Addition and Cycloaddition Reactions of the Chiral and Highly Nucleophilic Alkynyl Complex $[(\eta^5\text{-}C_5H_4Me)(CO)(PPh_3)MnC{\equiv}CMe]^-$

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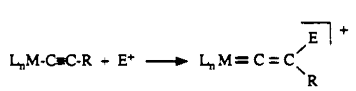
Abstract: The anionic alkynyl complex $[Cp'(CO)(PPh_3)MnC{\equiv}CCH_3]^-$ (**3**) can be generated in situ by the addition of 2 equiv of *n*-BuLi to a solution of the carbene complex $Cp'(CO)(PPh_3)Mn{=}C(OMe)CH_2CH_3$ (**2**). Complex **3** adds electrophiles such as H_2O, MeI, $MeOSO_2CF_3$, $[Et_3O][BF_4]$, EtI, Bu^tI, and RC{O}Cl (R = Me, Ph) to form vinylidene complexes $Cp'(CO)(PPh_3)Mn{=}C{=}CMe(R)$ (R = H, Me, Et, Bu^t (**5c**), C{O}Me (**6a**), and C{O}Ph). Alkylation of **6a** with MeOTf affords the vinyl carbyne complex $[Cp'(CO)(PPh_3)Mn{\equiv}CC(Me){=}C(OMe)Me]^+CF_3SO_3^-$. The β-carbon of the propynyl ligand of **3** also adds to the central carbon atom of the heterocumulenes TolNCO, Ph_2CCO, and CO_2 to form, after protonation or alkylation, the vinylidene complexes $Cp'(CO)(PPh_3)Mn{=}C{=}CMe(C\{O\}R)$ (R = NHTol, $CHPh_2$, OMe), and **3** undergoes conjugate addition with *trans*-4-phenyl-3-buten-2-one to give, after protonation, the vinylidene complex $Cp'(CO)(PPh_3)Mn{=}C{=}CMe(CH(Ph)CH_2C\{O\}Me)$, **13**. In the presence of $BF_3{\cdot}Et_2O$, complex **3** undergoes [2 + 3] cycloaddition of the C≡C bond of the propynyl ligand across the epoxide linkage of isobutylene oxide and cyclohexene oxide to form new cyclic carbene complexes **14** and **17**. A similar [2 + 4] cycloaddition occurs with 3,3-dimethyloxetane to give carbene complex **20**. These latter reactions are highly stereospecific due to the chiral nature of **3**, and they give a single pair of enantiomers of **14** and **20**. The mechanisms of these reactions are discussed, and complexes **2**, **5c**, **13′** (the Cp analogue of **13**), **14**, and **20** have been crystallographically characterized.

Introduction

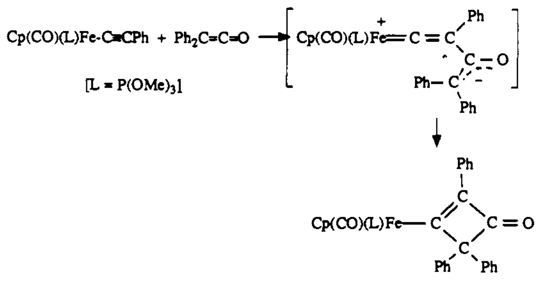
A large number of transition metal alkynyl complexes ($L_nMC{\equiv}CR$) are known, and it is well recognized that the reactivity of the alkynyl ligand is a sensitive function of the nature of the alkynyl substituent, the attached metal and its ligands, and the overall charge on the complex.[1] The reactivity of this ligand can be rationalized on the basis of resonance forms A and B, with

$$\underset{\textbf{A}}{L_nMC{\equiv}CR} \leftrightarrow \underset{\textbf{B}}{L_nM^+{=}C{=}C^-R}$$

form B becoming more important as the electron density on the complex increases upon moving from cationic to anionic complexes and as the ligands and the alkynyl substituents become more electron releasing. The importance of resonance form B is indicated by the reactions of electron-rich alkynyl complexes with electrophiles to form vinylidene complexes (eq 1).[1a,b] Alkynyl complexes have also been shown to undergo a series of [2 + 2] and [2 + 4] cycloaddition reactions with ketenes (eq 2[2a]), acid chlorides, 2-chloroacrylonitrile, dimethyl methylenemalonate, 1,3-dicyano-1,3-butadiene, nitrile oxides, and electron-deficient alkynes.[2]



$$L_nM\text{-}C{\equiv}C\text{-}R + E^+ \longrightarrow \left[L_nM{=}C{=}C\begin{matrix}E\\R\end{matrix}\right]^+ \quad (1)$$



(2)

We recently communicated the in situ generation of the anionic alkynyl complexes $[Cp'(CO)(PPh_3)MnC{\equiv}CR]^-$ ($Cp' = \eta^5\text{-}C_5H_4CH_3$; R = CH_3, Pr^n) which resulted from the addition of 2 equiv of *n*-BuLi to the carbene complex $Cp'(CO)(PPh_3)Mn{=}C(OR')CH_2R$.[3] These alkynyl complexes are highly nucleophilic as a result of the negative charge on the complex, the electron-releasing Cp and PPh_3 ligands and alkynyl substituents, and the fact that only one CO ligand is present to withdraw electron density. As a result, these alkynyl complexes have been found to undergo a series of new addition and cycloaddition reactions with electrophilic organic substrates and as such significantly extend the known chemistry of the alkynyl ligand. Full details of this study are reported herein, including a series of cycloaddition reactions with epoxides and 3,3-dimethyloxetane and the formation of a series of vinylidene complexes through the addition of the alkynyl complex to vinyl ketones, heterocumulenes, and a variety of other electrophilic reagents. An important feature of $[Cp'(CO)(PPh_3)MnC{\equiv}CR]^-$ is its chirality at the Mn center, which allows high stereocontrol of those reactions that generate a second chiral center in the resultant organic ligand.

The only other *anionic* alkynyl complexes of which we are aware are the $[(CO)_5MC{\equiv}CR]^-$ (M = Cr, Mo, W) compounds reported by Ruff[4a] and Mayr,[4b] Templeton's $[(dppe)(CO)_3WC{\equiv}CCH_3]^-$,[5a]

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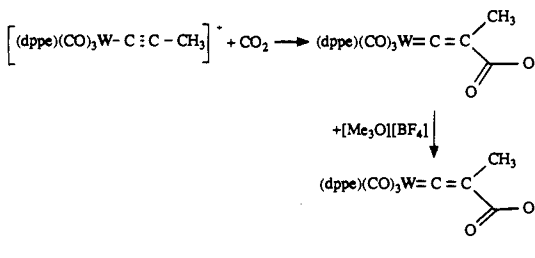
Table I. Crystallographic Data for Cp(CO)(PPh$_3$)Mn=C(OMe)Et (**2**), Cp(CO)(PPh$_3$)Mn=C=C(Me)Bu^t (**5c**), Cp′(CO)(PPh$_3$)Mn=C=C(Pr^n)CHPhCH$_2$C{O}CH$_3$ (**13′**), Cp′(CO)(PPh$_3$)Mn=C{OC(Me$_2$)CH$_2$CH(Me)} (**14**), and Cp′(CO)(PPh$_3$)Mn=C{OCH$_2$C(Me)$_2$CH$_2$CH(Me)} (**20**)[a]

	2	5c	13′	14	20
			(a) Crystal Parameters		
formula	$C_{28}H_{28}MnO_2P$	$C_{31}H_{32}OPMn$	$C_{40}H_{41}MnO_2P$	$C_{32}H_{37}MnO_2P$	$C_{32}H_{34}MnO_2P$
fw	482.44	506.51	639.68	539.56	536.53
cryst syst	triclinic	orthorhombic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$Pbca$	$P2_1/n$	$Pna2_1$	$P\bar{1}$
a, Å	10.0052 (26)	9.538 (3)	13.330 (3)	28.803 (9)	9.4698 (14)
b, Å	14.1401 (25)	18.932 (4)	16.081 (3)	10.018 (4)	10.3993 (18)
c, Å	17.409 (4)	29.869 (8)	16.420 (3)	9.803 (3)	14.8127 (23)
α, deg	91.964 (17)				86.576 (13)
β, deg	103.856 (20)		102.16 (1)		88.227 (12)
γ, deg	89.968 (18)				72.688 (12)
V, Å^3	2389.7 (9)	5394 (2)	3441 (1)	2828 (2)	1390.0 (4)
Z	4	8	4	4	2
D(calcd)	1.341	1.247	1.235	1.267	1.282
μ(Mo Kα), cm^{-1}	2.05	5.69	4.44	5.28	1.75
temp, K	296	296	296	296	296
size, mm	0.28 × 0.30 × 0.32	0.22 × 0.28 × 0.60	0.42 × 0.42 × 0.42	0.28 × 0.32 × 0.36	0.32 × 0.40 × 0.40
color	orange	orange-red	orange	orange	yellow-brown
T(max)/T(min)	1.101	1.088	1.086	1.092	1.186
			(b) Data Collection		
diffractometer	Nicolet R3m	Siemens P4	Nicolet R3m	Nicolet R3m	Nicolet R3m
monochromator			graphite		
wavelength, Å			0.71073		
radiation			Mo Kα		
scan method			ω		
scan limits	4° ≤ 2θ ≤ 46°	4° ≤ 2θ ≤ 45°	4° ≤ 2θ ≤ 47°	4° ≤ 2θ ≤ 48°	4° ≤ 2θ ≤ 50°
data collected	±h,±k,+l	+h,+k,+l	±h,+k,+l	+h,+k,+l	±h,±k,+l
rflns collected	6885	4006	5502	2576	5103
indpdt rflns	6627	3525	5080	2366	4894
obsd rflns	4805 (5σF$_o$)	1802 (5σF$_o$)	3434 (5σF$_o$)	1863 (5σF$_o$)	3500 (5σF$_o$)
std rflns			3 std/197 rflns		
var in stds, %	3	<2	<1	<1	4
			(c) Refinement		
R(F), %	5.70	5.34	4.59	11.71	4.53
R(wF), %	6.56	5.59	5.85	12.56	4.91
GOF	1.455	1.120	1.252	1.752	1.182
Δ/σ (max)	0.013	0.274	0.03	0.112	0.005
Δ(ρ), e Å^{-3}	0.795	0.001	0.30	2.436	0.318
N$_o$/N$_v$	9.5	6.0	9.9	7.0	12.3

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R(wF) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; $GOF = [\sum w||F_o| - |F_c||/N_o - N_v]^{1/2}$.

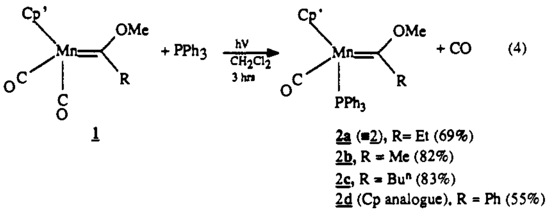
and Berke's [Cp(CO)$_2$MnC≡CR]$^-$.[5b,c] Each of these complexes has been shown to yield vinylidene complexes when treated with electrophiles (MeOSO$_2$CF$_3$, [Et$_3$O][BF$_4$], and HBF$_4$), and Templeton's compound also reacts with CO$_2$ to give, after alkylation, the vinylidene complex shown in eq 3.[5a]



(3)

Results

Preparation of the Chiral Carbene Complexes Cp′(CO)(PPh$_3$)Mn=C(OMe)(CH$_2$R). Although the chiral carbene complexes Cp′(CO)(PPh$_3$)Mn=C(OMe)R had not been previously reported in the literature,[6] we have found that they can be conveniently prepared by photoinduced substitution of PPh$_3$ for CO in the dicarbonyl complexes Cp′(CO)$_2$Mn=C(OR)R (eq 4).



The corresponding Cp complexes can be prepared in a similar manner, and preliminary studies indicate that Cp′(CO)(PPh$_3$)Mn=CPh$_2$ can also be formed by this method. The Cp analogue of complex **2a** has been crystallographically characterized (see Figure 1 and below), and the spectroscopic data given in the Experimental Section for **2a–d** are consistent with their indicated formulation. From here on, we focus only on complex **2a** (and occasionally its Cp analogue) and will refer to it simply as **2**.

In order to define the stereochemical influence of the PPh$_3$ ligand and the orientation of the carbene ligand in **2**, a crystallographic study was undertaken. The crystals used for the X-ray diffraction study were of the Cp analogue, Cp(CO)(PPh$_3$)Mn=C(OMe)Et, because of its greater ease of crystallization. The molecule crystallizes in the $P\bar{1}$ space group with two independent molecules per unit cell, which are differentiated by the use of primed and unprimed labels. Relevant crystallographic data are given in Tables I and II, and two different views of the unprimed

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(6) The related chiral carbene complexes (η-C$_5$H$_4$Me)(CO)(L)Mn=CS$_3$C$_2$(CO$_2$Me)$_2$ (L = P(OMe)$_3$, PMe$_3$, PMe$_2$Ph) have been described: Le Marouille, J.-Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. *J. Organomet. Chem.* **1980**, *191*, 133. (b) Also known are the chiral vinylidene complexes Cp(CO)(L)Mn=C=CHPh (L = PPh$_3$, P(OEt)$_3$, P(OPh)$_3$): Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55.

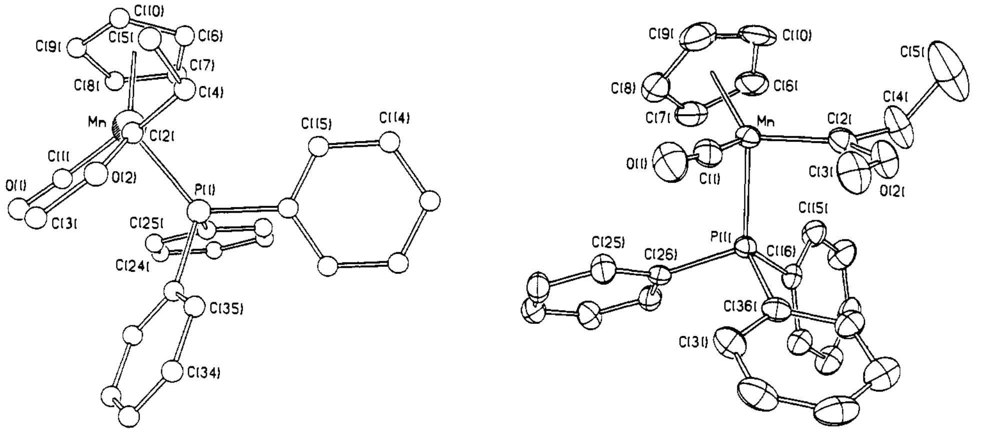
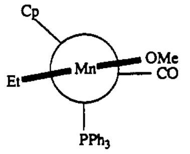


Figure 1. ORTEP drawings of one of the two independent molecules of Cp(CO)(PPh$_3$)Mn=C(OMe)Et (**2**).

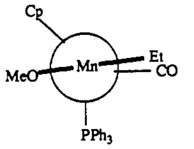
Table II. Selected Bond Lengths and Angles for Cp(CO)(PPh$_3$)Mn=C(OMe)Et (**2**)

	Bond Lengths (Å)		
Mn-C(1)	1.743 (7)	Mn′-C(1′)	1.737 (6)
Mn-C(2)	1.861 (6)	Mn′-C(2′)	1.865 (6)
Mn-P(1)	2.229 (2)	Mn′-P(1′)	2.232 (2)
C(1)-O(1)	1.166 (9)	C(1′)-O(1′)	1.170 (8)
C(2)-O(2)	1.372 (7)	C(2′)-O(2′)	1.359 (7)
O(2)-C(3)	1.420 (9)	O(2′)-C(3′)	1.419 (9)
	Bond Angles (deg)		
C(1)-Mn-C(2)	100.9 (3)	C(1′)-Mn′-C(2′)	100.8 (3)
P(1)-Mn-C(1)	90.6 (2)	P(1′)-Mn′-C(1′)	90.8 (2)
P(1)-Mn-C(2)	91.9 (2)	P(1′)-Mn′-C(2′)	90.1 (2)
Mn-C(2)-O(2)	133.6 (5)	Mn′-C(2′)-O(2′)	134.3 (5)
Mn-C(2)-C(4)	125.0 (4)	Mn′-C(2′)-C(4′)	123.5 (4)
C(2)-O(2)-C(3)	122.6 (5)	C(2′)-O(2′)-C(3′)	121.4 (5)
C(2)-C(4)-C(5)	114.9 (8)	C(2′)-C(4′)-C(5′)	114.4 (7)
Mn-C(1)-O(1)	171.7 (5)	Mn′-C(1′)-O(1′)	171.7 (5)

molecule are shown in Figure 1. The two molecules are structurally similar, as illustrated by the data given in Table II. The molecule possesses the usual pseudooctahedral geometry that has been established for other CpL$_3$M complexes and that is indicated by the P—Mn—C(1) [90.6 (2)°], P—Mn—C(2) [91.9 (2)°], and C(1)—Mn—C(2) [100.8 (2)°] bond angles. The drawing on the right of Figure 1 illustrates how the large PPh$_3$ ligand effectively shields the carbene ligand from below. The drawing on the left of Figure 1 shows that the carbene ligand and its substituents are coplanar with the CO ligand. This plane is perpendicular to the Mn-P bond [torsion angle {C(1)—Mn—C(2)}—{C(4)—C(2)—O(2)} = 5.0°; C(1′)—Mn—C(2′)}—{C(4′)—C(2′)—O(2′)} = 30°], an orientation that is preferred for electronic reasons and maximizes the π-bonding in the molecule, as has been rationalized for other carbene complexes.[7] The methoxy substituent of the carbene ligand is on the same side of the molecule as the CO ligand, whereas the ethyl substituent is oriented in the open region between the PPh$_3$ and Cp ligands, as indicated in the Newman projection **C**. The Mn—C(2) and Mn′—C(2′) distances of 1.861 (6) and 1.865 (6) Å compare well to the corresponding manganese–carbene distances found in other carbene complexes [Cp(CO)$_2$Mn=C(OEt)Ph, 1.865 (14) Å;[8a] Cp(CO)$_2$Mn=CPh$_2$, 1.885 (2) Å;[8b] Cp(CO)$_2$Mn=C(C{O}Ph)Ph, 1.88 (2) Å;[8c] Cp(CO)$_2$Mn=CMe$_2$, 1.872 (10) (molecule 1) and 1.864 (10) Å (molecule 2)[8d]]. All other metric parameters appear normal.



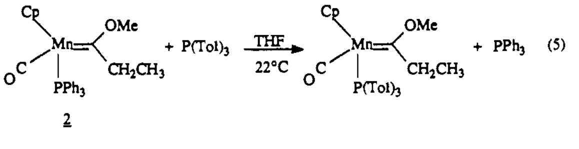
C
synclinal



D
anticlinal

Although ^{1}H NMR data for **2** indicate the presence of a single isomer at room temperature, a variable-temperature ^{1}H NMR study showed the presence of two species at low temperature. Thus, at −103 °C two Cp singlets were observed at δ 4.14 and 3.94, and upon warming these coalesced at −90 °C and then sharpened at 22 °C into a single Cp resonance at δ 4.4. From the NMR data, an activation barrier of 9.8 kcal/mol was calculated for this exchange process, which we attribute to syn–anti interconversion (**C** $\rightleftarrows$ **D**). This value compares well to similar low-energy barriers for rotation about M=C bonds in the complexes [Cp(CO)$_2$(PEt$_3$)W=CH$_2$]$^+$ ($\Delta G^{\ddagger}$ = 9.0 kcal/mol)[9] and [Cp(CO)(PPh$_3$)Fe=CHCH$_3$]$^+$ ($\Delta G^{\ddagger}$ = 7.8 kcal/mol).[7b] However, it is substantially lower than the corresponding 19–22 kcal/mol barriers found in rhenium carbene complexes of the type [Cp(NO)(PPh$_3$)Re=CRR′]$^+$.[7c,10] It should be noted that an alternative explanation of the variable-temperature NMR data is the freezing out of restricted rotation about the carbon–oxygen bond of the carbene ligand, but we view this as less likely than the proposed syn–anti interconversion.

In the course of these studies, it was observed that the Cp analogue of complex **2** undergoes slow phosphine exchange with P(Tol)$_3$ to form Cp(CO){P(Tol)$_3$}Mn=C(OMe)Et (eq 5). At



(5)

ambient temperature, 33% exchange was observed after 6.75 days, and ^{31}P NMR monitoring showed the reaction to proceed via an associative mechanism with the rate of exchange dependent on the P(Tol)$_3$ concentration. A linear plot of $1/[\mathbf{2}] - 1/[\mathbf{2}]_{t=0}$ versus time gave a second-order rate constant of 5.3×10^{-6} s^{-1} M^{-1} for this exchange process.

In Situ Generation of the Propynyl Complex [Cp′(CO)(PPh$_3$)MnC≡CCH$_3$]$^-$ (3). When treated with *n*-BuLi or lithium

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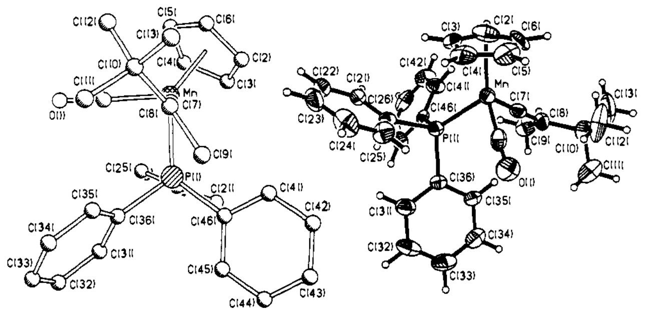
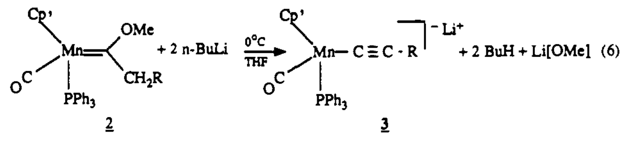


Figure 2. ORTEP drawings of Cp(CO)(PPh$_3$)Mn=C=C(Me)Bu^t (**5c**).

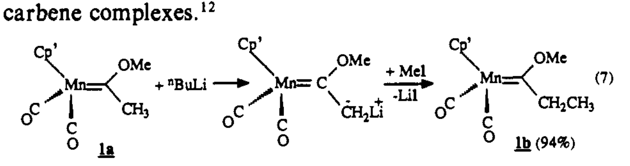
diisopropylamide (LDA), but not Et_3N, complex **2** forms the propynyl complex **3** shown in eq 6. A total of 2 equiv of base



(6)

was necessary to drive the complete conversion of **2** into **3**. IR monitoring of the reaction indicated that the addition of 1 equiv gave only an equimolar mixture of these two compounds. Although complex **3** could not be isolated in pure form due to its extreme moisture sensitivity (see below), its nature was inferred from its spectroscopic data and from its reactions described below. The IR spectrum of **3** shows two bands at 2049 (m) and 1779 (s) cm^{-1}, which are assigned to $\nu_{C\equiv C}$ and ν_{CO} vibrations, respectively. The former is in the region characteristic of alkynyl ligands and compares to the 2082 cm^{-1} band reported for the complex Cp(NO)(PPh$_3$)ReC≡CPh.[11] The very low energy ν_{CO} vibration (1779 cm^{-1}) is indicative of the high electron density on the metal. ^{1}H and ^{13}C NMR data (see the Experimental Section) are also consistent with the indicated formulation, and most notable in the ^{13}C NMR spectrum of **3** are resonances attributed to the α- and β-carbons of the propynyl ligand at δ 83.8 and 112.7. Although not investigated in as much detail, it was observed that complex **2b,c** also underwent a similar reaction to form the corresponding alkynyl complex and that this latter complex displayed reactivity patterns analogous to those described below for **3**.

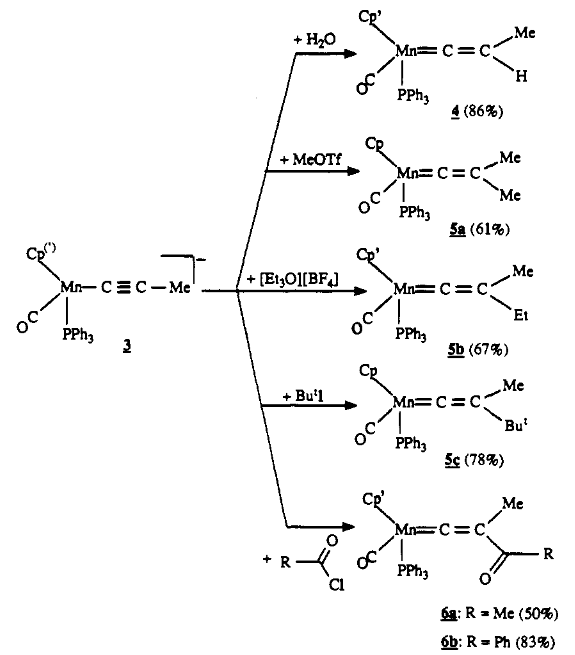
It is interesting to note that alkynyl complexes only form with the PPh$_3$-substituted carbene complexes **2a,b** and not with the less electron-rich dicarbonyl complex **1**. Treatment of this species with *n*-BuLi smoothly led to the anionic complex shown in eq 7, which cleanly gave the ethyl carbene complex **1b** when treated with MeI (see the Experimental Section). Similar reactions are well known for (CO)$_5$Cr=C(OMe)CH$_3$, (CO)$_5$W=C(OMe)CH$_3$, and related carbene complexes.[12]



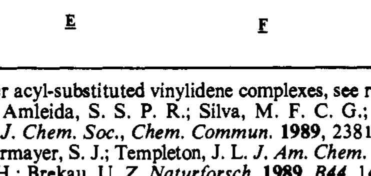
(7)

Protonation, Alkylation, and Acylation of Cp′(CO)(PPh$_3$)MnC≡CCH$_3$]$^-$ To Form Vinylidene Complexes. Complex **3** rapidly reacts with H$_2$O, [Et$_3$O][BF$_4$] (and EtI), MeOSO$_2$CF$_3$ (and MeI), Bu^{t}I, and RC{O}Cl to form the neutral vinylidene complexes **4–6** shown in Scheme I. These complexes were isolated as orange solids, except for **5b** which is an oil, and were spectroscopically characterized with the structure of **5c** fully defined by an X-ray diffraction study (see Figure 2 and below). Similar vinylidene complexes Cp(CO)(L)Mn=C=CHPh (L = PPh$_3$, P(OEt)$_3$, P(OPh)$_3$) were earlier prepared via thermal and photochemical substitution of L for CO in the complex Cp(CO)$_2$Mn=C=CHPh.[6b] Characteristic features of the IR spectra of **4**, **5a–c**, and all of the nonconjugated vinylidene complexes reported in subsequent paragraphs are bands in the 1890–1915 and 1630–1650 cm^{-1} regions, which are assigned to the ν_{CO} and vinylidene $\nu_{C=C}$ vibrations, respectively. The acyl-substituted vinylidene complexes **6a** and **6b** also show ν_{CO} bands in the 1890–1915 cm^{-1} region, but their $\nu_{C=C}$ vibrations are shifted to 1533 and 1550 cm^{-1}, respectively, due to their conjugation with the acyl group whose ν_{CO} bands appear at 1620 and 1640 cm^{-1}, respectively.[13] These assignments were verified by preparing complex **6a** from acetyl chloride enriched in ^{13}C in the carbonyl group, which induced a shift of the 1620 band to 1550 cm^{-1}. The $\nu_{C=C}$ band shifted far less, from 1553 to 1541 cm^{-1}. It is significant that the metal carbonyl $\nu_{C=O}$ bands of these vinylidene complexes are 50–85 cm^{-1} higher in energy than the corresponding bands of the parent carbene complexes **2a–d**, implying a stronger π-acidity of the vinylidene ligands as compared to the carbene ligands, as noted earlier for similar complexes.[6b] The ^{13}C NMR spectra of **4–6** and the other vinylidene complexes reported herein show Mn=*C* carbene carbon resonances in the δ 360–370 region with J_{PC} coupling constants of 26–30 Hz and Mn=C=*C* carbon resonances in the δ 125–140 region with smaller J_{PC} coupling constants of 7–12 Hz (see the Experimental Section).

Scheme I



In order to maximize π-bonding, the vinylidene ligand in these complexes should be oriented with the plane containing the vinylidene substituents coplanar with the Mn—P bond, as in **E**.[11] Steric arguments alone would predict orientation **F**, with the two vinylidene substituents located between the ligands. Of the two



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[11] (a) Wong, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4948. (b) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.

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[13] For other acyl-substituted vinylidene complexes, see ref 5c and Pombiero, A. J. L.; Amleida, S. S. P. R.; Silva, M. F. C. G.; Jeffrey, J. C.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1989**, 2381. Birdwhistell, K. R.; Nieter-Burmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789. Werner, H.; Brekau, U. *Z. Naturforsch.* **1989**, *B44*, 1438. Hohn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.

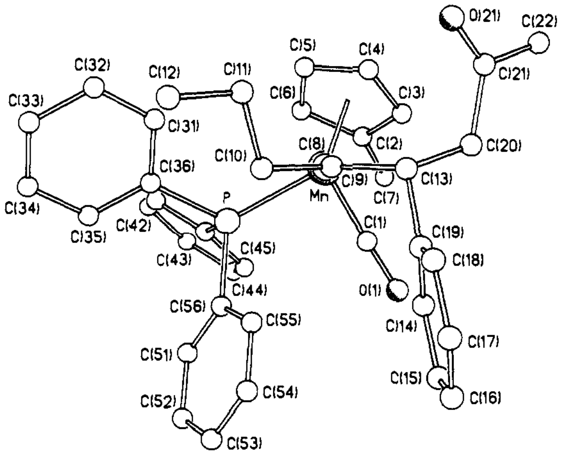


Figure 3. ORTEP drawing of $Cp'(CO)(PPh_3)Mn{=}C{=}C(Pr^n)CH(Ph)$-$CH_2C\{O\}Me$ (**13′**).

Table III. Selected Bond Lengths and Angles for $Cp(CO)(PPh_3)Mn{=}C{=}C(Me)Bu^t$ (**5c**)

Bond Lengths (Å)			
Mn-P(1)	2.225 (2)	Mn-C(1)	1.763 (9)
Mn-C(7)	1.764 (9)	Mn-CNT[a]	1.800 (9)
C(7)-C(8)	1.339 (11)	C(8)-C(9)	1.512 (12)
C(8)-C(10)	1.517 (14)		
Bond Angles (deg)			
P(1)-Mn-CNT	124.8 (3)	P(1)-Mn-C(1)	87.9 (3)
P(1)-Mn-C(7)	93.7 (2)	C(1)-Mn-CNT	124.3 (3)
C(1)-Mn-C(7)	92.3 (4)	C(7)-Mn-CNT	123.9 (3)
Mn-C(1)-O(1)	177.1 (7)	Mn-C(7)-C(8)	177.2 (7)
Mn-P(1)-C(26)	111.8 (2)	Mn-P(1)-C(36)	117.7 (2)
Mn-P(1)-C(46)	118.5 (2)	C(7)-C(8)-C(9)	118.9 (7)
C(7)-C(8)-C(10)	123.4 (8)	C(9)-C(8)-C(10)	117.5 (7)
C(8)-C(10)-C(11)	110.5 (9)	C(8)-C(10)-C(12)	111.7 (9)
C(8)-C(10)-C(13)	111.0 (9)		

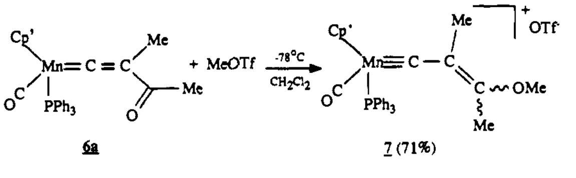
[a] CNT = centroid of atoms C(2) to C(6).

possible rotamers for each orientation, the one most sterically preferred would have the smaller of the two substituents located away from the phosphine ligand. Complex **5c** and the vinylidene complex $Cp(CO)(PPh_3)Mn{=}C{=}C(Pr^n)CHPhCH_2C\{O\}CH_3$ (**13′**), whose preparation is described below, have been crystallographically characterized. The ORTEP drawings of both complexes (see Figures 2 and 3) show that in each case the vinylidene ligand adopts the **F** orientation. Further evidence that electronic control of the orientation of the vinylidene ligand is not strong comes from the crystal structure of the bimetallic vinylidene complex $Cp(CO)(PPh_3)Mn{=}C{=}C(Me)CH(Et)C(Me){=}C{=}MnCp(CO)(PPh_3)$, whose preparation will be separately described,[14] which showed that one of the vinylidene ligands is oriented as in **F** whereas the other is coplanar with the Mn–P bond. A vinylidene ligand orientation similar to that in **F** was also observed crystallographically for $Cp^*(CO)(PPh_3)Os{=}C{=}CHBu^t$.[15]

Two different views of **5c** are shown in Figure 2, and relevant crystallographic data are given in Tables I and III. The molecule possesses the usual pseudooctahedral geometry about manganese. As illustrated in the drawing on the left, the vinylidene ligand is oriented with the bulky *tert*-butyl substituent between the Cp and the CO ligands and the smaller methyl substituent in the more hindered space between the PPh_3 and Cp ligands [torsion angle {P(1)—Mn—C(7)}—{C(7)—C(8)—C(9) = 33.5°]. The vinylidene ligand is essentially linear [Mn—C(7)—C(8) = 177.2 (7)°], and the Mn—C(7) and C(7)—C(8) distances of 1.764 (9) and 1.339 (11) Å, respectively, compare well to those found in related vinylidene complexes [$Cp(CO)_2Mn{=}C{=}CHPh$, Mn=C, 1.68 (2) Å; C=C, 1.34 (3) Å;[16a] $Cp(CO)_2Mn{=}C{=}CMe_2$, Mn=C, 1.79 (2) Å, C=C, 1.33 (2) Å;[16b] $Cp(CO)_2Mn{=}C{=}CH\{C_6H_4C(Br){=}CH_2\}$, Mn=C, 1.75 (2) Å; C=C, 1.32 (2) Å[16c]). All other metric parameters appear normal.

As noted above, there are two possible rotamers for each of the orientations **E** and **F** of the vinylidene complexes that have different substituents (A and B) on the vinylidene β-carbon. The observation of only a single set of ^1H and ^{13}C NMR resonances at 22 °C for vinylidene complexes **4**, **5a**,**b**, and **6a**,**b** indicates that only a single stereoisomer is formed in each case (**F** or **G**) or that rapid rotation of the vinylidene ligand occurs at this temperature and equilibrates the rotamers on the NMR time scale to give an averaged environment. Gladysz has shown that that rotation about the Re=C=C linkage can occur to equilibrate vinylidene rotamers in the complexes $[Cp(NO)(PPh_3)Re{=}C{=}CHR]^+$ (R = Me, Ph, 1-$C_{10}H_7$) and $[Cp(NO)(PPh_3)Re{=}C{=}CMe(Ph)]^+$, although the activation barrier is high (21–23 kcal/mol).[11] To probe the possibility of rotamer interconversion for the complexes described herein, variable-temperature ^1H NMR studies were conducted on the Cp analogues of complexes **4** and **5b**, and those results for the latter complex are shown in Figure A of the supplementary material. At 20 °C, the Cp analogue of **5b** shows a barely resolved doublet at δ 4.55 (J_{PH} = 1.5 Hz) due to the Cp protons, a multiplet at δ 2.01 due to the diastereotopic methylene protons, a singlet at δ 1.51 due to the vinyl methyl group, and a triplet at δ 1.05 due to the terminal methyl group, along with aromatic resonances. Upon cooling, these resonances broaden, coalesce, and by −80 °C have resolved into two distinct Cp resonances at δ 4.46 and 4.44, two broad methylene proton resonances at δ 2.14 and 1.72, two broad singlets at δ 1.87 and 1.31 for the vinyl methyl groups, and two broad triplets at δ 1.14 and 0.85 for the terminal methyl groups. The ratio of these two isomers is ~1.3:1. Similarly, complex **4** shows a doublet at δ 1.48 for the terminal methyl group and a doublet of quartets (J_{PH} = 1.2 Hz) at δ 5.2 for the vinyl proton, as well as aromatic and Cp resonances. As the sample is cooled, these resonances broaden and coalesce, and at −85 °C two broad signals at δ 1.71 and 1.25 are attributed to the terminal methyl groups of the two rotameric species and two broad signals at δ 5.37 and 5.10 are assigned to the vinyl protons of the two rotamers. The Cp resonance at δ 4.51 broadened over the temperature range but did not decoalesce. The isomer ratio at the low-temperature limit was ~2.1:1. Activation barriers of $\Delta G^{\ddagger}$ = 9.9 and 10.8 kcal/mol for the rotamer interconversion of the Cp analogues of **4** and **5b** were respectively calculated from the NMR data.

Alkylation of the Acyl Substituent of 6a To Form a Vinyl Carbyne Complex. The acyl group of complex **6a** can be alkylated to form the vinyl carbyne complex **7** shown in eq 8. This complex



(8)

was isolated in good yield as an orange solid and was spectroscopically characterized. It showed ^1H NMR resonances consistent with this structure, a parent ion at m/z = 521 in its FAB mass spectrum, and a ν_{CO} band at 1977 cm⁻¹ and a $\nu_{C=C}$ band at 1524 cm⁻¹ in its IR spectrum. However, the spectroscopic data, including that from a ^1H NMR NOE study, were insufficient to determine the *E* or *Z* configuration of the vinyl substituent. Related manganese complexes $[Cp(CO)_2Mn{\equiv}CCH{=}CR_2]^+$ (R

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[15] Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337.

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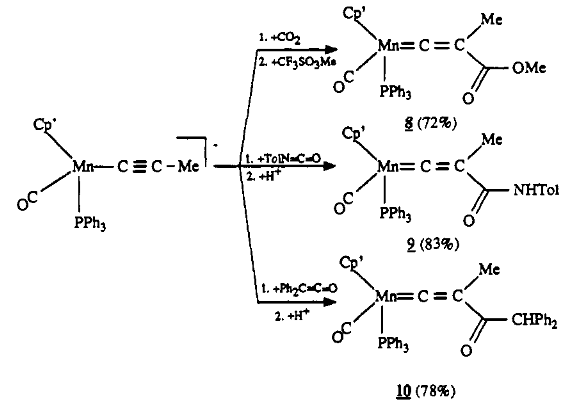
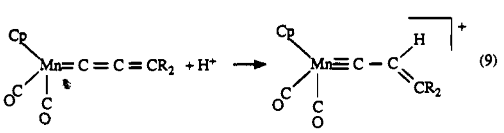
Scheme II

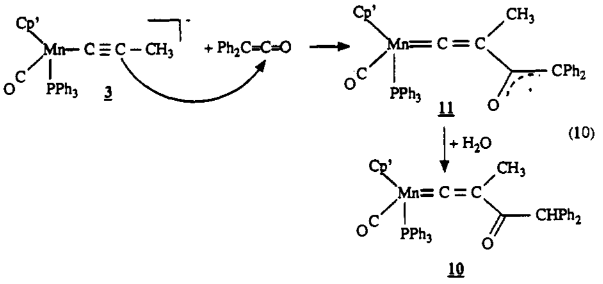


= Ph, Bu^t) were prepared by protonation of the allenylidene complexes illustrated in eq 9.[17]



(9)

Addition of 3 to Heterocumulenes. Complex **3** is also sufficiently nucleophilic to add to the heterocumulenes TolN=C=O, Ph_2C=C=O, and CO_2 to give, after protonation or alkylation, the vinylidene complexes **8–10** shown in Scheme II. These complexes result from nucleophilic attack of the β-carbon of the alkynyl ligand on the central carbon of the heterocumulene and most likely proceed via the intermediacy of vinylidene–enolate complexes such as **11** illustrated in eq 10. These intermediate complexes can be detected by IR but not isolated. For example, treatment of complex **3** with Ph_2C=C=O gave loss of the IR bands of **3** and the formation of an intermediate with IR bands at 1881 and 1629 cm^{-1}, which are in the regions characteristic of the other vinylidene complexes prepared in this study (e.g., **5b**, ν_{CO} = 1900 and $\nu_{C=C}$ = 1633 cm^{-1}). Addition of H_2O to this intermediate species induced the immediate disappearance of these bands and the appearance of IR bands characteristic of **10**. It should be noted that the intermediate vinylidene–enolate complex formed between **3** and CO_2 could only be trapped by treating it with an alkylating agent, as in the formation of **8**. When protonated, the only detectable product was the vinylidene complex Cp'(CO)(PPh_3)Mn=C=CH(CH_3) (**4**), which apparently formed by decarboxylation of the initially produced carboxylic acid Cp'(CO)(PPh_3)Mn=C=C(Me)(CO_2H).



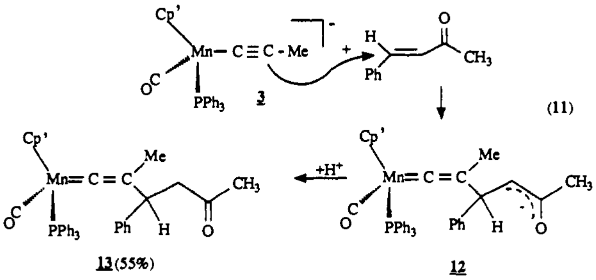
(10)

Vinylidene complexes **8–10** were isolated as orange solids and were spectroscopically characterized. Each gave acceptable C, H analyses, showed parent ions in their mass spectra, and exhibited IR bands and vinylidene ^{13}C NMR resonances in the regions characteristic of this general family of vinylidene complexes (see the Experimental Section).

Addition of 3 to *trans*-4-Phenyl-3-buten-2-one. The propynyl complex **3** is also sufficiently nucleophilic to undergo conjugate addition with *trans*-4-phenyl-3-buten-2-one to form, after protonation, the vinylidene complex **13** shown in eq 11. This reaction likely proceeds by nucleophilic attack of the β-carbon of the acetylide ligand on the vinyl carbon of the vinyl ketone to initially form the vinylidene–enolate complex **12**, which then gives **13** upon protonation with water. IR monitoring of the reaction showed the initial appearance of a ν_{CO} band at 1886 cm^{-1} assigned to **12**, which disappeared when water was added to form **13** (ν_{CO} = 1891 cm^{-1}). Complex **13** was isolated in good yield as a red solid and was spectroscopically characterized. In addition, its *n*-propyl analogue (**13'**), prepared from [Cp(CO)(PPh_3)MnC≡CPr^n]$^-$, was crystallographically characterized (see Figure 3 and below). Both the manganese and the benzylic carbon of **13** and **13'** are stereocenters giving rise to diastereomers, and each diastereomer can exist in two rotameric forms that result from rotation of the Mn=C=C unit. Thus, four stereoisomers could be observable if the rotamers did not readily interconvert. NMR data indicate the presence of only two isomers of both **13** and **13'**, and these are formed in a 9:1 ratio in each case. The crystallographically characterized isomer of **13'** is the *RR*/*SS* diastereomer in the rotameric form **G**, and ^1H NMR analysis of the crystals from which this sample was selected indicated selective crystallization of the major isomer. The minor isomer observed is either the rotameric form **H** or the *RS*/*SR* diastereomer. In either case, the reaction proceeds with relatively high stereocontrol due to the chirality of the manganese center.

Table IV. Selected Bond Lengths and Angles for Cp'(CO)(PPh_3)Mn=C=C(Pr^n)CHPhCH_2C{O}CH_3 (**13'**)

	Bond Lengths (Å)		
Mn-C(1)	1.756 (4)	Mn-C(8)	1.778 (4)
Mn-P	2.258 (1)	C(8)-C(9)	1.346 (5)
C(9)-C(10)	1.513 (5)	C(9)-C(13)	1.541 (6)
C(21)-O(21)	1.516 (7)	C(1)-O(1)	1.166 (5)
C(10)-C(11)	1.545 (6)	C(11)-C(12)	1.520 (6)
C(13)-C(20)	1.532 (5)	C(21)-C(22)	1.516 (7)
C(20)-C(21)	1.501 (5)		
	Bond Angles (deg)		
C(1)-Mn-C(8)	90.3 (2)	P-Mn-C(8)	93.9 (1)
P-Mn-C(1)	89.7 (2)	Mn-C(1)-O(1)	176.9 (4)
Mn-C(8)-C(9)	176.7 (3)	C(8)-C(9)-C(13)	123.8 (3)
C(8)-C(9)-C(10)	120.8 (4)	C(10)-C(9)-C(13)	115.3 (3)



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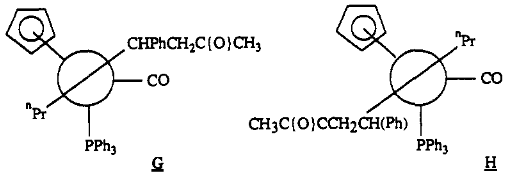

An ORTEP drawing of complex **13'** is shown in Figure 3, and the important crystallographic parameters are given in Tables I and IV. The molecule possesses the usual pseudooctahedral geometry about Mn, as indicated by the C(1)—Mn—C(8) and C(1)—Mn—P bond angles of 90.3 (2)° and 89.7 (2)°, respectively. The vinylidene ligand is linear with a Mn—C(8)—C(9) bond angle of 176.7 (3)°. As noted above, the plane containing the vinylidene substituents [C(10)—C(9)—C(13)] is not coplanar with the Mn—P vector as would be predicted on electronic grounds[7,11] and as has been found for the related complex [Cp(NO)(PPh_3)Re=C=CH(1-$C_{10}H_7$)]$^+$,[11] but instead is oriented

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[17] Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *262*, 39.

Table V. Selected Bond Lengths and Angles for $Cp'(CO)(PPh_3)Mn{=}\overline{C\{OC(Me)_2CH_2C}H(Me)\}$ (**14**)

	Bond Lengths (Å)		
Mn-C(1)	1.741 (19)	Mn-P(1)	2.229 (7)
Mn-C(8)	1.822 (20)	C(8)-C(9)	1.499 (26)
C(9)-C(12)	1.544 (35)	C(9)-C(10)	1.526 (32)
C(10)-C(11)	1.527 (39)	C(11)-O(2)	1.552 (27)
O(2)-C(8)	1.350 (25)	C(1)-O(1)	1.194 (26)
	Bond Angles (deg)		
Mn-C(1)-O(1)	170.5 (18)	C(8)-Mn-C(1)	92.5 (9)
C(8)-Mn-P(1)	93.4 (10)	C(1)-Mn-P(1)	92.4 (7)
Mn-C(8)-C(9)	132.4 (15)	C(8)-C(9)-C(10)	108.0 (16)
C(12)-C(9)-C(8)	109.3 (19)	C(12)-C(9)-C(10)	121.8 (19)
C(9)-C(10)-C(11)	106.3 (21)	C(10)-C(11)-O(2)	97.1 (18)
C(13)-C(11)-C(14)	104.4 (25)	C(11)-O(2)-C(8)	119.8 (16)
Mn-C(8)-O(2)	125.4 (15)		

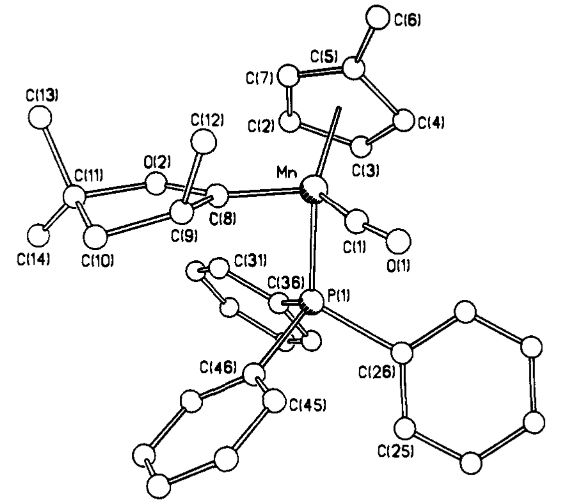
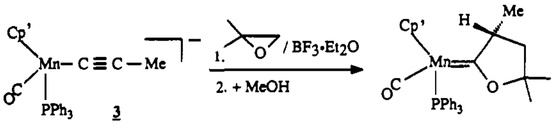


Figure 4. ORTEP drawing of $Cp'(CO)(PPh_3)Mn{=}\overline{C\{OC(Me)_2CH_2C}H(Me)\}$ (**14**).

such that the Pr^n substituent lies between the Cp and PPh$_3$ ligands and the CHPhCH$_2$C{O}CH$_3$ substituent lies between the Cp and CO ligands (see G above) with a [P—Mn—C(8)]—[C(10)—C(9)—C(13)] torsion angle of 30.1°. The Mn—C(8) and C(8)—C(9) distances of 1.778 (4) and 1.346 (5) Å within the vinylidene ligand compare well to the corresponding distances in the several $Cp(CO)_2Mn{=}C{=}CRR'$ vinylidiene complexes that have been structurally characterized (see the above discussion of the structure of **5c**).[16] All other metric parameters appear normal.

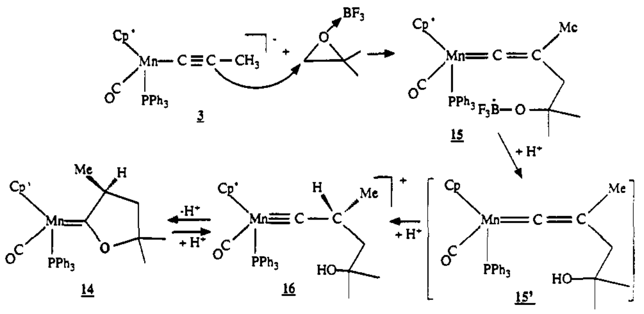
Cycloaddition of 3 with Epoxides. A particularly interesting reaction of complex **3**, and one which has no precedent for any other alkynyl complex, is the [2 + 3] cycloaddition reaction observed with epoxides. For example, treatment of **3** with isobutylene oxide gives, after protonation with methanol, the carbene complex **14** in excellent yield (eq 12). Although this reaction proceeds well in the absence of a Lewis acid, the presence of BF$_3$·Et$_2$O significantly decreases the reaction time and increases the yield. The BF$_3$·Et$_2$O likely assists the epoxide ring opening by coordinating to the epoxide oxygen and thus weakening the oxygen–carbon bond. Lewis acids are well known to promote reactions of epoxides with organic nucleophiles,[18] and BF$_3$·Et$_2$O has recently been shown to assist the reaction of epoxides with the carbene anion $(CO)_5Cr{=}C(OMe)CH_2^-Li^+$, a reaction which also forms cyclic carbene complexes similar to **14**.[19] Significantly, NMR data indicate that only a single pair (*RR*/*SS* or *RS*/*SR*) of enantiomers of **14** is produced, implying that the stereochemical configuration at Mn strongly controls the configuration adopted at the chiral carbon of the cyclic carbene ligand. Complex **14** was isolated in high yield as a yellow solid and has been spectroscopically (see the Experimental Section) and crystallographically characterized (see Tables I and V). The ORTEP drawing shown in Figure 4 indicates that it is the *RS*/*SR* pair that has formed with both of the enantiomers present in the centrosymmetric unit cell. Note that this configuration places the CH$_3$ substituent and the bulky PPh$_3$ ligand on opposite sides of the cyclic carbene ligand, as would be predicted on the basis of steric arguments. As with the carbene complex **2** (see Figure 1), the plane of the carbene ligand is oriented parallel to the Mn—CO vector, but in this case, the oxygen substituent of the carbene ligand is located on the opposite side of the molecule from the CO ligand. The Mn—C(8) distance is 1.822 (20) Å and compares well to the Mn—C(2) carbene distance of 1.861 (6) Å in **2** and to those listed above for the several crystallographically characterized $Cp(CO)_2Mn{=}CRR'$ complexes.[8] All other metric parameters appear normal.



(12)

14 (89%)

Scheme III



The mechanism proposed for the epoxide cycloaddition reaction is shown in Scheme III. The first step likely involves the Lewis acid assisted ring opening of the epoxide by nucleophilic **3** to form the anionic vinylidene complex **15**. Complex **15** was detected by IR after the reaction had run for 10 min under carefully controlled anhydrous conditions, and it shows IR bands in the regions characteristic of the other vinylidene complexes prepared in this study (ν_{CO} = 1886 cm^{-1}, $\nu_{C=C}$ = 1636 cm^{-1}). Complex **15** could not be isolated in pure form due to its instability. However, an impure solid sample was obtained by evaporation of solvent from these solutions, and this sample showed a ^{11}B NMR resonance at δ −0.75 (referenced to BF$_3$·Et$_2$O) attributed to the BF$_3$ group in **15**. Addition of MeOH to solutions of **15** gave a new species which showed a ν_{CO} band at 1998 cm^{-1}. The high-energy position of this band indicates this complex to be a cationic species, and we propose that double protonation occurs to form the cationic carbyne complex **16**. The position of this band compares well to the corresponding bands in the cationic carbyne complexes $[Cp(CO)(PPh_3)Mn{\equiv}CMe]^+$ (ν_{CO} = 1999 cm^{-1})[20] and $[Cp(CO)(PPh_3)Mn{\equiv}CPh]^+$ (ν_{CO} = 2003 cm^{-1})[20] and, as expected, is substantially higher in energy than the ν_{CO} band of neutral $Cp(CO)(PPh_3)Mn{=}C(OMe)Et$ (**2**) at 1826 cm^{-1}. The **15** to **16** conversion may proceed via the intermediacy of the vinylidene complex **15′**, although no direct evidence was obtained for this species. However, it was noted that the vinylidene complex $Cp(CO)(PPh_3)Mn{=}C{=}CMe_2$ (**5a**) reacts with MeOH *in the*

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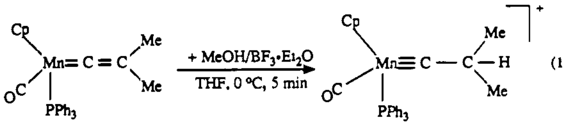
[18] (a) Smith, J. G. *Synthesis* **1984**, 629. (b) Winstein, S.; Henderson, R. B. In *Heterocyclic Compounds*; Elderfield, R. C., Ed.; John Wiley and Sons: New York, 1950; Vol. 1, pp 1–60. (c) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, 737. (d) Rosowsky, A. In *Heterocyclic Compounds with Three- and Four-Membered Rings*; Weissberger, A., Ed.; John Wiley and Sons: New York, 1964; Part 1, pp 1–523.

[19] Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807.

[20] (a) Terry, M. R.; Geoffroy, G. L. Unpublished data. (b) These cationic carbyne complexes were generated by addition of BCl$_3$ to carbene complexes **2b** and **2d** following the published procedures for the analogous dicarbonyl carbyne complexes $[Cp(CO)_2Mn{\equiv}CR]^+$: Fischer, E. O.; Besl, G. *Z. Naturforsch.* **1979**, *34B*, 1186. Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140.

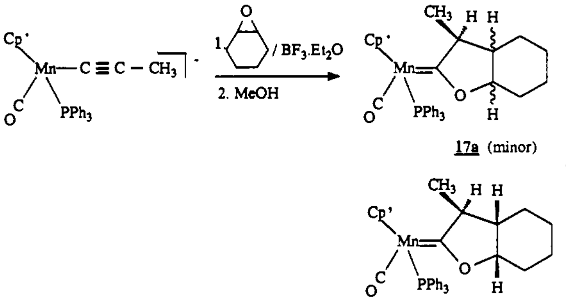
presence of $BF_3{\cdot}Et_2O$, but not in its absence, to give formation of the carbyne complex $[Cp(CO)(PPh_3)Mn{\equiv}CCHMe_2]^+$ [ν_{CO} = 2002 cm^{-1}; m/z (FAB) = 465 (M$^+$)] (eq 13). In this reaction,



(13)

and in that illustrated in Scheme III, the strong acid needed to protonate the vinylidene complex is presumably $H[MeOBF_3]$, resulting from the combination of MeOH and BF_3. Complex **16** also proved too unstable to be isolated in pure form, but it was observed that, when it was allowed to stand in THF, it slowly transformed into **14**, presumably by intramolecular addition of the oxygen atom of the OH substituent to the carbyne carbon with concomitant proton loss. Precedent for this step comes from the facile addition of many nucleophiles to the carbyne carbon in the related cationic dicarbonyl complexes $[Cp(CO)_2Mn{\equiv}CR]^+$.[21] It could be supposed that complex **14** forms directly from **15**′ by addition of the OH group across the vinylidene C═C bond, since many vinylidene complexes have been shown to give carbene derivatives by this type of reaction when treated with alcohols.[1] However, we do not believe this to be the case since none of the vinylidene complexes **4**–**6** prepared in this study have been found to react with alcohols, apparently because the electron-releasing PPh_3 ligand renders the α-carbon of the vinylidene ligand less electrophilic than in the vinylidene complexes that do undergo such reaction (see also Scheme V and the associated discussion). We thus suggest that the carbyne complex **16** must be an important intermediate in the formation of **14** and that ring closure occurs only from this cationic species which should have an highly electrophilic α-carbon. We note in passing that the **16** to **14** transformation can be reversed by protonating **14** with excess $HBF_4{\cdot}Et_2O$.

Cyclohexene oxide also reacts with **3** in the presence of $BF_3{\cdot}Et_2O$ to form, after protonation with MeOH, the isomeric carbene complexes **17a** and **17b** (eq 14). The use of the Lewis acid $BF_3{\cdot}Et_2O$ is essential in this case since the reaction does not proceed in its absence. Although there are four chiral centers in complex **15**, the Mn center and three carbons of the carbene ligand, ^{1}H NMR data indicate that only two diastereomers are present in a 7:3 ratio. Chromatography of this diastereomeric mixture gave a broad yellow band, from which a pure sample of **17b** was isolated by collecting the first half of the band from the column. The second half of the band gave a mixture of **17a** and **17b**. Pure **17b**, as well as the **17a**/**b** mixture, showed a single IR ν_{CO} band at 1850 cm^{-1} (compare to the ν_{CO} band of **14** at 1830 cm^{-1}) and a parent ion at m/z = 562 in its FAB mass spectrum. The ^{1}H and ^{13}C NMR spectra showed characteristic resonances for the Cp and PPh_3 ligands, as well as resonance patterns consistent with the carbene ligand structure drawn in eq 14. For example, the ^{1}H NMR spectrum of **17b** showed in addition to PPh_3 and Cp′ resonances, a triplet of doublets at δ 3.59 assigned to H_b (see drawing below), a broad doublet of quartets at δ 2.95 due to H_c, a multiplet at δ 2.29 assigned to H_a, a doublet at δ 1.05 due to the methyl group on the 5-membered ring, and a series of resonances in the 1.54–0.76 region assigned to the remaining hydrogens on the 6-membered ring. Although not as well resolved, the ^{1}H NMR spectrum of **17b** (see the Experimental Section) is similar to that of **17a**. Noteworthy in the ^{13}C NMR spectrum of **17b** is a carbene resonance at δ 335.3 (d, J_{PC} = 30.5 Hz). The relative stereochemistry of the three chiral centers in **17b** was determined from a ^{1}H NMR NOE experiment which showed that irradiation of the δ 3.59 resonance due to H_b gave enhancement of the resonances at δ 2.29 (H_a) and δ 1.05 (Mn═C(CHCH_3)), but not of the δ 2.95 resonance due to H_c. Similarly, irradiation of the resonance due to H_a gave enhancement of the resonances of H_b and the methyl group, but not that of H_c. Unfortunately, the stereochemistry of the minor isomer **17a** could not be similarly assigned, due to the small quantity of it present in the **17a**/**17b** mixture.

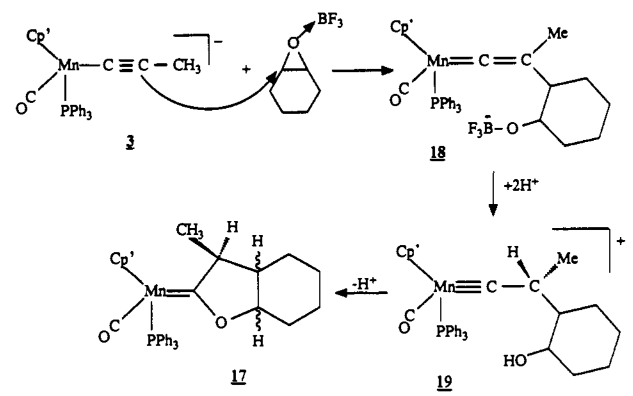


(14)

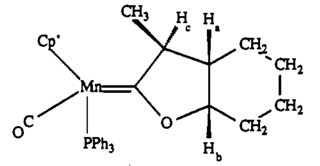
17a (minor)

17b (major)

Scheme IV

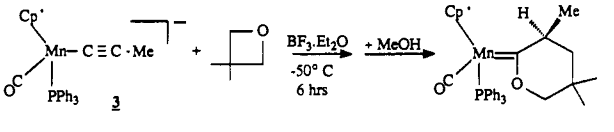


3 18 17 19



IR analysis of the reaction of cyclohexene oxide with the alkynyl complex **3** gave results similar to those discussed above for the reaction of **3** with isobutylene oxide and indicated a similar mechanism for the formation of **17a**,**b** (see Scheme IV). The IR spectrum of the reaction mixture after the addition of the cyclohexene oxide and $BF_3{\cdot}Et_2O$, but before the addition of MeOH, showed the presence of an intermediate with IR bands at ν_{CO} = 1891 and $\nu_{C=C}$ = 1657 cm^{-1} which are attributed to the vinylidene complex **18**. Addition of exactly 2 equiv of MeOH to this solution gave immediate replacement of these bands by a new band at ν_{CO} = 2003 cm^{-1}, which is attributed to the cationic carbyne complex **19**, and this species slowly transformed into **17a**,**b** when it was allowed to stir in THF solution for 12 h. IR data indicated that complexes **18** and **19** were present in solid samples obtained by solvent evaporation from their respective solutions, but we have not been able to obtain either sufficiently pure for NMR characterization.

Cycloaddition of 3 with 3,3-Dimethyloxetane. Complex **3** was also observed to undergo a net [4 + 2] cycloaddition with 3,3-dimethyloxetane to form, after protonation with MeOH, the carbene complex **20** (eq 15). As with cyclohexene oxide, this reaction does not proceed without the aid of $BF_3{\cdot}Et_2O$. Complex **20** was isolated as a yellow solid in good yield and was crystal-



(15)

3

20 (68%)

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(21) (a) Fischer, E. O.; Jiabi, C.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231. (b) Fischer, E. O.; Wanner, J. K. R. *Chem. Ber.* **1985**, *118*, 2489. (c) Fischer, E. O.; Schambeck, W. *J. Organomet. Chem.* **1980**, *201*, 311. (d) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51.

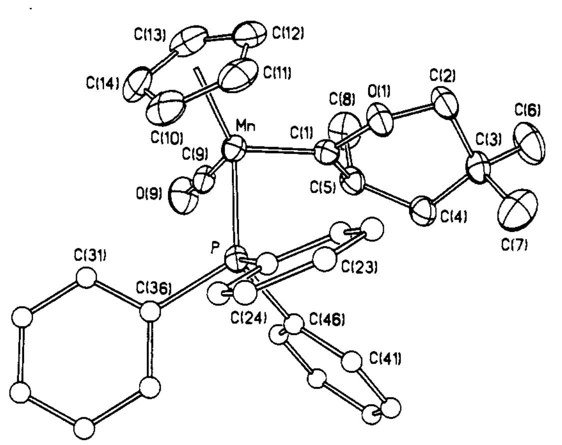


Figure 5. ORTEP drawing of $Cp'(CO)(PPh_3)Mn{=}\overline{C\{OCH_2C(Me)_2CH_2}CH(Me)\}$ (**20**).

Table VI. Selected Bond Lengths and Angles for $Cp'(CO)(PPh_3)Mn{=}\overline{C\{OCH_2C(Me)_2CH_2}CH(Me)\}$ (**20**)

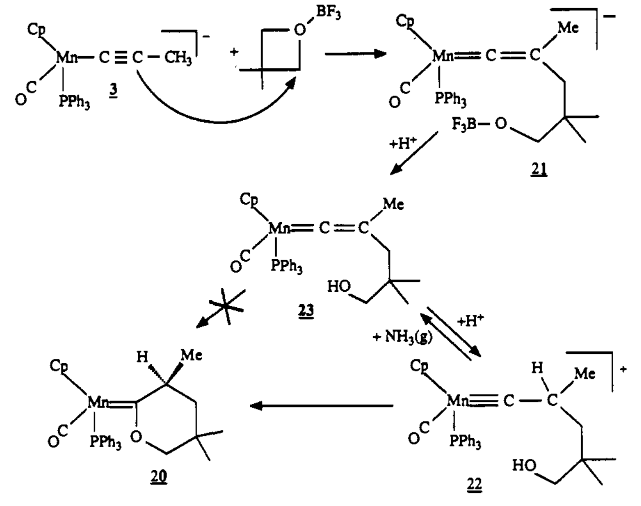
	Bond Lengths (Å)		
Mn-C(1)	1.861 (3)	C(2)-C(3)	1.511 (5)
Mn-C(9)	1.743 (4)	C(3)-C(4)	1.525 (5)
Mn-P	2.230 (1)	C(4)-C(5)	1.533 (5)
C(1)-O(1)	1.376 (4)	C(5)-C(1)	1.514 (4)
O(1)-C(2)	1.445 (4)		
	Bond Angles (deg)		
C(9)-Mn-C(1)	93.3 (1)	Mn-C(1)-C(5)	129.3 (2)
C(9)-Mn-P	92.7 (1)	C(1)-C(5)-C(4)	112.9 (3)
P-Mn-C(1)	93.7 (1)	C(5)-C(4)-C(3)	115.2 (3)
Mn-C(1)-O(1)	118.2 (2)	C(3)-C(2)-O(1)	112.7 (3)

lographically characterized (see Figure 5 and below). Its spectroscopic data given in the Experimental Section are consistent with the structure determined by the X-ray diffraction study, and both ^{1}H and ^{13}C NMR data indicate that only a single pair of enantiomers of **20** is formed, again demonstrating the high degree of stereochemical control induced by the chiral Mn center.

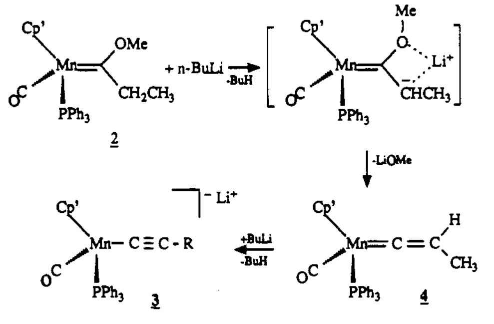
An ORTEP drawing of **20** is shown in Figure 5, and relevant crystallographic data are set out in Tables I and VI. The structure of the molecule is similar to those determined for **2** and **14** described above. The carbene carbon and the atoms attached to it are coplanar with the Mn—CO vector, and the oxygen substituent of the carbene ligand is on the opposite side of the molecule from the CO ligand, as in the case of **14** (but not **2**). The crystal structure shows that it is the *RS*/*SR* pair that has formed, with the CH_3 substituent and the bulky PPh_3 ligand located on opposite sides of the cyclic carbene ligand. The Mn=C(1) distance of 1.861 (3) Å compares well to that found in **2** (1.861 (6) Å) and **14** (1.822 (2) Å).

The mechanism proposed for this reaction is similar to that given above for the cycloaddition of **3** with epoxides and is shown in Scheme V (for the Cp analogue which gave more tractable compounds and better spectroscopic data). Nucleophilic ring opening of the BF_3-complexed oxetane by **3** was observed to give immediately the anionic vinylidene complex **21**, which was isolated as a light yellow solid. This compound showed a characteristic vinylidene IR spectrum (ν_{CO} = 1880 cm^{-1}, $\nu_{C=C}$ = 1651 cm^{-1}) and an $M^+ - BF_3$ ion at m/z = 535 in its FAB mass spectrum. Upon protonation by the addition of MeOH, **21** was converted into the cationic carbyne complex **22**, presumably via the intermediacy of **23**. Complex **22** was isolated as a bright yellow solid in 67% yield. This species gave a satisfactory C,H analysis and showed a parent ion at m/z = 537 in its FAB mass spectrum and a high-energy ν_{CO} band at 2010 cm^{-1}, consistent with its formulation as a cationic carbyne complex. When complex **22** was treated with excess NH_3(g), deprotonation occurred to form the neutral vinylidene complex **23**. This complex was isolated as an orange powder, and its IR, MS, and ^{1}H NMR data given in the Experimental Section are consistent with its proposed structure.

Scheme V



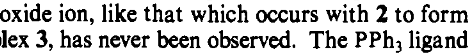
Scheme VI



Significantly, when separate THF solutions of **22** and **23** were stirred for 12 h at room temperature, the carbene complex **20** readily formed from the flask containing **22**, but there was no change in **23**. As discussed above for the formation of **14**, this result indicates that ring closure to form the cyclic carbene complexes **14**, **17**, and **20** occurs with the cationic carbyne intermediates and not with the neutral vinylidene complexes.

Discussion

The first major surprise in this study was the formation of the alkynyl complex **3** by treatment of the carbene complex $Cp'(CO)(PPh_3)Mn{=}C(OMe)CH_2CH_3$ (**2**) with base (eq 6). There are numerous reports in the literature of the deprotonation of carbene complexes to give relatively stable carbene anions, e.g., eq 16, and these latter compounds have proven to be useful reagents for the subsequent modification of the carbene ligand.[19,22]



$$(CO)_5Cr{=}C(OMe)(CH_3) + {}^nBuLi \xrightarrow{Et_2O} (CO)_5Cr{=}C(OMe)(\overset{-}{C}H_2\overset{+}{Li}) + {}^nBuH \quad (16)$$

However, to our knowledge a double deprotonation and loss of methoxide ion, like that which occurs with **2** to form the alkynyl complex **3**, has never been observed. The PPh_3 ligand is obviously influential in this reaction, since the unsubstituted complex

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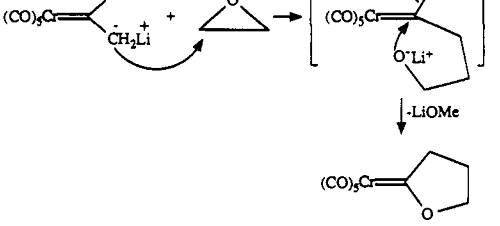
(22) (a) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230. (b) Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28. (c) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175. (d) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345. (e) Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391. (f) Casey, C. P.; Brunsvold, W. R.; Scheck, D. M. *Inorg. Chem.* **1977**, *16*, 3059. (g) Casey, C. P. *CHEMTECH* **1979**, 379. (h) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309. (i) Rudler-Chauvin, M.; Rudler, H. *J. Organomet. Chem.* **1981**, *212*, 203. (j) Alverez-Toledano, C.; Parlier, A.; Rose-Munch, F.; Rudler, H.; Daran, J. C.; Knobler, C.; Jeannin, Y. *J. Organomet. Chem.* **1987**, *323*, 371. (k) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263. (l) Macomber, D. W.; Madhukar, P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1275. (m) Macomber, D. W.; Hung, M.; Puttannachetty, M.; Liang, M.; Rogers, R. D. *Organometallics* **1991**, *10*, 737. (n) Macomber, D. W.; Hung, M. H.; Verma, A. G.; Rodgers, R. D. *Organometallics* **1988**, *7*, 2072.

$Cp'(CO)_2Mn{=}C(OMe)CH_3$ undergoes clean, single deprotonation to form a carbene anion which can be alkylated with CH_3I to yield $Cp'(CO)_2Mn{=}C(OMe)CH_2CH_3$ (**1b**, eq 7). Indeed, as outlined in the Experimental Section, this is the preferred synthesis of **1b**. The PPh_3 substitution must increase the electron density on the complex to such an extent that the methoxide ligand is more easily lost in the intermediate carbene anion formed from **2** (see Scheme VI) than it is from the carbene anion resulting from deprotonation of $Cp'(CO)_2Mn{=}C(OMe)CH_3$. Methoxide loss would generate the neutral vinylidene complex **4**, which could then be deprotonated to form **3** (Scheme VI). Indeed, IR analysis showed that treatment of the vinylidene complex **4** with *n*-BuLi did result in the clean formation of **3**. Furthermore, as described in the Experimental Section, vinylidene complex **5a** was prepared from **4** by deprotonation with MeLi and then treatment of the resultant **3** with MeOTf. The fact that **4** is not detected by IR in the formation of **3** from **2**, even with the use of just 1 equiv of *n*-BuLi, implies that deprotonation of **4** is more facile than the initial deprotonation of **2**.

The results described above show that the alkynyl complex **3** is highly electron rich, and it appears to be the most nucleophilic alkynyl complex yet prepared. Theoretical studies have shown that alkynyl complexes generally possess a partial negative charge on the β-carbon of the alkynyl ligand, with the magnitude of that charge dependent upon the nature of the complex. For example, Kostic and Fenske[23] have calculated that the atomic charge on the β-carbon of $Cp(CO)_2FeC{\equiv}CH$ is −0.27, and this value increased to −0.37 when the CO ligands were replaced by PH_3 ligands in the complex $Cp(PH_3)_2FeC{\equiv}CH$. The negative charge on the β-carbon of $[Cp(CO)(PPh_3)MnC{\equiv}CCH_3]^-$ should be greater still because of the overall negative charge on the complex and the electron-releasing methyl group on the alkynyl ligand. The reactions described above clearly indicate this to be the case and illustrate the importance of resonance form **B′**:

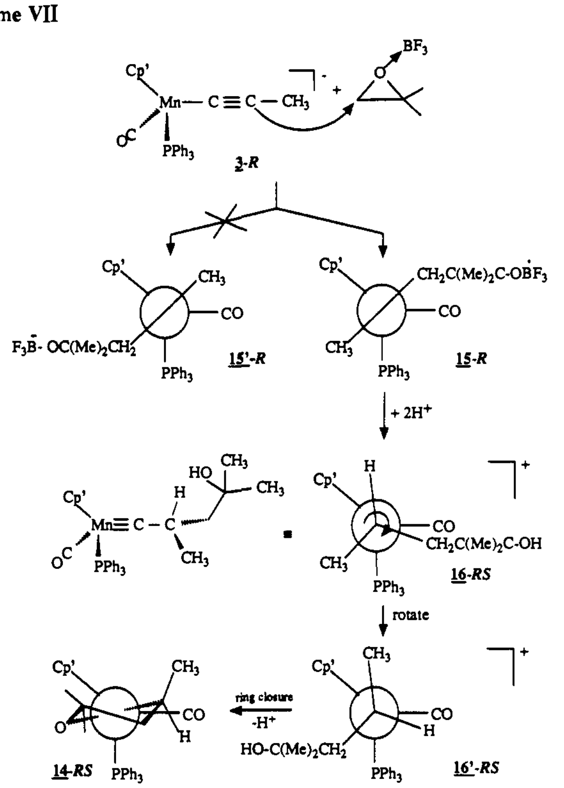
$$\underset{\mathbf{A'}}{L_nM^-C{\equiv}CR} \leftrightarrow \underset{\mathbf{B'}}{L_nM{=}C{=}C^-R}$$

The high nucleophilic character of **3** has given rise to a series of new addition and cycloaddition reactions and significantly extends the known chemistry of alkynyl ligands. The protonation and alkylation reactions illustrated in Scheme I to form vinylidene complexes have considerable precedent in other systems,[1] but the formations of vinylidene complexes by the addition of **3** to methyl styryl ketone (eq 11) and to $TolN{=}C{=}O$ and $Ph_2C{=}C{=}O$ (Scheme II) are unprecedented reactions, although the latter transformations are related to the reaction discovered by Templeton and shown in eq 3.[5a] Completely new are the net [2 + 3] and [2 + 4] cycloaddition reactions observed with epoxides (eqs 12 and 13) and 3,3-dimethyloxetane (eq 14), although cyclic carbene complexes similar to **14** and **17** have been shown to result from the addition of the carbene anions $(CO)_5Cr{=}C(OMe)CH_2^-Li^+$ to epoxides (eq 17)[19,22b,c,g,h] and from other routes as well.[24]

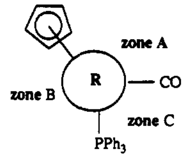


(17)

Scheme VII



The data presented herein also show that the chirality of **3** induces high stereocontrol in the reactions that form a new chiral center in the resulting organic ligand. Although a conformational analysis has not been conducted for $Cp(CO)(PPh_3)MnR$ complexes, the alkynyl complex **3** and the other Mn complexes described herein are closely related to the chiral-at-metal complexes of the type $Cp(CO)(PPh_3)FeR$ and $Cp(NO)(PPh_3)ReR$ that have been extensively studied by Davies[19,25] and Gladysz,[7c–e,10,11,26] respectively. These complexes have a pseudooctahedral geometry and can be depicted by Newman projections like that drawn here in which the circle represents the Mn center and the Mn–R vector is perpendicular to the plane of the paper. The mutually orthogonal geometry of the three sites not occupied by the Cp ligand is apparent from this view. A detailed analysis by Davies on the $Cp(CO)(PPh_3)FeR$ complexes has shown that zone C between the CO and the PPh_3 ligands is always the least accessible due to the small (∼90°) bond angle.[27] Due to the smaller size of the carbon monoxide ligand, zone A will always be more sterically



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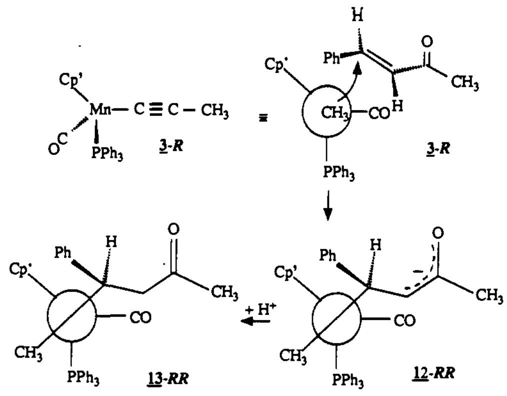
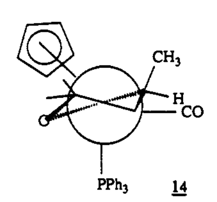
Scheme VIII



accessible than zone B. This effect is enhanced by the propeller structure of the triphenylphosphine which places a phenyl ortho hydrogen atom in zone B.[27]

The most significant stereochemical result of this study is the high degree of stereocontrol directed by the manganese center in the reaction of the alkynyl complex **3** with isobutylene oxide to form **14** and with 3,3-dimethyloxetane to give **20**. Recall that these reactions generated only one pair of the two possible diastereomeric pairs that could form. The crystal structures of both complexes **14** (Figure 4) and **20** (Figure 5) show that in each case the methyl group on the chiral ring carbon is located in the most sterically favorable zone A position between the Cp and the CO ligands, as illustrated below for **14**. The mechanisms given in Schemes III–V for the epoxide and oxetane reactions indicate that the stereochemsitry at the chiral carbon in the carbene ligand is established in the initial protonation of the intermediate vinylidene complexes **15**, **18**, and **21**, as illustrated in Scheme VII for the *R* enantiomer of **3** to yield the *RS* diastereomer of **14**. The initially formed vinylidene complex **15** can exist in the two rotameric forms **15** and **15′**, with the latter strongly disfavored because of steric repulsion between the PPh_3 ligand and the $BF_3OC(Me)_2CH_2$ substituent. Protonation of **15** will occur away from the bulky PPh_3 ligand, and if we assume that **15** is the predominant rotamer and the one protonated, this would form **16** with the *RS* configuration. Rotation about the carbon–carbon single bond of **16** would yield the rotamer **16′**, which upon ring closure would give the observed *RS* diastereomer of **14**.



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Scheme VIII presents an analysis of the reaction of **3** with methyl styryl ketone, which also occurs with high stereoselectivity. Unlike the reaction of **3** with epoxides, the stereochemistry in the final product is set in the initial addition of **3** to the vinyl ketone. As illustrated for the *R* enantiomer of **3**, the vinyl ketone should approach the acetylide complex on the side away from the PPh_3 ligand. The most sterically favored orientation would place the vinyl hydrogen substituent, rather than the phenyl group, toward the metal. This mode of addition leads directly to the observed *RR* diastereomer.

Experimental Section

General. The carbene complexes $Cp'(CO)_2Mn{=}C(OMe)R$ were prepared by the literature procedures,[28] except for complex **1b** which was most conveniently synthesized by the method described below. The reagents $[Me_3O]BF_4$, *n*-BuLi, CH_3I, PPh_3, acetyl chloride, *trans*-4-phenyl-3-buten-2-one, benzoyl chloride, $CH_3OSO_2CF_3$, *p*-tolyl isocyanate, $BF_3{\cdot}Et_2O$, cyclohexene oxide, 3,3-dimethyloxetane, $PhCH{=}NMe$, PhCHO, $LiN(Pr^i)_2$ (97%) (Aldrich Chemical Co.), $CpMn(CO)_3$, $Cp'Mn(CO)_3$, $P(Tol)_3$ (Strem Chemical), $[Et_3O]BF_4$ (Lancaster Synthesis), and isobutylene oxide (TCI American) were purchased from the indicated sources and used as received. Diphenylketene was prepared by the literature procedure.[29] Solvents were dried by refluxing over sodium/benzophenone ketyl (THF, Et_2O), CaH_2 (CH_2Cl_2, pentane, and hexane), or K_2CO_3 (acetone) and were freshly distilled prior to use. All manipulations were performed using standard Schlenk techniques under an N_2 atmosphere. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode, NMR spectra were obtained on a Bruker AM 300 FT NMR spectrometer, and mass spectra were recorded on AEI-MS9 (EI) and Kratos MS50 (FAB) mass spectrometers. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, and from Galbraith Analytical Laboratories, Knoxville, TN.

Preparation of $Cp'(CO)_2Mn{=}C(OMe)Et$ (1b). To a stirred solution of $Cp'(CO)_2Mn{=}C(OMe)Me$ (1.72 g, 6.9 mmol) in THF (40 mL) at −60 °C was added dropwise *n*-BuLi (4.75 mL of a 1.6 M solution in hexanes, 7.6 mmol). After the mixture was stirred for 15 min, MeI (1.19 mg, 8.4 mmol) was added, and the solution was warmed to room temperature and stirred for an additional 30 min. The THF was removed under vacuum to give an orange oil, which was dissolved in a small quantity of pentane and chromatographed on a neutral alumina column. Elution with pure pentane gave first a yellow band containing traces of $Cp'Mn(CO)_3$, followed by a second yellow band which left complex **1b** as an orange oil upon evaporation of solvent under vacuum (1.7 g, 6.5 mmol, 94% yield). For **1b**: IR (THF) ν_{CO} = 1942, 1878 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.75, 4.57 (4 H, $C_5H_4CH_3$), 4.36 (s, 3 H, $C(OCH_3)Et$), 2.94 (br m, 2 H, CH_2CH_3), 1.95 (s, 3 H, $C_5H_4CH_3$), 0.99 (br m, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 344.9 ($Mn{=}C$), 233.2 (CO), 103.3, 86.9, 85.9 ($C_5H_4CH_3$), 63.2 ($C(OCH_3)Et$), 52.4 (CH_2CH_3), 13.7 ($C_5H_4CH_3$), 12.3 (CH_2CH_3); MS (EI) *m/z* 262 (M^+), 234 (M^+ − CO). Anal. Calcd for $C_{12}H_{15}MnO_3$: C, 54.97; H, 5.77. Found: C, 54.63; H, 5.84.

Preparation of $Cp'(CO)(PPh_3)Mn{=}C(OMe)R$. In a typical reaction, complex **1b** (2.0 g, 6.9 mmol) and PPh_3 (2.7 g, 10.4 mmol) were dissolved in CH_2Cl_2 (25 mL) in a 40-mL Pyrex Schlenk flask. The solution was maintained at 0 °C under N_2 and irradiated with a Pyrex-filtered Hanovia 450-W medium-pressure Hg vapor lamp (Ace glass catalog no. 7825-35) contained in a water-cooled Pyrex immersion well for 3 h. The solvent was evaporated under vacuum to leave a red oil, which was chromatographed on alumina. Initial elution with neat pentane gave a single yellow band containing traces of $Cp'(CO)_3Mn$ and $Cp'(CO)_2(PPh_3)Mn$. The eluent was changed to 1:1 pentane/CH_2Cl_2 to elute a red band, which gave complex **2a** (≡ **2**) as an orange powder in 69% yield (2.36 g, 4.8 mmol). Complexes **2b** (82%), **2c** (83%), and **2d** (55%) were similarly prepared and isolated in the indicated yields following chromatography.

For **2a** (≡ **2**): IR (THF) ν_{CO} = 1832 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.38 (m, Ph), 4.46, 4.34, 4.28 (4 H, $C_5H_4CH_3$), 3.88 (s, 3 H, $C(OCH_3)Et$), 2.80 (dq, 1 H, J_{HH} = 14.3 Hz, $J_{HH(Me)}$ = 7.4 Hz, CH_2CH_3), 2.59 (dq, 1 H, J_{HH} = 14.3 Hz, $J_{HH(Me)}$ = 7.4 Hz, CH_2CH_3), 1.89 (s, 3 H, $C_5H_4CH_3$), 0.84 (t, 3 H, J_{HH} = 7.4 Hz, CH_2CH_3); ^{13}C NMR (CD_2Cl_2) δ 341.8 (d, J_{PC} = 26 Hz, $Mn{=}C$), 238.3 (d, J_{PC} = 26 Hz, CO), 139.1–128.1 (PPh_3), 98.1, 87.4, 87.1, 85.6, 84.8 ($C_5H_4CH_3$), 61.6 ($C(OCH_3)Et$), 51.6 (CH_2CH_3), 14.1 ($C_5H_4CH_3$), 12.4 (CH_2CH_3); ^{31}P NMR (CD_2Cl_2) δ 90.07; MS (EI) *m/z* 496 (M^+), 468 (M^+ − CO). Anal. Calcd for $C_{29}H_{30}MnO_2P$: C, 70.16; H, 6.09. Found: C, 70.65; H, 5.89.

For **2a** (Cp analogue): IR (CH_2Cl_2) ν_{CO} = 1826 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.43–7.27 (m, 15 H, Ph), 4.49 (d, 5 H, J_{PH} = 2 Hz, Cp), 3.85 (s, 3 H, OCH_3), 2.87 (dq, 1 H, J_{HH} = 14.8 Hz, $J_{HH(Me)}$ = 7.4 Hz, CH_2CH_3), 2.51 (dq, 1 H, J_{HH} = 14.8 Hz, $J_{HH(Me)}$ = 7.4 Hz, CH_2CH_3), 0.86 (t, 3 H, J_{HH} = 7.4 Hz, CH_2CH_3); ^{13}C NMR (CD_2Cl_2) δ 342.2 (d, J_{PC} = 25 Hz, $Mn{=}C$), 238.2 (d, J_{PC} = 30 Hz, CO), 139.2–128.2 (PPh_3), 85.6 (s, Cp), 61.8 (OCH_3), 52.1 (CH_2CH_3), 12.5 (CH_2CH_3); MS (+-FAB) *m/z* 482 (M^+), 454 (M^+ − CO). Anal. Calcd for $C_{28}H_{28}MnO_2P$: C, 69.71; H, 5.85. Found: C, 69.11; H, 5.91.

For **2b**: IR (THF) ν_{CO} = 1833 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.70 (m, 15 H, PPh_3), 4.70, 4.65, 4.58, 4.52 (4 H, $C_5H_4CH_3$), 4.00 (s, 3 H, $C(OCH_3)Me$), 2.71 (s, 3 H, $C(OMe)CH_3$), 2.19 (s, 3 H, $C_5H_4CH_3$); ^{13}C NMR (CD_2Cl_2) δ 333.9 (d, J_{PC} = 28 Hz, $Mn{=}C$), 238.1 (d, J_{PC} = 30 Hz, CO), 138.9–128.1 (PPh_3), 99.2, 88.3, 87.0, 86.4, 84.6 ($C_5H_4CH_3$), 60.1 ($C(OCH_3)Me$), 43.87 ($C(OMe)CH_3$), 14.0 ($C_5H_4CH_3$); ^{31}P NMR ($CDCl_3$) δ 90.88; MS (EI) *m/z* 482 (M^+), 454 (M^+ − CO). Anal. Calcd for $C_{28}H_{28}MnO_2P$: C, 69.71; H, 5.85. Found: C, 69.98; H, 5.27.

For **2c**: IR (THF) ν_{CO} = 1834 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (m, 15 H, Ph), 4.39, 4.31, 4.23 (4 H, $C_5H_4CH_3$), 3.86 (s, 3 H, $C(OCH_3)Bu$), 2.63 (m, 2 H, $C(OMe)CH_2CH_2CH_2CH_3$), 1.23 (m, 2 H, C(OMe)-

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$\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.07 (m, 2 H, $\mathrm{C(OMe)CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 0.74 (t, 3 H, J_{HH} = 7.0 Hz, $\mathrm{C(OMe)CH_2CH_2CH_2C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 341.0 (d, J_{PC} = 23 Hz, Mn=C), 238.0 (d, J_{PC} = 32 Hz, CO), 138.6–127.7 ($\mathrm{PPh_3}$), 97.5, 87.0, 86.7, 85.3, 84.5 ($\mathit{C}_5\mathrm{H_4CH_3}$), 61.6 (C(O$\mathit{C}\mathrm{H_3}$)Bu), 59.1 ($\mathrm{C(OMe)}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 29.8 ($\mathrm{C(OMe)CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 22.7 ($\mathrm{C(OMe)CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 10.2 (2 C, $\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$ and $\mathrm{C(OMe)CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$); ^{31}P NMR ($\mathrm{CDCl_3}$) δ 89.97; MS (EI) *m/z* 524 ($\mathrm{M^+}$), 496 ($\mathrm{M^+}$ − CO). Anal. Calcd for $\mathrm{C_{31}H_{34}MnO_2P}$: C, 70.99; H, 6.53. Found: C, 70.65; H, 6.41.

For **2d**: IR ($\mathrm{CH_2Cl_2}$) ν_{CO} = 1839 cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.41–6.63 (m, 15 H, Ph), 4.35 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 3.35 (s, 3 H, $\mathrm{OC}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 325.8 (d, J_{PC} = 29 Hz, Mn=C), 238.3 (d, J_{PC} = 32 Hz, CO), 154.7–124.7 (Ph and $\mathrm{PPh_3}$), 87.2 ($\mathit{C}_5\mathrm{H_5}$), 60.8 ($\mathrm{O}\mathit{C}\mathrm{H_3}$); MS (FAB) *m/z* 530 ($\mathrm{M^+}$), 502 ($\mathrm{M^+}$ − CO).

Substitution of $\mathrm{P(Tol)_3}$ for $\mathrm{PPh_3}$ in 2. In an NMR tube, complex **2** (≡ **2a**) (0.100 g, 0.21 mmol) and $\mathrm{P(Tol)_3}$ (0.07 g, 0.21 mmol) were dissolved in 1 mL of THF-d_8. The NMR tube was allowed to stand at ambient temperature, and the exchange reaction was monitored by ^{31}P NMR spectroscopy over a period of 7 days. The rate constant was derived from the slope of the line resulting from a plot of $1/[\mathbf{2}] - 1/[\mathbf{2}]_{t=0}$ vs time: IR ($\mathrm{Et_2O}$) ν_{CO} = 1840 cm^{-1}; ^{1}H NMR (THF-d_8) δ 7.9–7.1 ($\mathrm{C_6}\mathit{H}_4\mathrm{CH_3}$ and $\mathrm{PPh_3}$), 4.44 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 3.79 (s, 3 H, $\mathrm{Mn{=}C(OC}\mathit{H}_3)$), 2.87 (m, 1 H, $\mathrm{Mn{=}C(OMe)C}\mathit{H}_2\mathrm{CH_3}$), 2.49 (m, 1 H, $\mathrm{Mn{=}C(OMe)C}\mathit{H}_2\mathrm{CH_3}$), 2.33 (s, 3 H, $\mathrm{C_6H_4C}\mathit{H}_3$), 0.79 (t, 3 H, $\mathrm{Mn{=}C(OMe)CH_2C}\mathit{H}_3$); ^{31}P NMR (THF-$d_8$) δ 89.67.

In Situ Generation of $[\mathrm{Cp'(CO)(PPh_3)MnC{\equiv}CCH_3}]^-$ (3). In a typical reaction, complex **3** was formed in situ by adding 2.2 equiv of *n*-BuLi (3 mL of a 1.6 M solution in hexanes, 0.49 mmol) to a stirred solution of **2** (0.11 g, 0.22 mmol) in freshly distilled THF (10 mL) maintained at 0 °C. The color of the solution changed from orange to red as the reaction proceeded, and IR analysis indicated the complete formation of **3** within 30 min. Because of the extreme moisture sensitivity of **3**, samples for ^{1}H and ^{13}C NMR characterization were prepared by generating **3** directly in a 5-mm NMR tube in a dry box by placing complex **2** (0.05 g, 0.1 mmol) in the NMR tube, dissolving it in 1 mL of THF-d_8, and adding 2 equiv of lithium diisopropylamide (0.021 g, 0.2 mmol). The NMR tube was capped, sealed with parafilm, shaken, and then removed from the dry box. For **3**: IR (THF) $\nu_{C\equiv C}$ = 2049 (m), ν_{CO} = 1779 (s) cm^{-1}; ^{1}H NMR (THF-d_8) δ 6.54–6.92 (m, 15 H, Ph), 4.12, 3.95, 3.87, 3.81 ($\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$), 2.64 (s, $\mathrm{C_5H_4C}\mathit{H}_3$), 2.62 (s, $\mathrm{C{\equiv}CC}\mathit{H}_3$); ^{13}C NMR (THF-$d_8$) δ 238.6 (d, J_{PC} = 34 Hz, CO), 143.9–133.7 (Ph), 112.7 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_3}$), 97.6, 82.4, 80.8, 80.1, 76.5 ($\mathit{C}_5\mathrm{H_4CH_3}$), 83.8 ($\mathit{C}\mathrm{{\equiv}CCH_3}$), 14.6 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$), 8.0 ($\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_3}$).

Preparation of $\mathrm{Cp'(CO)(PPh_3)Mn{=}C{=}CH(Me)}$ (4). To a stirred 0 °C solution of **2** (2.1 g, 4.3 mmol) in THF (25 mL) was added 2.2 equiv of *n*-BuLi (5.88 mL of a 1.6 M solution in hexane, 9.42 mmol) to form complex **3**. This solution was stirred at 0 °C for 30 min, and then excess water was added to induce an immediate color change from red to clear orange. After 10 min, the THF was removed under vacuum to leave an orange oil, which was chromatographed on neutral alumina with 1:1 pentane/$\mathrm{Et_2O}$ as eluent to give an orange band of $\mathrm{Cp'(CO)(PPh_3)Mn{=}C{=}C(H)(Me)}$ (**4**). Evaporation of solvent from this band afforded **4** as an orange oil (1.70 g, 3.66 mmol, 86% yield). A similar preparation for the Cp analogue gave $\mathrm{Cp(CO)(PPh_3)Mn{=}C{=}CH(Me)}$ (**4′**) as an orange microcrystalline solid in 91% yield.

For **4**: IR (THF) ν_{CO} = 1892 (s), ν_{CC} = 1638 (w) cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.8–7.2 (m, 15 H, Ph), 5.26 (m, 1 H, $\mathrm{C{=}C}\mathit{H}\mathrm{(Me)}$), 4.59, 4.41, 4.25 (4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$), 1.99 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 1.63 (m, 3 H, $\mathrm{C{=}CH(}\mathit{Me}\mathrm{)}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 365.0 (d, J_{PC} = 30 Hz, Mn=C), 236.5 (d, J_{PC} = 33 Hz, CO), 138.8–128.3 (Ph), 133.5 (d, J_{PC} = 9 Hz, $\mathrm{C{=}}\mathit{C}\mathrm{H(Me)}$), 103.8, 89.2, 88.8, 86.6, 86.1 ($\mathit{C}_5\mathrm{H_4CH_3}$), 14.0 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$), 9.1 ($\mathrm{C{=}C(H)(}\mathit{C}\mathrm{H_3)}$); ^{31}P NMR ($\mathrm{CDCl_3}$) δ 92.99; MS (EI) *m/z* 464 ($\mathrm{M^+}$), 436 ($\mathrm{M^+}$ − CO).

For **4′**: IR (THF) ν_{CO} = 1894 (s), ν_{CC} = 1635 (w) cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.71–7.47 (m, 15 H, Ph), 5.31 (dq, 1 H, J_{PH} = 1.4 Hz, J_{HH} = 7.0 Hz, $\mathrm{C{=}C}\mathit{H}\mathrm{(Me)}$), 4.65 (d, 5 H, J_{PH} = 1.2 Hz, Cp), 1.63 (d, 3 H, J_{HH} = 7.0 Hz, $\mathrm{C{=}CH(}\mathit{Me}\mathrm{)}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 364.9 (d, J_{PC} = 32 Hz, Mn=C), 236.2 (d, J_{PC} = 42 Hz, CO), 138.8–128.3 (Ph), 112.8 (s, $\mathrm{C{=}}\mathit{C}\mathrm{H(Me)}$), 87.8 (s, Cp), 9.0 ($\mathrm{C{=}C(H)(}\mathit{C}\mathrm{H_3)}$); MS (+FAB) *m/z* 451 ($\mathrm{MH^+}$), 422 ($\mathrm{M^+}$ − CO). Anal. Calcd for $\mathrm{C_{27}H_{24}MnOP}$: C, 72.00; H, 5.37. Found: C, 71.67; H, 5.56.

Preparation of $\mathrm{Cp(CO)(PPh_3)Mn{=}C{=}C(Me)_2}$ (5a). Alkynyl complex **3** was generated by adding MeLi (1.2 equiv), 3.7 mmol, 2.63 mL of a 1.4 M solution in $\mathrm{Et_2O}$) to a stirred solution of **4** (1.38 g, 3.06 mmol) in freshly distilled $\mathrm{Et_2O}$ (100 mL). The resulting solution was cooled to 0 °C, and MeOTf (1.1 equiv, 3.4 mmol, 0.38 mL) was added dropwise via syringe causing a color change to light red. The solution was stirred for 15 min as it was warmed to room temperature, and the solvent volume was reduced to ~10 mL by evaporation under vacuum. This solution was chromatographed on neutral alumina with $\mathrm{Et_2O}$/pentane (1:1) to give a single red band. Removal of the solvent under vacuum left a red oil, which was redissolved in $\mathrm{Et_2O}$/pentane (1:1) and chromatographed again as above. Elution with $\mathrm{Et_2O}$/pentane (1:1) gave first a principal red band of **5a** followed by two smaller bands which were not identified. Removal of the solvent from the first band gave a red oil, which upon addition of pentane (5 mL) gave precipitation of an orange solid. The mixture was stirred at −20 °C for 12 h to facilitate further precipitation. The supernatant was then removed via cannula, and the remaining orange solid was washed with pentane (3 × 5 mL) and dried under vacuum to give **5a** in 61% yield (0.86 g, 1.85 mmol): IR ($\mathrm{Et_2O}$/pentane, 1:1) ν_{CO} = 1903, $\nu_{C=C}$ = 1670 cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.69–7.25 (m, 15 H, $\mathrm{P}\mathit{Ph}_3$), 4.65 (s, 5 H, *Cp*), 1.69 (s, 6 H, $\mathrm{C{=}C(C}\mathit{H}_3)_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 365.7 (d, J_{PC} = 31 Hz, Mn=C), 236.1 (d, J_{PC} = 31 Hz, CO), 139.1–128.2 (m, $\mathrm{P}\mathit{Ph}_3$), 129.5 (obscured doublet, $\mathrm{Mn{=}C{=}}\mathit{C}$), 87.5 (s, *Cp*), 15.4 (s, $\mathrm{C{=}C(}\mathit{Me}\mathrm{)_2}$); MS (+FAB) 464 ($\mathrm{M^+}$), 436 ($\mathrm{M^+}$ − CO). Anal. Calcd for $\mathrm{C_{28}H_{26}MnOP}$: C, 72.41; H, 5.64. Found: C, 72.69; H, 5.87.

Preparation of $\mathrm{Cp'(CO)(PPh_3)Mn{=}C{=}C(Me)(Et)}$ (5b). To a stirred solution of **2** (0.24 g, 0.48 mmol) in freshly distilled THF (15 mL) at 0 °C was added 2.2 equiv of *n*-BuLi (0.66 mL of a 1.6 M solution in hexanes, 1.1 mmol) to form **3**. This solution was stirred at 0 °C for 30 min, and then excess $\mathrm{[Et_3O][BF_4]}$ was added to induce an immediate color change to light orange. After 20 min, the THF was removed under vacuum to leave an orange oil, which was chromatographed on neutral alumina with 1:1 pentane/$\mathrm{Et_2O}$ as eluent to yield an orange band of **5b** which was isolated as an orange oil (0.16 g, 0.33 mmol, 67% yield) upon solvent evaporation.

For **5b**: IR (pentane) ν_{CO} = 1900, $\nu_{C=C}$ = 1633 cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.57–7.35 (m, 15 H, Ph), 4.55, 4.28, 4.22, 4.15 (4 H, $\mathrm{C_5}\mathit{H}_5\mathrm{CH_3}$), 2.06 (dq, 1 H, J_{HH} = 14.8 Hz, $J_{HH(Me)}$ = 7.4 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.91 (dq, 1 H, J_{HH} = 14.8 Hz, $J_{HH(Me)}$ = 7.4 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.90 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 1.52 (s, 3 H, $\mathrm{{=}C(C}\mathit{H}_3\mathrm{)}$), 1.01 (t, 3 H, J_{HH} = 7.4 Hz, $\mathrm{CH_2C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 365.0 (d, J_{PC} = 30 Hz, Mn=C), 237.0 (d, J_{PC} = 33 Hz, CO), 139.4–126.8 ($\mathrm{PPh_3}$), 133.5 (d, J_{PC} = 10 Hz, Mn=C=C), 103.6, 88.9, 88.1, 86.9, 85.7 ($\mathit{C}_5\mathrm{H_4CH_3}$), 23.9 ($\mathit{C}\mathrm{H_2CH_3}$), 14.0 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$), 13.9 ($\mathrm{{=}C(}\mathit{C}\mathrm{H_3)}$), 12.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$); MS (EI) *m/z* 492 ($\mathrm{M^+}$), 464 ($\mathrm{M^+}$ − CO). Anal. Calcd for $\mathrm{C_{30}H_{30}MnOP}$: C, 73.17; H, 6.14. Found: C, 73.25; H, 6.20.

For **5b** (Cp analogue): IR (1:1 $\mathrm{Et_2O}$/pentane) ν_{CO} = 1902, $\nu_{C=C}$ = 1665 cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.70–7.39 (m, 15 H, Ph), 4.55, 4.28, 4.22, 4.15 (4 H, $\mathrm{C_5}\mathit{H}_5\mathrm{CH_3}$), 2.07 (q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 4.62 (d, 5 H, J_{HP} = 1.43 Hz, Cp), 2.04 (dq, 1 H, J_{HH} = 14.6 Hz, $J_{HH(Me)}$ = 7.3 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.98 (dq, 1 H, J_{HH} = 14.6 Hz, $J_{HH(Me)}$ = 7.3 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.60 (s, 3 H, $\mathrm{{=}C(C}\mathit{H}_3\mathrm{)}$), 1.14 (t, 3 H, $\mathrm{CH_2C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 364.8 (d, J_{PC} = 31 Hz, Mn=C), 236.2 (d, J_{PC} = 33 Hz, CO), 139.4–127.5 ($\mathrm{PPh_3}$), 137.5 (d, J_{PC} = 11 Hz, $\mathrm{Mn{=}C{=}}\mathit{C}$), 87.4 (Cp), 23.9 ($\mathit{C}\mathrm{H_2CH_3}$), 14.0 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 12.5 ($\mathrm{{=}C(}\mathit{C}\mathrm{H_3)}$); MS (+FAB) *m/z* 478 ($\mathrm{M^+}$), 450 ($\mathrm{M^+}$ − CO).

Preparation of $\mathrm{Cp(CO)(PPh_3)Mn{=}C{=}C(Me)(Bu^t)}$ (5c). To a stirred solution of **2** (0.5 g, 1.04 mmol) in freshly distilled THF (15 mL) was added *n*-BuLi (2.28 mmol, 1.43 mL of a 1.6 M solution in hexanes) to generate **3**. The resulting solution was cooled to 0 °C, *tert*-butyl iodide (1.14 mmol, 0.14 mL) was added dropwise via syringe, and the solution was stirred for 3 h while warming to room temperature. Removal of the solvent under vacuum gave a red/brown oil, which was dissolved in $\mathrm{Et_2O}$ and chromatographed on neutral alumina with $\mathrm{Et_2O}$ as eluent to give a single red band which left a red oil upon solvent removal. This oil was dissolved in 1:1 pentane/$\mathrm{Et_2O}$ and rechromatographed on neutral alumina. The single orange product band was thoroughly washed by passing pentane down the column, and it was then eluted with $\mathrm{Et_2O}$. Evaporation of the solvent from this fraction left an orange flocculent solid, which was dried overnight under vacuum to leave **5c** as a free-flowing orange powder in 78% yield (0.41 g, 0.81 mmol): IR ($\mathrm{Et_2O}$/pentane, 1:1) ν_{CO} = 1901, $\nu_{C=C}$ = 1650 cm^{-1}; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.56–7.30 (m, 15 H, $\mathrm{P}\mathit{Ph}_3$), 4.59 (s, 5 H, Cp), 1.25 (s, 3 H, $\mathrm{C{=}C(}\mathit{Me}\mathrm{)(CMe_3)}$), 1.18 (s, 9 H, $\mathrm{C{=}C(Me)(C}\mathit{Me}_3\mathrm{)}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 364.7 (d, J_{PC} = 31 Hz, Mn=C), 237.6 (d, J_{PC} = 33 Hz, CO), 139.2–128.3 (m, $\mathrm{P}\mathit{Ph}_3$), 136.0 (s, $\mathrm{Mn{=}C{=}}\mathit{C}$), 87.7 (s, *Cp*), 32.7 (s, $\mathrm{Mn{=}C{=}C(Me)(}\mathit{C}\mathrm{Me_3)}$), 30.3 (s, $\mathrm{Mn{=}C{=}C(Me)(C}\mathit{Me}_3\mathrm{)}$), 9.0 (s, $\mathrm{Mn{=}C{=}C(}\mathit{Me}\mathrm{)(CMe_3)}$); MS (+FAB) 506 ($\mathrm{M^+}$), 478 ($\mathrm{M^+}$ − CO). Anal. Calcd for $\mathrm{C_{31}H_{32}MnOP}$: C, 73.51; H, 6.37. Found: C, 73.78; H, 6.20.

Preparation of the Acyl Vinylidene Complexes 6a and 6b. To prepare **6a**, acetyl chloride (0.022 mL, 0.30 mmol) was added to a −78 °C solution of complex **3** generated in situ from **2** (0.145 g, 0.28 mmol) in 10 mL of THF. The solution was stirred for 10 min at −78 °C and then allowed to slowly warm to room temperature as the color changed from red to clear yellow. The solvent was evaporated, and the residue was chromatographed on a neutral alumina column. Elution with 1:1 $\mathrm{CH_2Cl_2}$/pentane gave a small orange band containing traces of $\mathrm{Cp'(CO)_2(PPh_3)Mn}$. The eluent was changed to 1:1 $\mathrm{CH_2Cl_2}$/EtOAc to elute a yellow band of **6a**, which was obtained as a yellow microcrystalline powder by solvent evaporation (0.076 g, 1.5 mmol, 54% yield). Complex **6b** was prepared similarly in 48% yield from 0.273 g of **2** and 0.072 mL of benzoyl chloride.

In a similar manner, the ^{13}C-enriched complex **6a′** was prepared by the generation of complex **3** from **2** (0.20 g, 0.403 mmol) in THF (10 mL). Acetyl chloride that was enriched in ^{13}C at the carbonyl carbon (Aldrich, 0.032 mL, 0.484 mmol) was added to a −78 °C solution of complex **3**, and the solution was stirred for 15 min. The solvent was evaporated, and the residue was chromatographed on a neutral alumina column. Elution with 1:1 CH_2Cl_2/pentane gave a small orange band containing traces of $Cp'(CO)_2Mn(PPh_3)$. The eluent was changed to 1:1 CH_2Cl_2/EtOAc to elute a yellow band of **6a′**, which was obtained as a yellow microcrystalline powder by solvent evaporation (0.13 g, 0.256 mmol, 64% yield).

For **6a**: IR (CH_2Cl_2) $\nu_{CO} = 1911$ (s), $\nu_{C=C} = 1553$ (s), $\nu_{CO} = 1620$ (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.49–7.41 (m, 15 H, Ph), 4.70, 4.50, 4.48, 4.35 ($C_5H_4CH_3$), 2.35 (s, 3 H, $C\{O\}CH_3$), 1.94 (s, 3 H, $C_5H_4CH_3$), 1.33 (s, 3 H, $C{=}C(CH_3)$); ^{13}C NMR (CD_2Cl_2) δ 367.6 (d, $J_{PC} = 30$ Hz, $Mn{=}C$), 234.4 (d, $J_{PC} = 33$ Hz, CO), 199.9 ($C\{O\}Me$), 137.4–128.6 (Ph), 134.5 (d, $J_{PC} = 10$ Hz, $C{=}C(Me)$), 104.9, 89.8, 89.6, 89.1, 87.5 ($C_5H_4CH_3$), 28.9 ($C\{O\}CH_3$), 13.5 ($C_5H_4CH_3$), 9.4 ($=C(CH_3)$); ^{31}P NMR (CD_2Cl_2) δ 86.81; MS (EI) *m/z* 506 (M^+), 478 ($M^+ - CO$). Anal. Calcd for $C_{30}H_{28}MnO_2P$: C, 71.15; H, 5.57. Found: C, 71.25; H, 5.75. **6a′**: IR (CH_2Cl_2) $\nu_{CO} = 1914$ (s), 1550 (w) cm^{-1}, $\nu_{C=C} = 1541$ cm^{-1}.

For **6b**: IR (Et_2O) $\nu_{CO} = 1917$ (s), $\nu_{C=C} = 1550$ (s), $\nu_{CO} = 1617$ (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.80–7.42 (m, 20 H, Ph), 4.32, 4.26, 4.00, 3.70 (4 H, $C_5H_4CH_3$), 2.00 (s, 3 H, $C_5H_4CH_3$), 1.43 (s, 3 H, $=C(CH_3)$); ^{13}C NMR (CD_2Cl_2) δ 366.7 (d, $J_{PC} = 33$ Hz, $Mn{=}C$), 234.7 (br s, CO), 197.3 ($C\{O\}Ph$), 144.1–125.8 (Ph), 105.5, 90.4, 89.4, 88.1, 87.2 ($C_5H_4CH_3$), 13.0 ($C_5H_4CH_3$), 10.8 ($=C(CH_3)$); MS (EI) 568 (M^+), 540 ($M^+ - CO$). Anal. Calcd for $C_{35}H_{30}MnO_2P$: C, 73.94; H, 5.32. Found: C, 73.64; H, 5.44.

Preparation of the Vinyl Carbyne Complex 7. Complex **6a** (0.16 g, 0.32 mmol) was dissolved in a minimal amount of CH_2Cl_2 and pentane (5 mL), and the solution was cooled to −50 °C. MeOTf was added via cannula until a golden precipitate was observed. The solvent was removed under vacuum, and the remaining orange solid was recrystallized by dissolving it in a minimum of CH_2Cl_2, precipitating with pentane, and removing the supernatant via cannula to leave **7** (triflate salt) as an orange microcrystalline solid (0.15 g, 0.224 mmol, 71%): IR (CH_2Cl_2) $\nu_{CO} = 1977$ (s), $\nu_{C=C} = 1524$ (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.40 (m, 15 H, Ph), 4.68, 4.49, 4.33, 4.03 (4 H, $C_5H_4CH_3$), 2.32 (s, 3 H, OCH_3), 1.93 (s, 3 H, $C_5H_4CH_3$), 1.61 (s, 3 H, $=C(OCH_3)(CH_3)$), 1.15 (s, 3 H, $C(CH_3)$); MS (FAB) *m/z* 521 (M^+). Anal. Calcd for $C_{32}H_{31}MnO_5PF_3S$: C, 57.32; H, 4.66. Found: C, 56.54; H, 5.17.

Addition of 3 to CO_2 To Form Vinylidene Complex 8. Complex **3** was generated in THF (15 mL) from **2** (0.53 g, 1.07 mmol) and *n*-BuLi (1.5 mL of a 1.6 M solution in hexanes, 2.35 mmol). Gaseous CO_2 was bubbled through this solution at 0 °C for 5 min followed by the addition of $[Me_3O][BF_4]$ (0.20 g, 1.3 mmol) and then stirring for 1 h while slowly warming to room temperature. The solvent was removed by evaporation under vacuum to leave an orange oil, which was chromatographed on neutral alumina. Elution with 1:1 CH_2Cl_2/pentane gave a small orange band containing traces of $Cp'(CO)_2(PPh_3)Mn$. Subsequent elution with 1:1 CH_2Cl_2/EtOAc gave a yellow band of **8**, which was obtained as a yellow microcrystalline powder (0.40 g, 0.77 mmol, 72% yield) by solvent evaporation. IR analysis of the solution after the addition of CO_2, but before the addition of $[Me_3O][BF_4]$, showed the presence of an intermediate with IR bands at 1895 (ν_{CO}) and 1670 ($\nu_{C=C}$) cm^{-1}. For **8**: IR (Et_2O) $\nu_{CO} = 1911$ (s), 1681 (m), $\nu_{C=C} = 1593$ (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.56–7.4 (m, 18 H, Ph), 4.74, 4.42, 4.36, 4.35 (4 H, $C_5H_4CH_3$), 3.35 (s, 3 H, $C\{O\}OCH_3$), 1.94 (s, 3 H, $C_5H_4CH_3$), 1.65 (s, 3 H, $C(CH_3)$); ^{13}C NMR (CD_2Cl_2) δ 363.7 (d, $J_{PC} = 31$ Hz, $Mn{=}C$), 233.8 (d, $J_{PC} = 31$ Hz, CO), 173 ($C\{O\}OCH_3$), 138–128 (Ph), 133.6 (d, $J_{PC} = 10$ Hz, $Mn{=}C{=}C$), 104.6, 90.0, 89.3, 89.1, 87.1 ($C_5H_4CH_3$), 50.6 ($C\{O\}CH_3$), 13.9 ($C_5H_4CH_3$), 11.2 ($=C(CH_3)$); MS (EI) *m/z* 522 (M^+). Anal. Calcd for $C_{30}H_{28}MnO_3P$: C, 68.97; H, 5.40. Found: C, 69.10; H, 5.44.

Addition of 3 to $TolN{=}C{=}O$ To Form Vinylidene Complex 9. Acetylide complex **3** was generated in THF (15 mL) from **2** (0.14 g, 0.282 mmol) and *n*-BuLi (0.39 mL of a 1.6 M solution in hexanes, 0.62 mmol). $TolN{=}C{=}O$ (0.04 mL, 0.384 mmol) was added to this solution, which was maintained at 0 °C for 30 min, and then water (0.4 mL) was added. This reaction mixture was stirred for an additional 30 min while slowly warming to room temperature. The solvent was removed by evaporation under vacuum to leave an orange oil, which was chromatographed on neutral alumina. Elution with 1:1 CH_2Cl_2/pentane gave a small orange band containing traces of $Cp'(CO)_2(PPh_3)Mn$. Subsequent elution with 1:1 CH_2Cl_2/EtOAc gave a yellow band of **9**, which was obtained as a yellow microcrystalline powder (0.14 g, 0.234 mmol, 83% yield) by solvent evaporation. IR analysis of the solution after adding TolNCO, but before adding H_2O, showed the presence of an intermediate with IR bands at 1891 and 1636 cm^{-1}. For **9**: IR (THF) $\nu_{CO} = 1902$ (s), 1643 (m), $\nu_{C=C} = 1597$ (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.6 (s, 1 H, $C\{O\}NHTol$), 7.53–7.08 (m, 19 H, Ph and Tol), 4.74, 4.49, 4.43 (4 H, $C_5H_4CH_3$), 2.29 (s, 3 H, $C_6H_4CH_3$), 1.96 (s, 3 H, $C_5H_4CH_3$), 1.51 (s, 3 H, $=C(CH_3)$); ^{13}C NMR (CD_2Cl_2) δ 362.1 (d, $J_{PC} = 33$ Hz, $Mn{=}C$), 234.9 (d, $J_{PC} = 35$ Hz, CO), 169.7 ($=C(Me)C\{O\}NHTol$), 137.6–117.4 (PPh_3 and $C_6H_4CH_3$), 133.4 (d, $J_{PC} = 11$ Hz, $Mn{=}C{=}C$), 105.4, 89.8, 89.0, 88.9, 87.3 ($C_5H_4CH_3$), 20.8 ($C_6H_4CH_3$), 13.7 ($C_5H_4CH_3$), 9.22 ($=C(CH_3)$); MS (EI) 597 (M^+), 569 ($M^+ - CO$). Anal. Calcd for $C_{36}H_{33}MnNO_2P$: C, 72.36; H, 5.57. Found: C, 72.48; H, 5.76.

Addition of 3 to $Ph_2C{=}C{=}O$ To Form Vinylidene Complex 10. To a 0 °C solution of complex **3**, generated in THF (15 mL) from **2** (0.15 g, 0.302 mmol) and *n*-BuLi (0.38 mL of a 1.6 M solution in hexanes, 0.61 mmol), was added $Ph_2C{=}C{=}O$ (0.064 g, 0.332 mmol). This solution was stirred for 30 min, water (0.4 mL) was added, and the solution was stirred for an additional 30 min while slowly warming to room temperature. The solvent was removed by evaporation under vacuum to leave an orange oil, which was chromatographed on neutral alumina. Elution with 1:1 CH_2Cl_2/pentane gave a small orange band containing traces of $Cp'(CO)_2(PPh_3)Mn$. Subsequent elution with 1:1 CH_2Cl_2/EtOAc gave a yellow band of **10**, which was obtained as an orange microcrystalline powder (0.155 g, 0.23 mmol, 78% yield) by solvent evaporation. IR analysis of the solution after adding $Ph_2C{=}C{=}O$, but before adding H_2O, showed the presence of an intermediate with IR bands at 1881 and 1629 cm^{-1}. For **10**: IR (THF) $\nu_{CO} = 1913$ (s), 1634 (w), $\nu_{C=C} = 1556$ (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.52–7.19 (m, 25 H, Ph), 6.27 (s, 1 H, ($C\{O\}CHPh_2$), 4.53, 4.49, 4.45, 4.16 ($C_5H_4CH_3$), 1.78 (s, 3 H, $C_5H_4CH_3$), 1.42 (s, 3 H, $C{=}C(CH_3)$); ^{13}C NMR (CD_2Cl_2) δ 365.8 (d, $J_{PC} = 30$ Hz, $Mn{=}C$), 235.5 (d, $J_{PC} = 26$ Hz, CO), 199.5 ($C\{O\}CHPh_2$), 142.5–126.6 (Ph), 133.4 (d, $J_{PC} = 10$ Hz, $Mn{=}C{=}C$), 105.6, 89.6, 89.2, 88.5, 87.8 ($C_5H_4CH_3$), 61.1 ($CHPh_2$), 25.4 ($C{=}C(CH_3)$), 9.8 ($C_5H_4CH_3$); ^{31}P NMR (CD_2Cl_2) δ 86.17; MS (EI) *m/z* 658 (M^+), 630 ($M^+ - CO$). Anal. Calcd for $C_{42}H_{36}MnO_2P$: C, 76.59; H, 5.51. Found: C, 75.80; H, 5.47.

Addition of 3 to *trans*-4-Phenyl-3-buten-2-one To Form 13. *trans*-4-Phenyl-3-buten-2-one (0.05 g, 0.35 mmol) was added to a 0 °C solution of the complex **3** that was generated in situ from **2** (0.0202 g, 0.35 mmol) in THF (15 mL). The solution immediately turned orange, and after it stirred for 15 min, a few drops of water were added. The mixture was evaporated to dryness, and the residue was then chromatographed on a neutral alumina column. Elution with a 1:1 CH_2Cl_2/pentane mixture gave an orange band, which contained traces of $Cp'(CO)_2(PPh_3)Mn$. Subsequent elution with neat CH_2Cl_2 gave an orange band of **13**. This second band was evaporated to dryness and pumped on overnight to give 145 mg of crude material (0.24 mmol, 68%). NMR spectra of the crude compound shows two isomers in a 9:1 ratio. The crude material was recrystallized from a mixture of CH_2Cl_2/pentane to give 124 mg of red crystals (0.20 mmol, 57% yield). IR analysis of the solution after the addition of *trans*-4-phenyl-3-buten-2-one, but before the addition of H_2O, showed the presence of an intermediate with IR bands at $\nu_{CO} = 1886$ and $\nu_{C=C} = 1641$ cm^{-1}. For **13**: IR (THF) $\nu_{CO} = 1889$ (s), 1718 (w), $\nu_{C=C} = 1642$ (w) cm^{-1}; ^1H NMR (CD_2Cl_2; major isomer) δ 7.7–7.1 (m, 20 H, Ph), 4.67, 4.40, 4.19 (4 H, $C_5H_4CH_3$), 3.82 (t, 1 H, $J_{HH} = 8$ Hz, $CHPhCH_2C\{O\}Me$), 3.04 (d, 2 H, $J_{HH} = 16$ Hz, $CHPhCH_2C\{O\}Me$) 2.05 (s, 3 H, $C\{O\}CH_3$), 1.94 (s, 3 H, $C_5H_4CH_3$), 1.2 (s, 3 H, $C{=}C(CH_3)$); ^1H NMR (CD_2Cl_2; minor isomer) δ 7.7–7.1 (m, Ph), 3.88 (t, $J_{HH} = 7$ Hz, $CHPhCH_2C\{O\}Me$), 2.99 (m, $CHPhCH_2C\{O\}Me$), 2.10 (s, $C\{O\}CH_3$), 1.91 (s, $C_5H_4CH_3$), 1.2 (s, $C{=}C(CH_3)$); ^{13}C NMR (CD_2Cl_2; major diastereomer) δ 361.1 (d, $J_{PC} = 30$ Hz, $Mn{=}C$), 237.4 (d, $J_{PC} = 33$ Hz, CO), 208.2 ($C\{O\}Me$), 145.1–126.2 (Ph), 133.5 (d, $J_{PC} = 11$ Hz, $Mn{=}C{=}C$), 103.3, 89.2, 88.9, 87.6, 86.8 ($C_5H_4CH_3$), 49.3 ($CHPhCH_2C\{O\}Me$), 43.4 ($C{=}C(Me)CHPh$), 30.5 ($C\{O\}CH_3$), 13.9 ($C_5H_4CH_3$), 12.1 ($C{=}C(CH_3)$); ^{31}P NMR δ 91.97; ^{13}C NMR (CD_2Cl_2; minor diastereomer; unresolved resonances not reported) δ 207.6 ($C\{O\}Me$), 48.3 ($CHPhCH_2C\{O\}Me$), 42.7 ($C{=}C(Me)CHPh$), 30.6 ($C\{O\}CH_3$), 12.0 ($C_5H_4CH_3$), 11.3 ($C{=}C(CH_3)$); ^{31}P NMR (CD_2Cl_2; major diastereomer) δ 91.97; MS (EI) *m/z* 610 (M^+), 582 ($M^+ - CO$). Anal. Calcd for $C_{38}H_{36}MnO_2P$: C, 74.75; H, 5.94. Found: C, 74.76; H, 5.99.

Reaction of 3 with Isobutylene Oxide To Form 14. Complex **3** was generated from a solution of **2** (0.52 g, 1.05 mmol) in THF (15 mL) at 0 °C. The solution was then cooled to −78 °C, and isobutylene oxide (0.15 mL, 2.2 mmol) and $BF_3{\cdot}Et_2O$ (0.22 mL, 2.2 mmol) were added quickly in that order to the cold solution, which was then stirred for 2 h. This solution was then warmed to room temperature, excess MeOH (4 drops) was added, and the solution was stirred for an additional 30 min at room temperature. This solution was evaporated to dryness, and the residue was chromatographed on an alumina column. Elution with a 4:1 mixture of $\mathrm{Et_2O}$/pentane gave first a small yellow band of $\mathrm{Cp'(CO)_2(PPh_3)Mn}$ (by IR) followed by a yellow band which gave, after solvent evaporation, yellow microcrystalline **14** in 88% yield (0.495 mg, 0.92 mmol). For **14**: IR (THF) $\nu_{\mathrm{CO}} = 1830\ \mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.7–7.0 (m, 15 H, Ph), 4.41, 4.18, 3.99 (4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$), 2.67 (m, 1 H, $\mathrm{C(OC(Me)_2CH_2C}\mathit{H}\mathrm{(Me)))}$), 1.90 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 1.41 (s, 3 H, $\mathrm{C(OC(C}\mathit{H}_3\mathrm{)_2CH_2CH(Me))}$), 1.35 (d, 3 H, $J_{\mathrm{HH}} = 7$ Hz, $\mathrm{C(OC(CH_3)_2CH_2CH(C}\mathit{H}_3\mathrm{)))}$), 1.27 (s, 3 H, $\mathrm{C(OC(C}\mathit{H}_3\mathrm{)_2CH_2CH(Me)))}$), 1.14 (m, 2 H, $\mathrm{C(OC(Me)_2C}\mathit{H}_2\mathrm{CH(Me)))}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 334.5 (d, $J_{\mathrm{PC}} = 27$ Hz, $\mathrm{Mn{=}}\mathit{C}$), 236.9 (d, $J_{\mathrm{PC}} = 28$ Hz, $\mathit{C}\mathrm{O}$), 139.5–127.9 (Ph), 99.6, 88.3, 85.5, 85.1, 82.2 ($\mathit{C}_5\mathrm{H_4CH_3}$), 93.7 ($\mathrm{C(O}\mathit{C}\mathrm{(Me)_2))}$), 61.0 ($\mathrm{C(OC(Me)_2CH_2}\mathit{C}\mathrm{H(Me)))}$), 43.2 ($\mathrm{C(OC(Me)_2}\mathit{C}\mathrm{H_2CH(Me)))}$), 29.9, 29.7 ($\mathrm{C(OC(}\mathit{C}\mathrm{H_3)_2CH_2CH(Me)))}$), 23.1 ($\mathrm{C(OC(Me)_2CH_2CH(}\mathit{C}\mathrm{H_3)))}$), 14.3 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$); ^{31}P NMR ($\mathrm{CD_2Cl_2}$) δ 88.73; MS (EI) m/z 536 ($\mathrm{M^+}$), 508 ($\mathrm{M^+ - CO}$). Anal. Calcd for $\mathrm{C_{32}H_{34}MnO_2P}$: C, 71.64; H, 6.39. Found: C, 71.50; H, 6.59.

Reaction of 3 with Cyclohexene Oxide To Form Diastereomeric Carbene Complexes 17a and 17b. The acetylide complex **3** was generated in situ from 0.34 g (0.685 mmol) of **2** in 15 mL of THF. The solution was cooled to −50 °C, and $\mathrm{BF_3{\cdot}Et_2O}$ (0.10 mL, 1.09 mmol) and cyclohexene oxide (0.06 mL, 0.822 mmol) were added in that order. The solution was stirred overnight while it slowly warmed to room temperature. Excess MeOH was then added, and the solution was stirred for an additional 2 h. The THF was removed under vacuum to afford an orange oil, which was chromatographed on a neutral alumina column. Elution with a 1:4 mixture of $\mathrm{Et_2O}$/pentane gave a yellow band, which upon slow evaporation of solvent under reduced pressure left a 3:7 (by ^{1}H NMR) **17a**/**b** mixture as a yellow microcrystalline powder (0.26 g, 0.46 mmol, 68% yield). When the chromatography was conducted using 1:9 $\mathrm{CH_2Cl_2}$/pentane as eluent, a very broad yellow band moved down the column, and collection of the first half of this band yielded pure **17b**. The second half of the band gave a mixture of **17a** and **17b**.

For **17b**: IR (pentane) $\nu_{\mathrm{CO}} = 1850\ \mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{C_6D_6}$; see text for labeling scheme) δ 7.71–6.97 (m, 15 H, $\mathrm{PPh_3}$), 4.60, 4.41, 4.36, 4.20 (4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$), 3.59 (t of d, 1 H, $J(\mathrm{H_bH_a}) = 4$, $J(\mathrm{H_b,H_{CH_2}}) = 11$ Hz, $\mathrm{H_b}$), 2.95 (quintet, 1 H, $J(\mathrm{H_cH_{Me}}) = J(\mathrm{H_cH_a}) = 7$ Hz, $\mathrm{H_c}$), 2.29 (m, 1 H, $\mathrm{H_a}$), 1.94 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 1.54–0.76 (m, 8 H, ring H's), 1.05 (d, 3 H, $J_{\mathrm{HH}} = 7$ Hz, $\mathrm{{=}C(CH(C}\mathit{H}_3\mathrm{)))}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 335.3 (d, $J_{\mathrm{PC}} = 30$ Hz, $\mathrm{Mn{=}}\mathit{C}$), 236.5 (d, $J_{\mathrm{PC}} = 28$ Hz, $\mathrm{Mn}\mathit{C}\mathrm{O}$), 140.5–128.2 ($\mathrm{PPh_3}$), 101, 87.8, 86.6, 86.2, 83.4 ($\mathit{C}_5\mathrm{H_4CH_3}$), 89.0 ($\mathrm{{=}C(O}\mathit{C}\mathrm{H))}$), 61.8 ($\mathrm{{=}C(}\mathit{C}\mathrm{H(Me)))}$), 47.7 ($\mathrm{{=}C(CH(Me)}\mathit{C}\mathrm{H))}$), 32.2 ($\mathrm{{=}C(OCH}\mathit{C}\mathrm{H_2))}$), 26.6, 26.0, 25.0 (ring carbons), 14.8 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$), 13.0 ($\mathrm{{=}C(CH(}\mathit{C}\mathrm{H_3))}$); MS (FAB) 562 ($\mathrm{M^+}$), 534 ($\mathrm{M^+ - CO}$). Anal. Calcd for $\mathrm{C_{34}H_{36}MnO_2P}$: C, 72.59; H, 6.45. Found: C, 72.99; H, 6.66.

For **17a**: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.71–6.97 (m, $\mathrm{PPh_3}$), 4.58, 4.41, 4.33, 4.25 ($\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$), 3.20 (t of d, $J_{\mathrm{HH}} = 3$, 11 Hz, $\mathrm{H_b}$), 2.20 (m, $\mathrm{H_a}$), 1.88 ($\mathrm{C_5H_4C}\mathit{H}_3$), 1.53 (d, $J_{\mathrm{HH}} = 7$ Hz, $\mathrm{{=}C(CH(C}\mathit{H}_3\mathrm{))}$).

Reaction of 3 with 3,3-Dimethyloxetane To Form Carbene Complex 20. The acetylide complex **3** was generated in situ from **2** (0.210 g, 0.44 mmol) and *n*-BuLi in THF (15 mL). The solution was cooled to −50 °C, and $\mathrm{BF_3{\cdot}Et_2O}$ (0.12 mL, 0.88 mmol) and 3,3-dimethyloxetane (0.08 mL, 1.09 mmol) were added in that order. The solution was stirred overnight while being allowed to warm to room temperature. Excess MeOH was then added to the solution, and stirring was continued for an additional 2 h. The THF was removed under vacuum to leave an orange oil, which was chromatographed on a neutral alumina column. Elution with 1:4 $\mathrm{Et_2O}$/pentane as eluent gave a yellow band, which upon solvent evaporation under reduced pressure gave **20** as a yellow microcrystalline powder (0.16 g, 0.30 mmol, 68% yield). For **20**: IR (pentane) $\nu_{\mathrm{CO}} = 1849\ \mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.7–7.0 (m, 15 H, Ph), 4.49, 4.43, 4.29 (4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$), 3.67, 3.60 (AB pattern, 2 H, $J_{\mathrm{H_aH_b}} = 11$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{C(Me)_2}$), 3.63 (m, 1 H, $\mathrm{C}\mathit{H}\mathrm{(Me)CH_2}$), 1.98 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 1.34 (d, 3 H, $J_{\mathrm{HH}} = 8$ Hz, $\mathrm{CH(C}\mathit{H}_3\mathrm{))}$), 0.76 (dd, 1 H, $J_{\mathrm{HH}} = 2$, 14 Hz, $\mathrm{CH(Me)C}\mathit{H}_2$), 0.69 (s, 3 H, $\mathrm{OCH_2C(C}\mathit{H}_3\mathrm{)_2}$), 0.59 (s, 3 H, $\mathrm{OCH_2C(C}\mathit{H}_3\mathrm{)_2}$), 0.20 (dd, 1 H, $J_{\mathrm{HH}} = 7$, 14 Hz, $\mathrm{CH(Me)C}\mathit{H}_2$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 335.7 (d, $J_{\mathrm{PC}} = 30$ Hz, $\mathrm{Mn{=}}\mathit{C}$), 237.9 (d, $J_{\mathrm{PC}} = 30$ Hz, $\mathit{C}\mathrm{O}$), 140.7–128.2 (Ph), 100.6, 87.4, 86.8, 83.4, 78.2 ($\mathit{C}_5\mathrm{H_4CH_3}$), 90.7 ($\mathrm{O}\mathit{C}\mathrm{H_2CMe_2}$), 54.5 ($\mathit{C}\mathrm{H(Me)}$), 37.8 ($\mathrm{CH(Me)}\mathit{C}\mathrm{H_2}$), 30.4, 29.1 ($\mathrm{OCH_2C(}\mathit{C}\mathrm{H_3)_2}$), 29.7 ($\mathrm{OCH_2}\mathit{C}\mathrm{(Me)_2}$), 22.5 ($\mathrm{CH(}\mathit{C}\mathrm{H_3))}$), 14.9 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$); MS (FAB) m/z 550 ($\mathrm{M^+}$).

A light orange powder of intermediate **21** was obtained when the above procedure was followed for the Cp analogue of **3**, and the THF solvent was evaporated 10 min after the addition of $\mathrm{BF_3{\cdot}Et_2O}$ and 3,3-dimethyloxetane. This solid gave a parent ion at $m/z = 535$ ($\mathrm{M^+ - BF_3}$) in its mass spectrum and IR bands (THF) at $\nu_{\mathrm{CO}} = 1880$ and $\nu_{\mathrm{C=C}} = 1651\ \mathrm{cm^{-1}}$ and was observed by IR to cleanly transform into **22** upon the addition of MeOH. Similarly, intermediate **22** was obtained by stirring in THF (15 mL) at −50 °C for 10 min the Cp analogue of **3** (0.299 g, 0.62 mmol), 3,3-dimethyloxetane (0.127 1.28 mmol), and $\mathrm{BF_3{\cdot}Et_2O}$ (0.16 mL, 1.3 mmol). Excess MeOH was added to the cooled solution, it was stirred for another 25 min, and then the solvent was removed under reduced pressure to leave a yellow solid. This was purified by dissolution in $\mathrm{CH_2Cl_2}$ and precipitation with pentane to leave **22** as a bright yellow microcrystalline powder (0.2605 g, 0.42 mmol, 67% yield). Complex **22** smoothly converted into **20** (Cp analogue) when it was dissolved in freshly distilled THF and allowed to stir at room temperature for 12 h. For **22**: IR ($\mathrm{CH_2Cl_2}$) $\nu_{\mathrm{CO}} = 2010\ \mathrm{cm^{-1}}$; ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 383.5 ($\mathrm{Mn{\equiv}}\mathit{C}$), 225.1 ($\mathrm{Mn}\mathit{C}\mathrm{O}$), 135.5–130 (Ph), 94.3 (Cp); MS (FAB) m/z 537 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{32}H_{35}MnO_2PBF_4{\cdot}CH_2Cl_2}$: C, 55.88; H, 5.26. Found: C, 55.54; H, 5.30.

In a separate experiment, complex **22** (0.025 g, 0.04 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (10 mL) and cooled to −20 °C, and $\mathrm{NH_3}$ was bubbled through the yellow solution for 10 min as the color changed to orange. The $\mathrm{CH_2Cl_2}$ was removed under reduced pressure, and the resulting oil was chromatographed on a neutral alumina column. Elution with 1:1 $\mathrm{CH_2Cl_2}$/pentane afforded a single orange band, which left **23** as an orange microcrystalline solid upon solvent evaporation: IR (THF) $\nu_{\mathrm{CO}} = 1891$, $\nu_{\mathrm{C=C}} = 1639\ \mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.32 (m, 15 H, Ph), 4.33 (br s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 3.80 (br s, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 3.33 (br s, 1 H, $\mathrm{O}\mathit{H}$), 1.21 (br s, 3 H, $\mathrm{{=}C(C}\mathit{H}_3\mathrm{))}$), 0.78 (br s, 6 H, $\mathrm{C(C}\mathit{H}_3\mathrm{)_2CH_2OH}$), 0.62 (br s, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{C(Me_2))}$); MS (EI) m/z 536 ($\mathrm{M^+}$), 508 ($\mathrm{M^+ - CO}$).

Variable-Temperature ^{1}H NMR Study of 4 and 5b (Cp Analogues). In an inert atmosphere glove box, complex **4** or **5b** was dissolved in a minimal amount of $\mathrm{CD_2Cl_2}$, and the solution was filtered through a $^1/_2$-in. plug of neutral alumina directly into a flame-sealable 5-mm NMR tube. The prepared sample tube was placed in a 500-mL Schlenk tube, which was then sealed with a rubber septum and removed from the glove box. The NMR tube was then removed from the Schlenk vessel under a vigorous purge of nitrogen and was attached via rubber tubing to a Schlenk line. The sample tube was then quickly evacuated and backfilled with nitrogen three times to ensure an oxygen-free atmosphere. The sample solution was then frozen by immersion in liquid nitrogen, and the tube was fully evacuated for 10 min. The NMR tube was flame-sealed under vacuum, and the solution was allowed to warm to room temperture. For **4**, spectra were recorded at 5 or 10 °C increments from 20 to −90 °C. For **5b**, spectra were similarly recorded over the 20 to −85 °C range. $\Delta G^{\ddagger}$ was calculated from the equation $\Delta G^{\ddagger} = -RT[\ln(k/T) + \ln(h/\kappa)]$.[9,30]

X-ray Diffraction Studies of 2, 5c, 13′, 14, and 20. Crystal, data collection, and refinement parameters are collected in Table I. All crystals were mounted on fine glass fibers with epoxy cement. The unit cell parameters of **2**, **5c**, **13′**, **14**, and **20** were each obtained from the least-squares fit of 25 reflections ($20° \le 2\theta \le 25°$). Preliminary photographic characterization showed $\bar{1}$ Laue symmetry for **2** and **20**, $2/m$ Laue symmetry for **13′**, and *mmm* Laue symmetry for **5c** and **14**. All processing of the data for **2** and **20** was confined to the centrosymmetric space group, $P\bar{1}$, which provided the chemically reasonable structures reported. Systematic absences in the diffraction data for **13′** uniquely established the space group as $P2_1/n$ and as *Pbca* for **5c**. The systematic absences for **14** indicated either $Pna2_1$ (No. 33) or *Pnam* (nonstandard *Pnma* (No. 62)). The chemically sensible results of refinement indicated that $Pna2_1$ was the correct space group for **14**. The refinement of a multiplicative term (η) for $\Delta f''$ for **14** indicates that the enantiomorph reported is correct. No correction for absorption was applied to the data sets (low μ and $T_{\mathrm{max}}/T_{\mathrm{min}}$) except for **14**, for which a semiempirical absorption correction program XABS was applied.

The structures of **2** and **20** were solved by a Patterson map which located the Mn atoms. The structures of **5c**, **13′**, and **14** were solved by direct methods which located the Mn atoms. The remaining non-hydrogen atoms were located through subsequent least-squares and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions ($d\mathrm{CH} = 0.960$ Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The unit cell of **2** contains two crystallographically and chemically similar molecules. The overall restricted quality of **14** is the result of a crystal which diffracted weakly and diffusely, thus limiting the observable data available.

All computer programs and the sources of the scattering factors for **2**, **13′**, **14**, and **20** are contained in the SHELXTL program library (5.1, G. Sheldrick, Nicolet (Siemens), Madison, WI), and for **5c**, they are contained in the SHELXTL PLUS program library (4.21/V, G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: A variable-temperature NMR study for **5b** (Figure A) and tables of atomic positional parameters, anisotropic thermal parameters, bond lengths, and bond angles for **2**, **5c**, **13′**, **14**, and **20** (31 pages); tables of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

Contribution of Physical Blocking and Electronic Effect to Establishment of Strong Metal–Support Interaction in Rh/TiO_2 Catalysts

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Abstract: Establishment of strong metal–support interaction in Rh/TiO_2 catalysts has been studied by ^1H NMR spectroscopy as a function of conditions of reduction in H_2: temperature (373–773 K), time, and type of reduction (static or dynamic). Two consecutive stages have been identified: one when the catalyst is reduced below 673 K and the other when the temperature is above 673 K. In the first stage, elimination of hydrogen incorporated into the metal–support interface, by outgassing at 773 K, recuperates hydrogen adsorption on the metal. In the second stage, the outgassing treatment does not recover metal adsorption capacity. Physical blocking of metal adsorption sites by TiO_x species and electronic perturbation of the metal are responsible for the irreversible loss of hydrogen adsorption. From analysis of the NMR line assigned to hydrogen adsorbed on the metal, the relative contribution of both effects to adsorption suppression has been estimated.

Introduction

When catalysts consisting of group VIII metals supported on TiO_2 are reduced in H_2 at high temperatures (about 770 K), the metal capacity to adsorb H_2 and CO is suppressed. This metal behavior, ascribed initially to a strong metal–support interaction (SMSI),[1,2] was explained in terms of bonding between titanium cations and metal atoms, as deduced from theoretical calculations[3] and XPS, XANES, and EXAFS data.[4–11] The other source for the SMSI state consists in geometric blocking of metal adsorption sites[12–20] due to (i) migration of TiO_x ($1 < x < 2$) suboxide species onto the metal or (ii) burial of the metal into the support. In particular, it has been shown[21] by HRTEM that reduction of Rh/TiO_2 catalyst at 773 K produces an amorphization of the TiO_2 surface and a migration of TiO_x overlayers onto metal particles. However, some controversy still exists about the effect of TiO_x species on adsorption suppression. Thus, some authors[22,23] have found that the decrease in CO adsorption is proportional to the amount of metal surface covered by those species, while others[24] have observed a decrease higher than that expected for only geometric blocking. The two considered explanations, electronic and physical blocking, are not mutually exclusive for the SMSI state, and formation of chemical bondings between the metal and TiO_x species has been proposed[7,25,26] as the driving force for migration of those species onto metal particles.

In previous works[27,28] we have shown that incorporation of hydrogen into the metal–support interface decreases hydrogen adsorption on rhodium particles. When hydrogen is removed by outgassing the sample at 773 K, metal particles recover their initial adsorption capacity. Therefore, it seems that different processes such as hydrogen incorporation into the support, migration of TiO_x species onto the metal, and formation of rhodium–titanium bondings are involved during establishment of the SMSI state. The aim of this work is to analyze the experimental conditions in which they are operating and to evaluate their contribution to the metal chemisorption suppression. In this way, reduction in H_2 of an Rh/TiO_2 sample as a function of (i) temperature, (ii) time, and (iii) type of reduction (static and dynamic) has been

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