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Organonitrogen Groups in Metal Carbonyl Complexes. Part III.¹ Comparison of Alkylarylmethyleneamino-Complexes of Molybdenum and Tungsten with the Corresponding Dialkyl- and Diaryl-methyleneamino-Complexes

By M. Kilner * and J. N. Pinkney, Chemistry Department, The University of Durham, South Road, Durham

The properties and reactions of complexes of the type $[(\pi - C_5H_5)M(CO)_2N:CRR']$ (M = Mo, W; R = Ph, R' = Bu^t) closely resemble those of the di-t-butyl rather than the diphenyl derivatives. Complexes of the type $[(\pi - C_5H_5M - C_5H_5M$ $(CO)N:CBu^tPh]_2$ and $[(\pi-C_5H_5)M(CO)_2(PhBu^tCNCBu^tPh)]$ were not formed. With triphenylphosphine, the Mo complex formed a substitution product $[(\pi - C_{g}H_{\delta})Mo(CO)(PPh_{3})N:CBu^{t}Ph]$, in contrast to all other methyleneamino-complexes studied. With iodine, substitution analogous to that of the di-t-butyl complex, resulted in the formation of $[(\pi-C_5H_5)M(CO)I_2N:CBu^tPh]$. The reaction of PhBu^tC:NSiMe₃ with $[(\pi-C_5H_5)Mo(CO)_3CI]$ in monoglyme gave $[(\pi - C_5H_5)Mo(CO)_2(HN:CBu^{\dagger}Ph)Cl]$.

SUBSTITUENTS on the methyleneamino-group considerably influence the type of complex formed in the reactions of methyleneamino-derivatives with transitionmetal complexes. Diphenylmethyleneamino-derivatives give rise to complexes of three types for π -cyclopentadienvlcarbonyl-molybdenum and -tungsten systems, $(\pi - C_5H_5)M(CO)_2N:CPh_2, [(\pi - C_5H_5)M(CO)N:CPh_2]_2$ and $(\pi-C_{5}H_{5})M(CO)_{2}(Ph_{2}CNCPh_{2}),$ depending upon the methyleneamino-derivative used.² The first two result from reactions involving Ph₂C:NSiMe₃, whereas the 2-aza-allyl complex is formed exclusively in reactions involving Ph, C:NLi.2,3 In contrast, di-t-butylmethyleneamino-derivatives form only complexes of the first type.1

The different derivatives arising from the presence of different substituents, may be entirely due to steric rather than electronic factors. It was of interest, therefore, to study the mixed phenyl-t-butylmethyleneamino-system for which the steric requirements are somewhat less exacting than those for the di-t-butyl derivative. It was considered likely that the methyleneamino-group would again be prevented from bridging between two metals by the presence of one bulky group, but it was anticipated that the 2-aza-allyl group may be formed, and would provide information on the bonding of this group to the metal.

¹ Part II, M. Kilner and C. Midcalf, J. Chem. Soc. (A), 1971, 292; M. Kilner and C. Midcalf, Chem. Comm., 1970, 552.
² K. Farmery, M. Kilner, and C. Midcalf, J. Chem. Soc. (A), 1970, 2279.

Reactions of complexes of the type $[(\pi - C_5 H_5)M_5]$ (CO)₂N:CR₂] again depend on the substituent group. For R = Ph, no reaction occurred with PPh_3 under forcing conditions over many days,² but when $R = Bu^t$, reactions occurred which involved the solvent as a reactant. $(\pi - C_5 H_5) M(CO)_2 (PPh_3) H$ and [PPh₃Bu^t]- $[(\pi-C_5H_5)MCl_4]$ were formed in monoglyme and CCl_4 solvents respectively.¹ With iodine, diphenyl-derivatives produced $(\pi-C_5H_5)_3M_3I_3O_4$ complexes,² whereas t-butyl complexes gave (π-C₅H₅)M(CO)I₂N:CBu^t₂.¹

RESULTS AND DISCUSSION

Phenyl-t-butylmethyleneamine and (N-Trimethylsilyl)phenyl-t-butylmethyleneamine.—PhBu^tC:NH was obtained in good yield by a modified reaction of a Grignard reagent with a nitrile.⁴ 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 1, together with the relevant data for Ph₂C:NH and $Bu_2^tC:NH$. v_{CN} and v_{NH} Occur in the usual regions, and in the ¹H n.m.r. spectrum, single signals only are observed for both phenyl and t-butyl protons. No splitting of phenyl protons into meta and ortho/para

³ K. Farmery and M. Kilner, J. Organometallic Chem., 1969,

^{16, 51.} ⁴ P. L. Pickard and T. L. Tolbert, J. Org. Chem., 1961, 26,

sets was detected.⁵ The N-H signal was detected as a weak broad absorption at low field, the broadness arising from the electrical quadrupole moment of the nitrogen nucleus.

The pale yellow, moisture sensitive PhBu^tC:NSiMe₃ was obtained by a standard method⁶ in good yield. I.r. and ¹H n.m.r. spectroscopic data are recorded in Table 1 and compared with data for Ph₂C:NSiMe₃ and Bu^t₂C:NSiMe₃. In the ¹H n.m.r. spectrum, signals

actions of $(\pi$ -C₅H₅)M(CO)₃Cl (M = Mo, W) with PhBu^t-C:NLi, and the reaction of $(\pi-C_5H_5)W(CO)_3Cl$ with PhBu^tC:NSiMe₃ produced complexes of the type $[(\pi - C_5 H_5)M(CO)_8N:CBu^tPh]$, and thus closely resemble the reactions with But₂C:NLi and But₂C:NSiMe₃. The products are in contrast to those obtained using Ph₂C:NLi,^{1,2} and no evidence was found for complexes containing a 2-aza-allyl group. Also, the dicarbonyl complexes obtained showed no tendency to lose CO

TABLE 1

Spectroscopic data

	$Lr. (cm^{-1})$		¹ H n.m.r. (7)				
Compound	VCN	v _{NH}	Solvent	Ph	But	Others	
Ph,CNH "	1603	3236	$C_{6}D_{6}$	$2 \cdot 4(4) 2 \cdot 7(6)$		0.04(1)	
PhBu ^t C:NH	1618	3226	CČl₄	2.79(5)	8.81(9)	0 ∙09`́	
But,C:NH b	1610		CCl		8.70(18)	$6 \cdot 6(1)$	
Ph ₂ C:NSiMe ₃	1642 °		CDČl ₃	2.66	. ,	10·03	
PhBu ^t C:NSiMe ₃	1678		CDCl ₃	2.73(3) $3.03(2)$	8.85(9)	10.16(9)	
But ₂ C:NSiMe ₃	1733		CDCl ₃		8.72(2)	9.82(3)	
					8.87(4)		

^a (i) I. Pattison and K. Wade, J. Chem. Soc. (A), 1968, 57; (ii) K. Wade and B. K. Wyatt, J. Chem. Soc. (A), 1969, 1339; (iii) J. R. Jennings, I. Pattison, K. Wade, and B. K. Wyatt, J. Chem. Soc. (A), 1967, 1608. ^b R. Snaith and K. Wade, personal communication. ^c L.-H. Chan and E. G. Rochow, J. Organometallic Chem., 1967, 9, 231.

	I.r. spectral data			¹ H n.m.r. spectral data			
$Complex (-C, H, Mo(CO), N^{*}CButPh$	Phase	$v_{\rm CO}(\rm cm^{-1})$	$v_{\rm CN}(\rm cm^{-1})$	Solvent	$\tau(Ph)$	$\tau(\mathrm{Bu}^{t})$	Others
(<i>π</i> -0 ₅ 11 ₅)W0(CO) ₂ N-CDU-FII	Mull	1942vs, 1855vs, 1825w 1965sh, 1940vs, 1881sh, 1846vs, 1821sh	1636ms	CDCI ₃	2.99	0.00	4.11
$(-CH)W(CO) N^{*}CP$	Hexane	1967vs, 1887vs	1694.	CDCI	9.50	0.00	1.10
$(\pi - C_5 \Pi_5) W(CO)_2 N \cdot CD u^2 P \Pi$	Mull	1951vs, 1830vs, 1810w,sh 1951sh, 1929vs, 1869sh, 1835vs, 1808w,sh	1634m	CDCI ₃	2.99	8.90	4.40
	Hexane	1955vs, 1873vs		0D.01	a a a (a)	a - a(a)	
$(\pi$ -C ₅ H ₅)Mo(CO)(PPh ₃)N:CBu ^v Ph	KBr	1802vs	1547ms	CDCI ₃	2.70(5)	8.79(9)	4.61(5)
	Hovano	1802VS 1845vs	10471115				3.09(13)
$(\pi\text{-}\mathrm{C}_{5}\mathrm{H}_{5})\mathrm{Mo}(\mathrm{CO})\mathrm{I}_{2}\mathrm{N}\mathbf{:}\mathrm{CBu}^{t}\mathrm{Ph}$	Nujol	2041s, 2000w,sh	1660vw,br	$\text{CDCl}_3 (-40^\circ)$	2·29s 2·61w	8∙45s 8∙71w	4 ∙ 4 4s
				CDCl ₃ (40°)	2·38w 2·62s	8∙44w 8∙68s	4.56s
				CDCl ₃ (40°) *			5.78
$(\pi$ -C ₅ H ₅)W(CO)I ₂ N : CBu ^t Ph	Nujol	2016s	1667vw,br	$\text{CDCl}_3 (-40^\circ)$	2.44	8.66	4.42
	CHCl ₃	2031s		$\operatorname{CDCl}_{3}(-20^{\circ})$	2.57	8.67	4.50
				$CDCl_3 (0^\circ)$	2.51	8.63	4.48
				$CDCI_3 (20^\circ)$	2.99	8.69	4.57
$(-C \mathbf{H}) \mathbf{M}_{0}(\mathbf{C}O) (\mathbf{H}\mathbf{N}^{*}\mathbf{C}\mathbf{B}_{0}\mathbf{t}\mathbf{D}\mathbf{h}) C$	Nuiol	1051 ve 1845 ve 1818 v eb	1618m	$CDCI_3(40)$	3.00/5)	0.97/0)	0.40 5.31(2)
(#-05115/M0(00)2(1110.0DU-FII)CI	rujoi	100103, 104003, 10100,51	101011	C626	0 00(0)	0 21(0)	0 01(0)
		* After 3 hr.					

TABLE 2

I.r. and ¹H n.m.r. spectroscopic data for methyleneamino-carbonyl complexes

arising from the -SiMe₃ and But protons appeared as singlets, but phenyl protons gave two multiplets corresponding to meta and ortho/para sets.⁵ The parent ion was not observed in the mass spectrum of PhBut-C:NSiMe₃, the peak of highest mass (m/e 218) corresponding to $[PhBu^{t}C:NSiMe_{2}]^{+}$ or $[Ph(CMe_{2})C:NSiMe_{3}]^{+}$. A similar fragmentation occurred for But₂C:NSiMe₃ and again no parent ion was detected.7

Phenyl-t-butylmethyleneamino-complexes.—The re-

⁵ (a) I. Pattison and K. Wade, J. Chem. Soc. (A), 1968, 57; (b) K. Wade and B. K. Wyatt, J. Chem. Soc. (A), 1969, 1339; (c) J. R. Jennings, I. Pattison, K. Wade, and B. K. Wyatt, J. Chem. Soc. (A), 1967, 1608.

on heating to form dinuclear complexes. In these respects there is a close resemblance to the di-t-butylmethyleneamino-complexes, which is also reflected in many other properties.

Spectroscopic data on the complexes are recorded in Table 2. In the carbonyl stretching region, two strong absorptions are observed in hexane solutions at relatively low frequencies, indicating that the methyleneaminogroup is acting as a 3-electron donor to the metal. Both complexes are very soluble in hydrocarbon sol-

⁶ L.-H. Chan and E. G. Rochow, J. Organometallic Chem., 1967, 9, 231. 7 R. Snaith and K. Wade, personal communication.

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vents and the complex spectra recorded in Nujol arises because the sample was in part in solution, and in part in suspension. v_{ON} Were observed as medium-strong absorptions at positions little changed from the free methyleneamine (Table 1).

The positions and intensities of the carbonyl absorptions of a hexane solution of the molybdenum complex showed no variations over the temperature range -40° to 50° , nor were any changes observed in benzene at temperatures down to the freezing point. In this respect the complex differed from the analogous ditbuyl derivative for which two new low-frequency absorptions gradually replaced the original absorptions on cooling to -45° , the change being completely reversible. The changes were interpreted as indicating rotational changes about the M-N bond of the linear M-N-C skeleton. From the limited data available it is not possible to decide whether free rotation about the metal-nitrogen bond occurs or whether one preferred conformation is adopted under the conditions studied.

Molecular-weight measurements confirm the mononuclear formulations in solution, and the mass spectra similar formulations in the vapour state. In the mass spectra, parent ions were observed with isotopic distribution patterns corresponding to those computed for C₁₈H₁₉MNO₂ units, and each complex produced metal-containing ions of similar types as well as the expected organic ions resulting from fragmentation The fragmentation of the methyleneamino-group. pattern of the tungsten complex is worthy of note, since in addition to the loss of carbon monoxide from the parent ion, the fragmentation also proceeds by the more unusual loss of a methyl radical from the co-ordinated methyleneamino-group. The relatively low abundance of the resulting ion is similar to that found for another series of cyclopentadienyl carbonyl-molybdenum and -tungsten complexes e.g. $R_3GeM(CO)_3(\pi-C_5H_5)$, which lose alkyl radicals as an alternative fragmentation route to loss of carbon monoxide.8

The possible bonding modes of the methyleneaminogroup have been discussed,^{1,2} and for the di-t-butylmethyleneaminomolybdenum complex an X-ray crystal structure determination showed the M-N-C skeleton to be almost linear with considerable multiple bonding between the metal and nitrogen.⁹ No structural data is available for the phenyl-t-butylmethyleneaminocomplexes and the available spectroscopic data can be interpreted in terms of either a linear or a bent skeleton. 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).

The air-stable complex $(\pi-C_5H_5)Mo(CO)_2(HN:CPh-Bu^t)Cl$ was formed, surprisingly, in the reaction of $(\pi-C_5H_5)Mo(CO)_3Cl$ with PhBu^tC:NSiMe₃, in contrast

to the reaction with $(\pi-C_5H_5)W(CO)_3Cl$ and to reactions involving other N-silylmethyleneamines, which yield methyleneamino-complexes as discussed above. The identity of the complex was confirmed by comparison with material obtained from the reaction of $(\pi-C_5H_5)Mo(CO)_3Cl$ with the free methyleneamine in chloroform or toluene solutions.

I.r. and ¹H n.m.r. data are recorded in Table 2. Two carbonyl stretching frequencies were observed consistent with a *cis*-dicarbonyl complex, the weak absorption at 1818 cm⁻¹ being assigned to solid state effects. v_{CN} Is unchanged from that of the free methyleneamine, and consistent with results for other methyleneamine adducts of both main group and transition metal systems.¹⁰ Co-ordination of neutral methyleneamines appears to have little effect on v_{CN} . The presence of hydrogen attached to the nitrogen of the methyleneamino-group is indicated by i.r. but not ¹H n.m.r. spectroscopy. A medium intensity absorption at 3252 cm^{-1} is assigned to v_{NH} but in the n.m.r. spectrum no signal due to the N-H proton was detected, possibly because of the broadness of N-H signals and the only moderate solubility of the complex in deuteriobenzene. The source of the hydrogen is not known but like many hydrogen abstractions in solution possibly arises from the solvent, rather than from traces of moisture. Efforts were made to eliminate the latter, but the product still formed in reasonable yield.

The complex decomposed on heating. In vacuo a red oil, identified by i.r. spectroscopy as mainly PhBu^t-C:NH with an unknown metal carbonyl impurity, was condensed onto a cold finger. Elimination of HCl with the formation of $(\pi$ -C₅H₅)Mo(CO)₂N:CPhBu^t was not achieved by heating in the solid state, nor in solution in the presence of a base.

Substitution of triphenylphosphine for carbon monoxide could not be achieved for diphenyl-² nor di-tbutyl-methyleneamino¹-derivatives, but for the mixed phenyl-t-butyl molybdenum complex substitution occurs under relatively mild conditions to produce the complex $(\pi - C_5 H_5) Mo(CO)(Ph_3 P) N: CPhBu^t$. The corresponding tungsten complex failed to react. Spectroscopic data for the new complex is recorded in Table 2. v_{CO} and $v_{\rm ON}$ Occur at low frequencies and may indicate that the charge built up at the metal by the predominantly σ -donating phosphorus, is dissipated by both the carbonyl and methyleneamino-groups. v_{CN} Is considerably affected by this particular ligand and the decrease of ca. 89 cm⁻¹ may arise through steric effects involving the bulky PPh_3 and/or increased $d\pi - \pi^*$ bonding between the metal and the methyleneaminogroup. Steric interaction between PPh₃ and the methyleneamino-group in *cis*-positions may be relieved by a decrease in the M-N-C bond-angle of the methyleneamino-group which will tend to move the substituent

⁸ A. Carrick and F. Glockling, *J. Chem. Soc.* (A), 1968, 913; D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317.

⁹ H. M. M. Shearer and J. D. Sowerby, personal communication.

¹⁰ B. Samuel, R. Snaith, C. Summerford, and K. Wade, J. Chem. Soc. (A), 1970, 2019; K. Farmery and M. Kilner, unpublished results.

groups away from certain other co-ordinated ligands. A consequence of the increased deviation from a linear skeleton will be a weakening of the nitrogen \longrightarrow metal π -bonding, since the nitrogen orbital involved will tend to approach sp^2 hybridisation. Weakening of this type of bonding alone is expected to result in a lowering of $v_{\rm CN}$, and may contribute with increased $d\pi$ - π^* bonding, arising from the replacement of CO by a stronger σ -donor but weaker π -acceptor, to the considerable decrease observed.

The ¹H n.m.r. spectrum showed signals for the protons of Bu^t , π -C₅H₅ and two types of Ph groups in positions typical of these groups. The signal due to the π -C₅H₅ protons was observed at higher field ($\tau 4.67$) than in the parent dicarbonyl complex ($\tau 4.17$), and such movements are thought to reflect the ability of the π -C₅H₅ group and the limitation of the PPh3 group to remove electron density from the metal atom.¹¹ In the mass spectrum, the parent ion $(m/e \ 613)$ is observed, with an isotopic distribution pattern appropriate for C₃₅H₃₄MoNOP. A notable feature of the spectrum, and also that of all phenyl-t-butylmethyleneamino-complexes is the fragmentation of the methyleneamino-group, which occurs by initial loss of a t-butyl radical followed by PhCN. For no complex was loss of Ph radicals followed by Bu^tCN observed.

Reactions of methyleneamino-complexes with iodine have vielded complexes of two types $(\pi - C_5 H_5)M(CO)$ - $I_2N:CR_2^1$ and $(\pi-C_5H_5)_3M_3I_3O_4$,² depending on the substituent groups. The former complexes result from di-t-butyl complexes and the latter from diphenyl complexes, and consistent with the general tendency for the mixed alkylarylmethyleneamino-complexes to undergo reactions analogous to the di-t-butyl derivatives, complexes of the former type are produced (M = Mo, W). They are dark solids, insoluble in non-polar, but very soluble in polar, solvents, and on heating decompose without melting. The molybdenum complex is sensitive to air, but the tungsten complex was more resistant and decomposed only on prolonged exposure over many days. Mononuclear formulations were confirmed in the vapour state by the mass spectrum, but parent ions were not observed for either complex even at cool source temperatures. Similar results occurred for the corresponding di-t-butylmethyleneamino-complexes.¹

Co-ordination of the electronegative iodine atoms effectively decreases the electron density on the metal and has the expected effect on v_{CO} and v_{CN} . A decrease in electron density will increase σ - and π -donation to the metal but reduce $d\pi$ - π * back donation, and increases in v_{CO} and v_{CN} are consequently observed. The assignment of v_{CN} absorptions was difficult as absorptions are very weak and broad, and those recorded in Table 2 should be considered tentative.

The ¹H n.m.r. spectrum for the molybdenum complex showed two signals for Bu^t and Ph protons, the downfield ¹¹ K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, 1967, **6**, 294.

J. Chem. Soc. (A), 1971

signals of each pair being the much more intense at -40° . As the temperature was raised the up-field signals progressively increased in intensity and at $+40^{\circ}$ the relative intensities were reversed. The signal due to π -C₅H₅ protons remained fairly constant at $\tau 4.5$ over this temperature range. On standing at $+40^{\circ}$ for a few hours, solid material separated from the solution, and only a single signal at $\tau 5.78$ was observed, presumably due to π -C₅H₅ protons in a new environment, the complex having decomposed to remove the methyleneamino-group from solution.

The presence of two signals for both t-butyl and phenyl protons in the ¹H n.m.r. spectrum could be due to a number of causes. The increasing intensity of the up-field signals with increase in temperature followed by the final decomposition may be due to a gradual decomposition process in which the methyleneaminogroup is cleaved from the complex, remains in solution in some form before being finally removed from solution ageing at ambient temperature. This appears on unlikely on two accounts; firstly, cleavage of the methyleneamino-group from the complex would be expected to affect the shielding of the π -C₅H₅ 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 for which the complex ¹H n.m.r. spectrum was observed. Thus the change in form of the compound under study is such that the nature and bonding in the complex is little, if at all, changed.

Alternatively the spectral changes may be due to geometrical changes of the complex involving either isomers (I) and (II), or the positions of the substituents of a bent methyleneamino-group, but on the basis of the limited solution data, we are unable to interpret the spectra in terms of one type of structural change in preference to the other.

The tungsten complex showed only single signals for t-butyl and phenyl protons over a temperature range -40° to $+20^{\circ}$, the t-butyl signal being initially at $\tau 8.66 (-40^{\circ})$ but progressively moves to $\tau 8.69 (+20^{\circ})$,



the corresponding phenyl signals being observed at 2.44 and $\tau 2.55$ respectively. Again at $+40^{\circ}$ decomposition was observed leaving a single signal due to π -C₅H₅ protons at τ 5.46, this having moved upfield from the corresponding signal at lower temperatures

(τ 4·42 at -40°, τ 4·57 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.

EXPERIMENTAL

Hydrocarbon solvents and diethylether were dried over extruded sodium, monoglyme and methanol were distilled from lithium aluminium hydride; chloroform was 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.—I.r. spectra in the range $4000-400 \text{ cm}^{-1}$ 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 tetramethylsilane as reference. Mass spectra were obtained using an AEI MS9 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°. Isotope distribution patterns were computed using a programme kindly supplied to us by Dr. E. H. Brooks.

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 Macrolab Osmometer, in chloroform or benzene solution.

Starting Materials.— π -Cyclopentadienyltricarbonylmolybdenum- and -tungsten-chlorides were prepared from the corresponding hydride 12 by the action of carbon tetrachloride and recrystallised from chloroform-hexane mixtures before use.

Phenyl-t-butylmethyleneamine (2,2-Dimethyl-1-phenylpropylideneamine) PhButC=NH.-The detailed preparation of this compound has not been reported previously but its i.r. spectrum 13 and some of its reactions have been given.^{14, 15} Attempts to synthesise it from benzonitrile and t-butylmagnesium bromide following the method of Pickard and Tolbert⁴ resulted only in recovery of unchanged benzonitrile. The use of a toluene-ether solvent at a reflux temperature of 100° and decomposition of the Grignard-nitrile complex with anhydrous ammonia 16 resulted in the isolation of a white solid, identified by its melting point and i.r. spectrum as 2,4,6-triphenyl-1,3,5triazine, the trimer of benzonitrile. The tendency of benzonitrile to polymerise in the presence of organometallic compounds has been previously noted.^{17, 5a} The synthesis was successfully achieved in good yield using the method of Pickard and Tolbert,⁴ but with the aryl Grignard and alkyl nitrile. t-Butyl cyanide (18.67 g, 0.225 mol) was added dropwise to a solution of PhMgBr(130 ml, 0.25 mol) and the mixture heated under reflux for 12 h, during which

time a white solid separated. To the cooled mixture, anhydrous methanol (61.75 ml, 1.5 mol) was added dropwise. The pale yellow ether solution was separated by filtration from the bulky white precipitate, the solvent removed $(25^{\circ}, 0.1 \text{ mmHg})$ and the residual liquid distilled $(44-46^{\circ}, 1000 \text{ mmHg})$ 0.1 mmHg) to give the colourless phenyl-t-butylmethyleneamine (30.4 g, 75%) (Found: C, 82.3; H, 9.1; N, 8.5; Calc. for $C_{11}H_{15}N$: C, 82.0; H, 9.3; N, 8.7%). l.r. (liquid film), v_{ON} 1618 ms, v_{NH} 3226 wm cm⁻¹ (lit.,¹⁴ 1618, $32\bar{2}6$ cm⁻¹).

(N-Trimethylsilyl)-2,2-dimethyl-1-phenylpropylideneamine, PhBu^tC=NSiMe₃.—This was obtained in good yield by the method of Chan and Rochow.6

n-Butyl-lithium (50 mmol) was added to phenyl-t-butylmethyleneamine (8.05 g, 50 mmol) in anhydrous ether (250 ml) at -196° and the mixture allowed to warm to room temperature. To the resultant bright yellow solution was added trimethylchlorosilane (5.4 g, 50 mmol) and the mixture stirred at room temperature for 12 h. The yellow ether solution was filtered, the solvent removed (25°, 0.1 mmHg) and the residual liquid distilled (36-38°, 0.02 mmHg) to give the straw-coloured (N-trimethylsilyl)phenyl-t-butylmethyleneamine (6.0 g, 51.5%) (Found: C, 71.8; H, 9.6; N, 5.8. C₁₄H₂₃NSi requires C, 72.1; H, 9.87; N, 6.0). By analogy with absorptions observed in a number of similar N-organosilyl compounds ⁶ the following tentative assignments of the i.r. spectrum are made: $\nu_{\rm CN}$ 1678 cm⁻¹, $\nu_{\rm (Si-N)}$ 906 cm⁻¹, $\delta_{\rm sym}$ (Si-Me₃) 1250, 1261 cm⁻¹, ρ (Si-Me₃) 836, 755 cm⁻¹.

Mass spectrum (direct insertion at source temperature). The parent ion [PhBu^tC=NSiMe₃]⁺ was not observed in the spectrum; the peak at highest mass corresponded to loss of a methyl group from the parent *i.e.* [PhBu^tC=NSiMe₂]⁺ or $[PhC(CMe_2)=NSiMe_3]^+$ at m/e 218.

Reaction of (π -C₅H₅)Mo(CO)₃Cl with PhBu^tC=NLi.--A solution of PhBu^tC=NLi was prepared by adding n-butyllithium solution (8 mmol) to phenyl-t-butylmethyleneamine (1.288 g, 8 mmol) in anhydrous ether (150 ml) frozen at -196° and stirring the mixture at room temperature for 1 h. Addition of the resulting reactant to a solution of $(\pi$ -C₅H₅)Mo(CO)₃Cl (2·26 g, 8 mmol) in anhydrous ether (250 ml) frozen at -196° , and subsequent warming to room temperature caused slow evolution of carbon monoxide and a darkening in colour. After 4 h, evaporation of the solvent from the reaction mixture $(25^{\circ}, 0.1)$ mmHg) gave a dark red-brown oily residue which was extracted with hexane $(3 \times 10 \text{ ml})$ to give deep blue solutions. The residual red-brown solid, after hexane extraction, was shown by i.r. spectroscopy to be $[(\pi$ - C_5H_5 Mo(CO)₃]₂. Repetition of a process of removing the solvent from the hexane extracts (25°, 0·1 mmHg) followed by redissolving the product in hexane removed eventually all traces of the dimer, and cooling (-20°) the resulting deep blue solution produced deep blue-black crystals of $[(\pi - C_5 H_5) Mo(CO)_2 N = CPhBu^{t}], m.p. 63 = -64^{\circ} (0.4 \text{ g}, 13\%)$ [Found: C, 58·1; H, 5·2; N, $3\cdot7\%$; M (cyclohexane) 398. $C_{18}H_{19}MONO_2$ requires C, 57.0; H, 5.0; N, 3.65%; M, 379).

These blue-black crystals were extremely soluble in all common organic solvents, polar and non-polar, forming

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deep 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.

Mass spectrum (direct insertion at source temperature). The parent ion $[(\pi-C_5H_5)Mo(CO)_2N=CPhBu^t]^+$ was observed at m/e 379; the isotopic distribution pattern corresponded to that computed for $C_{18}H_{19}MoNO_2$. The most intense peak was due to $[C_5H_5MoPh]^+$.

Reaction of $(\pi-C_5H_5)Mo(CO)_3Cl$ with PhBu^tC=NLi in Monoglyme at Reflux Temperature.--The previous reaction led to the formation of the methyleneamino-complex $(\pi\text{-}C_5H_5)\mathrm{Mo}(\mathrm{CO})_2\mathrm{N}=\!\!\mathrm{CPhBu}^t$ with no sign of dinuclear or aza-allyl complexes.^{1,2} In order to investigate the possible formation of complexes containing the aza-allyl ligand [PhButCNCButPh], more forcing conditions were used. A solution of PhButC=NLi (8 mmol) in monoglyme (100 ml) was prepared as described above. The solution was heated to the reflux temperature and a solution of $(\pi$ -C₅H₅)Mo(CO)₃Cl (1·12 g, 4 mmol) in monoglyme (50 ml) was added dropwise over 1 h. The mixture darkened considerably during the addition. After 4 h the reaction mixture was cooled and the solvent removed (25°, 0.1 mmHg) 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 $[\pi$ -C₅H₅Mo(CO)₃]₂ and some unreacted chloride.

Reaction of $(\pi$ -C₅H₅)W(CO)₃Cl with PhBu^tC=NLi.—The reaction was performed in an analogous manner to the attempted reaction of the molybdenum complex using $(\pi - C_5 H_5) W(CO)_3 Cl (2.21 \text{ g}, 6.0 \text{ mmol}), PhBu^tC=NH (0.97 \text{ g}, 1.00 \text{ g})$ 6.0 mmol) and BunLi (6.0 mmol). Extraction of the residue with hexane $(3 \times 10 \text{ ml})$ produced deep green solutions and left an orange-red solid, identified by i.r. spectroscopy as $[(\pi-C_5H_5)W(CO)_3]_2$ with small amounts of unchanged chloride. The emerald green oil which resulted on removal of the solvent (25°, 0·1 mmHg) from the combined extracts was treated as for the $(\pi$ -C₅H₅)Mo(CO)₃Cl/LiN:CBu^tPh reaction 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° produced a crop of deep blue crystals of $(\pi\text{-}C_5H_5)\mathrm{W}(\mathrm{CO})_2\mathrm{N}=\!\mathrm{CPhBu^t},$ but further crops could not be obtained from the mother liquor. Yield of recrystallised material 0.1 g (4%), m.p. 94° (Found: C, 46.5; H, 4.05; N, 2.95%; M (cyclohexane), 477. Calc. for $C_{18}H_{19}NO_2W$: C, 46.45; H, 4.1; N, 3.0%; M, 465).

These 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.

Mass spectrum (direct insertion at source temperature). The parent ion $[(\pi-C_5H_5)W(CO)_2N=CPhBu^t]^+$ was observed at m/e 465; the isotopic distribution pattern corresponded to that computed for $C_{18}H_{19}NO_2W$. The most intense peak was due to $[C_5H_5WPh]^+$.

Reaction of $(\pi$ -C₅H₅)Mo(CO)₂N=CPhBu^t with Ph₃P.— $(\pi$ -C₅H₅)Mo(CO)₂N=CPhBu^t (0.379 g, 1.0 mmol) and Ph₃P (0.262 g, 1.0 mmol) were dissolved in hexane (50 ml) and the mixture was heated under the reflux. A slow evolution of gas was observed and the solution slowly went green.

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The reaction was shown by i.r. spectroscopy to be complete after 24 h. The deep emerald green solution formed was separated by filtration from a small amount of brown material and the bulk of the filtrate reduced in volume (25°, 0·1 mmHg). On cooling to -20° dark blue-green microcrystals of $(\pi$ -C₅H₅)Mo(CO)(Ph₃P)N=CPhBu^t, were obtained which were filtered off, washed with hexane (2 × 5 ml), and dried *in vacuo* (0·30 g, 50%), m.p. 118—120° (Found: C, 68·75; H, 5·7; N, 2·1. C₃₅H₃₄MoNOP requires C, 68·5; H, 5·55; N, 2·3%).

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.

Mass spectrum (direct insertion at source temperature). The parent ion $[(\pi-C_5H_5)Mo(CO)(Ph_3P)N=CPhBu^t]^+$ was observed at m/e 613; the isotopic distribution pattern corresponded to that computed for $C_{35}H_{34}MoNOP$. Metastable peaks were observed at m/e 558 and 476 and arise respectively from the loss of CO from $[P]^+$ and the loss of the t-butyl group from $[P - CO]^+$. The most intense peak was due to $[(C_5H_5)MOPh]^+$.

Reaction of $(\pi$ -C₅H₅)W(CO)₂N=CPhBu^t with Ph₃P.— Because of the difficulty in obtaining a sufficient quantity of the pure crystalline complex $(\pi$ -C₅H₅)W(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 $[(\pi$ -C₅H₅)W(CO)₃]₂. The impure $(\pi$ -C₅H₅)-W(CO)₂N=CPhBu^t (0.4 g, ca. 0.8 mmol) and Ph₃P (0.23 g, 0.84 mmol) were dissolved in hexane (70 ml) and heated under reflux. No reaction was detected by i.r. spectroscopy in the carbonyl stretching region after 22 h. The solvent was removed (25°, 0.1 mmHg), replaced by monoglyme (50 ml) and heated to the reflux temperature. No reaction was detected by i.r. spectroscopy after 15 h.

Reaction of (π -C₅H₅)Mo(CO)₂N=CPhBu^t with I₂.—The molybdenum complex (0.19 g, 0.5 mmol) was dissolved in hexane (10 ml) and the solution cooled in an ice-bath. A solution of iodine (0.127 g, 0.1 mmol) in hexane (200 ml), also cooled in an ice bath, was added dropwise during ca. 1 h with vigorous stirring. A rapid reaction occurred with the formation of a dark precipitate. The mixture was stirred for a further hour and the very dark brown complex, $(\pi-C_5H_5)Mo(CO)I_2(N=CPhBu^t)$, was filtered off and dried in vacuo. The yield was almost quantitative. Decomposition without melting at 79° (Found: C, 34.0; H, 3.35; I, 41.4; N, 2.15. Calc. for $C_{17}H_{19}I_2MoNO$: C, 33.7; H, 3.15; I, 42.0; N, 2.3). The air-sensitive dark brown solid was insoluble in hexane but very soluble in chloroform. A fresh mull of the aged solid (48 h under N₂) showed a weakened carbonyl absorption and the appearance of another weak broad absorption at 1623 cm⁻¹ indicating that the compound was thermally unstable even at ambient temperature. The ¹H n.m.r. spectrum in CDCl₂ solution (Table 3) showed a number of signals whose intensity varied with change in temperature.

Mass spectrum (direct insertion at 100°). The parent ion $[\pi-C_5H_5)Mo(CO)I_2(N=CPhBu^t)]^+$ was not observed even with a cool source temperature. The ion of highest mass observed (m/e 587) corresponded to $[(\pi-C_5H_5)MoI_2-(N=CPhBu^t)]^+$, and had an isotopic distribution pattern corresponding to that computed for $C_{16}H_{19}I_2MoN$. The most intense peak was due to $[(C_5H_5)MoI]^+$.

Reaction of $(\pi$ -C₅H₅)W(CO)₂N=CPhBu^t with I₂.—The

reaction was performed as described above for the molybdenum complex using solutions of $(\pi-C_5H_5)W(CO)_2N=CPh-$ But (0.133 g, 0.36 mmol) in hexane (10 ml) and iodine (0.073 g, 0.36 mmol) in hexane (100 ml) cooled in an ice bath. A rapid reaction occurred with the formation of a grey solid which was filtered off, washed with hexane $(3 \times 10 \text{ ml})$, and dried in vacuo. The yield of the complex, $(\pi-C_5H_5)W(CO)I_2(N=CPhBu^t)$, was almost quantitative (Found: C, 29.8; H, 2.7; I, 36.6; N, 1.85. C₁₇H₁₉I₂NOW requires C, 29.5; H, 2.8; I, 36.75; N, 2.05%). A sample of this solid exposed to air for a few days showed virtually no change in its i.r. spectrum; on prolonged exposure (7 days) 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°. The assignment of the i.r. spectrum was 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 $\nu_{\rm CN}$ by analogy with the corresponding molybdenum complex. The ¹H n.m.r. spectrum in CDCl₂ (Table 2) showed single signals for Bu^t protons (singlet), π -C₅H₅ protons (singlet) and Ph protons (multiplet) whose positions remained fairly constant over a range of temperature.

Mass spectrum (direct insertion at 100°). The parent ion $[(\pi-C_5H_5)W(CO)I_2(N=CPhBu^t)]^+$ was not observed even with a cool source temperature. The ion of highest mass $(m/e \ 663)$ corresponded to $[(\pi-C_5H_5)WI_2(N=CPhBu^t)]^+$ with the isotopic distribution pattern appropriate for $C_{16}H_{19}I_2NW$. The most intense peak was due to $[C_5H_5WI]^+$.

Reaction of (π-C₅H₅)Mo(CO)₃Cl with PhBu^tC=NSiMe₃.---The methyleneamine (1.24 g, 5.3 mmol) and $(\pi$ -C₅H₅)- $Mo(CO)_{3}Cl$ (1.50 g, 5.3 mmol) were dissolved in monoglyme (100 ml) and the temperature raised to 70° . The solution darkened at ca. 60° and evolution of gas was observed. The reaction was shown by i.r. spectroscopy to be complete after $2\frac{1}{2}$ h when a dark red solution resulted. The solution was filtered, leaving a small amount of dark brown material and the solvent was removed (25°, 0.1 mmHg) 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 gave dark red crystals of $(\pi - C_5 H_5) Mo(CO)_2$ -(HN=CPhBu^t)Cl (0.68 g, 31% yield). Decomposition without melting at 126-128° (Found: C, 52.45; H, 4.95; Cl, 8.7; N, 3.25%; M, 402, 385. Calc. for $C_{18}H_{20}Cl$ -MoNO₂: C, 52·1; H, 4·8; Cl, 8·45; N, 3·35%; M, 415).

The deep red crystals were stable even on prolonged

exposure to air. The crystals were insoluble in hexane and cyclohexane; soluble in benzene, toluene, and chloroform forming red solutions which were also air-stable.

Mass spectrum (direct insertion at 80°). Even at low source temperatures the parent ion $[(\pi-C_5H_5)Mo(CO)_2-(HN=CPhBu^t)Cl]^+$ was not observed. The ion of highest mass was centred at m/e 359, corresponding to $[(\pi-C_5H_5)-Mo(HN=CPhBu^t)Cl]^+$; the isotopic distribution pattern was appropriate for $C_{16}H_{20}CIMoN$. The most intense peak was due to $[C_5H_5MoCl]^+$.

Reaction of (π-C₅H₅)Mo(CO)₃Cl with PhBu^tC=NH. $(\pi-C_5H_5)Mo(CO)_3Cl$ (0.5 g, 1.78 mmol) and PhBu^tC=NH (0.288 g, 1.78 mmol) in chloroform (50 ml) were heated at 70°. Darkening of the solution occurred and gas was evolved. After 3 h, the solution was filtered, the solvent removed (25°, 0.1 mmHg), and the residual dark red solid dissolved in toluene (30 ml). Addition of hexane (10 ml) and cooling to -20° caused the separation of $(\pi - C_5 H_5)$ - $Mo(CO)_2(HN=CPhBu^t)Cl (0.1 g)$ (Found: C, 52.4; H, 5.15; Cl, 8.4; N, 3.35. Calc. for $C_{18}H_{20}ClMoNO_2$: C, 52.1; H, 4.8; Cl, 8.45; N, 3.35%). The product was shown by i.r. spectroscopy and elemental analysis to be identical with the product from the previous reaction. Further crops of solid mixed with unreacted chloride were obtained from the mother liquor. A similar reaction was performed in toluene and also gave the dark red crystals.

Reaction of (π -C₅H₅)W(CO)₃Cl with PhBu^tC=NSiMe₃.-The silylmethyleneamine (1.286 g, 5.52 mmol) and $(\pi$ -C₅H₅)- $W(CO)_{3}Cl$ (2.03 g, 5.52 mmol) in monoglyme (100 ml) were heated to 70°. The reaction mixture darkened quickly at this temperature and went green. After 5 h, the green solution was filtered and the solvent was removed $(25^{\circ},$ 0.1 mmHg). Extraction of the dark residue with hexane $(4 \times 10 \text{ ml})$ produced an intensely deep blue-green solution which. on reduction to small volume 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 identified by i.r. spectroscopy to be largely $[(\pi-C_5H_5)W(CO)_3]_2$ with some unreacted chloride. The clear blue solution was removed with a syringe from the oil and on cooling to -20° deposited dark blue crystals of the complex $(\pi-C_5H_5)W(CO)_2N=CPhBu^t$, identified by its i.r. spectrum (yield 0.15 g, 6%).

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