Organonitrogen Groups in Metal Carbonyl Complexes. Part VI. Studies on the Synthesis of (π-C_5H_5)Mo(CO)$_2$N:CR$_2$ complexes [†]

By H. R. Keable, M. Kilner,* and (Mrs.) E. E. Robertson, Department of Chemistry, The University of Durham, South Road, Durham City

In the presence of added substrates such as Ph_2CO, Me_2CO, PhCN, PhNCO, $PhNH_2$, and *trans*-PhCH=CHPh the reaction of $Ph_2C{:}NLi$ with (π-C_5H_5)M(CO)$_3$Cl (M = Mo, W) yields (π-C_5H_5)M(CO)$_2$(N:CPh$_2$) in contrast to the reaction without the added substrates which produces (π-C_5H_5)M(CO)$_2$(Ph$_2$CNCPh$_2$). Studies have been directed towards determining the role of the added substrates, and various types of involvement are discussed and tested. Two forms of the complex (π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) are compared, one being assigned a monomeric and the other a dimeric formulation.

We have reported previously [1] the synthesis and aspects of the chemistry of the complex (π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) which was obtained by the reaction of (π-C_5H_5)Mo(CO)$_3$Cl with $Ph_2C{:}NSiMe_3$ at *ca.* 80°. The reaction normally proceeds through to the dinuclear complex [(π-C_5H_5)Mo(CO)N:CPh$_2$]$_2$ under these conditions but on one occasion a sufficient quantity of the intermediate brown complex was isolated and characterised. The corresponding tungsten analogue (π-C_5H_5)W(CO)$_2$(N:CPh$_2$) was similarly prepared, but was the major product of the reaction and was converted into the dinuclear complex with loss of carbon monoxide only under more forcing conditions.[1] The most surprising feature of the two (π-C_5H_5)M(CO)$_2$(N:CPh$_2$) (M = Mo, W) complexes is their lack of similarity (illustrated by the spectroscopic data in the Table when small differences only occur for other series of complexes.[1-3]

The reactions of $Ph_2C{:}NLi$ with (π-C_5H_5)M(CO)$_3$Cl in ether solution lead predominantly to the aza-allyl/allene complexes (π-C_5H_5)M(CO)$_2$(Ph$_2$CNCPh$_2$) [1,4] with only a trace of the methyleneamino-complex remaining in solution. With *p*-tolyl$_2$C:NLi the following products were isolated, (π-C_5H_5)M(CO)$_2$N:C(*p*-tolyl)$_2$, (π-C_5H_5)M(CO)$_2${(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$}, and (π-C_5H_5)M(CO)$_2${(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$}(*p*-tolyl$_2$CO).[5] The proportion of each could be controlled by choice of the reaction conditions. In an attempt to increase the yield of the ketone adduct, free ketone was added to the initial reaction mixture but the result was that the methyleneamino-complex became the predominant product. Extention of this procedure to the $Ph_2C{:}NLi$ system allowed the synthesis of a blue form of (π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) which had distinctly different properties from the brown complex mentioned earlier. Here we compare the brown and blue complexes both formulated (π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) and report on studies directed towards establishing the role of the ketone and other added substrates on the course of the $Ph_2C{:}NLi$/(π-C_5H_5)M(CO)$_3$Cl reactions.

RESULTS AND DISCUSSION

Addition of a molar proportion of a range of added substrates to the reaction of $R_2C{:}NLi$ compounds with (π-C_5H_5)M(CO)$_3$Cl increases markedly the proportion of the methyleneamino-complex formed and in many cases this type of complex is the exclusive product. The range of added substrates studied include Ph_2CO, Me_2CO, PhCN, PhNCO, Ph_2C=NH, *trans*-PhHC=CHPh, $PhNH_2$, and $C_6H_{11}NC$; all except the last compound are effective at altering the course of the reaction. The products (π-C_5H_5)M(CO)$_2$N:CR$_2$ (I) are all blue solids exhibiting similar spectroscopic properties. For R = Ph, M = W and R = *p*-tolyl, M = Mo, W the products are identical in every respect to those formed with $R_2C{:}NSiMe_3$ as the starting material.[1] Differences occur, however, for (R = Ph, M = Mo), for which distinct differences in colour and other spectroscopic data are noted (see Table). The complexes prepared by the different routes both analyse satisfactorily for (π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) but it is apparent that the blue material from the preparative route involving $Ph_2C{:}NLi$ has a close similarity with those of other (π-C_5H_5)Mo(CO)$_2$(N:CR$_2$) complexes whereas the brown material is distinctly different with no known methyleneamino-analogues.

Spectroscopic data

Complex	ν(CO)/cm^{-1}	^{1}H n.m.r. (τ)
(π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) † brown form	1955vw,sh, 1920s, 1856s, 1802ms	2·48(10), 5·05, 5·11(5) §
(π-C_5H_5)Mo(CO)$_2$(N:CPh$_2$) † blue form	1964s, 1949s 1879s, 1874s	2·71(10), 4·22(5) ‡
*	1974s, 1897s	
(π-C_5H_5)W(CO)$_2$(N:CPh$_2$) †	1956s, 1940s 1869s, 1863s	2·63(10), 4·02(5) §
[(π-C_5H_5)W(CO)(N:CPh$_2$)]$_2$ †	1936s, 1847s	2·63(10), 4·64(5)
[(π-C_5H_5)W(CO)N:C(*p*-tolyl)$_2$]$_2$ †	1930s, 1836s	

* Hexane solution. † Nujol mull. ‡ CS_2 solution. § $CHCl_3$ solution.

Comparison between the Two Forms of (π-C_5H_5)Mo(CO)$_2$N:CPh$_2$.—The i.r. and ^{1}H n.m.r. data for the brown form (Table), particularly the three ν(CO) stretching

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[†] Preliminary report has been submitted as part of a contribution to the International Conference on Chemistry and Uses of Molybdenum, University of Reading, September 1973.

[1] K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc.* (*A*), 1970, 2279.

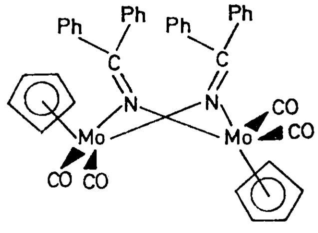
[2] M. Kilner and C. Midcalf, *J. Chem. Soc.* (*A*), 1971, 292.

[3] M. Kilner and J. N. Pinkney, *J. Chem. Soc.* (*A*), 1971, 2887.

[4] K. Farmery and M. Kilner, *J. Organometallic Chem.*, 1969, **16**, 51.

[5] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153.

frequencies and the two π-C_5H_5 ^1H n.m.r. signals, are inconsistent with a mononuclear formulation for which two ν(CO) stretching frequencies and one π-C_5H_5 ^1H n.m.r. signal are expected. In addition to the two higher frequency ν(CO) absorptions reported in a previous paper,[1] a lower medium-strong absorption (previously considered wrongly to be due to an unknown impurity) is now also assigned to the complex. The available data lead to the conclusion that the complex is not monomeric but oligomeric, and since it is readily converted into the dinuclear complex $[(\pi\text{-}C_5H_5)Mo(CO)(N{:}CPh_2)]_2$ it is most likely that the brown complex is also dimeric. Molecular-weight measurements were not possible using cryoscopic, ebullioscopic, and vapour pressure measurements because of the limited solubility of the complex in suitable solvents at and below ambient temperature and its thermal instability above ambient temperature. Since the relative intensity of the ^1H n.m.r. signals arising from the π-C_5H_5 protons are in the ratio 1 : 1,[1] different environments for the two rings in the dinuclear complex are indicated rather than two forms occurring in solution. Structure (I) satisfies these requirements. The C_s symmetry gives rise to four i.r.-active vibrations but one will have weak intensity. Three distinct ν(CO) stretching frequencies are observed, a weak shoulder occurring at 1955 cm^{-1} which may be assigned to the high-frequency symmetrical mode.



(I)

The mass spectral data require comment since both the brown and blue complexes give parent peaks and fragmentation patterns corresponding to $(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)$. The spectra are identical and neither show patterns for Mo_2 or higher molybdenum containing species. Thus inconsistencies appear to exist if the brown material is formulated as dimeric. One unusual feature apparent during the early work[1] was the unexpected recording of the mass spectrum of the brown complex under conditions which normally produce rapid conversion to $[(\pi\text{-}C_5H_5)Mo(CO)(N{:}CPh_2)]_2$. It is now believed that the spectrum is spurious and is due to the presence of trace amounts of the blue $(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)$ which is thermally stable above its m.p. of *ca.* 104°. A dimer→monomer dissociation is considered unlikely because of the ease with which the complex will lose carbon monoxide and undergo an alternative reaction. The presence of the blue isomer could not be detected as an impurity by i.r. nor by ^1H n.m.r. studies but since the preparative route has produced both brown and blue forms, it is possible that trace quantities of the blue complex could have been present in the sample of the brown complex isolated.

The series of blue complexes are all formulated as monomers whereas for the brown complex a dimeric formulation $[(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)]_2$ is most consistent with the data. The ready thermal reaction of the latter complex is then readily explicable since all that is involved in formation of the thermally stable $[(\pi\text{-}C_5H_5)Mo(CO)(N{:}CPh_2)]_2$ is loss of carbon monoxide and the formation of a planar Mo_2N_2 ring from a puckered Mo_2N_2 ring system. Interestingly the blue molybdenum complexes (R = Ph, *p*-tolyl) will not lose CO and form the dimeric complex although this can be achieved for the corresponding tungsten system.

Several other complexes of general formula $[(\pi\text{-}C_5H_5)M(CO)_2X]_n$ are known, some of which are dinuclear, but little similarity appears to exist between them and the brown complex discussed here. Indeed little similarity appears to exist between the previously reported complexes themselves, for example in the ν(CO) stretching region of the i.r. spectrum of $[(\pi\text{-}C_5H_5)M(CO)_2(SMe)]_2$ for M = Mo and W,[6] and $[(\pi\text{-}C_5H_5)Mo(CO)_2I]_n$[7] and consequently some of the reported data and/or structural interpretations must remain questionable. In general the complex $[(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)]_2$ exhibits lower ν(CO) stretching frequencies than the sulphur- and iodine-bridged complexes in keeping with the stronger σ- and π-donating properties of the nitrogen ligand, but it is surprising that the magnitude of the difference in the corresponding stretching frequencies between $[(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)]_2$ and $[(\pi\text{-}C_5H_5)W(CO)_2(SMe)]_2$, should amount to *ca.* 150 cm^{-1}. The difference when comparing the molybdenum complexes with sulphur and nitrogen ligands amounts in general to *ca.* 50 cm^{-1} which is more in keeping, if somewhat on the high side, with the difference expected; it is not clear, however, what stereochemical differences are responsible for some complexes exhibiting two and others four ν(CO) stretching frequencies.

The Effects of Added Substrates on the Reactions of $R_2C{:}NLi$ *with* $(\pi\text{-}C_5H_5)M(CO)_3Cl$.—A mechanism for the reaction of $(p\text{-tolyl})_2C{:}NLi$ with $(\pi\text{-}C_5H_5)M(CO)_3Cl$ in ether solution has been suggested in an earlier paper[5] to explain the range of products $(\pi\text{-}C_5H_5)M(CO)_2(N{:}CR_2)$, $(\pi\text{-}C_5H_5)M(CO)_2(R_2CNCR_2)$, $(\pi\text{-}C_5H_5)M(CO)_2(R_2CNCR_2)(R_2CO)$, R_2CO, LiNCO, LiCN, LiCl, and CO. Three stages of the process are relevant here: (1) an initial metathetical process generating $(\pi\text{-}C_5H_5)M(CO)_3(N{:}CR_2)$; (2) (*a*) subsequent loss of CO to form $(\pi\text{-}C_5H_5)M(CO)_2(N{:}CR_2)$ or (*b*) nucleophilic attack of a second $R_2C{:}NLi$ at the carbon atom of a carbonyl group to generate $(\pi\text{-}C_5H_5)M(CO)_2(N{:}CR_2)\{C(OLi)(N{:}CR_2)\}$; and (3) transfer of the CR_2 unit from the latterly introduced group either to (*a*) the adjacent methyleneamino-group to form

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[6] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 720.

[7] A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 431.

(π-C_5H_5)Mo$(CO)_2(R_2CNCR_2)$ with the elimination of LiNCO, or to (*b*) the oxygen of the attached carbonyl group to form (π-C_5H_5)Mo$(CO)_2$(N:CR_2), R_2CO, and LiCN. Since the aza-allyl/allene complex is formed almost exclusively using Ph_2C:NLi alone, processes (2*b*) followed by (3*a*) appears to be the dominant route for this system.

Several roles for the added substrates may be envisaged. (1) Reaction with R_2C:NLi to form an intermediate which on association with the metal displaces the added substrates in the same or in a changed form. (2) Modification of the lithio-reagent through changes in co-ordination of the lithium or changes in the degree of association. (3) Removal from the reaction solution of impurities which control the course of the reaction to form the aza-allyl/allene complex. (4) Substitution for a carbonyl group to form (π-C_5H_5)M$(CO)_2$LCl complexes which after subsequent reaction lose the added substrate, L.

To test the various possibilities a range of added substrates have been studied, and include Me_2CO, Ph_2CO, PhCN, PhNCO, $C_6H_{11}NC$, Ph_2C:NH, *trans*-PhCH=CHPh, and $PhNH_2$. Thus many types of ligand systems are represented including ligands with different donor atoms, ligands with and without π-systems, conventional-type and π-type ligand systems. All except $C_6H_{11}NC$ effectively alter the course of the reaction.

Before discussing the effects of each ligand type it is relevant to establish the procedure adopted in the reactions. The methyleneamine in ether and Bu^nLi in hexane are mixed, at or below −78° and the mixture is then stirred at ambient temperature for *ca.* ½ h before introduction of the additional substrate. The colour of the Bu^nLi/R_2C:NH mixture which starts to develop close to the m.p. of ether varied between yellow and orange-red depending on the commercial sample of Bu^nLi used—the colour is not considered to be due to R_2C:NLi compounds [8] but to arise from trace impurities, a conclusion confirmed by the present studies.

A lightening in the colour of the lithio-reagent was detected on addition of Ph_2CO and Me_2CO, but not on addition of PhCN or Ph_2C:NH; further, no changes were observed in the characteristic ν(CO), ν(C:N), or ν(C:N) stretching frequency of the substrate molecules, even on subsequent reaction with the carbonyl halide. No apparent changes occurred on the addition of *trans*-PhCH=CHPh but addition of $PhNH_2$ caused an immediate lightening in colour. After ½ h the original colour returned. Although a variety of different behaviours were detected towards the Ph_2C:NLi solution, nevertheless all the additional molecules proved very effective in producing (π-C_5H_5)Mo$(CO)_2$(N:CPh_2). In many reactions [(π-C_5H_5)Mo$(CO)_3]_2$ was a minor product.

Although addition of PhNCO increases the yield of the methyleneamino-complex it also reacts with Ph_2C:NLi to yield a yellow solution and a white solid. Drastic changes in the 1600—2200 cm^{-1} region of the spectrum were detected and at the end of the reaction the isocyanate is not regenerated. Chromatographic studies indicate that PhCN may be one of the products. In contrast the addition of $C_6H_{11}NC$ has no apparent effect on the course of the reaction and the aza-allyl complex remains the major product, although reaction of the isocyanide with (π-C_5H_5)Mo$(CO)_3$Cl occurs to a moderate extent to yield a mono-substitution product.

It is apparent that no single process is responsible for the change in course of the reaction. PhCN Effects no detectable change to the reaction solution whereas major changes occur for PhNCO where insertion across the N–C bond is expected to occur.[9] Thus although reaction may be responsible for the effects of some added substrates it is not the exclusive process. The presence of an impurity in the lithio-methyleneamine reagent which controls the course of the reaction has been tested by using various quantities of an additional substrate. If the latter reacts with the impurity and removes its effect from the solution, then only a small proportion of the added material should be consumed. Consequently the bulk of the material will be ineffective, and drastic reduction of the quantity should have no effect on the course of the reaction. This was shown by experiment to be the case, and addition of a 1/8 molar proportion of PhCN was found to be completely effective.

Two possible impurities in the lithiomethyleneamine reagent may thus control the course of the reaction, a slight excess of Bu^nLi or the species responsible for the orange-red colour. Since the latter colour is discharged with the introduction of some added substrates but not others, it is very unlikely that the coloured species is involved. The effect of Bu^nLi may also be eliminated. Although a slight excess of Bu^nLi could conceivably be present in the reaction of Ph_2C:NLi with (π-C_5H_5)-Mo$(CO)_3$Cl to yield the aza-allyl/allene complex, an excess of Bu^nLi reagent was also present in the reactions involving stoicheiometric proportions of Ph_2C:NLi, Bu^nLi, PhCN, or Ph_2CO, and (π-C_5H_5)Mo$(CO)_3$Cl which yielded the methyleneamino-complex. It has been shown that the reactions of Bu^nLi with PhCN and Ph_2CO do not progress completely with consumption of the nitrile or ketone, even after 24 h, at room temperature, so in the previous reaction unchanged Bu^nLi reagent will be present, particularly during the first hour when the composite reaction nears completion as indicated by the amount of the carbonyl chloride which remains. Although the involvement of excess of Bu^nLi can be eliminated, the possibility that other impurities in the Ph_2C:NLi solution are implicated cannot be completely dismissed.

The methyleneaminolithium reagents in ether will be oligomeric, and are considered to be tetramers or hexamers similar to the alkyl-lithium reagents.[9] Each lithium will be co-ordinated by ether molecules and since many of the added substrates are themselves potential ligands, stronger than ether, they may replace ether,

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[8] K. Wade, personal communication.

[9] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds: Volume I, The Main Group Elements,' Methuen, London, 1967.

thus altering the steric and electronic properties of the oligomer. Alternatively the degree of oligomerisation may be changed. Both effects may be to alter some delicate electronic or steric requirement necessary to generate the aza-allyl/allene complex for which the presence of two closely positioned methyleneamino-groups in the oligomeric lithio-reagent are considered necessary. It is relevant to mention that small changes in the substituents of the $R_2C:N$ group (*e.g. p*-tolyl for phenyl) are sufficient to produce distinct changes in the course of the reaction. If co-ordination of the additional molecules to the $Ph_2C:NLi$ oligomer does occur, then experimental data indicates that the attachment will be weak since changes in the $\nu(C:N)$ stretching frequency for PhCN and $\nu(CO)$ for Ph_2CO are negligible or very small.

The final possible explanation involves reaction of the added substrates with $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ to form dicarbonyl substitution products which undergo different reactions to the unsubstituted carbonyl chloride. Evidence for the transient formation of $(\pi\text{-}C_5H_5)Mo(CO)_2(Ph_2C:NH)Cl$ has been obtained, but not for similar complexes involving the other ligand molecules. Since the majority of additional molecules studied failed to react with $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ in ether solution under identical conditions to the $Ph_2C:NLi$ reactions, and since negligible changes were detected in the $\nu(CO)$ and $\nu(C:N)$ stretching frequencies of the ketones and nitrile respectively, substitution can also be eliminated as a predominant effect of the additional substrates.

Several possible roles for the additional substrates have been eliminated by experiment, but it has not proved possible to study the changes in the co-ordination or oligomerisation of the lithio-reagent under the conditions of the reaction. Changes in the nature of the lithio-reagent are believed to be responsible for the different reactions of $Ph_2C:NLi$ in the presence of added substrates and studies will continue in an effort to establish the identity of the reactive species.

EXPERIMENTAL

π-Cyclopentadienyltricarbonylmolybdenum chloride[10] and the methyleneamines[11] were prepared by standard methods. n-Butyl-lithium in hexane (*ca.* 2·5M), obtained from Phase Separation Ltd., was stored at ambient temperature under a nitrogen atmosphere and used without purification. Hydrocarbon solvents and diethyl ether were dried over extruded sodium and tetrahydrofuran was freshly distilled from lithium aluminium hydride. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed in oxygen-free atmospheres. Ph_2CO, Me_2CO, PhCN, $PhNH_2$, $C_6H_{11}NC$, Ph_2CNH, and *trans*-PhCH:CHPh were distilled or recrystallised as appropriate before use.

Spectra.—I.r. spectra in the range 4000—250 cm^{-1} were recorded on a Perkin-Elmer 457 spectrophotometer while mass spectra were obtained with an A.E.I. MS 9 instrument at 70 eV and an accelerating potential of 8 kV. Samples were inserted directly into the ion source at temperatures between 80 and 220°.

Chromatography.—Chromatograms were run on Merck silica gel GF_{254} and the components detected by their quenching of the fluorescence of the coating in u.v. light. Analytical and preparative plates had films of 0·25 and 1·0 mm thickness respectively. The plates were activated by drying at 100° for 12 h before use.

Reaction of Ph_2CNLi *with* $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$.—A solution of Ph_2CNLi was prepared by the addition of n-butyllithium (5 mmol) to a solution of Ph_2CNH (5 mmol) in ether (40 ml) at -78 °C. The solution was allowed to warm to room temperature and stirred for 20 min. The π-cyclopentadienyltricarbonylmolybdenum chloride (5 mmol, 1·40 g) in ether (40 ml) was added to the frozen deep red lithiomethyleneamine solution. The resultant solution was allowed to warm to room temperature with constant stirring, and the reaction mixture monitored by i.r. spectroscopy. After stirring for 20 h a greenish brown solution resulted with precipitation of brown-purple crystals in quantity, identified as the aza-allyl/allene complex $(\pi\text{-}C_5H_5)Mo(CO)_2(Ph_2CNCPh_2)$. The solution contained very minor quantities of the methyleneamino-complex, $(\pi\text{-}C_5H_5)Mo(CO)_2(N:CPh_2)$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

An identical reaction occurred using $(\pi\text{-}C_5H_5)W(CO)_3Cl$ in place of the molybdenum complex and $(\pi\text{-}C_5H_5)W(CO)_2(Ph_2CNCPh_2)$ was isolated.

Reaction of Ph_2CNLi *with* $(\pi\text{-}C_5H_5)M(CO)_3Cl$ *in the Presence of Added Substrates.*—The substrate, either neat or in ether solution, was added to the solution of Ph_2CNLi (5 mmol), prepared as above at -78 °C, and the solution stirred at room temperature for 20 min. The π-cyclopentadienyltricarbonyl-molybdenum or -tungsten chloride (5 mmol) in ether (40 ml) was added to the cooled lithiomethyleneamine solution (-78 °C) and the mixture stirred at ambient temperature. The course of the reaction was monitored by i.r. spectroscopy. In ether solution, the methyleneamino-complexes $(\pi\text{-}C_5H_5)M(CO)_2(N:CPh_2)$ show a characteristic absorption at *ca.* 1870—1880 cm^{-1}, and the aza-allyl/allene complexes a characteristic absorption at *ca.* 1840 cm^{-1}.

The molybdenum and tungsten complexes $(\pi\text{-}C_5H_5)M(CO)_2N:CPh_2$ were obtained as blue crystals, the tungsten complex being identical to the complex reported earlier.[1] $(\pi\text{-}C_5H_5)Mo(CO)_2(N:CPh_2)$ (m.p. 104—106°) formed air-stable, dark blue crystals which were moderately soluble in hexane and very soluble in most other common organic solvents to give intense, dark green air-sensitive solutions (Found: C, 60·35; H, 4·15; N, 3·8. $C_{20}H_{15}MoNO_2$ requires C, 60·5; H, 3·8; N, 3·55%).

Mass spectrum (direct insertion at *ca.* 200°): the isotopic distribution pattern observed for the parent ion corresponded to that computed for $C_{20}H_{15}MoNO_2$. Major ions observed were at 399 $[P^+]$, 371 $[(P-CO)^+]$, 343 $[(P-2CO)^+]$, 240 $[(C_5H_5MoPh)^+]$, 163 $[(C_5H_5Mo)^+]$, 199·5 $[(C_5H_5Mo(CO)_2NCPh_2)^{2+}]$, 171·5 $[(C_5H_5MoNCPh_2)^{2+}]$, m^* 344 $[P^+ - CO]$, m^* 317 $[(P-CO)^+ - CO]$, m^* 168 $[(C_5H_5MoNCPh_2)^+ - PhCN]$.

(i) *Addition of* PhCN. Introduction of the nitrile to the $Ph_2C:NLi$ solution produced no detectable reaction nor any colour change. Free nitrile persisted throughout the reaction with the carbonyl halide. The major product, identified spectroscopically, was $(\pi\text{-}C_5H_5)Mo(CO)_2(N:CPh_2)$,

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[10] E. O. Fischer, *Inorg. Synth.*, 1963, **7**, 136.

[11] P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, 1961, **26**, 4886.

with the aza-allyl/allene complex, $(\pi\text{-}C_5H_5)Mo(CO)_2(Ph_2CNCPh_2)$, and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ occurring as minor products in a proportion which varied from reaction to reaction.

(ii) *Addition of* Me_2CO, Ph_2CO, *and* p-tolyl$_2$CO. An immediate colour change from orange-red to pale yellow occurred on addition of these compounds to the ether solution of $Ph_2C{:}NLi$. Free ketone was detected throughout the course of the reaction with the carbonyl halide, and in all cases the major product was $(\pi\text{-}C_5H_5)Mo(CO)_2N{:}CPh_2$ with the occasional appearance of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ as a very minor product.

(iii) *Addition of* $Ph_2C{:}NH$. No initial colour change occurred on its addition to the $Ph_2C{:}NLi$ solution. $(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)$ was the predominant product, together with traces of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

Two ν(CO) absorptions at *ca.* 1880 and 1870 cm^{-1} were detected which varied in intensity during the later stages of the reaction. A variable-temperature study indicated that the 1870—1880 cm^{-1} fluctuations were not temperature dependent, and subsequent thin-layer chromatography resulted in the separation of very small quantities of the 1870 cm^{-1} component. Ultraviolet irradiation of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ and $Ph_2C{:}NH$ in ether solution during 1/4 h yielded a small quantity of a new carbonyl component with a carbonyl stretching frequency of *ca.* 1875 cm^{-1}. The major proportion of the carbonyl chloride remained unchanged even after irradiation for 3½ h and the relative proportion of the product was unchanged after 2 h. The data obtained for this derivative are consistent with it being formulated as $(\pi\text{-}C_5H_5)Mo(CO)_2(Ph_2C{:}NH)Cl$, by comparison with the previously reported complex $(\pi\text{-}C_5H_5)Mo(CO)_2(PhBu^tC{:}NH)Cl$.[3] Thus in the reaction of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ with $Ph_2C{:}NLi$ in the presence of $Ph_2C{:}NH$ the absorption detected at 1870 cm^{-1} is assigned to $(\pi\text{-}C_5H_5)Mo(CO)_2(Ph_2C{:}NH)Cl$. Its subsequent depletion may result from loss of HCl or alternatively by reaction with $Ph_2C{:}NLi$ and displacement of $Ph_2C{:}NH$. The latter route is preferred since all previous attempts to eliminate HCl from $R_2C{:}NH$ substitution derivatives of carbonyl halides to produce methyleneamino-complexes have been unsuccessful.[12]

(iv) *Addition of* trans-*stilbene*. Mixing of the $Ph_2C{:}NLi$ solution with the olefin produced no colour change. The sole product of the complete reaction with the carbonyl halide appeared to be the methyleneamino-complex, although transient formation of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ was detected.

(v) *Addition of* $C_6H_{11}NC$. No colour change occurred on addition of the isonitrile to the lithiomethyleneamine solution. The i.r. spectrum, following addition of the $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ solution, indicated some aza-allyl/allene formation, but reaction between the carbonyl chloride and the isonitrile was also detected. Subsequent reaction between the latter materials in ether solution under the conditions of the original reaction was confirmed, and the product identified as $(\pi\text{-}C_5H_5)Mo(CO)_2(C_6H_{11}NC)Cl$ by i.r. spectroscopy [(CO), hexane: 1987s and 1918s cm^{-1}].

(vi) *Addition of* $PhNH_2$. An immediate lightening of colour was noted on addition of aniline to the lithiomethyleneamine solution, although on ageing the solution darkened markedly. Addition of the carbonyl chloride produced the methyleneamino-complex together with a trace of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

(vii) *Addition of* PhNCO. A colour change from orange-red to yellow, accompanied by a clouding of the solution resulted on addition of the isocyanate to the lithiomethyleneamine solution. The characteristic ν(NCO) stretching frequency at 2260 cm^{-1} was lost and a new absorption appeared at 1690 cm^{-1} indicating reaction between the components. After completion of the reaction with $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ as indicated by the consumption of the latter complex, the methyleneamino-complex was observed to be the major product with a minor proportion of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. The isocyanate was not regenerated at the end of the reaction and PhC:N was identified by t.l.c. as one of the products.

Reaction of n-Butyl-lithium with PhC:N *and* Ph_2CO.—These reactions were performed to ascertain the extent of reaction and the amount of nitrile and ketone remaining at various times up to 24 h, the time allowed for complete reaction to occur in the $Ph_2C{:}NLi/(\pi\text{-}C_5H_5)Mo(CO)_3Cl$/added substrate reactions.

(i) PhCN. n-Butyl-lithium (5 mmol) in hexane (2 ml) was added to the nitrile (0·51 g, 5 mmol) in ether (50 ml) at −78°. On warming and stirring at ambient temperature a clear orange solution was produced which became cloudy during 24 h. The intensity of the ν(C:N) stretching frequency absorption decreased during the reaction time, but after 24 h unchanged nitrile remained to a significant extent.

(ii) Ph_2CO. n-Butyl-lithium (5 mmol) in hexane (2 ml) was added to the ketone (0·91 g, 5 mmol) in ether (50 ml) at −78°. On warming and stirring at ambient temperature a very pale cloudy yellow solution was produced. After 24 h an off-white precipitate had separated from the almost colourless supernatant liquid. Throughout the reaction most of the ketone persisted in the solution and at the end of the reaction was detected in an undiminished quantity by i.r. spectroscopy.

Possible impurities in Ph_2CO such as moisture, which would lead to the formation of the white precipitate, are eliminated since the same bulk sample of ketone was used with $Ph_2C{:}NH$ to react with Bu^nLi. The resultant reaction mixture when added to a solution of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ in ether, caused all the latter complex to be consumed and the exclusive formation of $(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)$. Had Bu^nLi been consumed in any way except by reaction with $Ph_2C{:}NH$, then some carbonyl chloride would remain, and products additional to the methyleneamino-complex would be formed.

Reaction of $(\pi\text{-}C_5H_5)W(CO)_3Cl$ *with* $Ph_2C{:}NH$.—Unlike the reaction referred to previously in which the corresponding carbonylmolybdenum chloride was irradiated with u.v. light, this reaction failed to proceed even at the refluxing temperature to produce a simple substitution product. No reaction occurred between $(\pi\text{-}C_5H_5)W(CO)_3Cl$ (1·84 g, 5 mmol) and $Ph_2C{:}NH$ (0·91 g, 5 mmol) in ether or ether–toluene solution except some decomposition.

Action of Heat on $(\pi\text{-}C_5H_5)Mo(CO)_2(N{:}CPh_2)$ *in Monoglyme Solution*.—The dark blue complex (0·4 g, 1 mmol) was dissolved in monoglyme (15 ml) and the resultant dark green solution was heated to 80 °C. No reaction was detected by i.r. spectroscopy during 24 h though the colour of the solution became green-brown through the presence of decomposition material. Removal of the solvent *in vacuo* yielded an oily residue which on mass spectroscopic examination showed the presence of starting material as the only carbonyl-containing species present.

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[12] M. Kilner, unpublished results.

Action of Heat on $(\pi\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{NC}(p\text{-tolyl})_2$ *in Monoglyme Solution.*—The complex (0·21 g, 0·5 mmol) in monoglyme (10 ml) was heated and processed as described above but no dinuclear complex was isolated.

Action of Heat on $(\pi\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{NC}(p\text{-tolyl})_2$ *in Monoglyme Solution.*—The dark blue complex (0·1 g, 0·2 mmol) in monoglyme (8 ml) was heated at 80° for 4 h during which time the dark green colour changed to orange-red. Addition of hexane (5 ml) and cooling to 0° gave a red powder which was identified by mass spectroscopy and i.r. spectroscopy as $[(\pi\text{-C}_5\text{H}_5)\text{W(CO)NC}(p\text{-tolyl})_2]_2$ (m/e 970). Ions detected in the spectrum: m/e 942 $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})\{\text{N}{\vdots}\text{C}(p\text{-tolyl})_2\}_2]^+$; m/e 914 $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2\{\text{N}{\vdots}\text{C}(p\text{-tolyl})_2\}_2]^+$; m/e 797 $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(p\text{-tolyl})\{\text{N}{\vdots}\text{C}(p\text{-tolyl})_2\}]^+$; m/e 680 $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(p\text{-tolyl})_2]^+$; m^* 915 $[P^+ - \text{CO}]$; m^* 886 $[(P - \text{CO})^+ - \text{CO}]$; m^* 696 $[(P - 2\text{CO})^+\text{-}p\text{-tolylCN}]$; m^* 680 $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(p\text{-tolyl})\{\text{N}{\vdots}\text{C}(p\text{-tolyl})_2\}^+\text{-}p\text{-tolylCN}]$.

Reaction of $(\pi\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{N}{\vdots}\text{C}(p\text{-tolyl})_2$ *with* Ph_3P.—The blue complex (0·09 g, 0·22 mmol) in hexane (15 ml) failed to react with Ph_3P (0·056 g) on stirring at room temperature. Warming the solution and finally heating at the reflux temperature led only to eventual decomposition.

Reaction of $(\pi\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{N}{\vdots}\text{C}(p\text{-tolyl})_2$ *with Iodine.*—The complex (0·425 g, 1 mmol) in monoglyme (30 ml) was added to a solution of iodine (0·25 g, 2 mmol) also in monoglyme (15 ml). Gas evolution occurred at room temperature and only a yellow-white solid non-carbonyl decomposition product was formed.

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