

# Synthesis and Characterization of the Asymmetric Complexes $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{R}') [R, R' = \text{Alkyl, Aryl}]$ and Regioselective Insertions of CO into Their W-C $\sigma$ Bonds<sup>1</sup>

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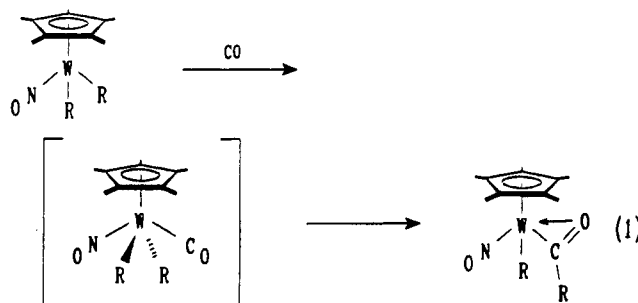
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Treatment of  $\text{Cp}^*\text{W}(\text{NO})(\text{Cl})_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) with 0.5 equiv of a  $\text{R}_2\text{Mg}\cdot x$  (dioxane) reagent ( $\text{R} = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ , Ph, *o*-tolyl) results in the formation of the alkyl and aryl chloro complexes  $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{Cl})$ , which have been isolated and fully characterized. Metathesis of these complexes with 0.5 equiv of another  $\text{R}'_2\text{Mg}\cdot x$  (dioxane) reagent ( $\text{R}' = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ , Me, Ph, *o*-tolyl) affords a series of 16-electron, mixed alkyl and aryl complexes,  $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{R}')$ , having all ten combinations of  $\text{R} \neq \text{R}'$ . These complexes have been characterized by conventional spectroscopic methods. The competitive reactivity of the different tungsten-carbon  $\sigma$  bonds in these species toward CO insertion has been investigated. Each complex reacts with 1 equiv of CO under ambient conditions to produce the corresponding  $\eta^2$ -acyl complex presumably via an initial carbonyl adduct. An X-ray diffraction analysis of  $\text{Cp}^*\text{W}(\text{NO})(\text{Ph})(\eta^2\text{-C(O)CH}_2\text{CMe}_3)$  has been performed to confirm the existence of the  $\eta^2$ -acyl linkage in one of these complexes: space group  $P2_1/n$ ,  $a = 11.759(3)$  Å,  $b = 16.028(3)$  Å,  $c = 12.022(2)$  Å,  $\beta = 107.95(2)^\circ$ ,  $Z = 4$ ,  $V = 2155.5$  Å<sup>3</sup>,  $R_F = 0.024$  for 3249 data ( $I_o \geq 2.5\sigma(I_o)$ ). These 18-electron acyl compounds are isolable except in the cases when the CO insertion occurs into a W- $\text{CH}_2\text{-SiMe}_3$  linkage. All complexes containing a (trimethylsilyl)methyl ligand form enolate species,  $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{OC}\{\equiv\text{CH}_2\}\text{SiMe}_3)$  upon reaction with CO, probably via formation of an intermediate acyl complex and subsequent rearrangement via a 1,2-silyl shift. The relative migratory aptitudes of the alkyl and aryl ligands have been established by conclusive identification of the inserted products. In order of decreasing migratory aptitude, the trend is  $\text{CH}_2\text{CMe}_3 > \text{CH}_2\text{SiMe}_3 > \textit{o}$ -tolyl > Ph > Me. The migratory aptitude of the various ligands appears to be primarily a function of the steric bulk of the ligand, the most sterically demanding ligands migrating to CO preferentially.

## Introduction

In previous work we have established that the monomeric  $\text{Cp}^*\text{M}(\text{NO})(\text{R})_2$  systems [ $\text{Cp}' = \text{Cp}$  ( $\eta^5\text{-C}_5\text{H}_5$ ),  $\text{Cp}^*$  ( $\eta^5\text{-C}_5\text{Me}_5$ );  $\text{M} = \text{Mo, W}$ ;  $\text{R} = \text{alkyl, aryl}$ ] constitute a unique family of 16-electron complexes possessing three-legged, piano-stool molecular structures.<sup>2</sup> The characteristic chemistry of these species is dominated by their ability to act as Lewis acids. Consequently, they form 1:1 adducts with small Lewis bases, and these adducts are either isolable as such or undergo subsequent intramolecular transformations involving the hydrocarbyl ligands. For instance, as we describe in the preceding paper in this issue, these complexes initially react with carbon monoxide in the manner summarized in eq 1. The intermediate CO adduct complexes are occasionally detectable spectroscopically.



A long-standing goal during our work with  $\text{Cp}^*\text{M}(\text{NO})(\text{R})_2$  complexes has been to develop a general synthetic route to mixed hydrocarbyl complexes of the type  $\text{Cp}^*\text{M}(\text{NO})(\text{R})(\text{R}')$  ( $\text{R, R}' = \text{alkyl, aryl}$ ) since such compounds would permit us to compare directly the relative reactivity of the two different M-C  $\sigma$  bonds at the same metal center. The attainability of this goal was indicated by our previous isolation of such mixed complexes during continuing

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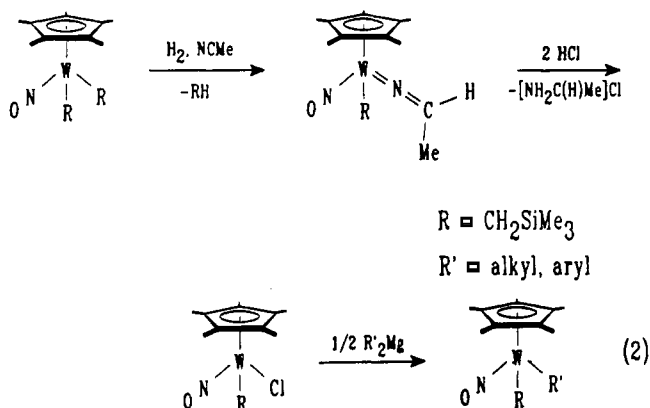
Table I. Numbering Scheme, Color, Yield, and Elemental Analysis Data for Complexes 1-14, Cp\*W(NO)(R)(X)

R	X	compd no.	color (yield %)	anal. found (calcd)		
				C	H	N
CH <sub>2</sub> SiMe <sub>3</sub>	Cl	1	violet (62%)	35.64 (35.97)	5.56 (5.59)	2.97 (2.92)
CH <sub>2</sub> CMe <sub>3</sub>	Cl	2	purple (53%)	39.54 (39.25)	5.75 (5.80)	3.07 (2.89)
<i>o</i> -tolyl	Cl	3	blue (40%)	42.92 (43.20)	4.66 (4.90)	2.95 (2.86)
Ph	Cl	4	blue (49%)	41.63 (42.10)	4.37 (4.47)	3.03 (3.10)
CH <sub>2</sub> SiMe <sub>3</sub>	CH <sub>3</sub>	5	violet (38%)	39.92 (39.76)	6.48 (6.49)	3.10 (3.11)
CH <sub>2</sub> SiMe <sub>3</sub>	<i>o</i> -tolyl	6	violet (31%)	47.82 (48.08)	6.31 (6.36)	2.66 (2.73)
CH <sub>2</sub> SiMe <sub>3</sub>	Ph	7	purple (38%)	46.79 (47.11)	6.09 (6.24)	2.73 (2.56)
CH <sub>2</sub> SiMe <sub>3</sub>	CH <sub>2</sub> CMe <sub>3</sub>	8	maroon (79%)	44.97 (44.72)	7.35 (7.29)	2.76 (2.87)
CH <sub>2</sub> CMe <sub>3</sub>	CH <sub>3</sub>	9	red (53%)	44.15 (43.67)	6.72 (6.54)	3.22 (3.36)
CH <sub>2</sub> CMe <sub>3</sub>	<i>o</i> -tolyl	10	purple (44%)	51.67 (51.93)	6.50 (6.55)	2.74 (2.72)
CH <sub>2</sub> CMe <sub>3</sub>	Ph	11	red (55%)	50.72 (50.68)	6.28 (6.38)	2.82 (2.78)
<i>o</i> -tolyl	CH <sub>3</sub>	12	violet (13%)	47.49 (47.60)	5.54 (5.40)	3.08 (2.99)
<i>o</i> -tolyl	Ph	13	blue (20%)	53.40 (53.43)	5.26 (5.31)	2.71 (2.80)
Ph	CH <sub>3</sub>	14	purple (-)			

Table II. Numbering Scheme, Color, Yield, and Elemental Analysis Data for the Carbonylation Products 5'-14', Cp\*W(NO)(R)(X)

R	X	compd no.	color (yield %)	anal. found (calcd)		
				C	H	N
CH <sub>3</sub>	OC(CH <sub>2</sub> )SiMe <sub>3</sub>	5'	colorless (45%)	40.09 (40.14)	6.10 (6.17)	2.92 (2.97)
<i>o</i> -tolyl	OC(CH <sub>2</sub> )SiMe <sub>3</sub>	6'	colorless (24%)	47.57 (47.27)	5.99 (5.83)	2.52 (2.56)
Ph	OC(CH <sub>2</sub> )SiMe <sub>3</sub>	7'	colorless (20%)	46.58 (46.83)	5.77 (5.85)	2.59 (2.54)
CH <sub>2</sub> SiMe <sub>3</sub>	C(O)CH <sub>2</sub> CMe <sub>3</sub>	8'	orange (46%)	44.69 (44.67)	6.94 (7.07)	2.61 (2.54)
CH <sub>3</sub>	C(O)CH <sub>2</sub> CMe <sub>3</sub>	9'	yellow (88%)	44.07 (43.91)	6.31 (6.48)	3.02 (2.97)
<i>o</i> -tolyl	C(O)CH <sub>2</sub> CMe <sub>3</sub>	10'	yellow (50%)	51.21 (50.95)	6.17 (6.24)	2.60 (2.55)
Ph	C(O)CH <sub>2</sub> CMe <sub>3</sub>	11'	yellow (95%)	50.29 (50.53)	5.95 (5.90)	2.67 (2.74)
CH <sub>3</sub>	C(O)- <i>o</i> -tolyl	12'	orange (52%)	47.22 (46.98)	5.21 (5.32)	2.90 (3.01)
Ph	C(O)- <i>o</i> -tolyl	13'	orange (75%)	52.86 (52.59)	4.99 (4.98)	2.57 (2.54)
CH <sub>3</sub>	C(O)Ph	14'	orange (10%)	45.16 (46.07)	4.90 (4.94)	2.88 (2.99)

investigations of the characteristic chemistry of Cp\*W-(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (eq 2).<sup>3</sup> However, this synthetic route



to the mixed hydrocarbyl complexes is cumbersome since it involves four steps from Cp\*W(NO)(Cl)<sub>2</sub>. It is also not generally applicable for the synthesis of a wide range of such compounds, only Cp\*W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(R) complexes being accessible in this manner if Cp\*W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> is the initial reactant.

In this paper we report a new and general, two-step synthetic methodology for the preparation of 16-electron Cp\*W(NO)(R)(R') complexes with a variety of alkyl and aryl ligands. As the initial step in the investigation of the chemical properties of these species, we have studied their reactivity toward carbon monoxide in order to establish the relative migratory aptitudes of the different  $\sigma$ -bound hydrocarbyl groups. The results obtained during this study not only contribute to the fundamental knowledge of such M-C  $\sigma$  bond reactivity<sup>4</sup> but also constitute an essential first step in our eventual tailoring of the reactivity of Cp\*M(NO)(R)(R') complexes in general.

## Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions in an atmosphere of prepurified argon. Conventional drybox and vacuum-line Schlenk techniques were utilized throughout.<sup>5</sup> General procedures routinely employed in these laboratories have been described in detail previously.<sup>6</sup> All reagents were purchased from commercial suppliers or were prepared according to literature methods. Thus, Cp\*W(NO)(Cl)<sub>2</sub> and R<sub>2</sub>Mg·x(dioxane) reagents<sup>6</sup> were synthesized by the published procedures. The gases CO (Matheson CP grade) and <sup>13</sup>CO (99 atom %, Sigma-Aldrich) were used as received.

**General Synthetic Procedures Employed during This Study.** Many of the new complexes described in this paper were synthesized using similar methodology. The syntheses are therefore grouped accordingly, with a representative example being described for each procedure. All solid reagents such as Cp\*W(NO)(Cl)<sub>2</sub> and R<sub>2</sub>Mg·x(dioxane) were weighed into a Schlenk tube contained in a glovebox. A magnetic stirbar was added, the tube was removed from the box, and subsequent chemistry was performed on a vacuum line. Unless indicated otherwise, solvents were added via syringe to the reaction vessel. Isolated yields for all products are listed in Tables I and II, and the spectroscopic and physical properties of all complexes are collected in Tables III-VI.

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Table III. NMR Data for Complexes 1–13

compd	<sup>1</sup> H NMR, δ <sup>d</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR, δ
1 <sup>a</sup>	2.00 (m, 2H, CH <sub>2</sub> ), 1.94 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 0.12 (s, 9H, SiMe <sub>3</sub> )	113.48 (C <sub>5</sub> Me <sub>5</sub> ), 63.62 (CH <sub>2</sub> ), 10.30 (C <sub>5</sub> Me <sub>5</sub> ), 1.38 (SiMe <sub>3</sub> )
2 <sup>b</sup>	3.42 (d (6), 1H, CH <sub>2</sub> ), 1.61 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.37 (s, 9H, CMe <sub>3</sub> ), -0.027 (d (6), 1H, CH <sub>2</sub> )	112.63 (C <sub>5</sub> Me <sub>5</sub> ), 96.59 (CH <sub>2</sub> ), 39.02 (CMe <sub>3</sub> ), 33.72 (CMe <sub>3</sub> ), 9.75 (C <sub>5</sub> Me <sub>5</sub> )
3 <sup>c</sup>	7.50 (m, 2H, <i>m/p</i> -ArH), 7.37 (m, 1H, <i>m</i> -ArH), 7.2 (br, 1H, <i>o</i> -ArH), 2.74 (s br, 3H, Me), 2.26 (s, 15H, C <sub>5</sub> Me <sub>5</sub> )	130.67, 129.65, 122.31 (Ar), 114.54 (C <sub>5</sub> Me <sub>5</sub> ), 25.41 (Me), 10.13 (C <sub>5</sub> Me <sub>5</sub> )
4 <sup>c</sup>	7.43 (m, 2H, <i>m</i> -ArH), 7.25 (m, 3H, <i>o/p</i> -ArH), 1.91 (s, 15H, C <sub>5</sub> Me <sub>5</sub> )	132.53, 128.84, 127.80 (Ar), 114.52 (C <sub>5</sub> Me <sub>5</sub> ), 10.07 (C <sub>5</sub> Me <sub>5</sub> )
5 <sup>b</sup>	2.03 (d (12), 1H, CH <sub>2</sub> ), 1.47 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.02 (d (12), 1H, CH <sub>2</sub> ), 0.57 (s, 3H, Me), 0.36 (s, 9H, SiMe <sub>3</sub> )	109.91 (C <sub>5</sub> Me <sub>5</sub> ), 72.47 (Me), 41.31 (CH <sub>2</sub> ), 9.67 (C <sub>5</sub> Me <sub>5</sub> ), 2.58 (SiMe <sub>3</sub> )
6 <sup>b</sup>	7.30 (m, 4H, Ar), 2.78 (br 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.56 (s, 18H, C <sub>5</sub> Me <sub>5</sub> + Me), 0.23 (s, 9H, SiMe <sub>3</sub> )	129.96, 128.97, 122.87 (Ar), 112.17 (C <sub>5</sub> Me <sub>5</sub> ), 26.05 (C <sub>6</sub> H <sub>4</sub> Me), 10.25 (C <sub>5</sub> Me <sub>5</sub> ), 2.37 (SiMe <sub>3</sub> )
7 <sup>b</sup>	7.71 (d (6), 2H, <i>o</i> -ArH), 7.2 (m, 3H, <i>m/p</i> -ArH), 2.25 (d (15), 1H, CH <sub>2</sub> ), 1.60 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 0.30 (s, 9H, SiMe <sub>3</sub> ), -0.55 (d (15), 1H, CH <sub>2</sub> )	188.93, 134.45, 128.47, 127.77 (Ar), 11.45 (C <sub>5</sub> Me <sub>5</sub> ), 71.76 (CH <sub>2</sub> ), 9.96 (C <sub>5</sub> Me <sub>5</sub> ), 2.85 (SiMe <sub>3</sub> )
8 <sup>b</sup>	3.28 (d (15), 1H, CH <sub>2</sub> ), 1.54 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.35 (s, 9H, CMe <sub>3</sub> ), 1.07 (d (12), 1H, CH <sub>2</sub> ), 0.38 (s, 9H, SiMe <sub>3</sub> ), -1.32 (d (12), 1H, CH <sub>2</sub> ), -2.08 (d (15), 1H, CH <sub>2</sub> )	109.91 (C <sub>5</sub> Me <sub>5</sub> ), 105.77 (CH <sub>2</sub> CMe <sub>3</sub> ), 51.13 (CH <sub>2</sub> SiMe <sub>3</sub> ), 39.82 (CMe <sub>3</sub> ), 34.24 (CMe <sub>3</sub> ), 9.87 (C <sub>5</sub> Me <sub>5</sub> ), 2.86 (SiMe <sub>3</sub> )
9 <sup>b</sup>	4.13 (d (18), 1H, CH <sub>2</sub> ), 1.52 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.34 (s, 9H, CMe <sub>3</sub> ), 0.54 (s, 3H, Me), -3.55 (d (18), 1H, CH <sub>2</sub> )	120.91 (CH <sub>2</sub> ), 109.56 (C <sub>5</sub> Me <sub>5</sub> ), 40.27 (CMe <sub>3</sub> ), 33.93 (CMe <sub>3</sub> ), 29.23 (Me), 9.70 (C <sub>5</sub> Me <sub>5</sub> )
10 <sup>b</sup>	7.16 (d (6), 1H, <i>o</i> -ArH), 7.0 (m, 3H, <i>m/p</i> -ArH), 2.7 (br, 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.52 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.43 (s, 9H, CMe <sub>3</sub> )	130.61, 128.17, 123.0 (br, Ar), 110.93 (C <sub>5</sub> Me <sub>5</sub> ), 40.9 (br, CMe <sub>3</sub> ), 34.17 (CMe <sub>3</sub> ), 27.2 (br, C <sub>6</sub> H <sub>4</sub> Me), 9.86 (C <sub>5</sub> Me <sub>5</sub> )
11 <sup>b</sup>	7.69 (d (6), 2H, <i>o</i> -ArH), 7.1 (m, 3H, <i>m/p</i> -ArH), 4.48 (d (15), 1H, CH <sub>2</sub> ), 1.53 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.22 (s, 9H, CMe <sub>3</sub> ), -2.07 (d (15), 1H, CH <sub>2</sub> )	182.14 (Ar), 137.24, 128.02, 127.64, 122.25 (CH <sub>2</sub> ), 110.90 (C <sub>5</sub> Me <sub>5</sub> ), 41.28 (CMe <sub>3</sub> ), 33.99 (CMe <sub>3</sub> ), 10.00 (C <sub>5</sub> Me <sub>5</sub> )
12 <sup>b</sup>	7.25 (m, 3H, <i>o/m</i> -ArH), 6.72 (d (6), 1H, <i>p</i> -ArH), 2.68 (s, 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.44 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.13 (s, 3H, Me)	149.20, 130.06, 129.33, 129.28, 122.63, 115.98 (Ar), 110.81 (C <sub>5</sub> Me <sub>5</sub> ), 41.06 (Me), 26.10 (C <sub>6</sub> H <sub>4</sub> Me), 9.85 (C <sub>5</sub> Me <sub>5</sub> )
13 <sup>b</sup>	8.16 (d (6), 2H, ArH), 7.97 (d (6), 1H, ArH), 7.1 (m, 6H, ArH), 2.83 (s, 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.58 (s, 15H, C <sub>5</sub> Me <sub>5</sub> )	150.43, 141.54, 130.06, 135.41, 129.98, 129.56, 127.93, 122.84, 119.81 (Ar), 112.14 (C <sub>5</sub> Me <sub>5</sub> ), 26.80 (C <sub>6</sub> H <sub>4</sub> Me), 10.01 (C <sub>5</sub> Me <sub>5</sub> )

<sup>a</sup> CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> CDCl<sub>3</sub>. <sup>d</sup> J<sub>H-H</sub> values (in Hz) are given in parentheses following multiplicities.

Table IV. NMR Data for Complexes 5'–14'

compd	<sup>1</sup> H NMR, δ <sup>d</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR, δ <sup>d</sup>
5' <sup>b</sup>	4.37 and 5.80 (s, 1H each, CH <sub>2</sub> ), 1.73 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.15 (s, 3H, Me), 0.82 (s, 9H, SiMe <sub>3</sub> )	182.82 (C=CH <sub>2</sub> ), 111.02 (C <sub>5</sub> Me <sub>5</sub> ), 66.35 (CH <sub>2</sub> ), 15.40 (Me), 10.28 (C <sub>5</sub> Me <sub>5</sub> ), -1.21 (SiMe <sub>3</sub> )
6' <sup>b</sup>	7.77 (d (6), 1H, <i>o</i> -ArH), 7.2 (m, 3H, <i>m/p</i> -ArH), 4.30 and 5.93 (s, 1H each, CH <sub>2</sub> ), 2.63 (s, 3H, Me), 1.68 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 0.04 (s, 9H, SiMe <sub>3</sub> )	184.85 (C=CH <sub>2</sub> ), 171.43 (ipso-Ar), 147.05, 139.56, 129.51, 125.72, 124.93 (Ar), 112.66 (C <sub>5</sub> Me <sub>5</sub> ), 66.26 (CH <sub>2</sub> ), 28.03 (C <sub>6</sub> H <sub>4</sub> Me), 10.70 (C <sub>5</sub> Me <sub>5</sub> ), -1.18 (SiMe <sub>3</sub> )
7' <sup>b</sup>	8.03 (t (8), 2H, <i>o</i> -ArH), 7.37 (t (8), 2H, <i>m</i> -ArH), 7.2 (t (8), 1H, <i>p</i> -ArH), 4.37 and 5.97 (s, 1H each, CH <sub>2</sub> ), 1.69 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 0.00 (s, 9H, SiMe <sub>3</sub> )	169.5 (ipso-Ar, <sup>1</sup> J <sub>WC</sub> = 118), 139.8, 127.8, 125.5 (Ar), 112.50 (C <sub>5</sub> Me <sub>5</sub> ), 67.18 (CH <sub>2</sub> ), 10.72 (C <sub>5</sub> Me <sub>5</sub> ), -1.20 (SiMe <sub>3</sub> )
8' <sup>b</sup>	2.64 and 3.35 (d (13), 1H each, CH <sub>2</sub> CMe <sub>3</sub> ), 1.58 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.03 (s, 9H, CMe <sub>3</sub> ), 0.48 (s, 9H, SiMe <sub>3</sub> ), -0.07 and 0.36 (d (13), 1H each, CH <sub>2</sub> SiMe <sub>3</sub> )	294.8 (C=O, <sup>1</sup> J <sub>WC</sub> = 77), 108.32 (C <sub>5</sub> Me <sub>5</sub> ), 53.48 (CH <sub>2</sub> CMe <sub>3</sub> ), 33.63 (CMe <sub>3</sub> ), 30.04 (CMe <sub>3</sub> ), 14.76 (CH <sub>2</sub> SiMe <sub>3</sub> , <sup>1</sup> J <sub>WC</sub> = 87, <sup>1</sup> J <sub>WSi</sub> = 51), 9.88 (C <sub>5</sub> Me <sub>5</sub> ), 3.46 (SiMe <sub>3</sub> )
9' <sup>b</sup>	2.78 and 3.06 (d (13), 1H each, CH <sub>2</sub> ), 1.67 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.27 (s, 3H, Me), 1.09 (s, 9H, CMe <sub>3</sub> )	296.22 (C=O), 108.90 (C <sub>5</sub> Me <sub>5</sub> ), 53.44 (CH <sub>2</sub> ), 33.33 (CMe <sub>3</sub> ), 29.98 (CMe <sub>3</sub> ), 11.04 (Me, <sup>1</sup> J <sub>WC</sub> = 88), 9.74 (C <sub>5</sub> Me <sub>5</sub> )
10' <sup>a</sup>	7.16 (d (6), 1H, <i>o</i> -ArH), 7.0 (m, 3H, <i>m/p</i> -ArH), 3.07 and 3.57 (d (12), 1H each, CH <sub>2</sub> ), 2.34 (br, 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.87 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.13 (s, 9H, CMe <sub>3</sub> )	295.2 (br, C=O), 148.0 (br), 138.85 (br), 129.98, 125.48, 123.79 (Ar), 110.28 (C <sub>5</sub> Me <sub>5</sub> ), 53.67 (CH <sub>2</sub> ), 33.98 (CMe <sub>3</sub> ), 30.08 (CMe <sub>3</sub> ), 10.24 (C <sub>5</sub> Me <sub>5</sub> )
11' <sup>a</sup>	7.65 (d (6), 2H, <i>o</i> -ArH), 7.26 (t (6), 2H, <i>m</i> -ArH), 7.12 (t (6), 1H, <i>p</i> -ArH), 3.11 and 3.46 (d (12), 1H each, CH <sub>2</sub> ), 1.84 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.14 (s, 9H, CMe <sub>3</sub> )	297.0 (C=O), 171.52 (ipso-Ar), 139.18, 127.87, 125.02 (Ar), 110.31 (C <sub>5</sub> Me <sub>5</sub> ), 53.47 (CH <sub>2</sub> ), 33.88 (CMe <sub>3</sub> ), 30.04 (CMe <sub>3</sub> ), 10.22 (C <sub>5</sub> Me <sub>5</sub> )
12' <sup>a</sup>	7.97 (d (7), 1H, <i>o</i> -ArH), 7.62 (t (7), 1H, <i>m</i> -ArH), 7.51 (t (7), 1H, <i>p</i> -ArH), 7.41 (d (7), 1H, <i>m</i> -ArH), 2.65 (s, 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.85 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 0.73 (s, 3H, Me)	282.8 (C=O), 181.0 (ipso-Ar), 141.0, 136.53, 135.48, 131.85, 127.06 (Ar), 109.30 (C <sub>5</sub> Me <sub>5</sub> ), 20.36 (C <sub>6</sub> H <sub>4</sub> Me), 10.50 (Me, <sup>1</sup> J <sub>WC</sub> = 90), 9.99 (C <sub>5</sub> Me <sub>5</sub> )
13' <sup>a</sup>	8.07 (d (8), 1H, ArH), 7.79 (d (8), 2H, ArH), 7.66 (t (8), 1H, ArH), 7.55 (t (8), 1H, ArH), 7.44 (d (8), 1H, ArH), 7.29 (t (7), 2H, <i>o</i> -C <sub>6</sub> H <sub>5</sub> ), 7.12 (t (7.5), 1H, <i>o</i> -C <sub>6</sub> H <sub>4</sub> Me), 2.74 (s, 3H, C <sub>6</sub> H <sub>4</sub> Me), 1.79 (s, 15H, C <sub>5</sub> Me <sub>5</sub> )	281.9 (C=O), 153.0 (ipso-C <sub>6</sub> H <sub>4</sub> Me), 149.2 (ipso-C <sub>6</sub> H <sub>5</sub> ), 139.63 ( <i>o</i> -C <sub>6</sub> H <sub>5</sub> ), 136.38 ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Me), 135.00, 131.48, 127.69, 126.67, 125.26 (Ar), 109.61 (C <sub>5</sub> Me <sub>5</sub> ), 20.23 (C <sub>6</sub> H <sub>4</sub> Me), 9.87 (C <sub>5</sub> Me <sub>5</sub> )
14' <sup>b</sup>	7.91 (d (7), 2H, <i>o</i> -ArH), 7.1 (m, 3H, <i>m/p</i> -ArH), 1.62 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.30 (s, 3H, Me)	280.63 (C=O), 135.13, 131.96, 129.28, 127.68 (Ar), 108.38 (C <sub>5</sub> Me <sub>5</sub> ), 11.95 (Me, <sup>1</sup> J <sub>WC</sub> = 95), 9.84 (C <sub>5</sub> Me <sub>5</sub> )

<sup>a</sup> CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> CDCl<sub>3</sub>. <sup>d</sup> J values given in Hz.

**Preparation of Cp\*W(NO)(R)(Cl) Complexes 1–4.** Cp\*W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(Cl) (1) and Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)(Cl) (2) were prepared in a similar manner. The synthesis of 2 is described as a representative example. THF (≈20 mL) was vacuum transferred onto a mixture of Cp\*W(NO)(Cl)<sub>2</sub> (2.10 g, 5.00 mmol) and (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>Mg·x(dioxane) (0.635 g, 2.50 mmol) at -196 °C. The stirred reaction mixture was allowed to warm to room temperature at which time the solvent was removed in vacuo. The purple solid remaining was extracted with pentane (100 mL) and filtered through Celite (2 × 4 cm) supported on a sintered glass frit. The filtrate was concentrated in vacuo and transferred

to a freezer (-30 °C). This cooling induced the formation of violet needles that were isolated from the mother liquor by cannulation and were dried in vacuo. Additional product was obtained by further concentrating and cooling the supernatant solution.

Cp\*W(NO)(*o*-tolyl)(Cl) (3) and Cp\*W(NO)(Ph)(Cl) (4) were prepared as described in the preceding paragraph except that CH<sub>2</sub>Cl<sub>2</sub> instead of pentane was used as the extracting solvent.

**Preparation of Cp\*W(NO)(R)(R') Complexes 5–13.** Cp\*W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(Me) (5), Cp\*W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(Ph) (7), Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>) (8), Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)-

Table V. Mass Spectral and Infrared Data for Complexes 1-13

compd	MS, $m/z^a$	temp, <sup>b</sup> °C	IR (Nujol) ( $\nu_{NO}$ ), $cm^{-1}$
1	471 [P <sup>+</sup> ]	120	1599
2	455 [P <sup>+</sup> ], 425 [P <sup>+</sup> - NO]	100	1582
3	475 [P <sup>+</sup> ], 441 [P <sup>+</sup> - Cl]	100	1588
4	461 [P <sup>+</sup> ], 425 [P <sup>+</sup> - Cl]	200	1591
5	451 [P <sup>+</sup> ]	100	1541
6	527 [P <sup>+</sup> ]	100	1539
7	513 [P <sup>+</sup> ]	180	1547
8	507 [P <sup>+</sup> ], 477 [P <sup>+</sup> - NO]	100	1555
9	435 [P <sup>+</sup> ]	180	1584
10	511 [P <sup>+</sup> ]	100	1545
11	497 [P <sup>+</sup> ]	100	1549
12	455 [P <sup>+</sup> ]	150	1536
13	517 [P <sup>+</sup> ]	150	1549

<sup>a</sup>  $m/z$  values are for the highest intensity peak of the calculated isotopic cluster, i.e. <sup>98</sup>Mo and <sup>184</sup>W. <sup>b</sup> Probe temperatures.

Table VI. Mass Spectral and Infrared Data for Complexes 5'-14'

compd	MS, $m/z^a$	temp, <sup>b</sup> °C	IR (Nujol), $cm^{-1}$
5'			1644 ( $\nu_{C-C}$ ) 1576 ( $\nu_{NO}$ )
6'			1645 ( $\nu_{C-C}$ ) 1574 ( $\nu_{NO}$ )
7'			1642 ( $\nu_{C-C}$ ) 1576, 1551
8'	535 [P <sup>+</sup> ], 507 [P <sup>+</sup> - CO]	150	1563, 1537
9'	463 [P <sup>+</sup> ], 435 [P <sup>+</sup> - CO]	120	1570, 1560, 1537
10'	539 [P <sup>+</sup> ], 511 [P <sup>+</sup> - CO]	180	1576, 1564, 1537
11'	525 [P <sup>+</sup> ], 497 [P <sup>+</sup> - CO]	180	1570, 1557
12'	483 [P <sup>+</sup> ], 455 [P <sup>+</sup> - CO]	120	1549, 1526
13'	545 [P <sup>+</sup> ], 517 [P <sup>+</sup> - CO]	120	1574, 1553, 1528
14' <sup>c</sup>	470 [PH <sup>+</sup> ]		1549, 1520

<sup>a</sup>  $m/z$  values are for the highest intensity peak of the calculated isotopic cluster, i.e. <sup>98</sup>Mo and <sup>184</sup>W. <sup>b</sup> Probe temperatures. <sup>c</sup> FAB<sup>+</sup> MS, 3-nitrobenzyl alcohol matrix.

(Me) (9), and Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)(Ph) (11) were prepared in a similar manner. The synthesis of 8 is described as a representative example. THF ( $\approx$ 15 mL) was vacuum transferred onto a mixture of Cp\*W(NO)(Cl)<sub>2</sub> (0.84 g, 2.00 mmol) and (CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Mg·x(dioxane) (0.254 g, 1.00 mmol) at -196 °C. The reaction mixture was then allowed to warm to room temperature with stirring. The solvent was removed under reduced pressure, and the residue was left under dynamic vacuum for 2 h. Et<sub>2</sub>O (30 mL) was added to the residue, and the resulting solution was cooled to -30 °C. A solution of (CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Mg·x(dioxane) (0.286 g, 1.00 mmol) in Et<sub>2</sub>O (20 mL) was slowly cannulated into the reaction vessel. The resulting mixture was stirred as it was allowed to warm to room temperature. The solvent was removed from the final reaction mixture in vacuo leaving a purple solid that was extracted with Et<sub>2</sub>O (30 mL) and filtered through Florisil (100-200 mesh, 2 × 3 cm) supported on a sintered glass frit. The filtrate was taken to dryness, and the solid was dissolved in a minimum amount of pentane. Cooling of this solution to -30 °C overnight induced the crystallization of red-purple needles of Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>) (8) which were isolated by cannulation.

Cp\*W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(*o*-tolyl) (6), Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)(*o*-tolyl) (10), and Cp\*W(NO)(*o*-tolyl)(Me) (12) were prepared in a manner identical to that described for complex 8 above. The only difference was that the product complex was crystallized directly from the Et<sub>2</sub>O filtrate after concentration and subsequent cooling.

Cp\*W(NO)(*o*-tolyl)(Ph) (13) was also prepared similarly to complex 8 above. However, after filtration of the Et<sub>2</sub>O solution through Florisil, the solvent was removed from the filtrate in vacuo and the remaining solid was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes to obtain analytically pure 13.

**Preparation of Cp\*W(NO)(Ph)(Me) (14).** THF ( $\approx$ 15 mL) was vacuum transferred onto a mixture of Cp\*W(NO)(Cl)<sub>2</sub> (0.84 g, 2.00 mmol) and (Ph)<sub>2</sub>Mg·x(dioxane) (0.300 g, 1.00 mmol) at -196 °C. Warming of the stirred reaction mixture to room temperature produced a deep blue solution. This solution was then cooled to -30 °C, and a solution of (Me)<sub>2</sub>Mg·x(dioxane) (0.50 mmol, 0.080 M, 6.3 mL) in Et<sub>2</sub>O was slowly cannulated into it. Warming of this solution to room temperature resulted in the formation of a deep violet solution of 14. All attempts to isolate 14 from this solution have failed. For instance, removal of the solvent from the violet solution under vacuum resulted in the formation of a brown intractable solid. Nevertheless, the complex thus generated may be utilized in situ for further chemistry (vide infra).

**Carbonylations of Complexes 5-13.** Approximately 30 mg of each complex was dissolved in 0.5 mL of C<sub>6</sub>D<sub>6</sub> contained in an NMR tube bearing a Teflon stopcock. The solution was freeze-pump-thaw degassed twice, and its <sup>1</sup>H NMR spectrum was recorded. Carbon monoxide (1 atm) was then introduced into the tube through the stopcock, and the solution was shaken until the reaction with CO was complete, as evidenced by the disappearance of the color of the starting material. The final solution was then degassed once, and its <sup>1</sup>H NMR spectrum was recorded.

**Preparation of Cp\*W(NO)( $\eta^2$ -C{O}R)(R') Complexes 8'-13'.** The synthesis of Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(Me) (9') is described as a representative example. Cp\*W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)(Me) (200 mg, 0.46 mmol) was dissolved in benzene (10 mL) in a Schlenk tube to produce a deep red solution. Carbon monoxide (1 atm) was introduced into the vessel, whereupon the solution turned yellow within minutes. The solvent was removed in vacuo, and the remaining orange powder was washed with cold pentane (2 × 5 mL). The crude product was then crystallized from Et<sub>2</sub>O/hexanes to obtain yellow crystals of 9'.

Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(*o*-tolyl) (10'), Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(Ph) (11'), Cp\*W(NO)( $\eta^2$ -C{O}(*o*-tolyl)(Me) (12'), and Cp\*W(NO)( $\eta^2$ -C{O}(*o*-tolyl)(Ph) (13') were prepared in a manner identical to that described for 9' in the preceding paragraph. The sole difference was that CH<sub>2</sub>Cl<sub>2</sub>/hexanes rather than Et<sub>2</sub>O/hexanes were used for the final crystallizations.

Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>) (8') was prepared similarly to 9' with the exception that the crude product was not washed with pentane. Instead, it was dissolved in a minimum of pentane and was placed in the freezer (-30 °C) to induce the crystallization of 8'.

**Preparation of Cp\*W(NO)( $\eta^2$ -OC{CH<sub>2</sub>SiMe<sub>3</sub>)(Me) (5'), Cp\*W(NO)( $\eta^2$ -OC{CH<sub>2</sub>SiMe<sub>3</sub>)(*o*-tolyl) (6'), and Cp\*W(NO)( $\eta^2$ -OC{CH<sub>2</sub>SiMe<sub>3</sub>)(Ph) (7').** The syntheses of these complexes were performed in a similar manner to those of the acyl complexes in the preceding paragraphs. However, one difference was that a minimum of CO was used during the reactions. Specifically, the atmosphere of CO was removed in vacuo as soon as the color of the starting material had disappeared. Solvent removal from the final reaction mixture afforded in each case a white powder which was washed once with cold pentane (5 mL). Complexes 5' and 7' were crystallized from hexanes, while 6' was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes. All three complexes formed clear, colorless crystals.

**Preparation of Cp\*W(NO)( $\eta^2$ -C{O}Ph)(Me) (14').** Carbon monoxide (1 atm) was introduced into a Schlenk tube containing a solution of 14 generated as described above. The solution quickly turned from deep purple to orange. The solvent was removed under reduced pressure, and the residue was extracted with pentane (100 mL). The extracts were filtered through Celite (2 × 4 cm) supported on a sintered glass frit, and the filtrate was concentrated and cooled (-30 °C). The orange powder that precipitated was isolated by cannulation, and was redissolved in pentane. Cooling of this solution to -30 °C overnight induced the deposition of 14' as an orange powder.

**X-ray Crystallographic Analysis of Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(Ph) (11').** A crystal of Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(Ph) was mounted on a Pyrex filament using epoxy resin. Data

were recorded at ambient temperature with an Enraf-Nonius CAD4F diffractometer using graphite-monochromatized Mo K $\alpha$  radiation. Unit cell dimensions were determined from 25 well-centered reflections ( $34^\circ \leq 2\theta \leq 50^\circ$ ). Two intensity standards were measured every 1 h of exposure time and increased systematically by 6% during the course of the measurements. The data were corrected analytically for absorption and checked against the measured  $\psi$  scans. Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

The structure was solved from the Patterson map by the heavy-atom method. After the non-hydrogen atoms were located and refined, hydrogen atoms were included at calculated positions (C-H 0.95 Å) with isotropic temperature factors assigned proportionately to those carbon atoms to which they were bound. In subsequent cycles of refinement, the hydrogen-atom coordinate shifts were linked with those for their respectively bonded carbon atoms, and a single parameter was refined for the net isotropic thermal motion of each of the following sets of hydrogen atoms: those of the Cp\* group; those of the Ph group; those of the lone methylene group; those of the isobutyl fragment. The final full-matrix least squares refinement of 240 parameters, using 3249 data ( $I_o \geq 2.5\sigma(I_o)$ ), also included an extinction parameter<sup>8a</sup> ( $r^* = 0.10(2)$ ) and anisotropic thermal parameters for all non-hydrogen atoms. Soft restraints were applied which helped keep the difference in along-bond thermal motion of pairs of bonded atoms near zero. An empirical weighting scheme based on counting statistics was applied such that  $\langle w(|F_o| - |F_c|)^2 \rangle$  was nearly constant as a function of both  $|F_o|$  and  $(\sin \theta)/\lambda$ . The refinement converged at  $R_F = 0.024$  and  $R_{wF} = 0.033$ .

The programs used for absorption corrections, data reduction, structure solution, refinement, and plot generation were from the NRCVAX Crystal Structure System.<sup>8b</sup> Final refinement was made using CRYSTALS.<sup>8c</sup> Complex scattering factors for neutral atoms<sup>8d</sup> were used in the calculation of structure factors. All computations were carried out on a MicroVAX-II computer. Experimental parameters are given in Table VII. Selected bond lengths and angles are listed in Table VIII. Atomic coordinates for the nonhydrogen atoms are listed in Table IX. A view of the solid-state molecular structure of Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)-Ph is presented in Figure 1.

## Results and Discussion

**Synthesis.** We initially undertook this study to synthesize a series of mixed alkyl and aryl complexes, Cp\*W(NO)(R)(R'), to be used in an investigation of the relative reactivities of the different metal-carbon  $\sigma$  bonds at the same metal center. Three alkyl and two aryl ligands were chosen, and ten complexes containing all possible combinations of the ligands were synthesized. Our choice of alkyl groups was limited to those that did not contain  $\beta$ -hydrogens, because the latter ligands decompose readily when attached to the 16-electron metal center, presumably via  $\beta$ -H elimination pathways.<sup>9</sup> Consequently, methyl, neopentyl, and (trimethylsilyl)methyl ligands were chosen as representative alkyl groups. Phenyl and *o*-tolyl were chosen as representative aryl ligands because of their differing steric properties, a feature that could possibly be an important factor in comparative reactivity studies.

(8) (a) Larson, A. C. In *Crystallographic Computing*; Munksgaard, Copenhagen, 1970; p 291. (b) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. NRCVAX—An interactive Program System for Structure Analysis. *J. Appl. Crystallogr.* 1989, 22, 384. (c) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS. Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1984. (d) *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England, 1975; Vol. IV, p 99.

(9) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* 1988, 7, 2394 and references therein.

**Table VII.** Crystallographic and Experimental Data<sup>a</sup> for Complex 11<sup>b</sup>

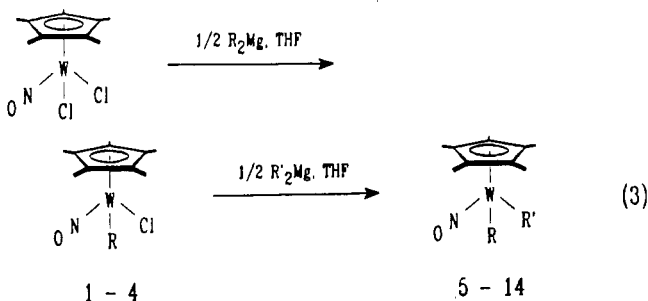
color	orange
formula	C <sub>22</sub> H <sub>31</sub> NO <sub>2</sub> W
fw	524.34
cryst syst	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	11.759(3)
<i>b</i> , Å	16.028(3)
<i>c</i> , Å	12.022(2)
$\beta$ , deg	107.95(2)
<i>V</i> , Å <sup>3</sup>	2155.5
<i>Z</i>	4
<i>d</i> <sub>calcd</sub> , Mg/m <sup>-3</sup>	1.619
<i>F</i> (000)	1039.70
$\lambda$ (Mo K $\alpha$ ), Å	0.709 30
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	54.9
<i>T</i> , K	294
cryst dimens, mm	0.36 × 0.37 × 0.38
transm factors	0.193–0.292
scan type	$\omega$ -2 $\theta$
scan range, deg	1.0 + 0.35 tan $\theta$
scan speed, deg/min	0.9–5.5
2 $\theta$ limits, deg	4 ≤ 2 $\theta$ ≤ 50
no. of unique rflns	3784
no. of rflns with <i>I</i> > 2.5 $\sigma$ ( <i>I</i> )	3249
no. of variables	240
<i>R</i> <sub>F</sub> <sup>b</sup>	0.024
<i>R</i> <sub>wF</sub> <sup>c,d</sup>	0.033
goodness of fit <sup>e</sup>	1.69
max $\Delta/\sigma$ (final cycle)	0.01
residual density, e/Å <sup>3</sup>	–0.7(1) to +1.7(1)

<sup>a</sup> Enraf-Nonius CAD4F diffractometer, Mo K $\alpha$  radiation, graphite monochromator. <sup>b</sup>  $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$ . <sup>c</sup>  $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ . <sup>d</sup>  $w = [\sigma(F_o)^2 + 0.0002F_o^{-2}]^{-1}$ . <sup>e</sup> GOF =  $[\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$ .

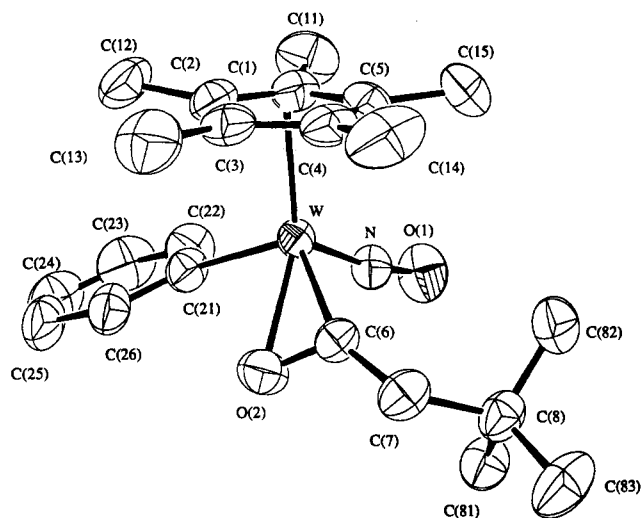
**Table VIII.** Selected Bond Lengths (Å) and Angles (deg) for Complex 11<sup>b</sup>

W–O(2)	2.202(3)	N–W–O(2)	103.9(1)
W–C(6)	2.046(4)	C(6)–W–O(2)	33.6(1)
W–N	1.779(4)	C(6)–W–N	95.5(2)
W–C(21)	2.183(4)	C(21)–W–N	93.6(2)
W–Cp	2.028	C(21)–W–O(2)	83.4(1)
O(1)–N	1.212(5)	C(21)–W–C(6)	116.5(2)
O(2)–C(6)	1.236(5)	O(1)–N–W	170.0(3)
C(6)–C(7)	1.502(6)	O(2)–C(6)–W	80.2(2)

The Cp\*W(NO)(R)(R') complexes are preparable by the sequential metatheses reaction summarized in eq 3. Both steps of reaction 3 are best effected at low temperatures. Very careful control over experimental conditions



is needed for the successful synthesis of both types of complexes. To this end, dialkyl- and diarylmagnesium reagents that can be stored and accurately weighed in a glovebox are used to ensure constant and precise stoichiometry. The use of vacuum-transferred THF as well as slow warming of the final reaction mixtures to room temperature are also vital for the success of these reactions. The first step of reaction 3 affords complexes 1–4, Cp\*W-



**Figure 1.** Solid-state molecular structure of Cp\*W(NO)( $\eta^2$ -C{O}CH<sub>2</sub>CMe<sub>3</sub>)(Ph) (11'). The hydrogen atoms have been omitted for clarity.

**Table IX.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Temperature Factors ( $\text{\AA}^2 \times 10^4$ ) for Complex 11'

atom	x/a	y/b	z/c	$U_{iso}$
W	2899.1(1)	1715.88(9)	1357.4(1)	341
O(1)	5502(3)	1684(2)	1617(4)	659
O(2)	2397(3)	3022(2)	1531(3)	535
N	4461(3)	1766(2)	1562(3)	434
C(1)	2714(4)	297(3)	1056(4)	509
C(2)	1714(4)	507(3)	1401(4)	483
C(3)	967(4)	1058(3)	560(4)	487
C(4)	1508(4)	1156(3)	-345(3)	456
C(5)	2580(4)	679(3)	-39(4)	499
C(11)	3657(6)	-338(3)	1626(5)	789
C(12)	1416(6)	152(3)	2443(5)	690
C(13)	-213(5)	1419(4)	558(6)	792
C(14)	936(6)	1596(3)	-1505(5)	647
C(15)	3412(5)	558(4)	-779(5)	724
C(6)	2511(4)	2857(2)	567(3)	407
C(7)	2340(4)	3507(3)	-370(4)	489
C(8)	3447(4)	3656(3)	-773(4)	488
C(81)	4525(4)	3874(3)	278(4)	550
C(82)	3747(5)	2882(4)	-1367(5)	651
C(83)	3151(5)	4372(4)	-1635(4)	674
C(21)	3132(4)	1673(2)	3229(4)	455
C(22)	4032(4)	1206(3)	3982(4)	595
C(23)	4132(6)	1145(4)	5172(4)	720
C(24)	3358(7)	1545(4)	5618(5)	748
C(25)	2452(6)	2019(4)	4886(5)	677
C(26)	2337(4)	2088(4)	3705(4)	563

(NO)(R)(Cl) (R = CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>CMe<sub>3</sub>, *o*-tolyl, Ph, respectively) whose characterization data are presented in Tables I, III, and V. Although the alkyl and aryl chloro complexes have been isolated to allow for their full characterization, their isolation is not necessary for the production of the mixed alkyl and aryl complexes 5–14. Thus, in the second step, another R<sub>2</sub>Mg alkylating agent can be added directly to a solution of the alkyl or aryl chloro complex generated in situ to produce the mixed compounds. The choice of which alkyl or aryl chloro intermediate should be generated first in any given synthesis is somewhat arbitrary. Although we synthesized all the complexes containing a methyl group by introducing it in the second step, we believe that the mixed complexes 5–14 can be made from either sequential route.

Characterization data for the mixed alkyl and aryl complexes 5–14 are listed in Tables I, III, and V. One of the mixed species used in the subsequent carbonylation study, Cp\*W(NO)(Ph)(Me) (14), has defied isolation to

date. Nevertheless, it can be generated in situ using the same methodology as for the other mixed species. That complex 14 is indeed present in solution is confirmed by the subsequent treatment of the solution with CO and the isolation of the expected acyl product, Cp\*W(NO)( $\eta^2$ -C{O}Ph)(Me) (14'). All of the isolable 16-electron mixed complexes 5–13 are air- and moisture-sensitive to varying degrees. The most stable members of this class of complexes are those with bulky alkyl ligands, a property previously observed for the related symmetric dialkyl and diaryl species Cp\*W(NO)(R)<sub>2</sub>.<sup>2</sup>

There are a few scattered reports of mixed alkyl or aryl transition-metal complexes in the literature,<sup>10–12</sup> but no systematic synthetic study of the scope reported here has yet been effected. The work most closely related to the current investigation is the recent study by Jordan and co-workers who synthesized the zirconocene complexes Cp<sub>2</sub>Zr(Ph)(R) [R = Me, or CH<sub>2</sub>Ph] and then investigated the comparative protonolysis of their metal–carbon bonds.<sup>10</sup>

**Spectroscopic Characterization of Complexes 1–13.** All of these complexes were characterized by standard spectroscopic techniques. The numbering scheme, yield, and elemental analysis data for these compounds are listed in Tables I and II, <sup>1</sup>H and <sup>13</sup>C NMR data are given in Tables III and IV, and mass spectral and infrared data are listed in Tables V and VI. All data are consistent with the Cp\*W(NO)(R)(Cl) and Cp\*W(NO)(R)(R') species being monomeric, 16-electron complexes.<sup>2,3</sup>

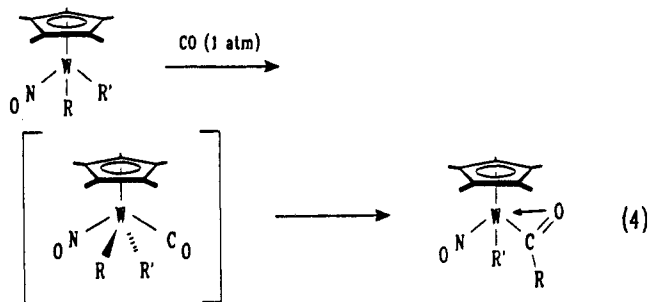
One notable characteristic of the <sup>1</sup>H and <sup>13</sup>C NMR data of the complexes containing an *o*-tolyl ligand is that signs of hindered rotation of the *o*-tolyl group about the ipso-carbon–tungsten bond are evident. Resonances due to both the ortho and methyl protons of the *o*-tolyl ligand appear broadened at room temperature. This phenomenon is mirrored in the <sup>13</sup>C NMR spectra where the ortho carbon and the methyl carbon signals are also broadened, even to the extent of not being observable in the spectrum of complex 10. We attribute this broadening to slow rotation (on the NMR time scale) about the ipso-carbon–tungsten bond so that the atoms affected are exchanged between different environments. Consistently, the broadening of these peaks becomes more pronounced as the steric congestion at the metal center increases. Thus, while the signal assignable to the methyl protons on the *o*-tolyl ligand in the <sup>1</sup>H NMR spectrum of Cp\*W(NO)(*o*-tolyl)(Cl) is sharp, the same peak in Cp\*W(NO)(*o*-tolyl)(CH<sub>2</sub>CMe<sub>3</sub>) is so wide that it is barely discernible from the baseline. The spectra of the latter complex recorded at 80 °C are almost identical to those taken at room temperature.

**Carbonylation Reactions.** Carbonylation reactions of the mixed complexes 5–13 were performed by exposing benzene solutions of these complexes to 1 atm of CO. In all cases, the insertion of 1 equiv of CO into one of the metal–carbon  $\sigma$  bonds occurs within minutes at room temperature. As indicated in eq 4, these processes probably proceed via initial adduct formation by the CO at the metal center's vacant orbital which bisects the R–M–

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R' angle<sup>13</sup> and subsequent competitive CO insertion. As noted above, the carbonylation of complex 14 was performed on a solution of the mixed complex generated in THF. The  $\eta^2$ -acyl product complexes formed by reaction 4 are numbered so as to reflect the mixed complex from which they originate, e.g. 8' results from treatment of 8 with CO. The compounds 8'–14' are thermally stable, monomeric species that can be handled in air for short periods of time. Spectroscopic data for these complexes are collected in Tables II, III, and VI. These data are consistent with the complexes being 18-electron species and possessing molecular structures analogous to that established for  $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{CH}_2\text{CMe}_2\text{Ph})(\text{CH}_2\text{CMe}_2\text{Ph})$ .<sup>1</sup> It should be noted, however, that for complexes 8'–14', the nitrosyl and carbonyl stretching bands in their IR spectra have not been assigned unambiguously. Most of the complexes have at least two strong absorptions in the region 1520–1560  $\text{cm}^{-1}$  due to the nitrosyl and  $\eta^2$ -acyl ligands (Table VI). The definitive assignment of IR bands is further complicated by the presence of aryl C=C stretching bands in the same region for those complexes containing either an *o*-tolyl or a phenyl group. Nevertheless, the absence of any  $\nu_{\text{CO}}$  bands at higher frequencies supports the description of these complexes as  $\eta^2$ - and not  $\eta^1$ -acyl species.<sup>1</sup>

Carbonylation reaction 4 of complexes 5–13 was first performed in NMR tubes in  $\text{C}_6\text{D}_6$  before being attempted on a preparative scale. In each case, the NMR data for the isolated product were compared to the spectra obtained in the NMR tube reactions to confirm that the same product was formed in both reactions. Unoptimized isolated yields for the preparative reactions are listed in Table II. In most cases, the reactions are quantitative, as judged by NMR spectroscopy. However, the spectroscopic yield of complex 6' is only ca. 50% based on the integration of the signals appearing in the  $\text{Cp}^*$  region of the  $^1\text{H}$  NMR spectrum after carbonylation. This low yield possibly reflects some thermal decomposition of the product complex in solution before the spectrum could be recorded. The NMR tube carbonylation of complex 8,  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$ , is also not quantitative. Along with signals attributable to the product of CO insertion into the tungsten–neopentyl bond, i.e. complex 8', one other  $\text{Cp}^*$  signal is observable along with some other minor peaks. This minor product, present in about 20% yield, is identifiable as the product of CO insertion into the tungsten–(trimethylsilyl)methyl bond. Its  $^1\text{H}$  NMR data<sup>14</sup> suggest that this minor product has undergone the same rearrangement as the other (trimethylsilyl)methyl-con-

taining complexes to form an enolate species (vide infra). The major acyl product, complex 8', crystallizes preferentially from the final reaction mixture, and no attempt was made to isolate the minor enolate product.

**Spectroscopic Characterization of Complexes 8'–14'.** Although it is generally easy to determine by mass spectroscopy and elemental analysis that one carbon monoxide molecule has been incorporated into the  $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{R}')$  complexes, it proves to be more difficult in some cases to determine which alkyl or aryl ligand has undergone the insertion. Fortunately,  $^{13}\text{C}\{^1\text{H}\}$  NMR data can be used to answer these questions. The presence of  $^{183}\text{W}$  satellites on the carbon signals in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the carbonylation products indicate which carbonyl carbon atoms, and therefore which ligands, are still attached directly to the metal center, thereby identifying the other ligand as the one which has undergone the CO insertion. For example, in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{CH}_2\text{CMe}_3)(\text{Me})$  (9'), the signal due to the methyl carbon contains  $^{183}\text{W}$  satellites ( $^1J_{\text{WC}} = 88$  Hz) while the methylene carbon signal of the neopentyl group does not. In some cases,  $^{183}\text{W}$  satellites on the carbonyl carbon signal are also discernible, as is the case in the latter example for which  $^1J_{\text{WC}} = 76$  Hz. Determining which ligand has inserted CO in complexes 8' and 13' is not quite as straightforward, however. The observation of  $^{29}\text{Si}$  satellites ( $^1J_{\text{CSi}} = 51$  Hz) in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$  (8') identifies the methylene carbon signal of the (trimethylsilyl)methyl ligand. The presence of another set of satellites due to coupling with  $^{183}\text{W}$  ( $J_{\text{WC}} = 87$  Hz) on the same methylene carbon signal provides evidence that the (trimethylsilyl)methyl ligand has not undergone insertion and is still attached directly to the metal center. For  $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{-}o\text{-tolyl})(\text{Ph})$  (13') it is impossible to differentiate the two ipso carbon signals in its  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum and thus determine which aryl group is still attached to the metal. To overcome this problem, a  $^1\text{H}, ^{13}\text{C}\{^1\text{H}\}$  COSY experiment must first be performed to correlate the ortho carbon signals to the ortho proton signals which are assignable by their differing integrations (one for *o*-tolyl and two for phenyl). A  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a sample of 13' synthesized with  $^{13}\text{CO}$  must then be obtained. In this spectrum the ortho carbon signal of the *o*-tolyl ligand appears as a doublet ( $^2J_{\text{CC}} = 7.3$  Hz) due to two-bond coupling to the labeled acyl carbon, thereby indicating that it is the *o*-tolyl group that has undergone CO insertion.

**Crystallographic Analysis of  $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{CH}_2\text{CMe}_3)(\text{Ph})$  (11').** Single crystals of  $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{CH}_2\text{CMe}_3)(\text{Ph})$  (11') were grown from  $\text{CH}_2\text{Cl}_2/\text{hexanes}$  and subjected to an X-ray diffraction analysis. This study was performed to establish conclusively the metrical parameters associated with the  $\eta^2$  bonding mode of the acyl ligand in this compound. The solid-state molecular structure established by this analysis is shown in Figure 1.

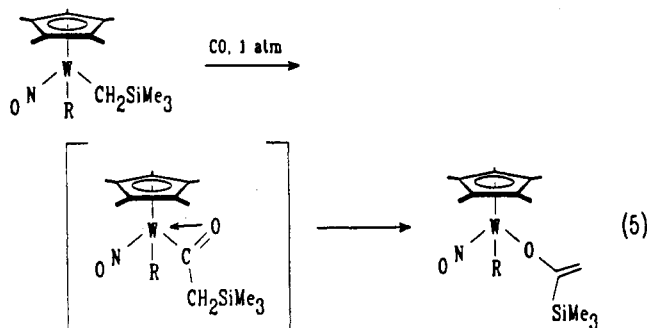
As expected, and consistent with the spectroscopic data discussed in the preceding sections, the acyl ligand is clearly bound to the metal in an  $\eta^2$  fashion, the carbonyl oxygen being within bonding distance of both the tungsten (2.202(3) Å) and the carbonyl carbon (1.236(5) Å). Not surprisingly, this oxygen donor is positioned trans to the NO group which is a strong  $\pi$ -acid ligand. The intramolecular dimensions of the  $\eta^2\text{-C}\{\text{O}\}\text{CH}_2\text{CMe}_3$  ligand resemble those

(13) Consistent with this view is the fact that the  $\text{Cp}^*\text{W}(\text{NO})(p\text{-tolyl})_2(\text{PMe}_3)$  adduct is a four-legged piano-stool molecule in which the NO and  $\text{PMe}_3$  ligands are trans to one another.<sup>7</sup>

(14)  $^1\text{H}$  NMR data for  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{OC}(\text{CH}_2)_2\text{SiMe}_3)$ :  $\delta$  0.16 (s, 9H,  $\text{SiMe}_3$ ), 1.44 (s, 9H,  $\text{CMe}_3$ ), 1.68 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 4.25 and 5.81 (s, 1H each,  $\text{OC}(\text{CH}_2)_2\text{SiMe}_3$ ), neopentyl methylene signals not observed.

determined previously for related systems<sup>15a</sup> and indicate that this ligand is acting as a formal 3-electron donor to the metal center in this 18-electron complex.

**Spectroscopic Characterization of Complexes 5'-7'.** The CO insertion product complexes 5'-7' are not spectroscopically or physically similar to the  $\eta^2$ -acyl complexes 8'-14'. Instead, the (trimethylsilyl)methyl group in these products has inserted carbon monoxide, and the resulting acyl ligand has then rearranged to give an enolate product via a 1,2-silyl shift (eq 5). There is



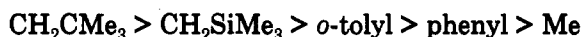
ample precedent for this type of rearrangement in the literature.<sup>15</sup> These types of rearrangements commonly occur with acyl intermediates at electron-deficient and oxophilic metal centers that give the  $\eta^2$ -acyl carbon a high degree of carbene-like character.<sup>15b-d</sup> Mechanistic speculation involving the proposed intermediacy of an acyl species has been proffered,<sup>15b,d,e</sup> and in one case the observed rearrangement of an isolated acyl complex to an enolate species provides support for this mechanism.<sup>15c</sup> We have obtained no evidence for the existence of the intermediate acyl complexes during the formation of compounds 5'-7' (eq 5) since the conversions involving these rearrangements are complete within seconds at ambient temperatures.

The enolate product complexes 5'-7', when pure, are colorless, while the acyl compounds are yellow to orange in color. The enolate complexes also have several unique spectroscopic features that distinguish them from simple  $\eta^2$ -acyl complexes, namely (1) their IR spectra show a sharp band at approximately 1640  $\text{cm}^{-1}$  assignable to the C=C stretch of the enolate ligand, (2) the inserted carbon signal in the <sup>13</sup>C NMR spectrum appears at approximately 180 ppm while analogous  $\eta^2$ -acyl carbons resonate near 300 ppm, and (3) the methylene proton signals in the <sup>1</sup>H NMR spectrum appear in the vinyl region as two singlets ( $J_{gem} = 0$ ). These enolate complexes prove to be thermally sensitive, and therefore satisfactory mass spectral data cannot be obtained for them. Nevertheless, comparisons of the spectroscopic data of complexes 5'-7' with those of related enolate complexes reported in the literature<sup>15b,c</sup> leave little doubt about their true natures.

**Migratory Aptitudes of the  $\sigma$ -Bound Ligands.** The results obtained during this study must be viewed in the context of the vast amount of previous work done on CO insertions by numerous other research groups.<sup>4,16</sup> Our investigation of the regioselective insertion of carbon

monoxide into the tungsten-alkyl and -aryl bonds was chosen so that a relative ranking of the migratory aptitudes of the different  $\sigma$ -bound ligands could be determined. The great majority of studies comparing migratory aptitudes of alkyl ligands have been performed on monoalkylated transition-metal complexes, and almost all have relied on kinetic data to compare the migratory aptitudes of various alkyl and aryl ligands in both carbonylation and decarbonylation processes.<sup>15c,16,17</sup>

Our study is different from the kinetic studies done in the past not only because ligand reactivities are being directly compared at the same metal center but also because the acyl ligands formed are  $\eta^2$ -bound in the product complexes. The direct formation of the  $\eta^2$ -acyl ligand simplifies the reaction considerably over those that rely on incoming ligands either to promote insertion or to fill the coordination site left at the metal center by the migrating ligand. By examining the products of carbonylation of all the mixed alkyl and aryl species, 5'-14', to determine which ligand inserts preferentially, we have established a relative ranking of the migratory aptitudes of the  $\sigma$ -bound ligands. In order of decreasing migratory aptitude, this ranking is



In other words, in all of the mixed complexes containing a neopentyl ligand, this group migrates preferentially over all other ligands upon treatment of the complex with CO. Conversely, if the complex contains a methyl ligand, CO does not undergo insertion into the methyl-tungsten bond, but rather into the other metal-alkyl or -aryl bond. The complexes containing the other ligands fill in the rest of the trend. For example, CO inserts into the tungsten-*o*-tolyl bond in Cp\*W(NO)(*o*-tolyl)(Ph), thereby indicating the preference to migration of *o*-tolyl over phenyl. On the other hand, the *o*-tolyl ligand in the complex Cp\*W(NO)(*o*-tolyl)(CH<sub>2</sub>SiMe<sub>3</sub>) does not insert, thereby indicating that the migratory aptitude of this ligand is less than that of the (trimethylsilyl)methyl ligand.

Although the differing M-C bond strengths of the inserting groups undoubtedly play a role, the above trend seems to reflect steric effects primarily, the most sterically demanding ligand inserting preferentially to decrease steric crowding at the metal center. The trend agrees with results found from kinetic studies where similar ligand choices allow some comparisons to be made. For example, in Cp<sub>3</sub>ThR systems the rate of carbonylation to form  $\eta^2$ -acyl products decreases as isopropyl > *sec*-butyl  $\gg$  neopentyl > *n*-butyl  $\gg$  CH<sub>2</sub>SiMe<sub>3</sub> > methyl > benzyl.<sup>15c</sup> A similar trend has been noted for the insertion rates in CpFe(CO)<sub>2</sub>R in Me<sub>2</sub>SO solutions to form  $\eta^1$ -acyls, i.e.: CH(SiMe<sub>3</sub>)<sub>2</sub>  $\gg$  CH<sub>2</sub>CMe<sub>3</sub> > *sec*-butyl > isopropyl > CH<sub>2</sub>SiMe<sub>3</sub> > *n*-butyl > CH<sub>2</sub>CH<sub>3</sub> > CH<sub>3</sub>.<sup>17a</sup>

Few examples of competitive carbonylation of two ligands attached to the same metal center exist in the chemical literature, but those that do generally corroborate

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the results found with the  $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{R}')$  systems. Thus, CO inserts into the more sterically demanding groups of  $\text{Cp}_2\text{Zr}(\text{CH}(\text{SiMe}_3)_2)(\text{Me})^{11}$  and  $\text{Cp}_2\text{Zr}(\text{Ph})(\text{Me})^{18}$  to relieve steric crowding at the metal center. Evidently, such steric factors are not dominant in the reaction of CO with  $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)(\text{Me})$ , and it inserts preferentially into the presumably weaker metal–methyl bond.<sup>19</sup> Interestingly, CO inserts into the Ir–Me bond in the complexes  $(\eta^5\text{-indenyl})\text{Ir}(\text{PMe}_3)(\text{Me})(\text{R})$  [R = Ph, *o*-tolyl],<sup>20</sup> a trend opposite to the one reported here. However, a complicated mechanism involving indenyl ring slippage and removal of coordinated CO with trimethylamine oxide is involved in this reaction, a fact which may well have some effect on determining the preferred reaction products.

The rearrangement of the (trimethylsilyl)methyl ligand to enolate complexes upon CO insertion does not appear to interfere with the ranking of migratory aptitudes established by this study. Nevertheless, it should be noted that the neopentyl and the (trimethylsilyl)methyl ligands have very similar migratory aptitudes. This feature is clearly evident during the carbonylation of  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$ , where a 4:1 ratio of products was observed, the major product arising from CO insertion into the tungsten–neopentyl bond and the minor one from tungsten–(trimethylsilyl)methyl insertion. The rearrangement of the (trimethylsilyl)methyl ligand after insertion may add some driving force toward insertion into this ligand over others, but evidently not enough to overcome the rate of CO insertion into the neopentyl ligand.

### Epilogue

Four alkyl and aryl chloro complexes of tungsten have been synthesized and characterized. These compounds

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have been used as precursors for the preparation of ten mixed alkyl and aryl complexes which provide us with the opportunity to compare directly the reactivities of different tungsten–carbon  $\sigma$  bonds at the same metal center with a variety of reagents. So far, carbonylation reactions under ambient conditions have been performed on these mixed species, and it has been found that each inserts one molecule of CO into one of the tungsten–carbon  $\sigma$  bonds. Conclusive identification of the carbonylation products leads to a ranking of the migratory aptitudes of the five ligands used in the study, i.e.  $\text{CH}_2\text{CMe}_3 > \text{CH}_2\text{SiMe}_3 > \text{o-tolyl} > \text{Ph} > \text{Me}$ . This trend appears to be sterically controlled, the most sterically demanding ligands inserting CO preferentially in each case. More reactivity studies of the mixed complexes designed to investigate further the regioselective reactivity of the different metal–carbon  $\sigma$  bonds in these complexes are currently underway. For instance, we are presently endeavoring to establish which of these complexes can insert a second molecule of CO into the other W–C  $\sigma$  bond under more forcing conditions. This knowledge is a prerequisite before we attempt such twin insertions by exposing the  $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{R}')$  systems to CO and its isoelectronic analogues sequentially.

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**Supplementary Material Available:** Tables of bond lengths and bond angles, hydrogen atom coordinates and isotropic temperature factors, non-hydrogen anisotropic temperature factors, intermolecular torsion angles, and least squares planes for complex 11' (8 pages). Ordering information is given on any current masthead page.

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