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Articles

η^2-Acyl and Methyl Complexes of Tungsten. Crystal and Molecular Structures of $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ and $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$

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Treatment of $WCl_2(CO)_2(PMe_3)_3$ with Grignard reagents affords the formally six-coordinate bidentate acyls $W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ (R = CH_2SiMe_3 (**1a**), CH_2CMe_3 (**1b**), CH_2CMe_2Ph (**1c**)), whereas the analogous reaction with LiMe furnishes a seven-coordinate methyl complex of composition $W(CH_3)Cl(CO)_2(PMe_3)_3$ (**1d**). Addition of $Me_2PCH_2CH_2PMe_2$ (dmpe) to solutions of **1d** effects PMe_3 substitution and formation of $W(CH_3)Cl(CO)_2(PMe_3)(dmpe)$ (**2**), but further reaction with dmpe does not take place even under rather forcing conditions (excess dmpe, 50 °C, 24 h). A related bis-dmpe complex, $[W(CH_3)(CO)_2(dmpe)_2]Cl$ (**3**), is obtained, however, by reaction of **1a** with 2 equiv of dmpe. Facile desilylation of **1a** to other related methyl complexes is also observed under appropriate conditions. Carbonylation of compounds **1b**–**d** under ambient conditions yields the η^2-acyl complexes $W(\eta^2\text{-}C(O)R)Cl(CO)_2(PMe_3)_2$ (R = CH_2CMe_3 (**5b**), CH_2CMe_2Ph (**5c**), CH_3 (**5d**)), while the Me_3SiCH_2 derivative **1a** again undergoes desilylation and furnishes the acetyl **5d**. The methyldithiocarbamate compound $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$ (**4**), prepared from **1a** and NaS_2CNMe_2, also converts into an acetyl complex, $W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (**6**), upon reaction with CO. The η^2-acyl complex **1a** and the methyl complex **4** have been characterized by X-ray studies. **1a** is orthorhombic, $P2_12_12_1$, with a = 10.717 (5) Å, b = 12.526 (5) Å, c = 18.870 (7) Å, Z = 4, and R = 0.027, while **4** is monoclinic, $P2_1/c$, with a = 14.318 (8) Å, b = 9.140 (2) Å, c = 16.267 (6) Å, β = 106.08 (4)°, Z = 4, and R = 0.029.

Introduction

Studies on carbonylation reactions of alkylmetal compounds have allowed the synthesis and characterization of a large number of stable acyl complexes. The preparation of these acyls is frequently based on the migration of an alkyl group to a coordinated carbon monoxide ligand, and this process can be assisted by a secondary interaction of the carbonyl oxygen atom either with a metal center, yielding bidentate acyl structures,[2] or with a strong Lewis acid.[3,4]

η^2-Acyl structures, although still rare for the late transition metals,[2,5] are common among the actinides[6] and the early transition metals, particularly group 4d metals.[7] In recent years and following Wilkinson's report on the first bidentate acyl of a group 6d metal[8] a growing number of η^2-acyl complexes of Mo have been characterized. These include $Mo(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ and other related derivatives,[9] some hydridotris(pyrazolyl)borate compounds,[10,11] and others.[12] Some related tungsten complexes have also been reported, but they are fewer in number.[13] The reactivity of the coordinated COR group has not yet been thoroughly investigated, although Templeton has recently disclosed some interesting transformations and has shown that the reactions of these complexes cover a very wide range of ligand transformations.[11]

Although as stated above many formally six-coordinate (6C) bidentate acyl complexes of Mo, and to a much lesser extent of W, have been reported to date, in no case, however, have the corresponding isomeric seven-coordinate

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(1) (a) Universidad de Sevilla-CSIC. (b) The University of Alabama. (c) Northern Illinois University.

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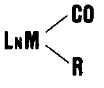
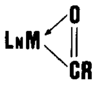
Table I. Analytical and IR Data for Complexes 1–6

	anal.,[a] %			IR[b]		
complex	C	H	N	ν(CO)	ν(COR)	ν(CN)
1a	30.5 (30.5)	6.5 (6.4)		1795 (s)	1465 (m)	
1b	32.8 (33.4)	6.6 (6.6)		1805 (s)	1480 (m)	
1b-Br	31.0 (31.0)	6.0 (6.1)		1810 (s)	1495 (m)	
1b-NCO	34.3 (35.1)	6.6 (6.5)		1820 (s)	1475 (m)	2220 (m)
1c	38.5 (39.6)	6.3 (7.0)		1790 (s)	1487 (m)	
1c-NCO	41.2 (41.0)	6.3 (6.2)		1798 (s)	1495 (m)	2210 (m)
1d	27.3 (27.8)	5.7 (5.8)		1890 (s) 1790 (s)		
1d-I	23.6 (23.6)	4.9 (4.9)		1895 (s) 1805 (s)		
1d-NCS	28.9 (28.8)	5.6 (5.5)		1895 (s) 1815 (s)		2070 (m)
2	28.3 (27.9)	5.2 (5.4)		1880 (s) 1800 (s)		
3	30.3 (30.5)	5.8 (5.9)		1910 (s) 1845 (s)		
4	27.3 (27.3)	5.1 (5.1)	2.7 (2.6)	1885 (s) 1795 (s)		1500 (m)
5b	29.8 (29.4)	5.0 (5.0)		1925 (s) 1820 (s)	1548 (m)	
5c	38.4 (38.7)	5.3 (5.3)		1938 (s) 1835 (s)	1555 (m)	
5d	25.5 (25.5)	4.5 (4.5)		1920 (s) 1820 (s)	1540 (m)	
6	25.1 (25.0)	3.9 (3.7)	3.1 (2.9)	1925 (s) 1835 (s)	1550 (m)	1530 (m)
6i	27.3 (28.1)	4.3 (4.9)	2.3 (2.5)	1900 (s) 1800 (s)	1555 (m)	1510 (m)

[a] Calculated values are given in parentheses. [b] Nujol mulls, cm^{-1}.

(7C) alkyl carbonyl compounds been detected.[14] Furthermore, and despite the relatively large number of transition-metal alkyl carbonyl and η^2-acyl compounds known to date, information on the relative stabilities of these two isomeric structures (A and B) and on the factors influencing their possible interconversion is very scarce.


A


B

Our interest in the chemistry of transition-metal acyl complexes and our successful approach to the study of η^2-acyls of molybdenum[9,12a] have led us to investigate the formation of related tungsten complexes by reactions of the chloro carbonyl compound $WCl_2(CO)_2(PMe_3)_3$ with various organomagnesium reagents, Mg(R)Cl. Preliminary results[15] have shown that both 7C methyl carbonyl and 6C η^2-acyl complexes of compositions $W(CH_3)X(CO)_2(PMe_3)_3$ and $W(\eta^2\text{-}C(O)R)X(CO)(PMe_3)_3$, respectively, can be readily obtained by this route. We have set out to prepare a number of compounds of these types with the hope of being able to alter the relative thermodynamic stability of the 7C alkyl carbonyl structure A and the 6C η^2-acyl formulation B by conveniently modifying the electronic and steric characteristics of the transition-metal center. These studies have generated a number of methyl carbonyl and η^2-acyl complexes of tungsten and have also shown that, in some cases, an equilibrium between structures A and B can be readily attained. In addition, for some of the complexes investigated, appropriate chemical transformations allow the smooth conversion of either structure to the other. The results of these studies are presented in this and in a subsequent publication.[16] Here we describe the formation of the η^2-acyl complexes $W(\eta^2\text{-}C(O)R)X(CO)(PMe_3)_3$ and some of their characteristic chemical reactions. Selected spectroscopic data for new complexes are given in Tables I–III.

Results and Discussion

As briefly noted in a previous publication,[9a] the bidentate acyls $W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ can be readily prepared by treating Et_2O suspensions of $WCl_2(CO)_2(PMe_3)_3$ with the corresponding Grignard reagents. This results in the incorporation of the alkyl group in the coordination sphere as an acyl ligand (eq 1). Compounds

$$WCl_2(CO)_2(PMe_3)_3 + Mg(R)Cl \xrightarrow{Et_2O} W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3 + MgCl_2 \quad (1)$$

$$R = CH_2SiMe_3\ (\mathbf{1a}),\quad CH_2CMe_3\ (\mathbf{1b}),\ CH_2CMe_2Ph\ (\mathbf{1c})$$

1a–c are orange to red diagmagnetic solids, freely soluble in common organic solvents. IR and NMR data (Tables I–III) are in accord with the proposed formulation. In particular, there is an IR absorption at ca. 1480 cm^{-1} due to ν(CO) of the acyl. This band is in the lower energy end of the approximate 1620–1450-cm^{-1} range typical of η^2-acyls[2-13,17] and is therefore indicative of bidentate coordination.

Several isomeric structures are in principle possible for the stoichiometry proposed for compounds **1a–c**, but NMR studies establish the existence of only one isomer in solution, one that has meridional phosphines. This rules out only the *fac* isomer and leaves three geometric isomers,

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(14) During the preparation of this paper, a preliminary communication that provides evidence for related observations concerning the equilibrium between a 6C alkyl carbonyl and a 5C η^2-acyl complex of Fe appeared: Jablonsky, C.; Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Am. Chem. Soc.* **1990**, *122*, 1632.

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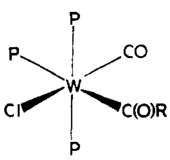
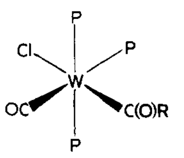
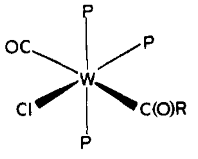


C



D



E

C–E, that contain respectively the acyl, the carbonyl, and the chloride ligands trans to the unique phosphine. A distinction among the three structures should in principle be possible on the basis of ^{13}C NMR studies, since the magnitudes of the $^2J_{CP}$ coupling constants should reveal whether the CO and the COR groups are cis or trans with respect to the equatorial phosphine ligand. The $^{13}C\{^1H\}$ NMR spectra of compounds **1a–c** show two signals of approximately equal intensity at ca. 270 (quartet; $^2J_{CP} \simeq$ 10–12 Hz) and 245 ppm (doublet of triplets, $^2J_{CP} \simeq 20$ and 7 Hz), confirming the presence of one acyl and one terminal carbonyl. The gated ^{13}C NMR spectra indicate the resonance at ca. 270 ppm corresponds to the acyl carbon, since it appears as a complex multiplet from which a value of $^2J_{CH} \simeq 6$ Hz can be computed. The value of 20 Hz found for the coupling of the CO ligand with the unique phosphine corresponds to a cis coupling,[18] and the even lower couplings of 10–12 Hz associated with the acyl ligand would accordingly suggest that this group is also cis to the phosphine ligands and therefore that compounds **1a–c** adopt a structure of type E. It should be noted, however, that the bidentate nature of the η^2-acyl group and its characteristic bite angle[9,10] of ca. 33° can give rise to P–M–C_{acyl} angles appreciably smaller than 180° in compounds where the acyl group is positioned trans to a phosphine ligand. Indeed in the analogous Mo complex $Mo(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$, which contains trans acyl and phosphine ligands, it is the acyl oxygen atom that occupies the trans position (P–Mo–O_{acyl} = 175.9 (1)°), while the P–Mo–C_{acyl} angle[9a] is appreciably smaller at 144.9 (2)°. This, coupled with the orientations of the acyl C–O vector with respect to other L–M or L–M–L′ vectors in the corresponding molecules, could complicate interpretation of the ^{13}C–^{31}P coupling constants. ^{13}C NMR data for the above Mo compound were not originally reported,[9a] but we have now found that this species displays carbonyl and acyl resonances almost identical with those of **1a**. This suggests that in compounds containing phosphine ligands and η^2-acyl groups the magnitudes of $^2J_{CP}$ can be deceptive and therefore of very little value to assess the stereochemistry of the acyl ligand. As shown below, an X-ray study carried out to confirm the geometry of **1a** shows that it has indeed a structure of type C. Deceptive ^{13}C–^{31}P couplings have been found recently in other η^2-acyl complexes, e.g. $Fe(\eta^2\text{-}C(O)R)X(CO)(dippe)$[19] (dippe = i-$Pr_2PCH_2CH_2P$-i-Pr_2) and especially in the hydridotris(pyrazolyl)borato complexes[10] $TpMo(CO)L(\eta^2\text{-}C(O)CH_3)$ (L = $P(OMe)_3$, PEt_3). In the $P(OMe)_3$ adduct the acyl and carbonyl carbons both appear as doublets at δ = 267.6 ($^2J_{PC}$ = 48 Hz) and 236.4 ppm ($^2J_{PC}$ = 14 Hz), respectively, while in the PEt_3 derivative they give singlets at 253.6 and 201.3 ppm, respectively. Subsequent X-ray determinations on these two compounds show they both have the acyl group cis to the P-donor, the only major difference between them being the orientation of the acyl group with respect to the P-donor ligand.[10]

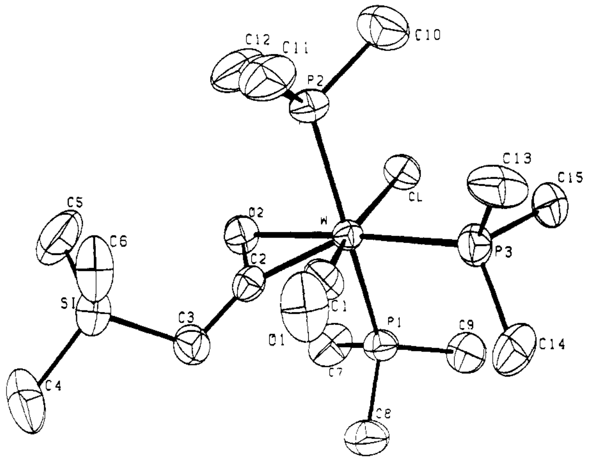


Figure 1. ORTEP diagram of complex **1a**.

In light of these results, it seems likely that the recently described bidentate acyl $Mo(\eta^2\text{-}C(O)CH_2CMe_3)Br(CN\text{-}t\text{-}Bu)(PMe_3)_3$,[9b] for which a structure having trans acyl and bromide ligands (i.e. of type D) has been proposed on the basis of the magnitude of the ^{13}C–^{31}P coupling constants, may also have a structure of type C in which the acyl ligand occupies a position that is trans with respect to the unique phosphine.

Figure 1 shows an ORTEP perspective view of **1a**; selected interatomic bond distances and angles are collected in Table V. The title compound is isostructural with its molybdenum analogue.[9a]

The W–η^2-CO plane is twisted 26.2° from the plane defined by W, Cl, P3, and C1, and as in other transition-metal acyl compounds,[7–9,12a,13a,19–22] the W–C2 distance (2.01 (1) Å) is shorter than the W–O2 separation of 2.334 (8) Å (a difference of 0.32 Å). In Th acyl complexes more oxycarbene character in the acyl linkage results in a Th–O distance shorter than the Th–C separation.[23]

In the related chloro-bridged dimer $[W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)_2(PMe_3)]_2$,[13a] the W–$O_{acyl}$ distance is shorter (2.289 (5) Å) and the W–C_{acyl} distance is longer (2.029 (7) Å) than found for **1a**. The difference in these values, 0.26 Å, is slightly smaller, while the dihedral angle between the acyl and the corresponding octahedral ligand plane is slightly larger at 32.1° than observed for compound **1a**. The differences in M–C and M–O distances for the structurally characterized Mo– and W–η^2-acyl complexes are all in the same range: $[Mo(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)_2(PMe_3)]_2$,[8] $Mo(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$,[9a] Δ = 0.30 Å; $[Mo(\eta^2\text{-}C(O)CH_2CMe_3)Br(PMe_3)_4$,[12a] Δ = 0.21 Å. The dihedral angles are also similar, except for the last compound, for which a dihedral angle of only 1.0° was observed. The last compound is also the only one in this series with the halide ligand trans to the acyl. All of them, including the title compound, have a PMe_3 group trans to the acyl and the halides trans to CO ligands.

The average W–P distance, 2.475 (7) Å, is normal and identical with the average observed in the chloro-bridged dimer. The W–CO separation of 1.91 (1) Å is also unexceptional. The W–Cl distance of 2.506 (3) Å is larger than the average W–Cl separation observed in $WCl_4(PMe_3)_3$

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Table II. ^1H and $^{31}P\{^1H\}$ NMR Data for Complexes 1–6

	^{31}P[a]			^1H[a]		
complex	Me–P	$^2J_{PP}$	$^1J_{PW}$	Me–P	$^2J_{HP}$	others
1a	−14.4[e]	10.4		1.34 d	7.8	2.90 s (CH_2)
	−14.8			1.15 t[i]	3.1	0.17 s ($SiMe_3$)
1b	−15.2 d	8.7	279.1	1.54 d	8.2	3.31 s (CH_2)
	−19.5 t		266.6	1.35 t[i]	3.0	1.33 s (CMe_3)
1b-Br[b]	−13.5 d	10.6	272.9	1.63 d	8.5	3.10 s (CH_2)
	−12.5 t		250.3	1.31 t[i]	3.3	1.06 s (CMe_3)
1b-NCO[b]	−9.5 d	7.7	278.7	1.60 d	8.7	3.08 s (CH_2)
	−10.8 t		256.6	1.23 t[i]	3.2	1.05 s (CMe_3)
1c	−14.9 d	9.1	275.2	1.30 d	8.2	3.81 s (CH_2)
	−15.6 t		237.4	1.00 t[i]	3.2	1.49 s (CMe_2)
						7.00 t (*Ph*)
						7.16 t (*Ph*)
						7.42 d (*Ph*)
1c-NCO	−9.6 d	7.3	278.4	1.57 d	8.5	3.59 s (CH_2)
	−10.9 t		252.3	1.07 t[i]	3.0	1.48 s (CMe_2)
						7.11 t (*Ph*)
						7.27 t (*Ph*)
						7.44 d (*Ph*)
1d[f]	−22.1 d	27.8	194.3	1.30 br s		0.39 q (J_{HP} = 6.9, CH_3)
	−27.2 t		122.9			
1d-I[c,f]	−34.5 br s			1.37 br s		0.55 q (J_{HP} = 7.8, CH_3)
	−40.8 br s					
1d-NCS[f]	−20.8 br s			1.35 br s		0.38 br s (CH_3)
	−31.2 br s					
2	−11.5 dd	155.8	207.8	1.34 d	9.0	0.46 dm (CH_3)[h]
		12.9		1.05 d[g]	8.5	
	15.9 dd[g]	19.5	182.3	1.21 d[g]	9.0	
	28.5 dd[g]		128.6	1.29 d[g]	7.9	
				1.50 d[g]	9.7	
				1.70 br m (CH_2)[g]		
3[d]	15.7 s[g]		173.4	1.50 br s[g]		−1.36 qt (J_{HP} = 10.4, CH_3)
				1.78 br m (CH_2)[g]		
4	−18.1 s		187.0	1.31 t[i]	4.0	0.61 t (J_{HP} = 8.1, CH_3)
						2.56 s ($CNMe_2$)
5b[b]	−10.8 d	9.0	254.9	1.74 d	9.4	3.38 d (CH_2)
	−16.9 d		224.4	1.34 d	7.9	3.19 d (CH'_2)
						1.01 s (CMe_3)
5c cis	−13.8 d	7.8	260.8	1.34 d	9.6	3.30 d (CH_2)
	−18.3 d		223.0	0.81 d	7.7	4.05 d (CH'_2)
						1.19 s (CMe_2)
						1.48 s (CMe'_2)
						6.99 t (*Ph*)
						7.12 t (*Ph*)
						7.27 d (*Ph*)
5c trans	−11.7 s		234.3	1.02 t[i]	3.9	3.50 s (CH_2)
						1.33 s (CMe_2)
5d cis	−13.6 d	8.3	263.1	0.96 d	7.5	2.65 s (CH_3)
	−17.5 d		226.8	1.31 d	9.6	
5d trans	−11.1 s		231.1	1.09 t[i]	3.8	2.45 s (CH_3)
6	−10.3 s		264.0	1.44 d	9.5	2.82 s (CH_3)
						2.43 s ($CNMe_2$)
6i	−15.0 br s			1.34 br s		2.75 s (CH_3)
						2.58 s ($CNMe_2$)

[a] δ in ppm, *J* in Hz; spectra recorded in C_6D_6 unless otherwise specified. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; dd, doublet of doublets; dc, doublet with some central intensity; br s, broad singlet; br m, broad multiplet. [b] In CD_3COCD_3. [c] In toluene-d_8. [d] In $CDCl_3$. [e] AB_2 pattern. [f] Main isomer. [g] Signals corresponding to dmpe ligands. [h] Doublet (J_{HP} = 13.4) of doublets with some central peaks ($J_{HP_{app}}$ = 8.7). [i] Values of *J* apparent.

(2.45 (3) Å).[24] This may be attributed to the trans carbonyl.

A final comment on compound **1a** refers to its solution behavior. If the solid-state structure were maintained in solution, inequivalence of the axial PMe_3 ligands would be expected due to the positioning of the acyl carbon slightly above the equatorial plane (i.e. the plane perpendicular to the trans P–W–P axis). NMR studies show, however, that they have identical chemical environments down to −80 °C. Hence, either the orientation of the acyl group has a negligible effect on the phosphines' environment or, more likely, there is a low-energy fluxional process, similar to that proposed by Curtis for some Tp–acyl complexes,[10] that equilibrates the two trans PMe_3 groups by creating an effective plane of symmetry.

Compounds **1b,c** readily undergo metathetical replacement of the chloride ligands by other halides or pseudohalides (eq 2). All these compounds display IR and NMR features very similar to those of **1a–c** and are therefore proposed to have similar structures.

$$W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3 + KX \rightarrow W(\eta^2\text{-}C(O)R)X(CO)(PMe_3)_3 + KCl \quad (2)$$

$$R = CH_2CMe_3,\ X = Br,\ NCO;\qquad R = CH_2CMe_2Ph,\ X = NCO$$

The analogous reaction of the (trimethylsilyl)methyl

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(24) Rogers, R. D.; Carmona, E.; Galindo, A.; Atwood, J. L.; Canada, L. G. *J. Organomet. Chem.* **1984**, *277*, 403.

Table III. $^{13}C\{^1H\}$ NMR Data[a] for Complexes 1-6

complex	Me–P	$^1J_{CP}$	others	CO	$^2J_{CP}$	COR	$^2J_{CP}$
1a	21.1 d	27.4	39.9 s (CH_2)	247.1 dt	20.1	267.8 q	10.9
	15.4 t^h	12.2	−0.5 s ($\mathrm{Si}Me_3$)		7.4		
1b	22.7 d	29.6	58.5 s (CH_2)	*e*		*e*	
	16.4 t^h	12.6	32.9 s ($C\mathrm{Me}_3$)				
			30.1 s ($\mathrm{C}Me_3$)				
1b-Br^b	22.1 d	29.5	58.5 s (CH_2)	245.1 dt	21.0	269.2 q	9.8
	16.3 t^h	12.8	32.7 s ($C\mathrm{Me}_3$)		7.3		
			30.0 s ($\mathrm{C}Me_3$)				
1b-NCO^b	21.2 d	29.9	59.2 s (CH_2)	249.0 dt	20.2	272.8 q	10.1
	16.1 t^h	12.4	32.7 s ($C\mathrm{Me}_3$)		6.9		
			30.1 s ($\mathrm{C}Me_3$)				
1c	21.2 d	28.4	59.0 s (CH_2)	247.8 dt	22.0	269.2 q	10.7
	15.3 t^h	12.2	38.3 s ($C\mathrm{Me}_2$)		6.6		
			29.2 s ($\mathrm{C}Me_2$)				
			125.6, 125.9, 128.2, 149.0 s (Ph)				
1c-NCO^b	21.3 d	28.6	59.5 s (CH_2)	248.3 m		270.5 q	8.4
	16.0 t^h	12.1	39.2 s ($C\mathrm{Me}_2$)				
			29.8 s ($\mathrm{C}Me_2$)				
			126.3, 126.5, 128.9, 149.8 s (Ph)				
1d^f	17.7 d	23.9	−0.1 m (CH_3)	*e*		*e*	
	14.2 t^h	12.8					
1d-I^{c,f}	17.4 br s		−6.2 br s (CH_3)	*e*		*e*	
1d-NCS	16.7 m		0.2 br s (CH_3)	*e*		*e*	
2	13.0 d	31.1	−4.4 t (J_{CP} = 17.6, CH_3)				
	27.5 m (CH_2)^g			259.7 m			
	16.1 d^g	30.8		229.9 m			
	13.5 d^g	25.6					
	10.6 d^g	25.0					
3^d	27.7 m (CH_2)^g		−2.2 br m (CH_3)	237.5 m			
	16.0 br s^g						
4	14.1 t^h	14.3	−4.9 t (J_{CP} = 7.0, CH_3)				
			207.8 s (S_2C)	250.6 t	13.1		
			38.0 s (CH_3)				
5b^b	19.6 d	33.2	58.8 s (CH_2)	226.6 dd	15.1, 8.7	263.0 dd	10.7, 4.9
	13.6 d	24.9	30.3 s ($C\mathrm{Me}_3$)	215.0 dd	58.3, 9.8		
			29.8 s ($\mathrm{C}Me_3$)				
5c cis	18.5 d	32.8	59.2 s (CH_2)	229.2 dd	13.9, 7.1	263.5 dd	9.7, 4.3
	12.5 d	23.4	38.2 s ($C\mathrm{Me}_2$)	214.3 dd	61.0, 10.2		
			30.7 s ($\mathrm{C}Me_2$)				
			27.2 s ($\mathrm{C}Me'_2$)				
			125.7, 125.0, 128.2, 148.2 s (Ph)				
5c trans	13.8 t^h	14.3	61.2 s (CH_2)	*e*		*e*	
			37.0 s ($C\mathrm{Me}_2$)				
			28.9 s ($\mathrm{C}Me_2$)				
5d cis	12.6 d	23.4	30.8 s (CH_3)	228.6 dd	13.7, 7.2	263.1 dd	10.6, 4.8
	18.5 d	33.0		214.1 dd	62.0, 10.1		
5d trans	13.8 t^h	14.5	32.7 s (CH_3)	*e*		*e*	
6	17.9 d	32.7	31.7 s (CH_3)	223.5 d	12.6	*e*	
			212.9 s (S_2C)				
			39.0 s ($\mathrm{CN}Me_2$)				
6i	15.2 br s		49.1 s (CH_3)	*e*		*e*	
			38.6 s ($\mathrm{CN}Me_2$)				

[a] δ in ppm, J in Hz; spectra recorded in C_6D_6 unless otherwise specified. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; br s, broad singlet; br m, broad multiplet. [b] In CD_3COCD_3. [c] In toluene-d_8. [d] In $CDCl_3$. [e] Not observed. [f] Main isomer. [g] Signals corresponding to dmpe ligands. [h] Values of J apparent.

complex **1a** with KX (X = I, NCS) fails to yield even spectroscopically detectable amounts of the expected acyls and produces instead the methyl complexes $W(CH_3)X(CO)_2(PMe_3)_3$, as a result of C–Si heterolysis prior to or following migration of the alkyl group to the metal. Although adventitious water possibly plays an important part in this transformation, catalytic processes involving traces of OH^- (or of chloride[25] when the desilylations are effected in chlorinated solvents or during metathetical replacements) cannot be ruled out as responsible for this reaction.

A more rational route to the methyl complex **1d** involves alkylation of $WCl_2(CO)_2(PMe_3)_3$ (eq 3). No evidence for

$$WCl_2(CO)_2(PMe_3)_3 + MeLi \rightarrow \underset{\mathbf{1d}}{W(CH_3)Cl(CO)_2(PMe_3)_3} + LiCl \quad (3)$$

an η^2-acetyl complex can be found either during the course of the reaction or during the thermal activation of **1d**. Therefore, it seems likely that this compound is both the kinetic and the thermodynamic product of the above reaction.

The methyl compounds $W(CH_3)X(CO)_2(PMe_3)_3$ (X = Cl, I, NCS) are yellow crystalline materials, soluble in nonpolar organic solvents, and somewhat unstable in solution, decomposing slowly even when kept under N_2, with formation of $WX_2(CO)_2(PMe_3)_3$, $W(CO)_2(PMe_3)_4$, and other unidentified products. IR studies show the presence of two carbonyl absorptions at ca. 1890 and 1800 cm^{-1}, but no evidence for the existence of an acyl ligand can be found. The tungsten-bonded methyl group gives rise to a characteristic high-field ^1H NMR signal at ca. 0.4 ppm. This appears as a pseudoquartet ($^3J_{HP} \simeq 8.5$ Hz) and is clearly in the region characteristic of alkyl groups directly bonded to a metal atom. A corresponding high-field ^{13}C-

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[25] (a) Ruiz, J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1986**, 862. (b) Fujita, M.; Hiyama, T. *J. Am. Chem. Soc.* **1985**, *107*, 4085.

$\{^1H\}$ resonance for each of these compounds is also observed (Table III).

The adoption of the 7C alkyl carbonyl structure A for the methyl complex **1d** and of the 6C η^2-acyl formulation B for compounds **1a–c**, containing bulkier alkyl groups, merits comment. Similar situations, although associated with the bulkiness of the ancillary ligands, have been found for some η^2-acyl complexes of iron[5] and ruthenium.[26] In the former case, the 5C acyl complexes $Fe(\eta^2\text{-}C(O)R)I(CO)L_2$ (L = phosphine ligand) were found to form for phosphines with cone angles[27] greater than 135°, while less sterically demanding phosphines ($\theta < 135°$) preferentially stabilized the 6C alkyl carbonyl structure $Fe(R)I(CO)_2L_2$. For these compounds the electronic properties of the ancillary ligand were found to have a negligible effect and the stabilization of the η^2-acyl structure was entirely ascribed to the number of d electrons at the metal and to the steric hindrance of the coligands.[5]

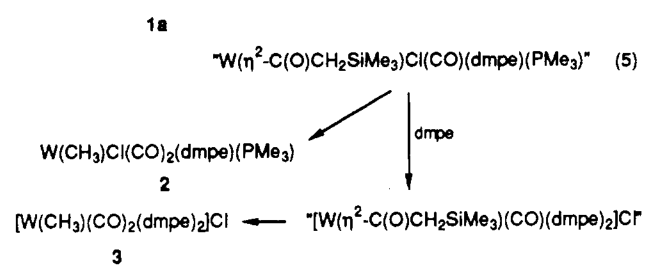
For compounds **1a–d** the η^2-acyl structure is evidently favored, with the only exception being the $W\text{-}CH_3$ derivative **1d**. The analogous Mo complexes[9a] all display the η^2-acyl structure. Both the strength of the M–C bond (5d > 4d) and the migratory aptitude of the alkyl group[28] favor structure A for **1d**, but apart from these obvious considerations, it should be evident that in series of related complexes the relative stability of structures A and B must be influenced by both steric and electronic effects. When compounds of Mo and W of the same composition are compared, the influence of the steric effects on any observed structural differences must be minimal, since the single-bond metallic radii of these elements differ by only 0.008 Å.[29] On electronic grounds, however, structure A should be more favorable than B in the order W > Mo because of the higher basicity of the tungsten derivatives.[30] Thus, it seems that whereas the stabilization of the η^2-acyl structure of **1a**,**b**, as compared to the alkyl carbonyl formulation of **1d**, is due to steric compression, the adoption of the latter structure by the tungsten complex **1d** and of the former by the Mo analogue $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ could possibly be due to electronic effects.

To confirm this assumption, some chemical reactions of compounds **1a–d** have been investigated and their outcomes are discussed below. Briefly, however, the substitution of one of the strongly basic PMe_3 ligands in the alkyl complexes $W(CH_3)Cl(CO)_2(PMe_3)_3$ (**1d**) and $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$ (see below), by the less sterically demanding and strong π-acid CO ligand, produces the η^2-acetyl complexes $W(\eta^2\text{-}C(O)CH_3)Cl(CO)_2(PMe_3)_2$ and $W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)$, respectively. Other related reactions that provide additional evidence on these matters are reported in a separate contribution.[16]

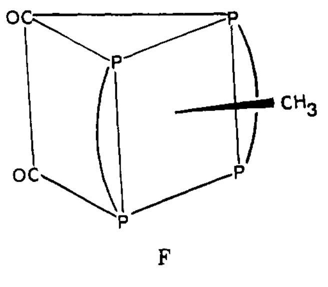
Some Chemical Reactions of Compounds 1a–d. Crystal and Molecular Structure of $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$ (4). Compound **1d** does not apparently react with PMe_3, neither migratory insertion nor carbon monoxide substitution reactions being observed, even in the presence of a large excess of PMe_3 (10 equiv). However, addition of $Me_2PCH_2CH_2PMe_2$ (dmpe) to diethyl ether solutions of **1d** affords the yellow complex $W(CH_3)Cl(CO)_2(dmpe)(PMe_3)$ (**2**), by the route of eq 4. Further substitution of PMe_3 does not take place even under rather forcing conditions (50 °C, 24 h), but a

$$\underset{\mathbf{1d}}{W(CH_3)Cl(CO)_2(PMe_3)_3} + \text{dmpe} \rightarrow \underset{\mathbf{2}}{W(CH_3)Cl(CO)_2(dmpe)(PMe_3)} + 2PMe_3 \quad (4)$$

cationic bis-dmpe complex of composition $[W(CH_3)(CO)_2(dmpe)_2]^+$ can be isolated as its chloride salt, **3**, by a different route that involves treatment of the (trimethylsilyl)methyl complex **1a** with 2 equiv of dmpe. Again, facile desilylation must occur at some stage. The equimolar reaction of **1a** and dmpe produces an incomplete transformation that furnishes unreacted **1a** together with **2** and **3**. Since as already indicated **2** is unreactive toward dmpe, the above transformation must follow the course depicted in eq 5.



Compounds **2** and **3** display two terminal carbonyl bands between 1910 and 1800 cm^{-1} (Nujol mulls), with the band at higher frequency being the more intense. This is indicative of a cis arrangement of the CO ligands. Only one isomer seems to exist in solution for either complex, and in the case of **2** this has nonequivalent dmpe phosphorus nuclei (approximately AMX spin system for the ^{31}P nuclei; see Table II) with the four methyl groups of the chelating dmpe ligand in different chemical environments and the two carbonyl ligands being also nonequivalent. The seven-coordinate nature of this species, which allows three idealized geometries (D_{5h} pentagonal bipyramid, C_{3v} monocapped octahedron, and C_{2v} monocapped trigonal prism), and its molecular complexity do not permit a unique structural proposal to be made with the present data. For **3**, however, the situation is much simpler and the complex can be proposed to have structure F on the basis of the IR and NMR data (two IR bands at 1910 and 1845 cm^{-1} (Nujol mull); $^{31}P\{^1H\}$ singlet at 15.7 ppm; ^1H quintet at −1.36 ppm, $^3J_{HP}$ = 10.4 Hz) and by similarity with the structures previously found for other related complexes, e.g. $TaCH_3(CO)_2(dmpe)_2$,[31] $[MoCl(CO)_2(diars)_2]I_3$,[32] and $[MoI(CO)_2(dmpe)_2]I$.[33]



F

Treatment of the methyl complex **1d** with sodium dimethyldithiocarbamate, NaS_2CNMe_2, results in the ex-

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[32] Drew, M. G. B.; Wilkins, J. C. *J. Chem. Soc., Dalton Trans.* **1973**, 2664.

[33] Connor, J. A.; McEwen, G. K.; Rix, C. J. *J. Chem. Soc., Dalton Trans.* **1974**, 589.

Table IV. Crystal and Refinement Data for 1a and 4

formula	$WC_{15}ClH_{38}O_2P_3Si$	$WC_{12}H_{27}NO_2P_2S_2$
mol wt	590.78	527.3
space group	$P2_12_12_1$	$P2_1/c$
temp, °C	22	20
cell constants	*a*	*b*
a, Å	10.717 (5)	14.318 (8)
b, Å	12.526 (5)	9.140 (2)
c, Å	18.870 (7)	16.267 (6)
β, deg		106.08 (4)
cell vol, Å^3	2533.1	2045.5
molecules/unit cell	4	4
D_{calc}, g cm^{-3}	1.55	1.71
μ_{calc}, cm^{-1}	51.71	63.2
diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ	Nicolet P3-F/ω
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
cryst dimens, mm	0.50 × 0.45 × 0.50	0.30 × 0.35 × 0.40
no. of rflns measd	2661	2225
2θ range, deg	$2 \le 2\theta \le 50$	$3 \le 2\theta \le 40$
no. of rflns obsd[c]	1981 [$I_o \ge 3\sigma(I_o)$]	1499 [$F_o \ge 5\sigma(F_o)$]
computer programs[d]	SHELX[e]	SHELX[e]
no. of params varied	208	181
weights	unit	$[\sigma(F_o)^2]^{-1}$
GOF	0.69	1.49
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.027	0.029
R_w	0.030	0.029

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections with $\theta > 19°$. [b] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections with $\theta > 13°$. [c] Corrections: Lorentz–polarization and absorption (empirical, ψ scan). [d] Neutral scattering factors and anomalous dispersion corrections from ref 43. [e] See ref 42.

Table V. Bond Distances (Å) and Angles (deg) for 1a

	Distances		
W–Cl	2.506 (3)	W–P1	2.474 (3)
W–P2	2.483 (3)	W–P3	2.467 (3)
W–O2	2.334 (8)	W–C1	1.91 (1)
W–C2	2.01 (1)	P1–C7	1.84 (1)
P1–C8	1.82 (1)	P1–C9	1.83 (1)
P2–C10	1.83 (2)	P2–C11	1.81 (2)
P2–C12	1.83 (1)	P3–C13	1.83 (1)
P3–C14	1.84 (1)	P3–C15	1.82 (1)
Si–C3	1.91 (1)	Si–C4	1.83 (1)
Si–C5	1.86 (2)	Si–C6	1.84 (2)
O1–C1	1.19 (1)	O2–C2	1.28 (1)
C2–C3	1.47 (2)		
	Angles		
Cl–W–P1	84.2 (1)	Cl–W–P2	83.6 (1)
P1–W–P2	165.9 (1)	Cl–W–P3	90.9 (1)
P1–W–P3	88.0 (1)	P2–W–P3	99.3 (1)
Cl–W–O2	89.2 (2)	P1–W–O2	88.1 (2)
P2–W–O2	84.7 (2)	P3–W–O2	176.0 (2)
Cl–W–C1	163.2 (3)	P1–W–C1	102.9 (4)
P2–W–C1	90.7 (4)	P3–W–C1	74.4 (4)
O2–W–C1	106.1 (4)	Cl–W–C2	119.8 (3)
P1–W–C2	79.6 (3)	P2–W–C2	100.4 (3)
P3–W–C2	145.1 (3)	O2–W–C2	33.2 (3)
C1–W–C2	76.8 (4)	W–P1–C7	111.2 (5)
W–P1–C8	117.8 (5)	C7–P1–C8	102.1 (7)
W–P1–C9	121.1 (5)	C7–P1–C9	100.8 (6)
C8–P1–C9	101.1 (6)	W–P2–C10	116.1 (6)
W–P2–C11	119.8 (5)	C10–P2–C11	100.3 (8)
W–P2–C12	113.5 (5)	C10–P2–C12	101.8 (8)
C11–P2–C12	102.7 (8)	W–P3–C13	117.2 (6)
W–P3–C14	119.0 (5)	C13–P3–C14	99.4 (6)
W–P3–C15	115.3 (5)	C13–P3–C15	98.6 (8)
C14–P3–C15	104.2 (7)	C3–Si–C4	107.2 (6)
C3–Si–C5	110.3 (8)	C4–Si–C5	110 (1)
C3–Si–C6	111.1 (6)	C4–Si–C6	108.5 (7)
C5–Si–C6	110 (1)	W–O2–C2	59.2 (6)
W–C1–O1	176 (1)	W–C2–O2	87.6 (7)
W–C2–C3	150.2 (9)	O2–C2–C3	122 (1)
Si–C3–C2	116.3 (9)		

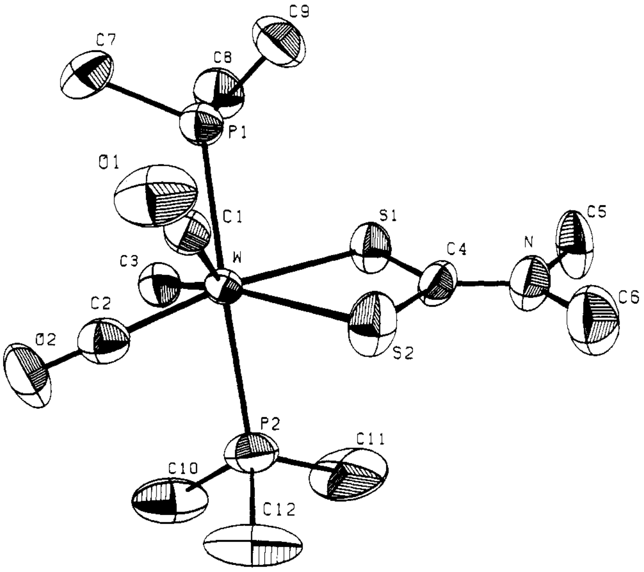

Figure 2. Molecular structure and labeling scheme for 4.

Table VI. Final Fractional Coordinates for 1a

atom	*x/a*	*y/b*	*z/c*
W	−0.35669 (4)	−0.00455 (4)	−0.11577 (2)
Cl	−0.5592 (3)	−0.1027 (2)	−0.1027 (2)
P1	−0.4635 (3)	0.0863 (3)	−0.2151 (2)
P2	−0.2833 (3)	−0.1327 (3)	−0.0244 (2)
P3	−0.4324 (3)	0.1394 (3)	−0.0376 (2)
Si	0.0154 (4)	−0.0803 (3)	−0.2330 (2)
O1	−0.1245 (8)	0.1362 (7)	−0.0854 (5)
O2	−0.2905 (8)	−0.1341 (6)	−0.1964 (4)
C1	−0.215 (1)	0.0852 (9)	−0.0987 (6)
C2	−0.241 (1)	−0.0410 (8)	−0.1959 (5)
C3	−0.142 (1)	−0.011 (1)	−0.2454 (5)
C4	0.119 (1)	−0.033 (2)	−0.3037 (8)
C5	−0.004 (2)	−0.227 (1)	−0.239 (1)
C6	0.086 (1)	−0.045 (1)	−0.147 (1)
C7	−0.491 (1)	−0.006 (2)	−0.2892 (6)
C8	−0.382 (1)	0.196 (1)	−0.2586 (7)
C9	−0.619 (1)	0.143 (1)	−0.2041 (7)
C10	−0.388 (2)	−0.155 (1)	0.051 (1)
C11	−0.138 (2)	−0.108 (1)	0.0220 (7)
C12	−0.262 (2)	−0.268 (1)	−0.0581 (8)
C13	−0.356 (2)	0.154 (1)	0.0485 (7)
C14	−0.423 (1)	0.279 (1)	−0.0686 (8)
C15	−0.593 (1)	0.125 (1)	−0.0069 (8)

pected substitution of the chloride ligand and of one of the PMe_3 groups by the powerful chelating, three-electron-donor ligand $SCNMe_2$, as indicated in eq 6. The proposed

$$\underset{\textbf{1d}}{W(CH_3)Cl(CO)_2(PMe_3)_3} + NaS_2CNMe_2 \rightarrow \underset{\textbf{4}}{W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2} + NaCl + PMe_3 \quad (6)$$

methyl carbonyl formulation for the resulting complex 4 is not unexpected in light of previous comments on the influence of electronic and steric effects in the relative stability of structures A and B and finds support in the observation of two strong IR bands at 1885 and 1795 cm^{-1} and of a relatively high-field ^1H resonance at ca. 1.3 ppm (t, $^3J_{HP}$ = 4 Hz). At low temperatures (−90 °C) the two carbonyl groups give separate ^{13}C resonances at ca. 265.6 (dd, $^2J_{CP}$ = 29 and 14 Hz) and 248.5 ppm (dd, $^2J_{CP}$ = 21 and 3.5 Hz), in accord with the solid-state geometry (see below), but at room temperature a fluxional process averages the two CO groups, which, under these conditions, give rise to a triplet centered at ca. 259 ppm ($^2J_{CP}$ = 13 Hz).

Table VII. Bond Distances (Å) and Angles (deg) for 4

	Distances		
W–S1	2.597 (3)	W–S2	2.568 (3)
W–P1	2.480 (3)	W–P2	2.563 (3)
W–C1	1.92 (1)	W–C2	1.94 (1)
W–C3	2.28 (1)	S1–C4	1.71 (1)
S2–C4	1.72 (1)	P1–C7	1.85 (1)
P1–C8	1.84 (1)	P1–C9	1.82 (1)
P2–C10	1.85 (2)	P2–C11	1.81 (2)
P2–C12	1.85 (1)	O1–C1	1.21 (1)
O2–C2	1.19 (1)	N–C4	1.32 (1)
N–C5	1.46 (1)	N–C6	1.42 (2)
	Angles		
S1–W–S2	67.2 (1)	S1–W–P1	79.8 (1)
S2–W–P1	113.4 (1)	S1–W–P2	89.3 (1)
S2–W–P2	77.6 (1)	P1–W–P2	159.3 (1)
S1–W–C1	121.6 (4)	S2–W–C1	77.0 (4)
P1–W–C1	74.0 (3)	P2–W–C1	126.5 (3)
S1–W–C2	165.0 (4)	S2–W–C2	118.2 (4)
P1–W–C2	108.4 (4)	P2–W–C2	78.9 (4)
C1–W–C2	73.2 (5)	S1–W–C3	89.5 (3)
S2–W–C3	150.6 (3)	P1–W–C3	77.6 (3)
P2–W–C3	84.8 (3)	C1–W–C3	132.1 (5)
C2–W–C3	80.4 (5)	W–S1–C4	89.6 (4)
W–S2–C4	90.3 (4)	W–P1–C7	116.0 (4)
W–P1–C8	118.8 (5)	C7–P1–C8	101.5 (6)
W–P1–C9	113.7 (5)	C7–P1–C9	103.0 (6)
C8–P1–C9	101.5 (6)	W–P2–C10	116.9 (5)
W–P2–C11	117.8 (5)	C10–P2–C11	100.3 (8)
W–P2–C12	115.7 (5)	C10–P2–C12	99.3 (7)
C11–P2–C12	104.2 (8)	C4–N–C5	121 (1)
C4–N–C6	122 (1)	C5–N–C6	117 (1)
W–C1–O1	176 (1)	W–C2–O2	179 (1)
S1–C4–S2	112.9 (7)	S1–C4–N	125.1 (9)
S2–C4–N	122.0 (9)		

Table VIII. Fractional Coordinates of the Non-Hydrogen Atoms of 4

atom	*x/a*	*y/b*	*z/c*
W	0.22278 (4)	0.48691 (5)	0.70196 (3)
S1	0.2656 (3)	0.6894 (4)	0.6064 (2)
S2	0.4026 (2)	0.4837 (4)	0.7037 (2)
P1	0.1761 (3)	0.7079 (4)	0.7697 (2)
P2	0.2247 (3)	0.2977 (4)	0.5861 (2)
O1	0.3283 (8)	0.456 (1)	0.8971 (6)
O2	0.1376 (7)	0.213 (1)	0.7707 (6)
N	0.4535 (8)	0.687 (1)	0.6069 (6)
C1	0.289 (1)	0.472 (1)	0.8214 (8)
C2	0.171 (1)	0.317 (1)	0.7448 (8)
C3	0.0622 (8)	0.513 (1)	0.6303 (7)
C4	0.3832 (9)	0.629 (1)	0.6339 (7)
C5	0.438 (1)	0.818 (1)	0.5533 (9)
C6	0.549 (1)	0.629 (2)	0.631 (1)
C7	0.1167 (9)	0.675 (1)	0.8554 (8)
C8	0.092 (1)	0.841 (1)	0.7019 (9)
C9	0.278 (1)	0.824 (1)	0.8215 (9)
C10	0.111 (1)	0.195 (2)	0.540 (1)
C11	0.250 (2)	0.362 (2)	0.490 (1)
C12	0.309 (1)	0.142 (2)	0.621 (1)

The crystal and molecular structure of complex 4 has been determined by an X-ray study, whose results are summarized in Figure 2 and Tables IV, VII, and VIII. The tungsten atom is seven-coordinate, and the complex most closely resembles a capped-octahedral geometry. C1 caps the trigonal face of P1, S2, and C2. The molecule also comes close to fitting an alternate monocapped-trigonal-prismatic geometry with C3 capping the rectangular face formed by P2, C2, P1, and S1.

The chelating dithiocarbamate ligand is planar to within 0.051 Å with W 0.018 Å out of this plane. Some delocalization of π-electron density is evident. The C–N bond is short (1.32 (1) Å), although not as short as a full C–N double bond. The N–C bonds average 1.44 (2) Å, while the C4–S bonds average 1.72 (1) Å.

The W–S distances 2.597 (3) Å (W–S1) and 2.568 (3) Å (W–S2) differ by 0.029 Å (roughly 10σ) and average 2.58 (1) Å. The difference may result from the trans influence of the C2 carbonyl group in S1 (the longer of the two W–S separations). The methyl group is trans to the closer S2. A large range of W–S dithiocarbamate separations has been observed, even within the same compounds. The W–S ranges and W–S average distances observed include the following: $W(S_2CNMe_2)_2(CO)_3$,[34] 2.501–2.569, 2.53 Å; $W(S_2CNMe_2)_2(PhC_2H)$(maleic anhydride),[35] 2.490–2.543, 2.51 Å; $W(S_2CNEt_2)_2(CO)_2(PPh_3)$,[36] 2.487–2.562, 2.53 Å; $W(S_2CNMe_2)(CO)\{(C_8H_{12})_2CO\}$,[37] 2.484–2.547, 2.52 Å; $W(S_2CNEt_2)(CO)(C_2H_2)$,[38] 2.399–2.588, 2.52 Å; $(\eta^5\text{-}C_5Ph_2H_2NMe_2)W(S_2CNMe_2)(S_2C_2PhH)$,[39] 2.460–2.468, 2.46 Å.

The W–CO distances are nearly identical and average 1.93 (1) Å, and the W–Me distance is 2.28 (1) Å. The W–P separations differ by 0.083 Å. The W–P1 bond length is 2.480 (3) Å, while W–P2 is 2.563 (3) Å. P2 may be affected by the C1 carbonyl group, which caps the opposite trigonal face. The average of 2.52 (4) Å is unexceptional.

The reactions of compounds **1a–d** with carbon monoxide have also been investigated. For the η^2-acyls **1a–c**, this transformation was of interest since it could either effect substitution of one of the PMe_3 ligands by CO or bring about an expansion of the coordination sphere around tungsten by coordination of an additional ligand, with concomitant change in the bridging mode of the acyl unit from η^2 to η^1. As for the methyl complex **1d**, it was of importance to ascertain whether the substitution of one of the strong σ-donor PMe_3 ligands[40] (cone angle $\theta = 118°$) for the strongly π-acidic and less sterically demanding CO ligand ($\theta = 95°$) could sufficiently alter the relative stability of structures A and B so as to induce formation of an η^2-acyl complex.

Compounds **1b,c** react smoothly with CO (eq 7), with formation of new bidentate acyls of composition $W(\eta^2\text{-}C(O)R)X(CO)_2(PMe_3)_2$ (X = Br, R = CH_2CMe_3, **5b-Br**; X = Cl, R = CH_2CMe_2Ph, **5c**). The IR spectra of these

$$\underset{\textbf{1b-Br, 1c}}{W(\eta^2\text{-}C(O)R)X(CO)(PMe_3)_3} + CO \rightarrow \underset{\textbf{5b-Br, 5c}}{W(\eta^2\text{-}C(O)R)X(CO)_2(PMe_3)_2} + PMe_3 \quad (7)$$

compounds present two bands of similar intensities in the range 1920–1820 cm^{-1}, as well as a medium-intensity absorption at ca. 1540 cm^{-1} for the acyl group. The latter has a frequency characteristic of η^2 coordination, and it is shifted by ca. 60 cm^{-1} to higher energy with respect to the frequencies for the monocarbonyls **1b-Br** and **1c**, in accord with the electronic changes foreseen upon substitution of PMe_3 by CO. In some instances the energy of $\nu(C(O)R)$ in bidentate acyls has been found to be insensitive to changes in the coordination sphere of the metal atom,[5,10] but the shifts found in these and other related η^2-acyls,[9,12a] in conjunction with substitution reactions involving the ancillary ligands, clearly demonstrate that this

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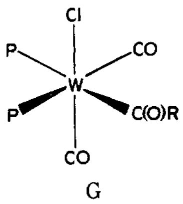
is not a general situation. In accord with the synergistic bonding model for the M–η^2-acyl linkages,[10,11] an increase in the electron density at the metal center is expected to produce a decrease in the value of ν(C(O)R). This effect is nicely illustrated in the compounds just discussed and, above all, in the series of compounds $Mo(\eta^2\text{-}C(O)CH_2CMe_3)Br(PMe_3)_{4-n}(CO)_n$ (n = 0–2), in which ν(C(O)R) shifts from one end of the η^2-acyl frequency range to the other upon substitution of two PMe_3 ligands by two CO molecules (1425 cm^{-1} for n = 0 to 1575 cm^{-1} for n = 2).

The analogous reaction of the methyl complex **1d** with CO produces the bidentate acetyl species **5d** (ν(C(O)R) = 1540 cm^{-1}), as represented in eq 8. Substitution of PMe_3 by CO should result in a decrease of the steric compression around the metal atom. Consequently, the above transformation must be entirely ascribed to electronic factors. This again demonstrates that the electronic properties of the coligands can have a considerable influence on the stability of the η^2-acyl structure. Complex **5d** is also obtained, as the only isolable product, in the reaction of **1a** with CO. The expected (trimethylsilyl)methyl derivative $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)_2(PMe_3)_2$ is extremely prone to hydrolytic cleavage of the C–Si bond and cannot be isolated in a pure form.

$$\underset{\mathbf{1d}}{W(CH_3)Cl(CO)_2(PMe_3)_3} + CO \rightarrow \underset{\mathbf{5d}}{W(\eta^2\text{-}C(O)CH_3)Cl(CO)_2(PMe_3)_2} + PMe_3 \tag{8}$$

NMR studies on compounds **5b–d** demonstrate the existence of two isomers that appear in a ratio of 6:1 or higher. The major component of this isomeric mixture exhibits two ^{1}H doublets for the two nonequivalent and mutually cis PMe_3 ligands (0.96 and 1.31 ppm, data for **5d**) and a singlet for the acyl protons (2.65 ppm in the acetyl complex **5d**). The neophyl derivative **5c** has diastereotopic methylene protons and methyl groups (Table II). This major cis isomer for compounds **5b–d** also exhibits three doublets of doublets in the $^{13}C\{^1H\}$ NMR spectrum due to the acyl and carbonyl carbons, which for compounds **5d** appear at 263.1 ($^2J_{CP}$ = 10.6 and 4.8 Hz), 228.6 ($^2J_{CP}$ = 13.7 and 7.2 Hz), and 214.0 ppm ($^2J_{CP}$ = 62 and 10 Hz). Although a unique structural proposal cannot be made with the present data, on electronic grounds, and also by similarity with the structures found for other related η^2-acyl complexes of Mo and W,[8,9,13a] which seem to have always trans Cl and CO ligands, a stereochemistry of type G can be proposed. As for the minor isomer, ^{1}H and $^{31}P\{^1H\}$ NMR studies indicate it has trans equivalent PMe_3 groups, but insufficient NMR data are available for its full structural characterization and hence speculation on its structure seems unwarranted.



G

In light of the above results concerning the conversion of the methyl complex **1d** into the η^2-acetyl species **5d**, it was of interest to ascertain whether the carbonylation of the dithiocarbamate complex $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$ (**4**) would also provide a bidentate acetyl. This was, in fact, the case, and yellow crystals of $W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (**6**) were isolated from the reaction of **4** with carbon monoxide (eq 9). Once again, a decrease in the electron density at the metal center, without augmentation of the steric requirements of the ancillary ligands, induces conversion of the alkyl carbonyl structure into the η^2-acyl formulation. Not unexpectedly, complex **6** can also be obtained by treatment of **5d** with NaS_2CNMe_2 (eq 10). The progress of these two reactions can be monitored by IR spectroscopy, following the emergence of the carbonyl absorptions at 1925 and 1835 cm^{-1}, characteristic of **6**, or the disappearance of those associated with **4** or **5d**. The formation of an intermediate species having two ν(CO) stretches at 1900 and 1800 cm^{-1} can be detected, but these bands gradually disappear and the final solution shows only the CO bands due to **6**. The above intermediate can be isolated under certain conditions (see Experimental Section) and is tentatively formulated as $W(\eta^2\text{-}C(O)CH_3)(\eta^1\text{-}S_2CNMe_2)(CO)_2(PMe_3)_2$ (**6i**), on the basis of analytical and spectroscopic data (Tables I–III) and of its chemical behavior. The two PMe_3 ligands give broad ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR signals, and one of them is slowly lost with formation of **6**. Conversely, addition of 1 equiv of PMe_3 to solutions of **6** produces this $\eta^1\text{-}S_2CNMe_2$ intermediate **6i**. The above data are in agreement with the equilibrium shown in eq 11 and further suggest that the reaction of the 7C alkyl carbonyl complex **4** with CO proceeds, at least in part, with initial attack of CO on the metal center, at the vacant coordination site generated by the transformation of the S_2CNMe_2 ligand from the bidentate S,S to the monodentate S bonding mode. The undetected intermediate species "$W(CH_3)(\eta^1\text{-}S_2CNMe_2)(CO)_3(PMe_3)_2$" would be formed in this way and would immediately rearrange to the intermediate acetyl **6i**. Loss of PMe_3 from **6i** would lead to the finally observed complex **6**.

$$\underset{\mathbf{4}}{W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2} + CO \rightarrow \underset{\mathbf{6}}{W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)} + PMe_3 \tag{9}$$

$$\underset{\mathbf{5d}}{W(\eta^2\text{-}C(O)CH_3)Cl(CO)_2(PMe_3)_2} + NaS_2CNMe_2 \rightarrow \underset{\mathbf{6}}{W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)} + PMe_3 + NaCl \tag{10}$$

$$\underset{\mathbf{6}}{W(\eta^2\text{-}C(O)CH_3)(\eta^2\text{-}S_2CNMe_2)(CO)_2(PMe_3)} \underset{-PMe_3}{\overset{+PMe_3}{\rightleftharpoons}} \underset{\mathbf{6i}}{W(\eta^2\text{-}C(O)CH_3)(\eta^1\text{-}S_2CNMe_2)(CO)_2(PMe_3)_2} \tag{11}$$

Concluding Remarks

Steric hindrance is likely responsible for the adoption of the 6C η^2-acyl structure B for compounds **1a–c**, containing the bulky alkyl ligands CH_2SiMe_3, CH_2CMe_3, and CH_2CMe_2Ph, and of the 7C alkyl carbonyl arrangement for the methyl complex **1d**. Electronic effects must, however, be invoked to account for the conversion of the methyl carbonyl compounds **1d** and **4** into the η^2-acetyl complexes **5d** and **6**, respectively. In accord with these observations, IR data for bidentate acyl complexes containing ancillary ligands of different electronic characteristics also show a significant influence of the electronic properties of the coligands on the metal–η^2-acyl linkage. Additional evidence for the influence of both the steric and the electronic effects on the relative stabilities of structures A and B is provided in a subsequent publication.[16]

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Remagen, Germany, and by the Analytical Service of The University of Seville. All preparations and manipulations were carried out under oxygen-free nitrogen, by conventional Schlenk techniques. Solvents were dried and degassed before use. All reagents were either purchased from commercial suppliers or prepared according to published procedures. Sodium dimethyldithiocarbamate was dried by heating at 70–90 °C for 2–3 days under vacuum. WCl$_2$(CO)$_2$(PMe$_3$)$_3$ was synthesized as described previously.[41]

IR spectra were recorded as Nujol mulls, or in an appropriate solvent, on Perkin-Elmer (Models 577 and 684) instruments. ^{1}H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200 spectrometer. ^{31}P NMR shifts were referenced to external 85% H$_3$PO$_4$, while ^{1}H and ^{13}C NMR shifts were referenced to the residual signals of the deuterated solvents employed, and are all reported in ppm downfield from Me$_4$Si.

Preparation of W(η^2-C(O)R)X(CO)(PMe$_3$)$_3$ (R = CH$_2$SiMe$_3$, X = Cl (1a); R = CH$_2$CMe$_3$, X = Cl (1b), Br (1b-Br), NCO (1b-NCO); R = CH$_2$CMe$_2$Ph, X = Cl (1c), NCO (1c-NCO)). The chloro acyl complexes were prepared by treating WCl$_2$(CO)$_2$(PMe$_3$)$_3$ with the corresponding Grignard reagents. The experimental procedure, with the W(η^2-C(O)CH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ complex as a representative example, was as follows.

W(η^2-C(O)CH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ (1a). To a stirred yellow suspension of WCl$_2$(CO)$_2$(PMe$_3$)$_3$ (5.4 g, 10 mmol) in 200 mL of diethyl ether (Et$_2$O), at 0 °C, was added a slight excess of Mg(CH$_2$SiMe$_3$)Cl (5.8 mL of a 1 M Et$_2$O solution). The supernatant solution gradually became red-orange as the quantitiy of insoluble starting material diminished and a white solid began to precipitate. The mixture was stirred for 2–3 h to ensure completion of the reaction, and the solvent was extracted with a 1:4 petroleum ether–Et$_2$O mixture (200 mL); further centrifugation and cooling at 0 °C overnight produced large red crystals of the desired product in 74% yield.

Complex **1a** is somewhat unstable in solution, and when it was stirred at room temperature in Et$_2$O for 3–4 h, a very finely divided golden shining precipitate was obtained. Crystallization of this solid from a concentrated 5:1 Et$_2$O–CH$_2$Cl$_2$ mixture at 5 °C afforded yellow crystals of composition [WCl(OH)(CO)$_2$(PMe$_3$)$_2$]$_n$.xEt_2O in 5–10% yield. The Et$_2$O of crystallization can be removed by grinding the crystals and drying under dynamic vacuum for 24 h. IR (Nujol mull, cm^{-1}): 3200 br (OH), 1890 s and 1790 s (CO). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 1.67 (filled-in d, $J_{\mathrm{HP}_{\mathrm{app}}}$ = 10.3 Hz, 2 PMe$_3$), 3.04 (s, OH). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 9.3 (br s, $^1J_{\mathrm{PW}}$ = 177 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 16.8 (pseudoquintet, $J_{\mathrm{CP}_{\mathrm{app}}}$ = 17.6 Hz, 2 PMe$_3$), 245.4 (t, $^2J_{\mathrm{CP}}$ = 27 Hz, CO). Anal. Calcd for W(OH)Cl(CO)$_2$(PMe$_3$)$_2$: C, 24.9; H, 5.0. Found: C, 25.5; H, 5.3.

W(η^2-C(O)CH$_2$CMe$_3$)Cl(CO)(PMe$_3$)$_3$ (**1b**) and W(η^2-C(O)CH$_2$CMe$_2$Ph)Cl(CO)(PMe$_3$)$_3$ (**1c**) were isolated similarly as red-orange crystals in 40% and 85% yields, respectively. W(η^2-C(O)CH$_2$CMe$_3$)Br(CO)(PMe$_3$)$_3$ (**1b–Br**) was the only product isolated in the reaction of WCl$_2$(CO)$_2$(PMe$_3$)$_3$ with Mg(CH$_2$CMe$_3$)Br after 4 h of stirring at room temperature; yield 80%.

The chloro acyl complexes can be converted into the corresponding bromo (**1b-Br**) and isocyanate derivatives (**1b-NCO** and **1c-NCO**) by metathesis reactions with the appropriate potassium salts. This requires reaction times of 12–20 h in acetone or tetrahydrofuran (THF) as the solvent.

The complexes W(η^2-C(O)CH$_2$SiMe$_3$)X(CO)(PMe$_3$)$_3$ (X = Br, I, NCO, NCS) could not be prepared by reactions of **1a** with the corresponding KX salts (see Results and Discussion).

Preparation of W(CH$_3$)X(CO)$_2$(PMe$_3$)$_3$ (X = Cl (1d), I (1d-I), NCS (1d-NCS)). W(CH$_3$)Cl(CO)$_2$(PMe$_3$)$_3$ (1d). To a yellow suspension of WCl$_2$(CO)$_2$(PMe$_3$)$_3$ (0.54 g, 1 mmol) in Et$_2$O (50 mL) was added LiMe (0.7 mL of a 1.8 M Et$_2$O solution) at −10 °C. The reaction mixture was stirred for 1 h at 5 °C, whereupon the solid slowly dissolved and a white precipitate formed. The solvent was evaporated in vacuo, and the residue was treated with 40 mL of Et$_2$O at 5 °C. This mixture was then centrifuged as rapidly as possible, and the volume of the resulting solution was reduced in vacuo to 10–15 mL. When the solution was cooled overnight at −30 °C, the title product was obtained as dark yellow crystals in 75% yield.

W(CH$_3$)I(CO)$_2$(PMe$_3$)$_3$ (1d-I). Complex **1d** (0.52 g, 1 mmol) and KI (4 mmol, an excess) were stirred at room temperature in 30 mL of THF over a period of 12 h. The resulting mixture was then evaporated to dryness and the residue extracted with 30 mL of a 1:1 petroleum ether–Et$_2$O mixture. After centrifugation and cooling at 0 °C the compound **1d-I** was obtained as yellow crystals in 80% yield.

W(CH$_3$)(SCN)(CO)$_2$(PMe$_3$)$_3$ (1d-NCS). This complex was the only product isolated in the reaction of W(η^2-C(O)CH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ (0.59 g, 1 mmol) with excess KSCN (0.15 g, 1.5 mmol) in THF (40 mL) after 10 h of stirring at 10 °C. The (trimethylsilyl)methyl derivative W(η^2-C(O)CH$_2$SiMe$_3$)(SCN)(CO)(PMe$_3$)$_3$ could not be isolated. Instead, doubtless due to the presence of adventitious water, **1d-NCS** was obtained and it was crystallized from Et$_2$O solutions at −30 °C in 45% yield. Complex **1d-NCS** can also be prepared in similar yields by metathesis of W(CH$_3$)Cl(CO)$_2$(PMe$_3$)$_3$ with KSCN in THF.

Preparation of W(CH$_3$)Cl(CO)$_2$(PMe$_3$)(dmpe) (2). To a stirred yellow solution of W(CH$_3$)Cl(CO)$_2$(PMe$_3$)$_3$ (0.50 g, 1 mmol) in 40 mL of Et$_2$O was added an excess of 1,2-bis(dimethylphosphino)ethane (dmpe; 0.6 mL, ca. 3 mmol). The resulting solution was stirred at room temperature for 8 h, the solvent was evaporated under reduced pressure, and the residue was extracted with a 1:1 petroleum ether–acetone mixture. After centrifugation and cooling at −35 °C, yellow crystals were collected, washed with petroleum ether, and dried in vacuo; yield 85%. Complex **2** does not react with more dmpe at room temperature over a period of 24 h, with Et$_2$O as the solvent, or at 40–50 °C in THF for ca. 24 h.

Preparation of [W(CH$_3$)(CO)$_2$(dmpe)$_2$]Cl (3). dmpe (0.4 mL, ca. 2 mmol) was added to a red solution of W(η^2-C(O)CH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ (0.59 g, 1 mmol) in 40 mL of Et$_2$O, and the reaction mixture was stirred at room temperature for 3–4 h. When the reaction was complete, a light red solution and a white finely divided solid resulted. This suspension was evaporated to dryness and the residue extracted with 30 mL of a 1:2 toluene–dichloromethane mixture; further centrifugation and cooling at −35 °C overnight produced the desired product as white crystals in ca. 85% yield.

The mixing of equimolar amounts of W(η^2-COCH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ and dmpe produced an incomplete reaction, which yielded a 1:1 mixture of the starting material and the bis-dmpe methyl compound. In some instances small amounts of W(CH$_3$)Cl(CO)$_2$(dmpe)(PMe$_3$) were obtained, but no evidence for the formation of the complexes W(η^2-C(O)CH$_2$SiMe$_3$)Cl(CO)(dmpe)(PMe$_3$) and [W(η^2-C(O)CH$_2$SiMe$_3$)(CO)(dmpe)$_2$]Cl was observed.

Preparation of W(CH$_3$)(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$ (4). The salt NaS$_2$CNMe$_2$ (0.17 g, 1 mmol) was added to a yellow solution of W(CH$_3$)Cl(CO)$_2$(PMe$_3$)$_3$ (0.54 g, 1 mmol) in Et$_2$O (40 mL). The reaction mixture was stirred at ca 10 °C for 8 h, during which time a pale red color developed. The volume was then reduced in vacuo and the residue extracted with 15–20 mL of Et$_2$O. After centrifugation and cooling at −10 °C complex **4** was obtained as orange crystals in 82% yield.

Preparation of W(η^2-C(O)R)X(CO)$_2$(PMe$_3$)$_2$ (X = Br, R = CH$_2$CMe$_3$ (5b); X = Cl, R = CH$_2$CMe$_2$Ph (5c); X = Cl, R = CH$_3$ (5d)). Carbon monoxide was passed through a solution of W(CH$_3$)Cl(CO)(PMe$_3$)$_3$ (0.51 g, 1 mmol) in Et$_2$O (40 mL). After it was stirred at 10 °C for ca. 40 min, the initially yellow solution became pale. The volume of the final solution was then reduced to 15 mL in vacuo and the solution cooled at −30 °C overnight to afford yellow crystals of W(η^2-C(O)CH$_3$)Cl(CO)$_2$(PMe$_3$)$_2$ (**5d**) in 78% yield.

Complex **5d** was also the product of the reaction of W(η^2-C(O)CH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ with CO in Et$_2$O. The complexes W(η^2-C(O)CH$_2$CMe$_3$)Br(CO)$_2$(PMe$_3$)$_2$ (**5b**) and W(η^2-C(O)CH$_2$CMe$_2$Ph)Cl(CO)$_2$(PMe$_3$)$_2$ (**5c**) were obtained in similar yields by the same procedure, as yellow crystals from Et$_2$O at −30 °C.

Preparation of W(η^2-C(O)CH$_3$)(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$) (6) and W(η^2-C(O)CH$_3$)(η^1-S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$ (6i). Through a solution of W(CH$_3$)(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$ (0.53 g, 1 mmol) in 40 mL of Et$_2$O was bubbled carbon monoxide at room temperature for 0.5 h. The color of the solution changed from orange to pale yellow. The solution was then filtered, and the residue obtained by removal of the solvent from the filtrate was crys-

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

tallized from a 1:1 petroleum ether–Et_2O mixture at 0 °C to afford $W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (6) as yellow crystals in 60% yield. The resulting mother liquor was collected and cooled at −30 °C, an operation that induced the precipitation of $W(\eta^2\text{-}C(O)CH_3)(\eta^1\text{-}S_2CNMe_2)(CO)_2(PMe_3)_2$ (6i) as lemon yellow microcrystals in 15% yield. Both complexes can also be prepared in similar yields by metathesis of $W(\eta^2\text{-}C(O)CH_3)Cl(CO)_2(PMe_3)_2$ with NaS_2CNMe_2 in Et_2O. Treatment of 6 with 1 equiv of PMe_3 afforded 6i in quantitative yield. Conversely, the heating of Et_2O solutions of 6i at 30 °C or the prolonged stirring of the complex in this solvent at room temperature caused extensive conversion back to 6.

Single-Crystal X-ray Diffraction Studies of 1a and 4. Crystal data and the parameters used during the collection and refinement of the diffraction data for 1a and 4 are summarized in Table IV. Single crystals of the compounds were sealed in thin-walled glass capillaries prior to X-ray examination.

The compound 1a was found to be isostructural with its molybdenum analogue, crystallizing in the space group $P2_12_12_1$. The final fractional coordinates of the Mo analogue were used as a starting point in the refinement of the tungsten compound. Refinement with isotropic thermal parameters led to a reliability index of $R = 0.054$. Refinement with anisotropic temperature factors gave $R = 0.048$. Conversion to the inverse configuration lowered the R value to 0.045. The hydrogen atoms were located with the aid of a difference Fourier and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.027$ and $R_w = 0.030$. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table VI.[42,43]

The space group of the complex 4 was uniquely determined as $P2_1/c$ from the systematic absences in $0k0$ for $k = 2n + 1$ and in $h0l$ for $l = 2n + 1$. Least-squares refinement with isotropic thermal parameters led to $R = 0.072$. Larger than normal thermal motion was found for the methyl carbons associated with P2. No resolvable disorder was found. The hydrogen atoms were located with the aid of a difference Fourier map and not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.029$ and $R_w = 0.029$. The final values of the positional parameters are given in Table VIII.[42,43]

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Supplementary Material Available: Tables of H atom coordinates, thermal parameters, and least-squares planes results for 1a and 4 (6 pages); tables of observed and calculated structure factors (18 pages).

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Synthesis and Properties of Alkyl and η^2-Acyl Complexes of Tungsten. Crystal and Molecular Structure of $W(CH_3)(acac)(CO)_2(PMe_3)_2$

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The acyl complexes $W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ react with NaS_2CNMe_2 with formation of the new acyls $W(\eta^2\text{-}C(O)R)(S_2CNMe_2)(CO)(PMe_3)_2$ ($R = CH_2CMe_3$ (2), CH_2CMe_2Ph (3)), but the (trimethylsilyl)methyl derivative affords an equilibrium mixture of an analogous bidentate acyl 1b and of the alkyl isomer $W(CH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$ (1a). Other dithiocarbamate and xanthate salts react similarly with $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ to yield analogous equilibrium mixtures of the alkyl, $W(CH_2SiMe_3)(S_2CX)(CO)_2(PMe_3)_2$ (4a–6a), and acyl, $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CX)(CO)(PMe_3)_2$ (4b–6b), isomers. Carbonylation of compounds 1 furnishes exclusively the bidentate acyl $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (7). The CH_2SiMe_3 group in acyls $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CX)(CO)(PMe_3)_2$ is extremely prone to hydrolytic cleavage of the CH_2–$SiMe_3$ bond and undergoes facile rupture in the presence of small amounts of water with formation of the methyl derivatives $W(CH_3)(S_2CX)(CO)_2(PMe_3)_2$ (8–12). The reaction of $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ with Tl(acac) gives directly $W(CH_3)(acac)(CO)_2(PMe_3)_2$ (13), which has been structurally characterized by X-ray crystallography. Crystals of 13 are orthorhombic, space group *Pbca*, with unit cell constants $a = 11.110$ (2) Å, $b = 13.779$ (3) Å, $c = 26.813$ (5) Å, and $D_{calcd} = 1.64$ g cm^{-3} for $Z = 8$.

Introduction

Whereas numerous formally six-coordinate (6C) η^2-acyl complexes of Mo and W have been characterized in recent years,[2-8] the corresponding isomeric seven-coordinate (7C) alkyl carbonyl compounds have only recently been de-

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(2) For a recent review on η^2-acyl complexes see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.