Organometallics **1993,** *12,* 2085–2093

Reactions of 16-Electron $Cp'M(NO)R_2$ Compounds [M = Mo, W; R = Alkyl, Aryl] with Carbon Monoxide[1,2]

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Received December 8, 1992

This paper reports the reactions of 16-electron $Cp'M(NO)R_2$ complexes [Cp′ = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = Mo, W; R = alkyl, aryl] with carbon monoxide. The reactions proceed in a stepwise fashion, and their outcomes are dependent on both the natures of Cp′ and R and the experimental conditions employed. Thus, treatment of solutions of $Cp'W(NO)R_2$ with CO under ambient conditions affords the corresponding 18-electron monoacyl species Cp′W(NO)(η^2-C{O}R)(R) (Cp′ = Cp*, R = CH_2CMe_2Ph, *p*-tolyl; Cp′ = Cp, R = CH_2CMe_2Ph, CH_2CMe_3, *p*-tolyl). An initially formed carbonyl adduct is isolable for Cp*W(NO)(*p*-tolyl)$_2$ at −38 °C, but at higher temperatures it converts to Cp*W(NO)(η^2-C{O}-*p*-tolyl)(*p*-tolyl). The atom connectivity in CpW(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) has been established by a single-crystal X-ray crystallographic analysis which was hampered by severe disorder. The cases having R = CH_2Ar (Ar = C_6H_5, C_6H_4-4-Me) are unique in that exposure of the Cp′M(NO)(CH_2Ar)$_2$ complexes to CO does not produce isolable acyl alkyl complexes but rather leads to the reductive elimination of $(ArCH_2)_2CO$ and formation of the well-known $Cp'M(NO)(CO)_2$ compounds. Upon exposure to CO at higher pressures, only the (perhydrocyclopentadienyl)tungsten monoacyl alkyl complexes undergo insertion of a second equivalent of CO, thereby affording the novel bis(acyl) complexes CpW(NO)(C{O}alkyl)$_2$, again probably via an initially formed carbonyl adduct. Such an adduct is detectable by IR spectroscopy for Cp*W(NO)(η^2-C{O}-*p*-tolyl)(*p*-tolyl), but it only persists in an atmosphere of CO. The spectroscopic properties of the CpW(NO)(C{O}alkyl)$_2$ complexes are consistent with their being stereochemically nonrigid molecules having the instantaneous 18-electron molecular structures CpW(NO)(η^2-C{O}alkyl)(η^1-C{O}alkyl). A unified rationale of how steric and electronic factors influence the eventual outcomes of the carbonylation reactions is presented.

Introduction

The migratory insertion of carbon monoxide into metal–carbon σ bonds is one of the most extensively studied reactions in organotransition-metal chemistry. The principal reason for this considerable expenditure of effort is the practical importance of both stoichiometric and catalytic carbonylation reactions in which the migratory insertion is the means by which the CO becomes activated by the transition-metal center.[3]

The prototypical example of migratory insertion of carbon monoxide is the conversion of an alkyl carbonyl complex into an acyl complex with concomitant incorporation of an external ligand, L, i.e.

$$\text{R–M–CO} + \text{L} \rightarrow \text{L–M–C\{O\}R} \qquad (1)$$

A number of mechanistic pathways are available for these reactions, the dominant path often being controlled by the nature of the solvent.[4] Much less common examples of carbon monoxide insertion are systems in which an external CO molecule is the source of the inserted CO and no incorporation of a trapping ligand is necessary for the insertion to occur, i.e.[4]

$$\text{M–R} + \text{CO} \rightarrow \text{M–C\{O\}R} \qquad (2)$$

In this paper we report the reactions of 16-electron $Cp'M(NO)R_2$ complexes [Cp′ = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = Mo, W; R = alkyl, aryl] with carbon monoxide. We have previously established that the chemistry of these complexes is dominated by their ability to form 1:1 adducts with small Lewis bases; these adducts are either isolable as such or undergo subsequent intramolecular transformations involving the hydrocarbyl ligands.[5] Hence, at the outset of this work we expected that the $Cp'M(NO)R_2$ compounds would at least react with CO to produce stable insertion products such as the acyl alkyl complexes, Cp′M(NO)(η^2-C{O}R)R. While we have found that this is indeed so in some cases, we have also discovered that the outcome of these insertion reactions is profoundly dependent on the natures of Cp′ and R. Thus, in some instances the monoinserted products are thermally unstable and re-

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[1] Organometallic Nitrosyl Chemistry. 56. For part 55, see: Legzdins, P.; McNeil, W. S.; Vessey, E. G.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1992,** *11,* 2718.

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[5] (a) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1988,** *7,* 2394 and references therein. (b) Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992,** *11,* 2583.

0276-7333/93/2312-2085$04.00/0

Table I. Elemental Analysis, Mass Spectral, and Infrared Data for Complexes 1-10

complex (compd no.)	anal. found (calcd)			MS,[a] m/z	IR,[b] cm^{-1}	
	C	H	N		ν_{NO}	ν_{CO}
Cp*W(NO)(C{O}-*p*-tolyl)(*p*-tolyl) (**1**)	53.72 (53.68)	5.17 (5.22)	2.42 (2.50)	531 $[P - CO]^+$, 501 $[P - CO - NO]^+$	1562	1526
Cp*W(NO)(C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) (**2**)	57.69 (57.86)	6.60 (6.42)	2.23 (2.18)	615 $[P - CO]^+$	1566	1547
CpW(NO)(C{O}-*p*-tolyl)(*p*-tolyl) (**3**)	48.82 (49.10)	3.91 (3.91)	2.79 (2.86)	461 $[P - CO]^+$	1592	1535
CpW(NO)(C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) (**4**)	54.54 (54.46)	5.47 (5.45)	2.43 (2.44)	545 $[P - CO]^+$, 515 $[P - CO - NO]^+$	1582	1553
CpW(NO)(C{O}CH_2CMe_3)(CH_2CMe_3) (**5**)	42.45 (42.77)	6.28 (6.06)	2.93 (3.12)	449 $[P]^+$, 434 $[P - CH_3]^+$, 421 $[P - CO]^+$	1582	1557
CpW(NO)(^{13}C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) (**6**)				574 $[P]^+$, 545 $[P - {}^{13}CO]^+$	1576	1520
CpW(NO)(^{13}C{O}CH_2CMe_3)(CH_2CMe_3) (**7**)				450 $[P]^+$, 435 $[P - CH_3]^+$, 421 $[P - {}^{13}CO]^+$	1575	1526
CpW(NO)(C{O}$CH_2CMe_2Ph)_2$ (**8**)	53.77 (53.92)	5.19 (5.20)	2.30 (2.33)	545 $[P - 2CO]^+$	1591	1633, 1552
CpW(NO)(C{O}$CH_2CMe_3)_2$ (**9**)	42.57 (42.78)	5.68 (5.70)	2.92 (2.93)	449 $[P - CO]^+$	1588	1632, 1553
CpW(NO)(C{O}{PMe_3}CH_2CMe_2Ph)-(CH_2CMe_2Ph) (**10**)	53.53 (53.63)	6.10 (6.20)	2.10 (2.16)	649 $[P]^+$, 621 $[P - CO]^+$, 545 $[P - CO - PMe_3]^+$	1493	1586

[a] Probe temperatures 80–150 °C. m/z values for the highest intensity peak of the calculated isotopic cluster. [b] Spectra are recorded in CH_2Cl_2.

ductively eliminate the ketones, R_2CO, whereas in others treatment with additional CO results in stable bis(acyl) complexes, Cp′M(NO)(C{O}R)$_2$.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen.[6] General procedures routinely employed in these laboratories have been described previously.[5b] All reagents were purchased from commercial suppliers or were prepared according to literature methods. Thus, Cp′M(NO)($CH_2Ph)_2$,[7,8] CpW(NO)R_2 [R = CH_2CMe_3, CH_2CMe_2Ph],[5a] Cp*W(NO)R_2 [R = *p*-tolyl, CH_2CMe_2Ph],[5b] and Cp*Mo(NO)($CH_2C_6H_4$-4-Me)$_2$[9] were synthesized by the published procedures. The gases CO (Matheson CP grade) and ^{13}CO (99 atom %, Sigma-Aldrich) were used as received. Solvents were dried according to conventional procedures,[10] distilled, and deaerated with argon prior to use. The column chromatographic materials used during this work were Florisil (60–100 mesh, Fisher) and silica gel 60 (230–400 mesh, Merck). Filtrations were performed through Celite 545 diatomaceous earth (Fisher) that had been oven-dried and cooled in vacuo.

A flow system for in situ IR monitoring of reactions was constructed using a Teflon diaphragm pump (Cole-Parmer 07090-62) and a NaCl IR flow cell (Wilmad 105A10-5, 0.2-mm path length).

Reaction of Cp*W(NO)(*p*-tolyl)$_2$ with CO (1 atm). A blue solution of Cp*W(NO)(*p*-tolyl)$_2$ (1.40 g, 2.63 mmol) in Et_2O (50 mL) was prepared in a flask equipped with a gas reaction bulb filled with CO (500 mL @ STP, ca. 20 mmol). The solution was cooled to −38 °C with a saturated $CaCl_2$(aq)/dry ice bath, and the CO was then admitted into the reaction flask. Over a 1-h period, the solution changed from a deep blue to a pale orange, and a pale yellow-green precipitate formed. The orange supernatant solution was removed by cannulation, and an IR spectrum of the remaining solid was recorded as a Nujol mull. This spectrum exhibited strong bands at 2014, 1603, and 1585 cm^{-1} in the region 2200–1400 cm^{-1}. As the mull warmed to room temperature, the 2014-cm^{-1} band diminished in intensity relative to the other two bands, and the color of the mull changed from yellow-green to orange. The cooling bath was removed from the solid, and after 3 h at ambient temperature, the solid had changed from yellow-green to orange. This solid was recrystallized from CH_2Cl_2/hexanes to obtain 0.66 g (45% yield) of analytically pure Cp*W(NO)(η^2-C{O}-*p*-tolyl)(*p*-tolyl) (**1**) in two fractions.

The characterization data for this and the other organometallic complexes synthesized during this work are collected in Tables I and II.

Reaction of Cp*W(NO)($CH_2CMe_2Ph)_2$ with CO (1 atm). A Schlenk tube containing a red solution of Cp*W(NO)($CH_2CMe_2Ph)_2$ (0.259 g, 0.42 mmol) in toluene (20 mL) was fitted with a gas reaction bulb filled with CO (500 mL @ STP, ca. 20 mmol). The CO in the bulb was admitted to the reaction tube, and the mixture was stirred for 6 h at room temperature whereupon it became yellow. The volume of the reaction mixture was then reduced in vacuo to about 3 mL, and hexanes (30 mL) were added. The resulting cloudy solution was left in a freezer (−10 °C) overnight to allow complete deposition of the product. The yellow precipitate that formed was collected by filtration and washed with hexanes (2 × 15 mL). This solid was dried in vacuo to obtain 0.17 g (63% yield) of Cp*W(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) (**2**).

Reaction of CpW(NO)(*p*-tolyl)$_2$ with CO (1 atm). A blue solution of CpW(NO)(*p*-tolyl)$_2$ was generated from CpW(NO)Cl_2 (0.70 g, 2.0 mmol) and Mg(*p*-tolyl)$_2$·*x*(dioxane)[5b] (2.0 mmol) in THF (25 mL) at −60 °C. The reaction solution was warmed to −10 °C and exposed to CO (1 atm) whereupon the solution quickly turned orange. The solvent was removed in vacuo, and the orange residue was extracted with CH_2Cl_2 (4 × 50 mL). The combined CH_2Cl_2 extracts were filtered through Florisil (2 × 8 cm) supported on a sintered glass frit. The filtrate was taken to dryness and was extracted with Et_2O (2 × 20 mL). These extracts were filtered through Celite (2 × 8 cm) supported on a sintered glass frit. The Et_2O filtrate was concentrated in vacuo and cooled to −10 °C to induce the crystallization of 0.038 g (4% based on CpW(NO)Cl_2) of CpW(NO)(η^2-C{O}-*p*-tolyl)(*p*-tolyl) (**3**) as orange microcrystals.

Reactions of CpW(NO)R_2 [R = CH_2CMe_2Ph, CH_2CMe_3] with CO (1 atm). Red solutions of CpW(NO)R_2 (1 mmol) in CH_2Cl_2 (15 mL) were prepared in Schlenk tubes fitted with gas reaction bulbs filled with CO (500 mL @ STP, ca. 20 mmol). After introduction of CO to the reaction vessels, the mixtures were stirred at ambient temperature for 0.5 h during which time the solutions became yellow. Removal of solvent from the yellow solutions in vacuo afforded sticky yellow powders which were dried in vacuo at 20 °C for 10 h.

In the case of R = CH_2CMe_2Ph, the resulting yellow solid was triturated with pentane (10 mL) and dried under reduced pressure for 2 h to obtain a 91% isolated yield of CpW(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) (**4**). Single crystals of this complex

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Table II. ^{1}H and ^{13}C{^{1}H} NMR Data ($\mathrm{C_6D_6}$) for Complexes 1–10

compd no.	^{1}H NMR, δ	^{13}C{^{1}H} NMR, δ
1	8.19 (d, 2H, ArH, $^3J_{\mathrm{HH}}$ = 8.0 Hz) 7.85 (d, 2H, ArH, $^3J_{\mathrm{HH}}$ = 8.0 Hz) 7.32 (d, 2H, ArH, $^3J_{\mathrm{HH}}$ = 8.0 Hz) 6.83 (d, 2H, ArH, $^3J_{\mathrm{HH}}$ = 8.0 Hz) 2.33 (s, 3H, $\mathrm{C(O)ArC}H_3$) 1.92 (s, 3H, $\mathrm{WArC}H_3$) 1.66 (s, 3H, $\mathrm{C_5(C}H_3)_5$)	279.16 (C=O) 168.22 (C_{ipso}) 147.08 (C_{para}) 139.58 (C_{arom}) 134.13 (C_{para}) 132.58 (C_{arom}) 130.10 (C_{arom}) 129.58 (C_{ipso}) 129.13 (C_{arom}) 109.56 ($C_5\mathrm{(CH_3)_5}$) 21.75 ($\mathrm{ArCH_3}$) 21.57 ($\mathrm{Ar'}C\mathrm{H_3}$) 10.11 ($\mathrm{C_5(}C\mathrm{H_3)_5}$)
2	7.78 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.2 Hz) 7.29 (t, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 7.2 Hz) 7.22 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.2 Hz) 7.16 (t, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 7.2 Hz) 7.09 (t, 1H, *p*-ArH, $^3J_{\mathrm{HH}}$ = 7.2 Hz) 7.02 (t, 1H, *p*-ArH, $^3J_{\mathrm{HH}}$ = 7.2 Hz) 3.34 (d, 1H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 13.2 Hz) 2.97 (d, 1H, $\mathrm{C(O)CH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 13.2 Hz) 2.20 (d, 1H, $\mathrm{WC}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 12.6 Hz) 1.63 (d, 1H, $\mathrm{WCH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 12.6 Hz) 1.41 (s, 15H, $\mathrm{C_5(C}H_3)_5$) 1.82, 1.68, 1.40, 1.30 (s, 4 × 3H, $\mathrm{C(C}H_3))$)	293.55 (C=O) 157.42 (C_{ipso}) 148.27 (C_{ipso}) 128.65 (C_{arom}) 128.05 (C_{arom}) 126.46 (C_{arom}) 126.20 (C_{arom}) 125.91 (C_{arom}) 124.74 (C_{arom}) 108.22 ($C_5\mathrm{(CH_3)_5}$) 54.30 ($C\mathrm{H_2}$) 53.75 ($C\mathrm{H_2}$) 44.52 (C_{quat}) 39.40 (C_{quat}) 32.49 ($\mathrm{C(}C\mathrm{H_3))}$) 30.93 ($\mathrm{C(}C\mathrm{H_3))}$) 28.87 ($\mathrm{C(}C\mathrm{H_3))}$) 28.41 ($\mathrm{C(}C\mathrm{H_3))}$) 9.60 ($\mathrm{C_5(}C\mathrm{H_3)_5}$)
3	8.23 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 9 Hz) 7.77 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 9 Hz) 7.35 (d, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 9 Hz) 6.85 (d, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 9 Hz) 5.22 (s, 5H, $\mathrm{C_5}H_5$) 2.34 (s, 3H, $\mathrm{C(O)ArC}H_3$) 1.93 (s, 3H, $\mathrm{WArC}H_3$)	
4	7.66 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.27 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.25 (t, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.15 (t, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.09 (t, 1H, *p*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.00 (t, 1H, *p*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 4.53 (s, 5H, $\mathrm{C_5}H_5$)[a] 3.21 (d, 1H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_X}$, $^2J_{\mathrm{HH}}$ = 15.0 Hz) 2.71 (d, 1H, $\mathrm{WC}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 12.9 Hz) 2.69 (d, 1H, $\mathrm{C(O)CH_A}H_{\mathrm{X}}$, $^2J_{\mathrm{HH}}$ = 15.0 Hz) 2.65 (d, 1H, $\mathrm{WCH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 12.9 Hz) 1.89, 1.80, 1.30, 1.13 (s, 4 × 3H, $\mathrm{C(C}H_3))$)	292.23 (C=O) 155.08 (C_{ipso}) 148.04 (C_{ipso}) 128.70 (C_{arom}) 128.11 (C_{arom}) 126.62 (C_{para}) 126.43 (C_{arom}) 126.30 (C_{arom}) 125.13 (C_{para}) 99.34 ($C_5\mathrm{H_5}$) 57.86 ($\mathrm{C(O)}C\mathrm{H_2}$) 44.48 ($\mathrm{W}C\mathrm{H_2}$, $^1J_{\mathrm{WC}}$ = 86 Hz) 44.18 (C_{quat}) 38.52 (C_{quat}) 35.23 ($C\mathrm{H_3}$) 31.79 ($C\mathrm{H_3}$) 30.40 ($C\mathrm{H_3}$) 27.56 ($C\mathrm{H_3}$)
5	5.01 (s, 5H, $\mathrm{C_5H_5}$)[a] 2.86 (d, 1H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 13.5 Hz) 2.55 (d, 1H, $\mathrm{C(O)CH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 13.5 Hz) 2.31 (d, 1H, $\mathrm{WC}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 13.2 Hz) 2.25 (d, 1H, $\mathrm{WCH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 13.2 Hz) 1.53 (s, 9H, $\mathrm{C(C}H_3)_3$) 0.97 (s, 9H, $\mathrm{C(C}H_3)_3$)	291.95 (C=O) 99.53 ($C_5\mathrm{H_5}$) 56.82 ($\mathrm{C(O)}C\mathrm{H_2}$) 43.35 ($\mathrm{W}C\mathrm{H_2}$) 37.77 ($C_{\mathrm{quat}}$) 34.66 ($\mathrm{C(}C\mathrm{H_3)_3}$) 33.10 ($C_{\mathrm{quat}}$) 29.85 ($\mathrm{C(}C\mathrm{H_3)_3}$)
6	7.68 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.8 Hz) 7.30, 7.27 (m, 4H, *m*,*o*-ArH, $^3J_{\mathrm{HH}}$ = 7.8 Hz) 7.18 (t, 2H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 7.8 Hz) 7.10 (t, 1H, *p*-ArH, $^2J_{\mathrm{HH}}$ = 7.8 Hz) 7.02 (t, 1H, *p*-ArH, $^3J_{\mathrm{HH}}$ = 7.8 Hz) 4.55 (s, 5H, $\mathrm{C_5}H_5$)[a] 3.24 (dd, 1H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_X}$, $^2J_{\mathrm{HH}}$ = 4.9 Hz, $^2J_{\mathrm{CH}}$ = 7.1 Hz) 2.73 (dd,[b] 1H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_X}$, $^2J_{\mathrm{HH}}$ = 14.9 Hz, $^2J_{\mathrm{CH}}$ = 4.8 Hz) 2.69 (m,[b] 2H, $\mathrm{WC}H_{\mathrm{A}}H_{\mathrm{B}}$) 1.89, 1.80, 1.31, 1.15 (s, 4 × 3H, $\mathrm{C(C}H_3))$)	292.21 (C=O, $^1J_{\mathrm{WC}}$ = 73 Hz) 155.05 (C_{ipso}) 148.06 (C_{ipso}) 128.73 (C_{arom}) 128.12 (C_{arom}) 126.60 (C_{para}) 126.44 (C_{arom}) 126.30 (C_{arom}) 125.12 (C_{para}) 99.34 ($C_5\mathrm{H_5}$) 57.82 ($\mathrm{C(O)}C\mathrm{H_2}$, $^1J_{\mathrm{CC}}$ = 28 Hz) 44.43 ($\mathrm{W}C\mathrm{H_2}$, $^1J_{\mathrm{WC}}$ = 92 Hz) 44.16 (C_{quat}) 38.51 (C_{quat}) 35.19 ($C\mathrm{H_3}$) 31.79 ($C\mathrm{H_3}$) 30.90 ($C\mathrm{H_3}$) 27.58 ($C\mathrm{H_3}$)
7	4.97 (s, 5H, $\mathrm{C_5}H_5$)[a] 2.83 (dd, 1H, $^{13}\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 13.5 Hz, $^2J_{\mathrm{CH}}$ = 7.1 Hz) 2.50 (dd, 1H, $^{13}\mathrm{C(O)CH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 13.5 Hz, $^2J_{\mathrm{CH}}$ = 4.4 Hz) 2.32 (dd, 1H, $\mathrm{WC}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 11.3 Hz, $^3J_{\mathrm{CH}}$ = 1.3 Hz) 2.26 (dd, 1H, $\mathrm{WCH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 11.3 Hz, $^3J_{\mathrm{CH}}$ = 2.4 Hz) 1.55, 0.97 (s, 2 × 9H, $\mathrm{C(C}H_3)_3$)	291.93 (C=O, $^1J_{\mathrm{WC}}$ = 72 Hz) 99.53 ($C_5\mathrm{H_5}$) 56.83 ($\mathrm{C(O)}C\mathrm{H_2}$, $^1J_{\mathrm{CC}}$ = 24 Hz) 43.35 ($\mathrm{W}C\mathrm{H_2}$) 37.77 (C_{quat}) 34.66 ($C\mathrm{(CH_3)_3}$) 33.09 (C_{quat}) 29.85 ($\mathrm{C(}C\mathrm{H_3)_3}$)
8[c]	7.43 (d, 4H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 8.1 Hz) 7.31 (t, 4H, *m*-ArH, $^3J_{\mathrm{HH}}$ = 7.8 Hz) 7.17 (t, 2H, *p*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 5.04 (s, 5H, $\mathrm{C_5H_5}$)[a] 3.49 (d, 2H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 15.9 Hz) 3.39 (d, 2H, $\mathrm{C(O)CH_{A'}}H_{\mathrm{B'}}$, $^2J_{\mathrm{HH}}$ = 15.9 Hz) 1.45 (s, 6H, $\mathrm{C(C}H_3)_{\mathrm{A}}$) 1.44 (s, 6H, $\mathrm{C(C}H_3)_{\mathrm{B}}$)	279.88 (C=O) 148.67 (C_{ipso}) 128.32 (C_{arom}) 126.01 (C_{para}) 125.90 (C_{arom}) 100.51 ($C_5\mathrm{H_5}$) 63.31 ($\mathrm{C(O)}C\mathrm{H_2}$) 38.42 ($C_{\mathrm{quat}}$) 30.49 (($C\mathrm{H_3})_{\mathrm{A}}$) 28.50 (($C\mathrm{H_3})_{\mathrm{B}}$)
9	5.11 (s, 5H, $\mathrm{C_5H_5}$)[a] 3.09 (d, 2H, $\mathrm{C(O)C}H_{\mathrm{A}}\mathrm{H_B}$, $^2J_{\mathrm{HH}}$ = 15.0 Hz) 2.39 (d, 2H, $\mathrm{C(O)CH_A}H_{\mathrm{B}}$, $^2J_{\mathrm{HH}}$ = 15.0 Hz) 1.11 (s, 18H, $\mathrm{C(C}H_3)_3$)	279.37 (C=O) 100.45 ($C_5\mathrm{H_5}$) 62.92 ($\mathrm{C(O)}C\mathrm{H_2}$) 32.51 ($C_{\mathrm{quat}}$) 30.49 (($C\mathrm{H_3})_3$)
10[d]	7.90 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.81 (d, 2H, *o*-ArH, $^3J_{\mathrm{HH}}$ = 7.5 Hz) 7.42–7.01 (m, 6H, ArH) 5.19 (s, 5H, $\mathrm{C_5H_5}$) 2.68 (d, 1H, $\mathrm{WC}H_2$, $^2J_{\mathrm{HH}}$ = 12.9 Hz) 2.37 (d, 1H, $\mathrm{WC}H_2$, $^2J_{\mathrm{HH}}$ = 12.9 Hz) 2.20 (dd, 1H, $\mathrm{C(O)C}H_2$, $^2J_{\mathrm{HH}}$ = 15.6 Hz, $^3J_{\mathrm{HP}}$ = 30.9 Hz) 2.09 (dd, 1H, $\mathrm{C(O)C}H_2$, $^2J_{\mathrm{HH}}$ = 15.6 Hz, $^3J_{\mathrm{HP}}$ = 10.8 Hz) 2.00, 1.98, 1.57, 1.31 (s, 4 × 3H, $\mathrm{C(C}H_3))$) 0.64 (d, 9H, $\mathrm{PMe_3}$, $^2J_{\mathrm{PH}}$ = 9.6 Hz)	155.41 (C_{ipso}) 149.67 (C_{ipso}) 128.33 (C_{arom}) 128.06 (C_{arom}) 127.90 (C_{arom}) 127.02 (C_{arom}) 126.26 (C_{arom}) 124.73 (C_{arom}) 58.14 (d, $^1J_{\mathrm{CP}}$ = 45.1 Hz, $C\mathrm{(O)(PMe_3)}$) 49.89 (d, $^2J_{\mathrm{CP}}$ = 26.8 Hz, $\mathrm{C(O)(PMe_3)}C\mathrm{H_2}$) 44.61 ($C_{\mathrm{quat}}$) 44.41 ($C_{\mathrm{quat}}$) 40.21 ($\mathrm{W}C\mathrm{H_2}$) 36.53, 32.79, 31.21, 29.69 (4 × $C\mathrm{H_3}$) 16.40 ($\mathrm{P(}C\mathrm{H_3)}$, $^1J_{\mathrm{CP}}$ = 13.2 Hz)

[a] A 10–20-s relaxation delay was necessary for proper integrated intensity. [b] The two overlapping signals are only partially resolved. [c] Spectra are recorded in $\mathrm{CDCl_3}$. [d] Exists in equilibrium with **4** and free $\mathrm{PMe_3}$.

suitable for an X-ray crystallographic analysis were grown by slow cooling of a saturated pentane solution.

In the case of R = $\mathrm{CH_2CMe_3}$, the yellow solid was redissolved in $\mathrm{CH_2Cl_2}$ and transferred to a Florisil column (2 × 8 cm) made up in $\mathrm{CH_2Cl_2}$. A single yellow band was eluted from this column using a 6:1 $\mathrm{CH_2Cl_2/Et_2O}$ mixture as eluant. The solvent was removed from the eluate in vacuo to obtain CpW(NO)(η^2-C{O}CH$_2$CMe$_3$)(CH$_2$CMe$_3$) (**5**) as a yellow solid (80% yield).

In Situ IR Monitoring of the Reaction of CpW(NO)(CH$_2$CMe$_2$Ph)$_2$ with CO (1 atm). A red solution of CpW(NO)(CH$_2$-

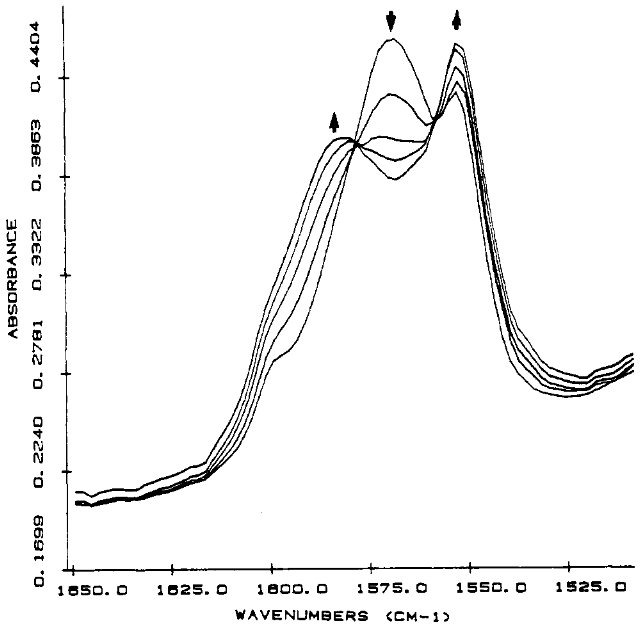

Figure 1. Spectra resulting from in situ IR monitoring of the reaction of $CpW(NO)(CH_2CMe_2Ph)_2$ with CO in CH_2Cl_2.

$CMe_2Ph)_2$ (0.55 g, 1.0 mmol) in CH_2Cl_2 (100 mL) was prepared in a 250-mL three-necked flask fitted with a gas reaction bulb filled with CO (500 mL @ STP, ca. 20 mmol) and an IR flow cell system. The flow cell was placed in the sample compartment of the IR spectrometer, and the solution was circulated through the cell. After an initial spectrum had been recorded, the reaction was started by opening the CO bulb to the reaction vessel. An IR spectrum of the reaction mixture was obtained periodically, and the collected spectra are displayed in Figure 1. The reaction was deemed to be complete after 45 min when the spectrum recorded did not differ from the preceding spectrum.

Preparation of $CpW(NO)(\eta^2\text{-}^{13}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (6) and $CpW(NO)(\eta^2\text{-}^{13}C\{O\}CH_2CMe_3)(CH_2CMe_3)$ (7). These complexes were prepared simultaneously by utilizing a single bulb of ^{13}CO. Solutions of $CpW(NO)(CH_2CMe_2Ph)_2$ (1.09 g, 2.0 mmol) and $CpW(NO)(CH_2CMe_3)_2$ (0.84 g, 2.0 mmol) were prepared in CH_2Cl_2 (45 mL each) in Schlenk tubes. The tubes were then connected to a bulb of ^{13}CO (100 mL, 4.46 mmol), and the reactions were initiated by breaking the glass break-seal on the gas bulb. The solutions were stirred for 18 h at ambient temperatures to utilize the maximum amount of ^{13}CO. At the end of that time, both solutions, although still slightly red, had noticeably lightened in color. The ^{13}CO bulb was removed, and the reaction mixtures were taken to dryness in vacuo. The two reaction residues were then worked up separately as follows.

For the neophyl complex, 6, the residue was dissolved in CH_2Cl_2 and transferred to a Florisil column (3 × 14 cm) made up in 3:1 hexanes/CH_2Cl_2. The column was eluted with mixtures of hexanes, diethyl ether, and CH_2Cl_2 so that the polarity of the eluting solvent gradually increased. A single red-orange band was eluted from the column and collected; its volume was reduced in vacuo until a precipitate began to form. The mixture was then placed in a freezer at −30 °C to complete the crystallization. Orange crystals of $CpW(NO)(\eta^2\text{-}^{13}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (6) (0.40 g, ca. 35% yield) were isolated by removal of the supernatant liquid via cannulation.

For the neopentyl complex, 7, the red residue was dissolved in a minimum of CH_2Cl_2 and transferred to the top of a Florisil column (3 × 9 cm) prepared in hexanes/CH_2Cl_2 (5:1). The column was eluted with solvent mixtures of hexanes, diethyl ether, and CH_2Cl_2 such that the polarity of the eluant gradually increased. An orange band containing the bis(neopentyl) starting material was eluted and collected first. A second yellow band was eluted, collected, and reduced in volume in vacuo until product precipitation began. This saturated solution deposited a yellow solid upon cooling in a freezer (−30 °C) overnight. $CpW(NO)(\eta^2\text{-}^{13}C\{O\}CH_2CMe_3)(CH_2CMe_3)$ (7) (0.43 g, ca. 47% yield) was isolated by removing the mother liquor via cannulation and drying the solid under reduced pressure.

General Synthetic Methodology Employed for the High-Pressure Carbon Monoxide Reactions. The following high-pressure CO reactions were all performed under similar reaction conditions. Specifically, in an inert atmosphere glovebox, a solution of the organometallic reactant in C_6H_6 (20 mL) was prepared in a Pyrex liner for a 300-mL Parr pressure reactor. The reactor was then assembled, removed from the glovebox, pressurized to 30 atm of CO, and left with its contents unstirred for 24 h. Excess CO pressure was then vented to a fumehood, and the reactor was taken back into the glovebox and disassembled. The final reaction solution was transferred into a flask and removed from the glovebox. The specific details of the workup of the individual reaction solutions are presented in the following paragraphs.

Reactions of $Cp^*W(NO)(\eta^2\text{-}C\{O\}\text{-}p\text{-tolyl})(p\text{-tolyl})$ (1) and $Cp^*W(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (2) with CO (30 atm). The reactions of 1 and 2 with CO were performed as described in the preceding paragraph. The solvent was removed from the final orange reaction solutions under reduced pressure. The IR spectrum of the remaining red-orange solid from 1 as a Nujol mull exhibited bands at 1970 (s), 1620 (m), 1605 (m), 1553 (s), 1540 (m, sh), and 1535 (m, sh) cm^{-1} in the region between 2200 and 1500 cm^{-1}. The corresponding IR spectral features of the orange solid from 2 were 2000 (s), 1733 (m), and 1606 (br) cm^{-1}. All attempts to crystallize these new materials afforded only the initial reactants, 1 and 2.

Treatment of $CpW(NO)(\eta^2\text{-}C\{O\}\text{-}p\text{-tolyl})(p\text{-tolyl})$ (3) with CO (30 atm). The treatment of 3 with CO was effected in the manner described above. Removal of solvent from the final reaction solution in vacuo afforded an orange solid. A Nujol mull IR spectrum of this solid only exhibited features diagnostic of the organometallic reactant, i.e. 1603, 1580, 1568, and 1524 cm^{-1}.

Reaction of $CpW(NO)(CH_2CMe_2Ph)_2$ with CO (30 atm). This reaction was effected in the manner described above using $CpW(NO)(CH_2CMe_2Ph)_2$ (0.50 g, 0.92 mmol). In this case, disassembly of the reactor revealed a final mixture consisting of long yellow fibers suspended in a light orange solution. The orange supernatant solution was cannulated away from the yellow solid. The solid (0.28 g) was washed with 3:1 Et_2O/hexanes (40 mL) and dried in vacuo. Removal of solvent from the supernatant solution under reduced pressure produced a yellow-brown powder. This powder was recrystallized from toluene/hexanes to obtain an additional 0.06 g of yellow product, thereby giving a 61% total isolated yield of $CpW(NO)(C\{O\}CH_2CMe_2Ph)_2$ (8) as a yellow, crystalline solid.

Reaction of $CpW(NO)(CH_2CMe_3)_2$ with CO (30 atm). This reaction was effected in the manner described above using $CpW(NO)(CH_2CMe_3)_2$ (0.56 g, 1.33 mmol). In this case, the final amber reaction solution was taken to dryness in vacuo and was redissolved in a minimum amount of toluene. The toluene solution was applied to the top of a silica column (2 × 8 cm) made up in toluene. The column was eluted with toluene/diethyl ether (1:1) whereupon a single orange band developed. This band was eluted and collected. Addition of hexanes to the eluate induced the deposition of $CpW(NO)(C\{O\}CH_2CMe_3)_2$ (9) (0.24 g, 38% yield) as a yellow solid.

Reactions of $Cp'M(NO)(CH_2Ph)_2$ [Cp = Cp, Cp*; M = Mo, W] with CO (30 atm). These reactions were all effected under similar experimental conditions. The reaction of $Cp^*Mo(NO)(CH_2Ph)_2$ with CO is described below as a representative example.

The high-pressure treatment of $Cp^*Mo(NO)(CH_2Ph)_2$ (1.32 g, 3.0 mmol) with CO was carried out in a Parr reactor (vide supra). The final amber solution was reduced to a yellow-brown, oily solid in vacuo. This solid was redissolved in pentane, and then transferred to the top of a silica gel column (2 × 8 cm) made up in pentane. The column was eluted with pentane, an operation which resulted in the elution of a single orange band which was collected and concentrated in vacuo. Cooling of this concentrated solution in a freezer (−10 °C) overnight resulted in the deposition of orange crystals (0.30 g, 32% yield) of Cp*Mo(NO)(CO)$_2$.

Anal. Calcd for $C_{12}H_{15}NO_3Mo$: C, 45.44; H, 4.77; N, 4.42. Found: C, 45.45; H, 4.80; N, 4.50. IR (Nujol mull): ν_{CO} 2000 (s), 1927 (s) cm^{-1}; ν_{NO} 1661 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.62 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 220.0 (CO), 106.1 ($C_5(CH_3)_5$), 10.4 ($C_5(CH_3)_5$). Low-resolution mass spectrum (probe temperature 80 °C): *m/z* 319 [P$^+$].

Subsequent elution of the silica column with Et_2O developed an amber band which was also collected and reduced to a amber oil in vacuo. The spectroscopic properties of this oil (0.15 g, 24% yield) were identical to those exhibited by an authentic sample of 1,3-diphenylacetone.

IR (neat): ν_{CO} 1717 (s), 754 (s), 733 (s), 698 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.20–6.90 (m, C_6H_5), 3.34 (s, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 204.8 (CO), 135.7 (C_{ipso}), 129.9 (C_{para}), 128.9 (C_{meta}), 127.0 (C_{ortho}), 49.0 (CH_2). Low-resolution mass spectrum (probe temperature 150 °C): *m/z* 210 [P$^+$].

The other Cp′M(NO)$(CH_2Ph)_2$ complexes also converted to Cp′M(NO)(CO)$_2$ and 1,3-diphenylacetone when exposed to CO under identical experimental conditions.

Reaction of Cp*Mo(NO)$(CH_2C_6H_4\text{-}4\text{-}Me)_2$ with CO (30 atm). The high-pressure treatment of Cp*Mo(NO)$(CH_2C_6H_4\text{-}4\text{-}Me)_2$ (0.60 g, 1.27 mmol) with CO was effected in the manner described above. The final amber solution was reduced to an amber-red oil in vacuo. An IR spectrum of the oil as a Nujol mull exhibited bands at 2000 (s), 1930 (m), 1726 (m), 1713 (m), 1663 (s), and 1515 (m) cm^{-1} in the region 2200–1500 cm^{-1}. The oil was dissolved in pentane and transferred to the top of a silica gel column (2 × 20 cm) made up in pentane. Elution of the column with pentane developed an orange band which was collected and concentrated in vacuo. Orange crystals (0.10 g, 25% yield) of Cp*Mo(NO)(CO)$_2$ (vide supra) were deposited from this solution upon cooling to −10 °C overnight.

Further elution of the column with Et_2O/pentane (1:1) afforded a pale yellow band which was collected and taken to dryness in vacuo. The resulting residue was recrystallized from pentane to obtain analytically pure $(4\text{-}Me\text{-}C_6H_4CH_2)_2CO$ (0.06 g, 20% yield) as a white, crystalline solid.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61; N, 0.00. Found: C, 85.68; H, 7.66; N, 0.00. IR (Nujol mull): 1726 (s), 1713 (s), 1514 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.92 (s, 8H, C_6H_4), 3.39 (s, 4H, CH_2), 2.10 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 204.0 (CO), 136.4, 131.8 (C_{ipso} and C_{para}), 129.7, 129.5 (C_{meta} and C_{ortho}), 48.6 (CH_2), 21.0 (CH_3). Low-resolution mass spectrum (probe temperature 180 °C): *m/z* 238 [P$^+$].

Preparation of CpW(NO)(C{O}{PMe$_3$}CH_2CMe_2Ph)(CH_2CMe_2Ph) (10). Excess PMe_3 was vacuum transferred into a CH_2Cl_2 (10 mL) solution of CpW(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) (4) (0.10 g, 0.17 mmol). The reaction mixture was stirred for 0.5 h whereupon the solution turned pale yellow. The final solution was taken to dryness in vacuo. The resulting solid was redissolved in 1:1 CH_2Cl_2/hexanes (20 mL) and filtered through Celite (2 × 4 cm) supported on a medium porosity glass frit. The filtrate was concentrated under reduced pressure and was placed in the freezer at −30 °C overnight to induce the precipitation of CpW(NO)(C{O}{PMe$_3$}CH_2CMe_2Ph)(CH_2CMe_2Ph) (10) as pale yellow flakes (0.07 g, 63% yield).

X-ray Crystallographic Analysis of CpW(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph). A yellow crystal of the complex was mounted in a Lindemann capillary tube using vacuum grease as adhesive. Intensity data (Mo Kα/graphite monochromator) were collected at ambient temperatures using an Enraf-Nonius CAD-4F diffractometer. The unit cell was determined from 25 well-centered reflections (14.2° ≤ 2θ ≤ 36.8°). Axial lengths were subsequently rechecked for doubled axes and lattice centering. Two intensity standards, measured every 1 h of exposure time, showed no systematic variations. The data were corrected analytically for the effects of absorption.[11] The data reduction included intensity scaling and Lorentz and polarization corrections.

The Patterson map showed an origin peak elongated in *y*. An initial (but unsatisfactory) structural model in the space group *Pcmn* was developed. Further Fourier and difference Fourier maps suggested a model with two complete complex molecules superimposed. However, this model could not account for the 28 observed weak reflections (out of 131) in the 0*kl* zone (odd *l*) with $I_o/\sigma(I_o) \geq 2.5$ with an average of 8σ which should be absent in *Pcmn*. After a variety of alternative models had been investigated, it was decided to refine the structure with a disordered model at equal occupancy in the space group $P2_12_12_1$ which required that the *c* glide plane as well as the mirror plane perpendicular to *b* be only approximately present. Because of the superimposition of the two disordered molecules, the resolution in the crystallographic data was poor, and so the model was stabilized using restraints on numerous bond lengths and angles. To keep a reasonable ratio of observations to variables, the final refinement was carried out using group refinement on the phenyl and the cyclopentadienyl groups and the temperature factors were equivalenced in a chemically reasonable way. Only the tungsten atoms were refined anisotropically with equivalenced thermal parameters according to the pseudomirror plane. The hydrogen atoms were placed in calculated positions and were given the same temperature factors as their respective carbon atoms. The maximum shift/esd ratio was smaller than 0.06 for the final cycle of refinement. The largest peak in the final difference map was 0.8 e Å^{-3}, 1.00 Å away from W(1). An empirical weighting scheme was applied such that $\langle w(|F_o|-|F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. Complex scattering factors for neutral atoms[12] were used in the calculation of the structure factors. The programs used for data reduction, structure solution, and initial refinement were from the NRC VAX Crystal Structure System.[13] The program suite CRYSTALS[14] was employed in the final refinement involing restraints. All computations were performed on a MICROVAX-II computer.

Pertinent crystallographic and experimental parameters for CpW(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) are summarized in Table III. The atomic coordinates and isotropic temperature factors for the non-hydrogen atoms of the complex are given in Table IV. Selected bond lengths (Å) and angles (deg) for the complex are presented in Table V. The remaining molecular dimensions and thermal parameters (including non-hydrogen atom parameters) for the compound are provided as supplementary material. A view of the solid-state molecular structure of CpW(NO)(η^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph) is presented in Figure 2.

Results and Discussion

The reactions of the various Cp′W(NO)R_2 complexes with carbon monoxide proceed in the stepwise fashion summarized in Scheme I. The first step involves the conversion of the 16-electron bis(alkyl) or bis(aryl) complex to the corresponding 18-electron monoacyl species, probably via an initially formed carbonyl adduct. The η^2-acyl-containing complex may be isolable as such or may undergo spontaneous reductive elimination of the symmetrical ketone. The second step involves the uptake of a second equivalent of CO and the formation of the 18-electron bis(acyl) complex, again via an initially formed carbonyl adduct. Exactly which path is followed in a particular instance is dependent upon the natures of Cp′ and R as well as the experimental conditions employed. These features are emphasized in the discussion that follows.

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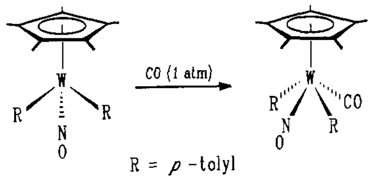
Table III. Crystallographic and Experimental Data for $CpW(NO)(C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (4)

color	yellow
formula	$C_{26}H_{31}NO_2W$
fw	573.39
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	9.158(3)
b, Å	14.603(4)
c, Å	17.230(6)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	2304
Z	4
D_x (Mg m^{-3})	1.653
$F(000)$	1135.69
μ(Mo Kα), cm^{-1}	51.40
T, K	298
cryst dimens, mm	0.20 × 0.29 × 0.33
transm factors	0.332–0.410
scan mode	$\omega/2\theta$
scan range, deg	$1.0 + 0.35 \tan\theta$
scan speed, deg/min	0.8–3.3
2θ limits, deg	$4 \leq 2\theta \leq 40$
no. of unique reflns	2064[c]
no. of reflns with $I_o > 2.0\sigma(I_o)$	1132
refined params	119
R_F[a]	0.068
R_{wF}[b]	0.058
GOF	1.02
max|shift/error|	0.06
residual density, e/Å^3	0.8(2)

[a] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] $0 \leq h \leq 8$, $0 \leq k \leq 14$, $0 \leq l \leq 16$.

Step 1: Formation of the Monoacyl Complexes. Treatment of $Cp^*W(NO)(p\text{-tolyl})_2$ with 1 atm of CO in Et_2O at −38 °C results in the formation of a yellow-green precipitate which we formulate as being the 18-electron, terminal carbonyl adduct of the starting complex (eq 3).



(3)

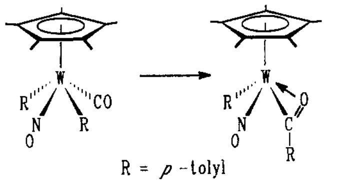
This formulation of the product is based on the presence of a distinctive IR absorption attributable to ν_{CO} = 2014 cm^{-1} in the Nujol mull IR spectrum of the green solid. Conversion 3 is also consistent with the documented ability of $Cp'M(NO)R_2$ complexes (M = Mo, W) to form 1:1 adducts with small Lewis bases.[5] The prior coordination of CO before subsequent insertion into a metal–carbon bond is generally assumed to occur during carbonylations of unsaturated alkyl complexes by external CO. However, only in a few instances have these terminal CO adducts been directly observed.[15]

As the terminal carbonyl adduct, $Cp^*W(NO)(CO)(p\text{-tolyl})_2$, warms to room temperature, the coordinated CO inserts into one of the tungsten–aryl bonds to form the corresponding red-orange acyl aryl complex, 1 (eq 4). While there are no CO adducts observed during the carbonylations of the other $Cp'W(NO)R_2$ complexes, it is likely that all the $Cp'W(NO)(\eta^2\text{-}C\{O\}R)(R)$ complexes synthesized during this work result from paths similar to that established for $Cp^*W(NO)(CO)(p\text{-tolyl})_2$ (eqs 3 and 4).

Table IV. Fractional Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for the Non-Hydrogen Atoms of $CpW(NO)(C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$[a]

atom	x/a	y/b	z/c	U(iso)
W(1)	900(6)	2786(3)	1035(1)	406
N(1)	−503(28)	2936(44)	1794(15)	575(72)
O(1)	−1417(43)	2886(45)	2292(21)	675(72)
C(1)	1275(62)	1193(9)	1081(19)	844(74)
C(2)	2635(41)	1606(24)	990(23)	844(74)
C(3)	2672(39)	2048(12)	276(30)	844(74)
C(4)	1341(63)	1925(20)	−96(8)	844(74)
C(5)	500(20)	1388(20)	403(32)	844(74)
C(10)	3260(28)	2496(20)	2708(6)	389(45)
C(11)	4588(29)	2043(24)	2616(7)	688(47)
C(12)	4818(40)	1113(24)	2762(9)	688(47)
C(13)	3595(49)	634(20)	3018(8)	688(47)
C(14)	2219(43)	1009(23)	3131(7)	688(47)
C(15)	2115(30)	1938(23)	2968(6)	688(47)
C(16)	3032(40)	3502(20)	2536(8)	688(77)
C(17)	4442(51)	4057(36)	2663(33)	763(80)
C(18)	1774(60)	3898(39)	3025(31)	763(80)
C(19)	2659(47)	3563(34)	1664(11)	640(114)
C(20)	−3026(8)	2613(18)	−170(15)	389(45)
C(21)	−3352(9)	2098(22)	487(15)	688(47)
C(22)	−3552(10)	1153(22)	481(22)	688(47)
C(23)	−3405(12)	726(18)	−237(26)	688(47)
C(24)	−3081(13)	1186(22)	−923(21)	688(47)
C(25)	−2899(10)	2129(21)	−862(15)	688(47)
C(26)	−2810(11)	3630(18)	−147(20)	485(77)
C(27)	−3842(53)	4059(37)	−750(34)	763(80)
C(28)	−3197(66)	3990(40)	666(26)	763(80)
C(29)	−1216(18)	3871(25)	−347(10)	733(136)
C(30)	−156(33)	3589(30)	274(10)	432(88)
O(2)	664(64)	4167(20)	527(27)	774(89)
W(101)	873(6)	2126(3)	956(1)	406
N(101)	−568(31)	2584(32)	1606(22)	575(72)
O(101)	−1465(40)	2701(40)	2133(24)	675(72)
C(101)	1512(64)	3682(12)	1074(15)	844(74)
C(102)	2766(33)	3205(24)	862(26)	844(74)
C(103)	2561(46)	2838(10)	127(27)	844(74)
C(104)	1179(59)	3073(23)	−139(12)	844(74)
C(105)	555(21)	3602(17)	447(34)	844(74)
C(110)	3272(31)	2476(20)	2695(6)	389(45)
C(111)	4705(31)	2756(24)	2561(7)	688(47)
C(112)	5217(38)	3652(27)	2647(9)	688(47)
C(113)	4174(50)	4286(21)	2888(9)	688(47)
C(114)	2718(47)	4090(21)	3039(7)	688(47)
C(115)	2329(34)	3179(22)	2933(6)	688(47)
C(116)	2737(42)	1503(20)	2588(8)	688(77)
C(117)	3895(62)	808(34)	2858(32)	763(80)
C(118)	1275(55)	1354(40)	3009(32)	763(80)
C(119)	2522(48)	1403(33)	1702(11)	640(114)
C(120)	−3096(8)	2396(18)	−96(15)	389(45)
C(121)	−3423(9)	2780(22)	623(15)	688(47)
C(122)	−3612(11)	3713(23)	747(20)	688(47)
C(123)	−3453(12)	4272(19)	98(25)	688(47)
C(124)	−3128(12)	3949(20)	−642(22)	688(47)
C(125)	−2958(10)	3006(21)	−711(16)	688(47)
C(126)	−2893(11)	1388(19)	−213(19)	485(77)
C(127)	−3899(55)	1065(37)	−875(33)	763(80)
C(128)	−3286(67)	868(37)	534(28)	763(80)
C(129)	−1311(18)	1188(28)	−457(10)	733(136)
C(130)	−230(31)	1386(31)	173(10)	432(88)
O(102)	613(62)	751(20)	439(27)	774(89)

[a] All atom sites have 0.5 occupancy. [b] All rings were refined as rigid groups and restraints were applied to other bond parameters.



(4)

Carbonylation of the bis(hydrocarbyl) complexes, $Cp'W(NO)R_2$, occurs irreversibly under very mild conditions in

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[15] Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. J. Chem. Soc. A 1967, 1347.

Table V. Selected Bond Lengths (Å) and Angles (deg) for $CpW(NO)(C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$[a]

W(1)-N(1)	1.85	W(101)-N(101)	1.86
W(1)-C(1)	2.35	W(101)-C(101)	2.36
W(1)-C(2)	2.35	W(101)-C(102)	2.35
W(1)-C(3)	2.35	W(101)-C(103)	2.35
W(1)-C(4)	2.36	W(101)-C(104)	2.36
W(1)-C(5)	2.34	W(101)-C(105)	2.34
W(1)-C(19)	2.25	W(101)-C(119)	2.25
W(1)-C(30)	2.01	W(101)-C(130)	2.00
W(1)-O(2)	2.21	W(101)-O(102)	2.21
W(1)-Cp1[b]	2.03	W(101)-Cp2	2.03
N(1)-O(1)	1.20	N(101)-O(101)	1.24
C(19)-W(1)-N(1)	96	C(119)-W(101)-N(101)	108
C(30)-W(1)-N(1)	93	C(130)-W(101)-N(101)	104
C(30)-W(1)-C(19)	111	O(102)-W(101)-N(101)	120
O(2)-W(1)-N(1)	96	C(130)-W(101)-C(119)	118
O(2)-W(1)-C(19)	79	O(102)-W(101)-C(119)	83
O(2)-W(1)-C(30)	33	O(102)-W(101)-C(130)	35
Cp1-W(1)-N(1)	130	Cp2-W(101)-N(101)	106
Cp1-W(1)-C(19)	112	Cp2-W(101)-C(119)	112
Cp1-W(1)-C(30)	112	Cp2-W(101)-C(130)	111
Cp1-W(1)-O(2)	129	Cp2-W(101)-O(102)	129
O(1)-N(1)-W(1)	170	O(101)-N(101)-W(101)	165

[a] These parameters were all subject to restraints during refinement and therefore no esd's are given. [b] Cp1 and Cp2 represent the center of mass of the appropriate C_5 rings.

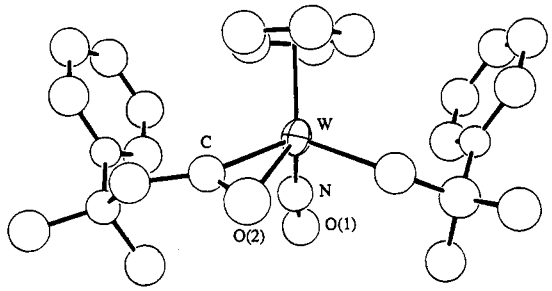


Figure 2. Solid-state molecular structure of $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (4), only one view of the disordered overlapping molecules being shown. Atoms refined isotropically are drawn as open circles; H atoms are omitted for clarity.

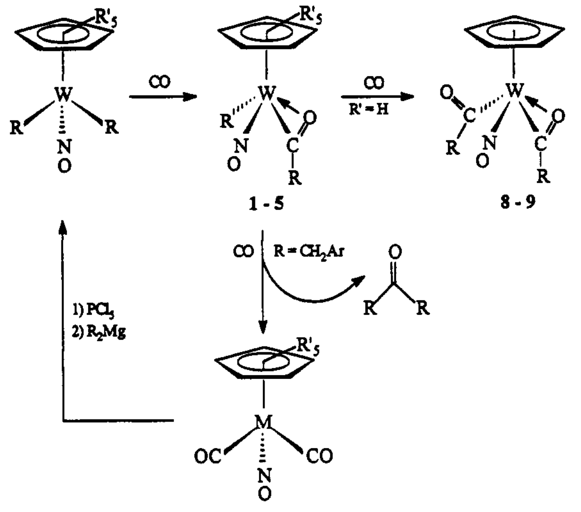
a variety of solvents to afford the monoacyl complexes, 1–5 (eq 5). These $Cp'W(NO)(\eta^2\text{-}C\{O\}R)R$ product com-

$$Cp'W(NO)(R)_2 \xrightarrow{\mathrm{CO\ (1\ atm)}} Cp'W(NO)(\eta^2\text{-}C\{O\}R)R \qquad (5)$$

plexes [Cp′ = Cp*, R = CH_2CMe_2Ph, p-tolyl; Cp′ = Cp, R = CH_2CMe_2Ph, CH_2CMe_3, p-tolyl] constitute a new family of thermally stable monoacyl organometallic compounds. The reactions of the thermally sensitive diaryl complexes with CO are best performed at lower temperatures since they are much more reactive than their congeneric dialkyl complexes. This higher reactivity has been attributed to the greater Lewis acidity of the diaryl species relative to the dialkyl complexes.[5b,16] The yellow acyl alkyl complexes and the red-orange acyl aryl complexes show reduced solubility in aliphatic hydrocarbon solvents when compared to their 16-electron precursors, but they are very soluble in aromatic and polar organic solvents.

Monitoring the carbon monoxide insertion reaction 5 by IR spectroscopy in the particular case of $CpW(NO)(CH_2CMe_2Ph)_2$ in CH_2Cl_2 demonstrates its clean conversion to $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$, as indicated by the observation of two isosbestic points (Figure 1). The monitoring of the reaction to form $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ by ^1H NMR spectroscopy in C_6D_6 also shows 100% conversion from the starting material. These observations indicate that the isolated yields of products reflect losses inherent in the workup procedures rather than incomplete formation of the product complexes.

Scheme I



Spectroscopic Properties of the Monoacyl Nitrosyl Complexes. The IR spectra of complexes 1–5 in CH_2Cl_2 (Table I) exhibit two strong bands in the region between 1595 and 1525 cm^{-1} due to the vibrations of the nitrosyl and η^2-acyl ligands. For instance, $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (4) exhibits bands at 1582 and 1553 cm^{-1} whereas the labeled complex, $CpW(NO)(\eta^2\text{-}{}^{13}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$, shows bands at 1576 and 1520 cm^{-1} in its IR spectrum. A simple two-atom harmonic oscillator model for the C–O stretch predicts a $\nu_{^{12}CO}/\nu_{^{13}CO}$ of 1.0227.[17] Using this frequency ratio, along with the $\nu_{^{13}CO}$ of 1520 cm^{-1}, a ν_{CO} of 1554 cm^{-1} would be calculated for $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$. This expected value is remarkably close to that of 1553 cm^{-1} found for one band of the unlabeled complex. Hence, this 1553-cm^{-1} band is assigned to the ν_{CO} of $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$, and by analogy, the lower energy band in the 1560–1520-cm^{-1} region is assigned to ν_{CO} for the monoacyl complexes 1–7. These ν_{CO} values (Table I) fall well within the range generally observed for η^2-acyls (1625–1453 cm^{-1}),[3] and thus all of the monoacyl complexes prepared in this work are formulated as the 18-electron species, $Cp'W(NO)(\eta^2\text{-}C\{O\}R)R$.

The ^1H NMR spectroscopic properties of the $Cp'W(NO)(\eta^2\text{-}C\{O\}R)R$ product complexes (Table II) are also consistent with their formulation as singly-inserted products. As expected, there are two different hydrocarbyl group environments for these complexes corresponding to the alkyl and acyl ligands, with the set of hydrocarbyl signals shifted to lower field being assigned to the acyl ligand due to the deshielding effect of the electron-withdrawing carbonyl group.[18] For example, the ^1H NMR spectrum of $CpW(NO)(\eta^2\text{-}C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (4) in C_6D_6 exhibits four signals due to the diastereotopic

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(16) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.*, in press.

(17) Herzberg, G. *Spectra of Diatomic Molecules*, 2nd ed.; D. Van Nostrand: New York, 1963; p 141.

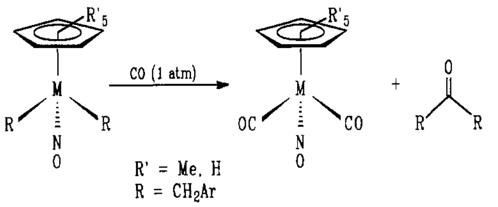
(18) (a) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. (b) Carmona, E.; Sánchez, L.; Marín, J. M.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214.

methyl groups. The inequivalent alkyl methylene protons manifest themselves as a doublet of doublets at 3.21 and 2.69 ppm ($J_{H_aH_x}$ = 15.0 Hz) whereas the inequivalent acyl methylene protons produce an AB pattern at 2.71 and 2.65 ppm ($J_{H_aH_b}$ = 13.5 Hz). The ^{1}H NMR data for the labeled complex, CpW(NO)(η^2-^{13}C{O}CH$_2$CMe$_2$Ph)-(CH$_2$CMe$_2$Ph) (**6**) (Table II), confirm the relative assignments of the methylene protons of the acyl and alkyl ligands by virtue of the different spin–spin couplings from the acyl carbon to these methylene protons. The acyl methylene protons exhibit the expected larger spin–spin coupling to the acyl carbon ($^2J_{CH}$ = 7.1 Hz) while the methylene protons of the alkyl group show the smaller coupling to the acyl carbon.[19]

The ^{13}C{^{1}H} NMR spectra of these complexes (Table II) are also consistent with the proposed η^2-acyl structures, the most important feature being the location of the resonance due to the carbon of the η^2-acyl group at 294–279 ppm for each of the acyl complexes. The chemical-shift range of this signal is more in accord with the existence of an η^2-rather than an η^1-type of acyl coordination given the generally observed range for the ^{13}C{^{1}H} signal of the η^2-acyl (i.e. 248–392 ppm)[3] ligand.

In order to establish the nature of the η^2-acyl linkage in CpW(NO)(η^2-C{O}CH$_2$CMe$_2$Ph)(CH$_2$CMe$_2$Ph), the complex was subjected to a single-crystal X-ray crystallographic analysis. Regrettably, two overlapping chemically equivalent, but crystallographically independent, molecules caused severe refinement problems of the molecular structure. Consequently, the most reliable information that can be extracted from the X-ray crystallographic study is the atom connectivity which establishes (Figure 2) that the acyl ligand is indeed coordinated to the tungsten atom in an η^2 fashion. The intramolecular metrical parameters of this monomeric complex (Table V) generally resemble those determined for other $^2\eta$-acyl complexes of the group 6 metals and are fully in accord with its formulation as an 18-valence-electron species.[18]

The Unique Case of R = CH$_2$Ar. The reactions of the bis(benzyl) complexes, Cp′M(NO)(CH$_2$Ar)$_2$ [Ar = C$_6$H$_5$, C$_6$H$_4$-4-Me], with CO do not proceed as depicted in eq 5, but rather lead to the reductive elimination of ketone and formation of the well-known dicarbonyl nitrosyl products as summarized in eq 6. These conversions occur slowly in benzene at 1 atm and ambient temperatures but are quite rapid at higher pressures of CO (e.g. 30 atm). Both the organometallic and the organic products of reaction 6 have been identified by comparison of their spectroscopic properties to those exhibited by authentic samples. We believe that reaction 6 proceeds via an intermediate acyl alkyl complex. However, unlike the other Cp′W(NO)(η^2-C{O}R)(R) complexes isolated during this work, the transient Cp′M(NO)(C{O}CH$_2$Ar)(CH$_2$Ar) species evidently eliminate (ArCH$_2$)$_2$CO spontaneously in the presence of excess CO. Since the Cp′M(NO)(CH$_2$Ar)$_2$ reagent complexes are prepared from Cp′M(NO)(CO)$_2$,[7,9] reaction 6 may be incorporated into a stoichiometric synthetic cycle, as shown in Scheme I.



(6)

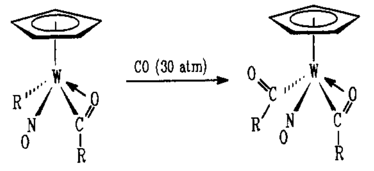
Step 2: Formation of the Bis(acyl) Complexes. Exposure of a C$_6$H$_6$ solution of Cp*W(NO)(η^2-C{O}-*p*-tolyl)(*p*-tolyl) (**1**) to elevated pressures (e.g. 30 atm) of CO results in the formation of an 18-electron 1:1 adduct, i.e.,

$$\text{Cp*W(NO)}(\eta^2\text{-C\{O\}-}p\text{-tolyl})(p\text{-tolyl}) \xrightarrow{\text{CO (30 atm)}} \text{Cp*W(NO)(CO)(C\{O\}-}p\text{-tolyl})(p\text{-tolyl}) \quad (7)$$

The formulation of the red-orange product of reaction 7 as the CO adduct is based on a terminal CO stretch at 1970 cm^{-1} evident in its Nujol mull IR spectrum.[20] This adduct is only stable under CO pressure, otherwise slowly reverting to Cp*W(NO)(η^2-C{O}-*p*-tolyl)(*p*-tolyl). Thus, all attempts to crystallize this new material afford only the reactant. The existence of the η^1-acyl ligand in the 1:1 adduct is indicated by a CO stretch in the IR spectrum at 1620 cm^{-1}.[21]

Interestingly, treatment of CpW(NO)(η^2-C{O}CH$_2$CMe$_2$Ph)(CH$_2$CMe$_2$Ph) with an excess of PMe$_3$ does not produce the related adduct CpW(NO)(C{O}CH$_2$CMe$_2$Ph)(CH$_2$CMe$_2$Ph)(PMe$_3$), but rather the ylide complex CpW(NO)-(C{O}{PMe$_3$}CH$_2$CMe$_2$Ph)(CH$_2$CMe$_2$Ph) (**10**). The existence of the ylide ligand in **10** is indicated by two spectroscopic features, namely a singlet at 22.3 ppm in the ^{31}P NMR spectrum due to the ylide PMe$_3$ fragment and a doublet at 58.14 ppm (J_{CP} = 45.1 Hz) in the ^{13}C NMR spectrum of the complex due to the ylide carbon (Table III). In these solutions, however, complex **10** exists in equilibrium (K = 0.43 at 23 °C in C$_6$D$_6$) with **4** and free PMe$_3$. It may be noted that this type of reactivity of an electrophilic dihaptoacyl group has been observed previously for the related CpMo(NO)(I)(η^2-C{O}-*p*-tolyl) complex.[22]

Upon exposure to CO at higher pressures, the cyclopentadienyl tungsten monoacyl alkyl complexes undergo insertion of a second equivalent of CO, thereby affording novel bis(acyl) complexes (eq 8). The bis(acyl) complexes probably result from initially formed CO adducts of the type CpW(NO)(C{O}alkyl)(alkyl)(CO) undergoing insertion into the remaining M–C$_{alkyl}$ bonds. For preparative purposes, the most convenient route to the bis(acyl) product complexes is via direct high-pressure carbonylation of their dialkyl precursors without isolation of the intermediate monoacyl alkyl complexes. The bis(acyl) complexes are thermally stable in solution and in the solid state, there being no evidence for the occurrence of decarbonylation processes.



(8)

4–5 **7–8**

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[19] Mann, B. E.; Taylor, B. F. *¹³C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 147.

[20] In the IR, terminal CO stretches range from 2100 to 1800 cm^{-1}. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons, Inc.: New York, 1986; p 261.

[21] (a) Hermes, A. R.; Girolami, G. S. *Organometallics* **1988**, *7*, 394. (b) Reference 4, p 107.

[22] Bonneson, P. V.; Yau, P. K. L.; Hersh, W. H. *Organometallics* **1987**, *6*, 1587.

The fact that only the cyclopentadienyl alkyl complexes undergo multiple insertions of CO can be rationalized on both steric and electronic grounds. For principally steric reasons, $CpW(NO)(CH_2CMe_2Ph)_2$ will insert 2 equiv of CO and $Cp^*W(NO)(CH_2CMe_2Ph)_2$ will not, presumably because the W center is more accessible in the former compound. For electronic reasons, $M-C_{alkyl}$ bonds are weaker than $M-C_{aryl}$ linkages and can thus be more readily cleaved during migratory insertion reactions.[23] Unlike the first insertion of CO (eq 5) which is driven primarily by the Lewis acidity of the starting bis(hydrocarbyl) complex, the second insertion evidently depends on the relative bond strengths of the remaining W–C bond since the 18-electron monoacyl reactant is not particularly Lewis acidic. In other words, the rate of the second insertion reaction (eq 8) depends principally on the relative bond strengths of a W-sp^2 vs a W-sp^3 carbon bond and not on the relative Lewis acidities of the monoacyl reactants. Consistent with this view is the fact that we have been able to isolate CpW(NO)(C{O}alkyl)$_2$ complexes but no CpW(NO)(C{O}aryl)$_2$ species during this work.

Spectroscopic Properties of the Bis(acyl) Nitrosyl Complexes 8 and 9. The most notable features in the IR spectra of complexes 8 and 9 are three strong bands in the range 1635–1550 cm^{-1} (Table I). The highest energy band for each complex is most certainly due to an η^1-acyl ligand.[21] The additional two bands can then be assigned to the nitrosyl and η^2-acyl ligands by analogy to the IR spectra of the monoacyl alkyl complexes (vide supra). These assignments lead to the description of these complexes as 18-electron species having the limiting molecular structures CpW(NO)(η^1-acyl)(η^2-acyl).

The bis(acyl) compounds exhibit intriguing ^1H NMR spectra which indicate that they are stereochemically nonrigid in solutions at ambient temperatures (Table II). Thus, the room-temperature spectra suggest the presence of symmetric molecules with identical acyl ligands, a feature apparently contrary to the η^1,η^2 configuration of the two acyl ligands indicated by their IR spectra. Consequently, it appears that the two acyl ligands are fluxional, with the acyl oxygen atoms quickly exchanging from η^1- to η^2-coordination in concert, thereby resulting in an NMR spectrum which is the time average of the two possible coordination geometries. The variable-temperature ^1H NMR spectra of $CpW(NO)(C\{O\}CH_2CMe_2Ph)_2$ confirm that the complex is still fluxional down to −50 °C.

The $^{13}C\{^1H\}$ NMR spectra of the bis(acyl) complexes, CpW(NO)(C{O}R)$_2$, also reveal a symmetric coordination mode for the acyl ligands. The signals for the acyl carbons in the bis(acyl) complexes are shifted ≈10 ppm upfield relative to the acyl carbons of the monoacyl alkyl complexes (Table II). This shift is a manifestation of fluxional η^1,η^2 bis(acyl) complexes, the observed chemical shift of the acyl carbon signal being roughly the average of the normal chemical shift for a tungsten η^2-acyl signal (≈292 ppm, vide supra) and a tungsten η^1-acyl signal (240–250 ppm).[19]

An X-ray crystallographic investigation[24] of $CpW(NO)(C\{O\}CH_2CMe_2Ph)_2$ indicates that its solid-state molecular structure does indeed possess the predicted η^1,η^2 bis(acyl) coordination mode around the metal center.[25] However there is a great deal of disorder in the alkyl residues, a problem which precludes refinement of the data below an R_F of 0.130. Although this level of refinement allows the gross connectivity of the ligands around the metal to be determined with some certainty, it is not sufficient to allow accurate metrical data to be derived and commented upon.

Epilogue

These studies have shown that the products obtained from the carbonylation of various $Cp'W(NO)R_2$ complexes are very dependent upon the nature of the ancillary ligands and the experimental conditions employed. The nature of the cyclopentadienyl ligand determines the extent of the reactivity, with only the Cp complexes inserting a second equivalent of CO. The nature of the hydrocarbyl group influences the rate of the reaction such that the greater Lewis acidity of the diaryl complexes results in their forming monoacyl products faster than do the related dialkyl complexes. However, only the monoacyl alkyl complexes possess a sufficiently weak M–C σ bond to undergo a second insertion of CO to form bis(acyl) species. The nature of the hydrocarbyl ligand also plays an influential role in the case when R = CH_2Ar in that putative reductive elimination of ketone occurs from the undetectable monoacyl intermediate complex. The steric and electronic factors mitigating this set of reactions allows us, in principle, the opportunity to fine tune the reaction conditions so as to obtain specific carbonylation products. The first step toward attaining this goal is to determine whether the insertions of CO into the asymmetric complexes Cp*W(NO)(R)(R′) occur regioselectively. Our results in this regard are presented in the following paper in this issue.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P. Legzdins, and F.W.B.E. and a postgraduate scholarship to N.H.D.

Supplementary Material Available: Tables of remaining molecular dimensions and thermal parameters (including non-hydrogen atom parameters) for $CpW(NO)(C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph)$ (2 pages). Ordering information is given on any current masthead page.

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[23] Debad, J. D.; Legzdins, P. *Organometallics*, following paper in this issue.

[24] Yee, V. C. University of British Columbia, personal communication. Some selected bond distances (Å) are W–N, 1.97(4); W–C1, 1.95(5); W–C2, 2.33(5); W–O1, 2.31; and W–O2, 2.84(5).

[25] A related acyl complex, CpMo(NO)(I)(C{O}-*p*-tolyl) has been shown to have an η^2-acyl ligand with a similar coordination geometry with the acyl oxygen bonding trans to the NO ligand.[22]