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Addition, Cycloaddition, and Metathesis Reactions of the Cationic Carbyne Complexes $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ and Neutral Vinylidene Complexes $Cp(CO)_2M{=}C{=}C(H)R$ (M = Mn, Re)

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The cationic alkylidyne complexes $[Cp(CO)_2M{\equiv}CCH_2R]^+$ (M = Re, R = H; M = Mn, R = H, Me, Ph) undergo facile deprotonation to give the corresponding neutral vinylidene complexes $Cp(CO)_2M{=}C{=}C(H)R$. For $[Cp(CO)_2Re{\equiv}CCH_3]^+$, this transformation occurs spontaneously at −78 °C upon the addition of solvent (CH_2Cl_2 or THF) to the solid carbyne complex, but the manganese complexes $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ (R = H, Me) require the addition of external base (*e.g.*, Et_3N) to induce their deprotonation. The manganese benzylcarbyne complex $[Cp(CO)_2Mn{\equiv}CCH_2Ph]^+$ is intermediate in behavior. Except for $Cp(CO)_2Mn{=}C{=}C(H)Ph$, these vinylidene complexes are thermally unstable and must be generated and studied at low temperature. They are potent dipolarophiles which undergo net [2 + 2] cycloaddition with imines to give cyclic carbene complexes of the general form $Cp(CO)_2M{=}\overline{CC(H)RC(H)PhN}(R')$ (M = Re, R = H, R′ = Me, Ph; M = Mn, R′ = Ph, R = H (**17a**), Me, Ph (**17c**)). Identical manganese products form upon treatment of the manganese carbyne complexes first with imine followed by addition of Et_3N. Permanganate oxidation of the manganese cyclic carbene complexes gives the corresponding β-lactams in excellent yield. Also formed in the reactions of the rhenium complex $Cp(CO)_2Re{=}C{=}CH_2$ with imines are the products $Cp(CO)_2Re{=}\overline{CC({=}C(H)Ph)C(H)PhN}(R')$ (R′ = Me, Ph (**15b**)), which have an exocyclic double bond formed via an aldol-type condensation between the initial cycloadduct and excess imine. The vinylidene complexes $Cp(CO)_2M{=}C{=}C(H)R$ react with $HN{=}C(Ph)_2$ to give imino–carbene complexes of the general form $Cp(CO)_2M{=}C(CH_2R)N{=}C(Ph)_2$, which are derived by addition of the N—H bond across the vinylidene C=C bond. Similar products form upon benzophenone imine addition to the manganese carbyne complexes, followed by addition of Et_3N. Also formed in the reaction of $Cp(CO)_2Mn{=}C{=}C(H)Ph$ or $[Cp(CO)_2Mn{\equiv}CCH_2Ph]^+$ with $HN{=}C(Ph)_2$ is the [2 + 2] cycloadduct $Cp(CO)_2Mn{=}\overline{CC(H)Ph\text{-}C(Ph)_2N}(H)$. Nitrile complexes, $Cp(CO)_2MnN{\equiv}CCH_2R$, result from an organometallic analogue of the Beckmann rearrangement upon treatment of $Cp(CO)_2Mn{=}C{=}C(H)R$ (R = H, Ph) or $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ (R = H, Me) with $Ph_2C{=}NNH_2$. Isocyanide complexes, $Cp(CO)_2ReC{\equiv}NR$, are the result of reaction of the vinylidene complex $Cp(CO)_2Re{=}C{=}CH_2$ with carbodiimides ($RN{=}C{=}NR$; R = Pr^i, Bu^t), a reaction that proceeds via net metathesis of the vinylidene Re=C bond with the carbodiimide C=N bond. A similar isocyanide product forms upon reaction of $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ with $Bu^tN{=}C{=}NBu^t$ and Et_3N, and a ^{13}C labeling experiment indicates a mechanism involving a 1,3-migration of the $[Cp(CO)_2Mn]$ fragment in the intermediate $[Cp(CO)_2MnC({=}CH_2)N(Bu^t){=}C{=}N(Bu^t)]$. Reaction of both $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ and $Cp(CO)_2Mn{=}C{=}CH_2$ with $Pr^iN{=}C{=}NPr^i$ gave the *ansa*-carbene complex $\{\eta^5\text{-}C_5H_4\overline{C({=}CH_2)\}(CO)_2Mn{=}C(N(H)Pr^i)(N}Pr^i)$ (**41**) by a path involving a similar 1,3-migration of the $[Cp(CO)_2Mn]$ fragment and insertion of the original vinylidene or carbyne α-carbon into the one of the C—H bonds of the cyclopentadienyl ligand. A byproduct of this reaction is the bis(amino)carbene complex $\{\eta^5\text{-}C_5H_4\text{-}C(O)CH_3(CO)_2Mn{=}C(NHPr^i)_2$ (**45**), with an acetyl substituent on the cyclopentadienyl ligand, a product that likely results from hydrolysis of the above-mentioned *ansa*-carbene complex. The unusual zwitterionic vinylidene complex $Cp(CO)_2Mn{=}C{=}C(Me)\overline{CN(Bu^t)B^-Cl_2N^+}(Bu^t)$ (**46**) is the principal product of the reaction of the propylidyne complex $[Cp(CO)_2Mn{\equiv}CCH_2Me]^+$ with $Bu^tN{=}C{=}NBu^t$ and Et_3N. With benzalazine, $Ph(H)C{=}NN{=}C(H)Ph$, the complexes $Cp(CO)_2Re{=}C{=}CH_2$ and $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ react to form the bimetallic bis(carbene) complexes $Cp(CO)_2M{=}\overline{CC(H)_2C(H)PhN}\overline{NC(H)\text{-}PhC(H)_2C}{=}M(CO)_2Cp$ (M = Re, Mn (**47**)), which result from consecutive [3 + 2] cycloaddition reactions of the azine with 2 equiv of the organometallic reagents. Crystal structures are reported for **15b**, **17a**, **41**, **45**, **46**, **47**, and the $\eta^5\text{-}C_5H_4Me$ analogue of **17c**.

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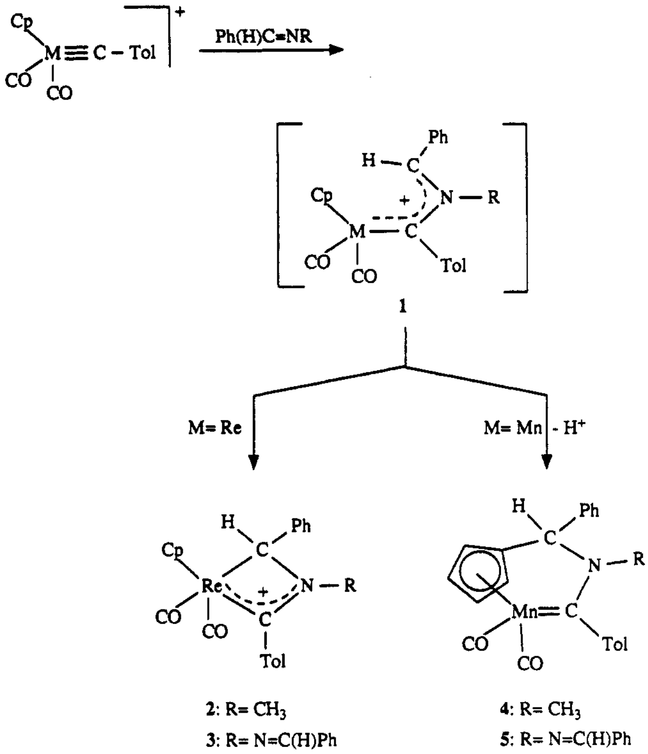
Introduction

In earlier work we demonstrated that the cationic aryl carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$ reacts with $Ph(H)C{=}NCH_3$ and $Ph(H)C{=}NN{=}C(H)Ph$ to give products arising from net [2 + 2] cycloadditions of the C=N bonds of these substrates across the Re≡C bond to form the metallacycles **2** and **3** shown in Scheme 1.[1] In contrast, the analogous Mn carbyne complex $[Cp(CO)_2Mn{\equiv}CTol]^+$ was observed to react with the same substrates to give the *ansa*-carbene complexes **4** and **5**, which result from insertion of the imine between the carbyne carbon and a C—H bond of the Cp ring, followed by deprotonation.[1] Both types of products are believed to form in a stepwise manner via the common intermediate **1**, which results from nucleophilic attack of the imine nitrogen at the electrophilic carbyne carbon atom.

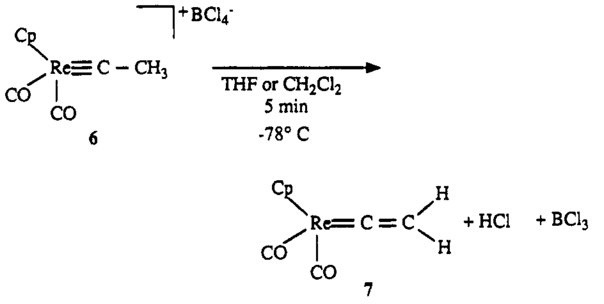
Following these and subsequent[2] investigations of the *aryl*carbyne complexes $[Cp(CO)_2Re{\equiv}CAr]^+$, we turned our attention to the corresponding *alkyl*carbyne complexes $[Cp(CO)_2M{\equiv}CCH_2R]^+$, which have in general been studied far less than their aryl analogues.[3] An important initial finding was the facile deprotonation of these species to generate the neutral vinylidene complexes $Cp(CO)_2M{=}C{=}C(H)R$. The parent vinylidene complexes with R = H had not been previously described, although many examples of substituted (R ≠ H) vinylidene complexes in this family are known.[4-6] Herein are described the reactions of the cationic carbyne complexes $[Cp(CO)_2M{\equiv}CCH_2R]^+$ and the neutral vinylidene complexes $Cp(CO)_2M{=}C{=}C(H)R$ with imines, carbodiimides ($RN{=}C{=}NR$), benzalazine ($Ph(H)C{=}NN{=}C(H)Ph$), and benzophenone hydrazone ($Ph_2C{=}NNH_2$). A preliminary account of part of this work has appeared.[7]

Scheme 1



Results

***In Situ* Generation of the Vinylidene Complexes $Cp(CO)_2M{=}C{=}C(H)R$.** The cationic rhenium carbyne complex $[Cp(CO)_2Re{\equiv}CCH_3]BCl_4$ (**6**) was observed to deprotonate rapidly upon dissolution in either CH_2Cl_2 or THF at −78 °C to give the vinylidene complex $Cp(CO)_2Re{=}C{=}CH_2$ (**7**) in near-quantitative yield by IR (eq 1).



(1)

Gas evolution occurred when THF or CH_2Cl_2 was added to a cooled (−78 °C) flask containing solid **6**, and this gas turned moistened litmus paper red, suggesting the release

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• Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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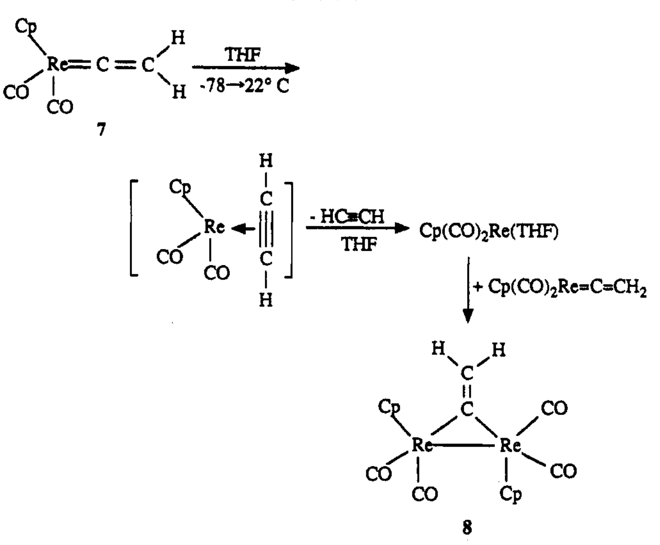
Scheme 2

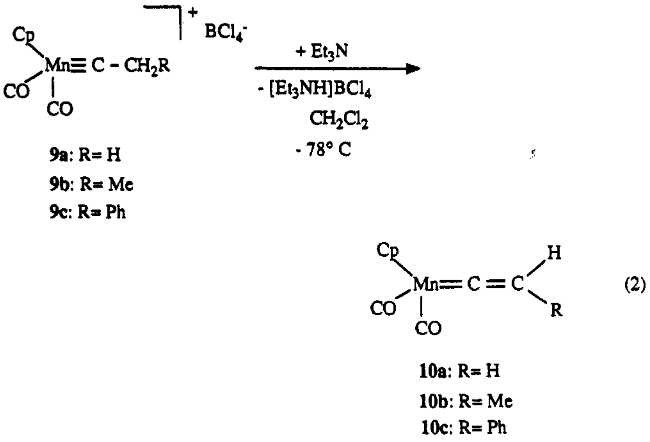


of HCl upon dissolution. Addition of Et_3N to CH_2Cl_2 or THF solutions of **6** also resulted in the instantaneous generation of **7**, although the general procedure employed in this work was simply to dissolve **6** in CH_2Cl_2 or THF and stir the solution for ~5 min at -78 °C to give **7**.

The vinylidene complex **7** could not be isolated, since when it was warmed to room temperature it decayed to give $CpRe(CO)_3$ and the binuclear μ-vinylidene complex **8** shown in Scheme 2, which also illustrates a likely mechanism for its formation. The complex $CpRe(CO)_2(\eta^2\text{-}HC{\equiv}CH)$ could form by rearrangement of the vinylidene ligand in **7** to an acetylene ligand, analogous to other known tautomerizations of vinylidene ligands,[4] and loss of acetylene would give $CpRe(CO)_2(THF)$. Addition of a second equivalent of $Cp(CO)_2Re{=}C{=}CH_2$ to $CpRe(CO)_2(THF)$ would then give the observed **8**. Complex **8** has not been previously reported, but the related complex $[Cp(CO)_2Re]_2(\mu\text{-}C{=}C(H)Ph)$ is known[5n] as is a manganese analogue which was proposed be formed by a mechanism similar to that of Scheme 2.[8a,b] The IR spectrum of **8** shows three ν_{CO} bands at 1982, 1960, and 1881 cm^{-1}, which compare reasonably well to those reported for $[Cp(CO)_2Re]_2(\mu\text{-}C{=}C(H)Ph)$ (ν_{CO} 1983, 1953, 1916 cm^{-1}).[5n]

The vinylidene complex **7** was characterized by IR and by its low-temperature ^1H NMR spectrum as well as by the detailed reactivity studies described below. Its IR spectrum shows two ν_{CO} bands at 1990 (s) and 1915 (s) cm^{-1} and a $\nu_{C=C}$ vibration at 1632 (w) cm^{-1}, which compare to the corresponding bands reported for the isolable complex $Cp(CO)_2Re{=}C{=}C(H)Ph$ at 2003 (s), 1938 (s), and 1594 (w) cm^{-1}.[5n] The -20 °C ^1H NMR spectrum of **7** showed singlets at δ 5.48 and 2.32 assigned to the Cp ligand and the terminal vinylidene CH_2 protons, respectively.

Mn–ethylidyne complex **9a** was previously prepared by Fischer *et al.*, and its reactions with several nucleophiles were investigated.[3a,b] However, complexes **9b** and **9c** have not been previously described, but they, and **9a**, were prepared in this study via addition of BCl_3 to the appropriate carbene precursor $Cp(CO)_2Mn{=}C(OEt)R$ at -78 °C.[3a,b] Each of these carbyne complexes is thermally unstable and must be handled at low temperature. They were deprotonated to form the neutral vinylidene complexes **10a–c** (eq 2) by suspending them in CH_2Cl_2 at -78 °C and adding Et_3N. This caused the solid to dissolve and gave homogeneous orange solutions of **10a** and **10b** and a purple solution of **10c**. IR analysis showed complete consumption of the cationic carbyne complexes and formation of neutral species. The benzylcarbyne complex **9c** undergoes slow deprotonation in CH_2Cl_2 even in the absence of added base to form **10c**, apparently due to the electron-withdrawing phenyl substituent, which increases the acidity of the adjacent benzyl protons.



The vinylidene complexes **10a** and **10b** have not been previously described, although **10c** was earlier prepared by an alternative route and is a stable compound.[5a,b] In contrast, **10a** and **10b** are unstable above ca. -50 °C and cannot be isolated. Like the rhenium vinylidene complex **7**, complex **10a** decomposed upon warming to form the known μ-vinylidene complex $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2)$,[8] although the yields were low (15–21%). Complex **10a** was earlier proposed as an intermediate in the preparation of $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2)$ from the reaction of $CpMn(CO)_3$ with acetylene[8a,b] and from treatment of $Cp(CO)_2Mn{=}C(OSO_2CF_3)Me$ with 1,8-bis(dimethylamino)naphthalene to eliminate $HOSO_2CF_3$.[8c] The vinylidene complexes **10a** and **10b** were characterized in solution by their IR data, and **10c** was identified by comparison of its spectroscopic data with those previously reported.[5a,b] IR analysis of the solution of **10a** generated as described above showed two ν_{CO} bands at 1996 (s) and 1932 (s) cm^{-1} and a $\nu_{C=C}$ band at 1624 (m) cm^{-1}, which compare favorably to the corresponding bands of the previously described complex $Cp(CO)_2Mn{=}C{=}CH\{C(Bu^t)_2H\}$ (ν_{CO} 1994 (s), 1937 (s) cm^{-1}; $\nu_{C=C}$ 1658 (s) cm^{-1}),[5l] as do the corresponding data for **10b** (ν_{CO} 1992 (s) and 1928 (s) cm^{-1}; $\nu_{C=C}$ 1662 (w) cm^{-1}).

Coordination of THF and Propylene Oxide to the Manganese Carbyne Complexes 9a and 9b. In addition to the deprotonation reactions described above, it was also observed that carbyne complexes **9a** and **9b** showed ν_{CO} band in THF solutions in the ranges more typical of neutral species (*e.g.*, **9a** (THF): ν_{CO} 1991 (s), 1926 (s) cm^{-1}), rather than in the cationic ranges observed in CH_2Cl_2 (*e.g.*, **9a** (CH_2Cl_2): ν_{CO} 2093 (s), 2053 (s) cm^{-1}). However, no $\nu_{C=C}$ bands were observed, suggesting that deprotonation to give the vinylidene complexes **10a** and **10b** did not occur under these conditions. However, the addition of Et_3N to these solutions caused the $\nu_{C=C}$ bands to appear as **10a** and **10b** formed. It was also found that the addition of just a small amount of THF (1.5–2.2 equiv) to CH_2Cl_2

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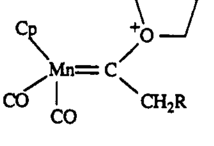
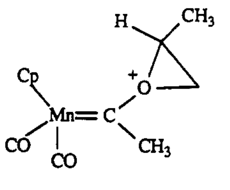
[8] (a) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483. (b) Lewis, L. N.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 403. (c) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628.

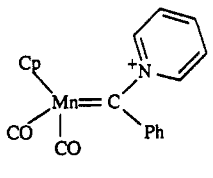
suspensions of the carbyne complexes **9a** and **9b** caused the ν_{CO} bands to shift to lower energy, but again the $\nu_{C=C}$ bands did not appear until Et_3N was added. Similar results were obtained when propylene oxide (1.1 equiv) was added to a −78 °C CH_2Cl_2 suspension of **9a**. This gave two ν_{CO} bands at 1992 (s) and 1925 (s) cm^{-1} but no evidence of the $\nu_{C=C}$ band characteristic of vinylidene complex **10a**. To account for these spectroscopic observations, we suggest that THF and propylene oxide coordinate via their oxygen atoms to the highly electrophilic carbyne carbon atoms in complexes **9a** and **9b** to give the adducts **11a**, **11b**, and **12**.



11a: R= H
11b: R= Me



12

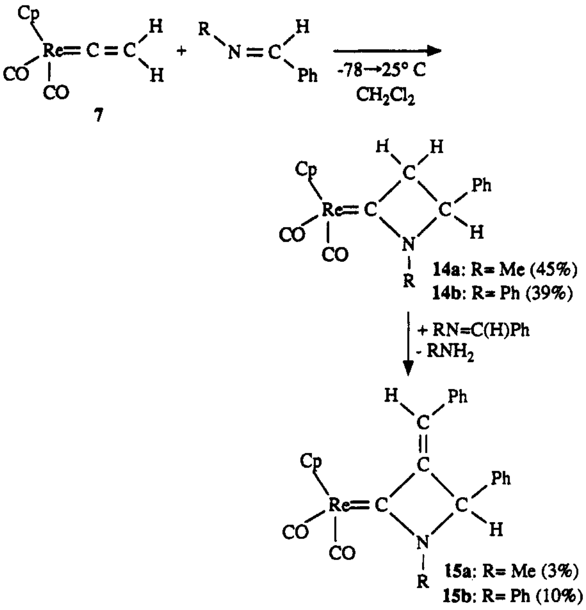


13

Similar adducts between the phenylcarbyne complex $[Cp(CO)_2Mn{\equiv}CPh]^+$ and pyridine (**13**)[9a] or PMe_3[9b] have been previously described. The IR spectra of **11a**, **11b**, and **12** compare reasonably well with that reported for the PMe_3 adduct $[Cp(CO)_2Mn{=}C(PMe_3)Ph]^+$ (ν_{CO} (CH_2Cl_2) 2010, 1944 cm^{-1}).[9b]

The observed IR changes could also be explained by deprotonation of the carbyne complexes **9a** and **9b** to form the vinylidene complexes **10a** and **10b** followed by their rapid tautomerization to give π-alkyne complexes. These would show ν_{CO} bands in the neutral region, but of course the vinylidene $\nu_{C=C}$ vibrations would be absent. However, the ν_{CO} bands observed when THF was added to CH_2Cl_2 suspensions of **9a** and **9b** (see above) are slightly different from the bands reported for the π-alkyne complexes $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CH)$ (ν_{CO} 1981 (s), 1919 (s) cm^{-1}) and $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CMe)$ (ν_{CO} 1975 (s), 1910 (s) cm^{-1}).[10] The complex $(\eta^5\text{-}C_5H_4Me)(CO)_2Mn(\eta^2\text{-}HC{\equiv}CH)$ has also been reported[10] to show a weak $\nu_{C\equiv C}$ band at 1730 cm^{-1} in pentane solution which was not observed in our samples of **9a** in CH_2Cl_2/THF. We thus do not believe that π-alkyne complexes are formed in the transformations of **9a** and **9b** described above but suggest instead formation of the adducts **11a**, **11b**, and **12**.

Reaction of $Cp(CO)_2Re{=}C{=}CH_2$ with the Imines $RN{=}C(H)Ph$ (R = Me, Ph). The vinylidene complex $Cp(CO)_2Re{=}C{=}CH_2$ (**7**), generated *in situ* as described above, reacts with the imines $PhN{=}C(H)Ph$ and $MeN{=}C(H)Ph$ to give mainly the cyclic carbene complexes **14a** and **14b**, which form via net [2 + 2] cycloaddition of the imine across the C=C bond of the vinylidene ligand (eq 3). Also formed in lower yields are the cyclic carbene complexes **15a** and **15b**, which are derived from **14a** and **14b** and excess imine via an aldol-like condensation reaction. Similar [2 + 2] cycloadditions of imines have been previously reported for the vinylidene complexes $(CO)_5W{=}C{=}CPh_2$[11] and $[Cp(CO)(L)Fe{=}C{=}CR_2]^+$ (L = PPh_3, $P(OMe)_3$; R = H, Me),[12a–c] and complexes analogous to **14** and **15** have also been prepared by the reaction of chromium carbene complexes with imines.[12d] As suggested in these earlier studies,[11,12] these reactions likely proceed in a stepwise fashion via initial addition of the imine nitrogen atom to the vinylidene α-carbon followed by ring closure to form the carbon–carbon bond. There was no evidence in this reaction for the formation of complexes analogous to **2** (Scheme 1) that would have resulted from a [2 + 2] cycloaddition of the C=N bond across the Re=C bond of **7**. Complexes **14** and **15** were not chromatographically separable, and these products were isolated as a mixture of the two compounds. These complexes have been spectroscopically characterized (see Experimental Section), and the yields given in eq 3 were determined by integration of the ^1H NMR spectra of the product mixtures. Complex **15b** selectively crystallized from the **14b**/**15b** mixture and has been fully defined by an X-ray diffraction study (see Figures 1–3 and below).



(3)

The ^1H NMR spectrum of the *N*-methyl complex **14a** exhibits an interesting five-bond homoallylic proton–proton coupling[13] between the methylene protons of the ring and the methyl substituent on the nitrogen atom. These groups are in a homoallylic-like arrangement as a result of the electron delocalization characteristic of aminocarbene complexes (A). Each of the diastereotopic methylene protons in the ^1H NMR spectrum of **14a** appears as a doublet of doublets of quartets, one at δ 2.39 ($^5J_{H_aH_d}$ = 1.2 Hz, $^3J_{H_aH_c}$ = 4.7 Hz, $^2J_{H_aH_b}$ = 14.7 Hz) and the other

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(9) (a) Meineke, E. W. Dissertation, Technische Universität München, 1975 (cited on page 115 of ref 3e). (b) Kreissl, F. R.; Stückler, P.; Meineke, E. W. *Chem. Ber.* **1977**, *110*, 3040.

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(13) (a) Pinhey, J. T.; Sternhell, S. *Tetrahedron Lett.* **1963**, *4*, 275. (b) Abraham, R. J.; Loftus, P. In *Proton and Carbon-13 NMR Spectroscopy*; Heyden and Son: Philadelphia, PA, 1980; pp 48–51. (c) van Tamelen, E. E.; Levin, S. H.; Brenner, G.; Wolinsky, J.; Aldrich, P. E. *J. Am. Chem. Soc.* **1959**, *81*, 1666. (d) Richards, J. H.; Beach, W. F. *J. Org. Chem.* **1961**, *26*, 623.

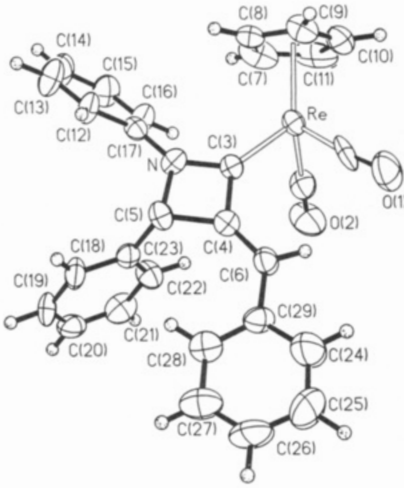


Figure 1. ORTEP drawing of the ordered molecule of **15b**.

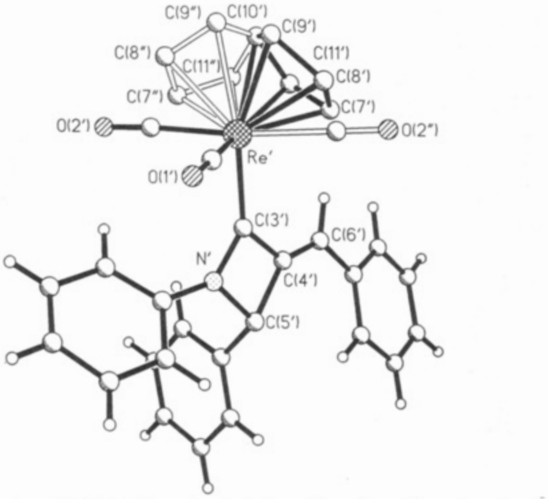
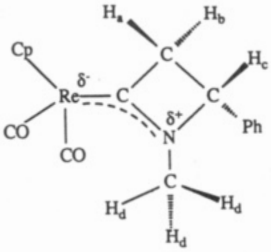


Figure 2. ORTEP drawing of the disordered molecule of **15b**.



A

at δ 1.99 ($^5J_{H_bH_d}$ = 1.2 Hz, $^3J_{H_bH_c}$ = 1.8 Hz, $^2J_{H_bH_a}$ = 14.7 Hz). These assignments have been verified by a homonuclear spin decoupling experiment in which irradiation of the signal due to the *N*-Me protons (δ 2.71) caused each of the resonances assigned to H_a and H_b to collapse into a simple doublet of doublets (see Figure 4). The magnitude of homoallylic coupling has been shown to be directly proportional to the dihedral angle (θ) between the planes defined by the bond vectors of the coupling nuclei and is strongest at θ = 90°.[13a,b] The crystal structures of **15b** and the related manganese compounds **17a** and **17c′** described below show these compounds to have a planar four-membered ring. The carbon atom of the nitrogen substituent is also in this plane, and free rotation about the C–N bond yields conformers such as **A**, which has the optimum 90° arrangement between the methylene and methyl protons.

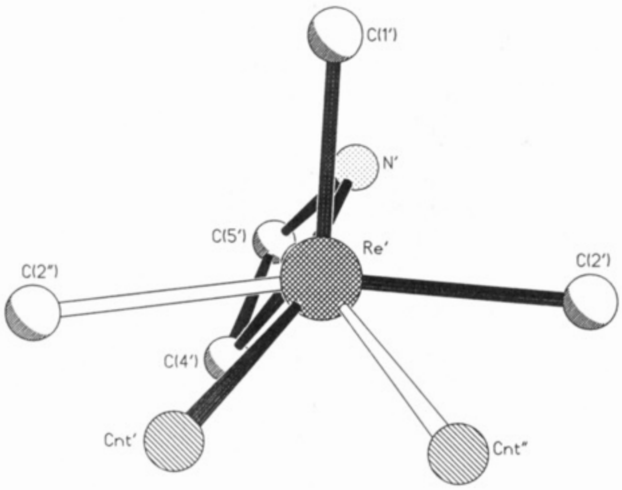


Figure 3. ORTEP drawing of the core of **15b** showing the Cp/CO disorder.

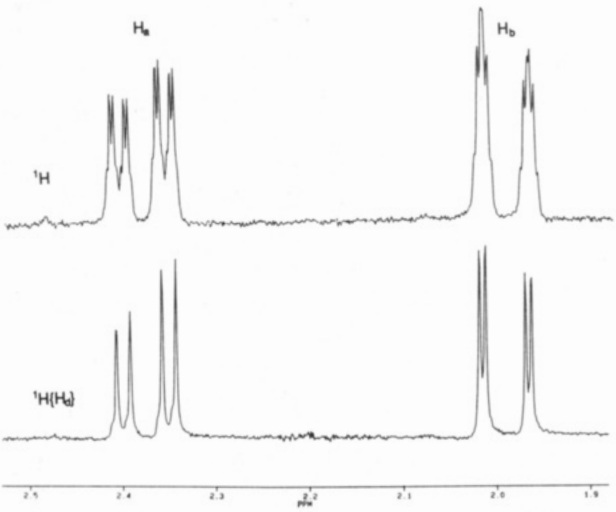


Figure 4. Homonuclear spin decoupling experiment for **14a**.

Crystal and Molecular Structure of 15b. Complex **15b** crystallizes in the $P\bar{1}$ space group with two crystallographically independent molecules per asymmetric unit. One of these is completely ordered and is shown in Figure 1 (unprimed molecule), and the other has an unusual Cp/CO disorder as illustrated in Figure 2. Figure 3 shows the core of the molecule and displays the Cp/CO disorder and the relative orientation of the cyclic carbene ligand. Relevant crystallographic data are set out in Tables 1 and 2. The disordered molecule has been refined using 64/36 occupancy factors for the primed and doubly primed atoms, respectively. The two forms of the disordered molecule are significantly different in the orientation of the cyclic carbene ligand. In the primed molecule, the plane of the carbene ligand and its substituents bisects the two carbonyl ligands ([C(3′)–Re′–C(Cnt′)]/[N′–C(3′)–C(4′)] dihedral angle 14.0°), but in the doubly primed molecule the plane of the carbene ligand is nearly perpendicular to the plane that bisects the carbonyls ([C(3′)–Re′–C(Cnt″)]/[N′–C(3′)–C(4′)] dihedral angle 67.7°). The unprimed molecule has the former orientation ([C(3)–Re–Cnt]/[N–C(3)–C(4)] dihedral angle 24.1°). Crystallographic studies of other carbene complexes within the $Cp(CO)_2M{=}CRR'$ (M = Mn, Re) family have shown both orientations to be possible, but the orientation found in the unprimed and primed molecules is generally preferred.[14] Otherwise, the three molecules possess the

Table 1. Crystal Data for 15b, 17a, 17c′, 41, 45, 46, and 47

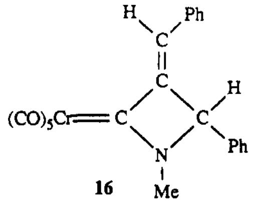
	15b	17a	17c′	41	45	46	47
formula	$C_{29}H_{22}NO_2Re$	$C_{22}H_{18}MnNO_2$	$C_{29}H_{22}MnNO_2$	$C_{16}H_{21}MnN_2O_2$	$C_{16}H_{23}MnN_2O_2$	$C_{19}H_{26}BCl_2MnN_2O_2$	$C_{22}H_{26}Mn_2N_2O_4$
fw	602.71	383.33	473.46	328.3	346.3	451.1	612.5
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$Pbca$	$Pca2_1$	$P\bar{1}$
a, Å	10.536(6)	10.403(1)	14.143(1)	8.539(2)	16.859(5)	16.362(3)	10.652(2)
b, Å	12.756(8)	19.283(2)	14.768(2)	10.928(1)	11.494(3)	10.068(2)	10.870(3)
c, Å	19.578(8)	9.284(2)	12.025(1)	9.562(1)	17.454(4)	28.004(3)	13.199(6)
α, deg	79.73(4)	96.53(1)	103.79(1)				75.966(33)
β, deg	83.32(4)	101.83(1)	91.64(1)	111.59(1)			67.850(32)
γ, deg	70.03(4)	84.29(1)	104.41(1)				82.542(32)
V, Å^3	2429(2)	1805.5(5)	2352.1(5)	829.6(2)	3382.4(15)	4613(1)	1372.0(9)
Z	4	4	4	2	8	8	2
D(calc), g cm^{-3}	1.648	1.41	1.34	1.314	1.360	1.299	1.482
μ(Mo Kα), cm^{-1}	50.30	7.16	5.63	7.68	7.57	8.2	4.75
radiation	Mo Kα (λ = 0.710 73 Å)						
$R(F)$, %[a]	4.7	5.1	6.2	4.0	4.34	6.5	3.91
$R_w(F)$, %[a]	5.3	5.1	6.2	4.3	4.79	7.91	4.40

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

Table 2. Selected Bond Distances and Angles for 15b

unprimed molecule		primed/doubly primed molecules	
	(a) Bond Distances (Å)		
Re–C(1)	1.786(18)	Re′–C(1′)	1.823(15)
Re–C(2)	1.912(14)	Re′–C(2′)	2.016(33)
Re–C(3)	2.013(11)	Re′–C(3′)	2.053(14)
N–C(3)	1.371(18)	N′–C(3′)	1.345(18)
N–C(5)	1.489(14)	N′–C(5′)	1.504(15)
N–C(17)	1.399(18)	N′–C(17′)	1.389(15)
C(3)–C(4)	1.509(15)	C(3′)–C(4′)	1.492(17)
C(4)–C(5)	1.534(21)	C(4′)–C(5′)	1.509(18)
C(4)–C(6)	1.309(21)	C(4′)–C(6′)	1.357(18)
C(5)–C(23)	1.507(15)	C(5′)–C(23′)	1.529(22)
C(6)–C(29)	1.478(17)	C(6′)–C(29′)	1.446(17)
		Re′–C(2″)	2.127(44)
	(b) Bond Angles (deg)		
C(1)–Re–C(2)	87.6(6)	C(1′)–Re′–C(2′)	92.6(9)
C(1)–Re–C(3)	91.5(5)	C(1′)–Re′–C(3′)	88.1(6)
C(2)–Re–C(3)	86.7(5)	C(2′)–Re′–C(3′)	90.0(9)
C(3)–N–C(5)	97.3(10)	C(3′)–N′–C(5′)	95.2(9)
C(5)–N–C(17)	125.9(10)	C(5′)–N′–C(17′)	128.9(10)
C(3)–N–C(17)	135.3(9)	C(3′)–N–C(17′)	135.9(10)
Re–C(3)–C(4)	135.8(10)	Re′–C(3′)–C(4′)	133.9(10)
Re–C(3)–N	135.2(8)	Re′–C(3′)–N′	135.3(9)
N–C(3)–C(4)	89.0(9)	N′–C(3′)–C(4′)	90.8(10)
C(3)–C(4)–C(5)	89.8(10)	C(3′)–C(4′)–C(5′)	89.2(9)
C(3)–C(4)–C(6)	131.8(12)	C(3′)–C(4′)–C(6′)	131.7(12)
C(5)–C(4)–C(6)	138.4(10)	C(5′)–C(4′)–C(6′)	139.0(11)
N–C(5)–C(23)	112.3(9)	N′–C(5′)–C(23′)	113.2(11)
C(4)–C(5)–C(23)	117.5(11)	C(4′)–C(5′)–C(23′)	119.4(10)
N–C(5)–C(4)	83.9(9)	N′–C(5′)–C(4′)	84.4(8)
C(4)–C(6)–C(29)	129.3(13)	C(4′)–C(6′)–C(29′)	128.4(13)
		C(2′)–Re′–C(2″)	168.7(11)
		C(2″)–Re′–C(3′)	91.4(12)
		C(1′)–Re′–C(2″)	98.6(11)

usual pseudooctahedral geometry about Re, as reflected in the 88.6° (unprimed molecule), 90.2° (primed molecule), and 95.0° (doubly primed molecule) average angle between the carbonyls and the carbene ligand. In each case the rhenium atom, the atoms of the four-membered ring, and the carbon atom and the phenyl *ipso* carbon of the exocyclic C(H)Ph group are essentially coplanar (primed molecule, maximum deviation of 0.098 Å associated with C(5′); unprimed molecule, maximum deviation of 0.012 Å associated with C(3)). The Re–C(3) and Re′–C(3′) bond lengths of 2.013(11) and 2.053(14) Å are slightly longer than typical Re=C double bonds (*e.g.*, for [Cp(NO)(PPh_3)Re=C(H)Ph]$^+$, R=C = 1.949(6) Å)[15] but are shorter than typical Re—C bonds single bonds (*e.g.*, for Cp(NO)(PPh_3)Re—CH_2Ph, Re—C = 2.203(8) Å),[16] consistent with a delocalized structure like that drawn in **A** (for **14a**). Similarly, the C(3)–N and C(3′)–N′ bond lengths of 1.371(18) and 1.345(18) Å are longer than typical C=N double-bond values (1.28 Å)[17] but are significantly shorter than the C(5)–N and C(5′)–N′ single-bond lengths of 1.489(14) and 1.504(15) Å, respectively. The C(4)–C(6) (1.309(21) Å) and C(4′)–C(6′) (1.357(18) Å) bond lengths associated with the exocyclic double bond are considerably longer than the C=C distance of isolated double bonds (1.299 Å),[17] but these compare well to the 1.330-Å value typical of conjugated systems.[17] In addition, the bond distances within the cyclic carbene ligand are similar to those found in the structurally similar complex **16**.[12d]



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Reactions of the Carbyne Complexes [Cp(CO)$_2$Mn$\equiv$CCH$_2$R]$^+$ and Vinylidene Complexes Cp(CO)$_2$Mn=C=C(H)R with PhN=C(H)Ph. As noted above, the manganese carbyne complexes **9a–c** do not deprotonate as readily as does the rhenium complex [Cp(CO)$_2$Re$\equiv$CCH$_3$]$^+$ (**6**). These carbyne complexes, and the vinylidene complexes that are derived from them (eq 2), both react with imines, but with some important differences. When treated with PhN=C(H)Ph and then Et$_3$N, the carbyne complexes **9a–c** yield the cyclic carbene complexes **17a–c** (eq 4). The products **17a–c** can also be formed by using excess imine (2.2 equiv) in the reaction instead of subsequently adding Et$_3$N, with the second equivalent of imine used to deprotonate the initially formed adduct complex (see below). Complexes **17a** and **17c** were isolated as orange-brown and yellow powders, respectively, and **17b** was obtained as a red oil. There was no evidence for the formation of 2:1 complexes analogous to **15** (see eq 3)

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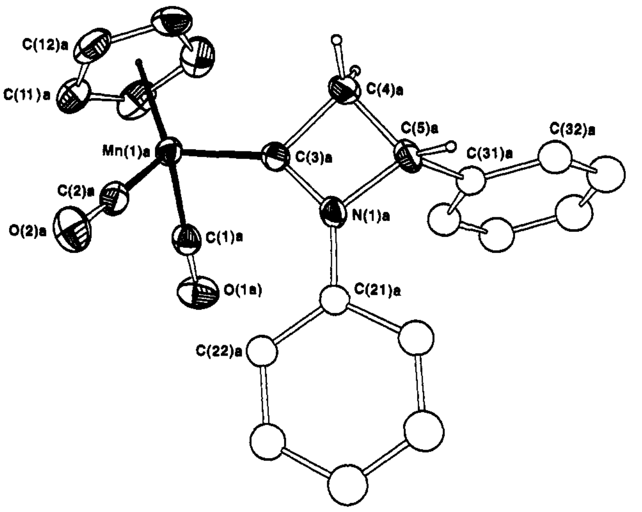
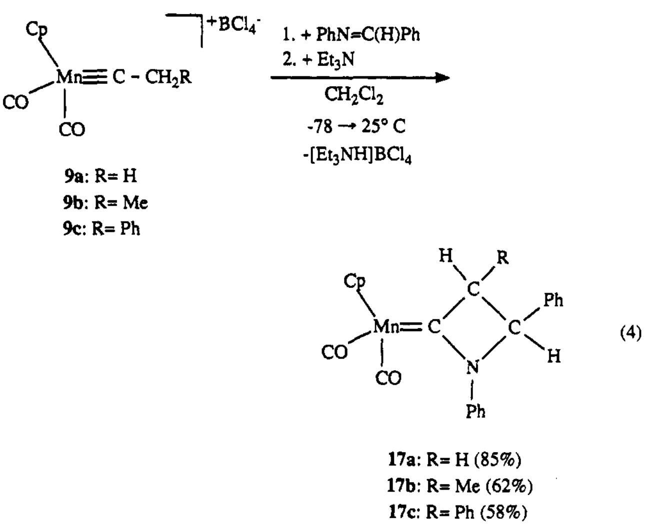


Figure 5. ORTEP drawing of **17a**.



in any of these reactions or for the formation of *ansa*-carbene complexes analogous to 4 that result from addition of Ph(H)C=NMe to the *aryl*carbyne complex [Cp(CO)$_2$Mn≡CTol]$^+$ (see Scheme 1). In addition to spectroscopic characterization (see Experimental Section), complexes **17a** and the Cp′ (Cp′ = η-C$_5$H$_4$Me) analogue of **17c** (**17c′**) were characterized by X-ray crystallographic studies (see Figures 5 and 6 and below). The NMR data indicate that complex **17b** forms as a mixture of diastereomers in a ratio varying from 9:1 to 4:1, depending upon the experimental conditions. The benzyl proton of the major isomer appears as a doublet at δ 4.79 (J_{HH} = 1.8 Hz) due to coupling with the C*H*Me proton, suggesting that the Me and Ph groups are trans to each other in this isomer (*RS*/*SR*) pair). The benzyl proton in the minor isomer appears as a doublet at δ 5.56 (J_{HH} = 5.0 Hz), establishing the cis arrangement of the Me and Ph groups in this diastereomer (*RR*/*SS* pair). The ^{1}H NMR spectrum of **17c** indicates the formation of a single diastereomer, and the appearance of the two benzyl protons as mutually coupled doublets at δ 5.52 (J_{HH} = 1.6 Hz) and δ 4.15 suggests that the two phenyl groups are in a *trans* arrangement (*RS*/*SR*), as observed in the crystal structure of the Cp′ (η^5-C$_5$H$_4$Me) analogue of **17c** (see Figure 6).

The mechanism proposed to account for the formation of **17a–c** is shown in Scheme 3. The first step is likely nucleophilic addition of the imine nitrogen to the electrophilic α-carbon of **9** to give **18**, analogous to the many

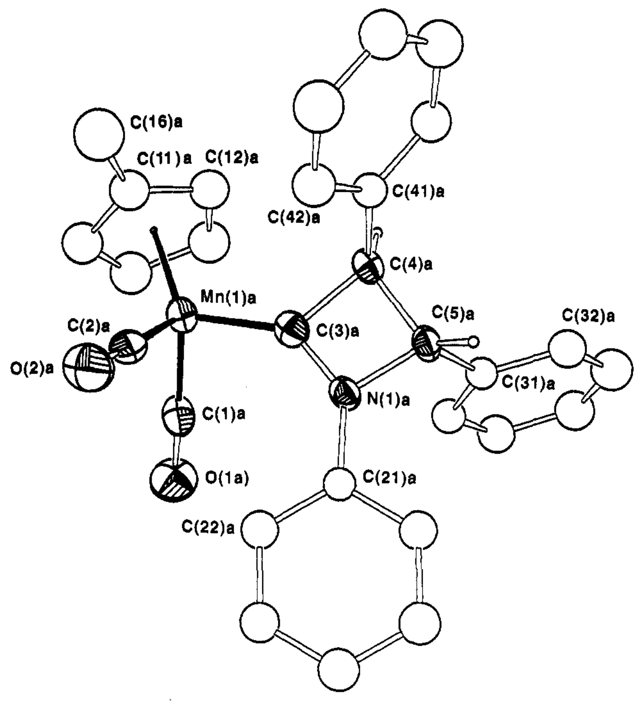
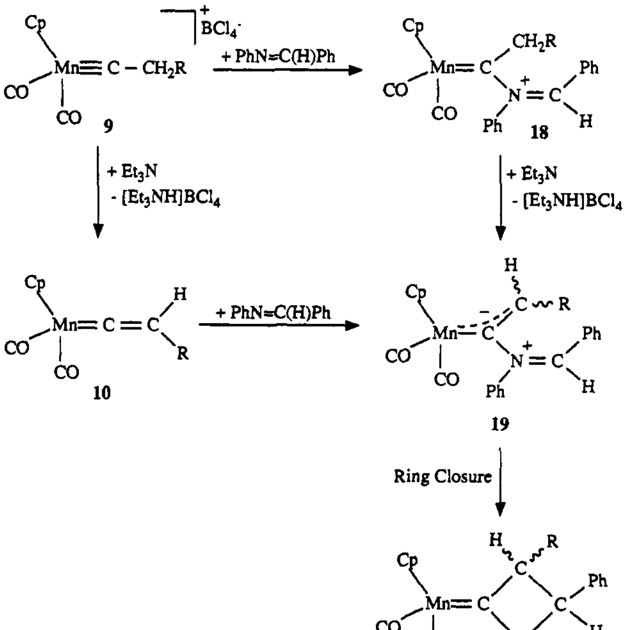


Figure 6. ORTEP drawing of **17c′**.

Scheme 3



other nucleophiles which have been shown to add to these electrophilic carbyne complexes.[1-3,9,18] Addition of base (Et$_3$N or excess imine) to this species should deprotonate the CH$_2$R group to give **19**, which upon ring closure would give the observed cyclic carbene complex. Experimentally, it was observed that the addition of 1.1 equiv of PhN=C(H)Ph to a −78 °C CH$_2$Cl$_2$ suspension of **9a** caused an instantaneous color change from pale yellow to orange and dissolution of much of the solid. This color persisted until Et$_3$N (1.5 equiv) was added, which then caused a further color change to deep red. At this point, the IR spectrum of the reaction mixture showed ν_{CO} bands at 1934 (s) and 1866 (s) cm^{-1} due to **17a**. Similar observations

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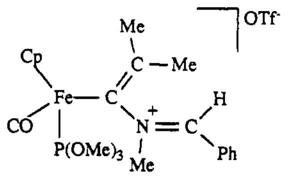
(18) Fischer, H.; Troll, C. *J. Organomet. Chem.* **1992**, *427*, 77.

were made in the reaction of PhN=C(H)Ph with **9b** and **9c**. We suggest that the initially formed orange solution contains the intermediate **18**, which persists at low temperature until base is added to induce its deprotonation to form **19** and from that the final product **17**.

Two complexes analogous to the proposed intermediate **19** have been isolated in other work. The first of these is **20**, reported by Barrett *et al.* to form upon addition of MeN=C(H)Ph to $[Cp(CO)\{P(OMe)_3\}Fe{=}C{=}CMe_2]^+$,[12a] and the second is **21**, which Fischer *et al.* have noted to result from the reaction of $(CO)_5W{=}C(H)Ph$ with $PhN{=}C{=}C(Ph)_2$ as well as from the combination of PhN=C(H)Ph with $(CO)_5W{=}C{=}CPh_2$.[11] Each of these complexes has been shown to undergo ring closure to give cyclic carbene complexes analogous to **17**.



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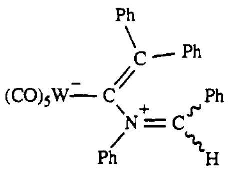
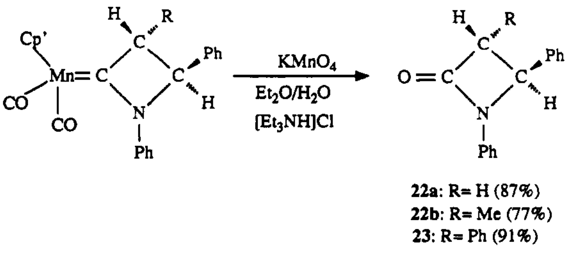


21

The vinylidene complexes **10a–c** also react with PhN=C(H)Ph to give the cyclic carbene products **17a–c**. These reactions were conducted by first generating **10a–c** via Et_3N addition to **9a–c** at −78 °C, followed by addition of PhN=C(H)Ph. Thus, the only difference in proceeding to **17** via **9** or **10** is the relative timing of the addition of imine and base, with imine addition occurring first from **9** and second from **10**. With the vinylidene complexes as starting materials, carbene complexes **17a–c** were isolated in 75%, 59%, and 48% yields, respectively, which compare to the 85%, 62%, and 58% yields from **9a–c**. For the formation of **17b**, we did not observe any significant changes in the diastereoselectivity of the reaction starting either from **9b** or **10b**. As illustrated in Scheme 3, the vinylidene reactions likely proceed via addition of the imine nitrogen atom to the electrophilic α-carbon of the vinylidene ligand to give **19**, which then undergoes ring closure to give **17**. As noted above, a similar mechanistic path has been proposed for the reactions of $[Cp(CO)\{P(OMe)_3\}Fe{=}C{=}CMe_2]^+$ [12a] and $(CO)_5W{=}C{=}CPh_2$[11] with imines.

It has also been observed that the Cp′ analogues of cyclic carbene complexes **17a–c** undergo smooth oxidation using a biphasic $Et_2O/H_2O/[Bu_3NH]Cl/KMnO_4$ system to give the β-lactams **22a,b** and **23** in excellent yields (eq 5). The yield given for **22b** is that for the purified *RS*/*SR* diastereomer.



(5)

22a: R= H (87%)
22b: R= Me (77%)
23: R= Ph (91%)

Table 3. Selected Bond Distances and Angles for 17a

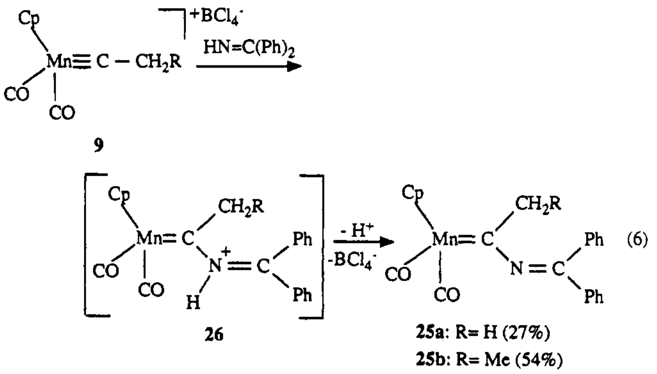
(a) Bond Distances (Å)			
Mn(a)–C(2a)	1.775(5)	Mn(b)–C(2b)	1.768(6)
Mn(a)–C(1a)	1.776(5)	Mn(b)–C(1b)	1.766(5)
Mn(a)–C(3a)	1.889(4)	Mn(b)–C(3b)	1.894(4)
C(3a)–N(1a)	1.369(6)	C(3b)–N(1b)	1.363(6)
C(3a)–C(4a)	1.534(6)	C(3b)–C(4b)	1.538(6)
C(4a)–C(5a)	1.531(7)	C(4b)–C(5b)	1.540(7)
C(5a)–N(1a)	1.476(5)	C(5b)–N(1b)	1.475(5)
C(5a)–C(31a)	1.507(6)	C(5b)–C(31b)	1.512(6)
N(1a)–C(21a)	1.410(6)	N(1b)–C(21b)	1.407(6)
(b) Bond Angles (deg)			
C(1a)–Mn(a)–C(2a)	93.6(2)	C(1b)–Mn(b)–C(2b)	93.6(2)
C(1a)–Mn(a)–C(3a)	90.3(2)	C(1b)–Mn(b)–C(3b)	90.8(2)
C(2a)–Mn(a)–C(3a)	96.1(2)	C(2b)–Mn(b)–C(3b)	96.2(2)
Mn(a)–C(3a)–C(4a)	129.2(3)	Mn(b)–C(3b)–C(4b)	129.7(3)
Mn(a)–C(3a)–N(1a)	141.4(3)	Mn(b)–C(3b)–N(1b)	140.6(3)
C(4a)–C(3a)–N(1a)	89.3(3)	C(4b)–C(3b)–N(1b)	89.7(3)
C(3a)–C(4a)–C(5a)	88.0(3)	C(3b)–C(4b)–C(5b)	87.5(3)
C(4a)–C(5a)–C(31a)	115.6(4)	C(4b)–C(5b)–C(31b)	116.1(3)
N(1a)–C(5a)–C(31a)	115.2(3)	N(1b)–C(5b)–C(31b)	115.4(4)
C(3a)–N(1a)–C(5a)	96.8(3)	C(3b)–N(1b)–C(5b)	97.2(3)
C(3a)–N(1a)–C(21a)	137.5(3)	C(3b)–N(1b)–C(21b)	137.4(3)
C(5a)–N(1a)–C(21a)	125.6(4)	C(5b)–N(1b)–C(21b)	125.4(3)

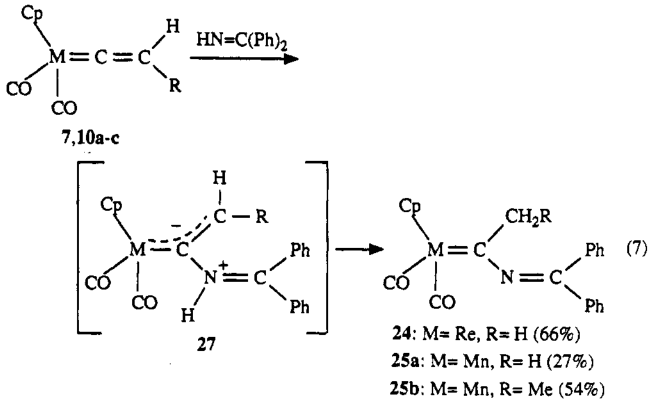
Table 4. Selected Bond Distances and Angles for 17c′

(a) Bond Distances (Å)			
Mn(a)–C(1a)	1.76(1)	Mn(b)–C(1b)	1.77(1)
Mn(a)–C(2a)	1.76(1)	Mn(b)–C(2b)	1.75(1)
Mn(a)–C(3a)	1.88(1)	Mn(b)–C(3b)	1.88(1)
C(3a)–N(1a)	1.37(1)	C(3b)–N(1b)	1.37(1)
C(3a)–C(4a)	1.55(1)	C(3b)–C(4b)	1.54(1)
C(4a)–C(41a)	1.51(1)	C(4b)–C(41b)	1.52(1)
C(4a)–C(5a)	1.54(1)	C(4b)–C(5b)	1.53(1)
C(5a)–N(1a)	1.47(1)	C(5b)–N(1b)	1.47(1)
C(5a)–C(31a)	1.51(1)	C(5b)–C(31b)	1.50(1)
N(1a)–C(21a)	1.41(1)	N(1b)–C(21b)	1.41(1)
(b) Bond Angles (deg)			
C(1a)–Mn(a)–C(2a)	92.6(4)	C(1b)–Mn(b)–C(2b)	93.3(4)
C(1a)–Mn(a)–C(3a)	93.9(4)	C(1b)–Mn(b)–C(3b)	95.1(4)
C(2a)–Mn(a)–C(3a)	92.9(4)	C(2b)–Mn(b)–C(3b)	91.3(4)
Mn(a)–C(3a)–C(4a)	130.2(5)	Mn(b)–C(3b)–C(4b)	130.5(6)
Mn(a)–C(3a)–N(1a)	140.4(6)	Mn(b)–C(3b)–N(1b)	139.9(6)
C(4a)–C(3a)–N(1a)	89.1(6)	C(4b)–C(3b)–N(1b)	89.3(6)
C(5a)–C(4a)–C(41a)	113.8(5)	C(5b)–C(4b)–C(41b)	114.3(6)
C(3a)–C(4a)–C(41a)	117.6(7)	C(3b)–C(4b)–C(41b)	116.0(5)
C(3a)–C(4a)–C(5a)	87.3(6)	C(3b)–C(4b)–C(5b)	87.5(6)
C(4a)–C(5a)–N(1a)	85.8(5)	C(4b)–C(5b)–N(1b)	86.1(5)
C(4a)–C(5a)–C(31a)	114.7(6)	C(4b)–C(5b)–C(31b)	116.7(6)
N(1a)–C(5a)–C(31a)	115.0(6)	N(1b)–C(5b)–C(31b)	114.4(5)
C(3a)–N(1a)–C(21a)	138.4(7)	C(3b)–N(1b)–C(21b)	138.5(6)
C(3a)–N(1a)–C(5a)	97.1(6)	C(3b)–N(1b)–C(5b)	96.6(6)
C(5a)–N(1a)–C(21a)	124.6(6)	C(5b)–N(1b)–C(21b)	124.9(6)

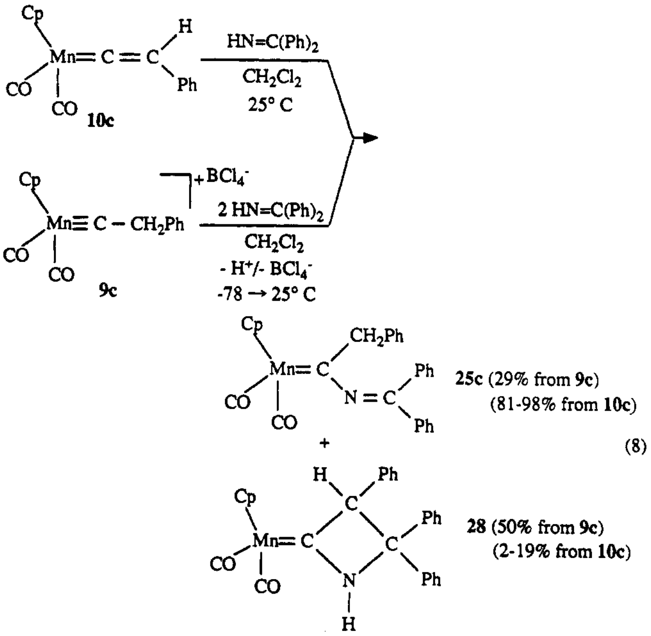
Crystal and Molecular Structures of 17a and 17c′ (Cp′ Analogue of 17c). In each of these complexes, the unit cell contains two chemically similar but crystallographically independent molecules which are designated with the labels a and b. ORTEP drawings of **17a** and **17c′** are shown in Figures 5 and 6, respectively, and relevant crystallographic data are set out in Tables 1, 3, and 4. Each of these complexes displays the usual pseudooctahedral geometry about manganese, and in both complexes, the Mn=C distances (**17a**, molecule a, 1.889(4) Å; **17a**, molecule b, 1.894(4) Å; **17c′**, molecules a and b, 1.88(1) Å) are values typical of $Cp(CO)_2Mn$–carbene complexes (*e.g.*, $Cp(CO)_2Mn{=}C(OEt)(Ph)$, Mn=C = 1.865(14) Å).[14e] In each complex, the atoms of the four-membered ring and the carbon atom attached to nitrogen are essentially coplanar (**17a**, molecule a, maximum deviation 0.036 Å associated with C(4a); **17a**, molecule b, maximum deviation 0.013 Å associated with C(4b); **17c′**, molecule a, maximum deviation 0.072 Å associated with C(4a); **17c′**, molecule b, maximum deviation 0.061 Å associated with C(4b)), and the plane defined by the atoms of the four-membered ring bisects the carbonyl ligands. As noted above, complex **17c** forms as a single pair of diastereomers, and the ^1H NMR spectrum of **17c′** indicates a similar result. Both the *RS* and *SR* enantiomers are present in the centrosymmetric unit cell of **17c′**, with the *SR* enantiomer illustrated in Figure 6.

Reaction of Cp(CO)$_2$M=C=C(H)R and [Cp(CO)$_2$Mn≡CCH$_2$R]$^+$ with HN=C(Ph)$_2$. In contrast to the results described above, reaction of the N—H imine HN=C(Ph)$_2$ with carbyne complexes **9a** and **9b** and vinylidene complexes **7**, **10a**, and **10b** did not give cyclic carbene complexes but instead gave the imino–carbene complexes **24**, **25a**, and **25b** (eqs 6 and 7). These complexes are apparently derived from the carbyne complexes via addition of the nucleophilic nitrogen atom to the electrophilic carbyne carbon followed by loss of the N—H proton (eq 6). With the vinylidene complexes, these products form by net addition of the N—H bond across the vinylidene C=C bond (eq 7) in analogy to the many examples of the addition of amines and alcohols across this bond in many other vinylidene complexes.[4] Complexes **24** and **25a** were isolated as orange and purple-brown microcrystalline solids, and **25b** was obtained as a brown oil. The spectroscopic data given in the Experimental Section are consistent with the proposed structures and are also similar to data reported for the related imino–carbene complex Cp(CO)$_2$Mn=C(Ph)N=C(Me)(NMe$_2$) earlier prepared by Fischer *et al.*[18] Imino–carbene complexes have been prepared by various routes, most of which involve carbene complexes as precursors,[19] but we can find no evidence for the prior formation of imino–carbene complexes from the reaction of imines with vinylidene and carbyne complexes.

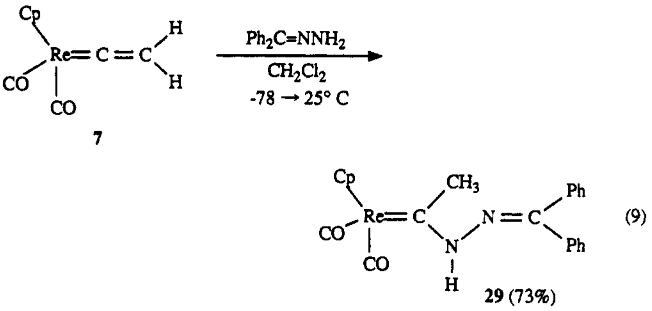




In contrast to the above reactions which gave only imino–carbene complexes, reaction of HN=C(Ph)$_2$ with the benzylcarbyne complex **9c** and the phenylvinylidene complex **10c** gave both imino–carbene (**25c**) and cyclic carbene (**28**) products (eq 8). Complexes **25c** and **28** were isolated as purple and yellow solids, respectively, and are spectroscopically similar to the complexes **25a,b** and **17a–c** described above (see Experimental Section). The formation of **28** from **10c** likely proceeds via an intermediate similar to **27** (eq 7) in which ring closure is competitive with hydrogen migration due to stabilization of the anionic center in this intermediate by the phenyl substituent.



Reaction of [Cp(CO)$_2$Mn≡CCH$_2$R]$^+$ and Cp(CO)$_2$Mn=C=C(H)R with Benzophenone Hydrazone, Ph$_2$C=NNH$_2$. In earlier work,[2] it was shown that the rhenium vinylidene complex **7** reacts with benzophenone hydrazone to give the hydrazonyl–carbene complex **29** via addition of an N–H bond across the vinylidene C=C bond (eq 9). In contrast, the manganese vinylidene complexes **10a** and **10c** and the carbyne complexes **9a** and **9b** react with this substrate to give the nitrile complexes **30a–c**[20] (eq 10). These complexes were isolated as yellow-orange solids and have been spectroscopically characterized. The acetonitrile complex **30a** is a known compound,[20b,c] and the spectroscopic data for **30b** and **30c** (see Experimental Section) are consistent with their formulations. These complexes result from a Beckmann-type rearrangement (Scheme 4)[21] via the intermediate **31**, which is analogous



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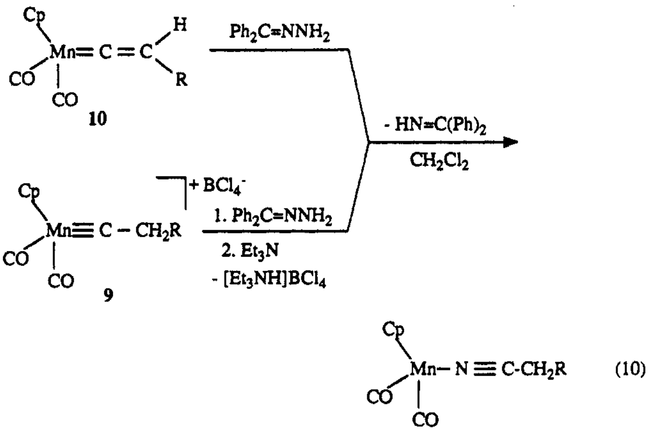
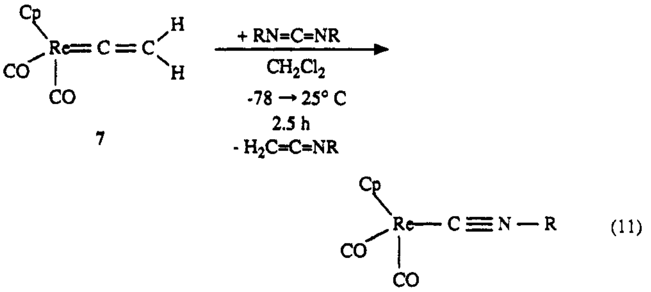


(10)

30a: R= H (62% from **9a**)
(32% from **10a**)
30b: R= Me (62% from **9b**)
30c: R= Ph (66% from **10c**)

to the crystallographically characterized rhenium complex **29** (eq 9).[2] A similar transformation of a vinylidene ligand into a nitrile ligand has been described by Barrett *et al.*[22]

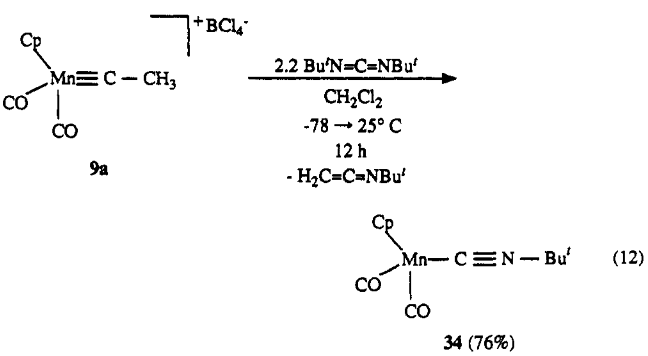
Formation of Isocyanide Complexes from the Reaction of $\mathrm{Cp(CO)_2M{=}C{=}CH_2}$ and $\mathrm{[Cp(CO)_2Mn{\equiv}CCH_2R]^+}$ with Carbodiimides. It was initially anticipated that carbodiimides (RN=C=NR) would undergo net [2 + 2] cycloaddition across the C=C bond of the vinylidene complex $\mathrm{Cp(CO)_2Re{=}C{=}CH_2}$ to form cyclic carbene complexes analogous to **14a** and **14b** described above, similar to the previously reported reaction of $\mathrm{(CO)_5Cr{=}C(OH)(Me)}$ with CyN=C=NCy (Cy = cyclohexyl) which gives a cyclic carbene product and which may proceed via $\mathrm{(CO)_5Cr{=}C{=}CH_2}$.[23] However, the reaction of **7** with RN=C=NR (R = Pr^i, Bu^t) led instead to the isocyanide complexes **33a** and **33b**, shown in eq 11.



(11)

33a: R= Pr^i (72%)
33b: R= Bu^t (67%)

These complexes were isolated as pale brown microcrystalline solids and are similar to other known complexes within the $\mathrm{Cp(CO)_2M(CNR)}$ family.[24] A similar isocyanide complex (**34**)[24a] resulted from the reaction of manganese ethylidyne complex **9a** with Bu^tN=C=NBu^t (eq 12), although the manganese vinylidene complex $\mathrm{Cp(CO)_2Mn{=}C{=}CH_2}$ (**10a**) failed to react with this substrate.

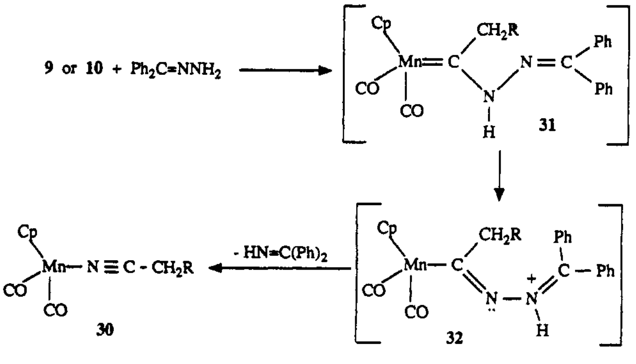


(12)

34 (76%)

The reactions outlined in eqs 11 and 12 represent a net metathesis of the N=C bond of the carbodiimide with either the C=C or M=C bond of the vinylidene ligand, via the two distinct mechanisms shown in Scheme 5 (illustrated for **9a**). The first step in the reaction is addition of the carbodiimide to **9a** to produce **35**, followed by deprotonation of the methyl substituent to give **36**. The rhenium analogue of this species (**36′**) would form in reaction 11 by direct addition of the carbodiimide to the α-carbon of the vinylidene ligand. Complex **36** could undergo a 1,3-shift of the metal to the carbon atom of the original carbodiimide to give **37**, which upon loss of the ketenimine fragment would yield the observed isocyanide product. This reaction represents metathesis of the carbodiimide N=C bond with the vinylidene Mn=C bond. Alternatively, **36** could undergo ring closure to give the cyclic carbene complex **38**, analogous to the complexes **14** and **15** discussed above. Complex **38** could decay via a retro-cycloaddition to give the isocyanide complex and free ketenimine, resulting in net metathesis of the carbodiimide N=C bond with the vinylidene C=C bond. As indicated in Scheme 5, if the α-carbon of the vinylidene ligand is labeled with ^{13}C, these paths are distinguishable since, in the former path, the label is transferred to the ketenimine product, whereas in the latter it is retained in the isocyanide ligand. Thus, when complex **9a**, labeled at both the CO ligands and C_α with ^{13}C (>15% enrichment by ^{13}C NMR), was allowed to react with 2.2 equiv of Bu^tN=C=NBu^t, isocyanide complex **34** was isolated in 85% yield. A ^{13}C NMR analysis of the product showed no ^{13}C incorporation at the isocyanide carbon, indicating that the reaction proceeds via the 1,3-shift path and not the cycloaddition path. Support for this mechanistic path also comes from a study by Fischer *et al.* of the reaction of $\mathrm{[Cp(CO)_2Mn{\equiv}CPh]^+}$ with dimethylcyanamide ($\mathrm{N{\equiv}CNMe_2}$; Scheme 6). This gave the *ansa*-carbene complex **39** via a similar 1,3-migration of the metal fragment in intermediate **40**.[18]

Scheme 4



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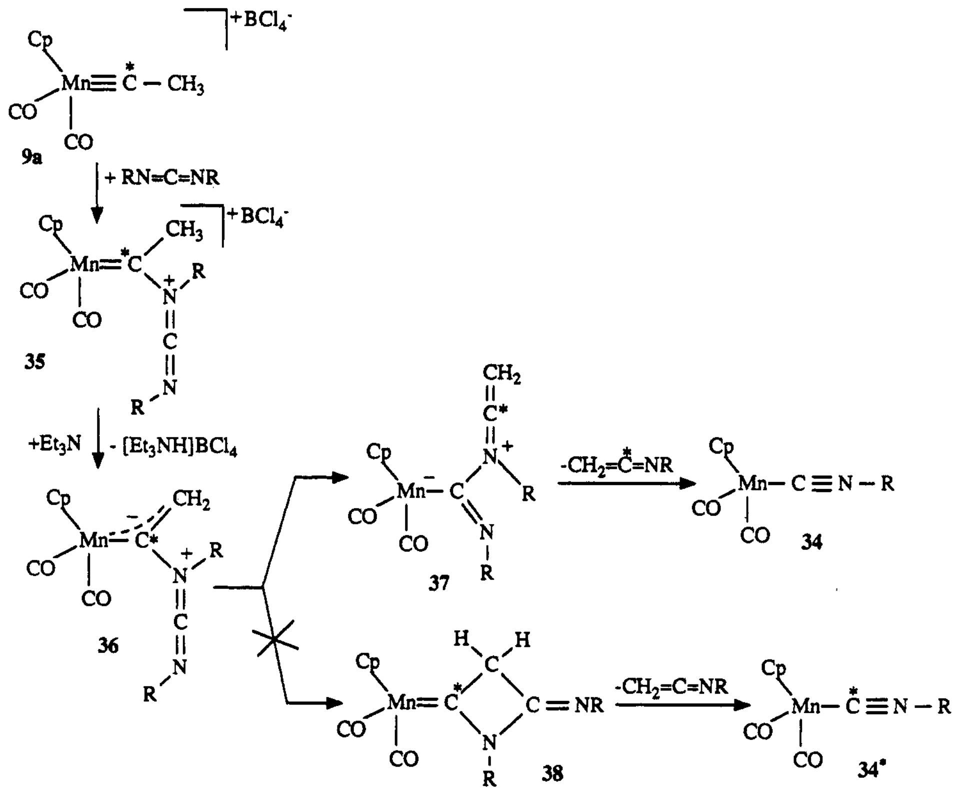
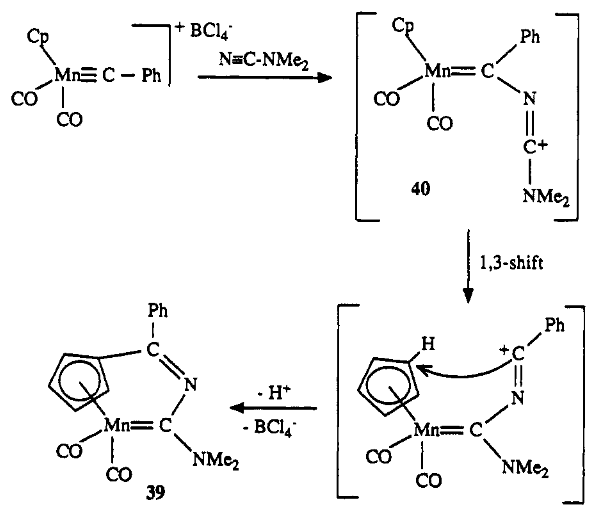
Scheme 5 (R = Bu^t)

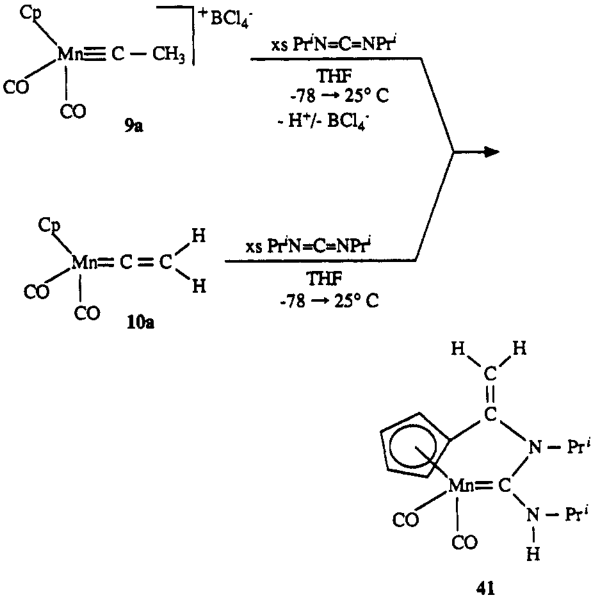


Scheme 6



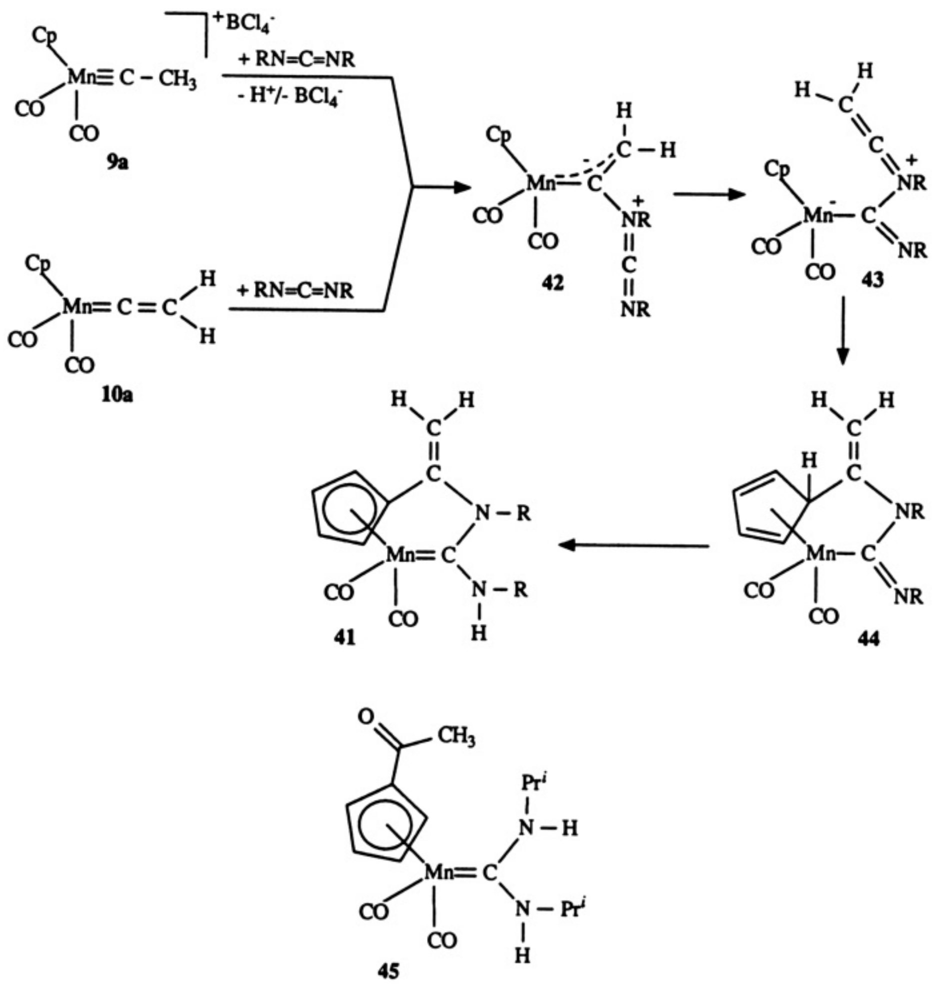
Infrared evidence was obtained for the presence of intermediate **35** (Scheme 5) via the addition of $\mathrm{Bu}^t\mathrm{N}{=}\mathrm{C}{=}\mathrm{NBu}^t$ (1.1 equiv) to a -78 °C CH_2Cl_2 suspension of **9a**, which gave a rapid change from a pale yellow suspension to an orange solution containing much undissolved solid material. The IR spectrum of this mixture showed the presence of a single species with ν_{CO} 1991 (s) and 1926 (s) cm^{-1}, which we suggest is **35**. This species persists at low temperature until Et_3N is added or the solution is warmed to room temperature in the presence of excess carbodiimide, which then gives the observed product **34**.

Formation of an *ansa*-Carbene Complex via Reaction of $[\mathrm{Cp(CO)_2Mn{\equiv}CCH_3}]^+$ and $\mathrm{Cp(CO)_2Mn{=}C{=}CH_2}$ with $\mathrm{Pr}^i\mathrm{N{=}C{=}NPr}^i$. It was noted above that an isocyanide complex (**34**; eq 12) resulted from the reaction of $[\mathrm{Cp(CO)_2Mn{\equiv}CCH_3}]^+$ with $\mathrm{Bu}^t\mathrm{N{=}C{=}NBu}^t$. Surprisingly, when the carbodiimide was changed to $\mathrm{Pr}^i\mathrm{N{=}C{=}NPr}^i$, none of this type of product formed, but instead an *ansa*-carbene complex (**41**) similar to those prepared earlier by us (Scheme 1)[1] and by Fischer *et al.* (Scheme 6)[18] was produced (eq 13). The same product also formed upon reaction of $\mathrm{Pr}^i\mathrm{N{=}C{=}NPr}^i$ with the vinylidene complex **10a**. Complex **41** was isolated in good yield as a yellow microcrystalline solid and has been characterized by spectroscopy (see Experimental Section) and by an X-ray diffraction study (see Figure 7 and below). The mechanism proposed to account for the formation of **41** is shown in Scheme 7. As discussed above, an intermediate such as **42** can be accessed via either the vinylidene or carbyne complex combined with the carbodiimide substrate. A 1,3-migration of the [Cp(CO)$_2$Mn] fragment



(13)

Scheme 7



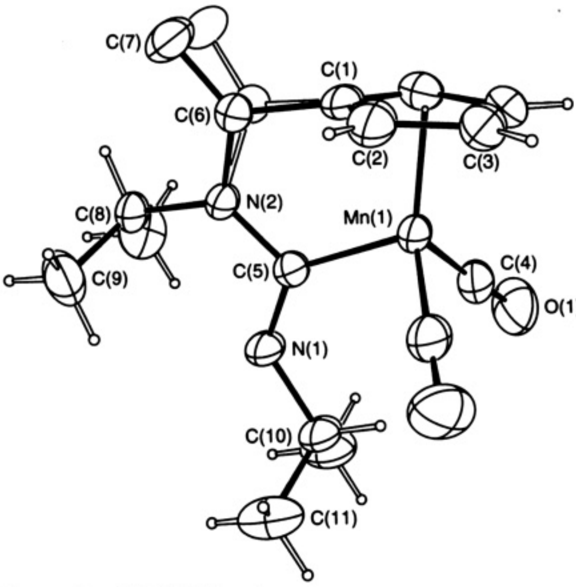


Figure 7. ORTEP drawing of **41**.

would give **43**, which could undergo electrophilic addition to the Cp ring to give **44**. Hydrogen migration, perhaps assisted by the excess carbodiimide present, to the imine nitrogen atom would then give the observed product **41**.

In one reaction, the bis(amino)carbene complex **45** with an acetyl substituent on the cyclopentadienyl ligand was obtained as a byproduct in the preparation of **41**. This species has been spectroscopically characterized (see Experimental Section) and has also been defined by an

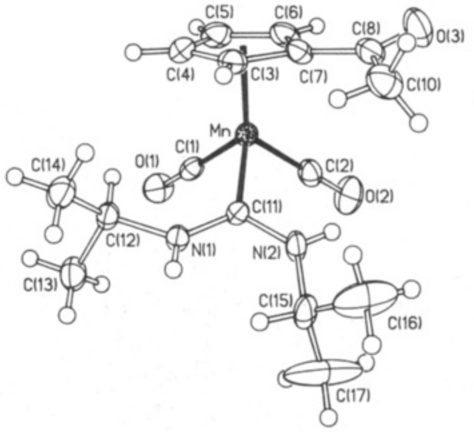


Figure 8. ORTEP drawing of **45**.

X-ray diffraction study (see Figure 8 and below). Its formation was not reproducible, but it would appear to be derived from hydrolysis of the *ansa*-carbene complex **41**.

Crystal and Molecular Structure of 41. An ORTEP drawing of complex **41** is shown in Figure 7, and the relevant crystallographic data are set out in Tables 1 and 5. This complex crystallizes in the $P2_1/m$ space group with a crystallographic plane of symmetry containing the Mn(1), C(5), N(2), and C(1) atoms and bisecting the carbonyl ligands. As illustrated in Figure 7, the structure is disordered with two different, equally populated orientations of the $CH_2{=}C$ unit on either side of the mirror plane. The Mn–C(5) distance of 1.965(4) Å is longer than the corresponding distance in $Cp(CO)_2Mn{=}C(OEt)Ph$

Table 5. Selected Bond Distances and Angles for 41

(a) Bond Distances (Å)			
Mn(1)–C(4)	1.755(5)	Mn(1)–C(5)	1.965(4)
N(1)–C(5)	1.331(6)	N(2)–C(5)	1.386(7)
N(1)–C(10)	1.465(8)	N(2)–C(8)	1.477(5)
N(2)–C(6)	1.433(8)	C(1)–C(6)	1.513(8)
C(6)–C(7)	1.328(12)	C(8)–C(9)	1.494(5)
C(10)–C(11)	1.487(6)		
(b) Bond Angles (deg)			
C(4)–Mn(1)–C(4a)	94.9(3)	C(4)–Mn(1)–C(5)	96.1(1)
C(5)–N(1)–C(10)	128.3(4)	C(5)–N(2)–C(6)	116.1(4)
C(5)–N(2)–C(8)	126.4(4)	C(6)–N(2)–C(8)	116.0(4)
C(2)–C(1)–C(6)	113.5(5)	Mn(1)–C(5)–N(1)	129.6(4)
Mn(1)–C(5)–N(2)	118.2(3)	N(1)–C(5)–N(2)	112.2(4)
N(2)–C(6)–C(1)	107.7(6)	N(2)–C(6)–C(7)	128.2(5)
C(1)–C(6)–C(7)	123.1(6)	N(2)–C(8)–C(9)	114.7(3)
N(1)–C(10)–C(11)	110.5(4)		

Table 6. Selected Bond Distances and Angles for 45

(a) Bond Distances (Å)			
Mn–C(1)	1.768(4)	Mn–C(2)	1.766(4)
Mn–C(11)	2.010(3)	N(1)–C(11)	1.331(5)
N(2)–C(11)	1.344(5)	C(7)–C(8)	1.463(6)
C(8)–C(10)	1.498(6)	O(3)–C(8)	1.208(5)
(b) Bond Angles (deg)			
C(1)–Mn–C(2)	88.1(2)	C(1)–Mn–C(11)	94.5(2)
C(2)–Mn–C(11)	93.4(2)	Mn–C(11)–N(1)	126.2(3)
Mn–C(11)–N(2)	119.7(3)	N(1)–C(11)–N(2)	114.0(3)
C(7)–C(8)–C(10)	118.9(4)	C(7)–C(8)–O(3)	120.6(4)
C(10)–C(8)–O(3)	120.5(4)		

(Mn═C = 1.865(14) Å)[14e] and in compounds **17a** (1.88 (1) Å) and **17c** (1.889 (4), 1.894 (4) Å) as a consequence of enhanced electron donation from the two attached amino substituents. The C(5)–N(1) distance of 1.331(6) Å is slightly shorter than the C(5)–N(2) distance of 1.386(7) Å, but both are similar to the C—N distances found in the cyclic aminocarbene complexes **15b**, **17a**, and **17c′** discussed above and are consistent with a delocalized structure. The N(2)–C(6) distance of 1.433(8) Å compares well to that expected for a C(sp^2)—N(pyramidal) single bond (1.416 Å),[17] and the C(6)–C(7) distance of 1.328(12) Å is typical for a $CH_2{=}C(X_2)$ double bond (1.321 Å).[17]

Crystal and Molecular Structure of 45. An ORTEP drawing of complex **45** is shown in Figure 8, and the relevant crystallographic data are set out in Tables 1 and 6. It has a geometry typical of $Cp(CO)_2Mn$(carbene) complexes, with the plane of the carbene ligand lying essentially perpendicular to the plane which bisects the carbonyl ligands. The Mn–C(11) distance of 2.010(3) Å is similar to the Mn–carbene distance of 1.966(3) Å found in compound **41** but is significantly longer than similar bonds in the reference compounds cited above. The C(11)–N(1) and C(11)–N(2) distances of 1.331(5) and 1.344(5) Å are similar to those found in **41** and imply a highly delocalized structure. The isopropyl groups attached to the two nitrogen atoms are arranged in an *anti* fashion and are nonequivalent. The presence of two isopropyl $CH(CH_3)_2$ resonances (δ 3.58, 4.38) in the ^1H NMR spectrum of **45** implies restricted rotation about the C—N bonds of the carbene ligand, although free rotation likely occurs about the Mn–C(11) bond. Bond parameters within the acetyl substituent of the cyclopentadienyl ligand appear normal.

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_2CH_3]^+$ with $Bu^tN{=}C{=}NBu^t$ and Et_3N. As described above, the reaction of the ethylidyne complex $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ (**9a**) with $Bu^tN{=}C{=}NBu^t$ gave an isocyanide complex, and an *ansa*-carbene complex resulted from the reaction of **9a** with $Pr^iN{=}C{=}NPr^i$. Yet a different type of product formed when the propylidyne complex **9b** was allowed to react with $Bu^tN{=}C{=}NBu^t$ and Et_3N (eq 14). This gave the unusual zwitterionic vinylidene complex **46**, which was isolated as a purple crystalline solid and has been fully characterized, including an X-ray crystallographic study (see Figure 9 and below). Complex **46** is remarkably stable and showed no evidence of decomposition even after several weeks of storage in air at room temperature. Its zwitterionic nature and the presence of the BCl_2 unit in a highly strained four-membered ring make its stability toward chromatography on neutral alumina even more surprising. Reaction of benzylcarbyne complex **9c** with excess $Bu^tN{=}C{=}NBu^t$ resulted only in deprotonation of the starting carbyne complex to produce vinylidene **10c**, which failed to react with this substrate.

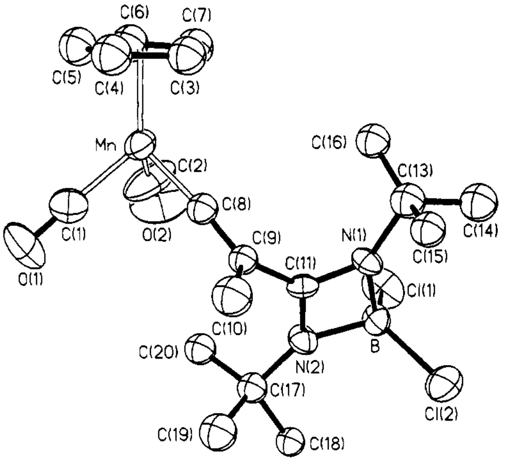
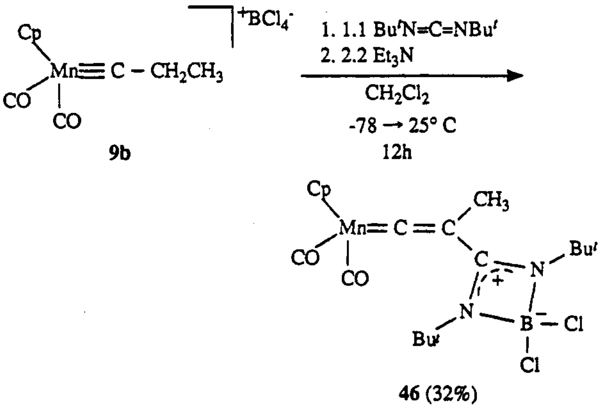


Figure 9. ORTEP drawing of **46**.



(14)

Crystal and Molecular Structure of 46. Complex **46** crystallizes in the $Pca2_1$ space group with two chemically similar but crystallographically independent molecules in the unit cell, which are designated with primed and unprimed labels. In each, the *tert*-butyl groups are significantly disordered over several rotationally related sites. An ORTEP drawing of the unprimed molecule is shown in Figure 9, and the relevant crystallographic data are set out in Tables 1 and 7. In both molecules, the vinylidene ligand is essentially linear (Mn(1)–C(8)–C(9) = 174.3(9)°; Mn(1′)–C(8′)–C(9′) = 176.1(9)°), and the Mn═C (1.756(11), 1.807(10) Å) and C═C (1.300 (14), 1.272(14) Å) distances are similar to those found in other manganese vinylidene complexes.[5b,c] The C(9)–C(10) (1.542(17) Å) and C(9′)–C(10′) (1.501(16) Å) distances are

Table 7. Selected Bond Distances and Angles for 46

unprimed molecule		primed molecule	
(a) Bond Distances (Å)			
Mn–C(1)	1.700(23)	Mn′–C(1′)	1.822(16)
Mn–C(2)	1.760(18)	Mn′–C(2′)	1.802(16)
Mn–C(8)	1.756(11)	Mn′–C(8′)	1.807(10)
Cl(1)–B	1.827(14)	Cl(1′)–B′	1.866(15)
Cl(2)–B	1.846(16)	Cl(2′)–B′	1.840(16)
N(1)–C(11)	1.334(11)	N(1′)–C(11′)	1.348(14)
N(1)–B	1.559(15)	N(1′)–B′	1.524(14)
N(1)–C(13)	1.450(16)	N(1′)–C(13′)	1.493(15)
N(2)–C(11)	1.325(13)	N(2′)–C(11′)	1.345(11)
N(2)–B	1.522(17)	N(2′)–B′	1.534(18)
N(2)–C(17)	1.460(14)	N(2′)–C(17′)	1.466(17)
C(8)–C(9)	1.300(14)	C(8′)–C(9′)	1.272(14)
C(9)–C(10)	1.542(17)	C(9′)–C(10′)	1.501(16)
C(9)–C(11)	1.486(14)	C(9′)–C(11′)	1.485(14)
(b) Bond Angles (deg)			
C(1)–Mn–C(2)	90.8(10)	C(1′)–Mn′–C(2′)	87.6(7)
C(1)–Mn–C(8)	89.7(9)	C(1′)–Mn′–C(8′)	86.0(6)
C(2)–Mn–C(8)	91.2(7)	C(2′)–Mn′–C(8′)	89.9(6)
C(11)–N(1)–B	86.9(8)	C(11′)–N(1′)–B	87.9(9)
C(11)–N(1)–C(13)	134.6(9)	C(11′)–N(1′)–C(13′)	131.6(8)
B–N(1)–C(13)	138.3(10)	B′–N(1′)–C(13′)	139.4(10)
C(11)–N(2)–B	88.8(8)	C(11′)–N(2′)–B′	87.5(8)
C(11)–N(2)–C(17)	133.6(9)	C(11′)–N(2′)–C(17′)	134.3(9)
B–N(2)–C(17)	137.5(9)	B′–N(2′)–C(17′)	138.2(8)
Mn–C(8)–C(9)	174.3(9)	Mn′–C(8′)–C(9′)	176.1(9)
C(8)–C(9)–C(10)	121.4(10)	C(8′)–C(9′)–C(10′)	122.8(10)
C(8)–C(9)–C(11)	120.3(9)	C(8′)–C(9′)–C(11′)	117.3(9)
C(10)–C(9)–C(11)	118.4(9)	C(10′)–C(9′)–C(11′)	119.9(9)
N(1)–C(11)–N(2)	100.9(8)	N(1′)–C(11′)–N(2′)	99.7(8)
N(1)–C(11)–C(9)	127.9(9)	N(1′)–C(11′)–C(9′)	131.3(9)
N(2)–C(11)–C(9)	131.2(9)	N(2′)–C(11′)–C(9′)	129.0(9)
Cl(1)–B–Cl(2)	111.1(7)	Cl(1′)–B′–Cl(2′)	109.3(6)
Cl(1)–B–N(1)	115.1(9)	Cl(1′)–B′–N(1′)	113.3(9)
Cl(2)–B–N(1)	114.1(9)	Cl(2′)–B′–N(1′)	115.7(10)
Cl(1)–B–N(2)	115.4(10)	Cl(1′)–B′–N(2′)	114.8(10)
Cl(2)–B–N(2)	115.3(9)	Cl(2′)–B′–N(2′)	117.5(10)
N(1)–B–N(2)	83.4(8)	N(1′)–B′–N(2′)	84.6(8)

typical C(sp^2)–C(sp^3) values (1.507 Å).[17] The plane defined by the vinylidene β-carbon and its substituents (C(10)–C(9)–C(11)) is nearly perpendicular to the plane which bisects the carbonyl ligands (dihedral angle [CNT–Mn–C(8)]/[C(10)–C(9)–C(11)] 81.1°; dihedral angle [CNT′–Mn′–C(8′)]/[C(10′)–C(9′)–C(11′)] 75.6°). A similar perpendicular arrangement exists between the plane of the vinylidene substituents and the four-membered BN$_2$C ring (dihedral angles: unprimed molecule, 85.6°; primed molecule, 84.0°). The latter rings and the attached carbon atoms of the *tert*-butyl substituents are also planar (unprimed molecule, maximum deviation of 0.024 Å associated with C(17); primed molecule, maximum deviation of 0.072 Å associated with N(1′)). The N—C distances within the four-membered ring (1.325(13)–1.348(14) Å; 1.338 Å average) are closer to typical C(sp^2)—N single bond (1.339 Å)[17] values than to typical C(sp^2)=N double-bond distances (1.313 Å).[17] The C(9)–C(11) and C(9′)–C(11′) distances of 1.486(14) and 1.485(14) Å are typical C(sp^2)—C(sp^2) single-bond values (1.460 Å),[17] and B—Cl (average 1.845 Å) and B–N (average 1.549 Å) are in the typical range for these bonds.[17] Although boron and carbon atoms are difficult to distinguish by X-ray crystallography, the presence of boron in the four-membered ring was verified by the ^{11}B NMR spectrum of **46**, which showed a single resonance at δ 4.51 (referenced to external BF$_3$·Et$_2$O), in the range typical of BX$_4$- ions.[25]

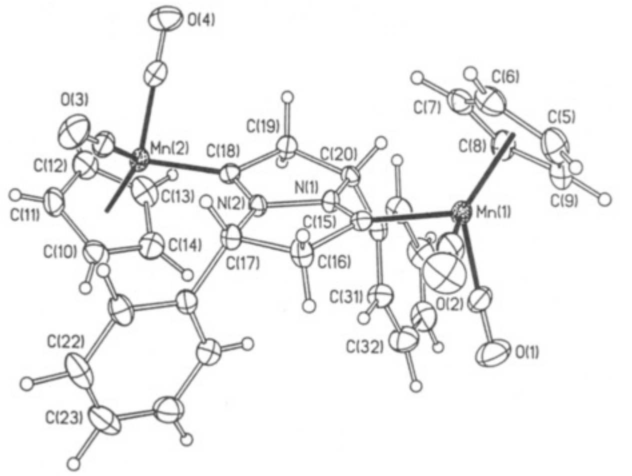
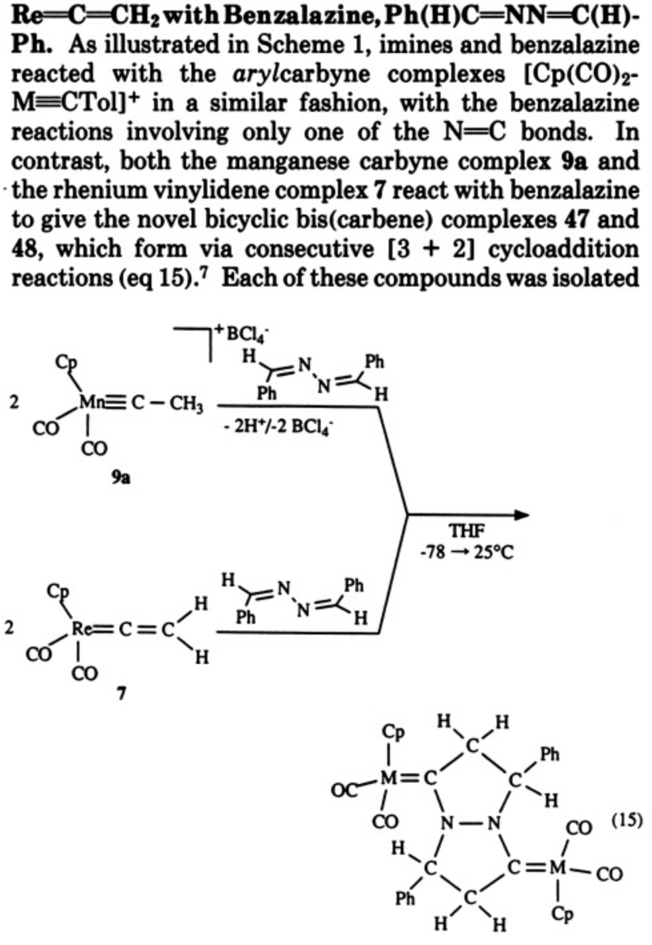


Figure 10. ORTEP drawing of **47**.

Reaction of [Cp(CO)$_2$Mn≡CCH$_3$]$^+$ and Cp(CO)$_2$Re=C=CH$_2$ with Benzalazine, Ph(H)C=NN=C(H)Ph. As illustrated in Scheme 1, imines and benzalazine reacted with the *aryl*carbyne complexes [Cp(CO)$_2$M≡CTol]$^+$ in a similar fashion, with the benzalazine reactions involving only one of the N=C bonds. In contrast, both the manganese carbyne complex **9a** and the rhenium vinylidene complex **7** react with benzalazine to give the novel bicyclic bis(carbene) complexes **47** and **48**, which form via consecutive [3 + 2] cycloaddition reactions (eq 15).[7] Each of these compounds was isolated



47: M= Mn (41%)
48: M= Re (53%)

as a yellow microcrystalline solid, and **47** has been characterized by an X-ray diffraction study (see Figure 10 and below). IR monitoring of the reaction of Re–vinylidene complex **7** with benzalazine indicated a clean reaction, with no other products detected. In the reaction of Mn–ethylidyne complex **9a** with benzalazine, *2* equiv of the substrate is required, with the second equivalent acting as a base. Alternatively, an external base (*e.g.* Et$_3$N, 1.1 equiv) may be added *after* the addition of benzalazine. The corresponding vinylidene complex **10a** (generated from **9a** by Et$_3$N addition prior to the addition of the

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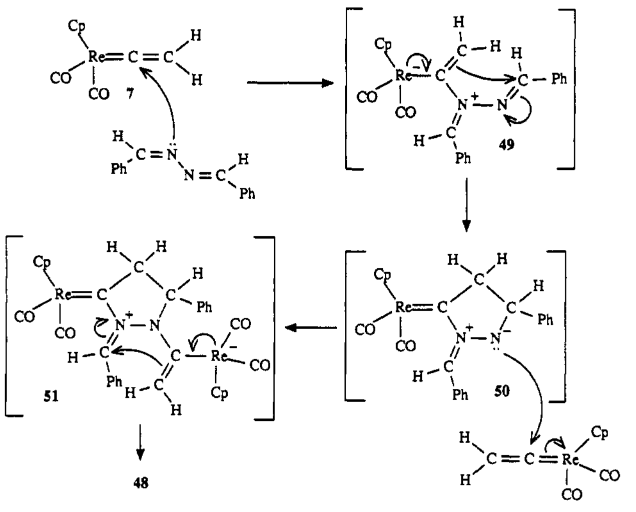
[25] Kidd, R. G. In *NMR of Newly-Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 49–77.

Scheme 8



substrate) failed to react with benzalazine. Reaction of propylidyne complex **9b** with 1 equiv of benzalazine, followed by 1.1 equiv of Et_3N and slow warming to room temperature, afforded an orange flocculent solid upon chromatographic workup. IR analysis of this fraction indicated the formation of a single product with ν_{CO} 1922 (s) and 1853 (s) cm^{-1} in CH_2Cl_2 solution, which compares favorably with the observed ν_{CO} bands of **47** (**47**: ν_{CO} 1926 (s), 1858 (s) cm^{-1}). The +FAB mass spectrum of the product showed a parent ion at *m/z* 640, consistent with the expected H/Me analogue of **47**. However, ^1H NMR analysis of the product showed it to be a complex mixture containing several byproducts, and this reaction was not further pursued. Vinylidene complexes **10b** and **10c** failed to react with benzalazine.

The mechanism proposed to account for the formation of **48**, and by analogy **47**, is shown in Scheme 8 and is similar to that which has been established for organic analogues of this reaction, which have often been termed "criss-cross" cycloadditions.[26] As in other reactions presented in this work, the first step is likely addition of one of the nucleophilic nitrogen atoms of benzalazine to the electrophilic α-carbon of the vinylidene ligand to give **49**. Intramolecular cyclization of this species would lead to the cyclic zwitterionic intermediate **50**, which should rapidly add to a second equivalent of **7** to give **51**. Subsequent cyclization would lead to the observed product **48**. The addition of benzalazine to the carbyne complex **9a** would proceed in a similar fashion, with the initial step involving addition of benzalazine to the electrophilic carbyne carbon followed by deprotonation of this species to form **47**.

Table 8. Selected Bond Distances and Angles for 47

(a) Bond Distances (Å)

Mn(1)–C(1)	1.783(3)	Mn(1)–C(2)	1.778(4)
Mn(1)–C(15)	1.945(3)	Mn(2)–C(3)	1.770(3)
Mn(2)–C(4)	1.769(4)	Mn(2)–C(18)	1.936(3)
C(15)–C(16)	1.518(5)	C(16)–C(17)	1.544(4)
C(16)–H(16a)	0.976(38)	C(16)–H(16b)	0.917(26)
C(17)–H(17)	0.933(24)	C(17)–C(26)	1.503(4)
C(18)–C(19)	1.524(5)	C(19)–C(20)	1.539(4)
C(19)–H(19a)	0.960(27)	C(19)–H(19b)	0.991(32)
C(20)–C(36)	1.518(3)	N(1)–N(2)	1.438(3)
N(1)–C(15)	1.312(4)	N(1)–C(20)	1.472(4)
N(2)–C(17)	1.473(4)	N(2)–C(18)	1.306(4)

(b) Bond Angles (deg)

C(1)–Mn(1)–C(2)	93.4(2)	C(1)–Mn(1)–C(15)	92.0(1)
C(2)–Mn(1)–C(15)	93.3(1)	C(3)–Mn(2)–C(4)	92.8(2)
C(3)–Mn(2)–C(18)	96.5(1)	C(4)–Mn(2)–C(18)	90.1(1)
N(2)–N(1)–C(15)	116.2(2)	N(2)–N(1)–C(20)	107.0(2)
C(15)–N(1)–C(20)	136.8(2)	N(1)–N(2)–C(17)	108.2(2)
N(1)–N(2)–C(18)	116.0(2)	C(17)–N(2)–C(18)	134.5(2)
Mn(1)–C(15)–N(1)	130.2(2)	Mn(1)–C(15)–C(16)	125.3(2)
N(1)–C(15)–C(16)	104.5(2)	C(15)–C(16)–C(17)	108.8(3)
N(2)–C(17)–C(16)	101.7(2)	C(16)–C(17)–C(26)	115.0(3)
N(2)–C(17)–C(26)	112.8(2)	Mn(2)–C(18)–N(2)	131.5(2)
Mn(2)–C(18)–C(19)	123.8(2)	N(2)–C(18)–C(19)	104.7(2)
C(18)–C(19)–C(20)	107.6(3)	N(1)–C(20)–C(36)	113.0(2)
N(1)–C(20)–C(19)	101.4(2)	C(19)–C(20)–C(36)	113.6(2)

Crystal and Molecular Structure of 47. An ORTEP drawing of **47** is shown in Figure 10, and the relevant crystallographic data are set out in Tables 1 and 8. The fused five-membered ring systems are nearly coplanar (dihedral angle 9.5°), and the Mn=C distances of 1.945(3) and 1.936(3) Å are similar to the Mn=C values found in the other Mn–carbene complexes described herein. The planes defined by the carbene atoms and their attached carbon and nitrogen atoms do not bisect the CO–Mn–CO angles, as is often found for $Cp(CO)_2Mn{=}C(R)(R')$ complexes,[14a] but instead appear to be oriented so as to minimize steric interactions ([CNT(2)–Mn(2)–C(18)]/[Mn(2)–C(18)–N(2)] dihedral angle 82.2°; [CNT(1)–Mn(1)–C(15)]/[Mn(1)–C(15)–N(1)] dihedral angle 42.3°). Each of the benzylic carbons of the bridging organic ligand is chiral, and thus the molecule could be present as a pair of enantiomers or in the *meso* form. The ^1H NMR spectrum of the product indicates the formation of a single spectroscopically detectable stereoisomer, and the ORTEP drawing shown in Figure 10 shows it to be the *RR*/*SS* pair with the two phenyl groups on the same side of the plane defined by the fused five-membered rings. The C(carbene)—N distances of 1.306(4) Å (C(18)–N(2)) and 1.312(4) Å (C(15)–N(1)) are similar to the corresponding C—N distances in the other aminocarbene complexes described herein. The N(1)–N(2) bond distance of 1.438(3) Å is intermediate between the N(pyramidal)—N(pyramidal) average distance of 1.454 Å and the N(pyramidal)—N(planar) average distance of 1.420 Å, but it is considerably longer than the N(planar)—N(planar) average distance of 1.401 Å.[17] When they are taken together, these structural features indicate a considerable degree of delocalization of the Mn=C bonds toward the nitrogen atoms of the fused-ring system.

Discussion

The original objective of this work was to compare the reactivity of *alkyl*carbyne complexes of Mn and Re with the previous studies of the corresponding *aryl*carbyne complexes conducted in these laboratories.[1,2] The important initial finding was that the alkylcarbyne complexes readily deprotonated to form the highly reactive vinylidene complexes $Cp(CO)_2Re{=}C{=}CH_2$ (**7**; eq 1) and $Cp(CO)_2Mn{=}C{=}C(H)R$ (**10a–c**; eq 2), and this deprotonation tendency rendered the chemistry of these complexes

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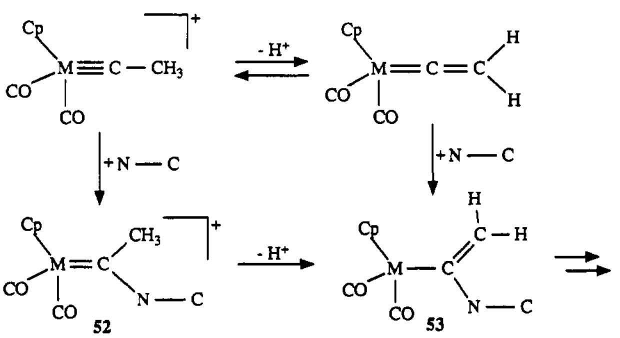
(26) (a) Bailey, J. R.; Moore, N. H. *J. Am. Chem. Soc.* **1917**, *39*, 279. (b) Bailey, J. R.; McPherson, A. T. *J. Am. Chem. Soc.* **1917**, *40*, 1322. (c) Padwa, A. *1,3-Dipolar Cycloaddition Chemistry*; Wiley: New York, 1984. (d) Wagner-Jauregg, T. *Synthesis* **1976**, 349. (e) Gieren, A.; Narayanan, P.; Burger, K.; Thenn, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 475. (f) Nuyken, O.; Maier, G.; Burger, K. *Makromol. Chem.* **1988**, *189*, 2245. (g) Nuyken, O.; Maier, G.; Burger, K. *Makromol. Chem.* **1989**, *190*, 623. (h) Burger, K.; Heink, F. *Liebigs Ann. Chem.* **1982**, 853. (i) Burger, K.; Schickaneder, H.; Hein, F.; Gieren, A.; Lamm, V.; Engelhardt, H. *Liebigs Ann. Chem.* **1982**, 845. (j) Burger, K.; Thenn, W.; Rauh, R.; Schickaneder, H.; Gieren, A. *Chem. Ber.* **1975**, *108*, 1460.

completely different from that observed for their arylcarbyne analogues. The generation of vinylidene complexes via deprotonation of alkylidyne complexes is a synthetic method with considerable precedent,[3c,d,4,27] but it has not been previously employed for the compounds described herein. This reaction has permitted the generation of the previously unreported parent vinylidene complexes **7** and **10a** and the methylvinylidene complex $Cp(CO)_2Mn{=}C{=}C(H)Me$. Although the phenylvinylidene complex $Cp(CO)_2Mn{=}C{=}C(H)Ph$ is a known compound, its reported yields by other routes are low (~10%),[5a,b] and its formation in 75–85% yields via deprotonation of $[Cp(CO)_2Mn{\equiv}CCH_2Ph]^+$ is clearly a superior synthetic method.

The cationic alkylidyne complexes $[Cp(CO)_2M{\equiv}CCH_2R]^+$ differ significantly in their relative acidity. As described above, the rhenium complex $[Cp(CO)_2Re{\equiv}CCH_3]^+$ undergoes spontaneous deprotonation upon dissolution in THF or CH_2Cl_2 at -78 °C, but the manganese complexes $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ (R = H, Me) require the addition of base to induce deprotonation at this temperature. This observation implies that the $Cp(CO)_2Re$ fragment is more electron withdrawing than is $Cp(CO)_2Mn$, a conclusion consistent with previous observations that the cyclopentadienyl ligand in $CpMn(CO)_3$ is far more reactive toward Friedel–Crafts acylation than is the Cp ligand of $CpRe(CO)_3$.[28] The Friedel–Crafts reaction is an electrophilic aromatic substitution reaction, and those results indicate a greater degree of electron density localized on the Cp ligand of $CpMn(CO)_3$ as a result of increased electronegativity of the $M(CO)_3$ fragment in moving from Mn to Re. The higher electron withdrawing property of $Cp(CO)_2Re$ as compared to $Cp(CO)_2Mn$ also accounts for the formation of azetidinylidene products (**15a**,**b**; eq 3) from the cyclic carbene complexes of rhenium, but not manganese. The azetidinylidene complexes presumably form an aldol-type condensation reaction with excess imine that proceeds via initial deprotonation of the β-carbon of the carbene ligand, and this site must be more acidic for Re than for Mn. The manganese benzylidyne complex $[Cp(CO)_2Mn{\equiv}CCH_2Ph]^+$ also spontaneously deprotonates in the absence of added base, a result of the phenyl substituent on the β-carbon which stabilizes the vinylidene ligand through conjugation.

The reactions of the organic substrates with the complexes described herein all likely proceed via initial addition of the nucleophilic substrate to the electrophilic α-carbon of the alkylidyne and vinylidene ligands to form intermediates **52** and **53**, respectively (Scheme 9). As illustrated, **52** can subsequently transform into **53** via deprotonation. The proposed initial steps in these reactions are consistent with the known electrophilic character of the α-carbon of vinylidene ligands[4,14b–e] and the previous studies that have demonstrated the high electrophilicity of the α-carbon of alkylidyne complexes within the $[Cp(CO)_2M{\equiv}CR]^+$ (M = Mn, Re) family.[1–3,7,9,18] As illustrated in Scheme 9, the details of the reaction course depend upon the timing of the deprotonation step—*i.e.*, whether deprotonation occurs prior or subsequent to addition of the organic substrate. The same product can result from either path, as illustrated by the formation of the cyclic carbene complexes **17a–c** (Scheme 3) in similar yields from the reaction of imines with either the alkylidyne or vinylidene precursors.

Scheme 9



The acid–base equilibrium of the manganese alkylidyne complexes complicates the interpretation of the mechanism by which they react with the various organic substrates. The complication arises from the fact that all of the organic substrates used in these reactions are themselves weak bases and can potentially deprotonate the alkylidyne ligand to form the vinylidene intermediates. Indeed, we have observed that several of the reactions of the alkylidyne complexes proceed in the absence of added base if excess organic substrate is employed. Because of its high acidity, we are certain that $[Cp(CO)_2Re{\equiv}CCH_3]^+$ reacts via initial deprotonation to form $Cp(CO)_2Re{=}C{=}CH_2$. In contrast, IR analyses of the reactions of $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ (R = H, Me) suggest that these complexes react via initial substrate addition followed by *subsequent* deprotonation, although we cannot be completely sure of this conclusion for all of the reactions examined. This uncertainty is even higher for the benzylidyne complex $[Cp(CO)_2Mn{\equiv}CCH_2Ph]^+$ due to its increased acidity compared to its ethylidyne and propylidyne analogues.

Because of their cationic nature, the manganese alkylidyne complexes are substantially more electrophilic than their neutral vinylidene derivatives. This is illustrated by the failure of the manganese vinylidene complexes **10a–c** to react with $Bu^tN{=}C{=}NBu^t$ and benzalazine, whereas these substrates readily underwent reaction with alkylidyne complexes **9a** and **9b**. In a comparison of the vinylidene complexes $Cp(CO)_2Mn{=}C{=}CH_2$ (**10a**) and $Cp(CO)_2Re{=}C{=}CH_2$ (**7**), the rhenium compound appears to be more electrophilic than the manganese derivative, as evidenced by the formation of $Cp(CO)_2Re{-}CNBu^t$ upon reaction of **7** with $Bu^tN{=}C{=}NBu^t$ and the lack of reactivity of **10a** with this substrate. The increased electrophilicity of **7** compared to **10a** is consistent with the $Cp(CO)_2Re$ fragment being more electron withdrawing than $Cp(CO)_2Mn$, as discussed above.

Although all of the organic substrates studied in this work have a reactive N=C double bond and a nucleophilic

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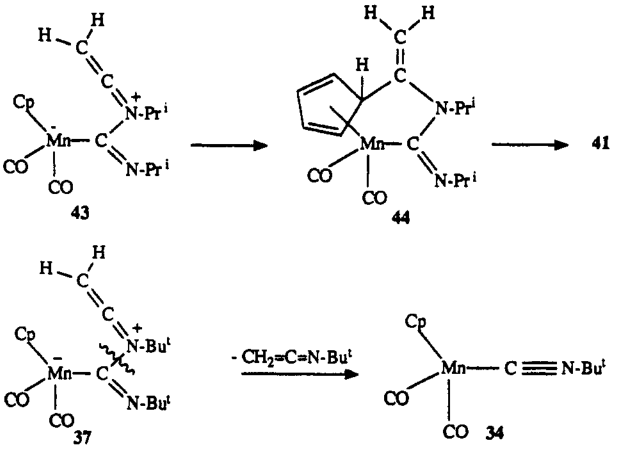
nitrogen atom, the reactions of these substrates with the alkylidyne and vinylidene complexes examined take widely different courses. N-substituted imines give net [2 + 2] cycloaddition across the C_α–C_β bond of the alkylidyne or vinylidene ligands to form the cyclic carbene complexes **14** (eq 3) and **17** (eq 4), whereas the unsubstituted imine HN=C(H)Ph gives mainly iminocarbene derivatives (eqs 6 and 7). Benzalazine reacts via consecutive [2 + 3] cycloaddition reactions to form the bicyclic bis(carbene) complexes **47** and **48** (eq 15), and carbodiimides give a variety of products depending upon the exact combination of reagents. Both Bu^{t}N=C=NBu^t and Pr^{i}N=C=NPr^i react with Cp(CO)$_2$Re=C=CH$_2$ to form isocyanide complexes via net metathesis of the Re=C bond with the N=C bond of the carbodiimide. A similar metathesis occurred between Bu^{t}N=C=NBu^t and the ethylidyne complex [Cp(CO)$_2$Mn≡CCH$_3$]$^+$ (eq 12). However, when the propylidyne complex [Cp(CO)$_2$Mn≡CCH$_2$CH$_3$]$^+$ was allowed to react with this substrate, the product formed was the unusual zwitterionic vinylidene complex **46**, which incorporated a BCl$_2$ fragment (eq 14). Finally, Pr^{i}N=C=NPr^i underwent reaction with [Cp(CO)$_2$Mn≡CCH$_3$]$^+$ and Cp(CO)$_2$Mn=C=CH$_2$ to give the *ansa*-carbene complex **41** (eq 13).

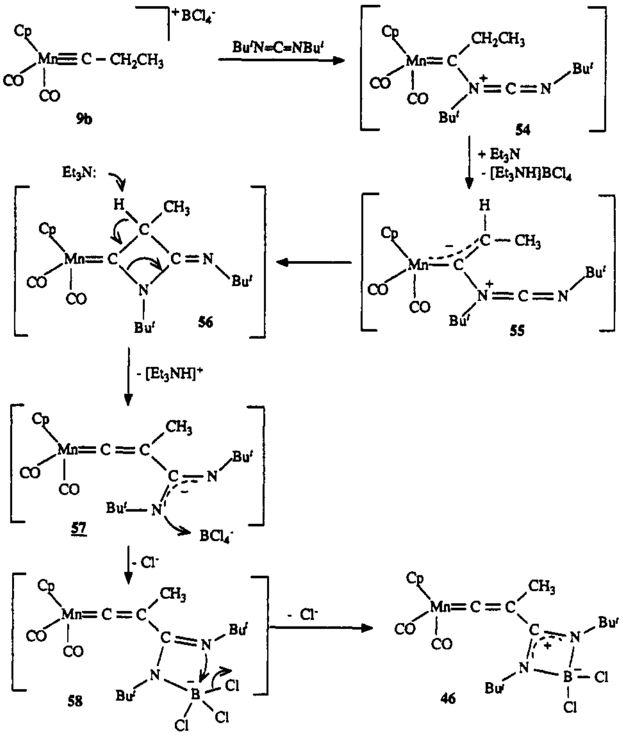
Although we do not fully understand the reasons for the differing reactions with the carbodiimide substrates, some rationalization can be presented. Both Cp(CO)$_2$Re=C=CH$_2$ and Cp(CO)$_2$Mn=C=CH$_2$ are believed to react with Pr^{i}N=C=NPr^i to give similar intermediates and initial reaction steps (Re, **36′** → **37′**, by analogy to Scheme 5; Mn, **42** → **43**, Scheme 7), but the final products differ markedly. In the case of rhenium, metathesis with the Re=C bond occurs to give the isocyanide derivative **33a** (eq 11), whereas with manganese the *ansa*-carbene complex **41** (eq 13) results. This difference is likely a consequence of the increased susceptibility of the Cp ligand in the manganese intermediate **43** to undergo electrophilic attack compared to that of the rhenium intermediate **37′**. As noted above, the Cp ligand of CpMn(CO)$_3$ is far more susceptible to electrophilic Friedel–Crafts reaction than is the Cp ligand of CpRe(CO)$_3$,[29] and as illustrated in Scheme 1, a similar difference between Mn and Re complexes was observed in our earlier study of their arylcarbyne derivatives.[1] That being the case, why then did not an *ansa*-carbene complex form upon reaction of [Cp(CO)$_2$Mn≡CCH$_3$]$^+$ and Cp(CO)$_2$Mn=C=CH$_2$ with Bu^{t}N=C=NBu^t? Recall that the product of these reactions was the isocyanide complex CpMn(CO)$_2$(CNBu^t) (**34**). Similar intermediates (**43** and **37**) have been invoked for the formation of both the *ansa*-carbene complex **41** and the isocyanide complex **34**, as illustrated in Scheme 10, but these are proposed to lead to the different products **41** and **34**. We can only presume that steric interactions involving the bulkier *tert*-butyl groups of **37** favor loss of the ketenimine to give **34**, rather than electrophilic addition to the Cp ring, which would have given an analogue of **41**.

As noted above, the propylidyne complex **9b** was observed to react with Bu^{t}N=C=NBu^t to give the zwitterionic complex **46** as the surprising product. We do not fully understand the mechanism by which **46** forms, but Scheme 11 presents a speculative mechanism. The initial intermediate is likely to be **54**, which would be the result of nucleophilic attack by a carbodiimide nitrogen at the electrophilic carbyne carbon of **9b**, as discussed above.

Scheme 10



Scheme 11



Deprotonation of this species would give **55**, which could then undergo ring closure to give **56**. A second deprotonation followed by ring opening would give **57**, which could displace chloride from the BCl$_4^-$ anion to give the observed **46**. Intermediate **56** is analogous to the product formed upon reaction of CyN=C=NCy with (CO)$_5$Cr=C(OH)(Me)[23] and is similar to the cyclic carbene complexes **17a–c**. Support for the proposed deprotonation of **56** comes from other work in these laboratories, in which it was shown that the cyclic carbene complex **17a** can be readily deprotonated at the β-carbon to give a highly reactive carbene anion.[29] The presence of both Mn=C and C=N bonds adjacent to the -C(H)CH$_3$- group in intermediate **56** should facilitate deprotonation at the β-carbon. An alternative mechanism, involving initial deprotonation of **9b** to give vinylidene **10b**, followed by a [2 + 2] cycloaddition between one of the C=N bonds of the carbodiimide and the terminal C=C bond of the vinylidene ligand to give intermediate **56** directly is less likely, given the observation that vinylidene complex **10b** (generated *prior* to the addition of Bu^{t}N=C=NBu^t by addition of Et$_3$N to a suspension of **9b**) failed to react with Bu^{t}N=C=NBu^t.

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The results presented in this work show that the vinylidene complexes $Cp(CO)_2Re{=}C{=}CH_2$ and $Cp(CO)_2Mn{=}C{=}CHR$ and their carbyne precursors are highly reactive species that undergo a variety of new types of addition and cycloaddition reactions. We suspect that they and related complexes within this family of compounds likely have much interesting chemistry that is yet to be discovered, and further studies along those lines are in progress in these laboratories.

Experimental Section

General Considerations. These carbene complexes $Cp(CO)_2Re{=}C(OSiMe_3)Me$ and $Cp(CO)_2Mn{=}C(OEt)CH_2R$ (R = H, Me, Ph) were prepared by modifications of the literature procedures for related complexes.[3a,30] Benzyllithium·TMEDA was prepared by the method of Eberhardt and Butte.[31] The reagents TMEDA, MeLi (1.4 M in Et_2O), MeI, Me_3SiCl, BCl_3 (1.0 M in hexanes), Et_3N, $MeN{=}C(H)Ph$, $PhN{=}C(H)Ph$, $HN{=}C(Ph)_2$, propylene oxide, $Ph_2C{=}NNH_2$, $Pr^iN{=}C{=}NPr^i$, and $Bu^tN{=}C{=}NBu^t$ were obtained from Aldrich Chemical Co. $[Et_3O]BF_4$ was obtained from Lancaster Synthesis, $CpM(CO)_3$ (M = Mn, Re) and $Cp'Mn(CO)_3$ were purchased from Strem Chemical Co., and $Ph(H)C{=}NN{=}C(H)Ph$ was obtained from Pfalz and Bauer. ^{13}CO (99.2% ^{13}C) was purchased from Isotech, Inc., and >15% ^{13}CO-enriched $CpMn(CO)_3$ was prepared by photolysis of $CpMn(CO)_3$ in Et_2O under a ^{13}CO atmosphere. This complex was then used to prepare $Cp(CO)_2Mn{=}C(OEt)CH_3$ that was >15% enriched in ^{13}C at the carbonyl and carbene carbon atoms. All reagents were used as received except for TMEDA, Et_3N, and $Pr^iN{=}C{=}NPr^i$, which were distilled prior to use. Solvents were dried by refluxing over Na/benzophenone ketyl (THF and Et_2O) or CaH_2 (hexane, pentane, CH_2Cl_2) and were freshly distilled prior to use. All manipulations were performed using standard Schlenk techniques under an atmosphere of dry N_2. A liquid N_2/2-propanol slush bath was used to maintain samples at −78 °C. Solution IR spectra were recorded between NaCl plates on an IBM FTIR-32 spectrometer or between CaF_2 plates on a Perkin-Elmer 225 spectrometer, both operating in the absorbance mode. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on Bruker AM-300, WH90, AC80, and AC200 FT NMR spectrometers in CD_2Cl_2 or C_6D_6 and were referenced to the residual solvent protons (^1H). Mass spectra were recorded on AEI-MS9 (EI), Kratos MS-50 (+FAB), and Hewlett-Packard 5970 mass spectrometers. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer or were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, or Galbraith Laboratories, Inc., Knoxville, TN.

***In Situ* Generation of $Cp(CO)_2Re{=}C{=}CH_2$ (7).** The carbyne complex $[Cp(CO)_2Re{\equiv}CCH_3]BCl_4$ (75.1 mg, 0.166 mmol), prepared from $Cp(CO)_2Re{=}C(OSiMe_3)Me$ and 2.2 equiv of BCl_3 (1.0 M in hexanes),[2,3,32] was dissolved in ~20 mL of CH_2Cl_2 at −78 °C. This gave gas evolution over the course of 5 min, after which time IR analysis of the mixture indicated quantitative consumption of $[Cp(CO)_2Re{\equiv}CCH_3]^+$ and the formation of 7. A similar reaction in THF at room temperature for 2 h gave formation of 7 and then its slow conversion to $[Cp(CO)_2Re]_2(\mu\text{-}C{=}CH_2)$ (ν_{CO} (hexane) 1982 (m), 1960 (s), 1881 (s) cm^{-1}) and $CpRe(CO)_3$ (ν_{CO} (CH_2Cl_2) 2023 (s), 1925 (s) cm^{-1}), which were isolated by chromatography on neutral alumina using 2:1 CH_2Cl_2/hexane as eluent.

7: IR (CH_2Cl_2) ν_{CO} 1992 (s), 1915 (s), $\nu_{C=C}$ 1632 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, −20 °C) δ 5.49 (s, 5H, *Cp*), 2.34 (s, 2H, CH_2).

***In Situ* Generation of $[Cp(CO)_2Mn{\equiv}CCH_2R]BCl_4$ (9) and $Cp(CO)_2Mn{=}C{=}C(H)R$ (10).** The appropriate carbene complex $Cp(CO)_2Mn{=}C(OEt)CH_2R$ was dissolved in ~15 mL of hexane, the solution was cooled to −78 °C, and BCl_3 (2.2 equiv of a 1.0 M solution in hexanes) was added dropwise via syringe, which caused formation of a light yellow precipitate of **9a** and **9b** and a brown precipitate of **9c**.[2,3,33] For the generation of **9a** and **9b**, the addition of BCl_3 must be performed rapidly after immersion in the low-temperature bath, as the carbene complexes precipitate from solution at this temperature. After the addition of BCl_3 was complete and while the flask was maintained at −78 °C, the supernatant was removed by means of a cannula tipped with filter paper and wrapped with poly(tetrafluoroethylene) tape. This procedure was facilitated by insertion of the free end of the cannula–filter into an empty Schlenk flask sealed with a septum and by periodic evacuation of the flask. The solid carbyne residue was then washed with 1:1 hexane/Et_2O (2 × 10 mL) at −78 °C, and the supernatant was similarly removed with a cannula–filter. The carbyne complexes were then suspended in ~20 mL of CH_2Cl_2 with the temperature maintained at −78 °C at all times. Addition of Et_3N (1.1 equiv) to the suspensions of the carbyne complexes resulted in dissolution of all solids and formation of homogeneous orange solutions of the vinylidene complexes **10a** and **10b** and a purple solution of **10c** in quantitative yield by IR. Complexes **10a** and **10b** are unstable at room temperature and could not be isolated. For the stable complex **10c**, the solution was warmed to room temperature, and a chromatographic workup on neutral alumina using 1:3 Et_2O/pentane as eluent gave pure **10c** in 80% yield as a purple microcrystalline solid. Trace amounts of violet $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}C(H)Ph)$[5a,b] were sometimes obtained. When they were warmed to room temperature, CH_2Cl_2 solutions of **9a** and **10a** both decomposed to give $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2)$, which was isolated as a maroon oil following silica gel chromatography with EtOAc as eluent in 18% and 21% yields, respectively (ν_{CO} (hexane) 1978 (w), 1950 (s), 1924 (s) cm^{-1}; lit.[8] ν_{CO} (hexane) 1975 (w), 1950 (s), 1921 (s) cm^{-1}).[8] Trace amounts of $CpMn(CO)_3$ were also formed.

$Cp(CO)_2Mn{=}C(OEt)CH_3$: ν_{CO} (CH_2Cl_2) 1947, 1875 cm^{-1}.

$Cp'(CO)_2Mn{=}C(OEt)CH_3$: IR (Et_2O) ν_{CO} 1952, 1890 cm^{-1}; ^1H NMR (C_6D_6) δ 4.42–4.24 (m, C_5H_4Me), 4.31 (q, 2H, J_{HH} = 7.0 Hz, OCH_2CH_3), 2.44 (s, 3H, CH_3), 1.72 (s, 3H, $C_5H_4CH_3$), 1.10 (t, 3H, J_{HH} = 7.0 Hz, OCH_2CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 337.0 ($Mn{=}C$), 233.8 ($Mn{-}CO$), 103.0, 87.2, 86.5 (C_5H_4Me), 71.1 (OCH_2CH_3), 14.9, 13.6 (OCH_2CH_3 and $C_5H_4CH_3$). Anal. Calcd for $C_{12}H_{15}MnO_3$: C, 54.97; H, 5.77. Found: C, 54.55; H, 5.76.

$Cp(CO)_2Mn{=}C(OEt)CH_2CH_3$: IR ($CH_2Cl_2$) ν_{CO} 1946, 1875 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.80 (s, 5H, *Cp*), 4.63 (q, 2H, J_{HH} = 7.0 Hz, OCH_2CH_3), 2.96 (q, 2H, J_{HH} = 7.5 Hz, CH_2CH_3), 1.48 (t, 3H, J_{HH} = 7.0 Hz, OCH_2CH_3), 0.99 (t, 3H, J_{HH} = 7.5 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 344.7 ($Mn{=}C$), 233.4 ($Mn{-}CO$), 86.7 (*Cp*), 72.7 (OCH_2CH_3), 53.3 (CH_2CH_3), 15.2 (OCH_2CH_3), 12.8 (CH_2CH_3); MS (EI) *m/z* 262 (M^+), 206 ($M^+ - 2$ CO).

$Cp'(CO)_2Mn{=}C(OEt)CH_2CH_3$: IR ($Et_2O$) ν_{CO} 1955, 1890 cm^{-1}; ^1H NMR (C_6D_6) δ 4.62 (q, 2H, J_{HH} = 7.0 Hz, OCH_2CH_3), 4.43–4.27 (m, C_5H_4Me), 2.78 (q, 2H, J_{HH} = 7.0 Hz, CH_2CH_3), 1.75 (s, 3H, $C_5H_4CH_3$), 1.19 (t, 3H, J_{HH} = 7.0 Hz, OCH_2CH_3), 0.94 (t, 3H, J_{HH} = 7.0 Hz, OCH_2CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 342.1 ($Mn{=}C$), 233.4 ($Mn{-}CO$), 103.3, 87.0, 86.1 (C_5H_4Me), 72.5 (OCH_2CH_3), 52.9 (CH_2CH_3), 15.0, 13.8, 13.0 (OCH_2CH_3, $C_5H_4CH_3$, and CH_2CH_3). Anal. Calcd for $C_{13}H_{17}MnO_3$: C, 56.53; H, 6.20. Found: C, 55.80; H, 6.09.

$Cp(CO)_2Mn{=}C(OEt)CH_2Ph$: ν_{CO} (CH_2Cl_2) 1950, 1880 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.33–7.15 (m, 5H, CH_2Ph), 4.83 (s, 5H, *Cp*), 4.66 (q, J_{HH} = 7.0 Hz, OCH_2CH_3), 4.32 (s, 2H, CH_2Ph), 1.44 (t, J_{HH} = 7.0 Hz, OCH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 338.4 ($Mn{=}C$), 233.1 ($Mn{-}CO$), 138.5 (*ipso-Ph*), 129.1 (*ortho-Ph*), 128.6 (*meta-Ph*), 126.4 (*para-Ph*), 86.9 (*Cp*), 73.3 (OCH_2CH_3), 65.2 (s, CH_2Ph), 15.1 (s, CH_2CH_3); MS (EI) *m/z* 324 (M^+), 268 ($M^+ - 2$ CO).

$Cp'(CO)_2Mn{=}C(OEt)CH_2Ph$: IR ($Et_2O$) ν_{CO} 1950, 1885 cm^{-1};

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(33) Auman, R.; Heinen, H. *Chem. Ber.* **1989**, *122*, 77.

^{1}H NMR (C_6D_6) δ 7.20–7.00 (m, Ph), 4.60 (q, 2H, J_{HH} = 7.0 Hz, $OC\mathit{H}_2CH_3$), 4.44–4.26 (m, $C_5\mathit{H}_4Me$), 4.12 (s, 2H, $C\mathit{H}_2Ph$), 1.68 (s, 3H, $C_5H_4C\mathit{H}_3$), 1.07 (t, 3H, J_{HH} = 7.0 Hz, $OCH_2C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 337.5 (Mn═*C*), 233.5 (Mn—*C*O), 103.5, 87.4, 86.5 (C_5H_4Me), 72.7 ($O\mathit{C}H_2CH_3$), 65.0 ($\mathit{C}H_2Ph$), 15.0, 13.8 ($OCH_2\mathit{C}H_3$ and $C_5H_4\mathit{C}H_3$). Anal. Calcd for $C_{18}H_{19}MnO_3$: C, 63.91; H, 5.66. Found: C, 62.74; H, 5.77.

9a: ν_{CO} (CH_2Cl_2) 2095, 2056 cm^{-1} (lit.[3a] ν_{CO} (CH_2Cl_2) 2084, 2043 cm^{-1}).

9b: ν_{CO} (CH_2Cl_2) 2093, 2053 cm^{-1}.

9c: ν_{CO} (CH_2Cl_2) 2095, 2054 cm^{-1}.

10a: ν_{CO} (CH_2Cl_2) 1996 (s), 1932 (s) $\nu_{C=C}$ 1624 (m) cm^{-1}.

10b: ν_{CO} (CH_2Cl_2) 1992 (s), 1928 (s), $\nu_{C=C}$ 1662 (w) cm^{-1}.

10c: IR (CH_2Cl_2) ν_{CO} 2003 (s), 1942 (s), $\nu_{C=C}$ 1646 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.28–7.04 (m, 5H, *Ph*), 6.71 (s, 1H, C═C(*H*)Ph), 5.11 (s, 5H, *Cp*); MS (EI) *m*/*z* 278 (M$^+$) 222 (M$^+$ – 2 CO) (lit.[5a] IR (cyclohexane) ν_{CO} 2009, 1955 cm^{-1}; ^{1}H NMR (CS_2) δ 7.40–7.00 (m, 5H, *Ph*), 6.91 (s, C═C(*H*)Ph), 5.27 (s, 5H, *Cp*)). Anal. Calcd for $C_{19}H_{11}MnO_2$: C, 64.76, H, 3.99. Found: C, 64.19; H, 3.91.

Reaction of $Cp(CO)_2Re{=}C{=}CH_2$ (7) with RN═C(H)Ph (R = Me, Ph). Carbyne complex **6** (88.0 mg, 0.181 mmol) was dissolved in ~20 mL of CH_2Cl_2 at –78 °C, and the solution was stirred for ~5 min as the vinylidene complex **7** formed. Excess MeN═C(H)Ph (0.5 mL, 4.06 mmol) was then added via syringe, and the resulting solution was stirred for 2 h. The solution was warmed to room temperature, the solvent was removed under vacuum, and the residue was chromatographed on neutral alumina (activity grade II). Elution with 1:1 CH_2Cl_2/pentane gave an orange band containing a mixture of complexes **14a** and **15a**. Removal of the solvent from this fraction gave the **14a**/**15a** product mixture as an orange solid (37 mg, 0.081 mmol); ^{1}H NMR indicated the yields of **14a** and **15a** to be 45% and 3%, respectively. A similar procedure for the reaction of **7** with PhN═C(H)Ph gave a **14b** (39%)/**15b** (10%) product mixture as an orange microcrystalline solid.

14a: IR (CH_2Cl_2) ν_{CO} 1919, 1843 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.89–7.07 (m, 5H, *Ph*), 4.87 (s, 5H, *Cp*), 4.41 (dd, 1H, J_{HH} = 1.8, 4.7 Hz, C(*H*)Ph), 2.71 (br t, 3H, $N(C\mathit{H}_3)$), 2.39 (ddq, 1H, J_{HH} = 1.2, 4.7, 14.7 Hz, $C\mathit{H}_2$), 1.99 (ddq, 1H, J_{HH} = 1.2, 1.8, 14.7 Hz, $C\mathit{H}_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 243.2 (Re═*C*), 204.2 and 204.0 (Re—*C*O), 137.7–126.3 (*aryl*), 85.8 (*Cp*), 72.0 (*C*(H)Ph), 54.8 ($\mathit{C}H_2$), 31.8 ($N(\mathit{C}H_3)$); MS (EI) *m*/*z* 453 (M$^+$).

15a: IR (CH_2Cl_2) ν_{CO} 1919, 1843 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 6.81 (C═C(*H*)Ph), 6.04 (N—C(*H*)Ph), 5.47 (*Cp*), 2.97 ($N(C\mathit{H}_3)$) (the aromatic protons were obscured by **14a**); MS (EI) *m*/*z* 540 (M$^+$).

14b: IR (CH_2Cl_2) ν_{CO} 1928, 1853 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 6.84–7.90 (m, 10H, *Ph*), 5.40 (s, 5H, *Cp*), 5.82 (dd, 1H, J_{HH} = 2.2, 5.1 Hz, C(*H*)Ph), 3.20 (dd, 1H, J_{HH} = 5.1, 15.4 Hz, $C\mathit{H}_2$), 2.67 (dd, 1H, J_{HH} = 2.2, 15.4 Hz, $C\mathit{H}_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 244.5 (Re═*C*), 205.3 and 203.8 (Re—*C*O), 150.8–121.8 (*aryl*), 86.7 (*Cp*), 71.7 (*C*(H)Ph), 55.8 ($\mathit{C}H_2$); MS (EI) *m*/*z* 515 (M$^+$).

15b: IR (CH_2Cl_2) ν_{CO} 1928, 1853 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.62–7.23 (m, 15H, *aryl*), 6.70 (d, 1H, J_{HH} = 1.2 Hz, C═C(*H*)Ph), 6.57 (d, 1H, J_{HH} = 1.2 Hz, N—C(*H*)Ph), 5.19 (s, 5H, *Cp*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 237.6 (Re═C), 204.6 (Re—*C*O), 150.8–121.8 (*aryl*), 86.1 (C═*C*(H)Ph), 85.5 (*Cp*), 80.3 (N-*C*(H)Ph) (the *C*═C(H)Ph resonance was not resolved); MS (EI) *m*/*z* 603 (M$^+$).

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_2R]BCl_4$ (9) with PhN═C(H)Ph. Carbyne complex **9a** was generated from $Cp(CO)_2Mn{=}C(OMe)CH_3$ (0.25 g, 1.01 mmol) and BCl_3 (2.2 equiv, 2.2 mL of a 1.0 M solution in hexanes) as described above and was suspended in ~20 mL of CH_2Cl_2 at –78 °C. To this was added via cannula PhN═C(H)Ph (1.1 equiv, 1.11 mmol, 0.20 g, dissolved in 5 mL of CH_2Cl_2), which caused much of the solid to dissolve and gave an orange solution. The reaction mixture was stirred for 10 min, and Et_3N (1.5 equiv, 0.21 mL) was then added via syringe, which caused formation of a deep red homogeneous solution. The reaction flask was then removed from the low-temperature bath, and stirring was continued while the reaction mixture was warmed to room temperature over 30 min. The mixture was then concentrated to ~2 mL under vacuum and chromatographed on neutral alumina. Elution with Et_2O gave a brown band, which was collected and concentrated to ~3 mL under vacuum. This solution was placed on a neutral alumina column, and the brown band was washed thoroughly with 100% pentane before being eluted with 100% Et_2O. Removal of solvent from this band gave a brown flocculent solid, and recrystallization from Et_2O/pentane left **17a** as a red-brown solid in 85% yield (0.33 g, 0.861 mmol). Similar procedures were used to prepare **17b** (62% yield, red oil), **17c** (58% yield, bright yellow powder), and the Cp′ analogues of **17a** (**17a′**; 80% yield, red-brown oil), **17b** (**17b′**; 80% yield, red oil), and **17c** (**17c′**; 75% yield, red-orange powder).

17a: IR (CH_2Cl_2) ν_{CO} 1934, 1865 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.49–7.20 (m, 10H, *aryl*), 5.86 (dd, 1H, J_{HH} = 2.1, 4.8 Hz, C(*H*)-Ph), 4.72 (s, 5H, *Cp*), 2.48 (dd, 1H, J_{HH} = 4.8, 15.7 Hz, $C\mathit{H}_2$), 2.93 (dd, 1H, J_{HH} = 2.1, 15.7 Hz, $C\mathit{H}_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 292.4 (Mn═*C*), 234.3 and 233.7 (2 × Mn—*C*O), 140.8–122.9 (*aryl*), 85.3 (*Cp*), 72.7 (*C*(H)Ph), 54.8 (CH_2); MS (EI) *m*/*z* 383 (M$^+$), 327 (M$^+$ – 2 CO). Anal. Calcd for $C_{22}H_{18}MnNO_2$: C, 68.93; H, 4.73. Found: C, 69.19; H, 4.84.

17a′: IR (Et_2O) ν_{CO} 1930, 1870 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.20–7.00 (m, 10H, *aryl*), 5.25 (dd, 1H, J_{HH} = 2.2, 5.0 Hz, C(*H*)Ph), 4.45–4.27 (m, $C_5\mathit{H}_4CH_3$), 2.72 (ABX pattern, 2H, J_{HH} = 2.2, 5.0, 15.6 Hz, $C\mathit{H}_2$), 1.84 (s, 3H, $C_5H_4C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 292.5 (Mn═*C*), 234.5 and 234.0 (2 × Mn—*C*O), 133.4–118.0 (*aryl*), 101.6, 85.9, 84.9, and 84.5 ($\mathit{C}_5H_4CH_3$), 72.1 (*C*(H)Ph), 54.5 ($\mathit{C}H_2$), 14.2 ($C_5H_4\mathit{C}H_3$).

17b (*RS*/*SR* diastereomer): IR (CH_2Cl_2) ν_{CO} 1930, 1861 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.3–6.5 (m, 10H, *aryl*), 4.79 (d, 1H, J_{HH} = 1.8 Hz, C(*H*)Ph), 4.36 (s, 5H, *Cp*), 2.66 (dq, 1H, J_{HH} = 7.3, 1.8 Hz, $C(\mathit{H})CH_3$), 1.25 (d, 3H, J_{HH} = 7.3 Hz, $C(H)C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 300.1 (Mn═*C*), 233.9 and 232.9 (2 × Mn—*C*O), 142.0–123.3 (*aryl*), 83.9 (*Cp*), 80.8 (*C*(H)Ph), 60.6 ($\mathit{C}(H)CH_3$), 16.8 (s, $C(H)\mathit{C}H_3$); MS (EI) *m*/*z* 397 (M$^+$), 341 (M$^+$ – 2 CO).

17b (*RR*/*SS* diastereomer): IR (CH_2Cl_2) ν_{CO} 1930, 1861 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.3–6.5 (m, *aryl*), 5.56 (d, 1H, J_{HH} = 5.0 Hz, C(*H*)Ph), 4.41 (s, 5H, *Cp*), 2.97 (dq, 1H, J_{HH} = 7.6, 5.0 Hz, $C(\mathit{H})$-CH_3), 0.84 (d, 3H, J_{HH} = 7.6 Hz, $C(H)C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (CD_2-Cl_2) δ 300.1 (Mn═*C*), 233.9 and 232.9 (2 × Mn—*C*O), 142.0–123.3 (*aryl*), 84.4 (*Cp*), 74.9 (*C*(H)Ph), 55.8 ($\mathit{C}(H)CH_3$), 14.0 ($C(H)\mathit{C}H_3$); MS (EI) *m*/*z* 397 (M$^+$), 341 (M$^+$ – 2 CO).

17b′ (*RS*/*SR* diastereomer): IR (Et_2O) ν_{CO} 1934, 1870 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.6–6.7 (m, 10H, *aryl*), 4.84 (d, 1H, J_{HH} = 1.8 Hz, C(*H*)Ph), 4.5–4.3 (m, $C_5\mathit{H}_4CH_3$), 2.68 (dq, 1H, J_{HH} = 7.1, 1.8 Hz, $C(\mathit{H})CH_3$), 1.81 (s, 3H, $C_5H_4C\mathit{H}_3$), 1.29 (d, 3H, J_{HH} = 7.1 Hz, $C(H)C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 300.7 (Mn═*C*), 233.9 and 233.4 (Mn—*C*O), 137.4–119.0 (*aryl*), 100.9, 88.1, 79.4 ($\mathit{C}_5H_4CH_3$), 80.4 (*C*(H)Ph), 60.3 ($\mathit{C}(H)CH_3$), 16.8, 14.1 ($C_5H_4\mathit{C}H_3$ and $C(H)\mathit{C}H_3$).

17b′ (*RR*/*SS* diastereomer): IR (Et_2O) ν_{CO} 1934, 1870 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.6–6.7 (m, 10H, *aryl*), 5.61 (d, 1H, J_{HH} = 5.0 Hz, C(*H*)Ph), 4.5–4.3 (m, 4H, $C_5\mathit{H}_4CH_3$), 3.03 (dq, 1H, J_{HH} = 7.1, 5.0 Hz, $C(\mathit{H})CH_3$), 1.79 (s, 3H, $C_5H_4C\mathit{H}_3$), 0.88 (d, 3H, J_{HH} = 7.1 Hz, $C(H)C\mathit{H}_3$).

17c: IR (CH_2Cl_2) ν_{CO} 1936, 1867 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.57–7.30 (m, 15H, *aryl*), 5.53 (d, 1H, J_{HH} = 1.6 Hz, C—C(*H*)Ph), 4.45 (s, 5H, *Cp*), 4.02 (d, 1H, J_{HH} = 1.6 Hz, N—C(*H*)Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 295.4 (Mn═*C*), 234.1 and 233.5 (2 × Mn—*C*O), 140.9–124.3 (*aryl*), 84.7 (*Cp*), 82.3 (C—*C*(H)Ph), 69.6 (N—*C*(H)-Ph); MS (EI) *m*/*z* 459 (M$^+$), 403 (M$^+$ – 2 CO). Anal. Calcd for $C_{28}H_{22}MnNO_2$: C, 73.20; H, 4.83. Found: C, 73.33; H, 4.93.

17c′: IR (Et_2O) ν_{CO} 1930, 1870 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.73–6.83 (m, 15H, *aryl*), 5.30 (d, 1H, J_{HH} = 1.9 Hz, C—C(*H*)Ph), 4.35–4.24 (m, $C_5\mathit{H}_4CH_3$), 3.86 (d, 1H, J_{HH} = 1.9 Hz, N—C(*H*)Ph), 1.70 (s, 3H, $C_5H_4C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 295.5 (Mn═*C*), 234.2 and 234.0 (2 × Mn—*C*O), 133.5–118.0 (*aryl*), 102.6, 85.2, 84.9, and 84.4 ($\mathit{C}_5H_4CH_3$), 82.0 (C—*C*(H)Ph), 69.8 (N—*C*(H)-Ph), 14.1 ($C_5H_4\mathit{C}H_3$). Anal. Calcd for $C_{29}H_{24}MnNO_2$: C, 73.57; H, 5.11; N, 2.96. Found: C, 73.53; H, 5.26; N, 2.81.

Reaction of $Cp(CO)_2Mn{=}C{=}C(H)R$ (10) with PhN═C(H)Ph. Vinylidene complex **10a** was generated from **9a** (from $Cp(CO)_2Mn{=}C(OMe)CH_3$ (0.25 g, 1.01 mmol) and BCl_3 (2.2 equiv, 2.2 mL of a 1.0 M solution in hexanes)) by the addition of Et_3N (1.5 equiv, 1.51 mmol, 0.21 mL) in CH_2Cl_2 (20 mL) at

−78 °C as described above. A solution of PhN=C(H)Ph (1.1 equiv, 1.11 mmol, 0.20 g in 5 mL of CH_2Cl_2) was then added via cannula, and the reaction flask was warmed to room temperature over 30 min with continuous stirring. The resulting brown solution was concentrated to ~3 mL and worked up as described above in the preparation of **17a** from **9a** to give **17a** in 75% yield (0.29 g, 0.76 mmol) as a red-brown solid. Complexes **17b** (54% yield, red oil) and **17c** (48% yield, yellow powder) were similarly prepared from **10b** and **10c**.

Oxidation of 17a′–c′ To Form the β-Lactams 22 and 23. The following oxidation procedure is a slight modification of that described in ref 33. Complex **17a′** (1.62 g, 4.05 mmol) was dissolved in 70 mL of Et_2O in an Erlenmeyer flask, and water (70 mL) and $[Bu_3NH]Cl$ (200 mg) were then added. The solution was vigorously stirred, and $KMnO_4$ was added in 100-mg portions every 5 min until the IR spectrum of the organic phase indicated the complete consumption of **17a′**. The mixture was then filtered, and the organic phase was separated, washed with H_2O (2 × 50 mL), and dried over $MgSO_4$. After filtration to remove the $MgSO_4$, the volatiles were removed under vacuum to give crude **22a** as a pale yellow powder. This solid was washed with hexane (100 mL) to remove traces of yellow $Cp'Mn(CO)_3$ formed during the oxidation step. After the hexane was decanted, the solid residue was dissolved in CH_2Cl_2 and filtered through a short alumina column. Removal of the solvent from the filtrate gave a colorless solid, which was recrystallized from Et_2O/hexane at −20 °C to give pure **22a** (782 mg, 3.50 mmol, 87% yield) as white crystals. Lactam **22b** was similarly prepared from a 3:22 mixture of diastereomers of **17b′**: the major *RS*/*SR* diastereomer of **22b** was obtained in pure form as white crystals in 77% yield. ^1H NMR data for the minor *RR*/*SS* diastereomer of **22b** was inferred from a ^1H NMR spectrum taken before the recrystallization step. Lactam **23** was prepared in a similar manner from **17c′** and was isolated as a white crystalline material in 91% yield.

22a: IR (Et_2O) ν_{CO} 1770 cm^{-1}; ^1H NMR (C_6D_6) δ 8.00–7.00 (m, 10H, *aryl*), 5.00 (dd, 1H, J_{HH} = 2.7, 5.7 Hz, C(*H*)Ph), 3.24 (ABX pattern, 2H, J_{HH} = 2.7, 5.7, 15.2 Hz, C*H*$_2$); MS (EI) *m*/*z* 223 (M$^+$), 180 ($C_6H_5CNC_6H_5^+$). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.58; H, 6.14; N, 6.03.

22b (*RS*/*SR* diastereomer): IR (Et_2O) ν_{CO} 1772 cm^{-1}; ^1H NMR (C_6D_6) δ 7.6–6.7 (m, *aryl*), 4.03 (d, 1H, J_{HH} = 2.5 Hz, C(*H*)Ph), 2.70 (dq, 1H, J_{HH} = 7.4, 2.5 Hz, C*H*CH$_3$), 1.03 (d, 3H, J_{HH} = 7.4 Hz); MS (EI) *m*/*z* 237 (M$^+$), 180 ($C_6H_5CNC_6H_5^+$). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.57; H, 6.24; N, 6.05.

22b (*RR*/*SS* diastereomer): IR (Et_2O) ν_{CO} 1772 cm^{-1}; ^1H NMR (C_6D_6) δ 7.6–6.7 (m, *aryl*), 4.43 (d, 1H, J_{HH} = 6.1 Hz, C(*H*)Ph), 3.09 (dq, 1H, J_{HH} = 7.6, 6.1 Hz, C*H*CH$_3$), 0.64 (d, 3H, J_{HH} = 7.6 Hz).

23: IR (Et_2O) ν_{CO} 1770 cm^{-1}; ^1H NMR (C_6D_6) δ 7.42–7.02 (m, 15H, *aryl*), 4.95 (d, 1H, J_{HH} = 2.5 Hz, N—C(*H*)Ph), 4.28 (d, 1H, J_{HH} = 2.5 Hz, C—C(*H*)Ph); MS (EI) *m*/*z* 299 (M$^+$), 180 ($C_6H_5CNC_6H_5$). Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.23; H, 5.84; N, 4.69.

Reaction of $Cp(CO)_2Re{=}C{=}CH_2$ (7) with $HN{=}C(Ph)_2$. Carbyne complex **6** (74.1 mg, 0.152 mmol) was dissolved in ~20 mL of CH_2Cl_2 at −78 °C and stirred for 5 min to give the vinylidene complex **7**. Excess $HN{=}C(Ph)_2$ (0.5 mL, 2.98 mmol) was then added via syringe, and the reaction mixture was stirred for 2 h while it was warmed to room temperature. The solvent was then removed under vacuum, and the crude product was column chromatographed on neutral alumina. Elution with a 1:5 CH_2Cl_2/hexane mixture gave a small yellow band containing unreacted $HN{=}C(Ph)_2$, and further elution with 1:1 CH_2Cl_2/hexane gave an orange band of the imino–carbene product **24**. Removal of the volatiles from this fraction under vacuum left imino–carbene complex **24** (52.3 mg, 0.102 mmol, 66% yield) as an orange microcrystalline solid.

24: IR (CH_2Cl_2) ν_{CO} 1930, 1854 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.81–7.48 (m, 10H, *aryl*), 5.16 (s, 5H, *Cp*), 2.78 (s, 3H, C*H*$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 228.3 (Re=*C*), 205.1 (Re—*C*O), 196.4 (N=*C*(Ph)$_2$), 137.7–128.4 (*aryl*), 87.2 (*Cp*), 43.6 (CH$_3$); MS (EI) *m*/*z* 515 (M$^+$). Anal. Calcd for $C_{22}H_{18}NO_2Re$: C, 51.35; H, 3.52. Found: C, 51.01; H, 3.59.

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ (R = H (9a), Me (9b)) with $HN{=}C(Ph)_2$. Carbyne complexes **9a** and **9b** were generated from the appropriate carbene precursor (0.50 g) and BCl_3 (2.2 equiv of a 1.0 M solution in hexanes) as described above and suspended in ~15 mL of CH_2Cl_2 at −78 °C. $HN{=}C(Ph)_2$ (1.1 equiv) was then added to this suspension via syringe, and the resulting deep red solution was stirred for 10 min. Et_3N (1.1–1.5 equiv) was then added via syringe, and the solution was stirred overnight while it was warmed to room temperature. The resulting red-brown solutions were then concentrated to ~2 mL and chromatographed on neutral alumina. Elution with 100% Et_2O gave red-brown bands in each case. The product band was collected, concentrated under vacuum to 2–3 mL, and reloaded onto the alumina column. The band was washed thoroughly with 100% pentane before being eluted with 1:3 Et_2O/pentane. The product band was collected, and the volatiles were removed under vacuum to give red-brown oils in each case. This procedure gave pure imino–carbene complexes **25a** and **25b** (0.41 g, 1.03 mmol, 54% yield) as red-brown oils. In the case of **25a**, dissolution of the oily product in a minimal amount of 1:1 Et_2O/pentane, followed by addition of 5 mL of pentane, induced the formation of red-brown crystals. The mixture was stored at −20 °C overnight to facilitate further crystal growth and the supernatant removed via cannula, leaving red-brown crystals of **25a** (0.21 g, 0.55 mmol, 27% yield). Similar treatment of **25b** failed to produce any crystalline material.

25a: IR (CH_2Cl_2) ν_{CO} 1927, 1857 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.81–7.48 (m, 10H, *aryl*), 4.47 (s, 5H, *Cp*), 2.69 (s, 3H, C*H*$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 250.7 (Mn=*C*), 234.6 (Mn—*C*O), 196.7 (N=*C*(Ph)$_2$), 138.0–128.4 (*aryl*), 85.1 (*Cp*), 38.0 (*C*H$_3$); MS (EI) *m*/*z* 383 (M$^+$), 327 (M$^+$ − 2 CO). Anal. Calcd for $C_{22}H_{18}MnNO_2$: C, 68.93; H, 4.73. Found: C, 69.05; H, 4.32.

25b: IR (CH_2Cl_2) ν_{CO} 1923, 1853 cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.81–7.48 (m, 10H, *aryl*), 4.46 (s, 5H, *Cp*), 2.99 (q, 2H, J_{HH} = 7.4 Hz, C*H*$_2$CH$_3$), 1.06 (t, 3H, J_{HH} = 7.4 Hz, CH$_2$C*H*$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 241.2 (Mn=*C*), 235.0 (Mn—*C*O), 196.7 (N=*C*(Ph)$_2$), 138.0–127.9 (*aryl*), 84.6 (*Cp*), 44.6 (*C*H$_2$CH$_3$), 12.6 (CH$_2$*C*H$_3$); MS (EI) *m*/*z* 397 (M$^+$), 341 (M$^+$ − 2 CO).

Reaction of $Cp(CO)_2Mn{=}C{=}C(H)R$ (R = H (10a), Me (10b)) with $HN{=}C(Ph)_2$. The vinylidene complexes **10a** and **10b** were generated from the appropriate carbyne precursor complex (**9a** and **9b** formed from 0.5 g of their carbene precursor complexes as described above) via addition of Et_3N (1.1 equiv) to a CH_2Cl_2 suspension of the carbyne complex at −78 °C. $HN{=}C(Ph)_2$ (1.1 equiv) was then added to the homogeneous orange solutions via syringe. Stirring was continued for 8–16 h while the reaction mixture was warmed slowly to room temperature. The resulting red-brown solutions were concentrated to 2–3 mL and worked up as described above to give imino–carbene complexes **25a** (0.21 g, 0.54 mmol, 27% yield) as a red-brown oil and **25b** (0.41 g, 1.03 mmol, 54% yield) as red-brown crystals.

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_2Ph]^+$ (9c) and $Cp(CO)_2Mn{=}C{=}C(H)Ph$ (10c) with $HN{=}C(Ph)_2$. Carbyne complex **9c** was generated from $Cp(CO)_2Mn{=}C(OMe)CH_2Ph$ (0.71 g, 2.19 mmol) in hexane at −78 °C via addition of BCl_3 (2.2 equiv, 4.8 mL of a 1.0 M solution in hexanes) and isolated at low temperature via the procedure described above. This complex was dissolved in 20 mL of CH_2Cl_2 at −78 °C, and $HN{=}C(Ph)_2$ (1.1 equiv, 2.41 mmol, 0.40 mL) was added via syringe, which caused formation of a deep red homogeneous solution within 15 min. The reaction mixture was warmed to room temperature, and a second equivalent of $HN{=}C(Ph)_2$ was added via syringe. The red-brown solution was stirred at room temperature for 3 days and concentrated to ~2 mL under vacuum, and 10 mL of Et_2O was added to give a red-brown solution with a white precipitate. The supernatant was removed via cannula and filtered through a plug of Celite into another Schlenk flask. The solid residue was washed with additional Et_2O until the washings were colorless, and the supernatants were combined into the flask containing the red-brown filtrate. This solution was then chromatographed on neutral alumina and eluted with 100% Et_2O to give a single brown band, which was collected, concentrated to 2–3 mL, and rechromatographed on the alumina column. Elution with 1:3 Et_2O/pentane gave first a red band of unreacted **10c** followed by a red-brown band of **25c**. A third yellow band of **28** was eluted with 100% Et_2O. These fractions were separately rechromatographed; each was washed with 100% pentane before it was eluted with 1:3 Et_2O/pentane (**25c**) or 100% Et_2O (**28**). Removal of the solvents from the collected product bands gave **25c** as a red-brown oil and **26** (0.44 g, 0.95 mmol, 50% yield) as a yellow microcrystalline solid. Dissolution of the oily residue of **25c** in a minimal amount of 1:1 Et_2O/pentane, followed by the addition of 5 mL of pentane, induced the formation of purple crystals of **25c**. This mixture was stored overnight at −20 °C to facilitate further crystallization and the slightly red-brown supernatant removed via cannula. The crystalline mass was washed with pentane (3 × 5 mL) and dried under vacuum to give purple-brown crystals of **25c** (0.29 g, 0.63 mmol, 29% yield).

In the reaction of **10c** with $HN{=}C(Ph)_2$, the vinylidene complex (0.50 g, 1.80 mmol) was dissolved in 15 mL of CH_2Cl_2 at room temperature and $HN{=}C(Ph)_2$ (1.1 equiv, 1.98 mmol, 0.33 mL) was added to the purple solution via syringe. The solution was stirred at room temperature for 1 h, after which time IR analysis of the red-brown solution indicated the complete consumption of **10c**. The solution was concentrated to 2–3 mL under vacuum and chromatographed on neutral alumina. Elution with 1:1 Et_2O/pentane gave first a large red-brown band of **25c**, and continued elution with 100% Et_2O gave a smaller yellow band of **28**. Removal of the solvents from the collected bands gave **25c** as a red-brown oil and **28** (0.16 g, 0.35 mmol, 19% yield) as a pale yellow solid. The **25c** thus obtained was crystallized as described above to give purple-brown crystals (0.66 g, 1.44 mmol, 80% yield).

25c: IR (CH_2Cl_2) ν_{CO} 1925, 1855 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.80–7.00 (m, 15H, *aryl*), 4.50 (s, 5H, *Cp*), 4.24 (s, 2H, CH_2Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 235.0 (Mn—CO), 234.8 (Mn═C), 196.7 ($N{=}C(Ph)_2$), 138.0–126.9 (*aryl*), 84.9 (*Cp*), 56.9 (CH_2Ph); MS (EI) *m/z* 459 (M^+), 403 ($M^+ - 2$ CO). Anal. Calcd for $C_{28}H_{22}MnNO_2$: C, 73.20; H, 4.83. Found: C, 72.84; H, 4.72.

28: IR (CH_2Cl_2) ν_{CO} 1936, 1864 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 9.80 (br s, 1H, N—*H*), 7.80–6.91 (m, 15H, *aryl*), 4.88 (s, 1H, C(*H*)Ph), 4.43 (s, 5H, *Cp*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 295.4 (Mn═C), 233.7 and 232.7 (2 × Mn-CO), 144.1–126.3 (*aryl*), 84.3 (*Cp*), 76.0 (*C*(H)-Ph); MS (EI) *m/z* 459 (M^+), 403 ($M^+ - 2$ CO). Anal. Calcd for $C_{28}H_{22}MnNO_2$: C, 73.20; H, 4.83. Found: C, 72.65; H, 5.11.

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_2R]^+$ (9) with $Ph_2C{=}NNH_2$. Carbyne complexes **9a** and **9b** were generated from the appropriate carbene precursor ($Cp(CO)_2Mn{=}C(OMe)CH_2R$, 0.35 g) and 2.2 equiv of BCl_3 in hexane at −78 °C and isolated at low temperature as described above. These complexes were suspended in ~15 mL of CH_2Cl_2 at −78 °C, and $Ph_2C{=}NNH_2$ (1.1 equiv in 5 mL of CH_2Cl_2) was added via cannula to give deep red-orange homogeneous solutions. These were stirred for 15 min at −78 °C, and Et_3N (1.5 equiv) was added via syringe. The reaction mixture was then removed from the low-temperature bath, warmed to room temperature over 30 min, concentrated to ~3 mL, and chromatographed on neutral alumina. Elution with 100% Et_2O gave in each case a single red-orange band, which was collected, concentrated to 2–3 mL under vacuum, and reloaded onto the chromatography column and rechromatographed. In the case of **30a**, the product band was washed thoroughly with pentane before elution with 1:3 Et_2O/pentane. This gave first two small red and purple bands, which were discarded, followed by elution with 1:1 Et_2O/pentane, which gave a large red band of **30a**. This latter band was rechromatographed using the same procedure to give **30a** (0.19 g, 0.88 mmol, 62% yield) as an orange-brown solid. In the case of **30b**, the product band was washed with 1:3 Et_2O/pentane, to elute a small orange-brown band, which was discarded, and continued elution with 1:1 Et_2O/pentane gave a large yellow-orange band of **30b**, which overlapped a small red band. The leading yellow-orange edge and trailing red-orange edge were collected separately, and the latter was rechromatographed as above. The yellow-orange bands of **30b** were combined and the solvents removed to give **30b** (0.19 g, 0.82 mmol, 62% yield) as an orange solid.

30a: IR (CH_2Cl_2) ν_{CO} 1934 (s), 1861 (s), ν_{CN} 2271 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.45 (s, 5H, *Cp*), 2.08 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 234.5 (Mn—CO), 132.5 (Mn—N≡*C*), 82.5 (*Cp*), 5.0 (N≡C—CH_3); MS (EI) *m/z* 217 (M^+), 161 ($M^+ - 2$ CO). Anal. Calcd for $C_9H_8MnNO_2$: C, 49.79; H, 3.71. Found: C, 49.80; H, 3.57.

30b: IR (CH_2Cl_2) ν_{CO} 1935 (s), 1858 (s), ν_{CN} 2260 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.44 (s, 5H, *Cp*), 2.40 (q, J_{HH} = 7.6 Hz, N≡C—CH_2CH_3), 1.14 (t, J_{HH} = 7.6 Hz, N≡C—CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 234.6 (Mn—CO), 136.8 (Mn—N≡*C*), 82.6 (*Cp*), 14.0 (N≡C—CH_2CH_3), 10.6 (N≡C—CH_2CH_3); MS (EI) *m/z* 231 (M^+), 175 ($M^+ - 2$ CO). Anal. Calcd for $C_{10}H_{10}MnNO_2$: C, 51.97; H, 4.36. Found: C, 51.86; H, 4.17.

Reaction of $Cp(CO)_2Mn{=}C{=}C(H)R$ (10) with $Ph_2C{=}N$-NH_2. Vinylidene complex **10a** was generated in CH_2Cl_2 at −78 °C from **9a** (formed from 0.25 g, 1.01 mmol of $Cp(CO)_2Mn{=}C$-$(OMe)Me$, as described above). $Ph_2C{=}NNH_2$ (1.1 equiv, 1.11 mmol, 0.22 g, in 5 mL of CH_2Cl_2) was then added to the orange solution via cannula, and the reaction mixture was stirred overnight while it was slowly warmed to room temperature. The resultant red-orange solution was concentrated under vacuum to ~3 mL and chromatographed on neutral alumina. Elution with 100% Et_2O gave a single red-orange band, which was collected, concentrated to ~3 mL under vacuum, reloaded onto the chromatography column, and washed thoroughly with 100% pentane before being eluted with 1:1 Et_2O/pentane. This gave a single orange band, which upon solvent removal left **30a** (0.07 g, 0.32 mmol, 32% yield) as an orange solid. A similar procedure from **10c** gave **30c** (0.20 g, 0.68 mmol, 66% yield) as an orange oil, which solidified to a waxy solid upon storage overnight at −20 °C.

30c: IR (CH_2Cl_2) ν_{CO} 1936 (s), 1863 (s) ν_{CN} 2264 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.40–7.20 (m, 5H, *aryl*), 4.49 (s, 5H, *Cp*), 3.83 (s, 2H, CH_2Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 234.3 (Mn—CO), 133.8 (Mn—N≡*C*), 130.4–128.0 (*aryl*), 82.6 (*Cp*), 26.5 (N≡C—CH_2-Ph); MS (EI) *m/z* 293 (M^+), 237 ($M^+ - 2$ CO). Anal. Calcd for $C_{15}H_{12}MnNO_2$: C, 61.45; H, 4.13. Found: C, 61.33; H, 4.09.

Reaction of $Cp(CO)_2Re{=}C{=}CH_2$ (7) with $RN{=}C{=}NR$ ($R = Pr^i, Bu^t$). Carbyne complex **6** (82.3 mg, 0.169 mmol) was dissolved in 20 mL of CH_2Cl_2 at −78 °C and the solution stirred for 5 min to generate vinylidene complex **7**. Excess $Bu^tN{=}C{=}NBu^t$ (0.5 mL, 2.59 mmol) was then added via syringe, and the reaction mixture was stirred for 2 h and then warmed to room temperature. The solvent was removed under vacuum, and the residue was loaded onto a neutral alumina chromatography column. The product band was first washed thoroughly with 1:3 CH_2Cl_2/hexane to remove excess carbodiimide before eluting with 2:1 CH_2Cl_2/hexane. This gave a light tan band from which the solvent was removed under vacuum to give isocyanide complex **33a** (44.3 mg, 0.113 mmol, 67% yield) as a tan microcrystalline solid. A similar procedure was followed for the reaction of **7** with $Pr^iN{=}C{=}NPr^i$ to give isocyanide complex **33b** in 72% yield.

33a: IR (CH_2Cl_2) ν_{CO} 1934 (s), 1874 (s), ν_{CN} 2121 (br) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.21 (s, 5H, *Cp*), 4.10 (sept, 1H, J_{HH} = 6.5 Hz, C(*H*)$(CH_3)_2$), 1.35 (d, 6H, J_{HH} = 6.5 Hz, C(H)$(CH_3)_2$); MS (EI) *m/z* 377 (M^+).

33b: IR (CH_2Cl_2) ν_{CO} 1934 (s), 1874 (s), ν_{CN} 2116 (br) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.21 (s, 5H, *Cp*), 1.43 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 199.3 (Re—CO), 145.3 (Re—*C*≡N), 83.3 (*Cp*), 57.4 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$); MS (EI) *m/z* 391 (M^+). Anal. Calcd for $C_{12}H_{14}NO_2Re$: C, 38.17; H, 3.96. Found: C, 37.92; H, 3.98.

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ (9a) with $Bu^tN{=}C{=}NBu^t$. Carbyne complex **9a** was generated by the reaction of $Cp(CO)_2Mn{=}C(OMe)Me$ (0.25 g, 1.01 mmol) with BCl_3 (2.2 equiv, 2.2 mL of a 1.0 M solution in hexanes) in hexane at −78 °C and isolated as described above. This was suspended in 15 mL of CH_2Cl_2 at −78 °C, and $Bu^tN{=}C{=}NBu^t$ (2.2 equiv, 2.22 mmol, 0.43 mL) was added via syringe. The resulting yellow-orange suspension was stirred overnight and warmed slowly to room temperature. The resultant red-brown solution was concentrated to ~3 mL under vacuum and chromatographed on neutral alumina. Elution with 100% Et_2O gave a single yellow band containing **34** and unreacted carbodiimide. This band was collected, concentrated to ~3 mL, and reloaded onto the chromatography column. The product band was first washed thoroughly with 100% pentane before being eluted with 1:3 Et_2O/pentane. Removal of the volatiles from the yellow band gave complex **34** (0.20 g, 0.72 mmol, 76% yield) as a yellow microcrystalline solid.

34: IR (CH_2Cl_2) ν_{CO} 1948 (s), 1889 (s) ν_{CN} 2100 (m br) cm^{-1} (lit.:[24] IR (hexane) ν_{CO} 1952, 1907, ν_{CN} 2114, 2078); ^1H NMR (CD_2Cl_2) δ 4.55 (s, 5H, *Cp*), 1.41 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 230.8 (Mn—*C*O), 177.5 ($Mn—N{\equiv}C$), 82.2 (*Cp*), 57.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$); MS (EI) *m/z* 259 (M^+), 203 ($M^+ - 2$ CO).

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ (9a) and $Cp(CO)_2Mn{=}C{=}CH_2$ (10a) with $Pr^iN{=}C{=}NPr^i$. Carbyne complex **9a** was generated by the reaction of $Cp(CO)_2Mn{=}C(OMe)Me$ (0.50 g, 2.00 mmol) with BCl_3 (2.2 equiv, 4.4 mL of a 1.0 M solution in hexanes) in hexane at −78 °C and isolated as described above. The complex was then dissolved in 15 mL of THF at −78 °C, and $Pr^iN{=}C{=}NPr^i$ (3.5 equiv, 7.0 mmol, 1.1 mL) was added to the orange solution via syringe. The solution was warmed slowly to room temperature while it was stirred overnight, and stirring was continued for an additional 1 day. The resultant orange solution was concentrated to ~3 mL and chromatographed on neutral alumina. Elution with 1:1 Et_2O/pentane gave first a small red-purple band, which was discarded, and then a second larger yellow band. Removal of solvents from this latter fraction left *ansa*-carbene complex **41** (0.51 g, 1.6 mmol, 78% yield) as a yellow microcrystalline solid. In one reaction of carbyne complex **9a** with $Pr^iN{=}C{=}NPr^i$, complex **45** was isolated in low yield following chromatographic separation of the reaction mixture on neutral alumina. Although this complex was isolated as a microcrystalline solid, its formation could not be reproduced in later reactions.

In a similar reaction, vinylidene complex **10a** was generated from a CH_2Cl_2 suspension of **9a** (from $Cp(CO)_2Mn{=}C(OMe)Me$, 0.50 g) via addition of Et_3N (1.1 equiv, 2.23 mmol, 0.31 mL) at −78 °C. $Pr^iN{=}C{=}NPr^i$ (2.5 equiv, 5.04 mmol, 0.79 mL) was then added to the orange solution via syringe, and the reaction mixture was stirred for ~4 h while it was warmed to 0 °C. The solution was stored overnight at −20 °C, stirred an additional 3 h at 0 °C, and then warmed to room temperature. The solution was filtered via cannula through a plug of Celite, and the resulting orange filtrate was concentrated to ~3 mL and chromatographed on neutral alumina as described above for the reaction of **9a** with $Pr^iN{=}C{=}NPr^i$. This gave **41** (0.36 g, 1.10 mmol) in 55% yield.

In order to distinguish between the peaks due to Mn=*C* and Mn—*C*O in the ^{13}C NMR spectrum, a sample of the product was stirred at room temperature in CH_2Cl_2 under an atmosphere of ^{13}CO for several days. The ^{13}C NMR spectrum of the product after treatment showed enhancement of the broad signal at δ 235.6, whereas the sharp singlet at δ 237.4 remained unchanged, establishing the former as the Mn—*C*O peak and the latter as the Mn=*C* peak.

41: IR (CH_2Cl_2) ν_{CO} 1915 (s), 1843 (s), $\nu_{C=C}$ 1523 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.16 (br d, 1H, J_{HH} = 9.2 Hz, N—*H*), 4.74 (t, 2H, J_{HH} = 2.1 Hz, H_2 and H_5 of *Cp*), 4.44 (d, 1H, J_{HH} = 1.4 Hz, $C{=}C(H_2)$ (note: The second doublet assignable to $C{=}C(H)_2$ is obscured by the signal due to H_3 and H_4 of the Cp ring at δ 4.40 (t, 2H, J_{HH} = 2.1 Hz, H_3 and H_4 of *Cp*), 4.24 (d sept, AMX pattern, 1H, J_{HH} = 9.2, 6.5 Hz, $N(H)C(H)(CH_3)_2$), 4.10 (sept, 1H, J_{HH} = 7.2 Hz, $N—C(H)(CH_3)_2$), 1.40 (d, 6H, J_{HH} = 7.2 Hz, $N—C(H)(CH_3)_2$), 1.26 (d, 6H, J_{HH} = 6.5 Hz, $N(H)C(H)(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 237.4 (Mn=*C*), 235.6 (Mn—*C*O), 146.2 ($C{=}C(H)_2$), 108.3 (C_1 of *Cp*), 91.8 ($C{=}C(H)_2$), 82.6 (C_2 and C_5 of *Cp*), 80.6 (C_3 and C_4 of *Cp*), 52.2 ($N(H)—C(H)(CH_3)_2$), 49.0 ($N—C(H)(CH_3)_2$), 24.0 ($N—C(H)(CH_3)_2$), 20.7 ($N(H)—C(H)(CH_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 146.4 (s, $C{=}C(H)_2$), 108.3 (br m, C_1 of *Cp*), 91.8 (t, J_{CH} = 159.9 Hz, $C{=}C(H)_2$), 82.9 (dq, J_{CH} = 6.9, 145.9 Hz, C_2 and C_5 of *Cp*), 80.7 (dq, J_{CH} = 6.5, 179.2 Hz, C_3 and C_4 of *Cp*), 52.2 (d, J_{CH} = 130.2 Hz, $N(H)—C(H)(CH_3)_2$), 49.0 (d, J_{CH} = 136.2 Hz, $N—C(H)(CH_3)_2$), 24.0 (q, J_{CH} = 126.6 Hz, $N—C(H)(CH_3)_2$), 20.8 (q, J_{CH} = 127.2 Hz, $N(H)—C(H)(CH_3)_2$); MS (+FAB) *m/z* 328 (M^+). Anal. Calcd for $C_{16}H_{21}MnN_2O_2$: C, 58.54; H, 6.45. Found: C, 58.54; H, 6.47.

45: IR (CH_2Cl_2) ν_{CO} 1918, 1848, 1653 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.66 (br, 2H, N*H*), 4.97 (t, 2H, J_{HH} = 2.2 Hz, $C_5H_4C\{O\}Me$), 4.58 (t, 2H, J_{HH} = 2.2 Hz, $C_5H_4C\{O\}Me$), 4.38 (br, 1H, C*H*Me_2), 3.58 (br, 1H, C*H*Me_2), 2.23 (s, 3H, $C_5H_4C\{O\}CH_3$), 1.65 (br, 12H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 233.0 (Mn—*C*O), 221.8 (Mn=*C*), 196.4 ($C_5H_4C\{O\}CH_3$), 90.4, 87.9, 87.7, 83.5, 83.4 ($C_5H_4C\{O\}CH_3$), 51.4 ($N—CPr^i$), 43.5 ($N\text{-}CPr^i$), 27.0 ($C_5H_4C\{O\}CH_3$), 24.3, 22.4 ($CH(CH_3)_2$); MS (EI) *m/z* 346 (M^+), 290 ($M^+ - 2CO$). Anal. Calcd for $C_{16}H_{23}MnN_2O_3$: C, 55.49; H, 6.69. Found: C, 56.02; H, 6.64.

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_2CH_3]^+$ (9b) with $Bu^tN{=}C{=}NBu^t$. Carbyne complex **9b** was generated in hexane at −78 °C from $Cp(CO)_2Mn{=}C(OEt)CH_2CH_3$ (0.50 g, 1.91 mmol) and BCl_3 (2.2 equiv, 4.20 mmol, 4.2 mL of a 1.0 M solution in hexanes) and isolated as described above. The carbyne thus obtained was suspended in 20 mL of CH_2Cl_2 at −78 °C, and $Bu^tN{=}C{=}NBu^t$ (1.1 equiv, 2.10 mmol, 0.40 mL) was added via syringe and the mixture stirred for 15 min, giving an orange suspension. Et_3N (2.2 equiv, 4.20 mmol, 0.58 mL) was then added via syringe, causing dissolution of all solids and formation of a homogeneous red-orange solution. This solution was stirred overnight and warmed to room temperature while the reaction flask remained immersed in the low-temperature bath. The deep red-purple solution was then concentrated to ~1 mL under vacuum and 10 mL Et_2O added, giving a violet solution with a large amount of solid precipitate. The supernatant was removed via cannula and filtered through a plug of Celite into another Schlenk flask. The solid residue was washed with additional Et_2O, and the supernatants were filtered through Celite and combined with the violet filtrate until the washings were nearly colorless. The combined filtrates were then chromatographed on neutral alumina. Elution with 100% Et_2O gave a large red-brown band, which was collected, concentrated to ~10 mL under vacuum, and rechromatographed. Elution with 1:1 Et_2O/pentane gave first a red-brown band, and removal of the volatiles from this fraction under vacuum gave a red oil. Continued elution with 100% Et_2O gave a violet band, and removal of the volatiles from this band under vacuum gave **46** as a violet crystalline solid. The red-brown oil from the first fraction was redissolved in minimal Et_2O and rechromatographed. Elution with 1:1 Et_2O/pentane gave a small purple band followed by a small brown band, both of which were discarded on the basis of their IR spectra. Elution with 100% Et_2O gave a small violet band, which was collected into the flask containing the previously isolated **46**, and removal of the volatiles from this mixture gave **46** (0.28 g, 0.62 mmol, 32% yield) as a violet crystalline solid.

46: IR (CH_2Cl_2) ν_{CO} 2012 (s), 1959 (s), $\nu_{C=C}$ 1652 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.02 (s, 5H, *Cp*), 1.99 (s, 3H, C*H*$_3$), 1.38 (s, 18H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 361.7 (Mn=*C*), 226.3 (Mn—*C*O), 168.1 ($C{=}C—(C)^+$), 118.7 ($Mn{=}C{=}C$), 88.5 (*Cp*), 83.4 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$), 14.6 ($C{=}C—CH_3$); ^{13}C NMR (CD_2Cl_2) δ 226.3 (br s, Mn—*C*O), 118.7 (br m, $Mn{=}C{=}C$), 88.5 (d, pent, J_{CH} = 8.0, 180.3 Hz, *Cp*), 30.3 (q, J_{CH} = 127.9 Hz, $C(CH_3)_3$), 14.6 (q, J_{CH} = 131.4 Hz, $C{=}C—CH_3$); ^{11}B NMR (CD_2Cl_2; vs. external $BF_3{\cdot}Et_2O$ at δ 0)[25] δ 4.51; MS (−FAB) *m/z* 451 (M^+, BCl_2 pattern), 422 (M^+ − CO; BCl_2 pattern). Anal. Calcd for $C_{19}H_{26}BCl_2MnN_2O_2$: C, 50.59; H, 5.81. Found: C, 50.78; H, 5.87.

Reaction of $Cp(CO)_2Re{=}C{=}CH_2$ (7) with Benzalazine. Carbyne complex **6** (79.4 mg, 0.163 mmol) was dissolved in CH_2Cl_2 at −50 °C, and the mixture was stirred for ~5 min to generate **7**. A 2-fold excess of benzalazine was then added, and the resulting solution was stirred at −50 °C for 1 h and then slowly warmed to room temperature. The solvent was then removed under vacuum to afford an orange oil, which was chromatographed on neutral alumina. Elution with 1:1 CH_2Cl_2/pentane gave first a yellow band containing unreacted Ph(H)C=NN=C(H)Ph, and continued elution with 100% CH_2Cl_2 gave a second orange band of **48**. Removal of the volatiles from this fraction afforded **48** (36.8 mg, 0.043 mmol, 53% yield) as an orange microcrystalline solid.

48: IR (CH_2Cl_2) ν_{CO} 1926, 1847 cm^{-1}; ^1H NMR (C_6D_6) δ 7.95–6.88 (m, 10H, *Ph*), 4.91 (s, 10H, *Cp*), 4.03 (dd, 2H, J_{HH} = 7.5, 2.4 Hz, C(*H*)Ph), 1.85 (dd, 2H, J_{HH} = 16.6, 7.5 Hz, C*H*$_2$), 1.81 (dd, 2H, J_{HH} = 16.6, 2.4 Hz, C*H*$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 228.3 (Re=*C*), 206.9, 206.5 (Re—*C*O), 148.2–125.9 (*aryl*), 87.5 (*Cp*), 38.3 (*C*(H)Ph), 22.6 (*C*H$_2$).

Reaction of $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ (9a) with Benzalazine. Carbyne complex **9a** was generated as described above from $Cp(CO)_2Mn{=}C(OMe)CH_3$ (0.44 g, 1.77 mmol) and excess BCl_3 (1.0 M in hexanes). The solid **9a** thus obtained was dissolved in ~25 mL of dry THF at -50 °C, and benzalazine (0.82 g, 3.9 mmol) was added. The resulting solution was stirred at -50 °C for 3 h and then slowly warmed to room temperature. Removal of the volatiles left a red oil, which was chromatographed on neutral alumina. Elution with 1:1 CH_2Cl_2/pentane gave first a yellow band containing unreacted Ph(H)C=NN=C(H)Ph, and continued elution with 100% CH_2Cl_2 gave a second yellow band of **47**. Removal of the volatiles from this fraction under vacuum left **47** (0.42 g, 0.72 mmol, 41% yield) as a yellow microcrystalline solid.

47: IR (CH_2Cl_2) ν_{CO} 1926, 1858 cm^{-1}; ^1H NMR (C_6D_6) δ 7.38–6.99 (10H, *Ph*), 5.34 (dd, 2H, J_{HH} = 10.2, 2.4 Hz, C(*H*)Ph), 4.03 (s, 10H, *Cp*), 3.34 (dd, 2H, J_{HH} = 18.4, 10.2 Hz, C*H*$_2$), 3.10 (dd, 2H, J_{HH} = 18.4, 2.4 Hz, C*H*$_2$); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ 245.5 (Mn=*C*), 234.0, 232.9 (Mn—*C*O), 140.6–126.6 (*aryl*), 84.0 (*Cp*), 66.3 (*C*(H)Ph), 59.3 (*C*H$_2$); MS (+FAB) *m/z* 612 (M^+). Anal. Calcd for $C_{32}H_{26}Mn_2N_2O_4$: C, 62.77; H, 4.28. Found: C, 62.88; H, 4.28.

X-ray Diffraction Studies of 15b, 45, 46, and 47 (University of Delaware). All specimens were mounted on glass fibers with epoxy cement, which also served as an atmospheric barrier. Preliminary photographic characterization revealed no symmetry higher than triclinic for **15b** and **47** and orthorhombic for **45** and **46**. For both of the triclinic structures centrosymmetry was initially assumed and was verified by the results of refinement. Systematic absences in the diffraction data for **46** allowed either of the space groups $Pca2_1$ or *Pcam* with the noncentrosymmetric setting preferred (Rogers test: η = 1.2(1)). Systematic absences in the diffraction data for **45** uniquely defined the space group *Pcba*. In **46**, no plane perpendicular to the *c* axis relates the two crystallographically independent molecules found. A semiempirical correction for absorption was applied to the data for **15b**, but not for the three Mn-containing structures (ψ-scan data showed a <10% variation).

The structures were solved by heavy-atom methods. Disorder found in one of the two independent molecules in **15b** is discussed in the text. The occupancies were refined as reported. In **46**, in both of the crystallographically independent molecules, the *tert*-butyl groups are rotationally disordered in two nearly equally occupied orientations. For **15b**, **45**, and **47** all non-hydrogen atoms were anisotropically refined, whereas for **46** all Mn, Cl, N, and O atoms and the C atoms in the CO groups plus C(8), C(9), C(10), and C(11) were anisotropically refined. All hydrogen atoms were found and refined for **47** and were idealized for the remaining structures. Hydrogen atom contributions were ignored for the disordered *tert*-butyl groups in **46** and the disordered Cp rings in **15b**.

All calculations used SHELXTL software (G. Sheldrick, Siemens, Madison, WI).

X-ray Diffraction Studies of 17a, 17c′, and 41 (CNRS, Toulouse, France). Crystals of **17a** suitable for X-ray diffraction analysis were obtained via recrystallization from Et_2O/hexane solution at -20 °C. Crystals of **17c′** were similarly obtained via recrystallization from pentane solution at room temperature. The initial diffraction data indicated triclinic symmetry for both compounds, and the centrosymmetric space group $P\bar{1}$ was initially assumed and was verified by the results of refinement. For **41**, initial diffraction data indicated monoclinic symmetry, and systematic absences in the diffraction data allowed either of the space groups $P2_1$ or $P2_1/m$. The latter centrosymmetric setting was verified by the presence of a crystallographic mirror plane. For each compound, the intensities were corrected for absorption by the semiempirical ψ-scan method.

The position of the Mn atoms in each compound were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. For **17c′**, the MeCp fragment in molecule b was found to be disordered, and two MeCp fragments were introduced with site occupancy factors fixed to 0.7 and 0.3, respectively, and the C_5H_4 rings were constrained as rigid planar pentagons (C–C = 1.420 Å). All non-hydrogen atoms except for the carbon atoms of the phenyl rings and the carbon atoms of the MeCp fragments in **17c′** were anisotropically refined. The hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements.

The structures were solved by using the SHELXS-86 package[34] and refined using the SHELXS-76 package.[35]

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Supplementary Material Available: For **15b**, **17a**, **17c′**, **41**, **45**, **46**, and **47**, tables of atomic coordinates, anisotropic temperature factors, all bond lengths and bond angles, and calculated hydrogen atom positions (49 pages). Ordering information is given on any current masthead page.

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[34] Sheldrick, G. Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.

[35] Sheldrick, G. Program for Crystal Structure Determination; University of Cambridge: Cambridge, U.K., 1976.