fluorenylideneamine,[76] the same product was obtained in almost quantitative yield by a much milder reaction with liquid ammonia at room temperature over a long period.[77]



More recently a number of perfluorodialkylmethyleneamines were obtained from the corresponding ketones by reaction with ammonia.[78] The intermediate ammonia adducts were stable to dehydration but the use of a basic medium (pyridine) and phosphorus oxychloride resulted in good yields of the methyleneamines.



$$(CF_3)_2C{=}O + NH_3 \longrightarrow (CF_3)_2\overset{OH}{\overset{|}{C}}{-}NH_2 \xrightarrow{B:} (CF_3)_2\overset{O^-}{\overset{|}{C}}{-}NH_2 + BH^+ \xrightarrow{POCl_3} (CF_3)_2C{=}NH$$

Catalytic ammonolysis of ketones has proved of limited success. Although benzophenone and ammonia vapours at $300-400^{\circ}$ in the presence of a thorium oxide catalyst gave an almost quantitative yield of diphenylmethyleneamine, other ketones gave poor yields.[79]

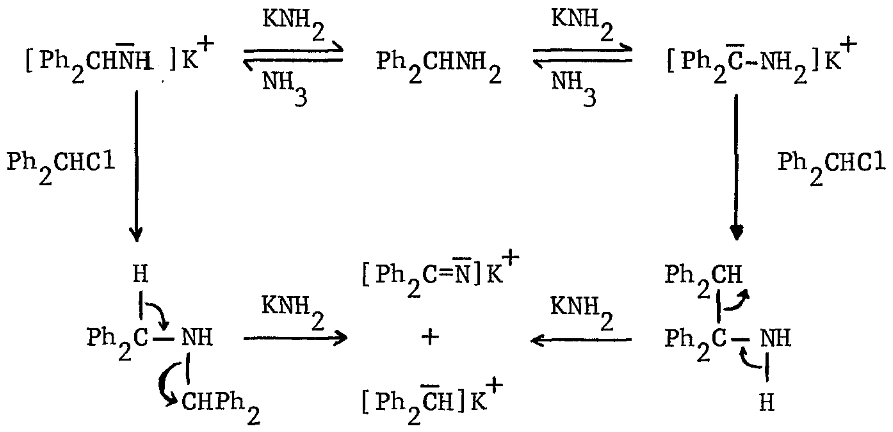
(ii) Dehydrogenation of amines

$$R{-}CHR'{-}NH_2 \xrightarrow{-H_2} RR'C{=}NH$$

This route to methyleneamines has not so far proved very successful due to competing reactions such as deammination. Catalytic dehydrogenation using platinised asbestos or Ni/Al_2O_3 at 320° or thorium oxide at 450° led to products which were presumed to contain the methyleneamines on the basis of their subsequent hydrolysis to ketones.[80] The use of sulphur as a dehydrogenating agent proved successful in producing 4,4'dimethoxydiphenylmethyleneamine,[81] the main product however being the corresponding thioketone.

(iii) Reactions with KNH_2

The reaction of halides having reactive α-hydrogen but no β-hydrogen atoms e.g. $PhCH_2Cl$, Ph_2CHCl and 9-chlorofluorene, with potassium amide in liquid ammonia to form the dimeric alkenes also formed amounts of the methyleneamines.[82] Good yields of diphenyl- and fluorenylidene-methyleneamines were obtained. The reaction products were explained by the scheme:



2C. From Oximes

(i) Reduction of oximes

Catalytic reduction of oximes by hydrogen (1 atm.) at room temperature in the presence of finely divided nickel as a catalyst gave good yields of diphenyl- and phenyl-α-naphthyl-methyleneamines.[83]

$$Ph_2C{=}N{-}OH + H_2 \xrightarrow{Ni} Ph_2C{=}NH + H_2O$$

Reduction of acetophenone and propiophenone failed due to the rapid hydrolysis of the methyleneamines but their hydrochloride salts were successfully obtained. Cyclohexanone oxime gave cyclohexanone as the major product.

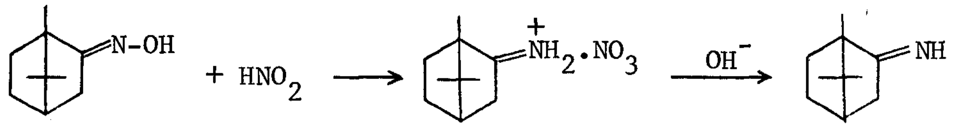
Controlled electrolytic reduction (pH $< 4{\cdot}0$, $1{\cdot}0\,\mu A$) of 2,4-dihydroxyacetophenone oxime to the corresponding methyleneamine was achieved by Lund.[84] The reduction consumed two electrons per molecule of oxime. The electrode reaction corresponded to reduction of the protonated oxime.

$$RR'C{=}N{-}OH + H^+ \rightleftharpoons RR'C{=}\overset{+}{N}H{-}OH$$

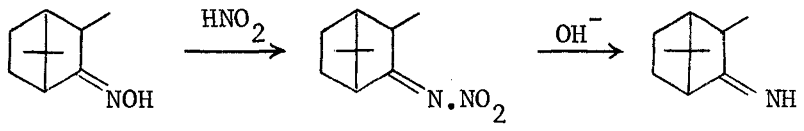
$$RR'C{=}\overset{+}{N}H{-}OH + 2e^- + 2H^+ \longrightarrow RR'C{=}\overset{+}{N}H_2 + H_2O$$

(ii) Action of nitrous acid on oximes

The only reported preparations of methyleneamines by this route have been from the oximes of camphor[85] and fenchone.[86] Camphor oxime formed "camphor imine" nitrate from which the free methyleneamine was obtained by treatment with aqueous alkali.



"Fenchimine" was obtained in a similar reaction but the initial product was reported as the nitrimine.



(iii) Action of Grignards on aldoximes

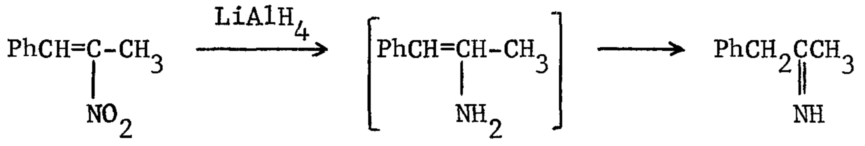
Small amounts of methyleneamines were produced by the action of excess of Grignard reagent on certain arylaldoximes.[87] Their formation was explained by the initial formation of the aryl nitrile which then reacted with the excess of Grignard in the usual way.

2D. Miscellaneous reactions producing methyleneamines

(i) The first reported synthesis of a methyleneamine was by Hantzsch and Kraft in 1891,[88] who obtained diphenylmethyleneamine by reaction of ethyl carbamate with dichlorodiphenylmethane.

$$Ph_2CCl_2 + H_2NCOOEt \xrightarrow{130^o} Ph_2C{=}NCOOEt \xrightarrow{HCl} Ph_2C{=}NH.HCl$$

(ii) Reduction of 1-phenyl-2-nitroprop-1-ene with $LiAlH_4$ and decomposition of the complex with aqueous sodium potassium tartrate was reported to give benzylmethylmethyleneamine in 60% yield.[89]



$$PhCH{=}\underset{\displaystyle NO_2}{\underset{|}{C}}{-}CH_3 \xrightarrow{LiAlH_4} \left[PhCH{=}\underset{\displaystyle NH_2}{\underset{|}{C}H}{-}CH_3\right] \longrightarrow PhCH_2\underset{\displaystyle NH}{\underset{\|}{C}}CH_3$$

The product reacted slowly with moist air to give a crystalline hydrate trimer $[PhCH_2C(=NH)CH_3.H_2O]_3$.

(iii) $Ph_2C{=}NH$ was obtained as the major product in the flash pyrolysis of benzophenone azine over the range 375-500°.[90] The initial formation of a diarylmethyleneamino-radical results from homolytic cleavage of the N-N bond. The radical then abstracted a proton from the reaction material; some charring of the reaction mixture was observed as a possible result of this process. The other main products of the reaction were benzonitrile and 6-phenylphenanthridine, the latter resulting from attack of phenyl radicals on unchanged azine.

$$\begin{tikzcd}
Ph_2C{=}N{-}N{=}CPh_2 \arrow[r, "\Delta"] & 2Ph_2C{=}N^{\bullet} \arrow[r, "\text{source of H}"] \arrow[d] & Ph_2C{=}NH \\
 & PhC{\equiv}N + Ph^{\bullet} &
\end{tikzcd}$$

(iv) N-chloro-difluoromethyleneamine was produced by loss of Cl_2 on heating N,N-dichloro-difluorochloromethylamine.[91]

$$CF_2Cl.NCl_2 \xrightarrow{100-150^{\circ}} CF_2{=}NCl$$

A summary of some of the methyleneamines prepared by the previous synthetic routes is given in Tables II.1.

Table II.1

References to preparations of methyleneamines

II.1(a) Diarylmethyleneamines. ArAr'C=NH

Ar	Ar'	Reference
Ph	Ph,o-tolyl,p-tolyl,α-naphth; 9-acridyl	27;48
Ph	2-, 3-, 4-pyridyl	40
Ph	p-Br.C_6H_4; 2,4,-$(OH)_2.C_6H_3$	52;84
o-,m-,p-tolyl	o-, m-, p-tolyl	30
C_6Cl_6	Ph, p-tolyl	55
p-Cl.C_6H_4	p-Cl.C_6H_4	112
p-MeO.C_6H_4	p-MeO.C_6H_4	81
2-thienyl	o-tolyl, 5-acridyl	36

II.1(b) Alkylarylmethyleneamines. RArC=NH

Ar	R	Reference
Ph	Et, Pr^n, Bu^i	27
o-,m-,p-tolyl	Pr^i, Bu^t	29
o-tolyl	Me, Et, Pr^n, Bu^t, Bu^i, Bu^s, Am^i	35
o-tolyl	$MeCPh_2$	33
2,4,6-$Me_3.C_6H_3$	CCl_3	58
2-,3-,4-pyridyl	Me, Et, Bu^n	40
Ph	Cy; 2,4,6-Me_3Cy *	27;38
Ph, 2-pyridyl	2-picolyl	51

* Cy = cyclohexyl

II.1(c) Dialkylmethyleneamines RR'C=NH

R	R'	Reference
$MeCPh_2$	Me, Et, Pr^n, Bu^n, Am^n, Am^i	33
Bu^t	Bu^t	52
Et	Et	36
Pr^n	Pr^i	36
$PhCH_2$	Me	89
CF_3	CF_3, CF_2Cl	78
CF_2Cl	CF_2Cl	78
C_2F_5	C_2F_5	78
Bu^s	$Cy(CH_2)_n$ (n = 2,3,4,5)*	31
Me	$2,4,6\text{-}Me_3Cy$*	38

3. Properties and reactions of methyleneamines

A. Spectroscopic properties

A systematic spectroscopic study of methyleneamines, RR'C=NH, has not been undertaken and the information available is, as yet, rather sparse. Pickard and Polly[92] reported C=N and N-H stretching frequencies for a number of methyleneamines and these, together with some recent data[52] are given in Table II.2. The stretching frequency of the $>$C=N group occurs intermediate between that of the more polar $>$C=O and the virtually non-polar $>$C=C$<$groups, being generally more intense than the latter but less intense than the former. $\nu_{C=N}$ absorptions for methyleneamines are usually in the range 1600-1650 cm^{-1}. A single N-H stretch is observed at 3200-3250 cm^{-1}.

Phenyl substituents tend to reduce the bond order and hence shift the $\nu_{C=N}$ absorption to lower frequencies; this is reflected in the data in Table II.2, dialkylmethyleneamines absorbing at ~1650 cm^{-1}, alkylaryl at ~1620 cm^{-1} and diaryl at ~1605 cm^{-1}. The effect of electron-withdrawing groups in the benzene ring further reduces the frequency e.g. di-p-chlorophenylmethyleneamine absorbs at 1590 cm^{-1},[52] (the value of $\nu_{C=N}$ 1653 cm^{-1} quoted by Pickard and Polly[92] has been suggested to be due to hydrochloride impurity[52]), whereas electron-donating groups increase the frequency e.g. di-p-methoxyphenylmethyleneamine ($\nu_{C=N}$ 1646 cm^{-1} [81]). Some discrepancy in the literature appears in the assignment of $\nu_{C=N}$ for diphenylmethyleneamine. Whilst Pickard and Polly[92] and Wade[52] assign a $\nu_{C=N}$ band at 1603 cm^{-1}, Cantarel[93] and Mathis-Noel[94] assign $\nu_{C=N}$ at 1649 cm^{-1} and 1660 cm^{-1} respectively. No explanation appears to have been offered for this discrepancy.

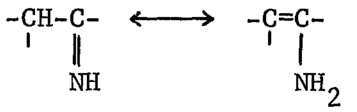
Table II.2

Stretching frequencies $\nu_{C=N}$ and ν_{N-H} for some methyleneamines RR'C=NH

R	R'	ν(C=N)	ν(N-H)	Reference
Ph	Ph	1603	3236	92
p-Cl.C_6H_4	p-Cl.C_6H_4	1590,[52] 1653	3247	92
p-Br.C_6H_4	Ph	1607		52
p-MeO.C_6H_4	p-MeO.C_6H_4	1646	3257	81
p-tolyl	p-tolyl	1610		52
Ph	Bu^t	1618	3226	92
o-tolyl	Et	1631	3205	92
o-tolyl	Bu^n	1629	3205	92
o-tolyl	Pr^n	1629	3226	92
Et	Bu^n	1645	3226	92
Pr^n	Pr^n	1645	3226	92
Bu^t	Bu^t	1610		52
CF_3	CF_3	1672		78
CF_2Cl	CF_2Cl	1672		78
C_2F_5	C_2F_5	1669	3289	78

B. Enamine tautomerism

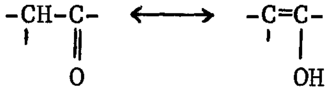
Methyleneamines of the type $-\overset{|}{C}H-\overset{|}{C}=NH$ may exist in tautomeric forms and the evidence for the two structural forms is reviewed below.



$$-\underset{|}{C}H-\underset{\underset{NH}{\|}}{C}- \longleftrightarrow -\underset{|}{C}=\underset{\underset{NH_2}{|}}{C}-$$

methyleneamine enamine

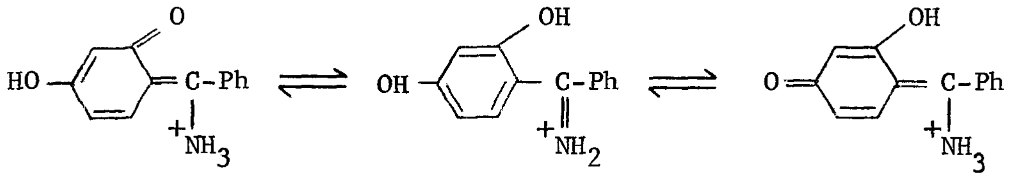
c.f.



$$-\underset{|}{C}H-\underset{\underset{O}{\|}}{C}- \longleftrightarrow -\underset{|}{C}=\underset{\underset{OH}{|}}{C}-$$

ketone enol

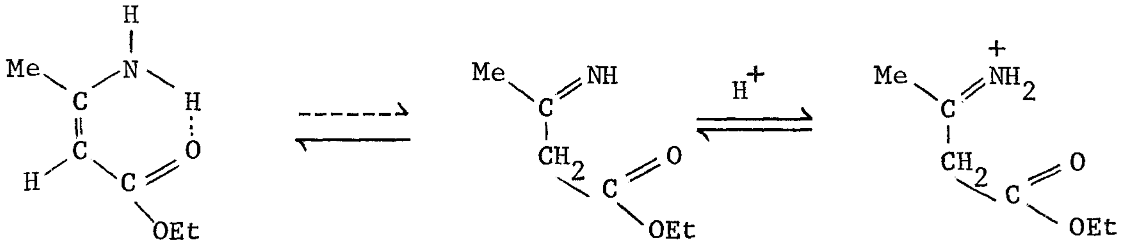
(i) Physical evidence: Due to lack of spectroscopic data on methyleneamines the evidence for such tautomerism is very sparse and somewhat conflicting. Culbertson[95] suggested the existence of the enamine forms of 2- and 4-hydroxydiphenylmethyleneamines to explain their resistance to hydrolysis. The ultra-violet absorption spectra showed distinct absorptions at 320-330 mμ whereas for 3-hydroxydiphenylmethyleneamine, where such tautomerism is impossible, only absorptions at 250-275 mμ were detected,



o-quinoid amine p-quinoid amine

Although Pickard and Polly[92] found no evidence of $\nu_{C=C}$ bands in the infrared spectra of methyleneamines arising from the enamine form, Mathis-Noel did find such evidence with pyridylalkylmethyleneamines.[94] He concluded that 2-pyridyl(n-butyl)methyleneamine was almost totally in the enamine form, and also that 4-pyridyl(n-butyl)- and 2-pyridyl(ethyl)-methyleneamines contained appreciable amounts of the enamine form.

Witkop[96] reported for $Ph_2CHCH=NH$ a single band in the 2000-1500 cm^{-1} region (assigned to $\nu_{C=N}$), and no indication of the enamine form, whereas for ethyl-β-aminocrotonate the one absorption at 1667 cm^{-1} ($\nu_{C=O}$) supports the enamine structure II instead of the imino form I. However, on addition of a trace of acid the compound was converted not to the expected enamine salt, but to the imino salt III which had an unconjugated ester band at 1715 cm^{-1}.



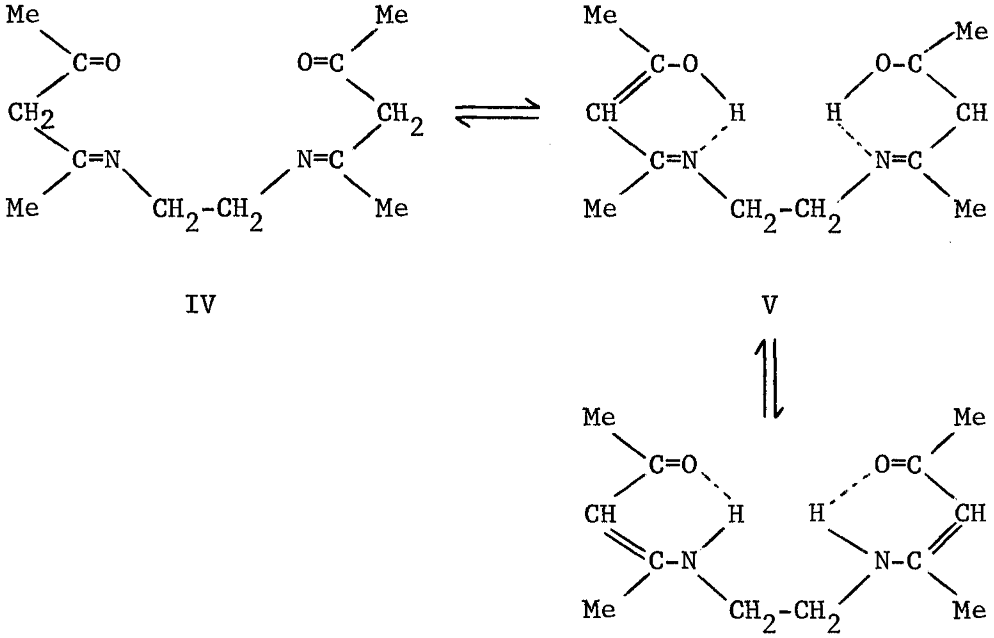
II I III

No evidence of tautomerism was seen in the i.r. spectra of a series of methyleneamines of the type $RR'NCH_2CH_2CPh_2C(=NH)Et$.[97]

The existence of the enamine form in N-substituted methyleneamines was detected by von Auwers and Wunderling[98] in 1932 from measurements of molar refractions. The enamine forms of N-cyclohexyl derivatives of cyclohexylidene- and phenylmethyl-methyleneamines were inferred from the presence of $\nu_{C=C}$ bands in the infrared.[99]

e.g.

Finally the limited ^1H n.m.r. data clearly shows the advantage of this technique in providing the much needed systematic study. Dudek and Holm[100a] reported the presence of vinylic protons and no $-CH_2-$ protons in the ^1H n.m.r. spectrum of bis-(acetylacetone)-ethylenediimine IV indicating the enol and enamine forms V or VI in > 95%.

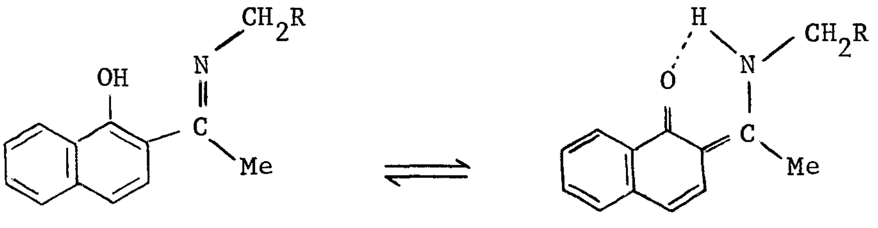


IV

V

VI

Similar studies on the derivatives of the o-hydroxynaphthylmethyleneamine VII showed that the stability of the enamine form VIII was sufficient to outweigh the loss in delocalisation produced in the ring system.[100b]

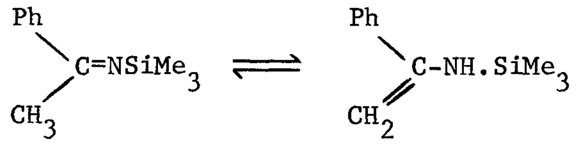


VII

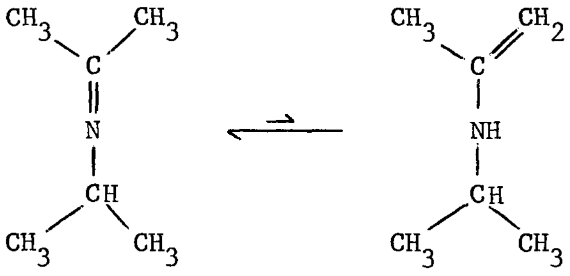
VIII

The presence of the enamine form of the N-organosilylmethyleneamine $PhMeC{=}NSiMe_3$ was detected by the presence of olefinic protons in the

^{1}H n.m.r. spectrum.[54]



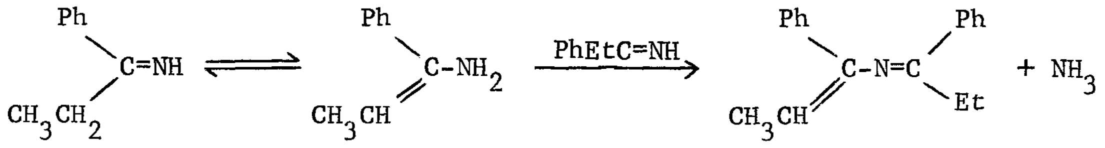
The reported spectrum of N-isopropyldimethylmethyleneamine measured in methanol at room temperature showed no vinylic protons but in CH_3OD there was immediate suppression of the signals due to the methyl protons attached to $>$C=N.[101] Thus, although the compound existed almost totally in form IX, rapid exchange of these six methyl protons for deuterium occurred via the enamine form X



IX X

Claims to have isolated both the two forms have also been made. Dabrowski reported[102] the separation of the enamine, n-PrCOCH=$CHNH_2$, by continuous extraction of the methyleneamine n-PrC(OH)=CH.CH=NH, with petroleum ether at -25° over a period of 18 hrs. Condensation of $PhMeCHNH_2$ with acetoacetic ester at -10° was reported[103] to give two isomeric products, a liquid assumed to be the enamine PhMeCHNHCMe=CHCOOEt, and a solid assumed to be the methyleneamine PhMeCHN=$CMeCH_2COOEt$, the enamine form being present to the extent of 68%.

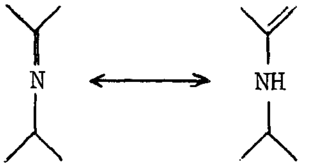
(ii) Chemical evidence: Evidence for a methyleneamine reaction occurring via the enamine form is furnished by the formation of "ketosoketimines". Phenylethylmethyleneamine was observed to become increasingly yellow on standing and evolution of ammonia occurred. On heating a greenish-yellow oil was obtained which was identified as the "ketosoketimine" XII.[104] It has been suggested that the reaction involved the enamine form XI.[95]

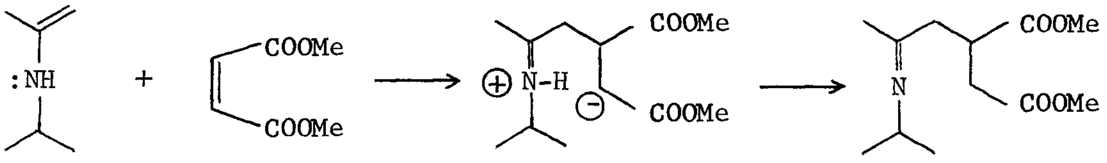


XI XII

"Ketosoketimines" were also observed to be formed during the isolation of 2-pyridyl(ethyl)methyleneamine.[40]

Also the reaction of N-isopropyldimethylmethyleneamine with dimethyl maleate was interpreted as involving the enamine form.[101]





C. Chemical reactions of methyleneamines

(i) The basicity of the nitrogen: pK_a measurements of only a few methyleneamines have been measured.[95] Diphenylmethyleneamine has a pK_a value of 7•18 and is obviously a weak base (ammonia 9•2, aniline 4•61, pyridine 5•20). From the values quoted[95] it is difficult to draw inferences concerning the effect of substituents on the basicity. The effect of electron withdrawing substituents e.g. chlorine produces the expected reduction in base strength but the effect of hydroxyl-, methoxyl- and alkyl-substituents does not reveal a consistent pattern.

All methyleneamines readily form salts of the form RR'C=NH.HCl on treatment with anhydrous hydrogen chloride.

(ii) Hydrolysis of methyleneamines

$$RR'C{=}NH + H_2O \longrightarrow RR'C{=}O + NH_3$$

The ease of hydrolysis of many methyleneamines and the consequent need for care in choosing reaction conditions for their synthesis is a main feature of the chemistry of these compounds. The reactivity towards hydrolysis appears to decrease in the order $R_2C{=}NH > RArC{=}NH > Ar_2C{=}NH$ but a wide range of rates of hydrolysis occurs even within these groups. Little kinetic work has so far been reported on the reaction. Cyclopropylphenylmethyleneamine hydrochloride gave values of k = 0•0252 min^{-1} (0•5M solution in 0•1M NaOH) and 0•0243 min^{-1} (0•1M solution in 0•1M NaOH) at 0^o .[28] The corresponding cyclopropylethylmethyleneamine compound was very rapidly hydrolysed, even more rapidly than the free base, and it was suggested that this might indicate the presence of a large proportion of the enamine form. A detailed kinetic study of the hydrolysis of various substituted diphenylmethyleneamines[95] revealed that substituents in the ortho-position resulted in much slower rates of hydrolysis, a possible reason being steric hindrance and this is confirmed by later work on substituted cyclohexylphenylmethyleneamines[105] and by qualitative observations.[29,30,38] All the kinetics studies showed a first order reaction.

(iii) Substitution reactions at the nitrogen

Organolithium compounds readily displaced the hydrogen atom forming the lithium derivative even at low temperatures.[53a]

$$R''Li + RR'C{=}NH \longrightarrow RR'C{=}NLi + R''H$$

The sodium derivative of diphenylmethyleneamine has also been made in an impure form by the action of sodium metal or sodium amide in liquid ammonia, but the potassium derivative could not be prepared.[106] Reaction of these lithium derivatives with trialkyl- or triaryl-chlorosilanes resulted in the formation of a series of N-organosilyl derivatives[53c,54] and similar derivatives containing Sn and Ge.[54]

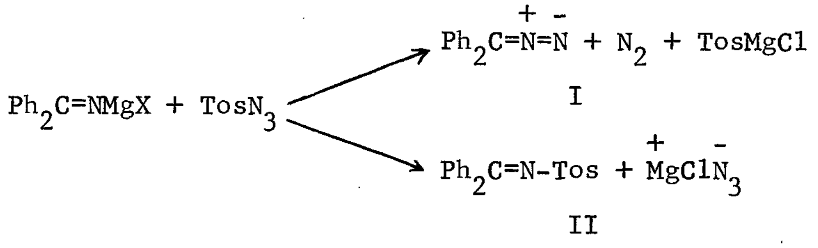
$$RR'C{+}NLi + R''_3SiCl \longrightarrow RR'C{=}NSiR''_3 + LiCl$$

These derivatives also resulted from the reaction of non-enolizable ketones on sodium bis-(triorganosilyl)amide.[107]

$$NaN(SiR_3)_2 + {>}C{=}O \longrightarrow {>}C{=}NSiR_3 + NaOSiR_3$$

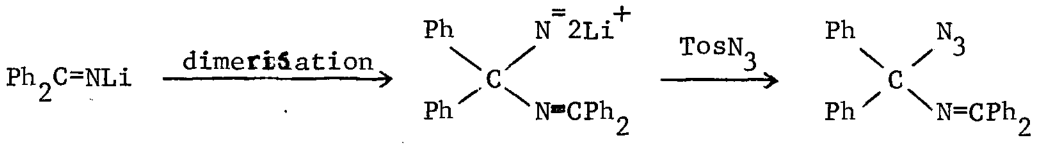
Grignard reagents similarly replaced the hydrogen atom forming the complex $RR'C{=}NMgX$ from which the methyleneamine could be recovered by cautious hydrolysis. The action of heat on T.H.F. solutions of this Grignard derivative with small amounts of copper(I) chloride resulted in the formation of the azines $RR'C{=}N{-}N{=}CRR'$, possibly via organocopper compounds of the type $RR'C{=}NCu$.[108]

Both the Grignard and lithium derivatives of $Ph_2C{=}NH$ reacted with azides,[109] the former producing diazomethanes I and N-substituted methyleneamines II. In addition compound III was produced following dimerisation of the lithium derivative.



I

II



III

Substitution of the hydrogen atoms for alkyl groups was achieved by reacting "camphor imine"[85] and "fenchone imine"[86] with methyl iodide, and also by reaction of methyleneamines with primary amines.[106,110]

$$Ph_2C{=}NH + H_2NR \longrightarrow Ph_2C{=}NR' + NH_3$$

Reaction with either acid anhydrides or ketene produced the corresponding N-acyl derivatives,[111] which with dry HCl in benzene reformed the parent compound

$$Ph_2C{=}NH + (RCO)_2O \longrightarrow Ph_2C{=}NCOR + RCOOH$$

$$Ph_2C{=}NH + CH_2{=}C{=}O \longrightarrow Ph_2C{=}NCOOCH_3$$

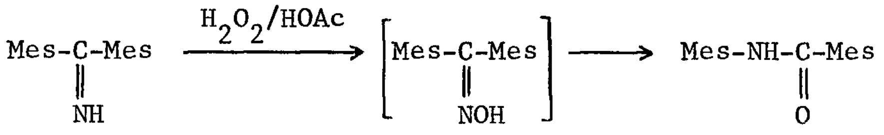
Substitution reactions at the nitrogen atom involving a variety of organic nitrogen compounds have been reported, thus phenylhydrazine yielded the N-substituted phenylhydrazone,[106] hydroxylamine yielded the oxime[39,106] and phenylisocyanate yielded, on hydrolysis, phenylurea and benzophenone[106]

$$Ph_2C{=}NH + PhNH.NH_2 \longrightarrow Ph_2C{=}N.NHPh + NH_3$$

$$Ph_2C{=}NH + NH_2OH \longrightarrow Ph_2C{=}NOH + NH_3$$

$$Ph_2C{=}NH + PhNCO \longrightarrow Ph_2C{=}NOCNPh \xrightarrow{H_2O} PhNHCONH_2 + Ph_2C{=}O$$

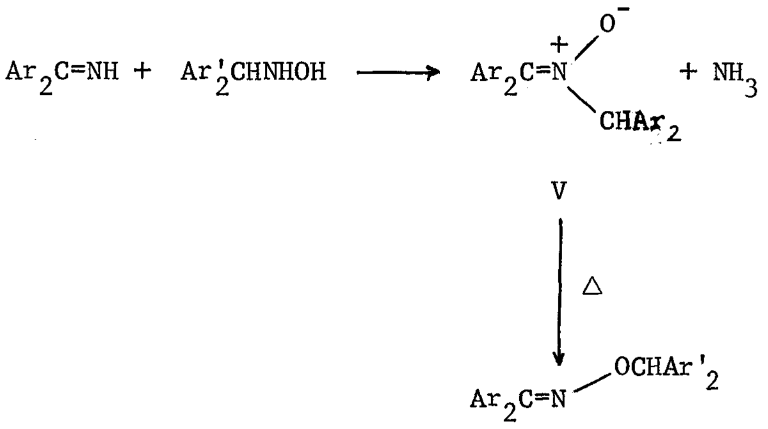
Dimesitylmethyleneamine did not yield the oxime on treatment with hydroxylamine. However, on treatment with hydrogen peroxide in glacial acetic acid (per-acetic acid) it produced a substituted amide IV, the Beckmann rearrangement product of the oxime.[39]



$$\underset{\underset{NH}{\|}}{Mes\text{-}C\text{-}Mes} \xrightarrow{H_2O_2/HOAc} \left[\underset{\underset{NOH}{\|}}{Mes\text{-}C\text{-}Mes}\right] \longrightarrow \underset{\underset{O}{\|}}{Mes\text{-}NH\text{-}C\text{-}Mes}$$

IV

With N-benzhydrylhydroxylamine the reaction produced a nitrone V which then rearranged to form the O-benzhydryloxime VI.[112]


V

VI

N-chloromethyleneamines were made by reaction of methyleneamines with hypochlorous acid[113] or t-butylhypochlorite.[114] $Ph_2C{=}NCl$ was found to be quite stable, being largely unchanged on heating at 130° in chlorobenzene solution, but $Ph_2MeCPhC{=}NCl$ under similar conditions broke down to form benzonitrile and 1,1-diphenylethylene.[114] Di-(trifluoromethyl)-methyleneamine underwent N-halogenation on treatment with halogens in the presence of metal fluorides as catalysts.[115]

$$(CF_3)_2C{=}NH + X_2 \longrightarrow (CF_3)_2C{=}NX + HX$$

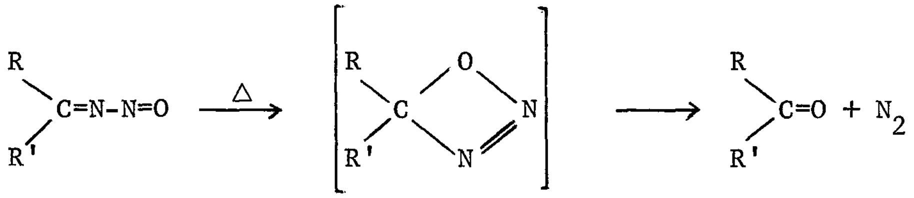
With fluorine some of the fully fluorinated amine $(CF_3)_2CF_2NF_2$ was produced. The N-bromo derivative was also prepared from the lithium derivative by the action of bromine.[78] This compound was light-sensitive forming the azine $(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$.

Substitution using phosgene produced a series of N-chlorocarbonyl derivatives VII together with their isomeric α-chloroisocyanates VIII.[116]

$$RR'C{=}NH + COCl_2 \xrightarrow[130^\circ]{\text{Toluene}} \underset{\text{VII}}{RR'C{=}NCOCl} \rightleftharpoons \underset{\text{VIII}}{RR'C(NCO)Cl}$$

Treatment of VII with SbF_3 produced, in some cases, the N-fluorocarbonyl derivative.[116] On hydrolysis VII reformed the parent methyleneamine,[116] alcoholysis of VII produced the N-alkoxycarbonyl derivatives and reaction with primary amines produced N-alkylamido-derivatives.[116]

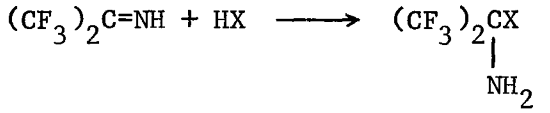
Substitution with nitrosyl chloride in carbon tetrachloride solution at -10° produced a number of deep blue or purple N-nitroso-derivatives[117] which were most unstable, decomposing slowly at room temperature to form the ketone and nitrogen via a first order reaction.



The same N-nitroso derivatives resulted from the treatment of ether solutions of the N-organosilyl derivatives with NOCl, the reagent causing cleavage of the Si-N bond.[118] The N-nitroso-t-butyl-o-tolylmethyleneamine decomposed forming σ-toluinitrile and t-butylchloride as well as the ketone. A free radical mechanism was suggested.[118]

(iv) Addition reactions

The reaction of hydrogen cyanide with methyleneamines is analogous to its reaction with carbonyl compounds, resulting in aminonitriles via nucleophilic attack at the carbon atom. Good yields of the aminonitriles were obtained from diphenylmethyleneamine[106,119] and fluorinylideneamine.[76,119] The carbon atom in $(CF_3)_2C{=}NH$ is particularly electron deficient and reaction with nucleophiles produced a number of stable addition compounds[78]

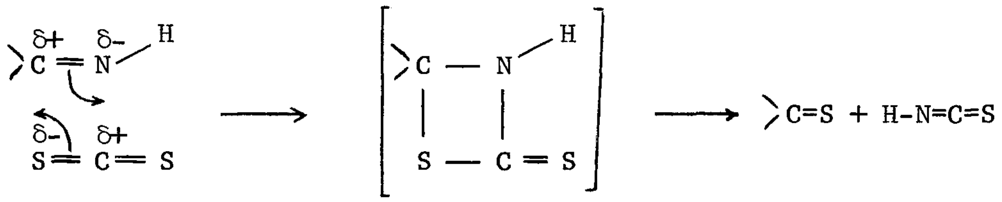


$$(CF_3)_2C{=}NH + HX \longrightarrow (CF_3)_2\underset{\displaystyle NH_2}{\underset{|}{C}}X \qquad [X = -NH_2,\ -NHNH_2,\ -NCO,\ -N_3,\ -OCH_3,\ -F]$$

Reaction of methyleneamines with compounds containing reactive methylene groups produced compounds with $>C{=}C<$ groupings.[120] For example, they reacted readily with cyanoacetic acid, cyanoacetic ester, cyanoacetamide and nitromethane to form the corresponding alkene, a reaction which is also shown by most aldehydes but is less readily shown by ketones, particularly diaryl ketones. The reaction was postulated as a nucleophilic addition followed by elimination.

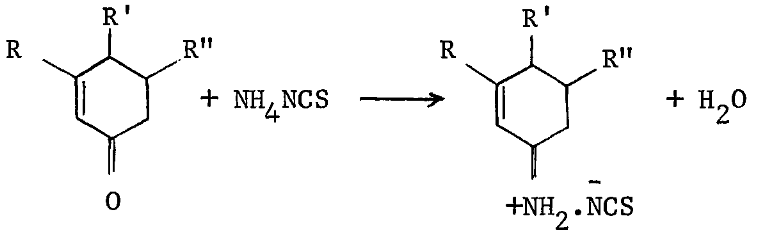
The vast majority of methyleneamines are reduced by hydrogen to form the primary amine.[30,32,33,35] Reduction readily occurs at room temperature in the presence of a platinum catalyst.

The reaction with carbon disulphide has been the subject of a number of reports, particularly in recent years. The reaction proceeded via a cyclic transition state to yield the corresponding thioketone and thiocyanic acid, the latter also reacting with more of the methyleneamine to produce the thiocyanate salt.[121,122]



$$\rangle C{=}NH + HNCS \longrightarrow \rangle C{=}\overset{+}{N}H_2\cdot\overset{-}{N}CS$$

The lithium derivative of methyleneamines also reacted with CS_2 to form the thioketone.[123] Reaction of 4,4-dimethoxydiphenylmethyleneamine with hydrogen sulphide also formed the corresponding thioketone[81] and the thiocyanate salt of methyleneamines was also produced indirectly by reaction of certain cyclohexen-1-ones with ammonium thiocyanate.[124]



(v) Radical reactions

The photochemical reduction[125] and oxidation[126] of $Ph_2C{=}NH$ was reported to occur via the same initial step involving proton abstraction from the solvent (isopropanol) forming a free radical.

$$Ph_2C{=}NH \xrightarrow[\text{photolysis}]{\text{solvent}} Ph_2\dot{C}{-}NH_2$$

In the absence of oxygen this radical further reacted to form Ph_2CHNH_2 and $Ph_2C{=}NCHPh_2$ as major products. In a stream of oxygen the sole product was benzophenone.

CHAPTER III

RESULTS AND DISCUSSION

In this chapter the synthesis of new methyleneamino-complexes of molybdenum and tungsten and some of their reactions are described.

1. Synthetic routes to methyleneamino-derivatives

The possible complication of enamine tautomerism in the methyleneamine has always been avoided by the use of such compounds with no hydrogen atoms in the α-position to the $>C=NH$ group. Diphenyl- and di-t-butyl-methyleneamines have been specifically studied previously[19,21] but in this work the intermediate mixed arylalkylmethyleneamine, $PhBu^tC=NH$, was used.

The method of introducing a formal 'anionic' ligand into metal carbonyl systems is generally achieved by use of a metathetical process, and some possible routes are listed below.

1.(a) $M(CO)_nNa + L\text{-}X \longrightarrow M(CO)_nL + NaX$ [X = halogen, etc.]

(b) $M(CO)_nX + L\text{-}M' \longrightarrow M(CO)_nL + M'X$ [M' = Li,Na]

2. $M(CO)_nX + L\text{-}M'R_3 \longrightarrow M(CO)_nL + R_3M'X$ [M' = Si,Sn]

3. $M(CO)_nX + L\text{-}H \xrightarrow{base} M(CO)_nL +$ salt of HX

4. $M(CO)_nH + L\text{-}H \longrightarrow M(CO)_nL + H_2$

5. $[M(CO)_n]_2 + L_2 \longrightarrow 2M(CO)_nL$

Methods 1(b) and 2 have been found most satisfactory[21] and are used in this work. A common by-product in both reactions is the dimeric carbonyl $[M(CO)_n]_2$.[21] Reaction 1(a) is not very satisfactory and leads largely to this dimeric carbonyl and the dimeric ligand (azine) as well as to small amounts of $M(CO)_nX$.[21] Method 3 results in the formation of complexes with the methyleneamine as a neutral ligand without the elimination of HX.[17]

$$Mn(CO)_5X + 2Ph_2C{=}NH \longrightarrow Mn(CO)_3(Ph_2C{=}NH)_2X + 2CO$$

Method 4 has not so far been investigated. Although method 5 was successfully used to prepare the iron carbonyl complex $[Fe(CO)_3N{=}C.C_6H_4.CH_3]_2$,[22] the method led to recovery of only the starting materials in previous work on the cyclopentadienyl Mo and W carbonyl systems.[21]

2. Experimental

Hydrocarbon solvents and diethylether were dried over extruded sodium, monoglyme and methanol were distilled from lithium aluminium hydride and chloroform dried over molecular sieve. Triphenylphosphine was recrystallised from hexane before use, and iodine purified by sublimation in vacuo. All solvents were pumped to remove dissolved air, stored under nitrogen and transferred by syringe against a counter current of nitrogen. All reactions were performed with rigorous exclusion of oxygen.

Spectra: Infrared spectra in the range 4000-400 cm^{-1} were recorded using a Grubb Parsons Spectromaster and ^1H n.m.r. spectra at 60 MHz. using a Perkin-Elmer R10 or Varian A56/60 spectrometer and using T.M.S. as a reference standard. Mass spectra were obtained using an A.E.I. MS9 instrument at 70 ev and an accelerating potential of 8 kv. Samples were inserted directly into the ion source at temperatures between 80^o and 220^o. Isotope distribution patterns were computed using a programme kindly supplied to us by Dr. E. Brook.

Analyses: Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Halogens were determined by fusion of the complex with potassium, followed by volumetric determination of the halide ions. Molecular weights were determined cryoscopically in benzene and cyclohexane, and osmometrically, using a Mecrolab Osmometer, in chloroform or benzene solution.

2A. Starting materials

π-cyclopentadienyl-molybdenum and tungsten- tricarbonylchlorides were prepared from the corresponding hydride[127] by the action of carbon tetrachloride and recrystallised from chloroform/hexane mixtures before use.

Phenyl-t-butylmethyleneamine, $PhBu^tC{=}NH$. The detailed preparation of this compound has not been reported previously in the literature but reference to its i.r. spectrum[92] and some of its reactions have been reported.[116,121] Attempts to synthesise it from benzonitrile and t-butylmagnesium bromide following the method of Pickard and Tolbert[36] resulted only in recovery of unreacted benzonitrile. The use of a toluene/ether solvent at a reflux temperature of 100° and decomposition of the Grignard/nitrile complex with anhydrous ammonia[29] resulted in the isolation of a white solid, identified by its melting point and i.r. spectrum as 2,4,6-triphenyl-1,3,5-triazine - the trimer of benzonitrile. This tendency of benzonitrile to polymerise in the presence of organometallic compounds has been previously noted.[49,50] The synthesis was successfully achieved in good yield using basically the method of Pickard and Tolbert[36] but using the aryl Grignard and alkyl nitrile.

Bromobenzene (39 g., 0•25 mole) in anhydrous ether (200 ml.) was added dropwise to magnesium (6•1 g., 0•26 mole) suspended in anhydrous ether (130 ml.) and the mixture stirred for 1 hr. to form the Grignard reagent. t-Butyl cyanide (18•67 g., 0•225 mole) was added dropwise and the mixture heated to reflux temperature for 12 hr., during which time a white solid separated. To the cooled mixture, anhydrous methanol (61•75 ml., 1•5 mole) was added dropwise. The pale yellow ether solution was separated by filtration from the bulky white precipitate, the solvent removed (25°, 0•1 mm.Hg) and the residual liquid distilled (44-6°, 0•1 mm.Hg) to give the colourless phenyl-t-butylmethyleneamine. Yield 30•4 g. (75%).

Analysis: Found, C,82•3; H,9•1; N,8•5; $C_{11}H_{15}N$ requires C,82•0; H,9•3; N,8•7%.

Infrared spectrum (liquid film): $\nu_{C=N}$, 1618 m-s; ν_{N-H}, 3226 w-m cm^{-1} (lit.[92] 1618, 3226 cm^{-1} respectively). Other absorptions: 3226w-m, 3081sh, 3067m, 3030m, 2976s, 2941sh, 2907m, 2890m, 1626sh, 1618m-s, 1607sh, 1579m, 1486s, 1471m, 1449m, 1401m, 1366sh, 1355s, 1235m, 1220m, 1188m-s, 1078w, 1033m, 1002m, 937s, 906sh, 897s, 808w, 772s, 739w, 703s,br, 685m, 586w, 578w, 562m cm^{-1}.

^1H n.m.r. spectrum in CCl_4 solution: singlets at 8•81(9), 2•75 broad (5) and 0•96 (broad) τ corresponding to Bu^t, Ph and N-H protons respectively. A good integration of the latter signal could not be obtained.

Mass spectrum (direct insertion at source temperature): The peaks due to the parent ion $[PhBu^tC{=}NH]^+$ at m/e 161 and that at m/e 160 due to $[PhBu^tC{:}N]^+$ were both very weak. The most intense peak in the spectrum corresponded to $[PhCHN]^+$ at m/e 104. The major peaks observed are listed in Table III.1.

Table III.1

Mass spectroscopic data for $PhBu^tC{=}NH$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
161	4•5	$[PhBu^tCNH]^+$	103	4•1	$[PhCN]^+$
160	2•0	$[PhBu^tCN]^+$	77	26•7	$[Ph]^+$
154	7•1	$[Ph_2]^+$	57	6•2	$[Bu^t]^+$
146	4•2	$[PhBu^tC]^+$	51	16•4	$[C_4H_3]^+$
105	16•4	$[PhCHNH]^+$	41	13•3	$[CH_3CN]^+$
104	100•0	$[PhCHN]^+$	39	9•8	$[CHCN]^+$

(N-trimethylsilyl)phenyl-t-butylmethyleneamine, $PhBu^tC{=}NSiMe_3$. This compound, which has not previously been reported, was obtained in good yield by the method of Chan and Rochow.[54]

Phenyl-t-butylmethyleneamine (8•05 g., 50 mmole) was dissolved in anhydrous ether (250 ml.) and the solution frozen to -196°. n-Butyllithium (50 mmole) was added by syringe against a counter flow of nitrogen and the mixture allowed to warm to room temperature. To the resultant bright yellow solution was added trimethylchlorosilane (5•4 g., 50 mmole) and the mixture stirred at room temperature for 12 hr. The yellow ether solution was separated by filtration from the white precipitate (LiCl) produced, the solvent removed (25°, 0•1 mm.Hg) and the residual liquid distilled (36-8°, 0•02 mm.Hg) to give the pale straw-coloured (N-trimethylsilyl)phenyl-t-butylmethyleneamine. Yield 6•0 g. (51•5%).

Analysis: Found, C,71•8; H,9•6; N,5•78; $C_{14}H_{23}NSi$ requires C,72•1; H,9•87; N,6•0%.

Infrared spectrum (liquid film): A strong absorption was observed at 1678 cm^{-1} ($\nu_{C=N}$). By analogy with absorptions observed in a number of similar N-organosilyl compounds[54] the following assignments are made: ν(Si-N) 906 cm^{-1}, $\delta_{sym}(Si\text{-}Me_3)$ 1250, 1261 cm^{-1}, $\rho(Si\text{-}Me_3)$ 836, 755 cm^{-1}.

The full infrared spectrum (contact film): 3077sh, 3062w, 3021w, 2967s, 2899m, 2874m, 1678s, 1604w, 1580w, 1481m, 1462m, 1391m, 1362m, 1348sh, 1261sh, 1250s, 1225w, 1199m, 1183sh, 1075m, 1036w-m, 1028w-m, 1000w, 965s, 935w, 906m-s, 873s, 836s, 823sh, 786m, 755m, 738m, 702s, 673m, 617w, 568w-m, 508w,br cm^{-1}.

^1H n.m.r. spectrum in $CDCl_3$ solution: singlets at 10•16(9) and 8•85τ(9) due to $SiMe_3$ and Bu^t protons respectively. Two signals due to phenyl protons were observed at 2•73(3) and 3•03(2)τ.

Mass spectrum (direct insertion at source temperature): The parent ion $[\mathrm{PhBu^tC{=}NSiMe_3}]^+$ was not observed in the spectrum, the peak at highest mass corresponded to loss of a methyl group from the parent i.e. $[\mathrm{PhBu^tC{=}NSiMe_2}]^+$ or $[\mathrm{PhC(CMe_2){=}NSiMe_3}]^+$ at m/e 218. The major peaks in the spectrum are summarised in Table III.2

Table III.2

Mass spectroscopic data for $\mathrm{PhBu^tC{=}NSiMe_3}$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
218	4·8	$[\mathrm{PhBu^tC{=}NSiMe_2}]^+$	78	13·4	$[\mathrm{PhH}]^+$
		or $[\mathrm{PhC(CMe_2){=}NSiMe_3}]^+$	74	14·8	$[\mathrm{Me_3SiH}]^+$
176	98·6	$[\mathrm{PhC{=}NSiMe_3}]^+$	73	100·0	$[\mathrm{Me_3Si}]^+$
149	10·9	$[\mathrm{Ph_2}]^+$	58	14·2	$[\mathrm{Bu^tH}]^+$
135	19·2	$[\mathrm{PhSiMe_2}]^+$	43	23·8	$[\mathrm{MeCHNH}]^+$
104	22·6	$[\mathrm{PhCHN}]^+$	41	15·9	$[\mathrm{MeCN}]^+$
103	7·7	$[\mathrm{PhCN}]^+$			

2B. Synthesis and reactions of phenyl-t-butylmethyleneamino-complexes of Mo and W

(i) Reaction of $\pi\text{-}\mathrm{C_5H_5Mo(CO)_3Cl}$ with $\mathrm{PhBu^tC{=}NLi}$

A solution of $\mathrm{PhBu^tC{=}NLi}$ was prepared by adding n-butyllithium solution (8 mmole) to phenyl-t-butylmethyleneamine (1·288 g., 8 mmole) in anhydrous ether (150 ml.) frozen at -196° and allowing the resultant mixture to warm slowly to room temperature. The resultant yellow solution was stirred for 1 hr. and then syringed into $\pi\text{-}\mathrm{C_5H_5Mo(CO)_3Cl}$ (2·26 g., 8 mmole) in anhydrous ether (250 ml.) frozen at -196°. On warming to room temperature, slow evolution of carbon monoxide and a darkening in colour were observed. The reaction was shown by i.r. spectroscopy to be complete after 4 hr. A whitish solid separated during this time and was found to be lithium chloride. The solvent was removed from the reaction mixture (25°, 0•1 mm.Hg) to leave a dark red-brown oily residue which was extracted with hexane (3 x 10 ml.) to give deep bluish solutions. The residual red-brown solid after hexane extraction was shown to be dimeric $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ by i.r. spectroscopy. Removal of the hexane from the bulked extracts left a dark bluish oil which was redissolved in hexane (10 ml.) to leave a small amount of undissolved material, also found to be dimer, which was removed by filtration. The process of removing the solvent followed by redissolving the product in hexane was repeated until no more undissolved dimer was detected. The remaining deep royal blue solution was reduced in bulk and on cooling to -20° deposited deep blue-black crystals. The mother liquor was removed by syringe and the crystals rapidly washed with a small amount of hexane and dried _in vacuo_. Yield 0•4 g. (13•2%). The crystals were identified as $\pi\text{-}C_5H_5Mo(CO)_2N{=}CPhBu^t$. (M.p. 63-64° to deep blue liquid).

Properties: The blue-black crystals were extremely soluble in all common organic solvents, polar and non-polar, forming deep royal blue solutions. The crystals were stable in air for short periods but prolonged exposure resulted in the formation of a brown coating. Solutions of the crystals were very air sensitive.

Analysis: Found, C,58•1; H,5•22; N,3•68; $C_{18}H_{19}MoNO_2$ requires C,57•0; H,5•0; N,3•67%.

Infrared spectrum: ν_{CO}, 1942vs, 1855vs, 1825w cm^{-1} (KBr disc); ν_{CN}, 1636m-s cm^{-1}. Several other absorptions were observed characteristic of π-cyclopentadienyl(*) and phenyl groups (†). The crystals gave a royal

blue mull with Nujol and the spectrum showed ν_{CO} 1965sh, 1940vs, 1881sh, 1846vs, 1821 cm^{-1}; ν_{CN} 1636 cm^{-1}. The strong shoulders at 1965 and 1881 cm^{-1} were shown to be due to solution in Nujol by comparison with other solution spectra e.g. in hexane solution, ν_{CO}, 1967vs, 1887vs cm^{-1}. The full i.r. spectrum (Nujol) is: 3096w*, 3067w†, Nujol, 1965sh, 1940vs, 1881sh, 1846vs, 1821sh, 1637m-s, 1596m†, 1493m, Nujol, 1433m, 1418sh, Nujol, 1366m, 1351sh, 1258m, 1215sh, 1202m, 1070w, 1062sh, 1059m-s, 1028m, 1014m-s, 1005m-s*, 958m, 902w, 839sh, 837m*, 825m*, 817w, 806s, 787m, 725s, 698s†, 685w, 645m-s, 613w, 604w,br, 579m, 544m, 508m,br, 495s, 466m,br, 458m,br cm^{-1}.
[* π-C_5H_5 absorptions, by comparison with π-$C_5H_5M(CO)_3Cl$;[128] † Ph absorptions, by comparison with $PhBu^tC$=NH].

<u>^{1}H n.m.r. spectrum</u> in $CDCl_3$ solution: signals at 8·80s, 4·17s, and 2·58m τ due to Bu^t, π-C_5H_5 and Ph protons respectively (s = singlet, m = multiplet). Good integration of the peaks was not obtained but indicated the presence of the groups in the expected ratio.

<u>Molecular weight</u>: A cryoscopic determination in cyclohexane gave a value for the molecular weight of 398 (theoretical 379).

<u>Mass spectrum</u> (direct insertion at source temperature): The parent ion $[\pi\text{-}C_5H_5Mo(CO)_2N{=}CPhBu^t]^+$ was observed centred at m/e 379; the isotopic distribution pattern corresponded to that computed for $C_{18}H_{19}MoNO_2$. The major peaks observed in the mass spectrum are listed in Table III.3.

(ii) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $PhBu^tC$=NLi in monoglyme at reflux temperature

The previous reaction led to the formation of the methyleneamino-complex π-$C_5H_5Mo(CO)_2N$=$CPhBu^t$ with no sign of dinuclear or aza-allyl complexes. In order to investigate the possible formation of complexes containing the aza-allyl ligand $PhBu^tCNCBu^tPh$, more forcing conditions were used. A solution of

Table III.3

Mass spectroscopic data for π-$C_5H_5Mo(CO)_2N{=}CPhBu^t$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
379	9•0	$[\pi\text{-}C_5H_5Mo(CO)_2N{=}CPhBu^t]^+$	161	-	$[PhBu^tCNH]^+$
351	2•0	$[\pi\text{-}C_5H_5Mo(CO)N{=}CPhBu^t]^+$	160	-	$[PhBu^tCN]^+$
323	16•7	$[\pi\text{-}C_5H_5MoN{=}CPhBu^t]^+$	104	-	$[PhCNH]^+$
266	7•3	$[\pi\text{-}C_5H_5MoN{=}CPh]^+$	103	-	$[PhCN]^+$
240	100•0	$[\pi\text{-}C_5H_5MoPh]^+$	98	11•0	$[Mo]^+$
163	16•7	$[\pi\text{-}C_5H_5Mo]^+$	77	-	$[Ph]^+$
			65	-	$[C_5H_5]^+$

In addition many organic ions were observed similar to those in the spectrum of $PhBu^tC{=}NH$ (Table III.1).

$PhBu^tC{=}NLi$ (8 mmole) in monoglyme (100 ml.) was prepared in a similar manner to that described in (i). The solution was heated to the reflux temperature and a solution of π-$C_5H_5Mo(CO)_3Cl$ (1•12 g., 4 mmole) in monoglyme (50 ml.) was added dropwise over 1 hr. The mixture darkened considerably during the addition. After 4 hr. the reaction mixture was cooled and the solvent removed (25°, 0•1 mm.Hg) leaving a dark red-brown residue which was insoluble in hexane. Extraction with chloroform gave a red-brown solution whose i.r. spectrum showed only the presence of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and some unreacted chloride.

(iii) Reaction of π-$C_5H_5W(CO)_3Cl$ with $PhBu^tC{=}NLi$

The reaction was performed in an analogous manner to reaction (i) using π-$C_5H_5W(CO)_3Cl$ (2•21 g., 6•0 mmole), $PhBu^tC{=}NH$ (0•97 g., 6•0 mmole) and n-BuLi (6•0 mmole). The reaction was complete after 5 hr. Extraction of the residue with hexane (3 x 10 ml.) produced deep green solutions and left an orange-red solid, identified by i.r. spectroscopy as $[\pi$-$C_5H_5W(CO)_3]_2$ with small amounts of unreacted chloride. The emerald green oil which resulted on removal of the solvent (25^o, 0•1 mm.Hg) from the combined extracts was treated as in (i) to remove traces of dissolved dimer but the purification of the oil proved a more difficult process; the dimer impurity appeared to be extremely soluble in the oil. Eventually a blue-green hexane solution was obtained which on cooling to -20^o produced a crop of deep blue crystals of π-$C_5H_5W(CO)_2N{=}CPhBu^t$, but further crops could not be obtained from the mother liquor. Yield of recrystallised material 0•1 g. (4%).

Although the yield of crystals is extremely low the initial amount of oil obtained by hexane extraction of the reaction product was 1-2 ml. and its i.r. spectrum showed it to contain relatively small amounts of dimer. However, it appeared that even such small amounts were extremely difficult to remove and prevented crystallisation of the bulk of the product. On several occasions the green oil defied all attempts to produce crystals, including prolonged freezing of the oil in liquid nitrogen and cooling concentrated solutions in solid carbon dioxide in the presence of 'seed' crystals.

Properties: The deep blue crystals were stable in air for short periods but the formation of a brown coating was observed on prolonged exposure. All common organic solvents readily dissolved the crystals to form blue-green solutions which were very air sensitive, turning brown after only a few minutes exposure. The crystals melted in a sealed tube at 94^o.

Analysis: Found, C,46·51; H,4·04; N,2·96; $C_{18}H_{19}NO_2W$ requires C,46·46; H,4·1; N,3·0%.

Infrared spectrum: The stretching frequencies ν_{CN} and ν_{CO} observed for the solid and solutions in hexane and cyclohexane are given in Table III.4. The solid (KBr) showed two strong (ν_{CO}) and one weak absorptions in the carbonyl region and extra bands were observed in the Nujol spectrum shown to be due to solution in Nujol by comparison with the solution spectra.

Table III.4

Infrared spectroscopic data for π-$C_5H_5W(CO)_2N{=}CPhBu^t$

Phase	ν_{CO}	ν_{CN}
KBr disc	1931vs, 1836vs, 1810wsh	1634m
Nujol mull	1951sh, 1929vs, 1869sh, 1835vs, 1808wsh	1634m-s
Hexane solution	1955vs, 1873vs	-
Cyclohexane solution	1958vs, 1875vs	-

Several bands due to π-C_5H_5* and phenyl† groups were observed in the spectra. The full spectrum (Nujol) is: Nujol, 1951sh, 1929vs, 1869sh, 1835vs, 1808wsh, 1634ms, 1587m†, 1493m, Nujol, 1445ms, 1437sh*, 1420m, Nujol, 1364m, 1263mw, 1222w, 1203m, 1157w, 1111w,br, 1073w, 1059ms, 1030m, 1012ms, 1006ms*, 992w, 964m, 910w, 844w*, 833m*, 817s, 792m, 732s, 702s†, 685w, 647m, 599w,br, 578m, 526m,br, 510m,br, 496ms, 472m,br cm^{-1}.

^{1}H n.m.r. spectrum in $CDCl_3$ solution showed signals at 8·80s, 4·04s and 2·59m τ due to Bu^t, π-C_5H_5 and Ph protons respectively. A good integration of the peaks was not obtained but indicated the presence of the groups in the expected ratio.

Molecular weight: Cryoscopic determination in cyclohexane gave a value for the molecular weight of 477 (theoretical 465).

Mass spectrum (direct insertion at source temperature): The parent ion $[\pi\text{-}C_5H_5W(CO)_2N{=}CPhBu^t]^+$ was observed centred at m/e 465; the isotopic distribution pattern corresponded to that computed for $C_{18}H_{19}NO_2W$. The major peaks observed in the spectrum are listed in Table III.5.

Table III.5

Mass spectroscopic data for $\pi\text{-}C_5H_5W(CO)_2N{=}CPhBu^t$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
465	36•1	$[\pi\text{-}C_5H_5W(CO)_2N{=}CPhBu^t]^+$	249	9•0	$[\pi\text{-}C_5H_5W]^+$
450	3•0	$[\pi\text{-}C_5H_5W(CO)_2N{=}C(Ph)CMe_2]^+$	184	5•3	$[W]^+$
437	3•8	$[\pi\text{-}C_5H_5W(CO)N{=}CPhBu^t]^+$	160	-	$[PhBu^tCN]^+$
409	45•1	$[\pi\text{-}C_5H_5WN{=}CPhBu^t]^+$	103	-	$[PhCN]^+$
352	12•0	$[\pi\text{-}C_5H_5WN{=}CPh]^+$	83	-	$[Bu^tCN]^+$
326	100•0	$[\pi\text{-}C_5H_5WPh]^+$	77	-	$[Ph]^+$
300	28•6	$[\pi\text{-}C_5H_5W(C_4H_3)]^+$?	65	-	$[C_5H_5]^+$

Many other organic ions were observed similar to those in the spectrum of $PhBu^tC{=}NH$ (Table III.1).

(iv) Reaction of $\pi\text{-}C_5H_5Mo(CO)_2N{=}CPhBu^t$ with Ph_3P

$\pi\text{-}C_5H_5Mo(CO)_2N{=}CPhBu^t$ (0•379 g., 1•0 mmole) and Ph_3P (0•262 g., 1•0 mmole) were dissolved in hexane (50 ml.) and the mixture heated to the reflux temperature. A slow evolution of gas was observed and the solution slowly assumed a green colouration. The reaction was shown by i.r. spectroscopy to be complete after 24 hr. The deep emerald green solution formed was separated by filtration from a small amount of brown solid (probably decomposition material) and the bulk of the filtrate reduced in volume (25°, 0•1 mm.Hg). On cooling to -20° a dark blue-green microcrystalline solid, π-$C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t$, was obtained which was separated by filtration, washed with hexane (2 x 5 ml.) and dried <u>in vacuo</u>. Yield 0•30 g. (50%).

<u>Properties</u>: The dark blue-green solid was quite air stable. It was only moderately soluble in hexane and cyclohexane, but very soluble in chloroform and benzene to give emerald green solutions which rapidly turned brown on exposure to air. The solid melted at 118-120°.

<u>Infrared spectrum</u>: The solid gave a deep emerald green mull with Nujol and the spectrum of the mull and also that of a KBr disc showed a single very strong absorption at 1802 cm^{-1} (ν_{CO}) and a medium-strong absorption at 1547 cm^{-1} (ν_{CN}). The position of the carbonyl absorption in solution was very dependent upon the solvent; in chloroform 1802 cm^{-1}, in ether 1836 cm^{-1}, and in hexane at 1845 cm^{-1}. The full Nujol spectrum is: 3067w, Nujol, 1802vs, 1757w, 1593w†, 1576w, 1547m-s, 1481sh, Nujol, 1439s, 1364m, 1311w, 1262w, 1215w, 1193m, 1155w, 1111w, 1089s, 1026m, 1014m, 1000m*, 962w, 823w*, 812m*, 789s, 754s, 741s, 703sh, 695s†, 683sh, 643m, 567m, 551m, 524s, 516s, 503s, 491m, 471w,br cm^{-1}. The absorptions at 1481, 1089, 754 and 741 cm^{-1} were due to the Ph_3P ligand by comparison with the spectrum of the free ligand.

<u>^1H n.m.r. spectrum</u> in $CDCl_3$ solution showed signals at 8•79s(9), 4•61s(5), 3•08m(15) and 2•70m(5) τ due to Bu^t protons, π-C_5H_5 protons, Ph protons (Ph_3P) and Ph protons (methyleneamino-groups) respectively.

<u>Mass spectrum</u> (direct insertion at source temperature): The parent ion $[\pi\text{-}C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t]^+$ was observed centred at m/e 613; the isotopic distribution pattern corresponded to that computed for $C_{35}H_{34}MoNOP$. The major peaks observed in the spectrum are listed in Table III.6.

<u>Analysis</u>: Found, C,68•75; H,5•71; N,2•12; $C_{35}H_{34}MoNOP$ requires C,68•5; H,5•55; N,2•23%.

Table III.6

Mass spectroscopic data for π-$C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t$

m/e	Relative intensity	Assignment	
613	24·4	$[\pi\text{-}C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t]^+$	m* 558
585	24·4	$[\pi\text{-}C_5H_5Mo(Ph_3P)N{=}CPhBu^t]^+$	m* 476
528	0·7	$[\pi\text{-}C_5H_5Mo(Ph_3P)N{=}CPh]^+$	
598	0·7	$[\pi\text{-}C_5H_5Mo(CO)(Ph_3P)N{=}C(Ph)CMe_2]^+$	
570	0·7	$[\pi\text{-}C_5H_5Mo(PH_3P)N{=}C(Ph)CMe_2]^+$	
425	23·4	$[\pi\text{-}C_5H_5MoPh_3P]^+$	
346	17·6	$[\pi\text{-}C_5H_5Mo(C_6H_3)_2P]^+$	
323	21·9	$[\pi\text{-}C_5H_5MoN{=}CPhBu^t]^+$	
317	24·4	$[\pi\text{-}C_5H_5MoPh_2]^+$	
262	-	$[Ph_3P]^+$	
240	100·0	$[\pi\text{-}C_5H_5MoPh]$	
185	-	$[Ph_2P]^+$	
183	-	$[(C_6H_4)_2P]^+$	
163	8·3	$[\pi\text{-}C_5H_5Mo]$	
108	-	$[PhP]^+$	
104	-	$[PhCNH]^+$	
103	-	$[PhCN]^+$	
98	1·7	$[Mo]^+$	
83	-	$[Bu^tCN]^+$	
77	-	$[Ph]^+$	
65	-	$[C_5H_5]^+$	
57	-	$[Bu^t]^+$	

(v) Reaction of π-$C_5H_5W(CO)_2N{=}CPhBu^t$ with Ph_3P

Due to lack of a sufficient quantity of the pure crystalline complex π-$C_5H_5W(CO)_2N{=}CPhBu^t$, this reaction was performed using a sample of the impure emerald green oil which contained a small quantity of the dissolved dimer $[\pi$-$C_5H_5W(CO)_3]_2$. The impure π-$C_5H_5W(CO)_2N{=}CPhBu^t$ (0•4 g., ~0•84 mmole) and Ph_3P (0•23 g., 0•84 mmole) were dissolved in hexane (70 ml.) and heated to the reflux temperature. No reaction was detected by i.r. spectroscopy in the carbonyl stretching region after 22 hr. The solvent was removed (25°, 0•1 mm.Hg), replaced by monoglyme (50 ml.) and heated to the reflux temperature. No reaction was detected by i.r. spectroscopy after 15 hr.

(vi) Reaction of π-$C_5H_5Mo(CO)_2N{=}CPhBu^t$ with I_2

The molybdenum complex (0•19 g., 0•5 mmole) was dissolved in hexane (10 ml.) and the solution cooled in an ice bath. A solution of iodine (0•127 g., 0•1 mmole) in hexane (200 ml.) cooled also in an ice bath was added dropwise over about 1 hr. with vigorous stirring. A rapid reaction occurred with the formation of a dark coloured precipitate. The mixture was stirred for 1 hr. after the addition and the very dark brown complex, π-$C_5H_5Mo(CO)I_2(N{=}CPhBu^t)$, separated by filtration and dried in vacuo. The yield was almost quantitative.

Properties: The dark brown solid appeared to be quite air sensitive. The solid was insoluble in hexane but very soluble in chloroform. On heating in a sealed tube it decomposed without melting at 79°.

Analysis: Found, C,34•0; H,3•36; I,41•4; N,2•13; $C_{17}H_{19}I_2MoNO$ requires C,33•7; H,3•14; I,41•98; N,2•31%.

Infrared spectrum: Both a Nujol mull and a chloroform solution spectrum showed a single strong absorption in the carbonyl region at 2041 cm^{-1}; a weak shoulder was observed in the Nujol spectrum at 2000 cm^{-1}. A very weak broad absorption at 1660 cm^{-1} was assigned to ν_{CN}. After 48 hr. under nitrogen, a fresh mull of the aged solid showed a weakened carbonyl absorption and the appearance of another weak broad absorption at 1623 cm^{-1}, indicating the compound was thermally unstable even at ambient temperature. The full Nujol spectrum is: 3077w, 3058sh, Nujol, 2041s, 2000w,sh, 1660vw,br, 1599w†, 1581w, Nujol, 1415m, Nujol, 1365s, 1259w, 1222w, 1200m-s, 1159w, 1075m, 1065m, 1029m, 1015m, 1000mw*, 995mw, 960m, 885w, 836s*, 826sh*, 788m, 730s, 699s†, 647m, 593w, 572m, 508m-s, 466m-s,br cm^{-1}.

^{1}H n.m.r. spectrum in $CDCl_3$ solution showed a number of signals which varied in intensity with change in temperature. The τ values for the signals observed at +40° and -40° are given in Table III.7.

Table III.7

^{1}H n.m.r. spectroscopic data (τ values) for π-$C_5H_5Mo(CO)I_2(N{=}CPhBu^t)$

Ph protons	π-C_5H_5 protons	Bu^t protons	Temperature
2•29s; 2•61w	4•44	8•45s; 8•71w	-40°
2•38w; 2•62s	4•56	8•44w; 8•68s	+40°
-	5•78	-	+40° (after few hr.)

(s = strong; w = weak)

Mass spectrum (direct insertion at 100°): The parent ion $[\pi\text{-}C_5H_5Mo(CO)I_2(N{=}CPhBu^t)]^+$ was not observed even with a cool source temperature. The ion of highest mass observed corresponded to $[\pi\text{-}C_5H_5MoI_2(N{=}CPhBu^t)]^+$, centred at m/e 587 and having an isotopic distribution pattern corresponding to that computed for $C_{16}H_{19}I_2MoN$. The major peaks observed in the spectrum are listed in Table III.8.

Table III.8

Mass spectroscopic data for π-$C_5H_5Mo(CO)I_2(N{=}CPhBu^t)$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
577	44•0	$[\pi\text{-}C_5H_5MoI_2(N{=}CPhBu^t)]^+$	127	-	$[I]^+$
520	12•1	$[\pi\text{-}C_5H_5MoI_2(N{=}CPh)]^+$	105	-	$[PhCHNH]^+$
417	62•6	$[\pi\text{-}C_5H_5MoI_2]^+$	104	-	$[PhCNH]^+$
290	100•0	$[\pi\text{-}C_5H_5MoI]^+$	103	-	$[PhCN]^+$
163	33•0	$[\pi\text{-}C_5H_5Mo]^+$	77	-	$[Ph]^+$
161	-	$[PhBu^tC{=}NH]^+$	65	-	$[C_5H_5]^+$
128	-	$[HI]^+$	57	-	$[Bu^t]^+$

(vii) Reaction of π-$C_5H_5W(CO)_2N{=}CPhBu^t$ with I_2

The reaction was performed in a similar manner to (vi) using solutions of π-$C_5H_5W(CO)_2N{=}CPhBu^t$ (0•133 g., 0•36 mmole) in hexane (10 ml.) and iodine (0•073 g., 0•36 mmole) in hexane (100 ml.) cooled in an ice bath. A rapid reaction occurred with the formation of a grey-black solid which was separated by filtration, washed with hexane (3 x 10 ml.) and dried in vacuo. The yield of the complex, π-$C_5H_5W(CO)I_2(N{=}CPhBu^t)$, was almost quantitative.

Properties: The grey-black solid was quite air stable, a sample exposed to air for a few days showed virtually no change in its i.r. spectrum; on prolonged exposure (one week) the solid attained a greenish tinge and appeared to be forming a non-carbonyl product. The solid was insoluble in hexane but very soluble in chloroform. On heating in a sealed tube it decomposed without melting at 110°.

Analysis: Found, C,29•8; H,2•70; I,36•6; N,1•87; $C_{17}H_{19}I_2NOW$ requires C,29•52; H,2•81; I,36•76; N,2•03%.

Infrared spectrum: The solid gave a black mull with Nujol and the spectrum showed a single strong absorption in the carbonyl region at 2016 cm^{-1} (ν_{CO}); a solution in chloroform showed this absorption at 2031 cm^{-1}. The assignment of a ν_{CN} absorption was more difficult, weak and very broad absorptions occurring in the 1600-1700 cm^{-1} region. A weak broad absorption at 1667 cm^{-1} was tentatively assigned to ν_{CN} by analogy with the corresponding molybdenum complex. The Nujol spectrum is: 3077m, Nujol, 2016vs, 1667w,br, 1623w,br, 1592w†, Nujol, 1410m, Nujol, 1261w, 1218sh, 1199m, 1182sh, 1159w, 1027w, 1013m-w, 1001w*, 990w, 962w, 843sh*, 833ms*, 786m-w, 697m-s†, 652w, 643w, 590vw, 571w,br, 522m,br, 480m-w,br cm^{-1}.

^{1}H n.m.r. spectrum in $CDCl_3$ showed single signals for Bu^t protons (singlet), π-C_5H_5 protons (singlet) and Ph protons (multiplet) whose positions remained fairly constant over a range of temperature. The data obtained is given in Table III.9. A good integration of the peaks was not obtained but appeared to indicate the groups in the expected ratio.

Table III.9

^{1}H n.m.r. spectroscopic data (τ values)
for π-$C_5H_5W(CO)I_2(N{=}CPhBu^t)$ in $CDCl_3$ solution

Ph protons	π-C_5H_5 protons	Bu^t protons	Temperature
2•44	4•42	8•66	-40°
2•57	4•50	8•67	-20°
2•51	4•48	8•63	0°
2•55	4•57	8•69	+20°
-	5•46	8•61vw	+40°

Mass spectrum (direct insertion at 100°): The parent ion $[\pi\text{-}C_5H_5W(CO)I_2(N{=}CPhBu^t)]^+$ was not observed even with a cool source temperature. The ion of highest mass was observed centred at m/e 663, corresponding to $[\pi\text{-}C_5H_5WI_2(N{=}CPhBu^t)]^+$ and having the isotopic distribution pattern corresponding to that computed for $C_{16}H_{19}I_2NW$. The major peaks observed in the spectrum are listed in Table III.10.

Table III.10

Mass spectroscopic data for $\pi\text{-}C_5H_5W(CO)I_2(N{=}CPhBu^t)$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
663	8·0	$[\pi\text{-}C_5H_5WI_2(N{=}CPhBu^t)]^+$	265	31·9	W_1 species; unassigned
648	7·2	$[\pi\text{-}C_5H_5WI_2(N{=}CPh.CMe_2)]^+$	161	-	$[PhBu^tCNH]^+$
606	23·2	$[\pi\text{-}C_5H_5WI_2(N{=}CPh)]^+$	160	-	$[PhBu^tCN]^+$
558	3·0	$[\pi\text{-}C_5H_5WI_2(C_4H_7)]^+$?	146	-	$[PhBu^tC]^+$
543	2·8	$[\pi\text{-}C_5H_5WI_2(C_3H_4)]^+$?	128	-	$[HI]^+$
517	47·8	$[\pi\text{-}C_5H_5WI_2(CH_2)]^+$?	127	-	$[I]^+$
503	65·2	$[\pi\text{-}C_5H_5WI_2]^+$	103	-	$[PhCN]^+$
392	53·6	$[(\pi\text{-}C_5H_5)_2WPhH]^+$?	77	-	$[Ph]^+$
376	100·0	$[\pi\text{-}C_5H_5WI]$	65	-	$[C_5H_5]^+$
350	31·9	W_1 species; unassigned	57	-	$[Bu^t]^+$

(viii) Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ with $PhBu^tC{=}NSiMe_3$

$PhBu^tC{=}NSiMe_3$ (1·24 g., 5·3 mmoles) and $\pi\text{-}C_5H_5Mo(CO)_3Cl$ (1·50 g., 5·3 mmoles) were dissolved in monoglyme (100 ml.) and the temperature raised to 70°. The solution darkened at ~60° and evolution of gas was observed. The reaction was shown by i.r. spectroscopy to be complete after 2½ hr. when a dark red solution was observed. The solution was filtered, leaving a small amount of dark brown decomposition material on the filter, and the solvent removed (25°, 0•1 mm.Hg) to leave a dark red solid which was dissolved in toluene (30 ml.). Addition of hexane (10 ml.) and cooling to -20° produced dark red crystals. Recrystallisation of the product from toluene/hexane mixtures gave dark red crystals of π-$C_5H_5Mo(CO)_2(HN{=}CPhBu^t)Cl$ (0•68 g., 31% yield).

Properties: The deep red crystals were air stable even on prolonged exposure. The crystals were insoluble in hexane and cyclohexane; soluble in benzene, toluene and chloroform forming red solutions which were also air stable. On heating it decomposed at 126-8°.

Analysis: Found, C,52•44; H,4•95; Cl,8•67; N,3•25; $C_{18}H_{20}ClMoNO_2$ requires C,52•1; H,4•82; Cl,8•44; N,3•37%.

Infrared spectrum: ν_{CO}, 1951vs, 1845vs, 1818w,sh cm^{-1} (Nujol); ν_{CN}, 1618m cm^{-1}, ν_{NH}, 3252m cm^{-1}. A chloroform solution showed ν_{CO}, 1970vs, 1876vs; ν_{CN} 1618w; ν_{NH}, 3245w,br cm^{-1}. The full Nujol spectrum is: 3252m, 3125w, 3086w*, Nujol, 1951vs, 1845vs, 1818sh, 1618m, 1602m†, Nujol, 1422m, Nujol, 1368sh, 1361sh, 1244m, 1190w, 1183sh, 1159w, 1075w, 1068m, 960w, 935w, 909w, 845w, 835w*, 829s, 820s*, 774m, 714s, 627vw,br 590w,br 572m, 542m, 510m,br cm^{-1}.

^1H n.m.r. spectrum in deuterobenzene solution: 9•27s(9), 5•31s(5) and 3•00m(5) τ due to Bu^t, π-C_5H_5 and Ph protons respectively. No signal due to the N-H proton was detected probably due to the moderate solubility of the compound in deuterobenzene.

Molecular weight: Osmometric determinations in chloroform and benzene solutions gave values of 402 and 385 respectively (theoretical 415). Cryoscopic determinations in benzene gave anomalous values probably due to moderate solubility of the solid in this solvent and the resultant separation of solid at or near the freezing point.

Mass spectrum (direct insertion at 80^o): Even at low source temperatures the parent ion $[\pi\text{-}C_5H_5Mo(CO)_2(HN{=}CPhBu^t)Cl]^+$ was not observed. The ion at highest mass was observed centred at m/e 359 corresponding to $[\pi\text{-}C_5H_5Mo(HN{=}CPhBu^t)Cl]^+$; the isotopic distribution pattern corresponded to that computed for $C_{16}H_{20}ClMoN$. The major peaks observed are listed in Table III.11.

Table III.11

Mass spectroscopic data for $\pi\text{-}C_5H_5Mo(CO)_2(HN{=}CPhBu^t)Cl$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
359	44•7	$[\pi\text{-}C_5H_5Mo(HN{=}CPhBu^t)Cl]^+$	146	-	$[PhBu^tC]^+$
240	29•5	$[\pi\text{-}C_5H_5MoPh]^+$	104	-	$[PhCNH]^+$
228	32•4	$[(\pi\text{-}C_5H_5)_2Mo]^+$	103	-	$[PhCN]^+$
198	100•0	$[\pi\text{-}C_5H_5MoCl]$	98	18•1	$[Mo]^+$
163	15•2	$[\pi\text{-}C_5H_5Mo]^+$	77	-	$[Ph]^+$
161	-	$[PhBu^tCNH]^+$	65	-	$[C_5H_5]^+$
160	-	$[PhBu^tCN]^+$	57	-	$[Bu^t]$

(ix) Reaction of $\pi\text{-}C_5H_5Mo(CO)_3Cl$ with $PhBu^tC{=}NH$

$\pi\text{-}C_5H_5Mo(CO)_3Cl$ (0•5 g., 1•78 mmole) and $PhBu^tC{=}NH$ (0•288 g., 1•78 mmole) in chloroform (50 ml.) were heated at 70^o. Darkening of the solution occurred and evolution of gas was observed. After 3 hr. no further decrease in the amount of chloride was observed by i.r. spectroscopy and the heating was stopped. The solution was filtered to remove a small amount of decomposition material, the solvent removed (25^{o}, 0•1 mm.Hg) and the residual dark red solid dissolved in toluene (30 ml.). Addition of hexane (10 ml.) and cooling to -20^{o} caused the separation of π-$C_5H_5Mo(CO)_2(HN{=}CPhBu^t)Cl$ (0•1 g.). The product was shown by i.r. spectroscopy and elemental analysis to be identical with the product from (viii). [Found, C,52•39; H,5•13; Cl,8•39; N,3•36; $C_{18}H_{20}ClMoNO_2$ requires C,52•1; H,4•82, Cl,8•44; N,3•37%]. Further crops of solid mixed with unreacted chloride were obtained from the mother liquor. A similar reaction was performed in toluene and gave the same dark red crystals.

(x) Reaction of π-$C_5H_5W(CO)_3Cl$ with $PhBu^tC{=}NSiMe_3$

$PhBu^tC{=}NSiMe_3$ (1•286 g., 5•52 mmole) and π-$C_5H_5W(CO)_3Cl$ (2•03 g., 5•52 mmole) in monoglyme (100 ml.) were heated to 70^{o}. The reaction mixture darkened quickly at this temperature and attained a greenish colour. After 5½ hr. no further changes was detected in the i.r. spectrum of the mixture. The greenish solution was filtered and the solvent removed (25^{o}, 0•1 mm.Hg) leaving a dark solid residue. Extraction with hexane (4 x 10 ml.) produced an intense deep blue-green solution which, on reducing to small bulk and cooling, resulted in the separation of a green viscous oil and a supernatant blue solution. The residual orange-red material after hexane extraction was found by i.r. spectroscopy to be largely $[\pi\text{-}C_5H_5W(CO)_3]_2$ with some unreacted chloride. The clear blue solution was syringed from the oil and on cooling to -20^{o} deposited dark blue crystals of the complex π-$C_5H_5W(CO)_2N{=}CPhBu^t$, identified by its i.r. spectrum. Yield 0•15 g. (6%).

3. Discussion

(i) $PhBu^tC{=}NH$: This compound was obtained in good yield by the standard reaction of a Grignard reagent with a nitrile[36] with the modification described in section 2A of this chapter. It is a colourless liquid, which slowly hydrolyses in moist air, and appears to be a typical alkylarylmethyleneamine in all respects. Features of the i.r. and ^1H n.m.r. spectra are given in Table III.12 together with the relevant data for $Ph_2C{=}NH$ and $Bu^t{}_2C{=}NH$.

Table III.12

Spectroscopic data for $Ph_2C{=}NH$, $PhBu^tC{=}NH$ and $Bu^t{}_2C{=}NH$

Compound	i.r. spectrum (cm^{-1})(liq. film)		^1H n.m.r. data (τ values)		
	ν_{CN}	ν_{NH}	Ph	Bu^t	=N-H
$Ph_2C{=}NH$[129]	1603	3236	2·4(4)br; 2·7(6)m	-	0·04(1)s*
$PhBu^tC{=}NH$	1618	3226	2·79(5)s	8·81(9)s	0·09s,br†
$Bu^t{}_2C{=}NH$[130]	1610		-	8·70(18)s	6·6(1)s,br†

† CCl_4 solution; * C_6D_6 solution; s = singlet; m = multiplet; br = broad relative intensities in parentheses.

ν_{CN} and ν_{NH} occur in regions typical of such methyleneamines - see Table II.2. The ^1H n.m.r. spectrum shows single signals for both phenyl and t-butyl protons; no sign of the splitting of the phenyl protons into meta and ortho/para sets was observed.[50,129] The N-H proton was observed as a weak broad signal at low field, the broadness of the signal being caused by the electrical quadrupole moment of the nitrogen nucleus (I = 1).

(ii) PhBu^{t}C=NSiMe$_3$ was obtained by a standard method[54] in good yield. It appeared to be a typical compound of its type, pale yellow in colour and quite moisture sensitive. Its i.r. and ^{1}H n.m.r. spectroscopic data are compared with those of Ph$_2$C=NSiMe$_3$ and Bu^t$_2$C=NSiMe$_3$ in Table III.13.

Table III.13

Spectroscopic data for Ph$_2$C=NSiMe$_3$, PhBu^{t}C=NSiMe$_3$ and Bu^t$_2$C=NSiMe$_3$

Compound	ν_{CN} (cm^{-1}) (liq.film)	^{1}H n.m.r. data (τ values)		
		Ph	Bu^t	SiMe$_3$
Ph$_2$C=NSiMe$_3$	1642[54]	2·66 m	-	10·03 s
PhBu^{t}C=NSiMe$_3$	1678	2•73(3)m; 3•02(2)m	8·55(9)s	10•16(9)s
Bu^t$_2$C=NSiMe$_3$[130]	1733	-	8•72(2)s; 8•87(4)s	9•82(3)s

CDCl$_3$ solutions; s = singlet; m = multiplet; br = broad; relative intensities in parentheses.

The signal due to -SiMe$_3$ protons in PhBu^{t}C=NSiMe$_3$ appeared at 10•16τ slightly higher than the reported position for the other compound. The phenyl protons appeared as two multiplets at 2•73(3) and 3•03(2)τ due to splitting into meta and ortho/para sets.[50,129] The ν_{CN} absorption appeared in a position intermediate between those of the corresponding diphenyl- and di-t-butyl-compounds.

The mass spectrum of PhBu^{t}C=NSiMe$_3$ showed no sign of the parent ion; the peak of highest mass was observed at m/e 218 corresponding to [PhBu^{t}C=NSiMe$_2$]$^+$ or [PhC(CMe$_2$)=NSiMe$_3$]$^+$. A similar phenomenon was observed in the mass spectrum of Bu^t$_2$C=NSiMe$_3$.[130]

(iii) The dicarbonyl complexes π-$C_5H_5M(CO)_2N{=}CPhBu^t$, [M = Mo,W]: The reaction of π-$C_5H_5Mo(CO)_3Cl_5$ with $PhBu^tC{=}NLi$ and the reaction of π-$C_5H_5W(CO)_3Cl$ with $PhBu^tC{=}NSiMe_3$ produced complexes of the type π-$C_5H_5M(CO)_2N{=}CPhBu^t$ and closely resembled the corresponding reaction with $Bu^t{}_2C{=}NLi$ and $Bu^t{}_2C{=}NSiMe_3$ which produced analogous di-t-butylmethyleneamino-complexes.[19] In contrast $Ph_2C{=}NLi$ produced dicarbonyl complexes containing the 2-aza-allyl ligand Ph_2CNCPh_2.[21,23] The diphenylmethyleneamino-complexes π-$C_5H_5M(CO)_2N{=}CPh_2$ were formed only by reacting the chlorides with $Ph_2C{=}NSiMe_3$ under controlled conditions and were converted by heat to the dinuclear complexes $[\pi$-$C_5H_5M(CO)N{=}CPh_2]_2$ by loss of carbon monoxide.[21]

No evidence was found in this work for the formation of complexes containing the 2-aza-allyl ligand $PhBu^tCNCBu^tPh$, and the dicarbonyl complexes obtained showed no tendency on heating to form dinuclear complexes, sublimation of the complex occurring under these conditions. In these respects there was a close resemblance to the di-t-butylmethyleneamino-complexes which was also reflected in many of their properties. A comparison of some physical properties of the various Mo complexes is given in Table III.14.

The complexes were formulated as π-$C_5H_5M(CO)_2N{=}CPhBu^t$ on the basis of considerable evidence. Analysis confirmed the empirical formula $C_{18}H_{19}MNO_2$ and cryoscopic determination of molecular weights suggested a mononuclear species. The presence of two strong absorptions in the carbonyl region of the infrared spectra at relatively low frequencies (Table III.15) indicates a dicarbonyl complex in which the methyleneamino-ligand acts as a three electron donor to the metal. The presence of a third weak carbonyl absorption in the spectra was probably due to a satellite ^{13}C ν_{CO} absorption.[131] The ν_{CN} absorptions were observed as medium-strong bands which were moved to only

Table III.14

Physical properties of methyleneamino-complexes of Mo

Compound	Appearance	m.p.	Action of heat	Solubility in hexane
π-$C_5H_5Mo(CO)_2N=CPh_2$[21]	Brown powder	150-155° (decomp)	Forms dinuclear complex	Insoluble
π-$C_5H_5Mo(CO)_2N=CPhBu^t$	Blue Crystals	63-4°	Sublimes	V.soluble
π-$C_5H_5Mo(CO)_2N=CBu^t_2$[19]	Blue Crystals	106-7°	Sublimes	V.soluble

Table III.15

Infrared absorptions, ν_{CO} and ν_{CN}, for methyleneamino-complexes (cm^{-1})

Compound	ν_{CO} (KBr)	ν_{CO} (Nujol)	ν_{CN} (Nujol)
π-$C_5H_5Mo(CO)_2N=CPh_2$[21]	-	1920s,1856s,	1534m
π-$C_5H_5W(CO)_2N=CPh_2$[21]	-	1942s,1873s	1587m
π-$C_5H_5Mo(CO)_2N=CPhBu^t$	1942s,1855s,1825w	1965sh, 1940s, 1881sh,1846s, 1821w	1636m-s
π-$C_5H_5W(CO)_2N=CPhBu^t$	1931s,1836s,1810w	1951sh,1929s, 1869sh,1835s, 1808w	1634m-s
π-$C_5H_5Mo(CO)_2N=CBu^t_2$[19]	1946s,1848s	1968s,1949s, 1884s,1851s	1618m-w
π-$C_5H_5W(CO)_2N=CBu^t_2$[19]	1934s,1834s	1946sh,1929s, 1866sh,1833s	1620m-w

slightly higher energy than in the free methyleneamine. This indicated that the formation of the σ- and (pπ-dπ) N ⟶ M bonding which results in electron donation to the metal is effectively balanced by the back donation via dπ-π* bonding. In general the ν_{CO} and ν_{CN} absorptions of the complexes show close similarity to those of the corresponding di-t-butylmethyleneamino-complexes (Table III.15). Both series of complexes are extremely soluble in hydrocarbon solvents and this produced absorptions in the Nujol spectra due to solution of the complexes. The i.r. spectra also showed bands characteristic of π-C_5H_5 and phenyl groups, no ν_{NH} absorption was observed.

The positions and intensities of the ν_{CO} absorptions of a hexane solution of the Mo complex showed no variations over a range of temperature -40^o to $+50^o$ and this was also observed for a benzene solution of the complex from room temperature down to the freezing point of benzene. In this respect the complex differed from the di-t-butylmethyleneamino-Mo complex where two new lower frequency absorptions gradually replaced the original absorptions on cooling to -45^o, the change being completely reversible. This phenomenon was interpreted as possibly indicating rotational changes about the M-N bond of the linear M-N=C skeleton.[19]

The mass spectra of the complexes confirmed the mononuclear formulation and the presence of two carbonyl groups per molecule. In both cases the parent ions were observed with isotopic distribution patterns corresponding to those computed for $C_{18}H_{19}MNO_2$. The spectra of the complexes showed the presence of metal containing ionic species of identical types as well as the expected organic ions resulting from fragmentation of the methyleneamino-group (Tables III.3 and III.5). The tungsten complex also showed the presence of a W_1 species which appeared to correspond to the ion $[\pi\text{-}C_5H_5W(CO)_2N{=}C(Ph)CMe_2]^+$ i.e. $[P\text{-}CH_3]^+$.

The ^{1}H n.m.r. spectra of the complexes showed single signals for Bu^t, π-C_5H_5 and Ph protons in positions typical of such groups. The ^{1}H n.m.r. data for the various methyleneamino-complexes and the free methyleneamines is given in Table III.16

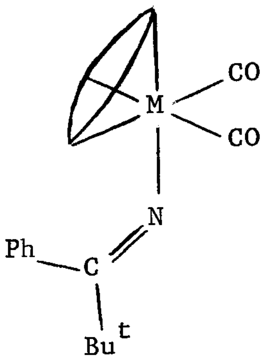
Table III.16

^{1}H n.m.r. data for methyleneamino-complex (τ values)

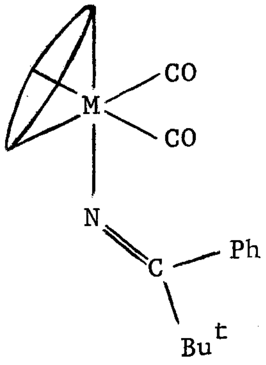
Compound	Ph	π-C_5H_5	Bu^t	N-H
$Ph_2C{=}NH$[129]	2•4; 2•73	-	-	0•04
π-$C_5H_5Mo(CO)_2N{=}CPh_2$[21]	2•48	5•05; 5•11	-	-
π-$C_5H_5W(CO)_2N{=}CPh_2$[21]	2•63	4•02	-	-
$PhBu^tC{=}NH$ *	2•75	-	8•81	0•96
π-$C_5H_5Mo(CO)_2N{=}CPhBu^t$	2•58	4•17	8•80	-
π-$C_5H_5W(CO)_2N{=}CPhBu^t$	2•59	4•04	8•80	-
$Bu^t{}_2C{=}NH$ [130]	-	-	8•70	6•6
π-$C_5H_5Mo(CO)_2N{=}CBu^t{}_2$ [19]	-	4•65	8•93	-
π-$C_5H_5W(CO)_2N{=}CBu^t{}_2$ [19]	-	4•55	8•88	-

* CCl_4 solution, all others in $CDCl_3$ solution

The crystal structure of π-$C_5H_5Mo(CO)_2N{=}CBu^t{}_2$[20] showed the presence of an almost linear M-N=C skeleton and the various spectral changes observed for this complex have been interpreted in terms of conformational changes about this linear unit.[20] No crystal structure data is available for the phenyl-t-butylmethyleneamino-complexes described here so the question of the bonding mode of this methyleneamino-group to the metals remains open to speculation as the data on the complexes could be interpreted in terms of either a linear or a bent skeleton. Assuming a bent skeleton, it is most likely that the methyleneamino-group will take up a position with the bulky t-butyl group at the greatest possible distance from the other groups attached to the metal atom i.e. I or II



I



II

The $p\pi$-$d\pi$ $N \rightleftharpoons M$ interaction with such a non-linear skeleton would be somewhat reduced compared with the linear form (see Figs.I.1(b) and I.2) but the overall steric interaction between the various groups would be reduced in the bent form. The structure adopted will undoubtedly be a compromise between achieving the strongest bonding between the metal and nitrogen (i.e. linear skeleton) and relieving steric interactions between bulky groups (i.e. bent skeleton). Thus a bent skeleton is to be expected with a M-N-C bond angle much greater than 120^{o} (sp^{2} nitrogen) but less than 180^{o} (sp nitrogen). Free rotation of the methyleneamino-group is possible because of the π-cylindrical symmetry of the metal orbitals, but for the PhBu^{t}C=N- group the barrier to rotation should be considerably less than that for the Bu$^{t}_{2}$C=N- group because of considerably less steric hindrance arising from the presence of only one Bu^{t} group, and the consequent increased ability of the M-N-C skeleton to become non-linear. Thus any spectral changes which are likely to result from conformational changes may only be detectable at much lower temperatures than those studied in this work.

(iv) The dicarbonyl complex π-$C_5H_5Mo(CO)_2(HN{=}CPhBu^t)Cl$: This complex was surprisingly formed in the reaction of π-$C_5H_5Mo(CO)_3Cl$ with $PhBu^tC{=}NSiMe_3$. Instead of the expected metathetical process occurring with elimination of Me_3SiCl and the formation of the complex π-$C_5H_5M(CO)_2N{=}CPhBu^t$ (as occurred with π-$C_5H_5W(CO)_3Cl$ and $PhBu^tC{=}NSiMe_3$), the complex containing the neutral methyleneamino-ligand resulted, the extra proton on the ligand presumably resulting from abstraction from the solvent. The identical complex was also formed from the reaction of π-$C_5H_5Mo(CO)_3Cl$ with the free methyleneamine in chloroform and toluene solutions.

The data obtained for the complex was in agreement with the stated formulation as a dicarbonyl complex containing the neutral methyleneamino-ligand as a two electron donor. Analysis confirmed the empirical formula $C_{18}H_{20}ClMoNO_2$ and molecular weight determinations indicated a mononuclear complex. The infrared spectrum showed two strong absorptions (ν_{CO}) at 1951 and 1845 cm^{-1}, (as well as a weak absorption at 1818 cm^{-1} assigned to a satellite ^{13}C ν_{CO} absorption[131]). Medium strong absorptions at 1618 cm^{-1} (ν_{CN}) and 3252 cm^{-1} (ν_{NH}) were also observed as well as absorptions typical of π-C_5H_5 and Ph groups. The carbonyl absorptions appeared in very similar positions to those of the complex π-$C_5H_5Mo(CO)_2N{=}CPhBu^t$ [ν_{CO} 1940s, 1846s, 1821w cm^{-1} (Nujol)] and the ν_{CN} absorption was identical with that of the free methyleneamine, suggesting that the N $\longrightarrow$ M σ-bonding was balanced by M $\longrightarrow$ N $d\pi$-π^* back bonding. The bonding mode of the neutral ligand is assumed to be similar to that shown in Fig.I.1(a).

The complex was found to be air stable even on prolonged exposure, as too were solutions in organic solvents. On heating, the complex underwent decomposition; on heating in vacuo a red oil was obtained as a sublimate and the i.r. spectrum of this oil indicated the presence of free $PhBu^tC{=}NH$ and also showed absorptions in the carbonyl region. Elimination of

HCl with the formation of the complex π-$C_5H_5Mo(CO)_2N{=}CPhBu^t$ was not achieved by heating.

(v) <u>The monocarbonyl complex π-$C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t$</u>: Reaction of the dicarbonyl complex π-$C_5H_5Mo(CO)_2N{=}CPhBu^t$ with Ph_3P in hexane produced the only complex of this type so far prepared in which simple substitution of CO by Ph_3P occurred. The corresponding reaction of the tungsten complex, however, did not give any indication of the formation of a corresponding tungsten complex. The corresponding diphenylmethyleneamino-complexes failed to react with Ph_3P[21] and the di-t-butylmethyleneamino-complexes reacted to form complexes in which the nature of the product depended on the solvent used (reference 19 and Fig.I.4) but in no case was simple substitution of CO by Ph_3P observed.

All the data obtained for the complex was in agreement with the formulation π-$C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t$. A single strong absorption, ν_{CO}, at 1802 cm^{-1} and a medium absorption, ν_{CN}, at 1547 cm^{-1} were observed in the i.r. spectrum (Nujol) as well as absorptions typical of π-C_5H_5 and Ph groups. The low frequencies of the ν_{CO} and ν_{CN} absorptions indicated that the Ph_3P ligand acted largely as a donor ligand and that M ⟶ P dπ-dπ back bonding occurred to only a very slight extent, if at all. The ^1H n.m.r. spectrum ($CDCl_3$ solution) showed signals for Bu^t, π-C_5H_5 and the two types of Ph group in positions typical of these groups. The signal due to the π-C_5H_5 protons was seen at a higher field ($4{\cdot}61\tau$) than that in the parent dicarbonyl complex ($4{\cdot}17\tau$) and this also reflects the limitations of the triphenylphosphine ligand to remove electron density from the metal atom.[132]

The mass spectrum showed the presence of the parent ion $[\pi\text{-}C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t]^+$ (m/e 613), consistent with the isotopic distribution pattern for $C_{35}H_{34}MoNOP$. The presence of two metastable peaks in the spectrum at m/e 558 and 476 confirmed the initial loss of carbon monoxide from the parent ion followed by further loss of a t-butyl fragment.

$$\begin{tikzcd}
{[\pi\text{-}C_5H_5Mo(CO)(Ph_3P)N{=}CPhBu^t]^+} \arrow[r, "-CO", "(m^{*}558)"'] & {[\pi\text{-}C_5H_5Mo(Ph_3P)N{=}CPhBu^t]^+} \\
613 & 585 \arrow[d, "\begin{array}{l}-Bu^t\\(m^{*}476)\end{array}"] \\
 & {[\pi\text{-}C_5H_5Mo(Ph_3P)N{=}CPh]^+} \\
 & 528
\end{tikzcd}$$

(vi) The monocarbonyl species π-$C_5H_5M(CO)I_2(N{=}CPhBu^t)$, [M = Mo,W]: Both the molybdenum and tungsten complexes were formed in very good yield by the rapid reaction of the dicarbonyl complexes with iodine in hexane solution at 0^o. In this respect there was considerable similarity to the di-t-butylmethyleneamino-complexes which similarly formed analogous monocarbonyl complexes. Reaction of the diphenylmethyleneamino-complexes π-$C_5H_5Mo(CO)_2N{=}CPh_2$, in contrast reacted with iodine in monoglyme solution to give the green complexes $[C_{15}H_{15}M_3I_3O_4]$.[21]

The complexes of the type π-$C_5H_5M(CO)I_2(N{=}CPhBu^t)$ were dark brown or black solids, insoluble in hexane but very soluble in chloroform, and on heating decomposed without melting. The molybdenum complex appeared to be air sensitive but the tungsten complex showed no change on standing in air for a few days; prolonged exposure did result in decomposition.

The data obtained for the complexes was in agreement with the stated formulation; analyses confirmed the empirical formula $C_{17}H_{19}MNO$ and the mass spectra confirmed a mononuclear species, although the parent ion was not observed for either complex even with cool source temperatures. This phenomenon has also been observed for the corresponding di-t-butylmethyleneamino-complexes.[19]

Co-ordination of the electronegative iodine atoms effectively decreases the electron density on the metal which increases σ- and pπ-dπ donation but reduces dπ-π* bonding to both carbonyl and methyleneamino-groups. This was reflected in the increase in frequency of the ν_{CO} and ν_{CN} absorptions in the i.r. spectra. The assignment of ν_{CN} absorptions was difficult as these absorptions are very weak and broad in these complexes.

Table III.17

Infrared spectroscopic data for

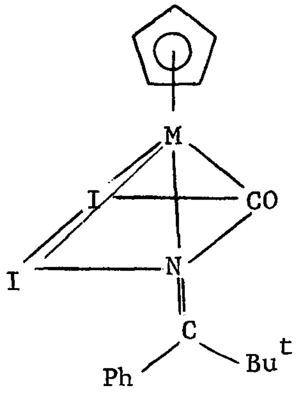
π-$C_5H_5M(CO)I_2(N{=}CPhBu^t)$ and π-$C_5H_5M(CO)I_2(N{=}CBu^t{}_2)$ complexes (cm^{-1})

Compound	ν_{CO}	ν_{CN}
π-$C_5H_5Mo(CO)I_2(N{=}CPhBu^t)$	2041s, 2000wsh	1660w,br
π-$C_5H_5W(CO)I_2(N{=}CPhBu^t)$	2016s	1667w,br
π-$C_5H_5Mo(CO)I_2(N{=}CBu^t{}_2)$	2027s	1639m-w,br
π-$C_5H_5W(CO)I_2(N{=}CBu^t{}_2)$	2000s, 1978sh	1644sh, 1640m

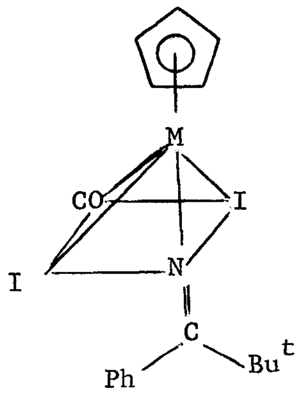
The ^1H n.m.r. data for the Mo complex showed two peaks for Bu^t and Ph protons. At -40° the Bu^t protons were observed as singlets at 8•45 and 8•71τ and the Ph protons as multiplets at 2•29 and 2•61τ, in both cases the downfield signals being much more intense than the upfield signals. As the temperature was raised the upfield signals gradually increased in intensity and at +40° the relative intensities had been progressively reversed. The signal due to the π-C_5H_5 protons remained fairly constant at 4•5τ over this temperature range. On standing at +40° for a few hours solid material separated out from solution and a single signal at 5•78τ was observed, presumably due to π-C_5H_5 protons in a new environment, the complex having decomposed in some way to remove the methyleneamino-group from solution.

The presence of two signals for both t-butyl and phenyl protons in the ^{1}H n.m.r. spectrum could be due to a number of causes. The increasing intensity of the upfield signals with increasing temperature followed by the final decomposition might be due to a gradual decomposition process in which the methyleneamino-group is cleaved from the complex, remains in solution in some form before being finally removed from solution on ageing at ambient temperature. This appears unlikely on two accounts; firstly, cleavage of the methyleneamino-group from the complex would be expected to affect the shielding of the π-C_5H_5 protons but a single cyclopentadienyl signal occurred at all temperatures. Secondly, only one carbonyl absorption was observed in the i.r. spectrum at ambient temperature under conditions when the complex ^{1}H n.m.r. spectrum was observed. Thus the change in form of the compound under study is such that the nature and bonding of the complex is little, if at all, changed.

Alternatively the spectral changes may be due to geometrical changes in the complex. Assuming a 9 co-ordinate structure various environments for the t-butyl and phenyl groups are possible depending on the bonding mode of the methyleneamino-group. Assuming a linear M-N-C skeleton, two geometrical arrangements may be possible, the <u>cis</u>-structure III and the <u>trans</u>-structure IV

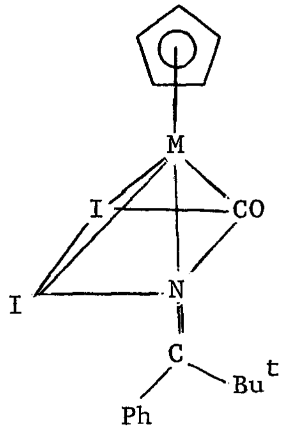


III

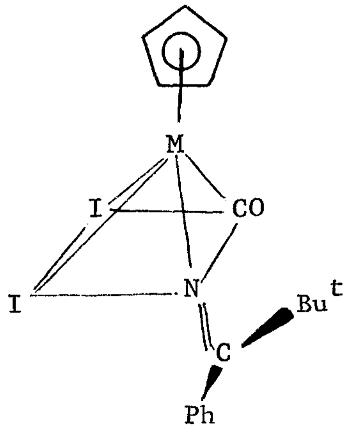


IV

The bulkiness of the Bu^t group would suggest that the cis structure III would be favoured because of its proximity to CO rather than the more bulky iodine. Rotation about the M-N axis in any of the geometrical isomers is probably unlikely under the conditions studied because of lack of metal d-orbitals available to constitute the π-cylindrical symmetry necessary for such rotation. Thus the conformation adopted will depend upon the spatial orientation of the metal orbital available for dπ-pπ bonding. Thus the plane of the methyleneamino-group may be in the positions shown (IIIa or IIIb), or in an intermediate position.



IIIa



IIIb

Alternatively, if the M-N-C skeleton is bent, the R-C-N angle to be reduced is expected for steric reasons to be the Ph-C-N angle. Again the conformation about the metal-nitrogen bond cannot be predicted.

The change in the ^1H n.m.r. spectrum can be interpreted in two ways (i) geometrical isomerism from structure III to IV (M-N-C skeleton may be linear or bent); (ii) 'syn-anti' type of isomerism involving a bent methyleneamino-group. Isomerism of the latter type is most likely for the geometrical arrangement III.

On the basis of the available data it is not possible to explain the spectral changes in terms of one of the two possibilities. Similar changes were observed for π-$C_5H_5Mo(CO)_2I_2(N{=}CBu^t{}_2)$ and a similar interpretation was suggested.[19]

The tungsten complex showed only single signals for the t-butyl and phenyl protons over a temperature range -40° to +20°, the t-butyl signal being initially at 8•66τ (-40°) but progressively moving to 8•69τ (+20°), the corresponding phenyl signals being at 2•44 and 2•55τ respectively. Again at +40° decomposition was observed leaving a single signal due to π-C_5H_5 protons at 5•46τ, this having moved upfield from the corresponding signal at lower temperatures (4•42τ at -40°, 4•57τ at +20°). It would appear that only one form of the complex is present under the conditions studied, probably corresponding to that of the higher temperature form of the molybdenum complex.

APPENDIX

EXPLORATORY INVESTIGATIONS ON THE DI-(TRIFLUOROMETHYL) METHYLENEAMINO-GROUP AS A LIGAND IN METAL CARBONYL SYSTEMS

Introduction

The purpose of this work was to obtain more information regarding the bonding mode of the methyleneamino-group in metal carbonyl complexes. The methyleneamino-complexes so far studied have raised interesting problems regarding the bonding mode but these problems have largely remained the subject of speculation due to lack of suitable data. The several possible bonding modes of the methyleneamino-group have been discussed in Chapter I. ^1H n.m.r. data could be a useful source of information regarding the actual bonding mode present. The diphenylmethyleneamino-complexes[21] provided little useful ^1H n.m.r. data due to the complex nature of the phenyl signals, and although the crystal structure of the di-t-butylmethyleneamino-complex π-$C_5H_5Mo(CO)_2N{=}CBu^t_2$ revealed an almost linear M-N-C skeleton,[20] this structure might well be favoured largely on the grounds of steric interactions. The data obtained for the phenyl-t-butylmethyleneamino-complexes described in this work provided no definite information regarding the bonding mode of the methyleneamino-group in the complexes mainly because the methyleneamine is unsymmetrically substituted.

Dimethylmethyleneamine, $Me_2C{=}NH$, would be an ideal compound to use to obtain such information as it has two small substituent groups and should give very informative ^1H n.m.r. spectral data. However this compound has never been successfully prepared due to its extreme reactivity arising from enamine tautomerism.[36] The corresponding perfluoroalkylmethyleneamine, $(CF_3)_2C{=}NH$, has been prepared;[78] and it has the advantage of the dimethyl derivative in providing a n.m.r. probe close to the co-ordinating methyleneamino-group, but is not subject to the complications of tautomerism. Thus exploratory investigations into the introduction of this group into cyclopentadienyl molybdenum- and tungsten carbonyl complexes were undertaken as a preliminary step to the structural investigations.

Experimental

A. Starting materials

(i) Di-(trifluoromethyl)methyleneamine, $(CF_3)_2C{=}NH$ was prepared using the method of Middleton and Krespan.[78] Anhydrous pyridine (50 ml.) was placed in a flask fitted with a condenser filled with solid carbon dioxide and cooled in a solid carbon dioxide-acetone bath. Sodium-dried liquid ammonia (4 ml., ~0•2 mmole) was condensed into the flask with vigorous stirring followed by hexafluoroacetone (29 g., ~0•2 mole) keeping the temperature between -25° and -30°. The mixture was warmed to room temperature and the flask fitted with a reflux condenser. Phosphorus oxychloride (20 ml., 0•24 mole) was added dropwise to maintain a steady reflux. The mixture was then heated to 100° and the water flow in the condenser stopped. The product distilled from the flask was collected as white crystals in a trap immersed in a solid carbon dioxide-acetone bath at -78°. The product was redistilled into an evacuated cylinder immersed in liquid nitrogen.
Yield 17g. (58%; lit.[78] 70%).

Infrared spectrum (gas cell, 10 cm. path length; KBr windows): 3333sh, 3279m, 3067w, 2747w, 2604w, 2500sh, 2430sh, 2410m-w, 2342m-w, 2160m-w, 2096m, 2033w, 1961w, 1852m, 1802m-w, 1672w, 1555m, 1515sh, 1385m, 1333w, 1258vs, 1212vs, 1195vs, 1072m, 971m-w, 939m, 797m,br, 719m-w, 709m, 704m, 699sh cm^{-1}.

Assignments: ν_{NH} 3279 cm^{-1}; ν_{CN} 1672 cm^{-1}. The value for ν_{CN} corresponded to that quoted by Middleton and Krespan[78] but conflicted with that quoted recently by Niedenzu[133] (ν_{CN} 1701 cm^{-1}).

Mass spectrum (direct insertion at source temperature): The peak at highest mass was observed at m/e 145 corresponding to $[CF_3C(CF_2){=}N]^+$ i.e. $[P\text{-}HF]^+$. The major peaks observed in the spectrum are listed in Table IV.1.

TABLE IV.1

Mass spectroscopic data for $(CF_3)_2C=NH$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
145	11•8	$[CF_3C(CF_2)N]^+$	45	5•9	$[FCN]^+$
96	5•9	$[CF_3CNH]^+$	31	53•0	$[CF]^+$
95	100•0	$[CF_3CN]^+$	27	100•0	$[HCN]^+$
76	11•8	$[CF_2CN]^+$	26	5•9	$[CN]^+$
50	70•1	$[CF_2]^+$			

^{19}F n.m.r. spectrum of the neat liquid showed two signals at 71•5 and 73•5 p.p.m. (56•5 MHz. reference compound $CFCl_3$). High resolution indicated some multiplicity of these peaks but could not be fully resolved (lit.[78] two quartets at 5•77 and 7•62 p.p.m. from reference $CFCl_2.CFCl_2$, lower field quartet split to a doublet).

(ii) $(CF_3)_2C=NSiMe_3$ was prepared using the method of Chan and Rochow[54] from $(CF_3)_2C=NLi$ and Me_3SiCl. The product was not isolated in a pure form but used directly for reactions. Vapour phase chromatography (10 ft. column, 10% A.P.L. at 62°) indicated the formation of the product in ~80% yield. Infrared spectrum: the ether/hexane solution obtained from the reaction showed a medium strong absorption at 1720 cm^{-1} (ν_{CN}). This compared with the literature value[54] of 1780 cm^{-1}.

B. (i) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $(CF_3)_2C=NLi$

A solution of $(CF_3)_2C=NLi$ was prepared in the usual manner from $(CF_3)_2C=NH$ (0•7 g., 4•24 mmole), anhydrous ether (100 ml.) and t-butyllithium (4•24 mmole). π-$C_5H_5Mo(CO)_3Cl$ (1•19 g., 4•24 mmole) was dissolved in anhydrous ether (60 ml.) and chloroform (20 ml.) and the solution frozen to -196°. The solution of $(CF_3)_2C=NLi$ was added to the frozen solution and the mixture allowed to warm to ambient temperature and stirred for 1 hr. The solution darkened considerably during this time and a white solid separated. The dark brown solution was filtered, reduced to small bulk (25°, 0•1 mm.Hg) and on cooling to -20° reddish-purple crystals separated which were identified by i.r. spectroscopy as [π-$C_5H_5Mo(CO)_3]_2$. Addition of hexane (20 ml.) caused further separation of the dimer. Removal of the solvent (25°, 0•1 mm.Hg) from the mother liquor produced a dark purplish oil which when dissolved in hexane (20 ml.) failed to produce crystals on prolonged cooling at -20°. The hexane solution was then subjected to chromatography (18 in. column of Silicar CC7 in CCl_4). Elution of three bands was achieved by use of carbon tetrachloride, 1:1 carbon tetrachloride/benzene and finally pure benzene. The fractions were respectively pale red, bluish-red and intense purple in colour.

Fraction 1 (pale red): the infrared spectrum of a concentrated solution in CCl_4 showed absorptions in the carbonyl region (ν_{CO}) at 1984s, 1931s and 1890sh cm^{-1}. On removal of the solvent (25°, 0•1 mm.Hg) a very small amount of a reddish oil was obtained.

Mass spectrum (direct insertion at source temperature): The molybdenum species at highest mass was a Mo_2 species observed at m/e 708 corresponding to [π-$C_5H_5Mo(CO)N=C(CF_3)_2]_2^+$. The peaks observed are recorded in Table IV.2.

Table IV.2

Mass spectroscopic data for Fraction 1

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
706	25·0 (Mo_2)	$[\pi\text{-}C_5H_5Mo(CO)N{=}C(CF_3)_2]_2^+$	150	-	$[C(CF_3)_2]^+$
650	100·0 (Mo_2)	$[\pi\text{-}C_5H_5MoN{=}C(CF_3)_2]_2^+$	96	-	$[CF_3CNH]^+$
327	83·3 (Mo_1)	$[\pi\text{-}C_5H_5MoN{=}C(CF_3)_2]^+$	95	-	$[CF_3CN]^+$
228	100·0 (Mo_1)	$[(\pi\text{-}C_5H_5)_2Mo]^+$	69	-	$[CF_3]^+$
201	71·5 (Mo_1)	$[\pi\text{-}C_5H_5MoF_2]^+$	65	-	$[C_5H_5]^+$
182	83·3 (Mo_1)	$[\pi\text{-}C_5H_5MoF]^+$	57	-	$[CFCN]^+$

Fraction 2 (bluish-red): Removal of the solvent (25°, 0·1 mm.Hg) left a dark coloured solid residue.

Infrared spectrum (Nujol): Intense absorptions(ν_{CO}) were observed at 2049, 1969sh and 1938 cm^{-1}. No absorption could be assigned to ν_{CN} as only very weak absorptions were observed in the 1500-1700 cm^{-1} region. The Nujol spectrum is: 3077w, Nujol, 2049vs, 1969sh, 1938vs, Nujol, 1292vw, 1256s, 1198w, 1053vs,br,952vw, 862m, 825sh, 803vs,br, 719w, 714w, 704mw, 690m,br, 662w,br, 562m, 522m, 467m,br cm^{-1}.

Mass spectrum (direct insertion at source temperature): A Mo_1 pattern was observed centred at m/e 472 but could not be assigned. At very high mass (m/e 850) two Mo_2 patterns were observed which appeared to differ by 19 units (i.e. F). These were the only Mo species detected in the spectrum.

Fraction 3 (intense purple): A chlorofrom solution showed a medium absorption at 1715 cm^{-1} which could be either ν_{CO} for a bridging carbonyl group or ν_{CN}. Removal of the solvent (25°, 0·1 mm.Hg) yielded a quantity of a dark coloured gummy material. This fraction appeared to be the major product of the reaction.

Mass spectrum (direct insertion at source temperature): A number of Mo species were detected but were largely unassigned. Mo_2 species were observed centred at m/e 534, 386 and 370 (the latter being the most intense species in the spectrum). Three Mo_1 species were observed at m/e 228, 198 and 179, the first tentatively assigned to $[(\pi-C_5H_5)_2Mo]^+$.

(ii) Similar reactions between $\pi-C_5H_5Mo(CO)_3Cl$ and $(CF_3)_2C{=}NLi$ in ether solution (a) with slow warming to ambient temperature by use of a 1,2-dichloroethane slush bath at -25° and final stirring at ambient temperature for 2 hr. (b) mixing reactants at -20° in a $C_2H_4Cl_2$ slush bath and stirring at ambient temperature for 2 hr. produced no reaction as indicated by i.r. spectroscopy although darkening of the solution was observed on each occasion.

(iii) Solutions of $(CF_3)_2C{=}NLi$ (2•5 mmole) in anhydrous ether (60 ml.) and $\pi-C_5H_5Mo(CO)_3Cl$ (0•7 g., 2•5 mmole) in anhydrous ether (100 ml.) were mixed at -20° ($C_2H_4Cl_2$ slush bath) and then warmed to ambient temperature. No reaction was observed by i.r. spectroscopy after stirring for 2 hr. The mixture was heated to the reflux temperature and after 33 hr. the chloride was shown by i.r. spectroscopy to have been consumed. Removal of the solvent (25°, 0•1 mm.Hg) from the dark brown solution left a brown residue which was extracted with chloroform (15 ml.) and the solution filtered from a light brown insoluble material (probably LiCl with some decomposition material). Addition of hexane (30 ml.) and cooling to -20° produced an amount of a brown solid.

Properties: On heating in vacuo in a sublimation apparatus a small amount of yellow solid was observed to condense onto the cold finger at 70°. On further heating to 140-150° sublimation of the brown material occurred to a slight extent, the bulk of the material remained unchanged on heating to 175°.

Infrared spectrum (Nujol): The solid showed no absorptions in the carbonyl region of the spectrum. The i.r. spectrum is: 3086m, Nujol, 1323m-w, 1266m, 1247m, 1232sh, 1220m, 1176s, 1093m, 1063w, 1020m, 1000m, 926sh, 913m-s, 836m-s, 830m-s, 806m-s, 712w, 701w, 690m.

Mass spectrum (direct insertion at source temperature): The peak at highest mass was an Mo_2 species centred at m/e 535 and weaker Mo_2 species were also observed centred at m/e 386 and 370. Intense Mo_1 species were observed centred at m/e 230 and 200 but none of the Mo_1 or Mo_2 species could be assigned.

(iv) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $(CF_3)_2C{=}NSiMe_3$.

π-$C_5H_5Mo(CO)_3Cl$ (1•12 g., 4•0 mmole) was dissolved in T.H.F. (20 ml.) and $(CF_3)_2C{=}NSiMe_3$ (~4•0 mmole) added. No reaction was observed by i.r. spectroscopy on stirring for 2 hr. The mixture was heated to the reflux temperature and after 4 hr. the i.r. spectrum showed the chloride to be almost entirely consumed. Removal of the solvent (25°, 0•1 mm.Hg) from the cooled solution left a dark brown oily residue which was dissolved in chloroform (20 ml.) and on addition of hexane (40 ml.) and cooling to -20° a brown solid separated. This was filtered from the solution, washed with hexane (10 ml.) and dried *in vacuo*.

Properties: The brown solid melted at 134-6° on heating in a sealed tube.

Analysis: Found, C,27•97; H,2•76; Cl,18•3; F,23•7; N,6•32%. No empirical formula could be obtained to satisfy these figures.

Infrared spectrum (Nujol): The solid appeared to be a non-carbonyl species as no absorptions were observed in the carbonyl region. The Nujol spectrum is: 3086m, Nujol, 1667vw,br, Nujol, 1323m, 1266m-s, 1247m-s, 1232sh, 1220m-s, 1176s, 1093m-s, 1063w, 1020m, 1000m, 926sh, 913s, 893s, 836s, 830s, 806m-s, 712w, 701w, 690m. cm^{-1}.

Mass spectrum (direct insertion at source temperature): Numerous Mo_2 species were observed centred at m/e 665, 638, 609, 581, 553, 515, 495, 467, 441 and 397 as well as a single Mo_1 species at 216. None of these species could be assigned.

(v) Reaction of π-$C_5H_5W(CO)_3Cl$ with $(CF_3)_2^tC{=}NSiMe_3$

The reaction was carried out in a similar manner to (iv) using π-$C_5H_5W(CO)_3Cl$ (1•0 g., 2•9 mmole), T.H.F. (20 ml.) and $(CF_3)_2C{=}NSiMe_3$ (~2•9 mole) and heating to the reflux temperature. No reaction was observed by i.r. spectroscopy after 5 hr.

(vi) Reaction of π-$C_5H_5Mo(CO)_3Cl$ with $(CF_3)_2C{=}NH$

$(CF_3)_2C{=}NH$ (0•33 g., 2 mmole) was condensed into a flask cooled in liquid nitrogen and dissolved in chloroform (50 ml.). A solution of π-$C_5H_5Mo(CO)_3Cl$ (0•56 g., 2 mmole) in chloroform (30 ml.) was added to the solution of $(CF_3)_2C{=}NH$ held below 0° and some magnesium carbonate added. The flask was fitted with a solid carbon dioxide condenser to prevent any loss of $(CF_3)_2C{=}NH$ from the reaction mixture. The mixture was stirred at ambient temperature for 20 hr. but no reaction was observed by i.r. spectroscopy.

Discussion

Although these preliminary experiments failed to produce any well defined complexes containing the di-(trifluoromethyl) methyleneamino-ligand some evidence was obtained for such complexes. It appeared that reaction of the lithium derivative with π-$C_5H_5Mo(CO)_3Cl$ did produce some carbonyl complexes and although the yield was very low and a mixture of products was formed, mass spectroscopic data did indicate the presence of carbonyl complexes containing the di-(trifluoromethyl) methyleneamino-ligand. The presence of chloroform as a solvent seemed necessary for this reaction to occur, no reaction occurring in either ether or ether/monoglyme mixtures. The reaction conditions seem to be a crucial factor in preparing these carbonyl complexes, low temperatures would seem to be favourable as the use of solvents at the reflux temperature tended to produce non-carbonyl materials. The abundance of Mo_2 species in the various mass spectra obtained would tend to indicate the possible tendency of the ligand to form bridges between metal atoms - the mass spectrum of Fraction 1 in reaction (i) did indicate the presence of a dinuclear complex $[\pi\text{-}C_5H_5Mo(CO)N{=}C(CF_3)_2]_2$ analogous to the dinuclear diphenylmethyleneamino-complexes which have been obtained.[21]

The reaction of the chlorides with $(CF_3)_2C{=}NSiMe_3$ showed no sign of carbonyl complexes being formed. The reaction with $\pi\text{-}C_5H_5Mo(CO)_3Cl$ gave a non-carbonyl compound of unknown constitution and with $\pi\text{-}C_5H_5W(CO)_3Cl$ no reaction was observed.

On the basis of these preliminary investigations it would appear that further studies on these systems would be worthwhile.

REFERENCES

1. H. Behrens and N. Harder, Chem. Ber., 1964, 97, 433.
2. H. Behrens and N. Harder, Chem. Ber., 1964, 97, 426.
3. D.C. Bradley and M.H. Gitlitz, J. Chem. Soc.(A), 1969, 980.
4. M. Ahmed, R. Bruce and G. Knox, Z. Naturforsch., 1966, 21b, 289.
5. N. Flitcroft, J. Organometallic Chem., 1968, 15, 254.
6. (a) M. Dekker and G. Knox, Chem. Comm., 1967, 1243.
   (b) R.J. Doedens, Inorg. Chem., 1969, 8, 570.
7. D.C. Bradley and E.G. Torrible, Canad. J. Chem., 1963, 41, 134.
8. B.L. Ross, J.G. Grasselli, W.T. Ritchey and H.D. Kaesz, Inorg. Chem., 1962, 2, 1023.
9. E.H. Schubert and R.K. Sheline, Inorg. Chem., 1966, 5, 1071.
10. S. Otsuka, A. Nakamura and T. Yoshida, Inorg. Chem., 1967, 6, 20.
11. H. Bock and H. tom Dieck, Z. anorg. Chem., 1966, 345, 9.
12. H. Bock, Angew. Chem. Internat. Edn., 1962, 1, 550.
13. H. Bock and H. tom Dieck, Chem. Ber., 1966, 99, 213.
14. K. Krogman and R. Mattes, Angew. Chem. Internat. Edn., 1966, 5, 1046.
15. E.A.V. Ebsworth, Chem. Comm., 1966, 530.
16. J.B. Culbertson, J. Amer. Chem. Soc., 1951, 73, 4818.
17. K. Farmery, Ph.D. Thesis, University of Durham, 1968.
18. E.O. Fischer and L. Knauss, Chem. Ber., 1970, 103, 1262.
19. M. Kilner and C. Midcalf, J. Chem. Soc.(A), in press.
20. M. Kilner and C. Midcalf, Chem. Comm., 1970, 552.
21. K. Farmery, M. Kilner and C. Midcalf, J. Chem. Soc.(A), in press.
22. D. Bright and O.S. Mills, Chem. Comm., 1967, 245.
23. K. Farmery and M. Kilner, J. Organometallic Chem., 1969, 16, 51.

24. R.W. Layer, Chem. Rev., 1963, 63, 489.

25. 'The Chemistry of the Carbon Nitrogen Double Bond' ed. S. Patai. Interscience, New York, 1970.

26. E.E. Blaise, Compt. rend., 1901, 132, 38; 1901, 133, 299.

27. C. Moureu and G. Mignonac, Compt. rend., 1913, 156, 1801.

28. J.B. Cloke, J. Amer. Chem. Soc., 1940, 62, 117.

29. P.L. Pickard and D.J. Vaughan, J. Amer. Chem. Soc., 1950, 72, 876.

30. P.L. Pickard and D.J. Vaughan, J. Amer. Chem. Soc., 1950, 72, 5017.

31. P.L. Pickard and C.W. Young, J. Amer. Chem. Soc., 1951, 73, 42.

32. P.L. Pickard and E.F. Engles, J. Amer. Chem. Soc., 1952, 74, 4607.

33. P.L. Pickard and E.F. Engles, J. Amer. Chem. Soc., 1953, 75, 2148.

34. I.R. Kaplan, H.N. Parton and J. Vaughan, J. Amer. Chem. Soc., 1953, 75, 4341.

35. P.L. Pickard and S.H. Jenkins, J. Amer. Chem. Soc., 1953, 75, 5899.

36. P.L. Pickard and T.L. Tolbert, J. Org. Chem., 1961, 26, 4886.

37. L.F. Fieser and A.M. Seligman, J. Amer. Chem. Soc., 1939, 61, 136.

38. H.L. Lockte, J. Horeczy, P.L. Pickard and A.D. Barton, J. Amer. Chem. Soc., 1948, 70, 2012.

39. C.R. Hauser and D.S. Hoffenburg, J. Amer. Chem. Soc., 1955, 77, 4885.

40. P. Bourbon and P. Puig, Compt. rend., 1964, 258, 3323.

41. C. Moureu and G. Mignonac, Compt. rend., 1920, 170, 1353

42. G. Charles, M. Mazet, Compt. rend., Cong. Soc. Savantes Dept., Sec. Sci., 1962, 87, 491. (Chem. Abs., 1964, 60, 14421).

43. P. Vittum, R. Anderson and J.B. Culbertson, Proc. Iowa Acad. Sci., 1929, 36, 296. (Chem. Abs., 1931, 25, 1230).

44. G.E. Coates, M.L.H. Green and K. Wade, 'Organometallic Compounds, Vol.1. The Main Group Elements', Methuen, 1967, p.91.

45. S.J. Storfer and E.I. Becker, J. Org. Chem., 1962, 27, 1868.

46. H. Edelstein and E.I. Becker, J. Org. Chem., 1966, 31, 3375.

47. H. Gilman and K.E. Marple, Rec. Trav. chim., 1936, 55, 133.

48. K. Lehmstedt and F. Dorstal, Ber., 1939, 72, 804.

49. R.H. Anker and A.H. Cook, J. Chem. Soc., 1941, 323.

50. I. Pattison and K. Wade, J. Chem. Soc.(A), 1968, 57.

51. J.P. Wibaut and J.I. de Jong, Rec. Trav. chim., 1949, 68, 485.

52. B. Samuel, R. Snaith, C. Summerford and K. Wade, J. Chem. Soc.(A), 1970, 2019.

53. (a) I. Pattison, K. Wade and B.K. Wyatt, J. Chem. Soc.(A), 1968, 837.
(b) J.R. Jennings, I. Pattison and K. Wade, J. Chem. Soc.(A), 1969, 565.
(c) C. Summerford and K. Wade, J. Chem. Soc.(A), 1969, 1487.

54. L-H. Chan and E.G. Rochow, J. Organometallic Chem., 1967, 9, 231.

55. D.J. Berry and B.J. Wakefield, Chem. Comm., 1969, 1273; J. Organometallic Chem., 1970, 23, 1.

56. (a) K. Hoesch, Ber., 1915, 48, 1122.
(b) K. Hoesch and T. von Zarzecki, ibid, 1917, 50, 462.

57. J. Houben, Ber., 1926, 59, 2878.

58. J. Houben and W. Fischer, J. prakt. Chem., 1929, 123, 313.

59. J. Houben and W. Fischer, Ber., 1931, 64, 2645.

60. D. Vorlander, Ber., 1911, 44, 2455.

61. I.G. Farbendindustrie A.G., F.P., 704,794/1930. (Chem. Abs., 1931, 25, 4717).

62. P.E. Spoerri and A.S. du Bois, Org. Reactions, 1949, 5, 387.

63. W. Ruske, 'Friedel Crafts and Related Reactions' ed. G.A. Olah, Interscience, New York, 1964, Vol.III, p.383.

64. E. Bresson and J.B. Culbertson, Proc. Iowa Acad. Sci., 1929, 36, 266. (Chem. Abs., 1931, 25, 1230).

65. E.A. Jeffrey and D.P.N. Satchell, J. Chem. Soc.(B), 1966, 579.

66. K. Zeigler, H. Ohlinger and E. Eberle, G.P., 591,269/1934. (Chem. Abs., 1934, 28, 2364).

67. T. Takata, Bull. Chem. Soc. Japan, 1962, 35, 1438. (Chem. Abs., 1963, 58, 2451).

68. H. Adkins and G.M. Whitman, J. Amer. Chem. Soc., 1942, 64, 150.

69. A. Dornow, I. Kuhlcke and F. Baxmann, Chem. Ber., 1949, 82, 254.

70. M.E. Baguley and J.A. Elvidge, J. Chem. Soc., 1957, 709.

71. J.R. Shelton and C.W. Uzelmeier, J. Amer. Chem. Soc., 1966, 88, 5222.

72. V.L. Hansley, U.S.P., 2,742,503/1956. (Chem. Abs., 1956, 50, 16830).

73. W.J. Chambers, C.W. Tullock and D.D. Coffmann, J. Amer. Chem. Soc., 1962, 84, 2337.

74. C. Thomae, Arch. Pharm., 1905, 243, 395.

75. H.H. Strain, J. Amer. Chem. Soc., 1930, 52, 820.

76. G.H. Harris, B.R. Harriman and K.W. Wheeler, J. Amer. Chem. Soc., 1946, 68, 846.

77. L.A. Pinck and G.E. Hilbert, J. Amer. Chem. Soc., 1934, 56, 490.

78. W.S. Middleton and C.G. Krespan, J. Org. Chem., 1965, 30, 1398.

79. G. Mignonac, Compt. rend., 1919, 169, 237.

80. A.A. Balandin and N.A. Vasyunina, Doklady. Akad. Nauk. S.S.R., 1955, 103, 831. (Chem. Abs., 1956, 50, 9283).

81. H.B. Williams, P. Koenig, G. Huddleston, T. Convillion and W. Castille, J. Org. Chem., 1963, 28, 463.

82. C.R. Hauser, W.R. Brasen, P.S. Skell, S.W. Kantor and A.E. Brodhag, J. Amer. Chem. Soc., 1965, 78, 1653.

83. G. Mignonac, Compt. rend., 1920, 170, 936.

84. H. Lund, Acta Chem. Scand., 1964, 18, 563.

85. F. Mahla and F. Tiemann, Ber., 1896, 29, 2807.

86. F. Mahla, Ber., 1901, 34, 3777.

87. P. Grammaticakis, Compt. rend., 1940, 210, 716.

88. A. Hantzsch and F. Kraft, Ber., 1891, 24, 3511.

89. R.T. Gilsdorf and F.F. Nord, J. Amer. Chem. Soc., 1950, 72, 4327.

90. S.S. Hirsch, J. Org. Chem., 1967, 32, 2433.

91. D.E. Young, L.R. Anderson and W.B. Fox, Chem. Comm., 1970, 395.

92. P.L. Pickard and G.W. Polly, J. Amer. Chem. Soc., 1954, 76, 5169.

93. R. Cantarel, Compt. rend., 1940, 210, 480.

94. R. Mathis-Noel, P. Puig and P. Bourbon, Compt. rend., 1967, 264C, 1252.

95. J.B. Culbertson, J. Amer. Chem. Soc., 1951, 73, 4818.

96. B. Witkop, J. Amer. Chem. Soc., 1956, 78, 2873.

97. A.F. Casey and M.M.A. Hassan, J. Chem. Soc.(B), 1969, 631.

98. K. von Auwers and H. Wunderling, Ber., 1932, 64, 70.

99. E.D. Bergmann, E. Zimkin and S. Pinchas, Rec. Trav. chim., 1952, 71,168.

100. (a) G.O. Dudek and R. Holm, J. Amer. Chem. Soc., 1961, 83, 2099;
(b) ibid, 1961, 83, 3914.

101. M. Pfau and C. Ribiere, Chem. Comm., 1970, 66.

102. J. Dabrowski, Bull. acad. polon. sci., Ser. Sci., Chim., geol. et geograph., 1957, 7, 93. (Chem. Abs., 1961, 55, 6414).

103. V.M. Potapov, F.A. Trofimov, A.P. Terent'ev, Doklady. Akad. Nauk. S.S.R. 1960, 134, 609. (Chem. Abs., 1961, 55, 6414).

104. C. Moureu and G. Mignonac, Compt. rend., 1914, 158, 1395.

105. J.B. Culbertson, D. Butterfield and O. Kolewe, J. Org. Chem., 1962, 27, 729.

106. G.E.P. Smith and F.W. Bergstrom, J. Amer. Chem. Soc., 1934, 56, 2095.

107. C. Kruger, E.G. Rochow and U. Wannagat, Chem. Ber., 1963, 96, 2132.

108. T. Kaufmann and D. Berger, Chem. Ber., 1968, 101, 3022.

109. J.P. Anselm, W. Fischer and N. Koga, Tetrahedron, 1969, 25, 89.

110. R. Cantarel, Compt. rend., 1940, 210, 403.

111. J.E. Banfield, G.M. Brown, F.H. Davey, W. Davies and T.A. Ramsey, Austral. J. Sci. Res., 1948, A1, 330. (Chem. Abs., 1952, 46, 5558).

112. E.J. Grubbs, J.D. McCullough, B.H. Weber and J.R. Maley, J. Org. Chem., 1966, 31, 1098.

113. J.J. Steiglitz and P.P. Peterson, Ber., 1910, 43, 782.

114. M.L. Poutsma and P.A. Ibarbia, J. Org. Chem., 1969, 34, 2848.

115. J.K. Ruff, J. Org. Chem., 1967, 32, 1675.

116. L.I. Samarai, O.V. Vishnevski and G.I. Derkach, Chem. Ber., 1969, 102,2972.

117. C.J. Thonan, S.J. and I. Moyer Hunsberger, J. Org. Chem., 1968, 33, 2852.

118. J. Jappy and P.M. Preston, Tetrahedron Letters, 1970, 1157.

119. A. Dornow and S. Lupfert, Chem. Ber., 1956, 89, 2718.

120. G. Charles, Bull. Soc. chim. France, 1963, 1559.

121. A. de Savignac and A. Lattes, Compt. rend., 1969, 268C, 2325.

122. H.B. Williams, K.N. Yarborough and K.L. Crochet, Tetrahedron, 1970, 26, 817.

123. R. Ahmed and W. Lwowski, Tetrahedron Letters, 1969, 3611.

124. G. Kabas, J. Org. Chem., 1967, 32, 218.

125. N. Toshima, H. Hirai and S. Makishima, J. Chem. Soc. Japan, Ind. Chem. Sec., 1969, 72, 184. (Chem. Abs., 1969, 70, 114378).

126. N. Toshima and H. Hirai, Tetrahedron Letters, 1970, 433.

127. Inorg. Synth., 1963, 7, 136.

128. H.P. Fitz, Adv. Organometallic Chem., 1964, 1, 239.

129. (a) K. Wade and B.K. Wyatt, J. Chem. Soc.(A), 1967, 1339.

(b) J.R. Jennings, I. Pattison, K. Wade and B.K. Wyatt, J. Chem.Soc.(A), 1967, 1608.

130. R. Snaith and K. Wade, personal communication.

131. M. Pankowski and M. Bigorgne, Compt. rend., 1966, 263C, 239.

132. K.W. Barnett and P.M. Treichel, Inorg. Chem., 1967, 6, 294.

133. K. Niedenzu, K.E. Blick and C.D. Miller, Inorg. Chem., 1970, 9, 975.