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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(1) (a) Universidad de Sevilla-CSIC. (b) CSIC and Universidad Complutense.

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

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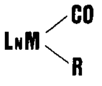
Table I. Analytical and IR Data for Complexes 1–13

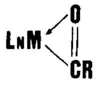
complex	anal. (%)[a] C	H	N	IR[b] ν(CO)	ν(COR)	others
1b	29.9 (30.0)	5.9 (5.8)	2.5 (2.3)	1465 (s)	1465 (m)	1500 (m) (ν(CN))
1a	31.2 (30.0)	5.9 (5.8)	2.5 (2.3)	1910 (s) 1815 (s)		1510 (m) (ν(CN))
2	32.9 (32.9)	5.9 (6.0)	2.4 (2.4)	1750 (s)	1455 (m)	1505 (m) (ν(CN))
3	38.8 (29.1)	6.0 (5.7)	2.3 (2.2)	1740 (s)	1470 (m)	1500 (m) (ν(CN))
4b	34.0 (34.8)	6.0 (6.6)	2.4 (2.1)	1750 (s)	1460 (m)	1475 (m) (ν(CN))
4a				1890 (s) 1800 (s)		
5b	28.1 (28.7)	5.0 (5.5)		1745 (s)	1465 (m)	
5a				1898 (s) 1805 (s)		
6b				1770 (s)	1468 (m)	
6a				1910 (s) 1820 (s)		
7	28.5 (28.3)	4.8 (4.7)	2.6 (2.5)	1920 (s) 1825 (s)	1455 (m)	1520 (m) (ν(CN))
8	32.7 (32.9)	6.0 (6.0)	2.4 (2.4)	1880 (s) 1800 (s)		1480 (m) (ν(CN))
9	32.6 (31.7)	5.8 (5.5)	2.2 (2.5)	1888 (s) 1795 (s)		1585 (m) (ν(CN))
10	25.8 (25.7)	4.7 (4.7)		1903 (s) 1812 (s)		
11	27.8 (27.3)	5.1 (4.9)		1885 (s) 1807 (s)		
12	29.2 (28.8)	5.2 (5.2)		1900 (s) 1815 (s)		
13	33.3 (33.2)	5.5 (5.5)		1883 (s) 1795 (s)		1582 (m) (ν(CO) acac) 1518 (m) (ν(CO) acac)

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

tected.[9] Since the interconversion of formulations A and B leaves unchanged the total number of electrons at the



A



B

metal center, it can be anticipated that, in series of analogous complexes, structure B should be favored over A for sterically demanding R groups, whereas an increase in the electron density at the metal center, i.e. in the metal basicity, should favor formulation A because of the strong acceptor properties of the carbonyl ligand. Despite the simplicity of these arguments and despite the relative large number of studies dealing with the formation and the chemical reactivity of alkyl carbonyl and η^2-acyl complexes of the transition metals, there is a dearth of information on the relative thermodynamic stabilities of these isomeric structures (A and B) and on the reaction conditions that allow their interconversion.[10] Recent work from our laboratory, based on methyl and η^2-acyl complexes of tungsten, has provided experimental evidence in accord with these observations.[9]

In order to obtain additional information on the influence of the steric and electronic effects on the relative stability of structures A and B, other related compounds have been investigated. The substitution of the chloride and of one of the PMe$_3$ ligands in the acyls Mo(η^2-C(O)R)Cl(CO)(PMe$_3$)$_3$ by the three-electron-donor S$_2$CNMe$_2$ group is known to produce an increase of the negative charge at the metal, as shown by a concomitant decrease in the value of ν(CO) from ca. 1810 cm^{-1} in Mo(η^2-C(O)R)Cl(CO)(PMe$_3$)$_3$ to ca. 1760 cm^{-1} in the corresponding Mo(η^2-C(O)R)(S$_2$CNMe$_2$)(CO)(PMe$_3$)$_2$.[4a] Accordingly, we have investigated whether a related transformation of the more basic tungsten acyl analogues, W(η^2-C(O)R)Cl(CO)(PMe$_3$)$_3$, could produce an increase in the electron density at tungsten large enough to induce their conversion into the alkyl carbonyl complexes W(R)(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$. For this purpose, the reactions of the above acyls (R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph) with various dithiocarbamate, xanthate (*O*-alkyl dithiocarbonate), and acetylacetonate salts have been carried out. The present contribution reports the results of these transformations, which, as discussed below, allow for some of the compounds investigated the observation of equilibrium mixtures[11] of the alkyl carbonyl and η^2-acyl structures, i.e. A $\rightleftharpoons$ B. In addition, we describe the formation of some methyl dicarbonyl complexes of tungsten analogous to the recently reported W(CH$_3$)(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$.[9b] The

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Table II. ^1H and $^{31}P\{^1H\}$ NMR Data for Complexes 1-13

	$^{31}P^a$		$^1H^a$			
complex	Me–P	$^1J_{PW}$	Me–P	$^2J_{HP}$	R	others
1b	–17.5 s	247.8	1.59 t^c	3.9	2.96 s (CH_2) 0.17 s ($SiMe_3$)	2.73 s (CH_3) 2.67 s (CH'_3)
1a	–16.0 br s	149.8	1.43 d	9.0	–0.06 t (J_{HP} = 5.4, CH_2) 0.47 s ($SiMe_3$)	2.57 s (CH_3)
2	–8.4 s	243.7	1.60 t^c	3.8	3.00 s (CH_2) 1.01 s (CMe_3)	3.17 s (CH_3) 3.17 s (CH'_3)
3^b	–13.4 s	243.4	1.53 t^c	3.7	3.31 s (CH_2) 1.48 s (CMe_2) 7.05 t (*Ph*) 7.20 t (*Ph*) 7.27 d (*Ph*)	2.69 s (CH_3) 2.67 s (CH'_3)
4b	–12.8 br s	*d*	1.59 t^c	3.8	2.95 s (CH_2) 0.11 s ($SiMe_3$)	1.13 br s (CH_3) 4.40 br s (CH)
4a	–13.5 s	144.6	1.42 d	8.7	–0.07 t (J_{HP} = 6.0, CH_2) 0.37 s ($SiMe_3$)	1.13 br s (CH_3) 4.40 br s (CH)
5b	–12.6 br s	*d*	1.49 t^c	3.9	2.94 s (CH_2) 0.11 s ($SiMe_3$)	3.55 s (CH_3)
5a	–11.3 s	139.7	1.34 dc^c	9.2	–0.37 t (J_{HP} = 5.3, CH_2) 0.45 s ($SiMe_3$)	3.47 s (CH_3)
6b	–11.2 br s	*d*	1.52 t^c	3.9	2.95 s (CH_2) 0.11 s ($SiMe_3$)	1.09 d (CH_3) 5.33 h (CH)
6s	–11.3 s	141.0	1.36 dc^c	9.2	–0.30 t (J_{HP} = 5.3, CH_2) 0.46 s ($SiMe_3$)	1.07 d (CH_3) 5.33 h (CH)
7	–11.8 s	254.0	1.47 d	9.1	3.25 s (CH_2) –0.16 s ($SiMe_3$)	2.45 s (CH_3)
8	–18.5 s	193.1	1.31 t^c	3.7	0.51 t (J_{HP} = 8.4, CH_3)	1.11 br s (CH_3) 4.52 br s (CH)
9	–18.3 s	189.1	1.33 t^c	3.8	0.60 t (J_{HP} = 8.1, CH_3)	1.09 br s (CH_2) 3.47 br s (CH_2)
10	–16.9 s	176.3	1.22 t^c	3.9	0.44 t (J_{HP} = 8.2, CH_3)	3.49 s (CH_3)
11	–16.8 s	176.5	1.24 t^c	4.0	0.93 t (J_{HP} = 8.2, CH_3)	0.93 t (CH_2) 4.13 q (CH_3)
12	–17.0 s	178.8	1.25 t^c	4.1	0.44 t (J_{HP} = 8.3, CH_3)	1.06 d (CH_3) 5.30 h (CH)
13	–1.8 s	132.4	1.30 d	8.6	0.31 t (J_{HP} = 3.5, CH_3)	1.73 s (CH_3) 5.13 s (CH)

[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; h, heptet; dc, doublet with some central intensity. [b] In CD_3COCD_3. [c] Values of J apparent. [d] Not observed.

crystal and molecular structure of the acetylacetonate derivative $W(CH_3)(acac)(CO)_2(PMe_3)_2$ is also discussed. Analytical and spectroscopic data for new compounds are collected in Tables I-III.

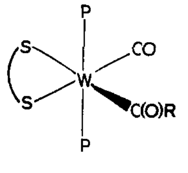
Results

η^2-Acyl Complexes, $W(\eta^2\text{-}C(O)R)(S_2CX)(CO)(PMe_3)_2$. As already mentioned, the reaction of the molybdenum complexes $Mo(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ with the strongly electron-releasing, powerfully chelating dimethyldithiocarbamate ligand has been shown to proceed[4a] with formation of compounds of composition $Mo(\eta^2\text{-}C(O)R)(S_2CNMe_2)(CO)(PMe_3)_2$. The analogous tungsten acyls $W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ display a similar behavior (eq 1) and afford, under appropriate conditions,

$$W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3 + NaS_2CNMe_2 \rightarrow W(\eta^2\text{-}C(O)R)(S_2CNMe_2)(CO)(PMe_3)_2 + PMe_3 + NaCl \quad (1)$$

$$R = CH_2SiMe_3\ (\mathbf{1b}),\ CH_2CMe_3\ (\mathbf{2}),\ CH_2CMe_2Ph\ (\mathbf{3})$$

compounds **1b**, **2**, and **3**. The formulation proposed for these complexes is based on analytical data and on IR and NMR (^1H, ^{13}C, ^{31}P) studies. For instance, the IR spectrum of **3** exhibits a strong $\nu(CO)$ stretch at ca. 1745 cm^{-1}, along with two medium-intensity bands at 1500 and 1475 cm^{-1} due to the dithiocarbamate and acyl ligands. The low frequency of the band associated with the terminal carbonyl ligand, which is shifted by ca. 50 cm^{-1} to lower energy with respect to that of the parent chloride complex, reflects the increase in the negative charge at the metal expected upon substitution of the chloride and one of the PMe_3 ligands by S_2CNMe_2. The ^1H NMR spectrum of **3** shows, in addition to resonances due to the acyl (3.31 and 1.48 ppm, singlets, CH_2CMe_2Ph and CH_2CMe_2Ph, respectively) and dithiocarbamate ligands (2.69 and 2.67 ppm), a pseudotriplet at 1.79 ppm ($J_{HP_{app}}$ = 3 Hz) corresponding to two equivalent PMe_3 ligands in an approximate trans distribution. This and the observation of a singlet in the room-temperature $^{31}P\{^1H\}$ NMR spectrum are in accord with structure C for these complexes, which accounts also for the appearance of two triplets at 277.7 ($^2J_{CP}$ = 13.2 Hz) and 235.4 ppm ($^2J_{CP}$ = 8.0 Hz) in the $^{13}C\{^1H\}$ NMR spectrum (data for **3**), due respectively to the acyl and terminal carbonyl ligands. Note, however, that in compounds of this type there is a preferred orientation of the acyl group with respect to the plane perpendicular to the P–W–P axis. By similarity with the solid-state structures found for the bidentate acyls $M(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ (M = Mo, W) and for other related derivatives,[3,4,9b] it is reasonable to expect that, in compounds **1b**, **2**, and **3**, the acyl carbon is adjacent to the carbonyl ligand and is slightly raised above the plane containing the acyl oxygen, the carbonyl group, and the dithiocarbamate sulfur atoms. If



C

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

complex	Me-P	$^1J_{CP}$	R	others	CO	$^2J_{CP}$
1b	15.5 t[c]	13.0	35.6 s (CH_2) −0.5 s $(SiMe_3)$ 14.1 t (J_{CP} = 14.5, CH_2)	38.9 s (CH_3) 39.5 s (CH'_3) 208.5 t (J_{CP} = 3.6, S_2C)	272.7 t (COR) 232.2 t (CO)	12.6 8.1
1a	16.7 d	32.4	4.8 s $(SiMe_3)$	38.1 s (CH_3) 211.9 t (J_{CP} = 4.7, S_2C)	240.6 t (CO)	21.0
2	15.8 t[c]	13.6	55.8 s (CH_2) 30.5 s (CMe_3) 32.7 s (CMe_3)	40.7 s (CH_3) 39.7 s (CH'_3) 211.9 d (J_{CP} = 4.6, S_2C)	280.1 t (COR) 236.5 t (CO)	12.9 8.3
3[b]	15.5 t[c]	13.1	55.6 s (CH_2) 39.4 s (CMe_2) 28.9 s (CMe_2)	38.7 s (CH_3) 211.6 s (S_2C)	277.7 t (COR) 235.4 t (CO)	13.2 8.0
4b	15.5 t[c]	11.9	37.6 s (CH_2) −0.6 s $(SiMe_3)$	19.4 s (CH_3) 49.3 s (CH) 207.3 s (S_2C)	272.8 t (COR) 232.4 t (CO)	12.7 8.2
4a	16.4 d	32.7	9.3 br s (CH_2) 4.3 s $(SiMe_3)$	19.4 s (CH_3) 49.3 s (CH) 211.4 s (S_2C)	241.7 t (CO)	15.6
5b	15.5 m		37.3 s (CH_2) −0.7 s $(SiMe_3)$	56.7 s (CH_3) 222.9 s (S_2C)	273.8 t (COR) 230.2 t (CO)	10.8 10.0
5a	17.0 m		4.6 s $(SiMe_3)$ 17.9 br s (CH_2)	55.8 s (CH_3) 224.1 s (S_2C)	237.9 t (CO)	21.6
6b	15.3 d	32.9	35.7 s (CH_2) −2.3 s $(SiMe_3)$ *d*	19.7 s (CH_3) 72.2 s (CH) 220.1 t (J_{CP} = 4.3, S_2C)	271.8 t (COR) 228.8 t (CO)	11.8 9.4
6a	13.6 m		2.8 s $(SiMe_3)$	19.5 s (CH_3) 72.5 s (CH) 221.7 t (J_{CP} = 5.4, S_2C)	236.4 t (CO)	21.7
7	17.9 d	33.0	0.9 s $(SiMe_3)$ 39.2 s (CH_2)	39.0 s (CH_3) 213.5 s (S_2C)	225.5 d (CO) 254.0 d (COR)	12.0 11.5
8	13.9 t[c]	13.7	−7.9 t (J_{CP} = 8.9, CH_3)	19.2 (CH_3) 49.3 s (CH) 206.4 s (S_2C)	251.8 t (CO)	11.9
9	13.9 t[c]	14.2	−6.2 t (J_{CP} = 7.6, CH_3)	23.9 s (CH_2) 25.5 s (CH'_2) 46.5 s (CH''_2) 206.1 s (S_2C)	251.0 t (CO)	13.1
10	14.7 t[c]	15.4	−2.0 br s (CH_3)	56.0 s (CH_3) 211.9 s (S_2C)	246.8 t (CO)	14.2
11	14.7 t[c]	15.0	−2.6 br s (CH_3)	13.4 s (CH_3) 66.1 s (CH_2) 221.5 s (S_2C)	248.0 t (CO)	13.9
12	14.6 t[c]	15.4	−3.2 t (J_{CP} = 7.5, CH_3)	21.2 s (CH_3) 74.3 s (CH) 221.0 t (J_{CP} = 4.0, S_2C)	247.4 t (CO)	16.0
13	16.0 d	31.2	17.0 br s (CH_3)	27.3 s (CH_3) 100.2 s (CH acac) 186.5 s (CO acac)	247.8 t (CO)	22.8

[a] δ in ppm, J in Hz; spectra recorded in C_6D_6 unless otherwise specified. Abbreviations: s, singlet; d, doublet; t, triplet, br s, broad singlet; m, multiplet. [b] In CD_3COCD_3. [c] Values of J apparent. [d] Not observed.

this structure were maintained in solution, the above orientation of the C–O acyl vector would create inequivalent environments for the PMe_3 ligands. Hence, a fluxional process that time-averages the effective symmetry to C_s must be operative. Similar dynamic behavior has been reported for η^2-acyl complexes of Mo and explained in terms of a libration of the acyl ligand coupled with a metal–ligand deformation.[5,6] The barrier estimated for this process by EHMO calculations is very low, and in fact the carbonyl ligands of the hydridotris(pyrazolyl)borate complex of molybdenum $TpMo(CO)_2(\eta^2\text{-}C(O)Me)$ give a single resonance down to −93 °C.[6] Although there are other mechanistic possibilities (see Discussion), a similar process can be assumed to be responsible for the equivalence of the PMe_3 groups in compounds **1b**, **2**, and **3** at room temperature. Interestingly, the barrier to this motion in these tungsten complexes is higher than for the Tp derivatives of molybdenum,[5,6] and the rigid structure of **1b**, **2**, and **3** can be frozen and observed at low temperatures. The characteristic dynamic behavior of these compounds is described below in detail for complex **1b**.

Complex **1b** exhibits a rather interesting behavior in solution, with relatively complex NMR spectra that can be interpreted in terms of an equilibrium mixture of two isomers,[10] the 6C η^2-acyl species **1b** and the 7C alkyl carbonyl complex **1a**, in a ca. 1:1 ratio (eq 2). Additional

$$\underset{\mathbf{1a}}{W(CH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)_2} \rightleftharpoons \underset{\mathbf{1b}}{W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2} \quad (2)$$

complications are introduced by the inevitable presence of small amounts of the methyl complex $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$,[9b] resulting from C–Si bond heterolysis by adventitious water. Disregarding the low-intensity signals associated with the latter species, it is found that in addition to resonances due to the η^2-acyl isomer, with chemical shifts very similar to those indicated above for the neophyl analogue **3**, the ^1H NMR spectrum shows a triplet at −0.06 ppm ($^3J_{HP}$ = 5.4 Hz) for the methylene protons of the Me_3SiCH_2 ligand, which is consistent with this group being directly bonded to the tungsten atom. Interestingly, the PMe_3 resonance of the alkyl complex **1a** appears as a doublet with little central intensity as a result of a cis or nearly cis distribution of the two equivalent PMe_3 groups in this 7C species. These and other spectroscopic data found for **1a** (see Tables I–III) are very similar to those observed for the analogous acac complex $W(CH_3)(acac)(CO)_2(PMe_3)_2$, whose structure has been determined by X-ray studies. This probably means that both compounds display similar structures (see below). Further support for the above equilibrium comes from IR and ^{31}P NMR studies. The solution IR spectrum displays absorptions at 1780 (acyl **1b**) and 1900 and 1810 cm^{-1} (alkyl **1a**) for the terminal carbonyl ligands in both complexes, while the $^{31}P\{^1H\}$ NMR spectrum exhibits two singlets at δ −17.5 ($^1J_{PW}$ = 248 Hz) and −16.0 ppm ($^1J_{PW}$ = 150 Hz) in a ca. 1:1 ratio for the PMe_3 ligands of **1b** and **1a**, respctively.

Although our original observations[9a] indicated that only the η^2-acyl structure seemed to exist in the solid state, in some instances crystals of both the yellow-orange 7C complex **1a** and the red 6C species **1b** have been obtained and separated manually inside the drybox. The IR spectra of the individual compounds show their characteristic ν(CO) and ν(C(O)R) bands along with an also very characteristic pattern at ca. 1245 cm^{-1} that invariably appears in compounds containing the CH_2SiMe_3 group. Upon dissolution of either species at room temperature, the equilibrium mixture **1a** $\rightleftharpoons$ **1b** is quickly attained, but interconversion of the two forms is slow at lower temperatures, and this allows their spectroscopic characterization. Typical NMR spectra of samples of either **1a** or **1b**, dissolved at −60 °C, contain the characteristic resonances corresponding to either of these main species together with minor signals due to the other isomer.

The η^2-acyl complex **1b** exhibits a rather complex dynamic behavior in solution that can be understood by considering the existence of two independent fluxional processes, one associated with the η^2-acyl ligand and the other, with higher activation energy, affecting the dithiocarbamate group. The $^{31}P\{^1H\}$ NMR spectrum of **1b**, recorded at −90 °C, consists of an AB quartet (J_{PP} = 102 Hz), which converts into a broad singlet upon warming at −15 °C. This signal is still broad below room temperature. Since tungsten satellites, arising from the coupling of the ^{31}P and the ^{183}W nuclei (^{183}W, $I = ^1/_2$, 14.3%), are observed in the temperature range studied (−90 to +70 °C), it is clear that the fluxional process responsible for this behavior does not involve dissociation of the trimethylphosphine ligands. From the value of the rate constant for this exchange, calculated at the coalescence temperature, a barrier of $\Delta G^{\ddagger}$ = 11.6 kcal mol^{-1} can be estimated for the above process. Related changes are observed in the ^1H NMR spectrum. Thus, the methyl protons of the PMe_3 ligands of **1b** yield two broad, partially superimposed signals at −60 °C and below. At these temperatures, the methylene protons of the acyl group are diastereotopic and provide an AB quartet. When the temperature is raised to −30 °C, the PMe_3 resonance converts into a sharp doublet with some central intensity. Further warming causes the appearance of a central resonance that merges in the middle of the doublet and gains in height when the temperature is increased, until at 0 °C a 1:2:1 triplet pattern is observed. This has, however, sharp outer lines and a broader central line, so that the three lines have approximately the same height. At higher temperatures (20 °C) a 1:2:1 triplet of sharp outer and central lines is observed.[12] Parallel to these changes, the diastereotopic methylenic protons of the acyl ligand transform into a broad singlet at −30 °C that becomes sharper upon warming and give a sharp resonance at temperatures near −10 °C. From these data a barrier of ca. 11.0 kcal mol^{-1} can be calculated for this exchange process, in good agreement with that estimated above from $^{31}P\{^1H\}$ NMR data. The above changes in the NMR spectra with temperature are reversible, and the low-temperature spectra can be regenerated upon cooling. These reversible changes can be followed for a number of cycles.

As for the dithiocarbamate ligand in compound **1b**, two singlets are observed at low temperatures for the nonequivalent methyl groups that convert into a single resonance at temperatures above 40 °C. The coalescence temperature, 35 °C, and the activation energy calculated for this process, $\Delta G^{\ddagger}$ = 16.3 kcal mol^{-1}, are well above the corresponding values found for the equilibration of the methylenic protons of the acyl ligand. It is therefore clear that both processes are independent. On the other hand, it seems likely that the inequivalence of the dithiocarbamate methyl groups at low temperatures is due to restricted rotation around the $\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N}$ bond. This is in agreement with the substantial double-bond character found by X-ray studies for the C–N bond of the dithiocarbamate ligand in the related complex $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$.[9b]

In order to ascertain the generality of the transformation of the chloride complex $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ into an equilibrium mixture of **1a** and **1b** by interaction with NaS_2CNMe_2, its reactions with other dithiocarbamate and xanthate salts and also with Tl(acac) have been investigated. In some cases the complexes resulting from these transformations are so susceptible to C–Si heterolysis by adventitious water that the methyl derivatives $W(CH_3)(L\text{-}L)(CO)_2(PMe_3)_2$ are the only products that can be isolated under the reaction conditions. However, for some of the reactions investigated, equilibria analogous to that described above for the S_2CNMe_2 ligand have been established (eqs 3 and 4).

$$W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3 + NaS_2CX \rightarrow W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CX)(CO)(PMe_3)_2 + PMe_3 + NaCl \quad (3)$$

$$X = N\text{-}i\text{-}Pr_2\ (\mathbf{4b}),\ OMe\ (\mathbf{5b}),\ O\text{-}i\text{-}Pr\ (\mathbf{6b})$$

$$\underset{\mathbf{4b\text{–}6b}}{W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CX)(CO)(PMe_3)_2} \rightleftharpoons \underset{\mathbf{4a\text{–}6a}}{W(CH_2SiMe_3)(S_2CX)(CO)_2(PMe_3)_2} \quad (4)$$

The instability of these compounds toward moisture makes it difficult to avoid contamination with the corresponding methyl complex $W(CH_3)(S_2CX)(CO)_2(PMe_3)_2$, resulting from the hydrolytic cleavage of the C–Si bond in compounds 4–6. The NMR properties of compounds 4–6 are very similar to those found for the related complexes 1. They are collected in Tables II and III and will not be further discussed.

The methyl complex $W(CH_3)(S_2CNMe_2(CO)_2(PMe_3)_2$ is known to react with CO, at room temperature and pressure, with formation of the bidentate acetyl complex $W(\eta^2\text{-}C(O)CH_3)(S_2CNMe_2)(CO)_2(PMe_3)$.[9b] In light of this result, it can be anticipated that the analogous reaction of an equilibrium mixture of the acyl and alkyl isomers of compounds 1 or 4–6 should exclusively provide the corresponding η^2-acyl complexes $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CX)(CO)_2(PMe_3)$. In accord with this, the carbonylation of **1a** $\rightleftharpoons$ **1b** takes place as depicted in eq 5 and allows the isolation of the acyl derivative $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (**7**). Spectroscopic data for this complex (Tables I–III) are consistent with

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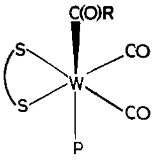
(12) Similar temperature-dependent exchange phenomena have been observed. See for example: (a) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021. (b) Casey, C. P.; Rutter, E. W., Jr.; Haller, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6886.

$$\mathbf{1a} + \mathbf{1b} \xrightarrow{CO} \underset{\mathbf{7}}{W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)} + PMe_3 \quad (5)$$

structure D. As discussed below, in the absence of steric constraints that could favor the alkyl carbonyl to η^2-acyl rearrangements, the transformation shown in eq 5 must be entirely ascribed to electronic factors.



D

W(CH$_3$)(L-L)(CO)$_2$(PMe$_3$)$_2$ Compounds. Crystal and Molecular Structure of W(CH$_3$)(acac)(CO)$_2$(PMe$_3$)$_2$. The compounds $W(CH_3)(S_2CX)(CO)_2(PMe_3)_2$ (X = NMe$_2$[9b] N-*i*-Pr$_2$ (**8**), NC$_5$H$_{10}$ (piperidine-derived dithiocarbamate, **9**), OMe (**10**), OEt (**11**), O-*i*-Pr (**12**)) can be obtained by addition of small amounts of water to solutions of the Me$_3$SiCH$_2$ complexes **1** or **4**–**6**, as exemplified in eq 6 for compounds **4**, or by reaction of the chloromethyl

$$\mathbf{4a} + \mathbf{4b} \xrightarrow{H_2O} \underset{\mathbf{8}}{W(CH_3)(S_2CN\text{-}i\text{-}Pr_2)(CO)_2(PMe_3)_2} \quad (6)$$

derivative $W(CH_3)Cl(CO)_2(PMe_3)_3$[9b] with the corresponding dithiocarbamate or xanthate salt (eq 7). For some of

$$W(CH_3)Cl(CO)_2(PMe_3)_2 + NaS_2COMe \rightarrow \underset{\mathbf{10}}{W(CH_3)(S_2COMe)(CO)_2(PMe_3)_2} + PMe_3 + NaCl \quad (7)$$

the reactions investigated, the hydrolytic cleavage of the C–Si bond shown in eq 6 is so facile that small amounts of adventitious water which cannot be removed from our reaction systems to such an extent are able to cause the depicted transformation. Compounds **8**–**12** are red-orange crystalline materials, very soluble in most common organic solvents. Their IR spectra display two strong CO absorptions in the range 1900–1800 cm^{-1} in addition to characteristic bands associated with the bidentate sulfur-containing ligand.[13] On the other hand, the metal-bonded methyl group in these complexes affords a high-field ^{1}H NMR resonance at ca. 0.9–0.3 ppm, which appears as a triplet ($^3J_{HP} \simeq 8.5$ Hz) as a consequence of its coupling with the two equivalent ^{31}P nuclei. Other spectroscopic data for these compounds are also similar to those reported for the related methyl complex $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$.[9b] They are collected in Tables I–III and require no additional comments.

With the aim of ascertaining whether the chelating acetylacetonate ligand could stabilize an alkyl carbonyl species analogous to the dithiocarbamate and xanthate complexes described above, the reaction of $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ with Tl(acac) has been carried out. However, and in spite of our efforts to completely remove traces of water from our reaction system, the expected (trimethylsilyl)methyl derivative could not be isolated, the reaction providing instead the methyl complex $W(CH_3)(acac)(CO)_2(PMe_3)_2$ (**13**). Spectroscopic data for this complex are in agreement with the proposed formulation. These data show some similarities with those found for compounds **8**–**12**, but there are also some noticeable differences. In particular, the two phosphine ligands give rise to a doublet, both in the ^{1}H and in the ^{13}C{^{1}H} NMR spectra, suggesting a cisoid distribution of these groups, in contrast with the transoid arrangement found for the same ligands in compounds **8**–**12**. For this reason and because of the scarcity of X-ray studies on alkyl derivatives of this type, an X-ray structural determination of **13** has been undertaken.

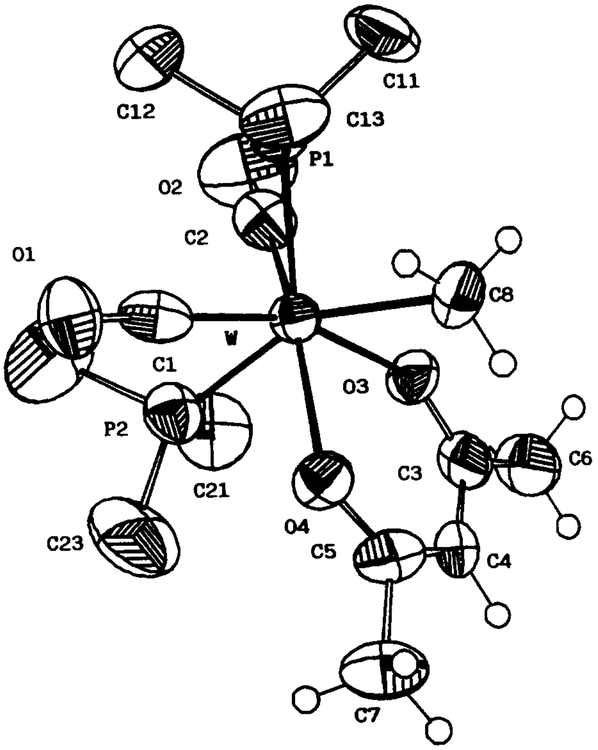


Figure 1. ORTEP drawing of complex **13**.

Table IV. Crystal and Refinement Data for 13

formula	$WC_{14}H_{28}O_4P_2$
cryst syst	orthorhombic
space group	*Pbca*
a, Å	11.110 (2)
b, Å	13.779 (3)
c, Å	26.813 (5)
V, Å^3	4105 (1)
Z	8
F(000)	1984
ρ(calcd), g cm^{-3}	1.64
temp, °C	22
μ, cm^{-1}	59.1
cryst dimens, mm	0.4 × 0.4 × 0.2
diffractometer	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
scan technique	$\Omega/2\theta$
data collected	(000)–(14,17,35)
no. of rflns collected	5458
no. of unique data	4786
no. of unique data ($I \geq 2\sigma(I)$)	2437
R(int), %	0.9
no. of std reflns	2/108 rflns
decay	≤11% variation
R_F, %	4.1
$R(w)_F$, %	5.0
av shift/error	0.2

Figure 1 shows an ORTEP perspective view of this complex that includes the atom numbering scheme. Selected interatomic bond distances and angles are summarized in Table V. The tungsten atom is in a seven-coordinate

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[13] (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233; **1979**, *26*, 301. (b) Paparizos, C.; Fackler, J. P. *Inorg. Chem.* **1980**, *19*, 2886. (c) Abrahamson, H. B.; Freeman, M. L.; Hossain, M. B.; Van der Helm, D. *Inorg. Chem.* **1984**, *23*, 2286.

Table V. Bond Distances (Å) and Angles (deg) for 13

W-P1	2.461 (4)	P2-C21	1.79 (2)
W-P2	2.554 (5)	P2-C22	1.80 (3)
W-O3	2.20 (1)	P2-C23	1.73 (2)
W-O4	2.16 (1)	O3-C3	1.28 (2)
W-C1	1.94 (2)	O4-C5	1.28 (2)
W-C2	1.92 (2)	O1-C1	1.22 (2)
W-C8	2.29 (2)	O2-C2	1.20 (2)
P1-C11	1.85 (2)	C3-O4	1.39 (2)
P1-C12	1.83 (2)	C3-C6	1.50 (3)
P1-C13	1.87 (1)	C4-C5	1.42 (2)
		C5-C7	1.52 (2)
C2-W-C8	116.5 (7)	P1-W-C2	73.4 (5)
C1-W-C8	117.7 (7)	P1-W-C1	73.2 (5)
C1-W-C2	102.0 (7)	P1-W-O4	130.5 (3)
O4-W-C8	78.1 (5)	P1-W-O3	129.8 (3)
O4-W-C2	156.0 (5)	P1-W-P2	132.1 (2)
O4-W-C1	85.7 (5)	W-O3-C3	133.0 (9)
O3-W-C8	78.0 (5)	W-O4-C5	130.7 (9)
O3-W-C2	83.9 (5)	W-C1-O1	174 (1)
O3-W-C1	156.7 (5)	W-C2-O2	174 (1)
O3-W-O4	80.7 (4)	O3-C3-C6	116 (1)
P2-W-C8	154.5 (5)	O3-C3-C4	124 (1)
P2-W-C2	76.8 (5)	C4-C3-C6	120 (1)
P2-W-C1	77.4 (6)	C3-C4-C5	124 (1)
P2-W-O4	82.9 (3)	O4-C5-C4	127 (1)
P2-W-O3	82.1 (3)	C4-C5-C7	118 (1)
P1-W-C8	73.5 (5)	O4-C5-C7	115 (1)

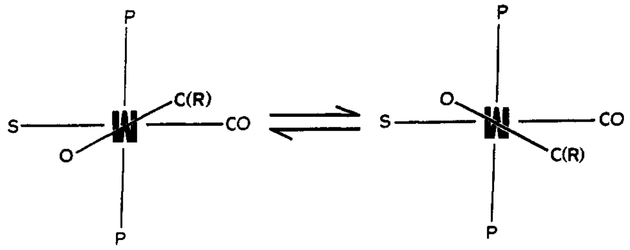
Table VI. Atomic Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for 13

atom	x/a	y/b	z/c	U_{eq}, Å^2
W	0.43872 (5)	0.17569 (4)	0.38019 (2)	390 (1)
P1	0.6049 (3)	0.2935 (3)	0.3761 (2)	487 (11)
P2	0.3682 (4)	0.0441 (3)	0.3198 (2)	623 (16)
O3	0.4025 (9)	0.0614 (8)	0.4355 (4)	563 (37)
O4	0.2474 (9)	0.1979 (7)	0.3901 (3)	523 (32)
O1	0.4025 (11)	0.2977 (9)	0.2818 (4)	813 (49)
O2	0.6661 (11)	0.0495 (9)	0.3599 (6)	1095 (67)
C1	0.4194 (15)	0.2467 (9)	0.3184 (8)	526 (51)
C2	0.5827 (15)	0.1024 (10)	0.3677 (6)	587 (59)
C3	0.3082 (15)	0.0373 (11)	0.4600 (6)	556 (54)
C4	0.1951 (14)	0.0778 (12)	0.4523 (5)	514 (51)
C5	0.1718 (13)	0.1555 (10)	0.4190 (6)	560 (54)
C6	0.3228 (17)	−0.0462 (15)	0.4952 (7)	857 (78)
C7	0.0425 (13)	0.1895 (12)	0.4137 (7)	720 (64)
C8	0.4330 (18)	0.2621 (15)	0.4530 (6)	873 (75)
C12	0.6969 (15)	0.2912 (15)	0.3194 (7)	786 (74)
C11	0.7244 (15)	0.2832 (14)	0.4239 (7)	760 (70)
C13	0.5661 (14)	0.4257 (9)	0.3790 (7)	650 (53)
C21	0.3802 (33)	−0.0809 (13)	0.3369 (12)	1962 (181)
C22	0.4387 (27)	0.0451 (17)	0.2592 (10)	1461 (132)
C23	0.2203 (20)	0.0521 (20)	0.2996 (9)	1412 (119)

environment that can approximately be described[14] as capped octahedral, with the phosphine ligand P1 capping the triangular face formed by the two carbonyls and the methyl group. The two oxygen atoms of the acac ligand are approximately trans with respect to the carbonyl groups (for instance, C-W-O angles of 85.7 (5) and 156.7 (5)° for the carbonyl carbon C1), while the remaining phosphine, P2, occupies the sixth vertex of the distorted octahedron. The structural parameters collected in Table V also allow an alternative description of the coordination polyhedron of **13** as approximately a capped trigonal prism, with P2 capping the quadrilateral face formed by the two carbonyls and the two oxygen atoms of the acac ligand.

The bond lengths from tungsten are not unusual and are of the same order of magnitude as those reported in the literature for related complexes. For example, the average W-C bond length for the carbonyl ligands is 1.93 (2) Å, very close to the values of 1.95 and 1.97 Å found respectively for the complexes $W(S_2CO\text{-}i\text{-}Pr\text{-}S)(S_2CO\text{-}i\text{-}Pr\text{-}S,S')(CO)_2(PMe_3)_2$[15] and $W(S_2CNEt_2)_2(CO)_2(PPh_3)$.[16] The W-$CH_3$ bond separation, at 2.29 (2) Å, is also similar to the value of 2.28 (1) Å found for the related complex $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$,[9b] while the W-P distance of 2.507 (5) Å (average) is in the range usually found in tungsten carbonyl phosphine complexes. On the other hand, the P-W-P angle of 132.1 (2)° corresponds to a cisoid distribution of the PMe_3 ligands and this explains the observation, already discussed, of a doublet for the phosphine methyl protons due to intermediate or low ^{31}P-^{31}P coupling. Finally, the bidentate acetylacetonate ligand exhibits a O-W-O bite angle of 80.7 (4)°, with W-O distances of 2.20 (1) and 2.16 (1) Å.

Scheme I. Rocking Motion of the Acyl Ligand in Complexes 1b, 2, and 3[a]



[a] The sulfur atom of the dithiocarbamate ligand trans to the acyl has been omitted for clarity.

Discussion

Some brief comments can be devoted at this point to the mechanism allowing for the exchange of the phosphine ligands and of the acyl methylene protons in compounds **1b**, **2**, and **3**. The available data indicate this process is intramolecular and does not involve phosphine dissociation. A fast equilibrium involving a short-lived 7C alkyl carbonyl intermediate can be disregarded on the basis of the data discussed for the equilibrium **1a** ⇌ **1b**. On the other hand, the intermediacy of a short-lived η^1-acyl complex, rapidly equilibrating the two isomeric η^2-acyl structures that respectively have the oxygen atom of the acyl in an exo and an endo position with regard to the adjacent carbonyl ligand seems unlikely on chemical grounds and moreover is not in agreement with the variable-temperature ^1H and $^{13}C\{^1H\}$ NMR data recorded for these compounds. Furthermore, isomerizations of this type are usually irreversible, one of the isomers being thermodynamically much more stable than the other.[17] The data are, however, consistent with a rocking motion of the acyl ligand around the Mo-η^2-C(O)R bond axis that effectively time-averages the symmetry to C_s, as shown in Scheme I. This process is analogous to that proposed by Curtis[6] to explain the dynamic behavior of related acyl species.

The characterization of the above and other related η^2-acyl complexes of Mo and W and, in some cases, of the isomeric 7C alkyl carbonyl derivatives (structure B and A, respectively) allow some generalizations to be made with respect to the influence of steric and electronic effects on the relative stability of these isomeric formulations.

The alkylation of complexes $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) with Grignard or organolithium reagents derived

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(14) Melník, M.; Sharrock, P. *Coord. Chem. Rev.* **1985**, *65*, 49.

(15) Carmona, E.; Contreras, L.; Sánchez, L. J.; Gútierrez-Puebla, E.; Monge, A. *J. Chem. Soc., Dalton Trans.* *1989*, 2003.

(16) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3743.

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from the alkyl groups CH_3, CH_2SiMe_3, CH_2CMe_3, and CH_2CMe_2Ph furnishes the bidentate Mo acyl complexes $Mo(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ in all the cases studied and the analogous tungsten complexes $W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$, with the only exception being the W–CH_3 derivative, which adopts the alkyl carbonyl structure, $W(CH_3)Cl(CO)_2(PMe_3)_3$. Clearly, the η^2-acyl structure is favored for the majority of the compounds investigated. These results can be accounted for by considering that the stability of the η^2-acyl structure is influenced by both steric and electronic effects. The former can be invoked to explain the formation of the η^2-acyl complexes of tungsten for the bulkier R groups (CH_2SiMe_3, CH_2CMe_3, and CH_2CMe_2Ph), while the adoption of the alkyl formulation for $W(CH_3)Cl(CO)_2(PMe_3)_3$, as opposed to the bidentate acyl structure of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$, can be attributed to the higher metal basicity of the tungsten compound.[18] In accord with this, the room-temperature carbonylation of $W(CH_3)Cl(CO)_2(PMe_3)_3$ yields exclusively the η^2-acetyl $W(\eta^2\text{-}C(O)CH_3)Cl(CO)_2(PMe_3)_2$.

The substitution in complexes of this type of the chloride and of one of the PMe_3 ligands by the three-electron-donor $S_2CNR'_2$ group has been shown to produce a significant increase in the electron density at the metal center (vide supra). Accordingly, $W(CH_3)(S_2CNR'_2)(CO)_2(PMe_3)_2$ compounds, obtained from $W(CH_3)Cl(CO)_2(PMe_3)_3$ and $NaS_2CNR'_2$, should only exist as methyl carbonyl derivatives, whereas the reaction of the acyl species $M(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ with $NaS_2CNR'_2$ could, in favorable instances, induce the η^2-acyl to alkyl carbonyl transformation. In accord with this, only the 7C structure A has been found for the compounds $W(CH_3)(S_2CNR'_2)(CO)_2(PMe_3)_2$. Their carbonylation produces, however, the η^2-acetyl complexes $W(\eta^2\text{-}C(O)CH_3)(S_2CNR'_2)(CO)_2(PMe_3)$. It is worth recalling at this point that the reaction of $Mo(\eta^2\text{-}C(O)CH_3)Cl(CO)(PMe_3)_3$ with NaS_2CNMe_2 furnishes the unique acetyl complexes $Mo(C(O)CH_3)(S_2CNMe_2)(CO)(PMe_3)_2$, in which there is a strong interaction between the Mo atom and a β-C–H bond of the acetyl group. Hence, it seems that the latter reaction induces the expected η^2-acyl to alkyl carbonyl transformation, although instead of the methyl carbonyl complex and "intermediate" agostic structure is obtained.

Finally, whereas the chloro derivatives $W(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph) exist only as the η^2-acyl isomers, their reactions with $NaS_2CNR'_2$ salts provide the η^2-acyls $W(\eta^2\text{-}C(O)R)(S_2CNR'_2)(CO)(PMe_3)_2$ where R = CH_2CMe_3 and CH_2CMe_2Ph but an isomeric mixture of the 6C η^2-acyl species and of the 7C alkyl carbonyl complex $W(R)(S_2CNR'_2)(CO)_2(PMe_3)_2$ for R = CH_2SiMe_3. Again the above chemical transformation produces an increase in the negative charge at the metal, thus favoring the alkyl carbonyl formulation. Nevertheless, the steric bulkiness of the neopentyl and neophyl groups prevents adoption of the 7C structure, while for the less bulky CH_2SiMe_3 group (note that the steric demands of the alkyl groups investigated in this work vary in the order $CH_3 < CH_2SiMe_3 < CH_2CMe_3 < CH_2CMe_2Ph$) an equilibrium between the two formulations is readily attained. In excellent accord with these observations, the carbonylation of this isomeric mixture produces exclusively an η^2-acyl complex, $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNR'_2)(CO)_2(PMe_3)$.

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Bonn, Germany, and by the Analytical Service of the University of Seville. All preparations and manipulations were carried out under oxygen-free nitrogen, by following the conventional Schlenk techniques. Solvents were dried and degassed before use. Sodium dialkyldithiocarbamate salts were 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.[20]

IR spectra were recorded as Nujol mulls, or in an appropriate solvent, on Perkin-Elmer Models 577 and 684 instruments. ^1H, ^{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_3PO_4, while ^1H 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_4Si.

Preparation of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CX)(CO)(PMe_3)_2$ (X = NMe_2 (1b), N-*i*-Pr_2 (4b), OMe (5b), O-*i*-Pr (6b)), $W(\eta^2\text{-}C(O)CH_2CMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (2), and $W(\eta^2\text{-}C(O)CH_2CMe_2Ph)(S_2CNMe_2)(CO)(PMe_3)_2$ (3). All of these preparations were performed in an identical manner. The procedure involving the reaction of $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ with NaS_2CNMe_2 is presented as a representative example.

$W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (1b). $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ (0.59 g, 1 mmol) was dissolved in 40 mL of Et_2O. A slight excess of anhydrous NaS_2CNMe_2 (0.17 g, 1.2 mmol) was added, and the reaction mixture was stirred for 8 h. The progress of the reaction was monitored by IR spectroscopy of the supernatant solution. Intermediate species were not detected, but three new carbonyl bands, characteristic of the mixture **1a** $\rightleftharpoons$ **1b**, gradually appeared at the expense of the single ν(CO) band of the starting material. A white solid that formed at this stage was discarded by centrifugation. The solvent was removed under vacuum and the residue crystallized from petroleum ether (15 mL) at 0 °C to afford red crystals of **1b** in 75% yield.

From the appropriate chloro acyl complexes and dithiocarbamate or xanthate salts the following compounds were obtained in similar yields by the above procedure: $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CN\text{-}i\text{-}Pr_2)(CO)(PMe_3)_2$ (**4b**), $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2COMe)(CO)(PMe_3)_2$ (**5b**), $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CO\text{-}i\text{-}Pr)(CO)(PMe_3)_2$ (**6b**), $W(\eta^2\text{-}C(O)CH_2CMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ (**2**), $W(\eta^2\text{-}C(O)CH_2CMe_2Ph)(S_2CNMe_2)(CO)(PMe_3)_2$ (**3**). They were isolated as dark red microcrystalline solids from petroleum ether, with the exception of the $S_2CO\text{-}i\text{-}Pr\text{–}CH_2SiMe_3$ derivative, which was obtained as a red oily mixture of the alkyl and η^2-acyl isomers.

In some instances yellow-orange crystals of the alkyl dicarbonyl isomers of **1b**, **4b**, and **5b** were also obtained from the above petroleum ether solutions and separated manually from their η^2-acyl carbonyl isomers inside the drybox. Their IR spectra (Nujol mulls) recorded immediately after their isolation revealed the presence of two carbonyl bands as well as that of the characteristic absorptions of the CH_2SiMe_3 ligand at ca. 1250 cm^{-1}. An equilibrium between the η^2-acyl and the alkyl carbonyl isomers was quickly attained in solution, at room temperature, for these CH_2SiMe_3 derivatives.

In spite of our efforts to eliminate traces of water from our reaction systems, the analogous reactions of $W(\eta^2\text{-}C(O)CH_2SiMe_3)Cl(CO)(PMe_3)_3$ with $NaS_2CNC_5H_{10}$, NaS_2COEt, and Tl(acac) provided directly the methyl complexes $W(CH_3)(L\text{-}L)(CO)_2(PMe_3)_2$ (L-L = $S_2CNC_5H_{10}$ (**9**), S_2COEt (**11**), acac (**13**)).

Preparation of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)$ (7). This complex has been obtained by reaction of Et_2O solutions of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2$ with CO under rigorously H_2O-free conditions. It was isolated from Et_2O at −20 °C as yellow crystals in ca. 70% yield.

Preparation of $W(CH_3)(L\text{-}L)(CO)_2(PMe_3)_2$ (L-L = $S_2CN\text{-}i\text{-}Pr_2$ (8), $S_2CNC_5H_{10}$ (9), S_2COMe (10), S_2COEt (11), $S_2CO\text{-}i\text{-}Pr$ (12), acac (13)). Method I. The salt $NaS_2CN\text{-}i\text{-}Pr_2$ (0.2 g, 1 mmol) was added to a yellow solution of $W(CH_3)Cl(CO)_2$-

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$(PMe_3)_3$ (0.54 g, 1 mmol) in Et_2O (40 mL). The reaction mixture was stirred at ca. 10 °C for 8 h, during which time a pale red color developed. The solvent was then reduced in vacuo to 10–15 mL. After centrifugation and cooling at −10 °C $W(CH_3)(S_2CN\text{-}i\text{-}Pr_2)(CO)_2(PMe_3)_2$ was obtained as orange crystals in 80% yield.

Method II. To a red solution of an equilibrium mixture of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CN\text{-}i\text{-}Pr_2)(CO)(PMe_3)_2$ and its alkyl isomer (0.65 g, 1 mmol) in acetone was added deaerated distilled water (1 drop), and the resulting solution was stirred for 1 h. Volatile components were then removed under reduced pressure, and the residue was extracted with Et_2O (15 mL). Crystallization at −10 °C afforded **8** in practically quantitative yield. From $W(CH_3)Cl(CO)_2(PMe_3)_3$ and the appropriate salts (NaS_2CNR_2, KS_2COR, and Tl(acac)) or by generation of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(L\text{-}L)(CO)(PMe_3)_2$ complexes in situ and subsequent addition of 1–2 drops of H_2O, the following compounds were obtained in similar yields by using analogous procedures: $W(CH_3)(S_2CNC_5H_{10})(CO)_2(PMe_3)_2$ (**9**), $W(CH_3)(S_2COMe)(CO)_2(PMe_3)_2$ (**10**), $W(CH_3)(S_2COEt)(CO)_2(PMe_3)_2$ (**11**), $W(CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)_2(PMe_3)_2$ (**12**), and $W(CH_3)(acac)(CO)_2(PMe_3)_2$ (**13**). They were isolated as yellow-orange crystalline solids by cooling Et_2O solutions of these complexes at −30 °C.

X-ray Structure Determination. A summary of the fundamental crystal data is given in Table IV. A single crystal was introduced in a glass capillary and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for W and P were taken from ref 21. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[22] was applied at the end of the isotropic refinement. Final refinement with fixed isotropic factors and coordinates for H atoms gave $R_F = 0.041$ and $R(w)_F = 0.050$. Most of the calculations were carried out with the X-Ray 80 system.[23]

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Note Added in Proof. Recent work carried out in our laboratory[19] has shown that in molybdenum complexes related to the tungsten compounds described in this contribution, the agostic acetyl formulation is indeed an alternative thermodynamic structure to their isomeric η^2-acyl and alkyl carbonyl formulations.

Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **13** (2 pages); a table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Vinylidene, Acetylide, and Carbene Complexes from Reactions of 2,5-Dithiahex-3-yne (MeSC≡CSMe) with $Cp(PMe_3)_2Ru^+$

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The alkyne MeSC≡CSMe initially displaces Cl^- in $Cp(PMe_3)_2RuCl$ at room temperature in MeOH to form the sulfur-bound alkyne complex $\{Cp(PMe_3)_2Ru[S(Me)C{\equiv}CSMe]\}PF_6$ (**1**). When it is warmed, **1** rearranges to the vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]PF_6$ (**2**). Complex **2** is reduced by $Na[HBEt_3]$ or Na/Hg to give the thioacetylide $Cp(PMe_3)_2Ru{-}C{\equiv}CSMe$ (**5**) and MeSSMe. The vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]^+$ (**6**, R = H; **7**, R = Me) are formed by electrophilic addition to the β-carbon of the thioacetylide **5**. Addition of CuCl to **5** forms $Cp(PMe_3)_2Ru(C{\equiv}CSMe)(CuCl)$ (**8**), in which the copper is π-bound through the C≡C group. Reaction of **6** with methanol and ethanol yields the alkoxycarbene complexes $[Cp(PMe_3)_2Ru{=}C(OR)(CH_2SMe)]BF_4$ (**11a**, R = Me; **11b**, R = Et). Deprotonation of **11a** with NaOMe yields the vinyl complex $Cp(PMe_3)_2Ru[C(OMe){=}C(H)SMe]$ (**12**). Addition of $[Me_3O]BF_4$ to complexes **6** and **7** yields the first examples of sulfoniovinylidene dicationic complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_2)](BF_4)_2$ (**9**, R = H; **10**, R = Me). An X-ray diffraction investigation shows that **9** crystallizes in space group $P2_1/n$ with $a = 16.641$ (2) Å, $b = 8.861$ (1) Å, $c = 18.168$ (2) Å, $\beta = 114.80$ (1)°, and $Z = 4$. Complexes **7** and **10** undergo one- and two-electron reductions, respectively, to give the acetylide $Cp(PMe_3)_2Ru{-}C{\equiv}CMe$ (**14**) and MeSSMe (for **7**) or SMe_2 (for **10**). Complexes **6** and **9** are readily deprotonated to give **5** and the sulfonioacetylide $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]BF_4$ (**13**), respectively. Mechanisms of the reactions and structural features of the vinylidenes are discussed.

Introduction

There has been considerable experimental and theoretical interest in reactions between transition-metal centers and alkynes.[2] Alkynes, when reacted with a single ruthenium metal center, are known to give a variety of reaction products: the alkyne can form π-alkyne complexes,[3-10] it can insert into a M–H or M–C bond of metal hydride or metal alkyl complexes,[11-18] 1-alkynes form metal-bound vinylidene complexes via a 1,2-hydrogen shift,[19-31] and a variety of alkynes are known to form

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