Inorg. Chem. **1990**, *29*, 700-706

Contribution from the Departamento de Química Inorgânica-Instituto de Ciencia de Materiales, Universidad de Sevilla-CSIC, 41071 Sevilla, Spain, Instituto de Ciencia de Materiales, Sede D, CSIC, Serrano 113, 28006 Madrid, Spain, and Facultad de Ciencias Químicas, Universidad Complutense de Madrid-CSIC, 28040 Madrid, Spain

Synthesis and Properties of Seven-Coordinate Isocyanide Complexes of Molybdenum(II) and Tungsten(II) Containing Carbonyl and Trimethylphosphine Ligands. X-ray Structure of $MoCl_2(CNBu^t)(CO)(PMe_3)_3$

Ernesto Carmona,*,[†] Leopoldo Contreras,[†] Enrique Gutiĕrrez-Puebla,[‡] Angeles Monge,[‡] and Luis Sânchez[†]

Received May 3, 1989

The reaction of the seven-coordinate compounds $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) with isocyanides (CNR) in the presence of PMe_3 affords the monoisocyanide derivatives $MCl_2(CNR)(CO)(PMe_3)_3$ (M = Mo, R = Bu^t (**1a**), Cy (**1b**), $C_6H_5CH_2$ (**1c**), 2,6-$C_6H_3Me_2$ (**1d**); M = W, R = Bu^t (**2**)). Complex **1a** has been characterized by a single-crystal X-ray structural determination. The complex is monoclinic, space group $P2_1/n$, with a = 15.217 (4) Å, b = 16.367 (3) Å, c = 9.804 (2) Å, β = 90.75 (2)°, and D_{calcd} = 1.38 g cm^{-3} for Z = 4. The bis(isocyanide) derivatives $MCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (M = Mo (**3**), W (**4**)) may be isolated from the reaction of $MCl_2(CO)_2(PMe_3)_3$ with 2 equiv of $CNBu^t$, in the absence of added PMe_3. These reactions proceed initially with substitution of a PMe_3 ligand by CNR to produce the reactive intermediate species $MCl_2(CNR)(CO)_2(PMe_3)_2$ that could react further with either PMe_3 or CNR (R = Bu^t) to afford compounds **1** and **2** or **3** and **4**, respectively. Indeed, one such intermediate, $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ (**5**) has been isolated. Action of an excess of $CNBu^t$ (>4 equiv) on the chlorocarbonyls $MCl_2(CO)_2(PMe_3)_3$ produces the electron-rich species $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ (M = Mo (**6**), W (**7**)) that undergo reductive coupling of two isocyanide ligands, as demonstrated by the conversion of **6** into $[MoCl(CNBu^t)_2(Bu^t(H)NC{\equiv}CN(H)Bu^t)(PMe_3)_2]Cl$ (**8**). On the other hand, compound **1a** reacts with $Mg(CH_2CMe_3)Br$ with formation of the η^2-acyl $MoBr(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ (**9**).

Introduction

Many examples of complexes of Mo(II) and W(II) with isocyanide ligands are known.[1,2] These include the seven-coordinate homoleptic cations[3] $M(CNR)_7^{2+}$ as well as various halo–isocyanide species such as $M(CNR)_6X^+$ (X = halogen) and others containing monodentate and bidentate tertiary phosphine ligands[4,5] or 2,2′-bipyridine and related ligands.[6] Mixed halo–carbonyl–isocyanide compounds, e.g. $MI_2(CO)_2(CNR)_3$, are also known.[3b]

Different synthetic procedures are available for such compounds,[3-6] which on the other hand, undergo some interesting transformations, among them dealkylation,[6] the so-called reductive coupling of two adjacent isocyanide groups to a coordinated bis(alkylamino)acetylene ligand[7,8] and protonation to aminocarbyne groups.[9] Another important transformation of coordinated isocyanides is their insertion into M–C bonds with formation of iminoacyl functionalities.[2,10,11]

We have been involved recently in the investigation of the seven-coordinated complexes $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W), in particular in the study of their alkylation with formation of monomeric η^2-acyl derivatives of composition $MCl(\eta^2\text{-}COR)(CO)(PMe_3)_3$ and related species.[12] The present work is a continuation of these and other studies on low-oxidation-state complexes of molybdenum and tungsten and had originally two main objectives: (1) the preparation of new halo–trimethylphosphine complexes of Mo(II) and W(II), containing in addition coordinated carbonyl and isocyanide ligands and (2) their alkylation to the corresponding acyl or iminoacyl derivatives. The first of these objectives has been fully achieved, and new compounds of composition $MCl_2(CNR)(CO)(PMe_3)_3$ (M = Mo, R = Bu^t (**1a**), Cy (C_6H_{11}) (**1b**), $C_6H_5CH_2$ (**1c**), 2,6-$Me_2C_6H_3$ (**1d**); M = W, R = Bu^t (**2**)), $MCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (M = Mo, (**3**), W, (**4**)), and $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ (**5**) have been obtained among others. As for the second, the reactions investigated have provided no isolable product, with the only exception being that of complex **1a** with $Mg(CH_2CMe_3)Br$, from which a η^2-acyl complex of composition $MoBr(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ (**9**) has been isolated, albeit in low yields. The crystal and molecular structure of compound **1a** has been determined, and it is also herein reported.

Results

Reactions of $MCl_2(CO)_2(PMe_3)_3$ Complexes with Isocyanides. Crystal and Molecular Structure of $MoCl_2(CNBu^t)(CO)(PMe_3)_3$ (1a).

Addition of 1 equiv of $CNBu^t$ to a tetrahydrofuran solution of the molybdenum derivative $MoCl_2(CO)_2(PMe_3)_3$, produces a mixture of two compounds for which analytical and spectroscopic evidence (see below) indicate composition $MoCl_2(CNBu^t)(CO)(PMe_3)_3$ (**1a**) and $MoCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (**3**) (eq 1).

$$MoCl_2(CO)_2(PMe_3)_3 \xrightarrow{CNBu^t} \underset{\mathbf{1a}}{MoCl_2(CNBu^t)(CO)(PMe_3)_3} + \underset{\mathbf{3}}{MoCl_2(CNBu^t)_2(CO)(PMe_3)_2} \quad (1)$$

Unreacted $MoCl_2(CO)_2(PMe_3)_3$ can also be recovered from the reaction mixture, which consistently contains the same products, in approximately the same ratio, regardless of the reaction temperature, within the relatively wide range of −30 to +60 °C, and of the presence or absence of CO in the reaction medium. However, if PMe_3 is added, the reaction proceeds exclusively with formation of **1a** (eq 2). Other related derivatives, e.g. $MCl_2(CNR)(CO)(PMe_3)_3$ (M = Mo, R = Cy (**1b**), $C_6H_5CH_2$ (**1c**), 2,6-$C_6H_3Me_2$ (**1d**); M = W, R = Bu^t (**2**)) can be similarly prepared by the route of eq 2.

$$MoCl_2(CO)_2(PMe_3)_3 + CNBu^t \xrightarrow{PMe_3} \underset{\mathbf{1a}}{MoCl_2(CNBu^t)(CO)(PMe_3)_3} + CO \quad (2)$$

[†] Universidad de Sevilla-CSIC.

[‡] Universidad Complutense de Madrid-CSIC.

(1) Leigh, G. J.; Richards, R. L. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England 1987; Vol. 3, p 1265.

(2) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(3) (a) Lam, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127. (b) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142.

(4) (a) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 2614. (b) Mialki, W. S.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1380. (c) Harwood, W. S.; Ju-Sheng Qi; Walton, R. A. *Polyhedron* **1986**, *5*, 15.

(5) Umland, P.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3580.

(6) Bell, A.; Lippard, S. J.; Roberts, M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562.

(7) (a) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617. (b) Corfield, P. W. R.; Baltusis, L. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 922.

(8) (a) Warner, S.; Lippard, S. J. *Organometallics* **1986**, *5*, 1716. (b) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263.

(9) Warner, S.; Lippard, S. J. *Organometallics* **1989**, *8*, 228.

(10) (a) Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544. (b) Legzdins, P.; Rettig, S. J.; Sânchez, L. *Organometallics* **1988**, *7*, 2394.

(11) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(12) Carmona, E.; Sânchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Riester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214.

0020-1669/90/1329-0700$02.50/0

Table I. Analytical and Spectroscopic Data for Complexes **1**–**9**

complex		anal.,[a] %			IR,[b] cm^{-1}		
no.	formula	C	H	N	ν(CO)	ν(CN)	other
1a	$MoCl_2(CNCMe_3)(CO)(PMe_3)_3$	35.6 (35.6)	7.2 (7.1)	2.6 (2.8)	1790	2100	
1b	$MoCl_2(CNC_6H_{11})(CO)(PMe_3)_3$	38.8 (38.3)	7.2 (7.1)		1790	2105	
1c	$MoCl_2(CNCH_2Ph)(CO)(PMe_3)_3$	40.2 (40.0)	6.3 (6.3)		1795	2120	
1d	$MoCl_2(CNC_6H_3\text{-}o,o'\text{-}Me_2)(CO)(PMe_3)_3$	40.7 (41.2)	6.4 (6.5)	2.4 (2.5)	1795	2060	
2	$WCl_2(CNCMe_3)(CO)(PMe_3)_3$	30.4 (30.3)	6.1 (6.1)		1780	2075	
3	$MoCl_2(CNCMe_3)_2(CO)(PMe_3)_2$	40.3 (39.8)	7.1 (7.0)		1845	2090[c]	
4	$WCl_2(CNCMe_3)_2(CO)(PMe_3)_2$	34.6 (33.9)	6.2 (6.0)	4.5 (4.7)	1845	1990[d]	
5	$WCl_2(CNCMe_3)(CO)_2(PMe_3)_2$	28.9 (28.5)	4.9 (4.9)	2.6 (2.6)	1930 1860	2130	
6	$[MoCl(CNCMe_3)_4(PMe_3)_2]Cl$	47.7 (47.9)	8.3 (8.3)			2120 2060	
7	$[WCl(CNCMe_3)_4(PMe_3)_2]Cl$	41.3 (42.2)	7.3 (7.3)	7.1 (7.6)		2100 2040 1880	
8	$[MoCl(CNCMe_3)_2(CMe_3(H)NC{\equiv}CN(H)CMe_3)(PMe_3)_2]Cl$	47.4 (47.8)	8.5 (8.6)	8.0 (8.6)		2180 2140	3200 (ν(NH)) 3160 (ν(NH)) $\left.\begin{matrix}1590\\1550\end{matrix}\right\}$ (ν(NCCN))
9	$MoBr(\eta^2\text{-}COCH_2CMe_3)(CNCMe_3)(PMe_3)_3$	40.5 (41.0)	8.2 (8.0)			1978[d]	1505 (ν(COR))

[a] Calculated values are given in parentheses. [b] Nujol mull. [c] Shoulder at 2110, 2060 cm^{-1}. [d] Broad signal.

When the tungsten complex $WCl_2(CO)_2(PMe_3)_3$ is reacted under mild conditions (−10 °C, 5–10 min) with slightly less than 1 equiv of $CNBu^t$ (eq 3), a complex of composition $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ (**5**) is formed. Interaction of **5** with PMe_3 and $CNBu^t$ affords respectively $WCl_2(CNBu^t)(CO)(PMe_3)_3$ (**2**) and $WCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (**4**).

$$WCl_2(CO)_2(PMe_3)_3 + CNBu^t \xrightarrow{-10\ ^\circ C} WCl_2(CNBu^t)(CO)_2(PMe_3)_2 + PMe_3 \quad (3)$$

The new compounds **1**–**5** are yellow or yellow-orange crystalline solids, of moderate stability to air in the solid state but very sensitive in solution. They are soluble in common organic solvents such as benzene, toluene, acetone, or dichloromethane but much less soluble in diethyl ether and petroleum ether. Spectroscopic studies are clearly in accord with the proposed formulations. Their IR spectra are dominated by strong absorptions due to the coordinated isocyanide and carbonyl ligands. The characteristic stretching frequencies of these unsaturated groups, in particular those of the carbon monoxide ligands, are much lower than those corresponding to the free molecules because of their coordination to an electron-rich metal center. Some expected trends are found in the values of $\nu(C{\equiv}N)$ and $\nu(C{\equiv}O)$ within this series of compounds, and they can be readily inferred from inspection of data in Table I. For instance, $\nu(C{\equiv}O)$ in the bis(isocyanides) **3** and **4** is ca. 60 cm^{-1} higher than in the mono(isocyanides) **1a** and **2**, while substitution of one of the carbonyl ligands in **5** by a PMe_3 group to afford **4** produces a decrease of $\nu(C{\equiv}N)$ from 2130 to 2075 cm^{-1}.

NMR studies for compounds **3**–**5** are uninformative with regards to their structural properties. ^1H, ^{13}C, and ^{31}P NMR spectra for these compounds display broad resonances indicative of complex behavior in solution. Variable-temperature $^{31}P\{^1H\}$ NMR measurements (−50 to +40 °C), carried out for some of these derivatives in $CDCl_3$, confirm their fluxional character. The two PMe_3 ligands in the molecules of these compounds appear at room temperature as a very broad AB pattern that becomes sharper upon cooling at −50 °C. The large ^{31}P–^{31}P coupling constant of 170–190 Hz found for these complexes is probably indicative of trans (or transoid) distribution of these ligands. Similar fluxional behavior has been reported for other related seven-coordinate isocyanide complexes of Mo(II) and W(II).[3b] In the $^{13}C\{^1H\}$ NMR spectrum of the tungsten species **5**, a very broad signal at ca. 240 ppm and a doublet at 156 ppm ($^2J(CP)$ = 22.5 Hz) are observed for the metal-bound carbon atoms of the carbonyl and isocyanide ligands, respectively.

At variance with this situation, the NMR spectroscopic properties of the tris(phosphine) complexes $MCl_2(CNR)(CO)(PMe_3)_3$ (**1a**–**d** and **2**) are more informative, suggesting the presence of only one isomer in solution. The ^1H NMR spectra display, in addition to the resonances due to the isocyanide protons, a filled-in doublet (i.e. a doublet with appreciable central intensity) and a second normal doublet for the phosphine methyl groups. The first corresponds to two symmetry-related PMe_3 ligands, and the second is assigned to a unique PMe_3 group. This is in accord with the observation of neat AX_2 patterns in the $^{31}P\{^1H\}$ NMR spectra, with relatively low values of $^2J(PP^*)$ of ca. 20 Hz, that correspond to small or intermediate ^{31}P–^{31}P coupling.

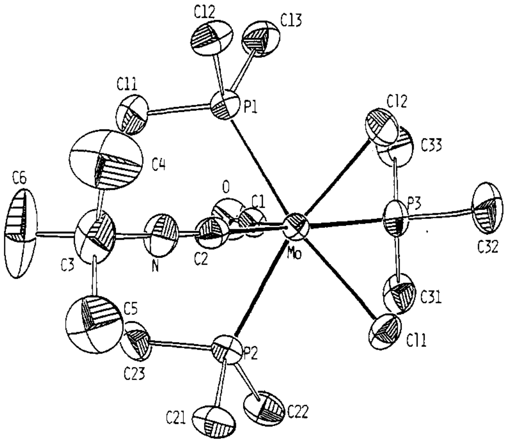


Figure 1. Structure by X-ray diffraction of the complex $MoCl_2(CNBu^t)(CO)(PMe_3)_3$.

On the other hand, the metal-bound isonitrile and carbonyl carbon atoms have chemical shifts in the range normally found in complexes of this type. The carbonyl resonance appears at low field, ca. 280–270 ppm, as a triplet of doublets due to coupling to the two equivalent PMe_3 groups with a coupling constant of about 50 Hz and to the unique phosphine with a lower coupling constant of ca. 35 Hz. In contrast, the M–CNR carbon, which resonates in the range 186–155 ppm, is more strongly coupled to the unique PMe_3 ligand ($^2J(CP) \simeq 66$ Hz) than to the other two ($^2J(CP) \simeq 30$ Hz), and this may suggest its positioning in a coordination site that is transoid with respect to the single PMe_3 group.

Since a unique structural proposal cannot be made with the above data, in order to ascertain the spatial distribution of the coordinated ligands an X-ray crystal structural determination has been undertaken. Complex **1a** readily provides single crystals suitable for this study and was therefore chosen for convenience. Figure 1 shows an ORTEP view of this complex that includes the atom numbering scheme. Relevant crystal data, interatomic bond distances and angles, and atomic coordinates are collected in

Table II. ^{1}H and ^{31}P{^{1}H} NMR Data for Complexes **1–9**

				^{1}H^a			
	^{31}P^a for PMe$_3$			Me–P			
complex	δ	$^2J_{PP}$	$^1J_{PW}$	δ	$^2J_{PH}$	CN*R*	other
1a	0.86 t^b	22.6		1.33 d	8.5^e	1.55 s (C*Me*$_3$)	
	23.87 d			1.49 d	9.4		
1b	0.43 t	22.0		1.17 d	8.3	3.84 m (C$_6$*H*$_{11}$)	
	26.76 d			1.34 d	9.6		
1c	−0.99 t	21.4		1.22 d	8.4^e	4.95 t (C*H*$_2$)	
	26.16 d			1.31 d	9.4	7.29 m (Ph)	
1d	−2.95 t	20.5		1.30 d	8.2^e	2.39 s (*Me*$_2$)	
	25.26 d			1.47 d	9.6	7.03 s (C$_6$*H*$_3$)	
2	−13.48 t	16.5	192.1	1.31 d	8.5^e	1.50 s (C*Me*$_3$)	
	−7.04 d		190.3	1.53 d	10.7		
3	−8.74^b	177.4^f		1.50 d	8.5^g	1.11 s (C*Me*$_3$)	
	7.21 d						
4	−10.64^b d	187.0^f		1.55 d	7.4^g	1.14 s (C*Me*$_3$)	
	−27.82 d						
5	−25.98^b d	167.0^f	151.2	1.39 d	9.8	1.00 s (C*Me*$_3$)	
	−11.7 d		167.5	1.46 d	9.9		
6	2.92 br			1.40 t	4.6^c	1.38 s (C*Me*$_3$)	
7	−23.56 br			1.62 t	4.2^c	1.48 s (C*Me*$_3$)	
8	−9.86^d s			1.19 t	3.3^c	1.57 s (C*Me*$_3$)	9.94 br (N*H*)
						1.59 s (C*Me*′$_3$)	
9	−2.40^b d	16.3		1.08 t	2.8	1.15 s (C*Me*$_3$)	1.27 s (C*Me*$_3$ COR)
	6.06 t			1.33 d	7.5		3.32 s (C*H*$_2$)

[a] Spectra registered in CDCl$_3$ unless otherwise specified. δ in ppm. J in Hz. [b] In C$_6$D$_6$. [c] Values of J apparent. [d] In CD$_2$Cl$_2$. [e] Doublet with some central intensity. [f] AB pattern doublet. [g] Very broad doublet.

Table III. ^{13}C{^{1}H} NMR Data^a for Complexes **1–9**

	Me–P			*C*NR		*C*O	
complex	δ	$^2J_{PC}$	CN*R*	δ	$^2J_{PC}$	δ	$^2J_{PC}$
1a	13.95^b d	25.0	29.48 s (C*Me*$_3$)	155.30 dt	66.2^f	270.7 td	51.3
	17.71 t	15.0^c	47.86 s (*C*Me$_3$)		30.5		34.9
1b	3.92 d	24.3	23.29 s (*C*H$_2$)	166.96 dt	66.6	280.3 td	48.7
	17.94 t	15.4^c	32.72 s (*C*H$_2$)		29.2		34.5
			42.63 s (*C*H$_2$)				
			55.25 s (*C*H)				
1c	13.88 d	23.9	49.07 s (*C*H$_2$)	171.00 dt	67.6^f	278.8 td	48.2
	17.94 t	15.6^c	127.71 s (*C*H ring)		30.2		33.9
			128.84 s (*C*H ring)				
			129.11 s (*C*H ring)				
			131.81 s (*C* ring)				
1d	13.76 d	23.8	19.44 s (*Me*$_2$)	186.12 dt	66.5	276.6 td	48.3
	17.98 t	16.0^c	127.76 m (*C*H ring)		33.0		33.4
			127.92 m (*C*H ring)				
			133.65 br (*C* ring)				
2	13.48 d	27.2	30.74 s (C*Me*$_3$)	*h*		*h*	
	17.77 t	16.6	57.77 br (*C*Me$_3$)				
3	4.00 br		20.95 s (C*Me*$_3$)	*h*		*h*	
4	12.70 d^g		30.84 s (C*Me*$_3$)	*h*		*h*	
			58.13 s (*C*Me$_3$)				
5	12.87^b t	33.2^c	29.91 s (C*Me*$_3$)	155.80 d	22.5	241.6 br	
			58.36 s (*C*Me$_3$)				
6	15.79 t	13.9^c	30.52 s (C*Me*$_3$)	173.60 m			
			57.71 s (*C*Me$_3$)				
7	15.72 t	16.2^c	30.66 s (C*Me*$_3$)	153.64 m			
			58.96 s (*C*Me$_3$)				
8	16.67^d t	11.9^c	29.99 s (C*Me*$_3$)	170.16 t	8.3	203.6 t	8.3 (*C*NH)
			30.31 s (C*Me*′$_3$)				
			52.80 s (*C*Me$_3$)				
			57.64 s (*C*Me′$_3$)				
9	16.39^b t	9.5^c	29.78 s (C*Me*$_3$) (CN*R*)	224.80 dt	36.4	278.7 q	11.7
	21.69 d	22.8	31.48 s (C*Me*$_3$) (CO*R*)		9.6		
			31.74 s (*C*Me$_3$) (CO*R*)				
			56.95 s (*C*H$_2$)				
			57.15 s (*C*Me$_3$) (CN*R*)				

[a] Spectra registered in CDCl$_3$ unless otherwise specified. δ in ppm. J in Hz. [b] In C$_6$D$_6$. [c] Values of J apparent. [d] Doublet with some central intensity. [f] Broad doublet of triplet. [g] Very broad doublet. [h] Not observed.

Tables IV–VI, respectively. The molybdenum atom is in a seven-coordinate environment composed of three PMe$_3$ groups, two chlorine atoms, one carbonyl group, and one isocyanide group, whose geometrical distribution can be approximately described as 4:3 "piano stool". The two coordinated carbon atoms, C1 and C2, and two of the phosphorus atoms, P1 and P2, are in an essentially planar distribution and compose the quadrilateral face while the remaining donor atoms, Cl1, Cl2, and P3, occupy the vertices of the trigonal cap. The two ligand mean planes are nearly parallel, the angle between them being only 2.0 (1)°. In an

Table IV. Crystallographic Data for $MoCl_2(CNBu^t)(CO)(PMe_3)_3$

chem formula	$MoC_{15}Cl_2H_{36}NOP_3$
fw	506.3
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	15.217 (4)
b, Å	16.367 (3)
c, Å	9.804 (2)
β, deg	90.75 (2)
V, Å^3	2441.5 (9)
Z	4
T, °C	22
λ, Å	0.710 69 (Mo Kα)
D_{calcd}, g cm^{-3}	1.38
μ, cm^{-1}	9.43
cryst dimens, mm	0.34 × 0.26 × 0.14
R_F, %	3.8
R_{wF}, %	4.8
scan technique	$\omega/2\theta$
two-scan range, deg	$2 < 2\theta < 46$
data collcd	$\pm h,+k,+l$
no. of unique reflcns	4792
no. of obsd reflcns	3193
R_{int}, %	0.95
no. of std reflcns	3
decay	≤1% var
ρ, e Å^{-3}	0.81
av shift/error	0.036

Table V. Selected Bond Distances (Å) and Angles (deg) in **1a**

Mo–Cl1	2.558 (2)	Mo–C2	2.113 (7)
Mo–Cl2	2.547 (2)	C1–O	1.190 (8)
Mo–P1	2.460 (2)	C2–N	1.167 (8)
Mo–P2	2.469 (2)	N–C3	1.458 (9)
Mo–P3	2.548 (2)	P–C (av)	1.813 (8)
Mo–C1	1.893 (7)	C3–C (av)	1.48 (1)
Cl1–Mo–Cl2	83.75 (6)	P1–Mo–C1	72.6 (2)
Cl1–Mo–P1	158.83 (6)	P1–Mo–C2	74.3 (2)
Cl1–Mo–P2	75.78 (6)	P2–Mo–P3	109.54 (6)
Cl1–Mo–P3	77.26 (6)	P2–Mo–C1	73.4 (2)
Cl1–Mo–C1	128.2 (2)	P2–Mo–C2	74.6 (2)
Cl1–Mo–C2	97.5 (2)	P3–Mo–C1	75.3 (2)
Cl2–Mo–P1	77.35 (6)	P3–Mo–C2	171.9 (2)
Cl2–Mo–P2	154.15 (6)	Mo–C1–O	177.1 (5)
Cl2–Mo–P3	80.51 (6)	Mo–C2–N	178.0 (5)
Cl2–Mo–C1	132.4 (2)	C2–N–C3	178.4 (7)
Cl2–Mo–C2	92.9 (2)	C–P–C (av)	100.8 (3)
P1–Mo–P2	119.09 (6)	C–C3–C (av)	110.6 (8)
P1–Mo–P3	108.50 (7)	C1–Mo–C2	112.8 (2)

Table VI. Atomic Coordinates for Non-Hydrogen Atoms for **1a**

atom	x/a	y/b	z/c
Mo	0.070 28 (3)	0.232 22 (3)	0.096 45 (5)
Cl1	−0.047 24 (10)	0.287 12 (11)	0.256 75 (17)
Cl2	0.175 36 (11)	0.309 60 (12)	0.254 09 (18)
P1	0.209 89 (10)	0.225 30 (11)	−0.026 57 (16)
C11	0.202 73 (49)	0.194 80 (51)	−0.204 19 (72)
C12	0.274 62 (45)	0.319 34 (51)	−0.041 13 (79)
C13	0.291 86 (47)	0.153 99 (51)	0.038 55 (78)
P2	−0.068 99 (10)	0.212 85 (10)	−0.031 42 (16)
C21	−0.140 63 (43)	0.300 48 (45)	−0.049 69 (77)
C22	−0.145 34 (45)	0.138 03 (45)	0.032 66 (80)
C23	−0.059 06 (50)	0.181 78 (52)	−0.207 18 (73)
P3	0.077 50 (12)	0.132 15 (11)	0.295 44 (17)
C31	−0.015 69 (51)	0.063 38 (47)	0.308 38 (75)
C32	0.083 33 (60)	0.173 61 (54)	0.467 30 (75)
C33	0.166 72 (56)	0.058 92 (50)	0.303 60 (85)
C1	0.076 42 (39)	0.127 93 (41)	0.013 79 (62)
O	0.081 38 (34)	0.060 88 (28)	−0.032 74 (52)
C2	0.065 55 (38)	0.328 29 (39)	−0.047 28 (64)
N	0.064 07 (37)	0.379 96 (33)	−0.129 74 (56)
C3	0.064 40 (56)	0.445 45 (44)	−0.230 53 (80)
C4	0.138 63 (68)	0.500 16 (58)	−0.199 21 (130)
C5	−0.020 87 (63)	0.490 51 (54)	−0.223 47 (106)
C6	0.073 83 (97)	0.407 77 (71)	−0.366 97 (93)

alternative description, the geometry of this molecule could be viewed as capped octahedral, with the carbonyl ligand capping the triangular face formed by the three molecules of PMe_3. Not surprisingly, the capping carbonyl ligand opens up the P1–P2–P3 face of the basic octahedron, so that the P–Mo–P angles have values well over the ideal 90° corresponding to regular octahedral coordination (in the range 108–119°; see data in Table V). Conversely, the C1–Mo–P angles are fairly acute, their values being 72.6 (2), 73.4 (2) and 75.3 (2)° respectively for P1, P2, and P3. In either of the above descriptions, the geometry of the ligand distribution is such that the mean plane passing through the molybdenum center and the ligand atoms C1, C2, and P3 is a plane of symmetry that relates the two chloride ligands, Cl1 and Cl2 as well as the phosphorus atoms P1 and P2. As expected, the bond lengths associated with these two atoms are very similar (2.460 (2) and 2.469 (2) Å, respectively) while that corresponding to Mo–P3 at 2.548 (2) Å is appreciably longer due possibly to the trans influence exerted by the isocyanide group (C2–Mo–P3 angle of 171.9 (2)°). These and other bond distances and angles within the coordination sphere of the molybdenum center appear normal and compare satisfactorily with those found in other complexes of molybdenum(II) containing similar ligands.[12]

Whether this solid-state structure persists in solution without appreciable change of the coordination polyhedron cannot be unambiguously ascertained with the available solution data. The solution IR spectrum of **1a** recorded in tetrahydrofuran (matched cells), in the region 2200–1700 cm^{-1}, is essentially identical with that obtained in the same frequency range for a Nujol mull. In addition, the trans distribution found for the isocyanide group and the unique phosphine ligand in the solid-state structure is in good agreement with the strong ^{13}C–^{31}P coupling of 66 Hz observed in solution between the corresponding nuclei. These observations suggest that the solid-state structure is maintained in solution, although the relative large value of 50 Hz detected for the $^2J(CP)$ coupling constant involving the carbonyl and the two equivalent PMe_3 ligands (vide supra) may seem typical of trans ^{13}C–^{31}P coupling.[13]

Synthesis of $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ (M = Mo (6), W (7)) and the Reductive Coupling of 6 to $[MoCl(CNBu^t)_2(Bu^t(H)NC{\equiv}CN(H)Bu^t)(PMe_3)_2]Cl$ (8). When the seven-coordinate compounds $MCl_2(CO)_2(PMe_3)_3$ are reacted with an excess of $CNBu^t$ (>4 equiv), *in the presence of* PMe_3 (0.5–1 equiv), full substitution of the coordinated CO groups and, in addition, of one PMe_3 and one chloride ligand is observed with formation of the new species $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ (eq 4). Although the stoichiometry of the reaction does not require the addition of PMe_3, the process is considerably accelerated in the presence of this added ligand. Compounds **6** and **7** can also be obtained from **1a** and **2**, by reaction with the isocyanide, also in the presence of added PMe_3 (eq 5), and have been independently prepared by other workers.[14] The new compounds are yellow diamagnetic species of low solubility in nonpolar organic solvents, as expected for 1:1 electrolytes. They exhibit spectroscopic data (Tables I–III) similar to those reported for other related complexes, and since these data provide no useful information with regard to their stereochemistry, they will not be further discussed.

$$MCl_2(CO)_2(PMe_3)_3 + 4CNBu^t \xrightarrow{PMe_3} [MCl(CNBu^t)_4(PMe_3)_2]Cl + 2CO + PMe_3 \quad (4)$$
$$M = Mo\ (\mathbf{6}),\ W\ (\mathbf{7})$$

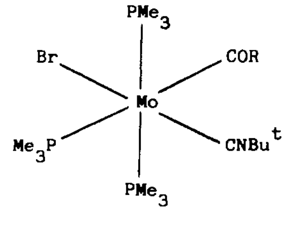
$$MCl_2(CNBu^t)(CO)(PMe_3)_3 + 3CNBu^t \xrightarrow{PMe_3} [MCl(CNBu^t)_4(PMe_3)_2]Cl + CO + PMe_3 \quad (5)$$

Compounds **6** and **7** are electron-rich complexes, having high coordination numbers and presumably short nonbonding contacts between the coordinated $CNBu^t$ molecules. We considered it of interest to ascertain if they could undergo the reductive coupling

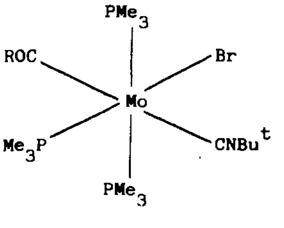
---

(13) Deaton, J. C.; Walton, R. A. *J. Organomet. Chem.* **1981**, *219*, 187.

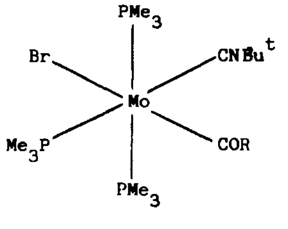
(14) Puerta, M. C. Personal communication.



A



B



C

of two isocyanide groups to a bis(alkylamino)acetylene ligand, an interesting transformation extensively studied by Lippard and co-workers in recent years[7,8] in similar complexes. Indeed, under reductive coupling conditions,[7,8] the molybdenum complex **6** that was chosen for this study experiences the expected transformation (eq 6) and provides orange, air-sensitive crystals of **8** in moderate

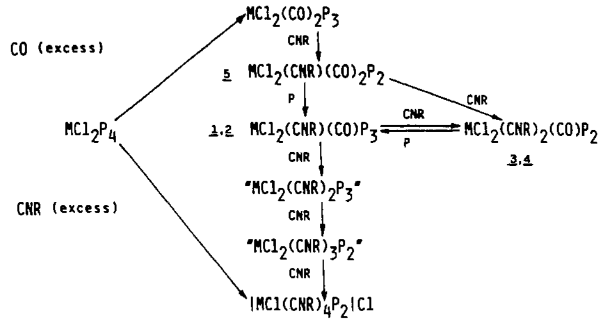
$$\underset{\textbf{6}}{[\mathrm{MoCl(CNBu^t)_4(PMe_3)_2}]\mathrm{Cl}} \xrightarrow{\mathrm{Zn,\ H_2O}} \underset{\textbf{8}}{[\mathrm{MoCl(CNBu^t)_2(Bu^t(H)NC{\equiv}CN(H)Bu^t)(PMe_3)_2}]\mathrm{Cl}} \quad (6)$$

yields (ca. 50%). The presence in the molecule of **8** of the coordinated *N,N'*-bis(*tert*-butylamino)acetylene ligand is inferred from spectroscopic evidence. Thus, in addition to absorptions due to the CNBu^t and PMe$_3$ ligand, bands are observed at 3200 and 3160 cm^{-1} (N–H) and 1590 and 1550 cm^{-1} (NCCN) in the IR spectrum of **8**. Furthermore, a ^{1}H NMR singlet at 9.94 ppm is assigned to the N–H proton, while a triplet that appears at 203.6 ppm in the ^{13}C NMR spectrum is due to the coordinated acetylene carbons (^2J(CP) = 8 Hz). Other relevant NMR parameters are collected in Tables II and III and are in accord with a structure similar to that found by Lippard for other related compounds.[7b,8a]

Alkylation Reactions of Compounds MCl$_2$(CNR)(CO)(PMe$_3$)$_3$. Synthesis of the η^2-Acyl MoBr(η^2-COCH$_2$CMe$_3$)(CNBu^t)(PMe$_3$)$_3$ (9). The reactions of compounds **1a–d** and **2** with organolithium or Grignard reagents, LiR' or Mg(R')X, lead, under different experimental conditions, to complex mixtures from which we have been unable to isolate pure products. The only exception to the above is the reaction of **1a** with Mg(CH$_2$CMe$_3$)Br, which provides the η^2-acyl MoBr(η^2-COCH$_2$CMe$_3$)(CNBu^t)(PMe$_3$)$_3$ (**9**) albeit in relatively low yields (25%). This complex is a red, air-sensitive crystalline material, very soluble in nonpolar organic solvents.

The IR spectrum shows a very broad and intense absorption between 2000 and 1800 cm^{-1}, attributed to a terminal isocyanide ligand. Similar broad bands are often encountered in other molybdenum complexes containing bent isocyanide groups.[15] A second, relatively low-intensity band centered at ca. 1500 cm^{-1} is assigned to the C═O frequency of the acyl ligand, and its low values suggests η^2 coordination.[12] ^{1}H and ^{31}P NMR studies for **9** establish the presence of two equivalent trans PMe$_3$ groups and of a third that is cis with respect to the others (Table II). Assuming that the η^2-acyl ligand occupies a single coordination position, an octahedral geometry with a meridional distribution of the PMe$_3$ ligands can be proposed for **9**. There are three possible isomers fulfilling these requirements (structures A, B, and C), but ^{1}H, ^{13}C, and ^{31}P NMR data for complex **9** unambiguously indicate the existence of only one isomer in solution. This displays two ^{13}C NMR resonances at 224.8 and 278.7 ppm that can be respectively assigned to the molybdenum-bound isocyanide and η^2-acyl carbon atoms. The first appears as a doublet of triplets, as a result of its coupling to the unique PMe$_3$, with the relatively large coupling constant of 36.4 Hz, and to the other two equivalent phosphines, with the smaller coupling of 9.6 Hz. The second is a quartet arising from coupling to the three ^{31}P nuclei with accidentally the same coupling constant of 11.7 Hz. These results suggest that the solution structure is that of isomer C. The related η^2-acyl–carbonyl complex WCl(η^2-COCH$_2$SiMe$_3$)(CO)(PMe$_3$)$_3$ displays similar NMR features suggesting an analogous solution structure[16] although an X-ray crystal structure determination shows that the solid-state structure corresponds to that of isomer A.

Scheme I



P = PMe$_3$; R = Bu^t

Discussion

Some comments can be made at this point on the reaction pathway leading to the isocyanide derivatives **1–7**. The results summarized in reactions 1 and 2 seem to suggest that compounds **1a–d** and **2** are the primary products of these substitution reactions and that the formation of **3** (eq 1) may result from the competitive substitution of one of the PMe$_3$ ligands in **1a** by a second molecule of CNBu^t. However, monitoring the progress of reaction 1 by IR spectroscopy reveals the formation of an intermediate species on the way to the final products. This exhibits a strong ν(C≡O) stretching at ca. 1940 cm^{-1} and presumably two additional bands at ca. 2100 and 1855 cm^{-1} that appear only as small shoulders due to overlapping with absorptions characteristic of **1a** and **3**. Although we have been unable to ascertain the precise conditions under which this intermediate can be isolated, relevant information about its nature can be gained from the analogous reaction of the tungsten complex WCl$_2$(CO)$_2$(PMe$_3$)$_3$, which as already indicated (see eq 3) leads to compound **5**. The IR spectrum of **5** shows three strong IR absorptions at 2120 cm^{-1} (CNR) and 1930 and 1860 cm^{-1} (C≡O), suggesting a composition similar to that of the Mo intermediate species detected during the course of reaction 1. Moreover, pure complex **5** can be readily converted into either the mono(isocyanide) species WCl$_2$(CNBu^t)(CO)(PMe$_3$)$_3$ (**2**) or the bis(isocyanide) WCl$_2$(CNBu^t)$_2$(CO)(PMe$_3$)$_2$ (**4**), by reaction with PMe$_3$ or CNBu^t, respectively. Therefore, it seems likely that the primary products of the reactions of MCl$_2$(CO)$_2$(PMe$_3$)$_3$ compounds with isocyanides could be the mono(isocyanide)–dicarbonyls MCl$_2$(CNR)(CO)$_2$(PMe$_3$)$_2$, which could further react with PMe$_3$ or CNBu^t as depicted in Scheme I.

With respect to the formation of compounds **6** and **7**, it is clear that the mono(isocyanide) complexes **1a** and **2** are intermediates in this process (see eq 5), but it seems that the next step does not involve the formation of the bis(isocyanide) species MCl$_2$(CNBu^t)$_2$(CO)(PMe$_3$)$_2$ (**3** and **4**) since the reaction of complex **2** with CNBu^t, *in the absence of PMe$_3$*, does not afford **7** but rather **4**, as depicted in eq 7. On the other hand **3** and **4** react only very slowly with more CNR. Therefore, in order to obtain **6** and **7**,

---

(15) Carmona, E.; Galindo, A.; Marín, J. M.; Gutiérrez, E.; Monge, A.; Ruiz, C. *Polyhedron* **1988**, *7*, 1831.

(16) Carmona, E.; Sánchez, L. To be submitted for publication.

$$\underset{\mathbf{2}}{WCl_2(CNBu^t)(CO)(PMe_3)_3} + CNBu^t \rightarrow \underset{\mathbf{4}}{WCl_2(CNBu^t)_2(CO)(PMe_3)_2} + PMe_3 \quad (7)$$

PMe_3 substitution must be avoided, and this suggests the intermediacy of the so far nonisolated species "$MCl_2(CNBu^t)_2(PMe_3)_3$". Additional although indirect evidence for this hypothesis comes from the facts that (i) the compounds *trans*-$MCl_2(PMe_3)_4$ provide an alternative and useful synthetic route to **6** and **7**, as shown in eq 8, and (ii) these chlorophosphine

$$trans\text{-}MCl_2(PMe_3)_4 + 4CNBu^t \rightarrow [MCl(CNBu^t)_4(PMe_3)_2]Cl + 2PMe_3 \quad (8)$$

complexes react with CO with formation of the seven-coordinate $MCl_2(CO)_2(PMe_3)_3$,[17] that is, the carbonyl analogue of the proposed isocyanide intermediate. In addition, a complex of composition $MoCl_2(CNBu^t)_3(PMe_3)_2$ has been recently isolated from the reaction of *trans*-$MoCl_2(PMe_3)_4$ and $CNBu^t$ under appropriate conditions.[14] The formation of these compounds is therefore proposed to take place by the stepwise sequence shown in Scheme I.

As stated in the Introduction, one of the objectives of the present work was the synthesis of acyl or iminoacyl complexes of Mo and W, and indeed the isolation of compounds **1**–**5**, containing both carbonyl and isocyanide ligands, provided the opportunity to study the preference of acyl vs iminoacyl formation in their reactions with organolithium or Grignard reagents. Although compounds **1a**–**d** and **2** react with various $Mg(R')X$ reagents, only for **1a** and $Mg(CH_2CMe_3)Br$ has a pure complex been isolated. This can be formulated as the η^2-acyl $MoBr(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ (**9**) on the basis of spectroscopic evidence (vide supra). Interestingly, this complex has been previously prepared in our laboratory[18] by addition of $CNBu^t$ to the η^2-acyl $MoBr(\eta^2\text{-}COCH_2CMe_3)(PMe_3)_4$[19] (eq 9).

$$MoBr(\eta^2\text{-}COCH_2CMe_3)(PMe_3)_4 + CNBu^t \rightarrow \underset{\mathbf{9}}{MoBr(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3} \quad (9)$$

Although preference for isocyanide over carbon monoxide insertion is generally observed when there is the choice,[20] the available IR and NMR data for **9** strongly support η^2-acyl rather than η^2-iminoacyl formulation. In this respect we note that (i) the reaction might not involve migratory insertion of a metal-bound alkyl group but rather direct attack of the alkylating agent onto the coordinated CO ligands, as proposed for other related systems,[21] and that (ii) there are reports in the literature where CO insertion is favored over CNR insertion.[22]

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Bonn, West Germany, and by the Analytical Service of the University of Seville. IR spectra were recorded as Nujol mulls or in an appropriate solvent on Perkin-Elmer Model 577 and 684 instruments. ^1H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200 instrument. ^{31}P NMR shifts were referenced to external 85% H_3PO_4. Conductivity measurements were carried out in CH_3CN solutions (ca. 5×10^{-3} M) at 20 °C.

All preparations and other operations were carried out under oxygen-free nitrogen or argon following conventional Schlenk techniques. Solvents were dried by standard techniques and degassed before use. The compounds $MCl_2(PMe_3)_4$ and $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) were synthesized as described elsewhere.[17,23] The Grignard reagents[24] and the $CNCMe_3$[25] and PMe_3[26] ligands were prepared by the published procedures. All other reagents were purchased from commercial suppliers and were used without further purification.

Preparation of the Complexes $MCl_2(CNR)(CO)(PMe_3)_3$ (M = Mo, R = Bu^t (1a), C_6H_{11} (1b), CH_2Ph (1c), 2,6-$Me_2C_6H_3$ (1d); M = W, R = Bu^t (2)). These complexes were synthesized in a similar manner. The experimental procedure, with that of the Mo–$CNBu^t$ complex used as a representative example, was as follows.

$MoCl_2(CNBu^t)(CO)(PMe_3)_3$ (1a). To a stirred solution of $MoCl_2(CO)_2(PMe_3)_3$ (0.45 g, 1.0 mmol) in 35 mL of THF were successively added an Et_2O solution of $CNBu^t$ (1.0 M, 1.0 mL, 1.0 mmol) and neat PMe_3 (0.1 mL, ca. 1.0 mmol). The resulting solution was stirred rapidly at room temperature for 1 h to obtain a light yellow solution whose IR spectrum exhibited a $\nu(C{\equiv}O)$ at 1790 cm^{-1} and a $\nu(C{\equiv}N)$ at 2100 cm^{-1}. The solvent was evaporated under reduced pressure and the residue extracted with 30 mL of THF. After centrifugation and cooling at 0 °C, 0.4 g of yellow crystals was collected, washed with Et_2O, and dried in vacuo. Yield: 80%. Starting with the appropriate chlorocarbonyl complex, $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W), and the CNR ligand, we obtained the following compounds by the above procedure: $MoCl_2(CNC_6H_{11})(CO)(PMe_3)_3$ (**1b**) (75%), $MoCl_2(CNCH_2Ph)(CO)(PMe_3)_3$ (**1c**) (82%), $MoCl_2(CN\text{-}2,6\text{-}Me_2C_6H_3)(CO)(PMe_3)_3$ (**1d**) (74%), and $WCl_2(CNBu^t)(CO)(PMe_3)_3$ (**2**) (65%). They were isolated as yellow crystalline solids from concentrated THF solutions with the exception of the less soluble Mo–CN-2,6-$Me_2C_6H_3$ derivative, which requires Et_2O–Cl_2CH_2 mixtures (ca. 1:1), and the more soluble W–$CNBu^t$ compound, which was isolated from Et_2O solutions.

Preparation of $MoCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (3). To a yellow solution of $MoCl_2(CO)_2(PMe_3)_3$ (0.45 g, 1.0 mmol) in THF (35 mL) was added a slight excess of $CNBu^t$ (1.5 mL of a 1.0 M Et_2O solution, 1.5 mmol). The resulting solution was stirred at room temperature under an intermittent dynamic vacuum to remove the PMe_3 released during the course of the reaction. The progress of the reaction was monitored by IR spectroscopy of the solution, measuring specifically the positions of the carbonyl-stretching absorptions. After 5 min, $\nu(C{\equiv}O)$'s were evident at 1940, 1935, 1855, 1835, and 1790 cm^{-1}. The bands at 1935 and 1835 cm^{-1} are characteristic of the parent $MoCl_2(CO)_2(PMe_3)_3$, while the other absorptions correspond to the new products formed. During the next 10 min, the characteristic absorptions of the starting material and the band at 1940 cm^{-1} rapidly disappeared while those at 1790 and 1855 increased in intensity at the expense of the 1940-cm^{-1} feature. Finally, after 1 h, only the absorptions at 1790 and 1855 cm^{-1} that correspond to the CO stretching frequencies in compounds **1a** and **3** persisted in the $\nu(C{\equiv}O)$ region.

The solvent was evaporated under reduced pressure, and compounds **1a** and **3** were separated by fractional crystallization from dilute THF solutions at 0 °C. Further recrystallization of these crystals afforded analytically pure **3** in 20–40% yield.

Starting with $WCl_2(CO)_2(PMe_3)_3$ allowed a mixture of the complexes **2**, **4**, and **5** to be obtained by using an analogous procedure.

Preparation of $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ (5). A yellow solution of $WCl_2(CO)_2(PMe_3)_3$ (0.54 g, 1.0 mmol) in THF (40 mL) was treated with slightly less than the stoichiometric amount of $CNBu^t$ (0.9 mL of a 1.0 M Et_2O solution, 0.9 mmol). The resulting solution was stirred at −15 °C for 10 min under a slight dynamic vacuum. The solvent was then evaporated under reduced pressure and the residue extracted with 40 mL of Et_2O. Further centrifugation and cooling at −30 °C overnight produced yellow crystals of $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ in 90% yield.

We have been unable to isolate the molybdenum complex $MoCl_2(CNBu^t)(CO)_2(PMe_3)_2$ using an analogous procedure. Instead, probably due to the facility with which it reacts either with more $CNBu^t$ or with the PMe_3 released during the course of the reaction, the bis(isocyanide) compound $MoCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (**3**), complex **1a**, and some unreacted starting material were isolated.

Reaction of $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ with $CNBu^t$. Preparation of $WCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (4). A yellow solution of complex **5** (0.54 g, 1.0 mmol) in THF (35 mL) was treated with an Et_2O solution of

---

(17) Carmona, E.; Doppert, K.; Marín, J. M.; Poveda, M. L.; Sánchez, L.; Sánchez-Delgado, R. *Inorg. Chem.* **1984**, *23*, 530.

(18) Carmona, E.; Muñoz, M. A. Unpublished results.

(19) Carmona, E.; Muñoz, M. A.; Rogers, R. D. *Inorg. Chem.* **1988**, *27*, 1598.

(20) (a) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 377.

(21) Desmond, T.; Lalor, F. J.; Ferguson, G.; Ruhl, B.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 55.

(22) Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84.

(23) (a) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430. (b) Carmona, E.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185.

(24) See, for instance: Withmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481.

(25) Gokel, G. W.; Widera, R. P.; Weber, W. P. *Organic Synthesis* **1976**, *55*, 96.

(26) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

$CNBu^t$ (1.0 M, 1.0 mL, 1.0 mmol) and the mixture was stirred at 50 °C for 5 h. Removal of the volatiles in vacuo and crystallization of the residue from Et_2O produced yellow crystals of $WCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (**4**) in 85% yield.

Reaction of $WCl_2(CNBu^t)(CO)_2(PMe_3)_2$ with PMe_3. A yellow solution of complex **5** (0.27 g, 0.5 mmol) in THF (30 mL) and neat PMe_3 (0.07 mL, 0.7 mmol) were stirred vigorously at room temperature for 4 h with no change in color. The final solution was taken to dryness, and the remaining residue was extracted with Et_2O (15 mL). Partial evaporation of the extracts and cooling at −30 °C induced the formation of yellow crystals, which were collected by filtration to afford analytically pure complex **2** in 90% yield.

Reaction of $MCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (M = Mo, W) with PMe_3. The reaction of $MoCl_2(CNBu^t)_2(CO)(PMe_3)_2$ with 1 equiv of PMe_3 in THF at room temperature for 2 h yielded, after workup, complex **1a** in 95% yield. The analogous conversion of $WCl_2(CNBu^t)_2(CO)(PMe_3)_2$ in complex **2** requires however higher temperatures (60 °C), an excess of PMe_3, and longer reaction times.

Reaction of $MCl_2(CNBu^t)(CO)(PMe_3)_3$ (M = Mo, W) with $CNBu^t$. In the absence of free added PMe_3, the complex $WCl_2(CNBu^t)(CO)(PMe_3)_3$ (**2**) reacts with 1 equiv of $CNBu^t$ in THF at room temperature to produce $WCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (**4**) in essentially quantitative yield. An analogous reaction using $MoCl_2(CNBu^t)(CO)(PMe_3)_3$ produces the cationic complex $[MoCl(CNBu^t)_4(PMe_3)_2]Cl$ (**6**) as the main reaction product, together with small amounts of $MoCl_2(CNBu^t)_2(CO)(PMe_3)_2$ (**3**) and unreacted starting material.

Preparation of $[MCl(CNBu^t)_4(PMe_3)_2]Cl$ (M = Mo (6), W (7)). Method A. A yellow solution of complex **1a** (0.5 g, 1.0 mmol) in THF (40 mL) was treated with an excess of $CNBu^t$ (4 mL of a ca. 1.0 M Et_2O solution, ca. 4.0 mmol) in the presence of 1 equiv of PMe_3 (0.1 mL, 1.0 mmol) at ambient temperature. As the mixture was stirred, a yellow solid began to precipitate, and after 6–7 h, the final reaction mixture consisted of a light yellow solution and a yellow, finely divided solid. This suspension was evaporated to dryness and the residue extracted with 30 mL of a 1:2 mixture of petroleum ether–dichloromethane. After centrifugation and cooling at −35 °C, yellow microcrystals were collected, washed with Et_2O, and dried in vacuo. Yield: 75%. This solid can be recrystallized from CH_2Cl_2 solutions by slow evaporation of the solvent. Conductivity: $\Lambda_M = 89\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Method B. Complex **6** can also be obtained by treating the compound $MoCl_2(PMe_3)_4$ with 5 equiv of $CNBu^t$, in THF, at room temperature for 4 h. Yield: 80%.

The analogous tungsten compound, $[WCl(CNBu^t)_4(PMe_3)_2]Cl$ (**7**), was obtained either from **2** (20 °C, 24 h) in 70% isolated yield or from $WCl_2(PMe_3)_4$ (at 40 °C, 3 h) in 80% yield, by using analogous procedures. The product crystallized from a 1:1 mixture of THF–CH_2Cl_2 at −35 °C as a yellow crystalline solid.

Preparation of $[MoCl(CNBu^t)_2(Bu^tC(H)NC{\equiv}CN(H)Bu^t)(PMe_3)_2]Cl$ (8). To a yellow, stirred suspension of complex **6** (0.65 g, 1.0 mmol) in THF (45 mL) at room temperature were added an excess of zinc dust (0.2 g, 3 mmol) and 1 mL of distilled, deaerated H_2O. This mixture was stirred and heated at reflux for 24 h. The supernatant solution gradually became red-orange in color as the quantity of insoluble solid diminished. The final mixture was permitted to cool to room temperature and centrifuged and was then taken to dryness in vacuo. The remaining residue was washed with Et_2O (2 × 15 mL) and crystallized from concentrated acetone solutions at −35 °C to obtain $[MoCl(CNBu^t)_2(Bu^t(H)NC{\equiv}CN(H)Bu^t)(PMe_3)_2]Cl$ (**8**) as analytically pure yellow-orange crystals in 45% yield.

Reactions of $MCl_2(CNR)(CO)(PMe_3)_3$ (M = Mo, W) with Alkylating Reagents. Preparation of $MoBr(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ (9). To a stirred suspension of yellow $MoCl_2(CNBu^t)(CO)(PMe_3)_3$ (**1a**) (0.5 g, 1.0 mmol) in Et_2O (40 mL) at 0 °C was added $Mg(CH_2CMe_3)Br$ (3.0 mL of a ca. 0.5 M Et_2O solution, 1.5 mmol). The cold bath was then removed and the mixture stirred at room temperature for 2–3 h. The solvent was evaporated in vacuo and the residue treated with 35 mL of a 2:1 mixture of petroleum ether–diethyl ether. The mixture was centrifuged and the product $MoCl(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ crystallized as red crystals by cooling overnight at −35 °C. Yield: 25%.

Attempts to prepare the tungsten complex analogue $WCl(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ and other related derivatives, $MCl(\eta^2\text{-}COR')(CNR)(PMe_3)_3$, by reaction of the corresponding $MCl_2(CNR)(CO)(PMe_3)_3$ complexes with organolithium or organomagnesium reagents were unsuccessful. Indeed, Grignard and lithium reagents did react with the carbonyl isocyanide complexes $MCl_2(CNR)(CO)(PMe_3)_3$, and solids displaying IR spectra similar to that recorded for $MoCl(\eta^2\text{-}COCH_2CMe_3)(CNBu^t)(PMe_3)_3$ were isolated. However, we have been unable to obtain analytically pure materials from these reactions.

X-ray Structure Determination of 1a. A summary of the fundamental crystal and refinement data is given in Table IV.

A yellow prismatic crystal of $MoCl_2(CNBu^t)(CO)(PMe_3)_3$ (**1a**) was resin epoxy coated and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of values of 24 reflections with $8° < \theta < 21°$. Study of the crystal on the diffractometer showed the systematic absences corresponding to the $P2_1/n$ space group. The data were corrected for Lorentz and polarization effects.

Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, P, and Cl were taken from ref 27.

The structure was solved by Patterson and Fourier methods.

An empirical absorption correction[28] (range max–min = 1.420–0.846) applied at the end of the isotropic refinement by using unit weights led to a conventional R value of 0.066.

Final refinement was carried out with anisotropic temperature factors for the non-hydrogen atoms and fixed isotropic temperature factors and positions for the H atoms, which were geometrically placed. No trends in ΔF vs F_o or $(\sin\theta)/\lambda$ were observed.

Most of the calculations were carried out with XRAY80.[29]

Acknowledgment. Generous support of this work by the Agencia Nacional de Evaluación y Prospectiva (Grant No. PB86-0653) is very gratefully acknowledged. L.C. thanks the Ministerio de Educación y Ciencia for support of a research grant.

Supplementary Material Available: Table SI, listing thermal parameters for **1a**, and Table SII, listing fractional atomic coordinates for hydrogen atoms of **1a** (2 pages); Table SIII, listing observed and calculated structure factors for **1a** (32 pages). Ordering information is given on any current masthead page.

---

(27) *International Tables for X-ray Crystallography*: Kynoch Press: Birminghan, U.K., 1974; Vol. IV, p 72.

(28) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(29) Stewart, J. M. *The X-ray System*; Computer Science Center, University of Maryland: College Park, MD, 1985.