Ti–Se distances average 2.759 (3) Å, while the P–Se are identical at 2.151 (4) Å. The bite angle (i.e., Se1–Ti–Se2) is slightly greater than the analogous S1–Ti–S2 angle found in **13**, while the Ti–Se–P angles (average 85.4 (1)°) is approximately three degrees smaller than the corresponding Ti–S–P angles. A comparison of the core structures of **1**, **13**, and **14** is illustrated in Figure 6.

Summary. Herein, we have described reactions of phosphine sulfides and selenides with Ti, Zr, and Hf metallocene dihalides. The chemistry of the titanium complexes is directed by the ease of reduction of Ti(IV) to Ti(III). In contrast, no corresponding redox chemistry was observed for Zr or Hf complexes. These observations are typical of the chemistry of group 4.

The utility of the chemistry described herein for the synthesis of heterobimetallic complexes is the subject of current studies. In particular, we have found that complexes **1–5** are capable of acting as metalloligands, chelating to late transition metals forming early–late heterobimetallic species. This chemistry will be the subject of a future publication.

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Supplementary Material Available: Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and bond distances and angles associated with cyclopentadienyl, cyclohexyl, and phenyl rings (Table S3) (10 pages); values of $10|F_o|$ and $10|F_c|$ (Table S4) (17 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of a Neutral Tungsten(0) Alkyl Complex. Insertion of CO_2 into the W–CH_3 Bond of *trans,trans*-$W(CH_3)(CO)_2(NO)(PPh_3)_2$ and the Structural Characterization of *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$

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Reaction of *trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ (**1**) with CH_3Li or $(CH_3)_2Zn$ affords *trans,trans*-$W(CH_3)(CO)_2(NO)(PPh_3)_2$ (**2**) in good yields. Treatment of **2** with DCl gives **1** and CH_3D quantitatively. Reaction of **2** with carbon monoxide (2 atm, 80 °C) results in a reversible substitution of CO for PPh_3 to give *mer*-$W(CH_3)(CO)_3(NO)(PPh_3)$ (**3**). Carbon dioxide undergoes a 1,2-insertion reaction with **2** to give the monodentate acetate complex *trans,trans*-$W[\eta^1\text{-}OC(O)CH_3](CO)_2(NO)(PPh_3)_2$ (**4**), which reversibly loses CO on heating to yield the bidentate acetate derivative *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$ (**5**). Monoclinic prisms of **5** were grown from a dichloromethane/benzene solution and crystallized in space group $P2_1/a$ with $Z = 4$, $a = 20.864$ (5) Å, $b = 9.729$ (2) Å, $c = 17.504$ (4) Å, and $\beta = 103.21$ (1)°. An X-ray diffraction study at −91 ± 3 °C showed that the acetate ligand is bound in an asymmetric fashion to the tungsten center and that the nitrosyl and carbonyl ligands are *not* substantially disordered. Salient metrical parameters of the structure include the following: W(1)–O(4) = 2.249 (5) Å, W(1)–O(5) = 2.217 (5) Å, O(4)–C(6) = 1.270 (10) Å, O(5)–C(6) = 1.302 (10) Å, W(1)–C(8) = 1.914 (8) Å, C(8)–O(9) = 1.171 (9) Å, W(1)–N(10) = 1.836 (7) Å, N(10)–O(11) = 1.203 (9) Å, and W(1)–N(10)–O(11) = 178.3 (6)°. The least-squares refinement converged to $R(F) = 0.036$ and $R_w(F) = 0.036$ for 3518 unique data with $F > 3\sigma(F)$.

Introduction

Insertion reactions of small molecules into transition-metal–carbon σ-bonds are key features in a variety of important stoichiometric and catalytic chemical processes. As a result, considerable research attention has been focused on the elucidation of the scope and the mechanistic details of the insertions of CO, CO_2, CS_2, C_2H_4, SO_2, etc. into M–R bonds.[1] Several simple metal systems have yielded valuable information in this regard, such as the classic studies of CO migratory insertion into the alkyl bond of $Mn(CO)_5R$,[2] as well as the more recent investigations of the insertions of CO and CO_2 into the tungsten–alkyl bond of $[W(CO)_5R^-]$ and $[W(CO)_4(PR_3)R^-]$.[3] Indeed, it has been sugggested by Darensbourg et al. that the group 6 metal anionic carbonyl aryl and alkyl complexes of the type $[M(CO)_5R^-]$ (M = Cr, W) might prove

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to be as useful for defining details of *carboxylation* reactions as the neutral group 7 metal analogues have been in studies of *carbonylation* reactions.[3b]

We undertook the synthesis of a *neutral* tungsten analogue of $[W(CO)_5CH_3^-]$ in order to examine the role that charge plays in the insertion reactions of carbon dioxide and related molecules. Such a complex will necessarily contain a formally positively charged ligand (to balance the uninegative formal charge of the alkyl ligand) if the metal center is to remain in the zerovalent oxidation state.[4] We have previously shown that the d^6 tungsten hydrido complex *trans,trans*-$WH(CO)_2(NO)(PPh_3)_2$,[5] a stable, neutral analogue of $[W(CO)_5H^-]$,[6] undergoes clean, facile insertion reactions with various heterocumulenes, so we chose as our target *trans,trans*-$W(CH_3)(CO)_2(NO)(PPh_3)_2$. Herein we detail the results of our efforts, including the synthesis of a stable, neutral tungsten(0) methyl complex, a preliminary description of its reactivity, and the structural characterization by single-crystal X-ray diffraction techniques of the product of its reaction with carbon dioxide.

It is noteworthy that alkyl derivatives of the group 6 metals (Cr, Mo, W) in their zerovalent oxidation states are quite rare, even though the first example, $(C_5H_5)Cr(NO)_2(CH_3)$, was prepared 30 years ago by Piper and Wilkinson;[7] related Mo and W complexes have been subsequently reported by Legzdins,[8] and accounts of the reactivities of these species have also appeared.[9] Additionally, we recently described the insertion reaction of O=C=C=C=O into a W—H bond to yield the novel σ-ketenyl complex *trans,trans*-$W\{\eta^1\text{-}C(CHO)CO\}(CO)_2(NO)(PPh_3)_2$.[10] The other examples belong to the class of anions previously discussed, which can be prepared by several routes.[11]

Experimental Section

General Considerations. Reactions were carried out under an argon atmosphere by using a combination of standard Schlenk and high-vacuum techniques, except where noted. Dry, air-free solvents were vacuum transferred from green "titanocene" (benzene, petroleum ether),[12] sodium benzophenone ketyl (THF, Et_2O), or CaH_2 (CH_2Cl_2) and used throughout. Infrared solution (KBr cells) and solid-state (CaF_2 plates; Fluorolube S-30 mulls) spectra were recorded on a Nicolet 20SX Fourier transform spectrophotometer automatically calibrated to the He/Ne laser line at 632.8 nm. ^1H NMR spectra were recorded in C_6D_6 by using a DS-1000 (Chicago built) 500-MHz instrument and chemical shifts referenced to the residual solvent protons (δ 7.15). ^{13}C NMR spectra were recorded in C_6D_6 by using a Varian XL-400 spectrometer operating at 100.6 MHz, with chemical shifts referenced to the solvent carbons (δ 128.0). $^{31}P\{^1H\}$ NMR spectra were obtained in C_6D_6 solution with a Nicolet NTC-200 instrument operating at 81-MHz, and chemical shifts reported with respect to external 85% H_3PO_4 (δ 0). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

cis,cis- and *trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ were prepared according to the literature method.[5b] Dimethylzinc was synthesized according to Wilkinson's procedure.[13] (*Caution*! $(CH_3)_2Zn$ inflames spontaneously on contact with the air!) Methyllithium (1.2 M in Et_2O; halide free) was purchased from Aldrich Chemical Co. Isotopically labeled methyllithium was prepared from lithium metal and $^{13}CH_3I$ (99% ^{13}C; Stohler Isotope Chemicals) in Et_2O. Carbon dioxide (bone dry) and carbon monoxide were used as purchased from Matheson.

Preparation of *trans,trans*-$W(CH_3)(CO)_2(NO)(PPh_3)_2$ (2). Method A. Into an evacuated 500-mL flask charged with *trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ (3.10 g, 3.74 mmol) were vacuum transferred 250 mL of dry THF, and then, under an argon counterflow, CH_3Li (5 mL, 6.0 mmol) was added via syringe to the cold (−78 °C), stirred solution. The reaction mixture was allowed to warm to ambient temperature during which time the yellow solid dissolved to give a homogeneous, orange solution. The solution was stirred for about 45 min at ambient temperature, and then 20 mL of absolute ethanol were added to quench the excess methyllithium. Subsequent workup was carried out in the air. The solvent was removed by using a rotary evaporator, and the resulting orange residue was dissolved in dichloromethane and filtered through a Celite pad and the product precipitated by the dropwise addition of absolute ethanol. The mixture was filtered, and the precipitate was washed sequentially with 30-mL portions of absolute ethanol, diethyl ether, and petroleum ether to yield 1.27 g (42%) of sparkling, lemon yellow microcrystals.

Method B. Into an evacuated 200-mL flask charged with *trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ (0.42 g, 0.51 mmol) were vacuum transferred 100 mL of dry THF. The solution was allowed to warm to ensure that all of the material would dissolve and recooled (−78 °C), and then neat $(CH_3)_2Zn$ (1 mL, 6.1 mmol) was added via syringe under an argon counterflow. The solution was allowed to warm to ambient temperature and was stirred for 10 h, after which time all of the solvent and volatiles were removed under vacuum. The yellow solid was recrystallized as in method A to yield 0.34 g (83%). Anal. Calcd for $C_{39}H_{33}NO_3P_2W$: C, 57.87; H, 4.11; N, 1.73. Found: C, 57.61; H, 4.04; N, 1.66. IR (mull): ν(CO) 2006 (vw), 1918 (vs), ν(NO) 1601 (vs) cm^{-1}. ^1H NMR δ −1.01 (t, 3 H, $^3J_{PH}$ = 8.2 Hz), 6.95 (m, 6 H), 7.05 (m, 12 H), 7.76 (m, 12 H). $^{31}P\{^1H\}$ NMR: δ 23.0 (s with W satellites, $^1J_{PW}$ = 280 Hz). ***trans,trans*-$W(^{13}CH_3)(CO)_2(NO)(PPh_3)_2$ (2-^{13}C)** was prepared as in method A except that freshly generated $^{13}CH_3Li$ was used. The labeled methyl group appeared as a doublet-of-triplets ($^1J_{CH}$ = 120.4, $^3J_{PH}$ = 8.2 Hz) and a triplet (δ −4.2 ($^2J_{PC}$ = 5.5 Hz)) in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively.

Reaction of 2 with CO. This reaction was conveniently monitored in a sealed-tube NMR experiment. A 10-mg (0.012-mmol) sample of **2** was placed in a 5-mm NMR tube sealed to a ground-glass joint and was attached to a vacuum line by way of a Teflon needle valve adapter. C_6D_6 (~0.4 mL) was vacuum transferred into the tube at −78 °C, then 700 torr of CO was admitted into the line, the needle valve above the tube was closed, and then the tube was cooled by using liquid nitrogen and sealed with a torch. The sealed tube was immersed in an oil bath (80 °C) and the reaction periodically monitored by using ^1H NMR spectroscopy. After several hours, a new *doublet* had appeared (δ −0.70 ($^3J_{PH}$ = 8.6 Hz)) and continued to grow at the expense of the CH_3 resonance of **2**. Furthermore, a $^{31}P\{^1H\}$ NMR spectrum showed the growth of two new resonances of approximately equal intensities assignable to free PPh_3 (δ −4.8 (s)) and *mer*-$W(CH_3)(CO)_3(NO)(PPh_3)$ (**3**) (δ 17.6 (s with W satellites, $^1J_{PW}$ = 267 Hz)). After 4 days at 80 °C, the ratio of **3**:**2** had stabilized at about 3:1, with several minor methyl peaks having emerged between δ +1 and δ +2 (these totaled about 10% of the integrated intensity for the CH_3 moieties). If the sealed tubes were allowed to sit for several days at ambient temperature, **3** partially reconverted to **2**, suggesting an equilibrium was operative. A solution IR (CD_2Cl_2) showed (in addition to the weaker bands of **2**) for

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[4] Isoelectronic, neutral d^6 rhenium complexes are well-known (e.g., *cis*-$Re(CH_3)(CO)_4(PPh_3)$ and *trans,mer*-$Re(CH_3)(CO)_3(PPh_3)_2$) but are less reactive than these anionic group 6 alkyls with regard to similar insertion reactions. (a) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066. (b) Chatt, J.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Organomet. Chem.* **1980**, *184*, C64. (c) Parker, D. W.; Marsi, M.; Gladysz, J. A. *Ibid.* **1980**, *194*, C1.

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3: ν(CO) 5072 (w), 1983 (s), 1955 (vs), ν(NO) 1633 cm^{-1}. Attempts to prepare pure isolated samples of **3** were unsuccessful.

Reaction of 2 with CO$_2$. Method A. The reaction was carried out and monitored (by using ^{1}H and ^{31}P{^{1}H} NMR spectroscopy) as described above (for CO) except that CO$_2$ was sealed in the tube with **2** and subsequently heated at 80 °C in an oil bath. During this period, the triplet CH$_3$ resonance of **2** (^{1}H NMR) disappeared in favor of two new singlet resonances at δ 1.21 (CH$_3$ of ***trans*,*trans*-W[η^1-OC(O)CH$_3$](CO)$_2$(NO)(PPh$_3$)$_2$** (**4**))[5] and δ 0.68 (CH$_3$ of ***trans*-W(η^2-O$_2$CCH$_3$)(CO)(NO)(PPh$_3$)$_2$** (**5**))[5] as well as a small doublet at δ −0.70 (CH$_3$ of **3**) which constituted about 3% of the total CH$_3$-intensity. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture likewise showed the disappearance of the resonance of **2** and the appearance of the resonances of **4** (δ 25.1 (s, $^1J_{PW}$ = 296 Hz) and **5** (δ 36.7 (s, $^1J_{PW}$ = 309 Hz)).

Method B. A 0.20-g (0.25-mmol) sample of **2** was placed in a Fischer-Porter pressure bottle along with 50 mL of dry toluene and 80 psig of CO$_2$. The solution was heated with an oil bath (80 °C) and stirred for 4 h, vented, and repressurized with a fresh CO$_2$ charge. This process was repeated three times, then the solution was cooled and filtered in the air, and the red filtrate was reduced in volume to about 10 mL. Absolute ethanol was added in a dropwise fashion to complete the precipitation of sparkling red crystals which were filtered and washed with ethanol to yield 0.15 g (73%) of **5**, which was identified by comparison with an authentic sample prepared by an independent method,[5] as well as by a single-crystal X-ray diffraction study (vide infra). IR (mull): ν(CO) 1891 (vs), ν(NO) 1610 (vs), ν(OCO) 1514 (m), 1464 (s) cm^{-1}. ^{1}H NMR: δ 0.68 (s, 3 H), 6.99 (m, 6 H), 7.05 (m, 12 H), 7.71 (m, 12 H).

Reaction of 2 with ^{2}HCl. A 5-mm NMR tube with an open-faced screw cap equipped with a Teflon-backed septum (Wilmad, Inc.) was charged with 10 mg of **2** and 0.4 mL of C$_6$D$_6$. A drop of concentrated DCl(aq) was added via a syringe, and the tube was shaken vigorously. Analysis of the solution by using ^{1}H and ^{31}P{^{1}H} NMR showed that **2** was completely converted to **1** and CH$_3$D within 5 min.

Crystallographic Characterization of 5. Ruby red prisms with well-formed faces were grown from a CH$_2$Cl$_2$/C$_6$H$_6$ (10:1, v/v) solution of **5** by allowing the solvent to slowly evaporate in a nitrogen-filled glovebox. Both solid and solution samples of **5** slowly decompose upon exposure to the atmosphere but can be handled for short periods without special precautions. A suitable small crystal was selected and transferred to the goniostat for characterization and data collection. Attempts to cool the crystal to our usual operating temperature of −156 °C resulted in a splitting of peaks caused by a phase transition. The crystal was warmed to −91 °C and maintained (±3 °C) at that temperature for the duration of the data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic symmetry and systematic extinctions of $0k0$ for $k = 2n + 1$ and of $h0l$ for $h = 2n + 1$ identifying the space group as $P2_1/a$. Data collection was carried out as described in Table I.

The structure was solved by using a combination of direct methods and Fourier techniques. The W atom was located by using MULTAN78, and the remaining atoms were located in successive difference Fouriers phased with the previously located atoms. All of the hydrogen atoms were located and refined by using isotropic thermal parameters. The least squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The final $R(F)$ was 0.036 by using 3518 reflections considered observed by the criterion $F > 3\sigma(F)$. The final difference map was essentially featureless, with the largest peak (1.2 e/Å^3) at the W position; otherwise, the maximum peak was 0.54 e/Å^3. General descriptions of the methods used in data collection, data reduction, and structure refinement have been previously reported.[14]

The identification of atoms 8 and 10 as C(8) and N(10) was based on several tests and observations during the solution and refinement of the structure. Initially, both atoms were assigned a carbon scattering factor, and an isotropic least-squares refinement resulted in thermal parameters of 2.28 and 1.25 Å^2 for atoms 8 and 10, respectively. At the same time, the thermal parameters for the acetate oxygen atoms were 2.78 Å^2 for O(4) and 2.69 Å^2 for O(5); thus the low value obtained for atom 10 indicated that it should properly be identified as a nitrogen atom. A subsequent isotropic refinement with the atoms identified as C(8) and N(10) resulted in thermal parameters of 2.3 and 2.7 Å^2, respectively. The indications were the same when anisotropic thermal values were used. In the model in which both atoms were refined as carbons, the root-mean-square displacements were much smaller for atom 10 (0.14, 0.17, 0.20) than for atom 8 (0.16, 0.19, 0.29). The root-mean-square displacements after the final refinement cycle were (0.12, 0.17, 0.22) for C(8) and (0.15, 0.18, 0.22) for N(10). In a difference Fourier computed with atoms 8 and 10 omitted, the peak heights for the respective atoms (6.10e vs. 6.45e) again indicated a higher electron density at atom 10. Finally, a comparison of the final W(1)–C(8), W(1)–N(10), C(8)–O(9), and N(10)–O(11) bond lengths (vide infra) also suggested that our assignments, with an ordered model, were correct.

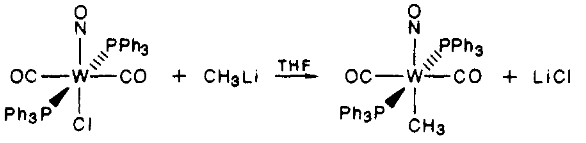
Table I. Summary of Crystallographic Data for 5

compd	*trans*-W(η^2-O$_2$CCH$_3$)(CO)(NO)-{P(C$_6$H$_5$)$_3$}$_2$
formula	C$_{39}$H$_{33}$NO$_4$P$_2$W
gfw	825.49
color of cryst	ruby red
a, Å	20.864 (5)
b, Å	9.729 (2)
c, Å	17.504 (4)
β, deg	103.21 (1)
V, Å^3	3459.11
Z	4
space group	C_{2h}—$P2_1/a$
cryst size, mm	0.20 × 0.20 × 0.20
radiation	Mo Kα (λ = 0.71069 Å) monochromatized with highly oriented graphite
μ, cm^{-1}	35.41
d(calcd), g/cm^3	1.585
temp, °C	−91 ± 3
aperture	3.0 mm wide × 4.0 mm high, 23.5 cm from crystal
takeoff angle, deg	2.0
scan speed, deg/min	6.0
scan range, deg	1.8 + dispersion
bkgd counting time, s	6
2θ limits, deg	6–45
unique data with $F > 3\sigma(F)$	3518
GOF	0.763
$R(F)$	0.036
$R_w(F)$	0.036

The final positional and thermal parameters for the refined nonhydrogen atoms appear in Table II. Table III lists the positional and thermal parameters for the refined hydrogen atoms.[15] A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[15]

Results and Discussion

Preparation and Reactivity of *trans*,*trans*-W(CH$_3$)(CO)$_2$(NO)(PPh$_3$)$_2$. The metathetical reaction of *trans*,*trans*-WCl(CO)$_2$(NO)(PPh$_3$)$_2$ (**1**) with methyllithium in THF results in formation of the bright yellow, air-stable tungsten(0) alkyl complex *trans*,*trans*-W(CH$_3$)(CO)$_2$(NO)(PPh$_3$)$_2$ (**2**) in ∼40–50% isolated yield (eq 1). Interestingly, neither *cis*,*cis*-WCl(CO)$_2$(NO)(PPh$_3$)$_2$ nor



1 2 (1)

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(15) Supplementary material.

Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for Non-Hydrogen Atoms of 5

atom	x	y	z	B_{iso}
W(1)	7514.8 (1)	107.7 (3)	2585.9 (2)	18
P(2)	8529 (1)	−133 (2)	3658 (1)	22
P(3)	6527 (1)	168 (2)	1449 (1)	18
O(4)	8068 (3)	−1162 (6)	1876 (3)	28
O(5)	7361 (2)	−2143 (5)	2457 (3)	27
C(6)	7780 (4)	−2254 (9)	2011 (5)	32
C(7)	7871 (5)	−3588 (11)	1644 (8)	60
C(8)	6975 (4)	592 (8)	3294 (4)	23
O(9)	6658 (3)	881 (7)	3742 (4)	42
N(10)	7737 (3)	1926 (8)	2536 (4)	27
O(11)	7889 (3)	3118 (6)	2524 (4)	40
C(12)	9222 (4)	821 (8)	3449 (5)	27
C(13)	9663 (4)	1577 (9)	4009 (5)	31
C(14)	10168 (5)	2308 (10)	3814 (6)	38
C(15)	10259 (5)	2268 (11)	3069 (6)	42
C(16)	9846 (5)	1482 (11)	2497 (5)	40
C(17)	9325 (4)	789 (10)	2691 (5)	33
C(18)	8855 (4)	−1868 (9)	3877 (4)	28
C(19)	9494 (5)	−2220 (10)	3919 (5)	36
C(20)	9706 (6)	−3577 (12)	4067 (6)	52
C(21)	9267 (7)	−4576 (12)	4154 (7)	61
C(22)	8624 (6)	−4231 (11)	4122 (7)	62
C(23)	8403 (5)	−2900 (11)	3970 (7)	53
C(24)	8453 (4)	581 (10)	4596 (5)	33
C(25)	8284 (5)	1956 (11)	4629 (5)	41
C(26)	8221 (5)	2550 (13)	5320 (7)	55
C(27)	8315 (6)	1785 (17)	5985 (6)	73
C(28)	8492 (8)	455 (18)	5972 (6)	96
C(29)	8538 (6)	−156 (13)	5279 (5)	61
C(30)	6261 (4)	1884 (8)	1079 (5)	23
C(31)	5993 (5)	2128 (9)	291 (5)	34
C(32)	5785 (5)	3433 (11)	41 (6)	42
C(33)	5842 (5)	4498 (10)	566 (7)	48
C(34)	6119 (4)	4272 (9)	1353 (6)	36
C(35)	6335 (4)	2984 (9)	1605 (5)	29
C(36)	6588 (4)	−805 (8)	561 (4)	21
C(37)	6104 (4)	−1700 (9)	179 (5)	29
C(38)	6196 (6)	−2425 (10)	−464 (5)	41
C(39)	6745 (6)	−2258 (10)	−744 (5)	41
C(40)	7233 (5)	−1340 (11)	−375 (5)	40
C(41)	7147 (4)	−639 (9)	274 (5)	29
C(42)	5777 (4)	−553 (8)	1686 (4)	21
C(43)	5192 (4)	130 (9)	1532 (5)	29
C(44)	4644 (4)	−457 (10)	1713 (6)	39
C(45)	4676 (4)	−1744 (11)	2051 (6)	37
C(46)	5258 (5)	−2416 (10)	2192 (6)	39
C(47)	5814 (4)	−1860 (9)	2022 (5)	31

[a] Fractional coordinates are ×10^4. [b] Isotropic values are ×10 and are calculated from the anisotropic values using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609. The units are Å^2. The anisotropic thermal parameters are available.[15]

mer-WCl(CO)$_3$(NO)(PPh$_3$)[5b] yielded isolable alkyl derivatives. Better yields of **2** (>80%) were obtained in the reaction of **1** with dimethylzinc (eq 2), but reaction of **1**

$$1 + (CH_3)_2Zn \xrightarrow{THF} 2 + CH_3ZnCl \qquad (2)$$

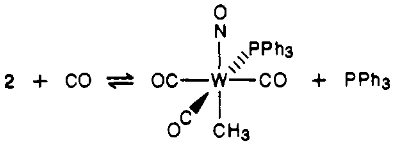
with either trimethylaluminum or with methyl Grignard reagents did not yield **2** in appreciable amounts. We were unable to prepare other alkyl or aryl derivatives from organolithium reagents (RLi; R = CH$_2$SiMe$_3$, *t*-Bu, Ph), which gave uncharacterized decomposition products; we have not yet tested the generality of the reaction of **1** with dialkylzinc reagents. The inability to prepare derivatives of **2** from these other RLi reagents is not too surprising. It is well recognized that metathesis reactions of the sort shown in eq 1 generally proceed via initial nucleophilic attack of "R$^-$" at a coordinated carbonyl ligand,[4c] followed by halide loss with alkyl migration. The intermediates are sometimes quite stable, however, and can be isolated as hydroxycarbene complexes upon acidic workup. Thus, treatment of *trans,trans*-ReCl(N$_2$)(CO)$_2$(PPh$_3$)$_2$ with CH$_3$Li followed by H$^+$ gives *trans*-Re[=C(OH)CH$_3$]Cl(N$_2$)(CO)(PPh$_3$)$_2$ in 60% yield;[4b] ReCl(CO)$_5$ likewise affords a hydroxycarbene complex, Re[=C(OH)CH$_3$]Cl(CO)$_4$.[16] This could very well be a complicating feature in some of the reactions of RLi with **1**. Additionally, nucleophilic attack at the nitrosyl ligand of **1** is also a distinct possibility.

The overall trans, trans geometry of **1** is maintained in **2** as judged by infrared (ν(CO) 2006 (vw), 1918 (vs) cm^{-1}) and ^{31}P{^{1}H} NMR (δ 23.0 (s, $^1J_{PW}$ = 280 Hz)) spectroscopy. Clear *spectroscopic* evidence for the presence of a methyl ligand is provided by the ^{1}H and ^{13}C{^{1}H} NMR spectra of the labeled isotopomer **2**–^{13}***C*** (prepared from **1** and ^{13}CH$_3$Li). The magnitudes of the observed coupling constants, the multiplicities, and the chemical shift values for the CH$_3$ group (^{1}H NMR δ −1.01 (doublet-of-triplets, $^1J_{CH}$ = 120.4, $^3J_{PH}$ = 8.2 Hz); ^{13}C{^{1}H} NMR δ −4.2 (t, $^2J_{PC}$ = 5.5 Hz)) indicates a methyl ligand is cis disposed with respect to the two PPh$_3$ ligands. Like many metal alkyls, the methyl moiety of **2** is sensitive to protic acids. As shown in eq 3, aqueous deuterium chloride quantitatively and

$$2 + DCl(aq) \xrightarrow{fast} 1 + CH_3D \qquad (3)$$

rapidly converts **2** to **1** with concomitant evolution of deuteriomethane (^{1}H NMR), providing *chemical* confirmation of the presence of the W–CH$_3$ linkage.

Carbon monoxide (2 atm) slowly undergoes a reversible phosphine displacement reaction on heating (80 °C) with benzene solutions of **2** to give *mer*-W(CH$_3$)(CO)$_3$(NO)(PPh$_3$) (**3**), which was identified by its characteristic infrared and ^{31}P{^{1}H} and ^{1}H NMR (δ −0.70 (d, $^3J_{PH}$ = 8.6 Hz)) spectra (eq 4). After 4 days at 80 °C, the conversion of

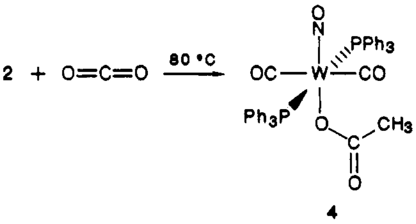


$$2 + CO \rightleftharpoons OC{-}\overset{\overset{O}{N}\ \ PPh_3}{\underset{OC\ \ CH_3}{W}}{-}CO + PPh_3 \qquad (4)$$

3

2 to **3** was 68% complete, with about 10% formation of several uncharacterized minor products that exhibited ^{1}H NMR singlet resonances between δ +1 and δ +2 (perhaps belonging to acyl products formed in methyl migration reactions). Our attempts to isolate pure samples of **3** (free of **2**) were unsuccessful because of the facile reassociation of PPh$_3$ in the absence of a carbon monoxide atmosphere. In fact, when an isolated mixed sample of **2** and **3** (1:1) was dissolved in C$_6$D$_6$ and heated to 40 °C in the presence of triphenylphosphine, **3** rapidly reconverted to **2** (<2 min, ^{1}H NMR).

Carbon dioxide (2 atm) undergoes an irreversible 1,2-insertion reaction with the methyl group of **2** at 80 °C to give, as the initial primary product, the yellow η^1-acetato derivative *trans,trans*-W[η^1-OC(O)CH$_3$](CO)$_2$(NO)(PPh$_3$)$_2$ (**4**), as shown in eq 5. The identification of the insertion



$$2 + O{=}C{=}O \xrightarrow{80\ ^\circ C} OC{-}\overset{\overset{O}{N}\ \ PPh_3}{\underset{Ph_3P\ \ OC(O)CH_3}{W}}{-}CO \qquad (5)$$

4

product as **4** follows by spectroscopic comparison with authentic samples prepared by the alternate routes de-

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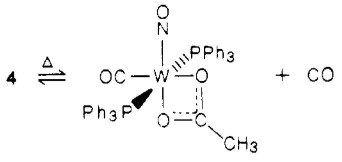
(16) Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65.

picted in eq 6 and 7.[5b] As we have previously described,

$$[W(CO)_3(NO)(PPh_3)_2][PF_6] + Na[O_2CCH_3] \rightarrow 4 + CO + NaPF_6 \quad (6)$$

$$WH(CO)_2(NO)(PPh_3)_2 + CH_3CO_2H \rightarrow 4 + H_2 \quad (7)$$

even on mild (40 °C) thermolysis the acetate ligand chelates with loss of CO to quantitatively yield the ruby-red complex *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$ (**5**); this CO loss is reversible, and stirring **5** under 1 atm of carbon monoxide at ambient temperature results in the regeneration of **4** (eq 8).[5b] Therefore, since the reaction of carbon dioxide with **2** is effected at 80 °C, **5** is also produced as a result of this secondary (decarbonylation) reaction (eq 8). The reaction of CO_2 with **2** can be cleanly driven to **5** simply by the occasional purging of CO from the system, and in this manner very good isolated yields (~75%) of **5** can be realized. When the carboxylation reaction is monitored in a sealed-tube ^1H NMR experiment, one also observes the transient appearance of small amounts (~3%) of **3**, formed from the carbon monoxide (see eq 4) liberated in the production of **5** (eq 8). This overall sequence is summarized in eq 9. When the carbonylation

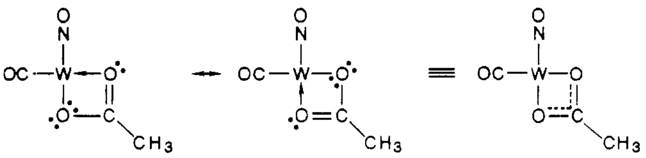

(8)

5

$$3 \underset{CO}{\overset{PPh_3}{\rightleftarrows}} 2 \xrightarrow{CO_2} 4 \overset{\Delta}{\rightleftharpoons} 5 + CO \quad (9)$$

or carboxylation reactions were attempted at higher temperatures (140 °C), decomposition of **2** with methane elimination occurred (presumably by an ortho-metalation process[4a]).

A comment on the reversible addition of CO to **5** (eq 8) is in order. The bidentate acetato group of **5** is coordinated trans to two strong π-acids, NO^+ and CO, in an otherwise symmetrical environment; thus the incoming carbon monoxide could hypothetically add trans to either the nitrosyl or the carbonyl ligand. (The only well-documented example of a complex having mutually trans NO and CO ligands is the very reactive vanadium species $V(CO)_5(NO)$.[17]) However, CO reacts *quantitatively* and *exclusively* to give **4** (i.e., with CO trans to CO).[18] This beautifully illustrates the well recognized ranking of the π-acidities of these isoelectronic ligands (NO^+ > CO) and supports the notion that valence formalism A is relatively more important than B. In order to examine whether this


A B

strong reactivity bias has an observable structural basis (i.e., if the acetato ligand is coordinated to tungsten in an asymmetric fashion), we undertook a single-crystal X-ray diffraction study of the crystal and molecular structure of **5**.

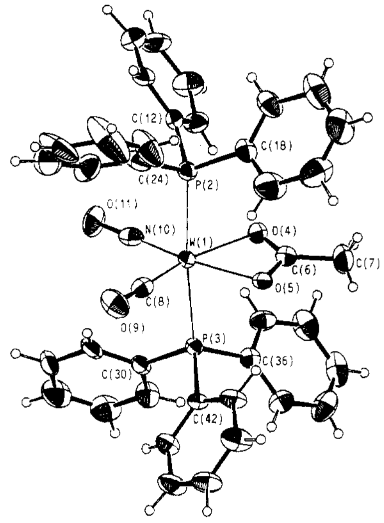


Figure 1. An ORTEP drawing of **5** showing the atom numbering scheme. Thermal elipsoids are drawn at the 50% probability level except those for the H atoms which are drawn artificially small for clarity. The complete numbering scheme (including all C and H atoms) is available.[15]

Table IV. Selected Bond Distances (Å) in 5

W(1)-P(2)	2.498 (2)	O(11)-N(10)	1.203 (9)
W(1)-P(3)	2.517 (2)	C(6)-C(7)	1.480 (15)
W(1)-O(4)	2.249 (5)	P(2)-C(12)	1.824 (9)
W(1)-O(5)	2.217 (5)	P(2)-C(18)	1.827 (8)
W(1)-N(10)	1.836 (7)	P(2)-C(24)	1.823 (8)
W(1)-C(8)	1.914 (8)	P(3)-C(30)	1.831 (8)
O(4)-C(6)	1.270 (10)	P(3)-C(36)	1.849 (8)
O(5)-C(6)	1.302 (10)	P(3)-C(42)	1.846 (8)
O(9)-C(8)	1.171 (9)	P-C(av)	1.833

Table V. Selected Bond Angles (deg) in 5

P(2)-W(1)-P(3)	174.92 (6)	W(1)-C(8)-O(9)	178.4 (7)
P(2)-W(1)-O(4)	84.84 (15)	W(1)-N(10)-O(11)	178.3 (6)
P(2)-W(1)-O(5)	93.55 (14)	W(1)-O(4)-C(6)	91.8 (5)
P(2)-W(1)-N(10)	86.9 (2)	W(1)-O(5)-C(6)	92.4 (5)
P(2)-W(1)-C(8)	93.4 (2)	O(4)-C(6)-O(5)	117.0 (7)
P(3)-W(1)-O(4)	90.39 (15)	O(4)-C(6)-C(7)	122.6 (10)
P(3)-W(1)-O(5)	82.47 (14)	O(5)-C(6)-C(7)	120.2 (10)
P(3)-W(1)-N(10)	96.3 (2)	W(1)-P(2)-C(12)	112.0 (3)
P(3)-W(1)-C(8)	90.6 (2)	W(1)-P(2)-C(18)	117.1 (3)
O(4)-W(1)-O(5)	58.8 (2)	W(1)-P(2)-C(24)	114.1 (3)
O(4)-W(1)-N(10)	109.6 (3)	W(1)-P(3)-C(30)	115.4 (3)
O(4)-W(1)-C(8)	161.0 (3)	W(1)-P(3)-C(36)	116.8 (3)
O(5)-W(1)-N(10)	168.3 (3)	W(1)-P(3)-C(42)	113.4 (2)
O(5)-W(1)-C(8)	102.5 (3)	W(1)-P-C(av)	114.8
N(10)-W(1)-C(8)	89.2 (3)		

Molecular Structure of *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$. The structure of **5** consists of discrete monomeric molecules in the unit cell. There are no significant inter- or intramolecular nonbonded contacts. A perspective view of the complex together with the labeling scheme is shown in Figure 1. The complex exhibits a six-coordinate, pseudo-octahedral geometry with the acetate ligand bound in an O,O-chelating fashion to W. Tables IV and V contain selected intramolecular bond distances and angles. A more complete listing of these parameters is available.[15] The linear carbonyl ligand is trans to one of the acetate's O atoms (C(8)-W(1)-O(4) = 161.0 (3)°), and the linear nitrosyl ligand is trans to the other one (N(10)-W(1)-O(5) = 168.3 (3)°). The two triphenylphosphine ligands are mutually trans disposed (P(2)-W(1)-P(3) = 174.92 (6)°). The constraints imposed by the four-membered metallacycle result in a typically contracted O(4)-W(1)-O(5) angle (58.8 (2)°). The W atom and the non-hydrogen atoms of the acetato, carbonyl, and nitrosyl ligands are nearly coplanar. Only O(4) (Δ = 0.10

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(17) (a) Hieber, W.; Peterhans, J.; Winter, E. *Chem. Ber.* **1961**, *94*, 2572. (b) Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2303.

(18) It is possible that CO adds trans to NO to give an unobserved kinetic intermediate that rapidly rearranges to the observed product 4.

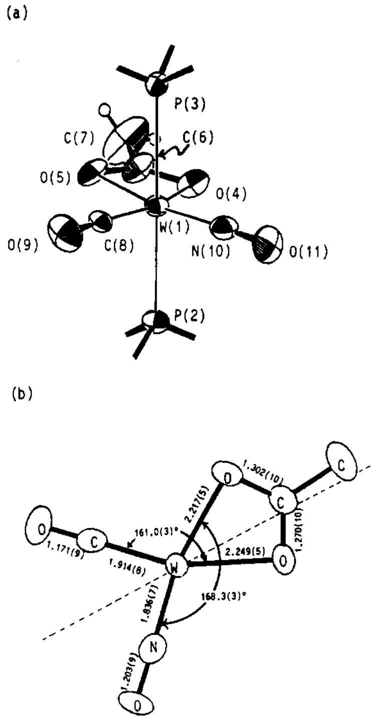

Figure 2. (a) A perspective view of the coordination sphere of 5 showing the asymmetry of the acetato ligand with respect to the pseudo-mirror plane that bisects the C(8)–W(1)–N(10) angle. (b) A view of 5 perpendicular to the plane that contains the tungsten, carbonyl, nitrosyl, and acetate atoms (the PPh_3 ligands have been omitted). The dashed line is the psuedo-mirror plane (or C_2 axis) that bisects the C(8)–W(1)–N(10) angle.

Å) and C(7) ($\Delta = 0.06$ Å) are displaced by more than 0.04 Å from the least-squares plane defined by these nine atoms.[15]

There are two noteworthy features of the structure: (1) it shows unequivocally that CO_2 has undergone a 1,2-insertion reaction with the W–CH_3 bond of 2, and (2) the acetato ligand is asymmetrically ligated to tungsten.

At 2.217 (5) Å, the W(1)–O(5) distance (trans to NO) is significantly shorter than the corresponding W(1)–O(4) distance of 2.249 (5) Å (trans to CO). These values can be compared to the W–O distance of 2.189 (9) Å found in the related structure of *trans,trans*-W{η^1-OPO(OH)$_2$}(CO)$_2$(NO)(PPh$_3$)$_2$;[19] the W(1)–O(5) distance in 5 is identical (within the error limits) and can be approximated as a simple W–O σ-interaction. The longer W(1)–O(4) distance suggests a relative increase in the dative character of this bond, as shown in a limiting case in formalism A. Thus, the best π-donor-type oxygen, O(5), is positioned trans to the strongest π-acceptor (NO^+). The larger errors associated with the C–O bond lengths (C(6)–O(4) = 1.270 (10) Å; C(6)–O(5) = 1.302 (10) Å) in the acetate ligand obscure any meaningful variation in these distances. Because of the different W–O bond lengths and since the C(8)–W(1)–O(4) angle is smaller than the N(10)–W(1)–O(5) angle ($\Delta = 7.3°$), the acetate's atoms are not symmetrically arranged with respect to the pseudo-C_2 axis (or mirror plane) that bisects the N(10)–W(1)–C(8) angle. This positional bias of the O_2CCH_3 group relative to the carbonyl and nitrosyl ligands is clearly illustrated in a perspective view of the coordination sphere of 5 oriented along this pseudo-mirror plane bisecting the C(8)–W(1)–N(10) angle (Figure 2). All of the acetate atoms except O(4) are closer to the CO than to the NO ligand, and it is probably this occurrence that gives rise to *ordered* (instead of disordered) carbonyl and nitrosyl ligands (vide supra).[20]

Both the nitrosyl (178.3 (6)°) and carbonyl (178.4 (7)°) are coordinated to W in a linear fashion. As expected, because NO^+ is a much better $d\pi \rightarrow p\pi^*$ acceptor ligand than is CO, the W(1)–N(10) distance (1.836 (7) Å) is shorter than the W(1)–C(8) distance (1.914 (8) Å) and the N(10)–O(11) bond length (1.203 (9) Å) is somewhat longer than that for C(8)–O(9) (1.171 (9) Å). These parameters are comparable to the analogous values found in *trans,trans*-W[η^1-OPO(OH)$_2$](CO)$_2$(NO)(PPh$_3$)$_2$ (W–N = 1.793 (13) Å; N–O = 1.19 (2) Å; W–C = 2.077 (15), 2.06 (2) Å; C–O = 1.11 (2), 1.14 (2) Å)[19] and *mer*-W(η^1-FSbF$_5$)(CO)$_3$(NO)(PMe$_2$Ph) (W–N = 1.80 (2) Å; N–O = 1.17 (2) Å; W–C = 2.09 (2), 2.09 (2), 2.05 (2) Å; C–O = 1.12 (2), 1.11 (2), 1.17 (2) Å).[21]

Conclusions

We have prepared the neutral, d^6 tungsten methyl complex *trans,trans*-W(CH$_3$)(CO)$_2$(NO)(PPh$_3$)$_2$ and shown that it undergoes reactions with CO and CO_2 to give, in the former case, a simple substitution product (*mer*-W(CH$_3$)(CO)$_3$(NO)(PPh$_3$)) and, in the latter case, the product of a 1,2-insertion (*trans,trans*-W[η^1-OC(O)CH$_3$](CO)$_2$(NO)(PPh$_3$)$_2$) which is subject to facile, reversible loss of CO with concomitant coordination of the pendent carbonyl functionality of the acetate ligand to give *trans*-W(η^2-O$_2$CCH$_3$)(CO)(NO)(PPh$_3$)$_2$. Since there is no substantial CO/NO^+ disorder, the molecular structure of this bidentate acetato complex affords the unique opportunity to examine and compare in some detail the *intramolecular electronic effects of CO and NO⁺ ligands on the structure of an otherwise symmetric molecule.* We are currently exploring the scope of this type of insertion reaction with other cumulated molecules like aryl azides (R—N=N=N) and carbon suboxide (O=C=C=C=O).

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Registry No. 1, 42536-21-0; 2, 108417-91-0; 2-^{13}C, 108417-92-1; 3, 108450-82-4; 4, 108234-42-0; 5, 108215-07-2.

Supplementary Material Available: A listing of anisotropic thermal parameters, Table III (fractional coordinates and thermal parameters for H atoms), Tables IVa and Va (tabulation of bond distances and angles), a listing of least-squares planes, and a VERSORT drawing showing the labeling scheme for 5 (7 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(19) Hillhouse, G. L., unpublished results.

(20) While the differences in the metrical parameters discussed above are small, they are nonetheless real and reflect the electronic differences between coordinated NO^+ and CO. This is the only molecular structure in which such differences have been probed; that the effect of trans NO vs. trans CO is subtle is itself a noteworthy result.

(21) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599.