Generation of Vinylcarbyne Complexes from Reaction of the Propynyl Complex $[Cp(CO)(PPh_3)MnC{\equiv}CMe]^-$ with Aldehydes and Ketones

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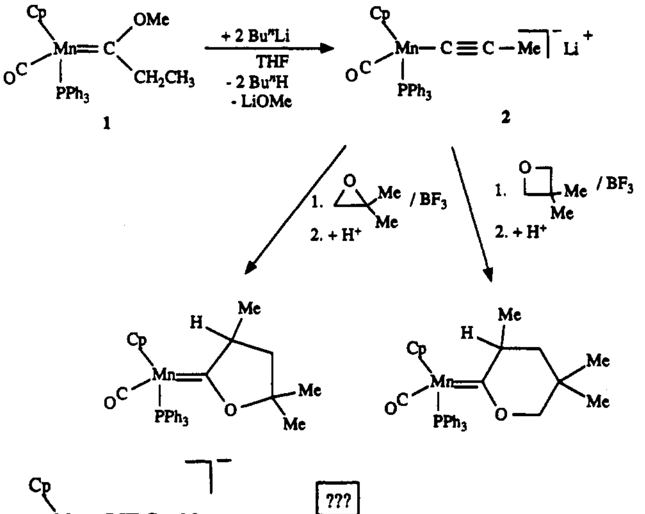
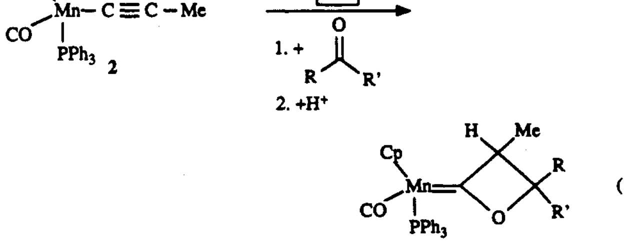
The highly nucleophilic propynyl complex $Li^+[Cp(CO)(PPh_3)MnC{\equiv}CMe]^-$ (**2**) reacts with a variety of aldehydes and ketones in the presence of $BF_3{\cdot}Et_2O$ to give, after quenching with MeOH, a series of cationic vinylcarbyne complexes of the general form $[Cp(CO)(PPh_3)Mn{\equiv}C\text{-}C(Me){=}C(R)(R')]BF_4$. The reactions of the R, R′ = Ph derivative (**5a**) with a series of nucleophiles ($LiAlH_4$, RMgX, $Bu^tC{\equiv}CLi$) have been studied, and addition occurs to both the α-carbon of the vinylcarbyne ligand to form vinylcarbene complexes $[Cp(CO)(PPh_3)Mn{=}C(R)C(Me){=}CPh_2]$ (R = H, Me, Et, $-C{\equiv}CBu^t$) and to the γ-carbon to give vinylidene complexes, with addition to C_α being electronically preferred but with addition to C_γ being favored sterically because of the bulky PPh_3 ligand. The vinylcarbyne complexes that have an acidic proton on the C_γ substituent undergo facile deprotonation to give vinylvinylidene derivatives of the general form $Cp(CO)(PPh_3)Mn{=}C{=}C(Me)C(R){=}C(R')_2$ (R′ = H, R = *p*-Tol (**14c**), Bu^t; R′ = Me, R = H). The propynyl complex **2** also adds to the γ-carbon of **5a** to form the binuclear bis(vinylidene) complex $[Cp(CO)(PPh_3)Mn{=}C{=}C(Me)\text{-}]_2\{C(Ph)_2\}$ as a separable mixture of diastereomers. The related binuclear bis(vinylidene) complex $[Cp(CO)(PPh_3)Mn{=}C{=}C(Me)\text{-}]_2\{C(H)(Et)\}$ (**13**) was also isolated in low yield from the reaction of propynyl complex **2** with both MeOH and Me_3SiCl. Also described is the preparation of the new PPh_3-substituted carbyne complexes $[Cp(CO)(PPh_3)Mn{\equiv}CR]X$ (R = Et, Ph, CH_2Ph; X = BF_4, OTf), and complexes **5a**, **13**, and **14c** have been crystallographically characterized.

Introduction

We recently reported that the carbene complex $Cp(CO)(PPh_3)Mn{=}C(OMe)Et$ (**1**) reacts with 2 equiv of Bu^nLi to generate *in situ* the chiral and highly nucleophilic propynyl complex $[Cp(CO)(PPh_3)MnC{\equiv}CMe]^-$ (**2**; Scheme I).[1] This latter complex is highly reactive and undergoes a number of addition and cycloaddition reactions with electrophilic organic substrates. Particularly interesting are the [2 + 3] and [2 + 4] cycloaddition reactions with epoxides and with 3,3-dimethyloxetane to give the cyclic carbene complexes shown in Scheme I.[1] As an extension of these cycloadditions, we considered the possibility of inducing a related [2 + 2] cycloaddition by allowing propynyl complex **2** to react with aldehydes and ketones (eq 1). However, as described herein, these reactions take a markedly different course and instead give a series of vinyl-substituted carbyne complexes, $[Cp(CO)(PPh_3)Mn{\equiv}CC(Me){=}C(R)(R')]^+BF_4^-$ (**5**), which form by coupling of the aldehyde or ketone with the alkynyl ligand of **2**.

Scheme I





(1)

Due to its conjugated and unsaturated nature, the vinylcarbyne ligand would appear to have potential for interesting addition and cycloaddition reactions of its own, but little is known about the chemistry of this ligand system.[2,3] The only previously described examples of mononuclear vinylcarbyne complexes are the dicarbonyl

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(1) (a) Lugan, N.; Kelley, C.; Terry, M. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3220. (b) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735.

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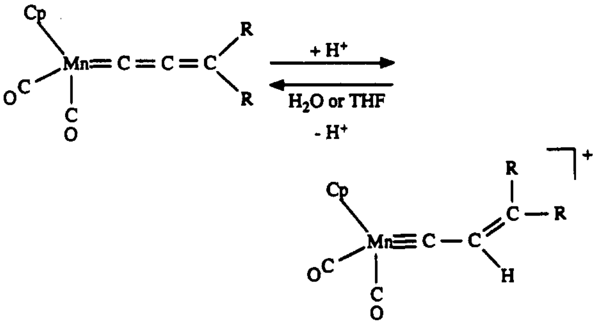
complexes $[Cp(CO)_2Mn{\equiv}CC(H){=}C(R)_2]^+$ (3), which were prepared by Kolobova and co-workers by protonation of neutral allenylidene complexes (eq 2),[2a] the complex $[Cp(CO)(PPh_3)Mn{\equiv}C\text{-}C(Me){=}C(OMe)Me]^+OTf^-$(4), synthesized in these laboratories by O-alkylation of an acyl-substituted vinylidene complex (eq 3),[1b] and the cationic vinylcarbyne complex $[(PPr^i_3)_2(Cl)Rh{\equiv}CC(H){=}C(Me)_2]^+$, recently reported by Werner *et al.* to form upon C_δ protonation of the vinylvinylidene complex $(PPr^i_3)_2(Cl)$-$Rh{=}C{=}C(H)C(Me){=}CH_2$.[2b] The complex $[Cp(CO)_2$-$Mn{\equiv}CC(H){=}C(Ph)_2]BF_4$ was crystallographically characterized by Kolobova *et al.*,[2a] but the only reported aspect of the reactivity of these complexes was their facile deprotonation upon treatment with H_2O or THF to regenerate the starting allenylidene complex (eq 2). Werner *et al.* also observed a similar deprotonation upon treatment of the above-mentioned Rh–vinylcarbyne complex with NaH.[2b] Reported herein are reactions of the vinylcarbyne complexes prepared in this study with nucleophiles to form carbene and vinylidene derivatives and with bases to yield vinyl-substituted vinylidene complexes.



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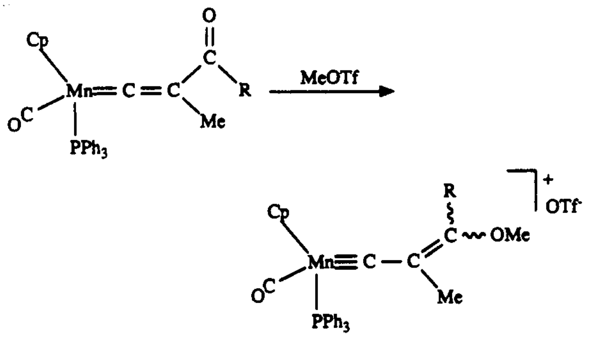

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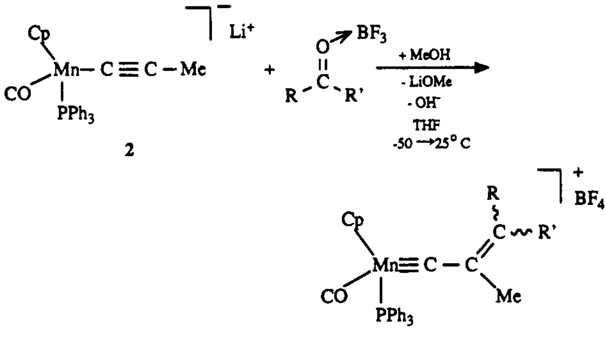
(3)

Results and Discussion

Formation of Cationic Vinylcarbyne Complexes via Reaction of $[Cp(CO)(PPh_3)MnC{\equiv}CMe]^-$ (2) with Aldehydes and Ketones. In the presence of $BF_3{\cdot}Et_2O$, propynyl complex 2, generated *in situ* from carbene complex 1 and Bu^nLi, rapidly reacts with a variety of ketones and aldehydes to form, after quenching with MeOH, the vinylcarbyne complexes **5a–g** as BF_4^- salts (eq 4). With the exception of **5a**, which was obtained analytically pure by crystallization, the remainder of the complexes **5b–g** were contaminated with varying amounts of the carbyne complex $[Cp(CO)(PPh_3)Mn{\equiv}CEt]BF_4$, which proved difficult to separate from **5**. This latter species readily forms by double protonation of any unreacted propynyl complex 2 by the strong acid HBF_3-OMe, which forms from the $BF_3{\cdot}Et_2O$ and MeOH used in the reaction. Integration of the ^1H NMR spectra indicated the yields of **5a–g** to be in the 80–90% range.



(4)

5a; R=R'=Ph
5b; R=R'=Me
5c; R=Me, R'=*p*-Tol
5d; R=Me, R'=Bu^t
5e; R=Ph, R'=Bu^t
5f; R=*p*-Tol, R'=H
5g; R=Pr^i, R'=H

The addition of the Lewis acid $BF_3{\cdot}Et_2O$ is essential for these reactions to occur. In the absence of $BF_3{\cdot}Et_2O$, reaction of the propynyl complex 2 with enolizable aldehydes or ketones results only in deprotonation of the ketone or aldehyde and formation of the previously described vinylidene complex $Cp(CO)(PPh_3)Mn{=}C{=}C$-$(H)(Me)$.[1] Reaction of 2 with the non-enolizable ketone $Ph_2C{=}O$ in the absence of $BF_3{\cdot}Et_2O$ also did not lead to the formation of **5a** but instead gave a color change from red-brown to deep blue-green, suggesting electron transfer to form $[Cp(CO)(PPh_3)Mn\text{-}C{\equiv}C\text{-}Me]^\bullet$ and the radical anion $[Ph_2CO]^{\bullet-}$. When this reaction was quenched with trifluoroacetic acid, $Cp(CO)(PPh_3)Mn{=}C{=}C(H)(Me)$ was formed, but the details of this reaction were not further investigated. Wulff and co-workers similarly observed the necessity of pretreating ketones and aldehydes with Lewis acids to render them susceptible to nucleophilic attack by the carbene anions $(CO)_5M{=}C(OMe)(CRR'^-Li^+)$ (M = Cr, W).[4]

Complexes **5a–g** have been spectroscopically characterized, and complex **5a** has been further defined by an X-ray diffraction study (see Figure 1 and below). Each compound gave a parent ion in its +FAB mass spectrum and also showed an ion resulting from loss of the CO ligand. Characteristic resonances for the Cp, CO, and PPh_3 ligands were observed in the ^1H and ^{13}C NMR spectra of the complexes along with resonances due to the substituents of the vinylcarbyne ligand. The ^{13}C NMR resonances for the C_α, C_β, and C_γ backbone carbons of the vinylcarbyne

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(2) (a) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *262*, 39. (b) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156. Note added in proof: For a recent report of vinylcarbyne complexes of osmium, see: Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683.

(3) *Binuclear μ-vinylcarbyne complexes of the form* $[\{Cp(CO)Fe\}_2(\mu\text{-}CO)(\mu\text{-}CC(R){=}CR_2)]^+$, $[Cp(CO)_2Cr{=}CC{=}C(Ph)]_2$, and $[\{CpFe\}_2(\mu\text{-}CO)(\mu\text{-}dppe)(\mu\text{-}CC(H){=}C(CN)_2)]^+$ are also known: (a) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620. (b) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411. (c) Casey, C. P.; Konings, M. S.; Palermo, R. D.; Colborn, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 5296. (d) Casey, C. P.; Konings, M. S.; Marder, S. R. *Polyhedron* **1988**, *7*, 881. (e) Casey, C. P.; Konings, M. S.; Marder, S. R.; Takezawa, Y. *J. Organomet. Chem.* **1988**, *358*, 347. (f) Casey, C. P.; Konings, M. S.; Marder, S. R. *J. Organomet. Chem.* **1988**, *345*, 125. (g) Etienne, M.; Talarmin, J.; Toupet, L. *Organometallics* **1992**, *11*, 2058. (h) Ustynyuk, N. A.; Vinogradova, V. N.; Andrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *268*, 73.

(4) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503.

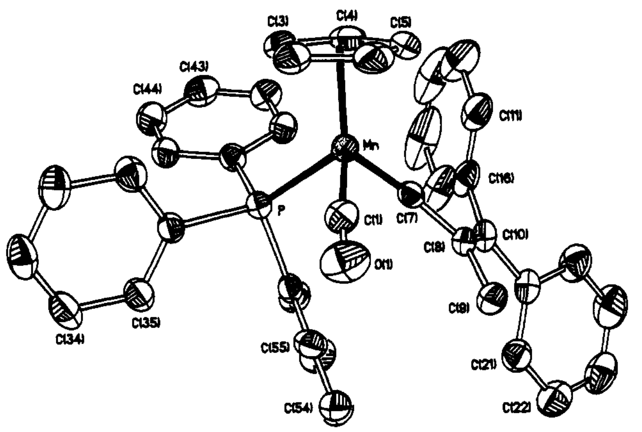
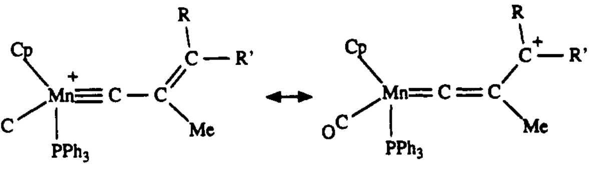


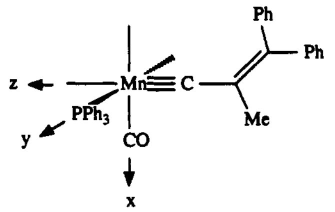
Figure 1. ORTEP drawing of $[Cp(CO)(PPh_3)Mn{\equiv}C(Me)C{=}CPh_2]BF_4{\cdot}CH_2Cl_2$ (**5a**).

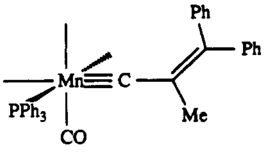
ligand appear in the following spectral regions for all the new complexes: δ_{C_α}, 345–349; δ_{C_β}, 145–148; δ_{C_γ}, 154–181. It has unfortunately not proven possible to determine the *E* or *Z* configuration of the vinyl group in these complexes, mainly because trace amounts of paramagnetic impurities, often a problem with Mn complexes, complicate the interpretation of ^1H NMR NOE experiments. In the IR, each compound showed a single ν_{CO} band in the 2010–1999-cm^{-1} region, with the high-energy position of this band indicative of a cationic complex. Also observed in all cases except for **5c** was a weak band in the 1570–1509-cm^{-1} region attributable to the $\nu_{C=C}$ vibration of the vinyl substituent. For comparison, the earlier described complex $[Cp(CO)(PPh_3)Mn{\equiv}CC(Me){=}C(Me)(OMe)]^+OTf^-$ (4; eq 3) showed corresponding bands at 1977 (s) and 1524 (w) cm^{-1}, respectively.[1b] The lower energy position of the ν_{CO} band in 4 as compared to that in **5a–g** is likely due to stabilization of resonance form **B** in 4 by electron donation from the OMe oxygen to the adjacent carbocation.



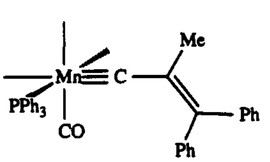
Crystal and Molecular Structure of $[Cp(CO)(PPh_3)Mn{\equiv}CC(Me){=}CPh_2]BF_4{\cdot}CH_2Cl_2$ (5a). An ORTEP drawing of **5a** is shown in Figure 1, and relevant crystallographic data are given in Tables I and II. Like other CpL_2MnX complexes, the overall coordination geometry about manganese is pseudooctahedral, as indicated by the 91.7° average angle between the CO, PPh_3, and carbyne ligands. The Mn–C(7) (1.668(5) Å) and C(8)–C(10) (1.357(7) Å) bond distances are similar to those reported by Kolobova *et al.*[2a] for $[Cp(CO)_2Mn{\equiv}CC(H){=}C(Ph)_2]^+$ (Mn–C_α, 1.665(5) Å; C_β–C_γ, 1.357(7) Å). However, the C(7)–C(8) (1.429(7) Å) distance in **5a** is slightly longer than the corresponding value found in this reference compound (C_α–C_β, 1.389(7) Å),[2a] but it compares well with the C(sp)–C(sp^2) single-bond distance characteristic of 1-en-3-ynes (1.431 Å).[5] Similarly, the vinyl C(8)–C(10) bond distance of 1.357(7) Å is longer than the C=C distance characteristic of isolated double bonds (1.299 Å)[5] but is close to the 1.330-Å value typical of conjugated systems.[5] The Mn–vinylcarbyne unit is planar (maximum deviation of 0.027 Å associated with C(7)), and this plane is aligned with the Mn–CO ligand ({Mn–C(7)–C(8)–C(10)}–{C(1)–Mn–C(7)} dihedral angle 13.3(2)°). This stands in contrast to the previously reported crystal structure of $[Cp(CO)_2Mn{\equiv}CC(H){=}CPh_2]^+$, which showed the plane of the vinylcarbyne ligand to bisect the OC–Mn–CO angle.[2a]

On the basis of only steric arguments, the vinylcarbyne fragment would be expected to be oriented with the CPh_2 fragment away from the PPh_3 ligand, between the Cp and the CO ligands in a Newman projection, and with the plane of the vinylcarbyne ligand containing the Mn–P vector. This is not the case in the present structure, which instead has the plane of the vinylcarbyne ligand perpendicular to the Mn–P vector (see Figure 1 and below). There must thus be an electronic preference for this orientation. Using the labeling scheme shown above, the p_x and p_y orbitals on the carbyne carbon in complex **5a** are nondegenerate due to conjugation of the p_y orbital with the π system of the vinyl substituent.[6] Also, as has been frequently noted for Cp(L)(CO)MX complexes, the metal d_{xz} and d_{yz} orbitals are not equivalent since the former is engaged in bonding to the strongly π-accepting CO ligand, where the latter interacts with the much more weakly π-accepting PPh_3 ligand.[7] The preferred orientation of any other π-accepting ligand on the metal is that which enhances π bonding with the d_{yz} orbtial.[7] The observed ligand orientation in **5a** indicates that this π bonding is enhanced when the d_{yz} orbital overlaps with the p oribtal on the carbyne carbon which is in conjugation with the vinyl substituent (p_y) rather than with the orthogonal p orbital (p_x), thereby creating a diene-like π system. Two isomers, **C** and **D**, are possible for this orientation, with the crystal structure showing **C** to be preferred in the solid state, presumably because **D** places one of the C_γ phenyl substituents in close proximity to the carbonyl ligand.





C



D

Mechanistic Considerations. The mechanism proposed to account for the formation of vinylcarbyne complexes **5a–g** is shown in Scheme II. The β-carbon of the propynyl ligand of **2** has been previously shown to be

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(5) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1981**, S1.

(6) The nondegenerate nature of the p_x and p_y orbitals has also been noted for arylcarbyne ligands: (a) Fenske, R. F.; Kostić, N. M. *J. Am. Chem. Soc.* **1981**, *103*, 4677. (b) Fenske, R. F.; Kostić, N. M. *J. Am. Chem. Soc.* **1982**, *104*, 3879. (c) Fenske, R. F.; Kostić, N. M. *Organometallics* **1982**, *1*, 489.

(7) (a) Hofmann, P. In *Carbyne Complexes*; VCH: New York, 1988; pp 59–98. (b) Kiel, W. A.; Lin, G.-H.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Einstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (c) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (d) Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879. (e) McCormick, F. B.; Kiel, W. A.; Gladysz, J. A. *Organometallics* **1982**, *1*, 405.

Table I. Crystallographic Parameters for [Cp(CO)(PPh$_3$)Mn≡C(Me)C=CPh$_2$]BF$_4$·CH$_2$Cl$_2$ (5a), [Cp(CO)(PPh$_3$)Mn=C=C(Me)–]$_2${C(H)(Et)} (13), and Cp(CO)(PPh$_3$)Mn=C=C(Me)(*p*-Tol)C=CH$_2$ (14c)[a]

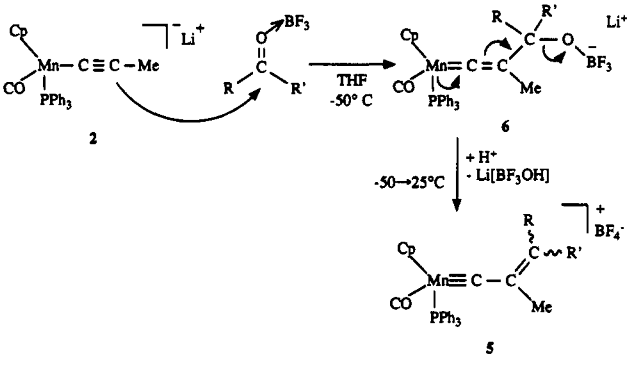
	5a	**13**	**14c**
	(a) Crystal Parameters		
formula	$C_{41}H_{35}BF_4OPMnCl_2$	$C_{57}H_{52}O_2P_2Mn_2$	$C_{36}H_{32}MnOP$
fw	787.35	940.86	566.56
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a, Å	10.602(3)	19.840(6)	8.563(2)
b, Å	11.798(4)	11.016(3)	17.267(3)
c, Å	16.422(6)	21.752(8)	19.928(4)
α, deg	70.391(28)		
β, deg	83.752(27)	98.76(3)	
γ, deg	79.298(29)		
V, Å^3	1898.9(11)	4698.5(36)	2946.5(10)
Z	2	4	4
cryst dimens, mm	0.30 × 0.30 × 0.41	0.32 × 0.32 × 0.42	0.31 × 0.31 × 0.36
cryst color	red	red	orange-red
D(calc), g/cm^3	1.377	1.330	1.277
μ(Mo Kα), cm^{-1}	5.66	6.23	5.08
F(000)	808	1960	1184
temp, K	298	298	298
T(max)/*T*(min)	1.21	1.17	1.32
	(b) Data Collection		
diffractometer	Nicolet R3m	Nicolet R3m	Siemens P4
monochromator	graphite	graphite	graphite
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
2θ scan range, deg	4–48	4–48	4–55
data (*hkl*)	±13,±14,+19	±22,+12,+24	+11,+22,+25
no. of rflns collected	6183	8167	3829
no. of indpt rflns	5864	7271	3824
no. of indpt obsd rflns	4052 (*n* = 5)	3912 (*n* = 5)	2460 (*n* = 4)
no. of std rflns	3 std/197	3 std/197	3 std/197
var in stds, %	2.7	3.6	2.6
	(c) Refinement		
R(*F*), %	5.82	6.40	5.25
R(w*F*), %	6.41	6.43	5.92
Δ/σ(max)	0.026	0.019	0.002
Δ(ρ), e Å^{-3}	0.657	0.676	0.450
N_o/N_v	10.1	7.9	7.0
GOF	1.581	1.370	1.180

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

Table II. Selected Bond Distances and Angles for [Cp(CO)(PPh$_3$)Mn≡C(Me)C=CPh$_2$]BF$_4$·CH$_2$Cl$_2$ (5a)

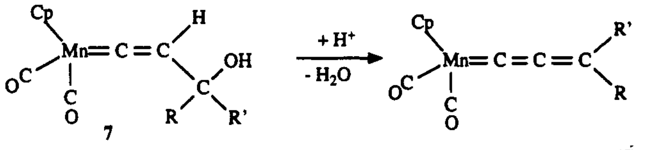
	(a) Bond Distances (Å)		
Mn–P	2.288(1)	Mn–C(1)	1.808(5)
Mn–CNT	1.808(4)	Mn–C(7)	1.668(5)
C(7)–C(8)	1.429(7)	C(8)–C(9)	1.515(6)
C(8)–C(10)	1.357(7)	C(10)–C(16)	1.470(6)
C(10)–C(26)	1.489(7)		
	(b) Bond Angles (deg)		
P–Mn–C(1)	92.7(2)	P–Mn–CNT	122.4(3)
C(1)–Mn–CNT	119.1(2)	C(7)–Mn–CNT	130.3(3)
C(1)–Mn–C(7)	90.3(2)	C(7)–Mn–P	92.2(3)
Mn–C(7)–C(8)	169.9(3)	C(7)–C(8)–C(9)	113.5(4)
C(7)–C(8)–C(10)	121.7(4)	C(9)–C(8)–C(10)	124.8(5)
C(8)–C(10)–C(16)	120.9(5)	C(8)–C(10)–C(26)	123.8(4)
C(16)–C(10)–C(26)	115.2(4)		

Scheme II



highly nucleophilic[1] and should thus readily add to the carbonyl carbon of the BF$_3$-activated ketone or aldehyde to form the vinylidene intermediate **6**. This species can be observed by IR analysis of the reaction mixture immediately after the addition of the ketone or aldehyde and BF$_3$·Et$_2$O but before quenching with MeOH. For example, the IR spectrum of the reaction mixture resulting from the addition of acetone/BF$_3$·Et$_2$O to **2** at −50 °C showed a ν_{CO} band at 1896 (s) cm^{-1} and a $\nu_{C=C}$ band at 1599 (w) cm^{-1}. The ν_{CO} band is similar in position to that observed for other vinylidene complexes within this family (*e.g.*, Cp(CO)(PPh$_3$)Mn=C=CMe$_2$, ν_{CO} = 1903 (s) cm^{-1}),[1b] but the $\nu_{C=C}$ band is substantially lower in energy than that typically found (Cp(CO)(PPh$_3$)Mn=C=CMe$_2$, $\nu_{C=C}$ = 1670 (w) cm^{-1}),[1b] an apparent consequence of the presence of the OBF$_3$ group.

Protonation of **6** by MeOH addition should lead to displacement of [HOBF$_3$]$^-$ and formation of the vinylcarbyne complex **5**. There are a number of examples of related hydroxide elimination reactions to form conjugated organic ligands.[2b,8] For example, stable hydroxy-substituted vinylidene complexes of the form Cp(CO)$_2$Mn=C=C(H)C(OH)RR′ (**7**) have been shown to dehydrate in the presence of catalytic amounts of mineral acids as well as on SiO$_2$ or Al$_2$O$_3$ chromatography to give the allenylidene complexes Cp(CO)$_2$Mn=C=C=CRR′ (eq 5).[8a] It should also be noted that a similar mechanism has



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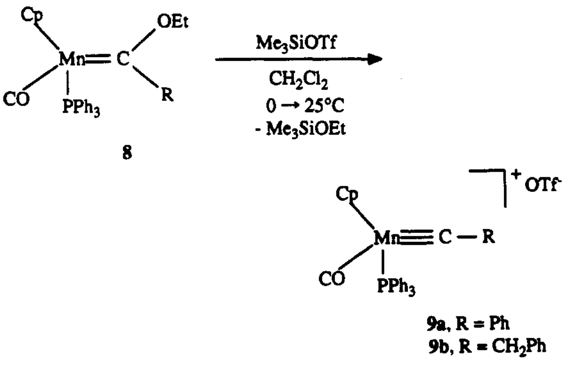
(5)

been invoked to explain the formation of bridging vinylcarbyne ligands from the condensation of μ-carbyne ligands with aldehydes and ketones.[3c,d]

Preparation of the Carbyne Complexes $[Cp(CO)(PPh_3)Mn{\equiv}CR]^+$ (R = Et, Ph, CH_2Ph). For spectroscopic comparison to the vinylcarbyne complexes described above, we have prepared the related carbyne complexes $[Cp(CO)(PPh_3)Mn{\equiv}CR]^+$ (R = Et, Ph, CH_2Ph) via Me_3SiOTf-induced loss of ethoxide from ethoxycarbene complexes (eq 6) and protonation of a vinylidene complex[1b] with the acid formed upon mixing BF_3 and methanol (eq 7).[9] Although similar dicarbonyl analogues are known,[10] these PPh_3-substituted derivatives have not been previously reported. These complexes were isolated as microcrystalline solids in near-quantitative yield and were spectroscopically characterized (see Experimental Section). In the infrared, each showed a single ν_{CO} band in the 2013–2018-cm^{-1} spectral region, with these bands slightly higher in energy than those of the vinylcarbyne complexes **5a–g** (ν_{CO} = 1999–2010 cm^{-1}). In the ^{13}C NMR, the carbyne carbon resonance of the phenylcarbyne complex **9a** is at δ 343.7, substantially upfield of those of **9b** (δ 362.6) and **9c** (δ 372.5) but near the δ 345–349 range observed for C_α in the vinylcarbyne complexes **5a–g**. For comparison, the corresponding resonance for the related dicarbonyl complex $[Cp(CO)_2Mn{\equiv}CPh]^+$ is at δ 356.9.[10]



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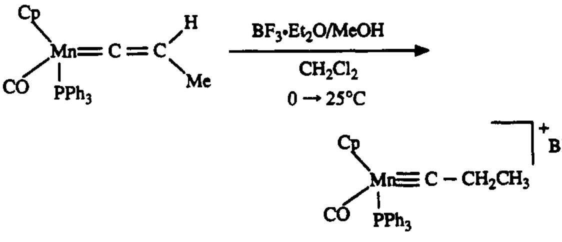
(6)

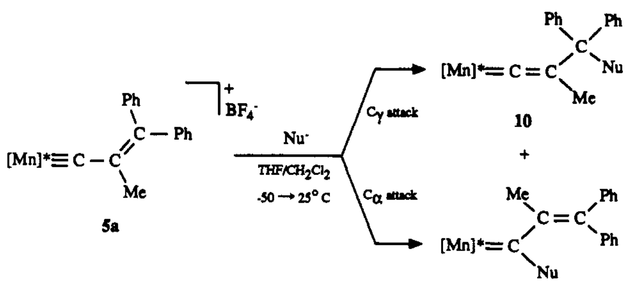
9a, R = Ph
9b, R = CH_2Ph



(7)

9c

Scheme III



5a, **10**, **11**

Nucleophile	Isolated Yields 10	11
$LiAlH_4$ (a)	10a/11a = < 5/95*	
MeMgI (b)	20%	56%
EtMgCl (c)	24%	31%
Pr^iMgCl (d)	67%	--
$LiC{\equiv}C\text{-}Bu^t$ (e)	--	32%

*Product not isolated, relative yields based on IR data

Reactions of $[Cp(CO)(PPh_3)Mn{\equiv}CC(Me){=}CPh_2]BF_4$ (5a) with Nucleophiles. It is well-known that cationic carbyne complexes within the $[Cp(CO)_2Mn{\equiv}C\text{—}aryl]^+$ family readily add nucleophiles to the carbyne carbon to form carbene derivatives.[10,11] Similar reactions have not been reported for the more electron-rich PPh_3-substituted derivatives $[Cp(CO)(PPh_3)Mn{\equiv}C\text{—}aryl]^+$, although a brief study of complexes **9a–c** indicated that they are substantially less electrophilic than are their dicarbonyl analogues.[12] *A priori*, the vinylcarbyne complexes **5a–g** might also be expected to add nucleophiles to the carbyne carbon, but addition to C_γ could also occur due to the importance of the resonance form **B** illustrated above. Nucleophilic addition to C_α would yield carbene derivatives, whereas vinylidene complexes would result from addition to C_γ. It should be noted that previous studies of μ-vinylcarbyne complexes have shown that nucleophiles add to the γ-carbon to form μ-vinylidene complexes, but C_α addition was not observed.[3d,f]

It has been found that addition to *both* sites occurs for the vinylcarbyne complex **5a**, with addition to C_α being electronically preferred but with addition to C_γ being favored sterically because of the bulky PPh_3 ligand. This is illustrated by the data given in Scheme III, which show that, within the limits of IR and ^1H NMR analysis, hydride and the *tert*-butylacetylide group add only to C_α, the large isopropyl group adds only to C_γ, and the intermediate-sized methyl and ethyl anions add to both positions, with the smaller methyl group favoring C_α addition more so than the larger ethyl group. With the exception of **11a**, which is unstable and decomposes near room temperature, each of the indicated products was isolated as a spectroscopically characterized microcrystalline solid (see Ex-

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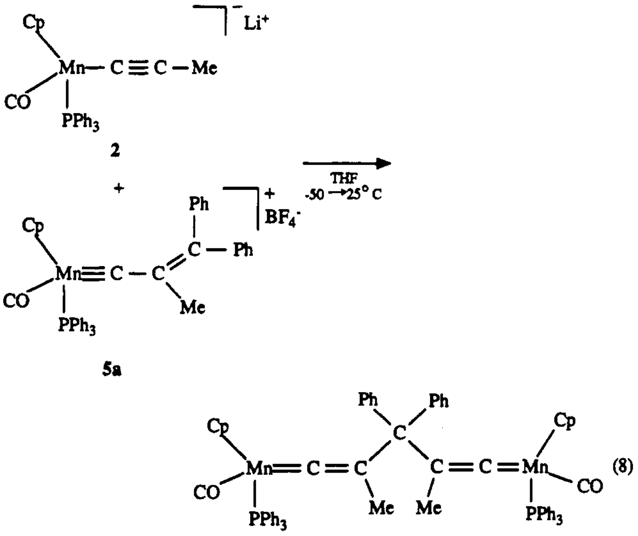
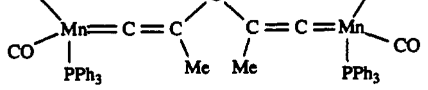
(12) Terry, M.; Geoffroy, G. L., unpublished observations.

perimental Section). Although **11a** could not be isolated, IR analysis of the reaction mixture showed only the presence of a single species with a ν_{CO} band at 1848 (s) cm^{-1}, similar in position to the bands of **11b** (1842 (s) cm^{-1}), **11c** (1855 (s) cm^{-1}), and **11e** (1853 (s) cm^{-1}) but different from those of **10b–d** (1890–1898 (s) cm^{-1}). The vinylidene complexes **10b–e** are similar to earlier reported examples within this Cp(CO)(PPh$_3$)Mn=C=CRR′ family.[1]

Reaction of Vinylcarbyne Complex 5a with Propynyl Complex 2. The propynyl complex **2** is a potent nucleophile,[1] and it was thus of interest to determine if it would likewise add to **5a**, most likely to the γ-carbon because of its larger size. Indeed, as illustrated in eq 8, such reaction does occur to form the binuclear bis(vinylidene) complex **12**, in which the vinylidene ligands are connected through a diphenylmethylene unit. Each of the manganese centers in **12** is chiral, and ^{1}H NMR data indicate that this complex forms as a 1:1 mixture of diastereomers. These were separated by a combination of chromatography and extraction and obtained as stable red and brown solids. They show identical IR spectra (ν_{CO} = 1888 (s) cm^{-1}; $\nu_{C=C}$ = 1614 (w) cm^{-1}), and each gave the same parent ion at *m/z* 1065 in their +FAB mass spectra. The ^{1}H and ^{13}C NMR spectra of the two diastereomers are similar, but not identical, and are consistent with the indicated formulations (see Experimental Section).



12 (48%)



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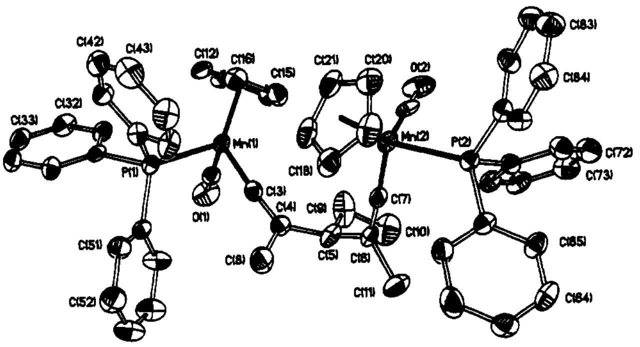


Figure 2. ORTEP drawing of [Cp(CO)(PPh$_3$)Mn=C=C(Me)–]$_2${C(H)(Et)} (**13**).

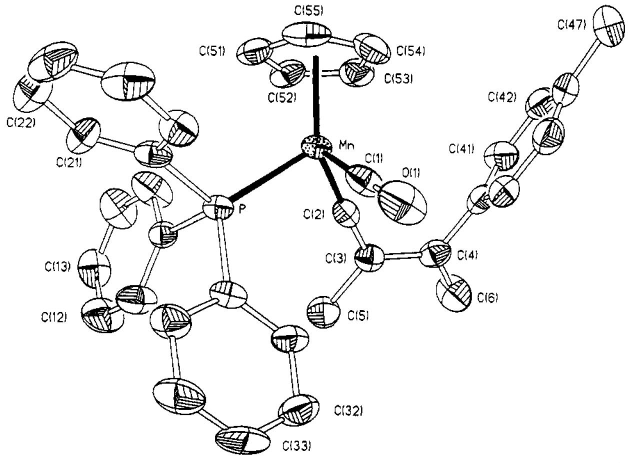


Figure 3. ORTEP drawing of Cp(CO)(PPh$_3$)Mn=C=C(Me)(*p*-Tol)C=CH$_2$ (**14c**).

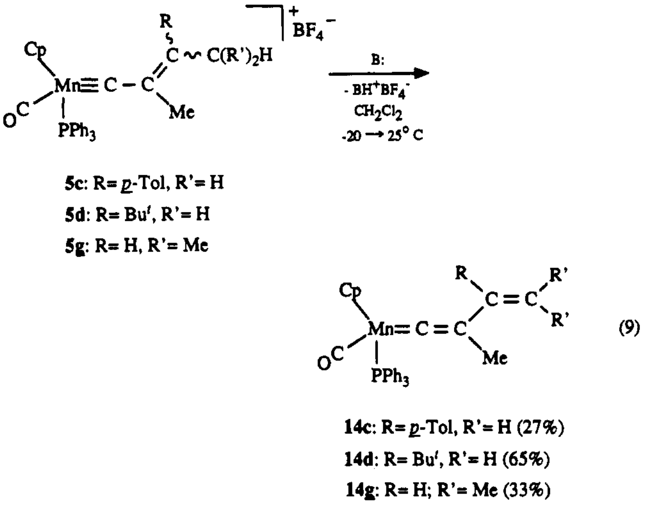
Table III. Selected Bond Distances and Angles for [Cp(CO)(PPh$_3$)Mn=C=C(Me)–]$_2${C(H)(Et)} (13)

(a) Bond Distances (Å)			
Mn(1)–P(1)	2.239(2)	Mn(1)–C(3)	1.793(7)
Mn(1)–C(1)	1.758(8)	Mn(2)–P(2)	2.222(2)
Mn(2)–C(2)	1.756(7)	Mn(2)–C(7)	1.772(7)
C(3)–C(4)	1.317(10)	C(4)–C(5)	1.506(11)
C(4)–C(8)	1.517(11)	C(5)–C(6)	1.535(11)
C(5)–C(9)	1.465(13)	C(6)–C(7)	1.311(11)
C(6)–C(11)	1.529(10)	C(9)–C(10)	1.544(14)
Mn(1)–CNT(1)	1.789(7)	Mn(2)–CNT(2)	1.794(6)
(b) Bond Angles (deg)			
C(1)–Mn(1)–C(3)	92.8(3)	C(2)–Mn(2)–C(7)	92.7(3)
CNT(1)–Mn(1)–C(3)	123.7(2)	CNT(2)–Mn(2)–C(7)	123.3(3)
P(1)–Mn(1)–CNT(1)	122.4(2)	P(2)–Mn(2)–CNT(2)	124.2(3)
C(1)–Mn(1)–CNT(1)	123.8(3)	C(2)–Mn(2)–CNT(2)	124.6(4)
P(1)–Mn(1)–C(3)	93.0(2)	P(2)–Mn(2)–C(7)	93.5(2)
C(1)–Mn(1)–P(1)	92.4(3)	C(2)–Mn(2)–P(2)	80.1(3)
Mn(1)–C(1)–O(1)	175.6(6)	Mn(2)–C(2)–O(2)	178.4(7)
Mn(1)–C(3)–C(4)	175.9(6)	C(3)–C(4)–C(5)	123.4(7)
C(3)–C(4)–C(8)	121.6(7)	C(5)–C(4)–C(8)	114.9(6)
C(4)–C(5)–C(6)	111.7(6)	C(4)–C(5)–C(9)	115.8(7)
C(6)–C(5)–C(9)	115.0(8)	C(5)–C(6)–C(7)	122.4(6)
C(5)–C(6)–C(11)	116.1(7)	C(7)–C(6)–C(11)	121.4(7)
Mn(2)–C(7)–C(6)	177.2(6)	C(5)–C(9)–C(10)	112.7(8)

The closely related compound **13** was serendipitously obtained via an unknown mechanism and in very low yield as a byproduct from the separate reactions of **2** with MeOH and with Me$_3$SiCl. The ^{1}H NMR data indicate that **13** forms as a ~3:1 mixture of diastereomers, but no attempt was made to separate these. The spectroscopic data for **13** are similar to those for **12** (see Experimental Section), and this species was also fully characterized by an X-ray diffraction study. An ORTEP drawing is shown in Figure 2, and the important crystallographic data are given in Tables I and III. The molecule possesses the usual pseudooctahedral geometry about each of the Mn centers, and the vinylidene ligands are oriented such that the planes defined by their β-carbons (C(4) and C(6)) and their attached substituent atoms approach coplanarity with the Mn–P vectors, as illustrated by the torsion angles between the planes defined by P(1)–Mn(1)–C(3) and C(3)–C(4)–C(8) (11.0(3)°) and P(2)–Mn(2)–C(7) and C(7)–C(6)–C(11) (29.4(3)°). This is the orientation predicted by electronic arguments, since the strongly electron-withdrawing vinylidene and carbonyl ligands π-bond with different metal d$_\pi$ orbitals and thus do not compete for the metal electron density.[7] The vinylidene ligands are essentially linear (Mn-

(1)–C(3)–C(4) = 175.9(6)° and Mn(2)–C(7)–C(6) = 177.2(6)°), and the Mn=C bond distances of 1.793(7) (Mn(1)–C(3)) and 1.772(7) Å (Mn(2)–C(7)) compare well to that of the related vinylidene complex Cp(CO)(PPh$_3$)Mn=C=C(Me)(Bu^t) (Mn=C = 1.764(9) Å).[1b] The C(3)–C(4) and C(7)–C(6) distances of 1.317(10) and 1.311(11) Å, respectively, compare favorably with the corresponding C=C distance of 1.339(1) Å found in this reference compound. The bis(vinylidene) ligand is twisted about the C(4)–C(5)–C(6) linkage (torsion angle {C(8)–C(4)–C(5)}–{C(11)–C(6)–C(5)} = 89.3(3)°) so as to minimize steric interactions between the terminal methyl groups. The two Mn centers are chiral and are of opposite configuration with both the *RS* and *SR* diastereomers present in the centrosymmetric unit cell. The diastereomer drawn in Figure 2 has the *R* configuration about Mn(1) and *S* about Mn(2).

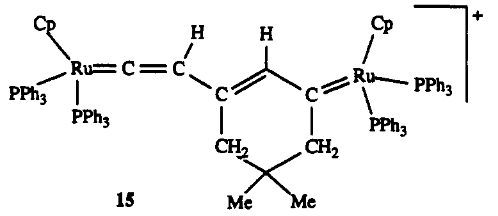
Formation of Vinylvinylidene Complexes via Deprotonation of Complexes 5c,d,g. The vinylcarbyne complexes that have an alkyl substituent on the γ-carbon can be deprotonated to form the vinylvinylidene complexes shown in eq 9. This reaction is reversible, and the vinylcarbyne complexes can be re-formed in near-quantitative yield by protonation of 14 with HOTf. These new complexes were isolated as spectroscopically characterized microcrystalline solids, and complex 14c was further defined by an X-ray diffraction study (see Figure 3 and below). In the infrared, each complex showed a single ν_{CO} band (1883–1890 (s) cm^{-1}), and 14d and 14g showed two $\nu_{C=C}$ vibrations (14d 1635 (w), 1599 (w), cm^{-1}; 14g, 1653 (w), 1601 (w) cm^{-1}), with the higher energy band attributed to the terminal C=C bond of the vinylidene ligand and the lower energy vibration attributed to the C=C bond of the vinyl substituent. In the case of 14c, these bands overlap and appear as a single broad band at 1592 (m) cm^{-1}. The $\nu_{C=C}$ bands compare well to the 1626- and 1601-cm^{-1} values reported for the vinylidene and vinyl C=C vibrations in the ruthenium vinylvinylidene complex 15.[13] The ^{1}H and ^{13}C NMR data for these new vinylvinylidene complexes are consistent with their proposed structures, and particularly important in the ^{13}C NMR are the resonances assigned to the unsaturated carbon atoms of the vinylvinylidene ligand (δ_{C_α} = 362–370 (d, J_{PC} = 29–32 Hz); δ_{C_β} = 134–137; δ_{C_γ} = 119–157; δ_{C_δ} = 103–120). These values compare to the values reported for 15 as follows: δ_{C_α} = 356.0; δ_{C_β} = 110.8; δ_{C_γ} = 129.3; δ_{C_δ} = 123.6.[13]



5c: R= p-Tol, R'= H
5d: R= Bu^t, R'= H
5g: R= H, R'= Me

(9)

14c: R= p-Tol, R'= H (27%)
14d: R= Bu^t, R'= H (65%)
14g: R= H; R'= Me (33%)



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Crystal and Molecular Structure of 14c. An ORTEP drawing of 14c is shown in Figure 3, and the important crystallographic data are set out in Tables I and IV. The molecule possesses the usual pseudooctahedral geometry about Mn. The manganese atom and the carbon atoms of the vinylvinylidene ligand are coplanar (maximum deviation of 0.039 Å associated with C(6) from the plane defined by Mn and C(2–6)). This plane is also nearly coplanar with the Mn–P vector, as indicated by the {P–Mn–C(2)}–{C(2)–C(3)–C(5)–C(4)} torsion angle of 14.2(2)°. As noted above, this is the orientation of the vinylidene ligand predicted by electronic arguments.[7] The Mn–C(2) and C(2)–C(3) distances of 1.761(6) and 1.336(9) Å, respectively, compare well to those found in 13 and in the related vinylidene complex Cp(CO)(PPh$_3$)Mn=C=C(Me)(Bu^t) (Mn=C = 1.764(9); C=C = 1.339(11) Å).[1b] The C(3)–C(4) distance of 1.474(10) Å and the C(4)–C(6) distance of 1.333(11) Å are typical values for organic dienes (1.460 and 1.330 Å).[5]

Concluding Remarks

The most important aspects of the work described herein are the formation of vinylcarbyne complexes 5a–g by the surprising reaction of the propynyl complex [Cp(CO)(PPh$_3$)MnC≡CMe]$^-$ with BF$_3$-activated aldehydes and ketones and the observed reactions of this class of vinylcarbyne complexes with nucleophiles. Vinylcarbyne complexes has never before been prepared via a synthetic method like that employed herein, and although these products were unexpected, in retrospect the mechanism for the reaction shown in Scheme II is quite reasonable on the basis of the previously demonstrated nucleophilicity of [Cp(CO)(PPh$_3$)MnC≡CMe]$^-$ and related OH$^-$-elimination reactions reported in the literature.[1,2b,8] Although the scope of this synthetic reaction leading to vinylcarbyne complexes in this manganese family has not been extensively explored, it should be relatively large, given the range of nucleophilic manganese acetylide complexes which can be prepared[1] and the range of ketones and aldehydes demonstrated to work in the reactions reported herein (eq 4). A major limitation of this method is the difficulty in separating the complex salts obtained from the byproduct [Cp(CO)(PPh$_3$)Mn≡CEt]BF$_4$. These salts do not survive chromatography, and separation is thus dependent upon selective crystallization, which in our hands has not worked well (except for 5a).

Of particular interest in the reactivity of the vinylcarbyne complex 5a is the demonstration that nucleophiles can add to either the α-carbon to form carbene complexes or to the γ-carbon to form vinylidene derivatives, with the site of nucleophilic addition strongly influenced by steric factors. The data presented in Scheme III indicate that small nucleophiles prefer to add to the α-carbon but that when this is restricted due to steric interactions between the nucleophile and the crowded manganese center, addition readily occurs at the γ-carbon. In passing, we note that weaker nucleophiles such as imines, benzalazine, azoxybenzene, carbodiimides, and Bu^{t}NCO, which could

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(13) (a) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921. (b) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.

Table IV. Selected Bond Distances and Angles for $Cp(CO)(PPh_3)Mn{=}C{=}C(Me)(p\text{-}Tol)C{=}CH_2$ (14c)

(a) Bond Distances (Å)			
Mn–P	2.239(2)	Mn–C(1)	1.745(8)
Mn–C(2)	1.761(6)	Mn–CNT	1.813(6)
C(2)–C(3)	1.336(9)	C(3)–C(4)	1.474(10)
C(3)–C(5)	1.526(9)	C(4)–C(6)	1.333(11)
C(4)–C(46)	1.495(10)		
(b) Bond Angles (deg)			
P–Mn–CNT	123.8(1)	C(1)–Mn–CNT	125.1(4)
C(2)–Mn–CNT	122.4(5)	C(1)–Mn–P	89.6(2)
C(2)–Mn–P	94.1(2)	C(1)–Mn–C(2)	92.7(3)
Mn–C(1)–O(1)	176.1(7)	Mn–C(2)–C(3)	176.5(5)
C(2)–C(3)–C(4)	123.5(6)	C(2)–C(3)–C(5)	117.8(6)
C(4)–C(3)–C(5)	118.6(6)	C(3)–C(4)–C(6)	123.7(7)
C(3)–C(4)–C(46)	117.7(6)	C(6)–C(4)–C(46)	118.6(7)

have led to cycloaddition reactions across the vinylcarbyne ligand, did not react with complex **5b**. In other work, we have shown that imines and related organics readily undergo a variety of interesting cycloaddition reactions with the cationic carbyne complexes $[Cp(CO)_2M{\equiv}CTol]^+$ (M = Mn, Re),[14] but the presence of the electron-releasing PPh_3 ligand in **5b** apparently reduces the electrophilicity of the vinylcarbyne ligand to such an extent that these weak nucleophiles do not add to this ligand in these complexes. To counter this problem, we are currently developing alternative routes to the dicarbonyl complexes $[Cp(CO)_2Mn{\equiv}CC(R'){=}CR_2]^+$ (R′ ≠ H) which should be more electrophilic and perhaps capable of undergoing the desired cycloaddition reactions with these weaker organic nucleophiles.[15]

Experimental Section

General Considerations. The carbene complexes $Cp(CO)(PPh_3)Mn{=}C(OR)R'$ (R = Et, R′ = Me, Ph, CH_2Ph; R = Me, R′ = Et)[1b,16] and the vinylidene complex $Cp(CO)(PPh_3)Mn{=}C{=}CHMe$[1b] were prepared by modifications of the published procedures. Benzyllithium·TMEDA was prepared by the method of Eberhardt and Butte.[17] The reagents Bu^nLi, $BF_3{\cdot}Et_2O$, Me_3SiOTf, HOTf, pinacolone, 4′-methylacetophenone, acetone, isobutyraldehyde, *p*-tolualdehyde, 2,2,2-trimethylacetophenone, $Li[AlH_4]$ (1.0 M in THF), MeMgI (3.0 M in Et_2O), EtMgCl (2.0 M in Et_2O), Et_3N, Et_2NH, Pr^iMgCl (2.9 M in THF), and $Li[BEt_3H]$ (1.0 M in THF) were obtained from Aldrich Chemical Co., and benzophenone was obtained from Fisher Scientific Co. $CpMn(CO)_3$ was obtained from Strem Chemicals, Inc. Lithium *tert*-butylacetylide was prepared by the reaction of $Bu^tC{\equiv}CH$ (Aldrich) with Bu^nLi. All reagents were used without further purification, except acetone, which was distilled from K_2CO_3 under an N_2 atmosphere, MeOH, which was distilled from BaO under an N_2 atmosphere, and isobutyraldehyde, which was distilled under N_2 at atmospheric pressure. Solvents were dried by refluxing over Na/benzophenone ketyl (THF, Et_2O) or CaH_2 (CH_2Cl_2, pentane, hexane) and distilled under an N_2 atmosphere prior to use. All manipulations were performed using standard Schlenk techniques under an N_2 atmosphere. Solution IR spectra were recorded between NaCl plates on an IBM FTIR-32 spectrometer operated in the absorbance mode. NMR spectra (^1H and ^{13}C) were obtained on a Bruker AM-300 FT NMR in CD_2Cl_2 and referenced to the residual solvent protons (^1H). Mass spectra were recorded on AEI-MS9 (EI) and Kratos MS-50 (+FAB) mass spectrometers. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, and from Galbraith Analytical Laboratories, Knoxville, TN.

Preparation of Vinylcarbyne Complexes 5a–g via Reaction of $[Cp(CO)(PPh_3)MnC{\equiv}CMe]^-$ with Aldehydes and Ketones. To a stirred solution of $Cp(CO)(PPh_3)Mn{=}C(OMe)Et$ in THF was added *n*-BuLi (2.2 equiv) via syringe to generate propynyl complex **2**. This solution was stirred at room temperature for ~15 min and then cooled to −50 °C with a 2-propanol/liquid N_2 bath. In a separate flask, a THF solution containing the desired ketone or aldehyde (1.1 equiv) and $BF_3{\cdot}Et_2O$ (2.2 equiv) was prepared and cooled to 0 °C. This latter solution was then added to the cooled solution of **2** via cannula, and the reaction mixture was stirred for 15 min at −50 °C. An excess (2.2 equiv) of dry MeOH was added to the reaction mixture, which was then warmed to room temperature over ~30 min. The solution was filtered through dry Celite, and the volatile components were removed under vacuum to leave an orange-brown flocculent solid containing the vinylcarbyne product along with some $[Cp(CO)(PPh_3)Mn{\equiv}CEt]BF_4$ (**9c**). ^1H NMR analysis of the products indicated the overall yields of the vinylcarbyne complexes to be in the 80–90% range in all cases. Partial purification was accomplished by repeated dissolution of the solid in minimal CH_2Cl_2, reprecipitation of the product, usually as an oil, by addition of hexane, and removal of the supernatant via cannula. Thorough drying of the residue under vacuum gave the products as orange-brown flocculent solids which left free-flowing microcrystalline solids upon crushing with a spatual and washing with hexane. Analytically pure **5a** (CH_2Cl_2 solvate) was obtained by layering a concentrated CH_2Cl_2 solution of the complex with hexane and allowing slow solvent diffusion to occur at room temperature, which induced crystallization of **5a** as purple cubes. Complexes **5c,d,g** were preferentially obtained as their OTf^- salts as described in the following paragraph. ^1H and ^{13}C NMR analysis of **5b,e,f** showed the presence of varying amounts of **9c** as an impurity, and no procedures were found which would allow the clean separation of these complex salts. In the cases of **5b–d**, ^1H and ^{13}C NMR assignments were verified by means of two-dimensional C–H correlation NMR experiments.

5a. Anal. Calcd for $C_{40}H_{33}BF_4MnOP{\cdot}CH_2Cl_2$: C, 62.55; H, 4.48. Found: C, 63.00; H, 4.37. IR (CH_2Cl_2): ν_{CO} = 1999 (s), $\nu_{C=C}$ = 1509 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.63–6.85 (m, 25H, *Ph*), 5.06 (d, J_{PH} = 1.4 Hz, *Cp*), 1.84 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 345.5 (d, J_{PC} = 33.6 Hz, Mn≡*C*), 226.4 (d, J_{PC} = 27.2 Hz, Mn-*C*O), 166.5 (C_γ), 145.4 (C_β), 140.1–128.6 (aryl), 93.1 (*Cp*), 18.34 (CH_3). MS (+FAB): *m/z* 615 ($M^+ - BF_4^-$), 587 ($M^+ - BF_4^- - CO$).

5b. IR (CH_2Cl_2): ν_{CO} = 2004 (s), $\nu_{C=C}$ = 1564 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.75–7.32 (m, 15H, *Ph*), 5.17 (s, 5H, *Cp*), 2.32 and 1.92 (s, 3H, $C(CH_3)_2$), 1.55 (s, 3H, $C(CH_3){=}CMe_2$). $^{13}C\{^1H\}$NMR (CD_2Cl_2): δ 347.2 (d, J_{PC} = 33.3 Hz, Mn≡*C*), 225.1 (d, J_{PC} = 27.7 Hz, Mn–*C*O), 172.6 (s, C_γ), 145.9 (s, C_β), 134.7–129.6 (aryl), 92.4 (s, *Cp*), 24.7 and 23.4 (s, $C(CH_3)_2$), 14.2 (s, $C(CH_3){=}CMe_2$). MS (+FAB): *m/z* 491 ($M^+ - BF_4^-$), 463 ($M^+ - BF_4^- - CO$).

5e. IR (CH_2Cl_2): ν_{CO} = 2010 (s), $\nu_{C=C}$ = 1522 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.57–7.20 (m, 20H, *Ph*), 5.19 (s, 5H, *Cp*), 1.77 (s, 3H, $C(CH_3)$), 1.08 (s, 9H, ${=}C(Ph)(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 348.6 (d, J_{PC} = 36.1 Hz, Mn≡*C*), 227.1 (d, J_{PC} = 25.0 Hz, Mn–*C*O), 180.5 (s, C_γ), 146.4 (s, C_β), 133.8–129.5 (aryl), 92.3 (s, *Cp*), 38.9 (s, $C(CH_3)_3$), 28.7 (s, $C(CH_3)_3$). MS (+FAB): *m/z* 595 ($M^+ - BF_4^-$), 567 ($M^+ - BF_4^- - CO$).

5f. IR (CH_2Cl_2): ν_{CO} = 2008 (s), $\nu_{C=C}$ = 1541 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.55–7.26 (m, 19H, aryl), 5.24 (s, 5H, *Cp*), 2.40 (s, 3H, $p\text{-}(CH_3)C_6H_4$), 2.06 (s, 3H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 347.1 (d, J_{PC} = 36.1 Hz, Mn≡*C*), 226.6 (br s, Mn–*C*O), 154.1 (s, C_γ), 147.1 (s, C_β), 144.0–128.9 (aryl), 92.5 (s, *Cp*), 21.9 (s, $p\text{-}(CH_3)C_6H_4$), 15.3 (s, $C(CH_3)$). ^{13}C NMR (CD_2Cl_2): δ 346.9 (d, J_{PC} = 36.1 Hz, Mn≡*C*), 226.5 (d, J_{PC} = 27.7 Hz, Mn–*C*O), 153.9 (br d, J_{CH} = 155.4 Hz, C_γ), 147.1 (s, C_β), 143.9–128.5 (m, aryl), 92.5 (d, J_{CH} = 179.8 Hz, *Cp*), 21.8 (q, J_{CH} = 130.4 Hz, $p\text{-}(CH_3)C_6H_4$), 14.1 (q, J_{CH} = 122.1 Hz, $C(CH_3)$. MS (+FAB): *m/z* 595 ($M^+ - BF_4^-$), 567 ($M^+ - BF_4^- - CO$).

Formation of the Vinylcarbyne Complexes 5c,d,g as Their

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OTf$^-$ Salts via Protonation of Vinylvinylidene Complexes with HOTf. The appropriate vinylvinylidene complex (**14c,d,g**; 0.2–0.3 mmol), whose preparations are described below, was dissolved in CH_2Cl_2 (10 mL), the solution was cooled to 0 °C, and 1 equiv of HOTf was added via syringe. The reaction mixture was stirred for 10 min at 0 °C and then warmed to room temperature over 15 min. IR analysis of the reaction mixtures showed complete consumption of the vinylvinylidene complex and indicated formation of a single cationic product in each case. The solution was then concentrated under vacuum to ~2 mL, and the product was precipitated as an oil by addition of 1:1 Et_2O/hexane (10 mL). The supernatant was removed via cannula, and the precipitation procedure was twice repeated. The resulting red-orange oil was thoroughly dried under vacuum to leave a flocculent solid which was crushed with a spatula and washed with hexane (2 × 5 mL). Thorough drying of this solid gave the corresponding vinylcarbyne complexes as OTf$^-$ salts in near-quantitative yields as free-flowing microcrystalline powders.

5c (OTf$^-$ Salt). IR (THF): ν_{CO} = 1999 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.89–7.16 (m, 19H, aryl), 5.00 (s, 5H, *Cp*), 2.55 (s, 3H, *p*-(CH_3)C_6H_4), 2.11 (s, 3H, C(CH_3)), 1.72 (s, 3H, C(*p*-Tol)(CH_3)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 346.1 (d, J_{PC} = 33.3 Hz, Mn$\equiv$*C*), 227.1 (d, J_{PC} = 27.7 Hz, Mn–*C*O), 169.2 (s, C_γ), 146.1 (s, C_β), 141.7–127.6 (aryl), 92.7 (s, *Cp*), 31.9 (s, C(*C*H$_3$)(*p*-Tol)), 21.6 (s, *p*-(*C*H$_3$C$_6$H$_4$), 14.2 (s, C(*C*H$_3$). MS (+FAB): *m/z* 567 (M$^+$ – BF$_4^-$), 539 (M$^+$ – OTf$^-$ – CO).

5d (OTf$^-$ Salt). IR (CH_2Cl_2): ν_{CO} = 1999 (s), $\nu_{C=C}$ = 1524 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.57–7.30 (m, 15H, *Ph*), 5.19 (d, 5H, J_{PH} = 1.6 Hz, *Cp*), 2.37 (s, 3H, C(CH_3)), 1.82 (s, 3H, C(CH_3)(Bu^t)), 1.13 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 372.5 (d, J_{PC} = 38.8 Hz, Mn$\equiv$C), 227.1 (d, J_{PC} = 30.5 Hz, Mn–*C*O), 180.1 (s, C_γ), 146.4 (s, C_β), 133.9–129.5 (aryl), 92.3 (s, *Cp*), 38.9 (s, *C*(CH$_3$)$_3$), 28.7 (s, C(*C*H$_3$)$_3$), 23.0 (s, C(*C*H$_3$)). MS (+FAB): *m/z* 533 (M$^+$ – OTf$^-$), 505 (M$^+$ – OTf$^-$ – CO).

5g (OTf$^-$ Salt). Anal. Calcd for $C_{32}H_{31}F_3MnO_4PS$: C, 58.72; H, 4.77. Found: C, 58.63; H, 4.61. IR (CH_2Cl_2): ν_{CO} = 2008 (s), $\nu_{C=C}$ = 1570 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.69–7.09 (m, aryl), 5.19 (br s, *Cp*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 347.5 (d, J_{PC} = 41.6 Hz, Mn$\equiv$*C*), 226.0 (d, J_{PC} = 25.0 Hz, Mn–*C*O)), 166.5 (s, C_γ), 147.5 (s, C_β), 137.7–128.2 (aryl), 92.5 (s, *Cp*). MS (+FAB): *m/z* 505 (M$^+$ – OTf$^-$), 477 (M$^+$ – OTf$^-$ – CO).

Preparation of the Carbyne Complexes [Cp(CO)(PPh$_3$)-Mn$\equiv$CR]OTf (R = Ph (9a), CH$_2$Ph (9b)). The appropriate carbene complex (Cp(CO)(PPh$_3$)Mn=C(OEt)Ph 0.50 g, 0.95 mmol; Cp(CO)(PPh$_3$)Mn=C(OEt)CH$_2$Ph, 0.25 g, 0.45 mmol) was dissolved in CH_2Cl_2 (10–15 mL), the solution was cooled to 0 °C, and Me$_3$SiOTf (1.1 equiv) was then added via syringe. The solution was stirred for 10 min, warmed to room temperature over ~15 min, and then concentrated under vacuum to ~1–2 mL. Addition of 10 mL of a 1:3 Et_2O/hexane mixture gave a red/orange oily precipitate. The supernatant was removed via cannula, and the oily residue was dried under vacuum to give a flocculent solid which was crushed with a spatula, washed with hexane, and dried under vacuum to yield **9a** (red, 0.62 g, 0.95 mmol) and **9b** (yellow-brown, 0.30 g, 0.45 mmol) as microcrystalline solids.

9a. Anal. Calcd for $C_{32}H_{25}F_3MnO_4PS$: C, 59.27; H, 3.89. Found: C, 59.18; H, 4.01. IR (CH_2Cl_2): ν_{CO} = 2014 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.68–7.38 (m, 20H, *Ph*), 5.29 (s, 5H, *Cp*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 343.7 (d, J_{PC} = 36.1 Hz, Mn$\equiv$*C*), 225.5 (d, J_{PC} = 22.2 Hz, Mn–*C*O), 147.3–129.3 (aryl), 93.1 (s, *Cp*). MS (+FAB): *m/z* 499 (M$^+$ – OTf$^-$), 471 (M$^+$ – OTf$^-$ – CO).

9b. Anal. Calcd for $C_{33}H_{27}F_3MnO_4PS$: C, 59.82; H, 4.11. Found: C, 59.79; H, 3.90. IR (CH_2Cl_2): ν_{CO} = 2018 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.54–7.04 (m, 20H, *Ph*), 5.12 (s, 5H, *Cp*), 4.27 (br d, AB pattern, 1H, C*H*$_2$Ph), 4.09 (br d, AB pattern, 1H, C*H*$_2$Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 362.6 (d, J_{PC} = 36.1 Hz, Mn$\equiv$C), 224.9 (d, J_{PC} = 25.0 Hz, Mn–CO), 135.8–128.7 (aryl), 92.7 (s, *Cp*), δ 64.2 (s, *C*H$_2$Ph). MS (+FAB): *m/z* 513 (M$^+$ – OTf$^-$), 485 (M$^+$ – OTf$^-$ – CO).

Preparation of the Carbyne Complex [Cp(CO)(PPh$_3$)Mn$\equiv$CEt]BF$_4$ (9c). The complex Cp(CO)(PPh$_3$)Mn=C=CHMe (0.40 g, 0.89 mmol) was dissolved in CH_2Cl_2 (10 mL) at room temperature. In a separate flask, MeOH (0.98 mmol, 0.04 mL) and BF$_3$·Et$_2$O (0.98 mmol, 0.12 mL) were combined in CH_2Cl_2 (5 mL) at 0 °C and stirred for 5 min. The MeOH/BF$_3$·Et$_2$O solution was then added to the solution of the vinylidene complex via cannula, and the resultant solution was stirred for 15 min at room temperature, during which time the color changed from deep red to light orange. The solution was concentrated to ~3 mL under vacuum and filtered through a 1-in. plug of dry Celite. The clear orange filtrate was then concentrated to ~2 mL, and 10 mL of a 1:1 hexane/Et_2O solution was added, causing precipitation of **9c** as an orange oil. The supernatant was removed via cannula, the solid was dissolved in minimal CH_2Cl_2, and the precipitation step was repeated. The resultant oily orange residue was then dried under vacuum to give a flocculent yellow solid, which was crushed with a spatula, washed with hexane (2 × 5 mL), and dried under vacuum to give **9c** (0.48 g, 0.89 mmol) as a yellow solid.

9c. Anal. Calcd for $C_{27}H_{25}MnOPBF_4$: C, 60.26; H, 4.68. Found: C, 59.96; H, 4.66. IR (CH_2Cl_2): ν_{CO} = 2013 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.56–7.11 (m, 15H, P*Ph*$_3$), 5.18 (s, 5H, *Cp*), 3.06–2.97 (br m, ABX$_3$ pattern, 1H, C*H*$_2$CH$_3$), 2.78–2.69 (br m, ABX$_3$ pattern, 1H, C*H*$_2$CH$_3$), 1.18 (t, J_{HH} = 7.0 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 372.5 (d, J_{PC} = 33.3 Hz, Mn$\equiv$*C*), 225.1 (d, J_{PC} = 19.4 Hz, Mn–*C*O), 133.7–129.6 (m, P*Ph*$_3$), 92.3 (s, *Cp*), 52.3 (s, *C*H$_2$CH$_3$), 10.8 (s, CH$_2$*C*H$_3$). MS (+FAB): *m/z* 451 (M$^+$ – BF$_4^-$), 423 (M$^+$ – BF$_4^-$ – CO).

Reaction of Vinylcarbyne Complex 5a with Li[AlH$_4$]. Complex **5a** (0.55 g, 0.783 mmol) was dissolved in 20 mL of 4:1 THF/CH_2Cl_2, the solution was cooled to –50 °C, and LiAlH$_4$ (1.1 equiv, 0.86 mmol, 0.87 mL of a 1.0 M solution in THF) was added dropwise via syringe, which caused the purple solution to darken. The reaction mixture was stirred for ~30 min while it was warmed to room temperature. IR analysis showed the complete consumption of **5a** and the appearance of a single ν_{CO} band at 1848 (s) cm^{-1}, indicating the formation of **11a** (see text). Removal of solvent from this solution under vacuum gave extensive decomposition, and no tractable products were obtained. Similar results were obtained using Li[HBEt$_3$] as the hydride source.

Reaction of Vinylcarbyne Complex 5a with MeMgI. Complex **5a** (0.5 g, 0.712 mmol) was dissolved in 20 mL of 4:1 THF/CH_2Cl_2, the solution was cooled to –50 °C, MeMgI (1.1 equiv, 0.783 mmol, 0.26 mL of a 3.0 M solution in Et_2O) was added dropwise via syringe, and the reaction mixture was stirred for ~1 h while it was warmed to room temperature. The solvents were removed under vacuum to leave a brown solid, which was dissolved in Et_2O and chromatographed on neutral alumina. Elution with 1:1 Et_2O/pentane gave first a bright yellow band of an unidentified compound. Continued elution with 100% Et_2O gave a single brown band containing both **10b** and **11b** (by IR). Extraction of this mixture with pentane/Et_2O (3:1) gave a red solution of **10b** and an olive-green precipitate of **11b** (0.25 g, 56% yield after drying). The supernatant was removed via cannula, and the remaining solid was washed with the 3:1 pentane/Et_2O mixture until the washings were colorless. The washings and supernatant were combined and rechromatographed as above, giving a single red band of **10b**. Removal of solvent from this fraction under vacuum gave a red-brown oil which left an orange precipitate of **10b** (0.09 g, 20% yield) upon stirring with pentane.

10b. Anal. Calcd for $C_{41}H_{36}MnOP$: C, 78.09; H, 5.75. Found: C, 78.09; H, 6.04. IR (THF): ν_{CO} = 1890 (s), $\nu_{C=C}$ = 1641 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.81–7.20 (m, 25H, *Ph*), 4.49 d, 5H, J_{PH} = 1.5 Hz, *Cp*), 1.89 (s, 3H, C(C*H*$_3$)Ph$_2$), 0.99 (s, 3H, Mn=C=C(C*H*$_3$)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 362.6 (d, J_{PC} = 30.5 Hz, Mn=*C*), 237.1 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 134.4–125.7 (aryl), 138.5 (br s, Mn=C=*C*), 88.0 (s, *Cp*), 51.2 (s, *C*(CH$_3$)Ph$_2$), 31.2 (s, C(*C*H$_3$)Ph$_2$), 12.0 (s, Mn=C=C(*C*H$_3$). MS (+FAB): *m/z* 602 (M$^+$ – CO).

11b. Anal. Calcd for $C_{41}H_{36}MnOP$: C, 78.09; H, 5.75. Found: C, 77.82; H, 5.50. IR (CH_2Cl_2): ν_{CO} = 1842 (s), $\nu_{C=C}$ = 1596 (vw) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.52–7.09 (m, 25H, *Ph*), 3.99 (s, 5H, *Cp*), 2.79 (s, 3H, Mn=C(C*H*$_3$)), 1.01 (s, 3H, C(C*H*$_3$)=CPh$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 350.8 (d, J_{PC} = 27.7 Hz, Mn=*C*), 237.2 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 162.5 (s, C(CH$_3$)=*C*Ph$_2$), 145.5 (s,

$\mathit{C}(CH_3){=}CPh_2)$, 145.5–128.6 (aryl), 90.4 (s, *Cp*), 47.6 (d, J_{PC} = 11.1 Hz, $Mn{=}C(\mathit{C}H_3))$, 19.2 (s, $C(\mathit{C}H_3){=}CPh_2)$. MS (+FAB): *m/z* 631 (M + H$^+$), 602 (M$^+$ – CO).

Reaction of Vinylcarbyne Complex 5a with EtMgCl. Vinylcarbyne complex **5a** (0.50 g, 0.71 mmol) was dissolved in 20 mL of THF/CH_2Cl_2 (4:1) and cooled to −50 °C. EtMgCl (1.0 equiv, 0.36 mL of a 2.0 M solution in Et_2O) was then added dropwise via syringe, and the resulting solution was stirred for ~30 min while it was warmed to room temperature. The solvents were then removed under vacuum to give a brown oil, which was dissolved in Et_2O/CH_2Cl_2 (3:1) and chromatographed on neutral alumina. Elution with a 1:1 mixture of Et_2O/pentane gave first a bright yellow band of an unknown compound, and elution with neat Et_2O gave a single brown band containing both **10c** and **11c** (by IR). Removal of the solvent from this fraction gave a brown solid, which was redissolved and chromatographed again. Elution with a 3:1 solution of pentane/Et_2O gave first a small red band containing **10c**. Continued elution with neat Et_2O gave a second green-brown band containing **11c**. Removal of solvent from the first fraction gave a red-orange oil which upon trituration with a minimum of pentane left an orange precipitate of **10c** (0.11 g, 24% yield). Removal of solvent from the second fraction gave **11c** (0.14 g, 31% yield) as an olive green solid.

10c. Anal. Calcd for $C_{42}H_{38}MnOP$: C, 78.25; H, 5.94. Found: C, 78.62; H, 5.27. IR (Et_2O): ν_{CO} = 1898 (s), $\nu_{C=C}$ = 1633 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.50–7.20 (m, 25H, *Ph*), 4.56 (s, 5H, *Cp*), 2.64 (br m, AMX_3 pattern, 1H, $C\mathit{H}_2CH_3$), 2.03 (br m, AMX_3 pattern, 1H, $C\mathit{H}_2CH_3$), 0.90 (s, 3H, $C{=}C(C\mathit{H}_3))$, 0.76 (t, J_{HH} = 6.9 Hz, 3H, $CH_2C\mathit{H}_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 362.5 (d, J_{PC} = 30.2 Hz, $Mn{=}\mathit{C}$), 237.3 (d, J_{PC} = 34.0 Hz, Mn–*C*O), 138.3 (br d, $Mn{=}C{=}\mathit{C}$), 145.7–125.5 (aryl), 88.1 (s, *Cp*), 33.6 (s, $\mathit{C}H_2CH_3$), 11.8 (s, $CH_2\mathit{C}H_3$), 10.4 (s, $C{=}C(\mathit{C}H_3))$. MS (+FAB): *m/z* 644 (M$^+$), 616 (M$^+$ – CO).

11c. Anal. Calcd for $C_{42}H_{38}MnOP$: C, 78.25; H, 5.94. Found: C, 78.06; H, 6.03. IR (CH_2Cl_2): ν_{CO} = 1842 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.53–7.06 (m, 25H, *Ph*), 4.05 (s, 5H, *Cp*), 3.75 (br m, AMX_3 pattern, 1H, $C\mathit{H}_2CH_3$), 2.09 (br m, AMX_3 pattern, 1H, $C\mathit{H}_2CH_3$), 1.19 (t, J_{HH} = 7.3 Hz, 3H, $CH_2C\mathit{H}_3$), 1.04 (s, 3H, $C(C\mathit{H}_3){=}C(Ph)_2)$. ^{13}C{^{1}H} NMR ($CD_2Cl_2$): δ 357.1 (d, J_{PC} = 27.5 Hz, $Mn{=}\mathit{C}$), 237.1 (d, J_{PC} = 34.9 Hz, Mn–*C*O), 159.7 (s, $C(CH_3){=}\mathit{C}Ph_2$), 146.6 (s, $\mathit{C}(CH_3){=}CPh_2$), 145.1–125.3 (aryl), 89.6 (s, *Cp*), 19.6 (s, $C(\mathit{C}H_3){=}CPh_2$), 15.2 (s, $CH_2\mathit{C}H_3$). *Note*: The peak assignable to $\mathit{C}H_2CH_3$ was obscured by the solvent peak (δ 53.8 (5)), as verified by the proton-coupled ^{13}C NMR spectrum. ^{13}C NMR ($CDCl_3$): δ 357.1 (br s, $Mn{=}\mathit{C}$), 236.7 (d, J_{PC} = 31.7 Hz, Mn–*C*O), 159.3 (s, $C(CH_3){=}\mathit{C}Ph_2$), 146.1 (s, $\mathit{C}(CH_3){=}CPh_2$), 144.7–123.9 (aryl), 88.7 (d, J_{CH} = 176.4 Hz, *Cp*), 53.8 (d of t, J_{CH} = 130.4 Hz, J_{PC} = 8.3 Hz, $\mathit{C}H_2CH_3$), 19.4 (q, J_{CH} = 127.6 Hz, $C(\mathit{C}H_3){=}CPh_2$), 15.2 (q, J_{CH} = 119.3 Hz, $CH_2\mathit{C}H_3$). MS (+FAB): *m/z* 644 (M$^+$), 616 (M$^+$ – CO).

Reaction of Vinylcarbyne Complex 5a with Pr^{i}MgCl. Complex **5a** (0.5 g, 0.712 mmol) was dissolved in 20 mL of THF/CH_2Cl_2 (4:1) and cooled to −50 °C. Pr^{i}MgCl (1.1 equiv, 0.783 mmol, 0.27 mL of a 2.9 M solution in THF) was then added dropwise via syringe, which induced a color change from deep purple-brown to red. The solution was stirred for ~1 h while it was warmed to room temperature, and the solvent was removed under vacuum to give a red solid, which was dissolved in Et_2O/CH_2Cl_2 (3:1) and chromatographed on neutral alumina. Elution with neat Et_2O gave a single red band of **10d**. Removal of solvent from this band left **10d** (0.31 g, 67% yield) as a red microcrystalline solid.

10d. Anal. Calcd for $C_{43}H_{40}MnOP$: C, 78.41; H, 6.12. Found: C, 78.44; H, 6.36. IR (THF): ν_{CO} = 1892 (s), $\nu_{C=C}$ = 1621 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.50–7.23 (m, 25H, *Ph*), 4.51 (d, 5H, J_{PC} = 1.5 Hz, *Cp*), 3.05 (sept, J_{HH} = 6.4 Hz, 1H, $C\mathit{H}(CH_3)_2$), 0.93 (d, J_{HH} = 6.6 Hz, 3H, $CH(C\mathit{H}_3)_2$), 0.89 (s, 3H, $C{=}C(C\mathit{H}_3))$, 0.78 (d, J_{HH} = 6.5 Hz, 3H, $CH(C\mathit{H}_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 346.3 (d, J_{PC} = 30.5 Hz, $Mn{=}\mathit{C}$), 237.7 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 138.5 (br s, $Mn{=}C{=}\mathit{C}$), 144.3–125.6 (aryl), 88.1 (s, *Cp*), 32.4 (s, $\mathit{C}H(CH_3)_2$), 20.7 and 20.4 (s, $CH(\mathit{C}H_3)_2$), 12.4 (s, $C(\mathit{C}H_3){=}CPh_2Pr^i$). MS (EI): *m/z* 658 (M$^+$), 630 (M$^+$ – CO).

Reaction of Vinylcarbyne Complex 5a with LiC≡CBu^t. Vinylcarbyne complex **5a** (0.5 g, 0.712 mmol) was dissolved in 4:1 THF/CH_2Cl_2 (15 mL), and the resulting solution was cooled to −50 °C. In a separate flask, LiC≡CBu^t (1.1 equiv, 0.78 mmol, 0.07 g) was dissolved in 10 mL of THF and cooled to 0 °C, and this solution was added to the flask containing **5a** via cannula. This mixture was stirred for ~30 min while it was warmed to room temperature, during which time the color changed drom deep purple to green-brown. The solvents were removed under vacuum to give a green-brown solid residue, which was redissolved in Et_2O and chromatographed on neutral alumina. Elution with neat Et_2O gave a single band of **11e**. Removal of the solvent from this fraction gave a green solid, which was washed with pentane (3 × 5 mL) and dried under vacuum to give **11e** (0.16g, 32% yield) as an emerald green microcrystalline powder.

11e. Anal. Calcd for $C_{46}H_{42}MnOP$: C, 79.30; H, 6.08. Found: C, 79.35; H, 5.81. IR (Et_2O): ν_{CO} = 1862 (s). ^{1}H NMR (CD_2Cl_2): δ 7.52–7.17 (m, 25H, *Ph*), 4.10 (d, 5H, J_{PC} = 2.0 Hz, *Cp*), 1.39 (s, 9H, $C{\equiv}CC(C\mathit{H}_3)_3$), 0.93 (s, 3H, $C(C\mathit{H}_3){=}CPh_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 304.0 (d, J_{PC} = 29.6 Hz, $Mn{=}\mathit{C}$), 237.1 (d, J_{PC} = 34.0 Hz, Mn–*C*O), 159.5 (s, $C(CH_3){=}\mathit{C}Ph_2$), 145.4 (s, $\mathit{C}(CH_3){=}CPh_2$), 138.1–125.6 (aryl), 97.7 (s, $-C{=}\mathit{C}Bu^t$), 93.3 (s, *Cp*), 87.9 (s, $-\mathit{C}{=}CBu^t$), 31.4 (s, $C{\equiv}CC(\mathit{C}H_3)_3$), 30.8 (s, $C{\equiv}C\mathit{C}(CH_3)_3$), 19.1 (s, $C(\mathit{C}H_3){=}CPh_2$). MS (+FAB): *m/z* 697 (M + H$^+$), 668 (M$^+$ – CO).

Reaction of Vinylcarbyne Complex 5a with Propynyl Complex 2. The carbene complex $Cp(CO)(PPh_3)Mn{=}C(OMe)Et$ (0.57 g, 1.17 mmol) was dissolved in freshly distilled THF (15 mL), and Bu^{n}Li (2.2 equiv, 2.58 mL of a 1.6 M solution in hexanes) was added dropwise via syringe to generate propynyl complex **2**. In a separate flask, vinylcarbyne complex **5a** (0.75 g, 1.07 mmol) was dissolved in THF (20 mL). Both solutions were cooled to −50 °C, the solution of **2** was added to the **5a** solution via cannula, and the reaction mixture was stirred for 30 min while it was warmed to room temperature. Removal of solvent under vacuum gave a red oily residue, which was then redissolved in a minimal amount of Et_2O and chromatographed on neutral alumina. Elution with a 1:1 mixture of pentane/Et_2O gave first an orange-brown band containing $Cp(CO)(PPh_3)Mn{=}C{=}C(H)(Me)$ (**6**), which was discarded. Continued elution with neat Et_2O gave a single red-brown band containing both diastereomers of **12** (designated **12′** and **12″**). The product mixture was rechromatographed, first with a 1:1 mixture of Et_2O/pentane as eluent and then with gradual increases in the Et_2O concentration. The leading edge of the product band was collected, and the solvents were removed under vacuum to give the brown diastereomer **12′** as an orange-brown flocculent solid. The middle portion of this band was collected in a separate flask, and removal of solvent from this fraction gave a mixture of the diastereomers as a red-brown solid. The trailing edge of this band was then collected, and the solvents were removed to give the red diastereomer **12″** as a red solid. The solid residue from the mixture of diastereomers from the middle fraction was washed with 3:1 Et_2O/pentane to leave a red precipitate to **12″** and an orange-brown solution containing **12′**. The supernatant was removed from this mixture via cannula and added to the previously isolated **12′**. The remaining red solid (**12″**) was washed with 3:1 Et_2O/pentane until the washings were colorless, and all of the washings were added to the flask containing **12′**. Removal of the solvents from this solution gave an orange-brown flocculent solid, which was washed with pentane (3 × 5 mL) and dried under vacuum to give **12′** (0.26 g, 23% yield). The remaining red solids were combined, washed with pentane (3 × 5 mL), and dried under vacuum to give **12″** as a light red powder (0.29 g, 25% yield).

12′. Anal. Calcd for $C_{67}H_{56}Mn_2O_2P_2$: C, 75.56; H, 5.30. Found: C, 75.64; H, 5.76. IR (THF): ν_{CO} = 1888 (s), $\nu_{C=C}$ = 1614 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.89–7.10 (m, 40H, *Ph*), 4.21 (d, 10H, J_{PH} = 1.6 Hz, *Cp*), 1.51 (s, 6H, $C{=}C(C\mathit{H}_3)$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 364.8 (d, J_{PC} = 29.4 Hz, $Mn{=}\mathit{C}$), 236.6 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 147.9 (s, $Mn{=}C{=}\mathit{C}$), 146.9 (s, $Mn{=}C{=}\mathit{C}$), 139.0–125.3 (aryl), 87.9 (s, *Cp*), 87.7 (s, *Cp*), 66.0 (s, $\mathit{C}Ph_2$), 15.0 (s, $Mn{=}C{=}C(\mathit{C}H_3)$). MS (+FAB): *m/z* 1065 (M$^+$), 1038 (MH$^+$ – CO).

12″. Anal. Calcd for $C_{76}H_{56}Mn_2O_2P_2$: C, 75.56; H, 5.30.

Found: C, 75.96; H, 5.07. IR (THF): ν_{CO} = 1888 (s), $\nu_{C=C}$ = 1614 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.69–7.07 (m, 40H, *Ph*), 3.94 (d, 10H, J_{PH} = 1.5 Hz, *Cp*), 1.61 (s, 6H, C=C(C*H*$_3$)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 365.6 (d, J_{PC} = 30.6 Hz, Mn=*C*), 236.7 (d, J_{PC} = 33.5 Hz, Mn–*C*O), 147.3 (s, Mn=C=*C*), 134.2–125.3 (aryl), 87.5 (s, *Cp*), 63.9 (s, *C*Ph$_2$), 14.3 (s, Mn=C=C(*C*H$_3$)). MS (+FAB): *m/z* 1065 (M$^+$), 1037 (M$^+$ – CO).

Preparation of Bis(vinylidene) Complex 13. The carbene complex Cp(CO)(PPh$_3$)Mn=C(OMe)Et (3.0 g, 6.22 mmol) was dissolved in dry THF (~100 mL), and Bu^{n}Li (2.2 equiv, 13.7 mmol, 8.6 mL of a 1.6 M solution in hexanes) was added dropwise via syringe to generate propynyl complex **2**. Excess dry MeOH was then added to the reaction mixture, which was stirred for 15 min, after which the volatiles were removed under vacuum to give a red oily residue. This residue was taken up in a minimal amount of Et_2O and chromatographed on alumina. Elution with a 3:1 mixture of pentane/Et_2O gave a single red band, and removal of the solvents from this band under vacuum gave a red oil. The oil was rechromatographed as above; the product band was first washed thoroughly with pentane before it was eluted with the same 3:1 pentane/Et_2O mixture. This gave a first small red band of **13**, followed by a larger orange band of Cp(CO)(PPh$_3$)-Mn=C=C(H)(Me) (**6**). Removal of the solvents from the first band left **13** as a deep red microcrystalline solid, which was washed with pentane (3 × 5 mL) and dried under vacuum (0.55 g, 0.58 mmol, 9.4% yield). Complex **13** was similarly isolated in 5.8% yield from the reaction of **2** with Me_3SiCl.

13. Anal. Calcd for $C_{57}H_{52}Mn_2O_2P_2$: C, 72.22; H, 5.57. Found: C, 72.50; H, 5.42. IR (hexane): ν_{CO} = 1900 (s), $\nu_{C=C}$ = 1637 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.60–7.13 (m, 30H, P*Ph*$_3$), 4.51 (d, J_{PH} = 1.6 Hz, 5H, *Cp*), 4.50 (obscured doublet, *Cp*), 2.80 (t, C(*H*)CH$_2$CH$_3$), 2.62 (t, C(*H*)CH$_2$CH$_3$), 1.68–1.55 (overlapping dm, 2H, 2 × C(H)C*H*$_2$CH$_3$), 1.43 (s, 3H, C=C(C*H*$_3$)), 1.38 (s, 3H, C=C(C*H*$_3$)), 1.12 (t, J_{HH} = 7.2 Hz, 3H, C(H)CH$_2$C*H*$_3$), 0.89 (t, J_{HH} = 7.2 Hz, 3H, C(H)CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 363.6 (d, J_{PC} = 30.5 Hz, Mn=*C*), 236.7 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 236.6 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 139.2–127.8 (aryl), 87.6 (s, *Cp*), 46.8 (s, *C*(H)(CH$_2$CH$_3$)), 25.2 (s, C(H)(*C*H$_2$CH$_3$)), 14.1 (s, C(H)(CH$_2$*C*H$_3$)), 11.3 (s, C=C(*C*H$_3$)). ^{13}C NMR (CD_2Cl_2): δ 363.9 (br s, Mn=*C*), 236.7 (d, J_{PC} = 33.1 Hz, Mn–*C*O), 139.2–126.7 (m, aryl), 89.0–88.7 and 86.6–86.3 (2 dm, J_{CH1} = 182.7 Hz, J_{CH2} = 7.3 Hz, *Cp*), 46.7 (d, J_{CH} = 130.8 Hz, *C*(H)(CH$_2$CH$_3$)), 25.2 (t, J_{CH} = 162.8 Hz, C(H)(*C*H$_2$CH$_3$)), 13.0 (q, J_{CH} = 132.4 Hz, C(H)-(CH$_2$*C*H$_3$)), 12.5 (q, J_{CH} = 134.9 Hz, 2 × C=C(*C*H$_3$)). MS (–FAB): *m/z* 939 (M – H$^+$).

Deprotonation of Vinylcarbyne Complexes 5c,g,f with Et_3N and Et_2NH. The vinylcarbyne complex (**5c** or **5g**, 0.25 g; **5d**, 0.5 g) was dissolved in 15 mL of CH_2Cl_2, and the resulting solution was cooled to 0 °C. An excess of base (Et_2NH or Et_3N, 2.2 equiv) was then added dropwise via syringe, which caused the color of the solution to lighten to orange-red. The reaction mixture was stirred for ~30 min while it was warmed to room temperature, and the solvent and excess base were removed under vacuum to give red-orange oily residues. The residue was dissolved in Et_2O and chromatographed on neutral alumina to give a single orange band in each case. Removal of the solvent from these fractions gave orange solids, which were dissolved in Et_2O and rechromatographed, the product band being washed thoroughly with neat pentane before it was eluted with neat Et_2O. Removal of the solvents from these fractions gave **14c** as an orange solid (0.10 g, 27% yield), **14d** (0.28 g, 65% yield) as a red microcrystalline solid, and **14g** as a flocculent red solid (0.07 g, 33% yield).

14c. Anal. Calcd for $C_{36}H_{32}MnOP$: C, 76.32; H, 5.69. Found: C, 76.37; H, 5.99. IR (CH_2Cl_2): ν_{CO} = 1890 (s), $\nu_{C=C}$ = 1592 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.50–7.09 (m, 19H, aryl), 4.46 (d, 1H, J_{HH} = 1.4 Hz, C(*p*-Tol)=C*H*$_2$), 4.37 (d, 1H, J_{HH} = 1.4 Hz, C(*p*-Tol)=C*H*$_2$), 4.13 (d, 5H, J_{PC} = 1.48 Hz, *Cp*), 2.35 (s, 3H, *p*-(C*H*$_3$)-C$_6$H$_4$), 1.44 (s, 3H, C=C(C*H*$_3$)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 369.7 (d, J_{PC} = 31.5 Hz, Mn=*C*), 235.2 (d, J_{PC} = 32.0 Hz, Mn–*C*O), 149.2 (s, *C*(*p*-Tol)=CH$_2$), 141.2–128.2 (P*Ph*$_3$ and *p-Tol*), 136.4 (s, Mn=C=*C*(CH$_3$)), 103.6 (s, C(*p*-Tol)=*C*H$_2$), 88.2 (s, *Cp*), 21.2 (s, *p*-(*C*H$_3$)C$_6$H$_4$), 12.4 (s, C=C(*C*H$_3$). MS (+FAB): *m/z* 567 (M + H$^+$), 538 (M$^+$ – CO).

14d. Anal. Calcd for $C_{33}H_{34}MnOP$: C, 74.43; H, 6.43. Found: C, 74.20; H, 6.21. IR (CH_2Cl_2): ν_{CO} = 1883 (s), $\nu_{C=C}$ = 1635 (w), 1599 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.55–7.36 (m, 15H, P*Ph*$_3$), 4.74 (d, 1H, J_{HH} = 1.64 Hz, C(Bu^t)=C*H*$_2$), 4.64 (d, 1H, J_{HH} = 1.53 Hz, C(Bu^t)=C*H*$_2$), 4.56 (d, J_{PC} = 1.49 Hz, *Cp*), 1.44 (s, 3H, C=C-(C*H*)$_3$), 1.22 (s, 9H, C(C(C*H*$_3$)$_3$=CH$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 362.9 (d, J_{PC} = 29.2 Hz, Mn=*C*), 237.2 (d, J_{PC} = 30.5 Hz, Mn–*C*O), 156.2 (s, *C*(Bu^t)=CH$_2$), 138.8–128.2 (P*Ph*$_3$), 106.3 (s, C(Bu^t)=*C*H$_2$), 88.1 (s, *Cp*), 37.6 (s, *C*(CH$_3$)$_3$), 30.9 (s, C(*C*H$_3$)$_3$), 16.4 (s, C=C(*C*H$_3$)). MS (+FAB): *m/z* 532 (M$^+$), 504 (M$^+$ – CO).

14g. Anal. Calcd for $C_{31}H_{30}MnOP$: C, 73.81; H, 5.99. Found: C, 74.45; H, 6.04. IR (CH_2Cl_2): ν_{CO} = 1883 (s), $\nu_{C=C}$ = 1653 (w), 1601 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.56–7.32 (m, 15H, P*Ph*$_3$), 5.32 (s, 1H, C(*H*)=C(CH$_3$)$_2$), 4.56 (d, 5H, J_{PH} = 1.4 Hz, *Cp*), 1.85 (s, 3H, C(H)=C(C*H*$_3$)$_2$), 1.78 and 1.56 (s, 3H, C(H)=C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 370.1 (d, J_{PC} = 30.5 Hz, Mn=*C*), 236.0 (d, J_{PC} = 33.3 Hz, Mn–*C*O), 138.8–125.8 (P*Ph*$_3$), 134.2 (s, Mn=C=*C*), 119.8 (s, *C*(H)=C(CH$_3$)$_2$), 87.8 (s, *Cp*), 27.1 and 20.6 (2 s, C(H)=C(*C*H$_3$)$_2$), 14.4 (s, Mn=C=C(*C*H$_3$)). MS (+FAB): *m/z* 505 (M + H$^+$), 476 (M$^+$ – CO).

Crystal and Molecular Structures of 5a, 13, and 14c. 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 were obtained from the least-squares fit of 25 reflections (20° ≤ θ ≤ 25°). Systematic absences in the diffraction data uniquely determined the monoclinic space group of $P2_1/n$ for **13** and the orthorhombic space group of $P2_12_12_1$ for **14c**. For compound **5a**, photographic evidence and cell reduction routines indicated $\bar{1}$ Laue symmetry. The chemically sensible results of refinement established the space group as $P\bar{1}$. No correction for absorption was required for any of the three crystals (low μ, well-shaped crystals).

The structures were solved by direct methods, which located the Mn atoms. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl rings in compounds **13** and **5a** were constrained as rigid planar hexagons. All hydrogen atoms were treated as idealized isotropic contributions (d_{CH} = 0.960 Å, U = 1.2U for attached C). All software is contained in the SHELXTL (5.1, 1983) program library for structures **13** and **5a** and SHELXTL PLUS (4.21, 1990) program library for **14c** (G. Sheldrick, Siemens (Nicolet) XRD Corp., Madison, WI).

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Supplementary Material Available: For **5a**, **13**, and **14c**, tables of atomic coordinates and isotropic parameters, anisotropic thermal parameters, bond lengths, bond angles, and hydrogen atom coordinates (19 pages). Ordering information is given on any current masthead page.

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