chloride, $(CH_3)_2ZrCl_2{\cdot}C_{10}H_{24}N_4$, with trimethylaluminum, dimethylaluminum chloride, and $(CH_3)Al(OCH_3)Cl$, as illustrated in Figure 4, could readily provide $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II).

Several points regarding structure and bonding in I and II are worthy of note. The Al–Cl bond distance of 2.130 (3) Å involving the four-coordinate aluminum atom Al(2) in II is considerably shorter than the corresponding Al–Cl bond distance of 2.368 (2) Å involving the six-coordinate aluminum atom Al(1). Moreover, it is interesting to note that the six-coordinate aluminum–chlorine bond distance in II is shorter than the analogous Al(1)–Cl(1) bond distance of 2.394 (1) Å observed in I. Indeed, the Al–Cl bond distances involving the six-coordinate aluminum atoms in I and II are considerably longer than the Al–Cl distances of 2.202 (5) and 2.197 (7) Å reported for the seven-coordinate aluminum atom in the $[Cl_2Al{\cdot}15\text{-crown-}5]^+$ complex.[44]

Organoaluminum chemistry relative to amines is currently experiencing great activity principally due to the utilization of Al–N compounds as potential precursors to ceramic materials.[45-47] For example, a novel six-coordinate aminoalane complex has recently been reported that, upon pyrolysis, provides aluminum nitride and silicon carbide.[48] Future contributions from this laboratory will continue to examine the interactions of organoaluminum species with various amines.

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Registry No. I, 122699-35-8; II, 122699-37-0; *N*,*N*-bis(3-aminopropyl)ethylenediamine, 10563-26-5; diethylaluminum chloride, 96-10-6; cyclam, 295-37-4; trimethylaluminum, 75-24-1.

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters, molecular plots, and a summary of data collection and refinement (33 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Isocyanide Insertion Reactions of Manganese(I) Alkyl and Iminoacyl Complexes

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The reaction of $(CO)_5MnCH_2C_6H_4$-*p*-X (X = Cl, OMe) with *p*-tolyl isocyanide in the presence of PdO affords the products of double insertion $(CO)_4Mn[C({=}N$-*p*-tolyl$)C({=}N$-*p*-tolyl$)CH_2C_6H_4$-*p*-X] (**2a,b**). Also isolated was **3a**, $(CO)_4Mn[C\{{=}CH(C_6H_4$-*p*-Cl$)\}N($*p*-tolyl$)C(NH$-*p*-tolyl)], the product of intramolecular imino N attack on a coordinated *p*-tolyl isocyanide. **2a,b** react with an additional equivalent of isocyanide affording products which depend on the identity of the isocyanide. With *p*-tolyl isocyanide and cyclohexyl isocyanide, carbene complexes $(CO)_4Mn[C({=}N$-*p*-tolyl$)C\{{=}CH(C_6H_4$-*p*-X$)\}N($*p*-tolyl$)C(NHR)]$ (**4a**, X = Cl, R = *p*-tolyl; **4b**, X = OMe, R = C_6H_{11}; **4c**, X = Cl, R = C_6H_{11}) and $(CO)_4Mn[C({=}N$-*p*-tolyl$)C(NH$-*p*-tolyl$)C(C_6H_4$-*p*-X$)C(NHR)]$ (**5a**, X = Cl, R = *p*-tolyl; **5b**, X = OMe, R = C_6H_{11}) are isolated. With bulky *t*-BuNC, $(CO)_4(CN$-*t*-Bu$)Mn[C({=}N$-*p*-tolyl$)C({=}N$-*p*-tolyl$)CH_2C_6H_4$-*p*-Cl] (**7a**) and $(CO)_3(CN$-*t*-Bu$)$-$Mn[C({=}N$-*p*-tolyl$)C({=}N$-*p*-tolyl$)CH_2C_6H_4$-*p*-Cl] (**8a**) are obtained. **4a** can be protonated at the iminoacyl N giving a bis(carbene) complex, **6a**. Mechanisms for the formation of **2**, **3**, and **4** are proposed. The last is supported by isolation of **7**. The structures of **2b**, **3a**, **4a**, **4b**, **4c**, and **6a** have been solved by single-crystal X-ray diffraction methods. Crystallographic data [space group, *a* (Å), *b* (Å), *c* (Å), *β* (deg), *Z*, observed reflections, R_w]: for **2b**, $P2_1/n$, 19.616 (2), 12.287 (2), 11.368 (2), 103.13 (1), 4, 1985, 0.0379; for **3a**, $P2_1/c$, 6.611 (1), 18.937 (2), 20.510 (2), 90.111 (8), 4, 2119, 0.0407; for **4a**, $P2_1/n$, 16.354 (5), 13.273 (2), 15.513 (4), 108.96 (2), 4, 2292, 0.0388; for **4b**, $P2_1/n$, 15.986 (2), 13.748 (2), 15.681 (2), 108.01 (1), 4, 2033, 0.0370; for **4c**, $P2_1/n$, 15.915 (2), 13.550 (2), 15.611 (2), 108.723 (9), 4, 3303, 0.0382; and for **6a**, $P2_1/c$, 13.054 (2), 15.721 (2), 17.798 (3), 104.79 (1), 4, 2026, 0.0392.

Introduction

Insertion reactions are of fundamental importance in organometallic chemistry.[1,2] The most completely studied insertion reaction is that of carbon monoxide which plays a key role in many reactions homogeneously catalyzed by transition-metal species—for example, hydroformylation,[3] homologation,[4] and oxygenate production by hydrogenation of CO.[5] CO insertion chemistry has been reviewed.[6-8]

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Table I. Spectral Data

compd	IR, cm^{-1}	^1H NMR δ
2a	2064 (s), 1995 (s), 1985 (s), 1954 (s) ($C{\equiv}O$); 1620 ($C{=}N$)^a	7.24–6.78 (m, 12 H), C_6H_4; 3.80 (s, 2 H), CH_2; 2.37 (s, 3 H), CH_3; 2.35 (s, 3 H), CH_3
2b	2072 (m), 1989 (s), 1980 (s), 1954 (s) ($C{\equiv}O$); 1624 (w), 1615 (w) ($C{=}N$)^b	7.22–6.80 (m, 12 H), C_6H_4; 3.74 (s, br, 5 H), CH_2 + OCH_3; 2.35 (s, br, 6 H), CH_3
3a	3315 (m) (N–H); 2067 (s), 1989 (s, br), 1942 (s) ($C{\equiv}O$); 1592 (m), 1531 (s) ($C{=}N$)^c	7.75 (s, br, 1 H), NH; 7.40–7.06 (m, 12 H), C_6H_4; 6.54 (s, 1 H), $C{=}CH$; 2.46 (s, 3 H), CH_3; 2.35 (s, 3 H), CH_3
4a	3288 (w), N–H; 2060 (m), 1976 (s, br) ($C{\equiv}O$); 1589 (m, br), 1518 (m) ($C{=}N$)^c	7.85 (s, br, 1 H), NH; 7.52–7.02 (m, 16 H), C_6H_4; 5.28 (s, 1 H), $C{=}CH$; 2.47 (s, 3 H), CH_3; 2.30 (s, 3 H), CH_3
4b	3310 (w), N–H; 2058 (w), 1987 (s), 1973 (s), 1939 (s) ($C{\equiv}O$); 1559 (m), 1550 (m), 1530 (m), 1523 (m) ($C{=}N$)^b	7.45–6.60 (m, 14 H), C_6H_4 + NH; 5.21 (s, 1 H), $C{=}CH$; 3.8–4.1 (m, br, 1 H), CH of C_6H_{11}; 3.73 (s, 3 H), OCH_3; 2.46 (s, 3 H), CH_3; 2.32 (s, 3 H), CH_3; 2.24–1.15 (m, 10 H), CH_2 of C_6H_{11}
5a	2055 (m), 1990 (s), 1969 (s), 1957 (s) ($C{\equiv}O$); 1595 (m), 1522 (m) ($C{=}N$)^a	7.14–6.70 (m, 18 H), C_6H_4 + NH; 2.33 (s, 6 H), CH_3; 2.23 (s, 6 H), CH_3
5b	2059 (m), 1992 (s), 1972 (s), 1941 (s) ($C{\equiv}O$); 1600 (m, br), 1520 (m) ($C{=}N$)^a	7.17–6.32 (m, 14 H), C_6H_4 + NH; 4.02–3.77 (m, br, 1 H), CH of C_6H_{11}; 3.60 (s, 3 H), OCH_3; 2.27 (s, 3 H), CH_3; 2.12 (s, 3 H), CH_3; 1.79–1.15 (m, 10 H), CH_2 of C_6H_{11}
7a	2168 (m) ($C{\equiv}N$); 2068 (s), 1997 (s), 1975 (s), 1962 (s) ($C{\equiv}O$); 1643 (w), 1638 (w) ($C{=}N$)^a	7.11–6.71 (m, 12 H), C_6H_4; 3.88 (s, br, 1 H), CH_2; 3.74 (s, br, 1 H), CH_2; 2.32 (s, 6 H), CH_3; 1.35 (s, 9 H), $C(CH_3)_3$
8a	2148 ($C{\equiv}N$); 2010 (s), 1953 (s), 1928 (s) ($C{\equiv}O$); 1618 (w, br) ($C{=}N$)^b	7.31–6.78 (m, 12 H), C_6H_4; 3.72 (dd, 2 H, J = 13.2 Hz), CH_2; 2.32 (s, 6 H), CH_3; 1.34 (s, 9 H), $C(CH_3)_3$

^{a} In hexane. ^{b} In CCl_4. ^{c} In $CHCl_3$.

A general feature of CO insertion into metal–carbon bonds seems to be the migration of the alkyl group to an already coordinated CO ligand in the cis position. Carbonylation of early d-block, lanthanide and actinide complexes often leads to η^2-acyls[9] while later d-block complexes are more likely to generate η^1 species, although there are some exceptions.[10–14]

Isocyanides are isoelectronic with CO, and a good deal of interest in their insertion reactions into metal–carbon bonds has been evident.[15,16] Recent examples of isocyanide insertion involve the metal–carbon bonds formed by Ti,[17,18] Zr,[19] V,[20] Cr, Mo, W,[21,22] Fe,[23–25] Ni,[26] Pd,[27–37] Pt,[38] Zn,[39] Y,[40] and U.[41–43] Isocyanides have also been found to insert into metal–nitrogen bonds in amide complexes of Mo[44] and U[45,46] as well as in a Pd formamidinato complex.[47] Other modes of reactivity recently reported include insertion into a U-ylide C bond,[48] a U–Ge bond,[49] a Y–H bond,[50] M–H–M bonds,[51,52] and M–M bonds[53,54] as well as

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catalyzed insertion into benzene C–H bonds.[55,56] With the exception of work by Adams,[57] who obtained a diazabutadiene complex by treating $[Mn(CO)_4(CNCH_3)]^-$ with CH_3I, and by Kuty,[58] who found that reaction of $RMn(CO)_4(CNR')$ with a phosphite gave carbonyl insertion exclusively, information on isocyanide insertion in Mn complexes seems to be lacking in the literature.

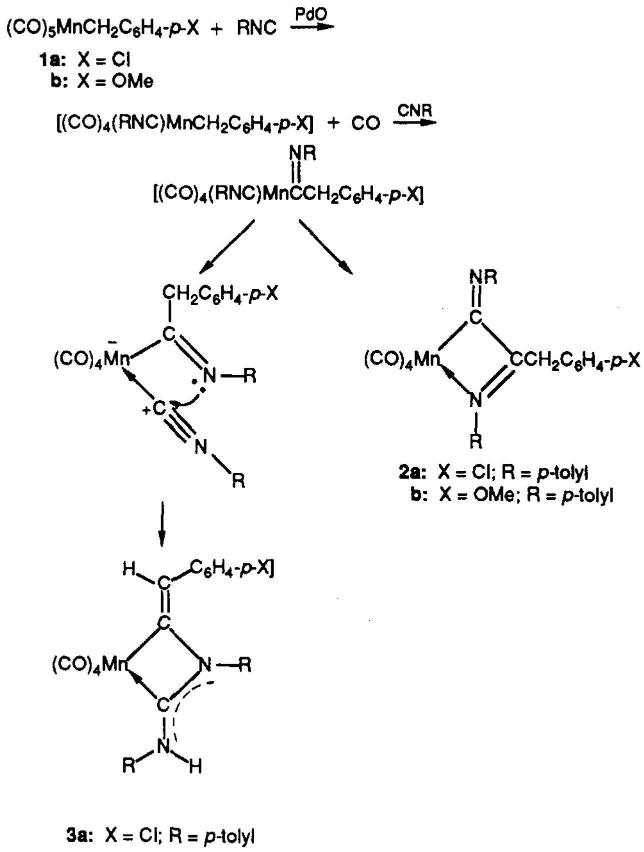
We report herein the results of reactions of manganese carbonyl complexes with isocyanides which lead to insertions into both Mn–C and Mn–N bonds.

Results and Discussion

Reaction of Isocyanide with Alkyl Manganese Pentacarbonyls. We have previously reported[58] that n-C_4H_9NC, t-C_4H_9NC, and $C_6H_{11}NC$ react with p-$XC_6H_4CH_2Mn(CO)_5$ (X = H, Cl) to afford the products of carbonylation, p-$XC_6H_4CH_2C(O)Mn(CO)_4(CNR)$, which undergo smooth thermal decarbonylation yielding p-$XC_6H_4CH_2Mn(CO)_4(CNR)$. Recently, we found[59] that p-$XC_6H_4CH_2C(O)Mn(CO_4)(CN$-$p$-tolyl) (X = H, Cl, OCH_3), prepared from the alkyl Mn complexes and the aromatic isocyanide, produced dimeric compounds containing a coordinated 1,4-diazabuta-1,3-diene ligand on thermolysis.

In seeking to understand the remarkable change in chemistry brought about by the aromatic isocyanide as contrasted with the aliphatic ones, we set out to prepare complexes of the type p-$XC_6H_4CH_2Mn(CO)_4(CN$-p-tolyl). We intended to test the possible intermediacy of these in the dimerization reaction. Coville and co-workers[60] have lately shown that several binary carbonyls undergo CO replacement by a variety of alkyl and aryl isocyanides in the presence of catalytic amounts of PdO. Furthermore, the number of CO's replaced corresponded to the stoichiometry in which the reactants were mixed. We decided to try to achieve direct replacement of CO by CN(p-tolyl) (instead of carbonyl insertion) by treating **1a,b** with an equimolar quantity of the aromatic isocyanide in the presence of PdO. Whether the reagents were mixed in 1:1 or 1:2 ratio, the result was that shown in Scheme I.

Scheme I



Apparently, PdO does catalyze direct replacement of CO by isocyanide; however, rapid and exclusive insertion of isocyanide occurs creating a vacant coordination position that is occupied by a second mole of isocyanide. At this point, two possible pathways are available. The major one is insertion of a second isocyanide to afford the bis(iminoacyl) complexes **2a,b**. The reaction stops when the N lone pair occupies the coordination site on Mn vacated by the second inserting isocyanide resulting in a 1-mangana-2-azacyclobutene ring. In the minor pathway, an isocyanide polarized by coordination is attacked by the lone pair of the iminoacyl N producing **3**, which contains a four-membered ring. Transfer of one of the benzylic hydrogens to the isocyanide occurs creating a ligand that is a vinyl at one end and a diaminocarbene at the other. This ring can be described as a 1-mangana-3-azacyclobutane. Rothwell and co-workers[61] have observed transfer of a benzylic hydrogen to the carbon of an iminoacyl group that then rearranges to give a vinylamide ligand in Zr and Hf complexes. Complexes **2a,b** are stable to this type of rearrangement.

Spectral data for **2a,b** (Table I) are consistent with the structure shown in Scheme I. Both compounds exhibit four terminal CO stretches in the IR, as expected for a cis-disubstituted octahedral carbonyl. Multiplets due to phenyl protons of benzyl groups as well as p-tolyl isocyanide phenyl groups are present in the ^1H NMR. Two p-tolyl methyl signals are resolved in **2a**, but not in **2b**. Neither compound shows separate signals for the diastereotopic benzylic protons.

The IR spectrum of **3a** has a sharp N–H stretch at 3315 cm^{-1} as well as strong bands attributable to terminal CO stretches at 2067, 1989 (br), and 1942 cm^{-1}. The broad band at 1989 cm^{-1} evidently contains the fourth band expected for a cis-disubstituted octahedral geometry. Bands at 1592 and 1531 cm^{-1} are in the correct region for C=N stretches. The ^1H NMR spectrum displays an N–H signal at 7.75 ppm, a phenyl multiplet from 7.40 to 7.06 ppm, an olefinic proton signal at 6.45 ppm, and two methyl signals at 2.46 and 2.35 ppm. The X-ray crystal structures for **2b** and **3a** (vide infra) confirm the proposed atomic arrangements. (**2b** was prepared because **2a** could not be crystallized. Hence, no effort was made to isolate the analogous compound **3b**.)

3a is rather unstable in solution converting to **2a** and decomposing to unidentified products. Our experiments

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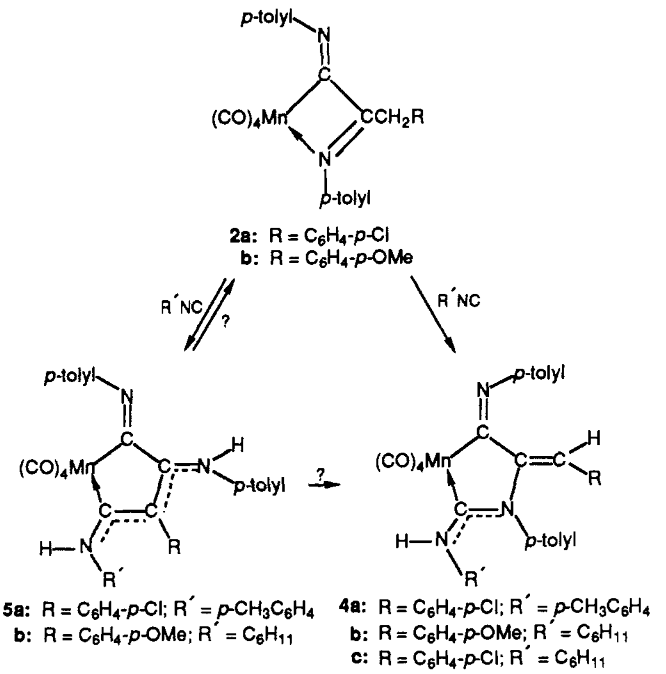
Scheme II

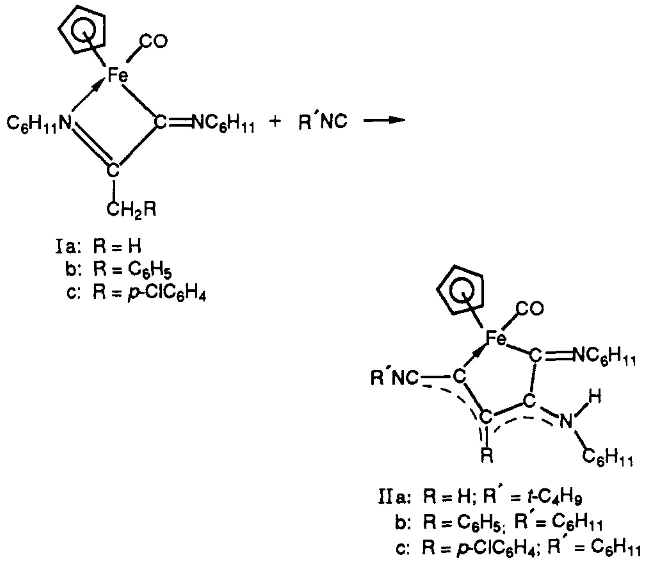


2a: R = C_6H_4-p-Cl; **b**: R = C_6H_4-p-OMe

5a: R = C_6H_4-p-Cl; R′ = p-$CH_3C_6H_4$; **b**: R = C_6H_4-p-OMe; R′ = C_6H_{11}

4a: R = C_6H_4-p-Cl; R′ = p-$CH_3C_6H_4$; **b**: R = C_6H_4-p-OMe; R′ = C_6H_{11}; **c**: R = C_6H_4-p-Cl; R′ = C_6H_{11}

Scheme III



Ia: R = H; b: R = C_6H_5; c: R = p-ClC_6H_4

IIa: R = H; R′ = t-C_4H_9; b: R = C_6H_5; R′ = C_6H_{11}; c: R = p-ClC_6H_4; R′ = C_6H_{11}

do not rule out the possibility that **3a** is the intermediate on the pathway to the major product **2a**, but we find it difficult to believe that this is indeed the case. First, multiple insertion products of Fe,[62] Ni, and Pd[15,16] are known in which no products analogous to **3** were obtained. Second, **2a,b** react with additional isocyanide affording only **4** and **5**, products analogous to **3** (vide infra), suggesting that insertion of a third isocyanide is not competitive with the intramolecular attack on coordinated ligand. Moreover, neither **4** nor **5** rearranges to tris(iminoacyl) species. Finally, Cardaci and co-workers[23-25] have recently reported the preparation of $[\overline{Fe(CO)(CNC_6H_{11})(PMe_3)_2\{C(=CH_2)N(C_6H_{11})C}(NHC_6H_{11})\}]^+$ analogous to **3a** by rearrangement of the product of double isocyanide insertion $Fe(CO)(PMe_3)_2(CNC_6H_{11})I(C\{=NC_6H_{11}\}C\{=NC_6H_{11}\}CH_3)$. That is, the rearrangement in the six-coordinate Fe complex proceeds with intramolecular attack on one of the isocyanides giving the carbene complex which does not rearrange to a product of multiple insertions.

In order to investigate whether **2a,b** would insert another isocyanide and/or behave as polymerization catalysts for isocyanide, we allowed **2a** to react with 1 equiv of p-tolyl isocyanide in toluene at ambient temperature. Two products were isolated as shown in Scheme II.

4a was the major product (43% yield) while **5a** was the minor product (17% yield). Spectroscopic properties (Table I) are in accord with the structure for **4a** shown in Scheme II. In particular, a signal at 5.28 ppm in the ^{1}H NMR shows the presence of an olefinic proton while an N*H* proton signal (which disappears on treatment with D_2O) is seen at 7.85 ppm with the N-H stretch appearing at 3288 cm^{-1} in the IR. An X-ray crystal structure (vide infra) confirms the atomic arrangement. **4a**, like **3a**, is the product of a formal insertion of isocyanide into a Mn-N bond.

We lack conclusive evidence for the structure proposed for **5a**. Four stretches in the terminal CO region are typical of a *cis*-$M(CO)_4L_2$ molecule of local C_s symmetry. Stretches assignable to C=N double bonds are also observed at 1595 and 1522 cm^{-1}, but no N—H stretches are seen in the IR. The ^{1}H NMR displays methyl proton signals at 2.23 and 2.33 ppm and a broad multiplet (7.14–6.70 ppm) which integrates for the total number of protons expected in phenyl rings and N-H bonds. **5a** has the same elemental composition as **4a** since it converts to **4a** both in solution and as an oil stored in the refrigerator over a period of months. We were unable to grow crystals of **5a** possibly because of the continual presence of a small amount of **4a**. Also, the isomerization of **5a** to **4a** prevented us from obtaining meaningful elemental analysis. However, as pointed out above, the conversion of **5a** to **4a** does indicate identity of atomic composition. The structure of **5a** is proposed by analogy with chemistry depicted in Scheme III in which Aoki and Yamamoto[62] allowed Fe complexes analogous to **2** to react with an additional equivalent of isocyanide.

The ^{1}H NMR spectra of II display signals in the 7.6–7.7 ppm region that disappear on treatment of the sample with D_2O and are thus assigned as N-H. This is consistent with the N-H signals in **5a,b** being buried in the multiplet from 6.3 to 7.2 ppm which includes phenyl protons.

In an effort to trap **5a**, a freshly chromatographed sample was treated with HBF_4 which was expected to protonate the imino N. Crystals of the product were grown, but the X-ray structure revealed that rearrangement to **6a**, the N-protonated form of **4a**, had occurred.

In order to establish that the carbene C is indeed the one from the final equivalent of isocyanide, we allowed **2b** to react with $C_6H_{11}NC$ affording **4b** and **5b** which have spectroscopic properties closely matching those of **4a** and **5a**. In addition, the low-resolution mass spectrum of **5b** showed the presence of a weak parent peak at *m/e* 631 which was not seen for **4b**. As expected, the carbene C is the one containing the cyclohexyl ring as shown by the X-ray crystal structure (vide infra).

Isomerization of **5** to **4** could occur directly or **5** could revert to **2** + R′NC which rereact giving **4**; these two possibilities are indicated in Scheme II. We were unable to detect any odor of isocyanide above samples of **5**. Also, samples of **5** remained yellow without visibly detectable amounts of red **2** being present. Neither was any **2** detectable on TLC of samples of **5** partially isomerized to **4**. Hence, if the isomerization pathway does involve re-

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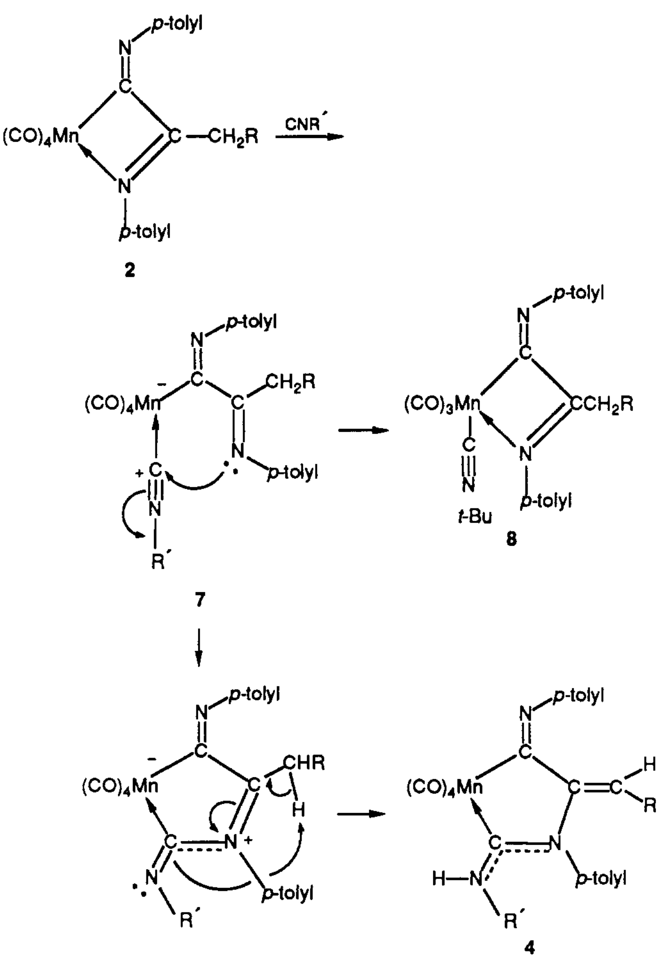
[62] (a) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1972**, *11*, 211. (b) Aoki, K.; Yamamoto, Y. *Inorg. Chem.* **1976**, *15*, 48. (c) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1977**, *16*, 3182.

Scheme IV



version to starting materials, these never accumulated to experimentally observable quantities.

The cyclopentadienyl Fe complexes prepared by Yamamoto and co-workers feature five-membered rings containing only Fe and C atoms which are the formal products of isocyanide insertion into C–H bonds of the alkyl group. The reaction of $Fe(CO)_2(PMe_3)_2(CH_3)I$ with isocyanide by Cardaci et al.[23-25] produces $[Fe(CO)_2(PMe_3)_2\{C(=CH_2)N(C_6H_{11})C(NH(C_6H_{11})\}]^+$ while $Fe(CO)(PMe_3)_2(CNC_6H_{11})I(C\{=NC_6H_{11}\}C\{=NC_6H_{11}\}CH_3)$ rearranges to $[Fe(CO)(CNC_6H_{11})(PMe_3)_2\{C(=CH_2)N(C_6H_{11})C(NHC_6H_{11})\}]^+$, both products resulting from attack on a coordinated isocyanage by a mono(iminoacyl) N. Both feature a four-membered Fe–C–C–N ring. In contrast, Mn exhibits both of the above-mentioned modes of reactivity as well as attack on a coordinated isocyanide by a bis(iminoacyl) N affording a five-membered Mn–C–C–N–C ring. The reasons for the greater versatility in Mn chemistry as compared to Fe are not completely clear at present but are probably related to the greater reactivity of Mn complexes with nucleophiles.

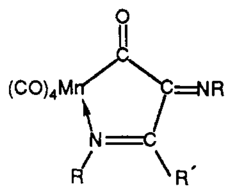
In contrast to the behavior of Pd and Ni complexes that undergo multiple insertions into M–C bonds, Mn complexes seem to form only bis(iminoacyl) species. Thus, there was no detectable competition between insertion of the third isocyanide into the M–C and M–N bonds as was seen for addition of the second isocyanide (vide supra). Only insertion into the Mn–N bond occurs.

Scheme IV depicts a possible mechanism to account for the formation of **4**. The first step involes displacement of the coordinated N of **2** by the entering isocyanide giving **7** with a "dangling" bis(iminoacyl) group. Nucleophilic attack on the positively polarized isocyanide C by the imino N lone pair closes the ring. The reaction is completed by transfer of a benzylic H to the isocyanide N giving **4**. It is possible that the hydrogen is first transferred to the imino N. It is also possible that the hydrogen transfer is not intramolecular. We have no experimental evidence that rules out either of these latter possibilities. An attempt to test whether the hydrogen transfer is intramolecular was unsuccessful because $(CO)_4Mn[C(=N\text{-}p\text{-tolyl})C(=N\text{-}p\text{-tolyl})CD_2C_6H_4\text{-}p\text{-Cl}]$ exchanged D for H on purification by chromatography on silica gel.[63]

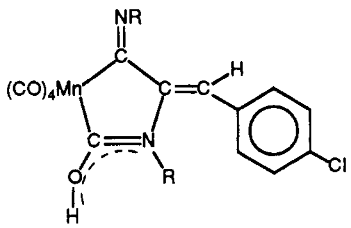
7a ($R = p\text{-ClC}_6H_4$; $R' = t\text{-C}_4H_9$) was isolated in 40% yield when **2a** was allowed to react with 1 equiv of $t\text{-C}_4H_9NC$ in toluene at room temperature. Also obtained was a 27% yield of **8a**. Formation of **7a** is consistent with displacement of coordinated N in **2a** by an entering isocyanide as depicted in Scheme IV. The bulkiness of the *tert*-butyl group hinders nucleophilic attack at the isocyanide C. Formation of **8a** results from intramolecular displacement of CO by the imino lone pair. In solution **7a** converts to **8a** under Ar, but the transformation is impeded under CO.

The IR spectrum of **7a** contains four sharp bands in the range from 1962 to 2068 cm^{-1}, assignable to four terminal carbonyls, as well as sharp band at 2168 cm^{-1} due to a terminal isocyanide and a pair of bands at 1643 and 1638 cm^{-1} due to the two imino double bonds. In the ^{1}H NMR spectrum, the benzylic protons appear as two broad singlets at 3.88 and 3.74 ppm suggesting the possibility of rotomers in solution. For **8a**, the IR spectrum contains three bands of equal intensity due to terminal CO's in the 1928–2010 cm^{-1} region consistent with a facial geometry. These bands are all ca. 40 cm^{-1} lower in energy than those of **7a**, consistent with the replacement of CO by a poorer π-acceptor. A terminal isocyanide band appears at 2148 cm^{-1} and a C=N stretch at 1618 cm^{-1}.

We attempted unsuccessfully to prepare compounds such as III (which would result from CO insertion into the Mn iminoacyl bond of **2**) or IV (which would result from displacement of coordinated imino N in **2** by CO followed by nucleophilic attack on CO polarized by coordination). Benzene solutions of **2a** underwent no carbonyl insertion either at room temperature and 20 psi of CO or at 70 °C and 1000 psi of CO for 24 h. It may be that CO does displace coordinated N at high pressure but that coordinated CO is not sufficiently polarized for intramolecular nucleophilic attack by N and so the system undergoes decarbonylation when pressure is released.



III



IV

Shriver has shown that Lewis acids accelerate alkyl migration in $CH_3Mn(CO)_5$ by a factor of 1 × 10^8.[64] In addition, use of $AlBr_3$ by Lindner and von Au[65] led to the

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[63] Slater, C. P., unpublished results.

[64] Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.

[65] Lindner, E.; von Au, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 824.

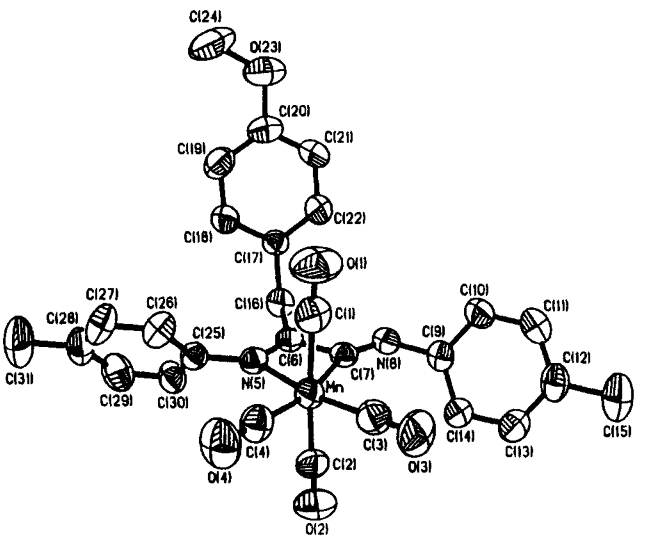

Figure 1. Molecular structure of (CO)$_4$Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)CH$_2$C$_6$H$_4$-*p*-OCH$_3$] (**2b**).

first example of CO insertion into a Re–alkyl bond. However, attempted carbonylation of **2a** using AlCl$_3$ in benzene was also unsuccessful and led only to decomposition of the sample as evidenced by the IR spectrum of the reaction mixture.

A mechanism for the formation of Fe complexes analogous to **5** has been given by Aoki and Yamamoto.[62]

Molecular Structure of (CO)$_4$Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)CH$_2$C$_6$H$_4$-*p*-OCH$_3$] (2b). The molecular structure of **2b** is shown in Figure 1 while atomic coordinates appear in Table II and relevant bond distances and angles in Table III. The complex contains a four-membered metallacyclic ring composed of Mn, N(5), C(6), and C(7). Chelation of the organic moiety occurs through a Mn–iminoacyl C bond and a Mn–iminoacyl N donor–acceptor bond.

The geometry around Mn is a distorted octahedron with the two carbonyl groups along the axis perpendicular to the manganacyclic ring slightly bent back (∠C(1)–Mn–C(2) = 171.3 (2)°) and the carbonyl groups in the plane of the ring having ∠C(3)–Mn–C(4) = 92.8 (2)°. All other C–Mn–C angles are close to, but slightly larger than, the ideal 90°. The carbonyl ligands are all linear. The bite of the bis(iminoacyl) ligand is rather small, the N(5)–Mn–C(7) angle being only 64.4 (1)°. The ∠C(6)–N(5)–C(25) and ∠C(7)–N(8)–C(9) are 124.4 (3)° and 121.3 (3)°, respectively, as expected for sp^2 imino nitrogens. The angle Mn–N(5)–C(25) is larger at 137.4 (3)°. The geometry at C(16) is tetrahedral with ∠C(6)–C(16)–C(17) = 108.9 (3)° and the face of the phenyl ring roughly perpendicular to the metallacyclic ring.

The Mn–C(7) bond distance of 2.067 (4) Å falls within the expected range for a Mn–acyl C bond.[66] The Mn–C(7) distance is shorter than the Mn–acyl C distance in (CO)$_5$MnC(O)CH$_3$ (2.10 Å)[67] and the Mn–benzoyl C distance (2.09 (1) Å) in [Me$_4$N][(CO)$_4$Mn{C(O)Ph}{C(O)Me}][68] but longer than the Mn–acetyl C distance (2.05 (1) Å) in the latter compound. The C(7)–N(8) and C(6)–N(5) distances of 1.274 (4) and 1.287 (4) Å, respectively, are those expected for C–N double bonds (1.28 Å) in which both atoms are sp^2 hybridized. The C(7)–C(6) distance of 1.490 (5) Å agrees with the single C–C bond length for two formally sp^2-hybridized carbons (1.48 Å).[69] The Mn–N(5) distance

Table II. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (CO)$_4$Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)CH$_2$C$_6$H$_4$-*p*-OCH$_3$] (2b)

atom	*x*	*y*	*z*
Mn	728.2 (3)	1866.8 (5)	4721.6 (6)
O(1)	2029 (2)	2150 (3)	3809 (4)
O(2)	−657 (2)	1940 (3)	5382 (3)
O(3)	194 (2)	307 (3)	2755 (3)
O(4)	1306 (2)	87 (3)	6441 (3)
C(1)	1539 (3)	2030 (3)	4165 (4)
C(2)	−124 (2)	1892 (3)	5144 (4)
C(3)	397 (2)	924 (4)	3509 (4)
C(4)	1083 (2)	773 (4)	5780 (4)
N(5)	1034 (2)	3200 (3)	5842 (3)
C(6)	819 (2)	3955 (3)	5062 (4)
C(7)	462 (2)	3372 (3)	3941 (4)
N(8)	173 (2)	3923 (3)	3013 (3)
C(9)	−190 (2)	3408 (3)	1935 (4)
C(10)	−24 (2)	3697 (3)	864 (4)
C(11)	−376 (2)	3239 (4)	−214 (4)
C(12)	−908 (2)	2504 (4)	−264 (4)
C(13)	−1088 (2)	2251 (4)	809 (4)
C(14)	−735 (2)	2684 (3)	1888 (4)
C(15)	−1277 (3)	1975 (4)	−1447 (4)
C(16)	967 (2)	5158 (3)	5164 (4)
C(17)	1671 (2)	5374 (3)	4866 (4)
C(18)	2278 (2)	5375 (3)	5775 (4)
C(19)	2921 (2)	5563 (3)	5513 (5)
C(20)	2967 (2)	5745 (3)	4341 (5)
C(21)	2370 (3)	5738 (3)	3444 (5)
C(22)	1733 (2)	5544 (3)	3708 (4)
O(23)	3579 (2)	5954 (3)	3983 (3)
C(24)	4203 (3)	6037 (5)	4899 (6)
C(25)	1406 (2)	3391 (3)	7059 (4)
C(26)	2053 (2)	2938 (3)	7475 (4)
C(27)	2423 (2)	3129 (3)	8635 (4)
C(28)	2150 (3)	3747 (4)	9428 (4)
C(29)	1488 (3)	4182 (4)	8991 (4)
C(30)	1115 (2)	4014 (3)	7828 (4)
C(31)	2548 (3)	3936 (5)	10717 (5)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (CO)$_4$Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)CH$_2$C$_6$H$_4$-*p*-OCH$_3$] (2b)

Bond Distances			
Mn–C(1)	1.851 (5)	C(3)–O(3)	1.147 (5)
Mn–C(2)	1.841 (5)	C(4)–O(4)	1.148 (5)
Mn–C(3)	1.805 (5)	N(5)–C(6)	1.287 (4)
Mn–C(4)	1.832 (5)	N(5)–C(25)	1.428 (5)
Mn–N(5)	2.079 (3)	C(6)–C(7)	1.490 (5)
Mn–C(7)	2.067 (4)	C(7)–N(8)	1.274 (4)
C(1)–O(1)	1.135 (5)	C(6)–C(16)	1.506 (5)
C(2)–O(2)	1.139 (4)	N(8)–C(9)	1.419 (5)
Bond Angles			
C(1)–Mn–C(2)	171.3 (2)	N(5)–C(6)–C(7)	105.1 (3)
C(1)–Mn–C(3)	89.8 (2)	C(6)–C(7)–Mn	92.3 (3)
C(1)–Mn–C(4)	94.4 (2)	Mn–N(5)–C(6)	98.1 (3)
C(2)–Mn–C(3)	91.1 (2)	Mn–N(5)–C(25)	137.4 (3)
C(2)–Mn–C(4)	94.2 (2)	C(6)–N(5)–C(25)	124.4 (3)
C(3)–Mn–C(4)	92.8 (2)	N(5)–C(6)–C(16)	128.8 (4)
C(1)–Mn–N(5)	88.5 (1)	C(7)–C(6)–C(16)	125.6 (4)
C(1)–Mn–C(7)	84.8 (2)	C(6)–C(16)–C(17)	108.9 (3)
C(2)–Mn–N(5)	88.9 (1)	C(6)–C(7)–N(8)	119.2 (3)
C(2)–Mn–C(7)	86.6 (2)	Mn–C(7)–N(8)	148.5 (3)
C(3)–Mn–N(5)	167.9 (2)	C(7)–N(8)–C(9)	121.3 (3)
C(3)–Mn–C(7)	103.6 (2)	Mn–C(1)–O(1)	178.4 (4)
C(4)–Mn–N(5)	99.3 (2)	Mn–C(2)–O(2)	177.7 (4)
C(4)–Mn–C(7)	163.6 (2)	Mn–C(3)–O(3)	178.5 (4)
N(5)–Mn–C(7)	64.4 (1)	Mn–C(4)–O(4)	179.8 (2)

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(66) Treichel, P. M. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 4, pp 1–159.

(67) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441.

(68) Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436.

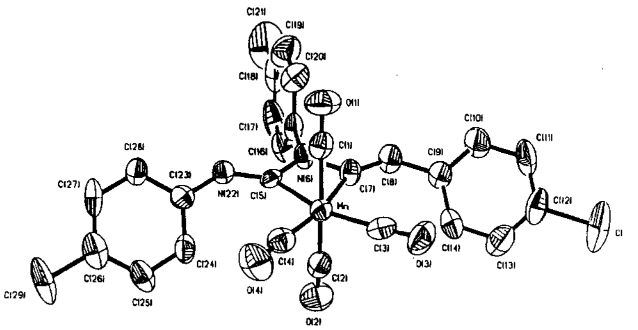

Figure 2. Molecular structure of $(CO)_4Mn[C\{=CH(C_6H_4\text{-}p\text{-}Cl)\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]$ (**3a**).

Table IV. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in $(CO)_4Mn[C\{=CH(C_6H_4\text{-}p\text{-}Cl)\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]$ (3a)

atom	*x*	*y*	*z*
Mn	2383 (1)	1082 (1)	1003 (1)
Cl	7265 (4)	1379 (1)	4363 (1)
O(1)	−1715 (7)	746 (3)	1507 (3)
O(2)	6171 (7)	1727 (3)	515 (3)
O(3)	4109 (7)	201 (3)	2062 (2)
O(4)	2483 (8)	−131 (3)	87 (3)
C(1)	−151 (10)	868 (3)	1303 (3)
C(2)	4746 (10)	1458 (3)	716 (3)
C(3)	3496 (9)	550 (3)	1643 (4)
C(4)	2413 (10)	344 (4)	428 (3)
C(5)	1013 (8)	1874 (3)	505 (3)
N(6)	898 (7)	2338 (3)	1005 (3)
C(7)	2002 (9)	2000 (3)	1520 (3)
C(8)	2270 (11)	2324 (4)	2091 (4)
C(9)	3475 (11)	2072 (3)	2645 (4)
C(10)	2817 (13)	2151 (4)	3278 (4)
C(11)	3958 (14)	1936 (4)	3805 (4)
C(12)	5790 (13)	1641 (4)	3694 (4)
C(13)	6520 (12)	1546 (4)	3080 (4)
C(14)	5338 (12)	1769 (4)	2555 (4)
C(15)	3 (11)	3031 (3)	999 (3)
C(16)	980 (13)	3592 (4)	734 (3)
C(17)	72 (17)	4247 (5)	736 (4)
C(18)	−1838 (18)	4348 (5)	987 (5)
C(19)	−2784 (14)	3773 (5)	1251 (4)
C(20)	−1883 (12)	3119 (4)	1253 (4)
C(21)	−2813 (19)	5078 (5)	993 (5)
N(22)	192 (8)	2051 (3)	−60 (3)
C(23)	330 (10)	1660 (3)	−652 (3)
C(24)	2123 (11)	1343 (3)	−834 (3)
C(25)	2298 (13)	991 (4)	−1423 (3)
C(26)	680 (13)	961 (3)	−1852 (3)
C(27)	−1105 (12)	1292 (3)	−1667 (3)
C(28)	−1290 (11)	1633 (4)	−1072 (3)
C(29)	858 (15)	596 (4)	−2507 (3)

Table V. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for $(CO)_4Mn[C\{=CH(C_6H_4\text{-}p\text{-}Cl)\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]$ (3a)

Bond Distances			
Mn–C(1)	1.831 (7)	C(4)–O(4)	1.140 (8)
Mn–C(2)	1.816 (7)	C(5)–N(6)	1.352 (8)
Mn–C(3)	1.809 (7)	C(5)–N(22)	1.323 (9)
Mn–C(4)	1.829 (7)	N(6)–C(7)	1.434 (8)
Mn–C(5)	2.027 (6)	C(7)–C(8)	1.333 (10)
Mn–C(7)	2.053 (6)	N(6)–C(15)	1.439 (8)
C(1)–O(1)	1.140 (8)	C(8)–C(9)	1.466 (11)
C(2)–O(2)	1.148 (8)	C(8)–H(8)	0.893 (53)
C(3)–O(3)	1.157 (9)		
Bond Angles			
C(1)–Mn–C(2)	169.7 (3)	Mn–C(5)–N(6)	97.2 (4)
C(1)–Mn–C(3)	90.3 (3)	Mn–C(5)–N(22)	144.3 (5)
C(1)–Mn–C(4)	93.3 (3)	N(6)–C(5)–N(22)	118.4 (5)
C(2)–Mn–C(3)	96.0 (3)	C(5)–N(6)–C(7)	103.8 (5)
C(2)–Mn–C(4)	94.6 (3)	C(5)–N(6)–C(15)	127.7 (5)
C(3)–Mn–C(4)	92.2 (3)	C(7)–N(6)–C(15)	128.4 (5)
C(1)–Mn–C(5)	85.7 (3)	N(6)–C(7)–Mn	93.4 (4)
C(1)–Mn–C(7)	84.3 (3)	N(6)–C(7)–C(8)	120.6 (6)
C(2)–Mn–C(5)	86.0 (3)	Mn–C(7)–C(8)	145.8 (5)
C(2)–Mn–C(7)	86.7 (3)	C(7)–C(8)–C(9)	127.0 (7)
C(3)–Mn–C(5)	163.3 (3)	Mn–C(1)–O(1)	177.8 (6)
C(3)–Mn–C(7)	98.4 (3)	Mn–C(2)–O(2)	175.8 (6)
C(4)–Mn–C(5)	104.2 (3)	Mn–C(3)–O(3)	176.5 (6)
C(4)–Mn–C(7)	169.1 (3)	Mn–C(4)–O(4)	177.2 (6)
C(5)–Mn–C(7)	65.1 (3)		

of 2.079 (3) Å is quite similar to the 2.070 Å reported for the Mn–imine N distance in $(CO)_4Mn[C_6H_4\text{-}o\text{-}(CH{=}NPh)]$[70] which is shorter than the Mn–amine N distance of 2.139 Å in $(CO)_4Mn[C_6H_4\text{-}o\text{-}CH_2NMe_2]$.[71]

The four terminal CO's all exhibit bond distances typical for alkylmanganese carbonyl complexes.[72] The Mn–C distances range from 1.805 (5) to 1.851 (5) Å with Mn–C$_{av}$ = 1.832 Å. The four C–O triple bond distances range from 1.135 (5) to 1.148 (5) Å with C–O$_{av}$ = 1.142 Å.

Molecular Structure of $(CO)_4Mn[C\{=CH(C_6H_4\text{-}p\text{-}Cl)\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]$ (3a). Figure 2 shows the molecular geometry of **3a**. Atomic coordinates are reported in Table IV and bond distances and bond angles of interest in Table V. The coordination geometry around Mn is, like that in **2b**, a distorted cis-disubstituted octahedron. The most interesting structural feature is the four-membered manganacyclic ring which includes the atoms Mn, C(5), N(6), and C(7). The mean deviation from the best least-squares plane through this ring is 0.034 Å with a maximum deviation of 0.046 Å exhibited by N(6). In contrast, Mn, C(5), C(7), C(8), and N(22) form an excellent plane (average deviation 0.0048 Å) with N(6) ~0.1 Å out of the plane. Adding C(3) and C(4) gives a plane with average deviation 0.148 Å with N(6) lying 0.12 Å out of the plane.

The ring structure is related to that of **2b**. However, the C(5)–N(6) distance of 1.352 (8) Å, the C(5)–N(22) distance of 1.323 (9) Å, and the N(6)–C(7) distance of 1.434 (8) Å indicate appreciable delocalization around the ring. These distances are to be contrasted with the comparable ones in **2b** (N(5)–C(6) = 1.287 (4), N(5)–C(25) = 1.428 (5), and C(6)–C(7) = 1.490 (5) Å).

That transfer of a benzylic H has occurred is clearly revealed by the C(7)–C(8) distance of 1.33 (1) Å, indicative of a C–C double bond, and by the location of H(22) bonded to N(22) from the density map.

The geometry at the carbene carbon C(5) differs from that in other carbene complexes of Mn(I) such as $Cp(CO)_2MnC(CH_3)_2$[73] which has Mn–C–C(methyl) angles of 124.1 (5)° and 126.2 (5)° and ∠C(methyl)–C(carbene)–C(methyl) = 109° with a Mn–C(carbene) distance of 1.872 (1) Å. In **3a**, the Mn–C(carbene) distance is considerably longer at 2.027 (6) Å while ∠Mn–C(5)–N(6) is 97.2 (4)° and ∠Mn–C(5)–N(22) is 144.3 (5)° with ∠N(6)–C(5)–N(22) = 118.4 (5)°. These parameters are probably related to strain in the four-membered ring since they are extremely similar to those in $[(PMe_3)_2(CO)_2Fe\{C(=CH_2)N(C_6H_{11})C(NHC_6H_{11})\}]^+$,[25] the major difference between the two structures being in the bond distances of 1.97 (1) Å for

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Table VI. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)] (4a)

atom	*x*	*y*	*z*
Mn	7511.2 (5)	229.7 (6)	8924.9 (6)
Cl	2223 (1)	3100 (1)	7755 (1)
O(1)	8313 (3)	597 (3)	10915 (3)
O(2)	6575 (3)	-292 (3)	6988 (3)
O(3)	8033 (3)	2224 (3)	8416 (3)
O(4)	9219 (3)	-333 (4)	8772 (4)
C(1)	7999 (3)	468 (4)	10149 (4)
C(2)	6941 (4)	-71 (4)	7724 (4)
C(3)	7795 (3)	1477 (5)	8625 (4)
C(4)	8556 (4)	-185 (5)	8849 (4)
C(5)	7045 (3)	-1105 (4)	9186 (3)
N(6)	6173 (3)	-1154 (3)	9015 (3)
C(7)	5708 (3)	-229 (4)	8849 (3)
C(8)	6329 (3)	640 (4)	9032 (3)
N(9)	6030 (3)	1436 (3)	9276 (3)
C(10)	6444 (3)	2387 (4)	9440 (4)
C(11)	6920 (3)	2694 (4)	10309 (4)
C(12)	7231 (3)	3671 (4)	10464 (4)
C(13)	7072 (3)	4361 (4)	9771 (5)
C(14)	6603 (4)	4047 (4)	8903 (5)
C(15)	6283 (4)	3073 (4)	8738 (4)
C(16)	7401 (4)	5438 (4)	9951 (4)
C(17)	4847 (3)	-230 (4)	8569 (4)
C(18)	4226 (3)	610 (4)	8345 (3)
C(19)	3470 (3)	510 (4)	8566 (3)
C(20)	2852 (3)	1263 (4)	8389 (3)
C(21)	2981 (3)	2126 (4)	7971 (3)
C(22)	3700 (3)	2245 (4)	7703 (3)
C(23)	4311 (3)	1483 (4)	7891 (3)
C(24)	5719 (3)	-2102 (3)	8903 (4)
C(25)	5403 (3)	-2482 (4)	9554 (3)
C(26)	4957 (3)	-3388 (4)	9393 (4)
C(27)	4818 (3)	-3916 (4)	8590 (4)
C(28)	5153 (3)	-3519 (4)	7952 (4)
C(29)	5597 (3)	-2622 (4)	8102 (4)
C(30)	4309 (4)	-4897 (4)	8415 (4)
N(31)	7446 (3)	-1975 (3)	9478 (3)
C(32)	8303 (3)	-2273 (3)	9536 (4)
C(33)	8929 (4)	-2360 (5)	10353 (5)
C(34)	9711 (4)	-2763 (7)	10393 (5)
C(35)	9893 (4)	-3104 (5)	9652 (5)
C(36)	9249 (4)	-3008 (5)	8845 (4)
C(37)	8457 (4)	-2599 (5)	8786 (4)
C(38)	10746 (4)	-3595 (6)	9707 (5)

Fe–C(carbene) and 1.98 (1) Å for Fe–C(vinyl) due to the slightly smaller (~0.06 Å) radius for Fe(II) as compared to Mn(I). The Mn–C(7) distance of 2.053 (6) Å in **3a** is to be compared with the Mn–vinylic C distance of 2.057 Å in $Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7$.[74] This distance is in the range ordinarily observed between Mn and an sp^2 acyl C.[66,67]

The Mn–C (carbonyl) distances are in the range 1.816 (7)–1.831 (7) Å. All the carbonyls are linear with Mn–C–O angles between 175.8 (6)° and 177.8 (6)°.

Molecular Structures of (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)] (4a), (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-OMe)}N(*p*-tolyl)C(NHC$_6$H$_{11}$)] (4b), and (CO)$_4$ Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NHC$_6$H$_{11}$)] (4c). The structures of these three compounds are all extremely similar. Selected bond distances and bond angles appear in Table IX, and Tables VI, VII, and VIII give atomic coordinates for **4a**, **4b**, and **4c**, respectively. The geometries are depicted in Figures 3–5. Because of the similarity of the structures, this discussion quotes only average and approximate values of bond angles and bond lengths. Actual values are presented in the tables.

Each molecule is a distorted cis-disubstituted octahedron containing a five-membered manganacyclic ring. The ring is attached to Mn via an iminoacyl group on one end and by a diaminocarbene on the other. The Mn–C(5) (carbene C) bond length of 2.03 Å is slightly shorter than the Mn–C(8) (iminoacyl C) σ bond length of 2.07 Å reflecting more

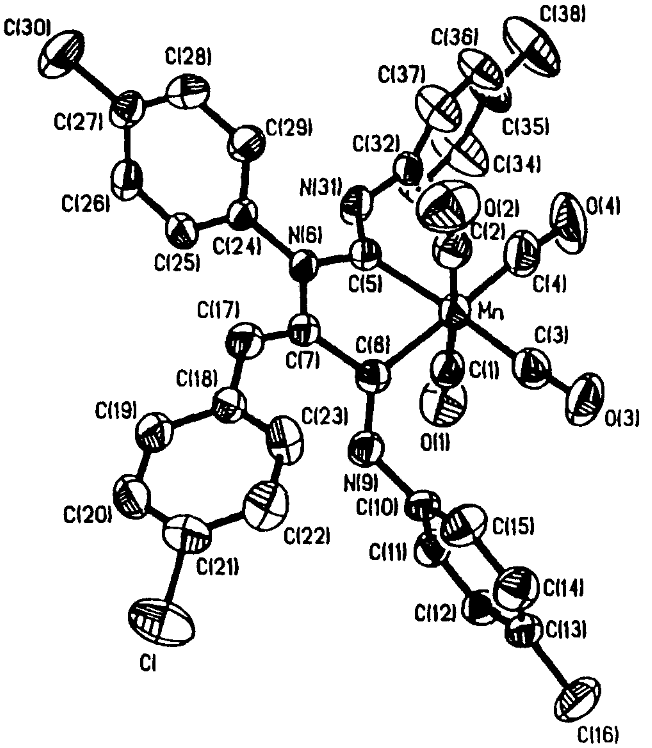

Figure 3. Molecular structure of (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)] (**4a**).

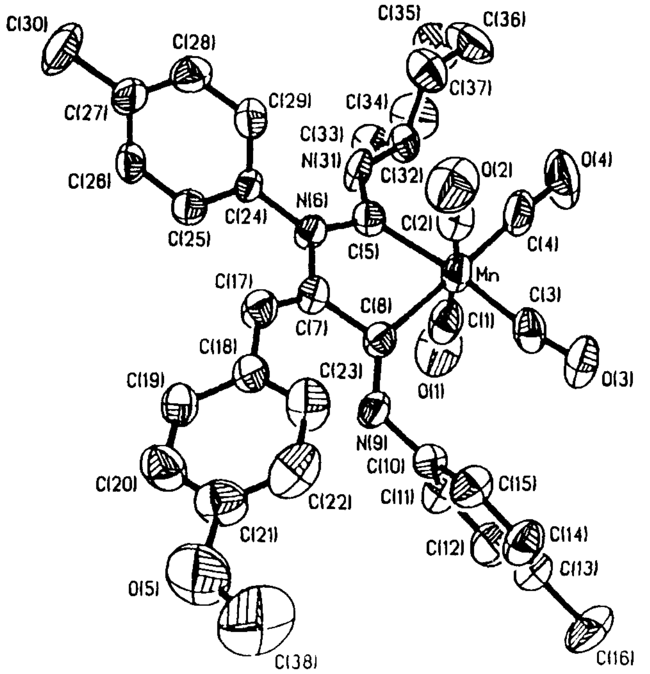

Figure 4. Molecular structure of (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-OMe)}N(*p*-tolyl)C(NHC$_6$H$_{11}$)] (**4b**).

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Table VII. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-OMe)}N(*p*-tolyl)C(NHC$_6$H$_{11}$)] (4b)

atom	*x*	*y*	*z*
Mn	8785.9 (6)	−341.1 (7)	7560.1 (6)
O(1)	10696 (3)	−642 (4)	8503 (3)
O(2)	6957 (3)	143 (4)	6444 (3)
O(3)	8238 (3)	−2343 (3)	7888 (3)
O(4)	8403 (4)	98 (3)	9255 (3)
O(5)	8044 (4)	−2547 (5)	2151 (3)
C(1)	9959 (5)	−548 (5)	8136 (4)
C(2)	7648 (5)	−49 (5)	6880 (5)
C(3)	8472 (4)	−1592 (5)	7728 (4)
C(4)	8563 (5)	−26 (4)	8590 (5)
C(5)	9108 (4)	992 (4)	7198 (4)
N(6)	9007 (3)	1105 (3)	6306 (3)
C(7)	8869 (3)	245 (5)	5778 (4)
C(8)	9016 (4)	−645 (4)	6360 (4)
N(9)	9289 (3)	−1380 (4)	6038 (3)
C(10)	9427 (5)	−2310 (5)	6445 (4)
C(11)	10223 (5)	−2570 (5)	7041 (4)
C(12)	10361 (5)	−3516 (6)	7374 (4)
C(13)	9717 (6)	−4215 (5)	7128 (5)
C(14)	8937 (5)	−3937 (5)	6532 (5)
C(15)	8780 (5)	−3008 (5)	6182 (4)
C(16)	9883 (5)	−5237 (5)	7511 (5)
C(17)	8638 (4)	292 (5)	4877 (4)
C(18)	8438 (4)	−488 (5)	4199 (4)
C(19)	8721 (4)	−371 (5)	3449 (4)
C(20)	8559 (5)	−1055 (6)	2785 (4)
C(21)	8123 (5)	−1879 (6)	2851 (5)
C(22)	7801 (5)	−2015 (5)	3554 (5)
C(23)	7953 (4)	−1310 (5)	4230 (4)
C(24)	8952 (5)	2041 (4)	5862 (4)
C(25)	9609 (4)	2362 (5)	5555 (4)
C(26)	9490 (5)	3230 (5)	5076 (4)
C(27)	8731 (5)	3768 (5)	4899 (4)
C(28)	8089 (4)	3425 (5)	5238 (4)
C(29)	8190 (4)	2568 (5)	5717 (4)
C(30)	8587 (5)	4685 (5)	4332 (4)
N(31)	9371 (4)	1799 (4)	7671 (3)
C(32)	9549 (4)	1958 (4)	8635 (4)
C(33)	10416 (4)	2487 (5)	9011 (4)
C(34)	10604 (5)	2702 (6)	10002 (4)
C(35)	9867 (6)	3271 (6)	10177 (5)
C(36)	9003 (5)	2741 (6)	9804 (5)
C(37)	8800 (4)	2514 (5)	8801 (4)
C(38)	7718 (5)	−3419 (6)	2227 (6)

Table VIII. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NHC$_6$H$_{11}$)] (4c)

atom	*x*	*y*	*z*
Mn	8812 (1)	−304 (1)	7528 (1)
Cl	7775 (1)	−3041 (1)	2175 (1)
O(1)	10745 (2)	−585 (2)	8478 (2)
O(2)	6955 (2)	168 (2)	6410 (2)
O(3)	8255 (2)	−2325 (2)	7858 (2)
O(4)	8444 (2)	142 (2)	9230 (2)
C(1)	10005 (3)	−506 (3)	8113 (2)
C(2)	7654 (3)	−15 (3)	6838 (3)
C(3)	8497 (3)	−1568 (3)	7704 (2)
C(4)	8598 (3)	10 (3)	8567 (3)
C(5)	9135 (2)	1048 (3)	7154 (2)
N(6)	9008 (2)	1161 (2)	6253 (2)
C(7)	8856 (2)	288 (3)	5722 (2)
C(8)	9042 (2)	−609 (3)	6325 (2)
N(9)	9334 (2)	−1348 (2)	6010 (2)
C(10)	9483 (3)	−2281 (3)	6435 (2)
C(11)	10298 (3)	−2556 (3)	7009 (3)
C(12)	10441 (3)	−3506 (3)	7352 (3)
C(13)	9777 (3)	−4200 (3)	7126 (3)
C(14)	8971 (3)	−3926 (3)	6547 (3)
C(15)	8818 (3)	−2979 (3)	6194 (3)
C(16)	9944 (4)	−5245 (3)	7504 (3)
C(17)	8576 (2)	316 (3)	4819 (2)
C(18)	8359 (2)	−506 (3)	4173 (2)
C(19)	8615 (2)	−473 (3)	3403 (2)
C(20)	8431 (3)	−1241 (3)	2779 (3)
C(21)	7988 (2)	−2054 (3)	2936 (3)
C(22)	7702 (2)	−2111 (3)	3673 (3)
C(23)	7880 (2)	−1333 (3)	4278 (3)
C(24)	8934 (2)	2112 (2)	5812 (2)
C(25)	9578 (2)	2453 (3)	5478 (2)
C(26)	9442 (3)	3331 (3)	5002 (2)
C(27)	8680 (3)	3878 (3)	4850 (2)
C(28)	8052 (3)	3533 (3)	5216 (2)
C(29)	8172 (3)	2657 (3)	5691 (2)
C(30)	8520 (3)	4818 (3)	4286 (3)
N(31)	9408 (2)	1853 (3)	7644 (2)
C(32)	9592 (2)	2007 (3)	8612 (2)
C(33)	10471 (2)	2527 (3)	9013 (2)
C(34)	10658 (3)	2733 (4)	10013 (3)
C(35)	9920 (4)	3300 (4)	10190 (3)
C(36)	9050 (3)	2767 (5)	9799 (3)
C(37)	8844 (3)	2565 (3)	8795 (3)

multiple-bond character in the Mn–carbene C bond even through both C(5) and C(8) are both formally sp^2-hybridized. These values are in agreement with other Mn–C(sp^2) distances[67,73] but are longer than Mn–isocyanide C distances found in *fac*-MnBr(CO)$_3$(CNMe)$_2$ (1.99 (1) and 1.95 (1) Å[75]) and in *fac*-MnBr(CO)$_3$(CNPh)$_2$ (1.92 (3) and 1.93 (4) Å[76]). The angles at the carbene C(5) are distorted from ideal values: ∠Mn–C(5)–N(6) = 115°, ∠Mn–C(5)–N(31) = 130°, and ∠N(6)–C(5)–N(31) = 113°. The distortions here are smaller than those in the four-membered ring of **3a** and are comparable in magnitude to those seen in at least one Cr carbene complex.[77] The C(5)–N(6) distance of 1.37 Å and the C(5)–N(31) distance of 1.33 Å are similar to aminocarbene bond lengths in **3a** and in Cr carbene complexes[76,78] and reflect double-bond character. Nevertheless, as expected, these are longer than the iminoacyl C(8)–N(9) bond length of 1.27 Å but shorter than the 1.48 Å C–N single bond length in organic amides.[68] H(31), the hydrogen transferred to the isocyanide N, was located from the electron density map in each of the structures. ∠C(5)–N(31)–C(32) was around 129° in all three structures, indicative of sp^2 hybridization at the aminocarbene N as is the ∠C(5)–N(6)–C(24) of 123°.

The bond angles around the iminoacyl C(8) are distorted from the ideal 120° with ∠Mn–C(8)–N(9) = 135°, ∠Mn–C(8)–C(7) = 111°, and ∠C(7)–C(8)–C(9) = 114°. The distortion is in contrast with *cis*-[Mn(CO)$_4${C(O)Me}{C(O)Ph}]$^-$ [67] where all the angles are 120° around the acyl carbons. This is presumably due to the chelating nature of the ligand which forces a C(5)–Mn–C(8) angle of only 78°. For comparison, the C(5)–Mn–C(7) angle in **3a** is only 65° with correspondingly larger distortions around the vinylic C(5).

Other distances around the manganacyclic ring are C(7)–C(8) = 1.50 Å and C(7)–N(6) = 1.42 Å. The former distance is that expected for a C–C single bond while the latter is smaller than the C–N single bond length of 1.48 Å.[68] C(7) and C(17) are 1.34 Å apart as expected for double-bonded C.

As seen in Figures 3–5, the phenyl and cyclohexyl rings attached to the manganacyclic rings are oriented similarly in all three molecules. Mn, C(5), C(8), and the carbonyl carbons C(3) and C(4) form a least-squares plane with a mean deviation of 0.03, 0.01, and 0.01 Å in **4a**, **4b**, and **4c**, respectively. Both N(6) and C(7) lie out of the plane by

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Table IX. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for $(CO)_4Mn[C(=N\text{-}p\text{-tolyl})C\{=CH(C_6H_4\text{-}p\text{-Cl})\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]$ (4a), $(CO)_4Mn[C(=N\text{-}p\text{-tolyl})C\{=CH(C_6H_4\text{-}p\text{-OMe})\}N(p\text{-tolyl})C(NHC_6H_{11})]$ (4b), and $(CO)_4Mn[C(=N\text{-}p\text{-tolyl})C\{=CH(C_6H_4\text{-}p\text{-Cl})\}N(p\text{-tolyl})C(NHC_6H_{11})]$ (4c)

	4a	4b	4c		4a	4b	4c
			Bond Distances				
Mn–C(1)	1.833 (7)	1.834 (8)	1.843 (5)	C(5)–N(6)	1.366 (5)	1.366 (6)	1.364 (4)
Mn–C(2)	1.836 (7)	1.846 (7)	1.855 (5)	C(5)–N(31)	1.332 (6)	1.329 (6)	1.323 (4)
Mn–C(3)	1.820 (6)	1.833 (7)	1.830 (4)	N(6)–C(7)	1.423 (6)	1.421 (6)	1.420 (4)
Mn–C(4)	1.836 (6)	1.811 (7)	1.811 (4)	N(6)–C(24)	1.442 (6)	1.452 (6)	1.447 (4)
Mn–C(5)	2.021 (5)	2.032 (6)	2.038 (3)	C(7)–C(17)	1.332 (6)	1.347 (7)	1.335 (4)
Mn–C(8)	2.067 (5)	2.068 (6)	2.067 (3)	C(7)–C(8)	1.501 (6)	1.501 (7)	1.508 (4)
C(1)–O(1)	1.144 (6)	1.148 (7)	1.138 (4)	C(8)–N(9)	1.272 (5)	1.266 (6)	1.268 (4)
C(2)–O(2)	1.141 (6)	1.136 (6)	1.126 (4)	C(17)–H(17)	0.94 (5)	0.91 (5)	0.94 (3)
C(3)–O(3)	1.150 (6)	1.152 (6)	1.147 (4)	N(31)–H(31)	0.84 (5)	0.85 (5)	0.78 (3)
C(4)–O(4)	1.145 (6)	1.159 (6)	1.152 (4)				
			Bond Angles				
C(1)–Mn–C(2)	174.6 (2)	173.1 (3)	173.1 (2)	N(6)–C(5)–N(31)	113.1 (4)	113.2 (5)	114.6 (3)
C(1)–Mn–C(3)	92.7 (2)	93.9 (3)	94.3 (2)	C(5)–N(6)–C(7)	117.2 (4)	116.7 (5)	116.7 (3)
C(1)–Mn–C(4)	91.0 (3)	93.0 (3)	92.9 (2)	C(5)–N(6)–C(24)	121.9 (4)	124.2 (5)	123.6 (3)
C(2)–Mn–C(3)	91.5 (2)	91.3 (3)	90.9 (2)	C(7)–N(6)–C(24)	120.5 (4)	118.8 (5)	119.4 (3)
C(2)–Mn–C(4)	92.6 (3)	91.9 (3)	91.9 (2)	N(6)–C(7)–C(8)	109.9 (4)	110.9 (5)	110.1 (2)
C(3)–Mn–C(4)	86.4 (2)	87.6 (3)	86.9 (2)	N(6)–C(7)–C(17)	120.2 (5)	120.9 (6)	122.0 (3)
C(1)–Mn–C(5)	90.5 (2)	88.2 (3)	87.8 (1)	C(8)–C(7)–C(17)	129.9 (5)	128.2 (6)	127.9 (3)
C(1)–Mn–C(8)	88.6 (2)	88.5 (3)	88.8 (1)	C(7)–C(8)–Mn	112.1 (3)	110.5 (4)	110.5 (2)
C(2)–Mn–C(5)	85.0 (2)	86.1 (3)	86.4 (1)	C(7)–C(8)–N(9)	113.1 (4)	114.6 (5)	114.7 (3)
C(2)–Mn–C(8)	87.6 (2)	86.5 (3)	87.0 (1)	Mn–C(8)–N(9)	134.6 (4)	134.8 (5)	134.7 (3)
C(3)–Mn–C(5)	173.1 (2)	172.2 (2)	172.2 (1)	C(5)–N(31)–C(32)	128.6 (4)	128.8 (5)	129.6 (3)
C(3)–Mn–C(8)	95.9 (2)	94.2 (2)	95.0 (1)	C(7)–C(17)–C(18)	130.6 (5)	130.5 (6)	129.0 (4)
C(4)–Mn–C(5)	99.7 (2)	99.8 (2)	100.5 (2)	C(8)–N(9)–C(10)	125.8 (4)	124.4 (5)	123.6 (3)
C(4)–Mn–C(8)	177.7 (2)	177.5 (3)	177.8 (2)	C(7)–C(17)–H(17)	119 (3)	116 (4)	118 (2)
C(5)–Mn–C(8)	78.0 (2)	78.3 (2)	77.6 (1)	C(18)–C(17)–H(17)	111 (3)	113 (3)	113 (2)
Mn–C(5)–N(6)	116.1 (4)	115.4 (4)	115.4 (2)	C(5)–N(31)–H(31)	120 (4)	120 (4)	117 (2)
Mn–C(5)–N(31)	130.7 (4)	131.4 (4)	129.9 (3)	C(32)–N(31)–H(31)	110 (4)	111 (4)	113 (2)

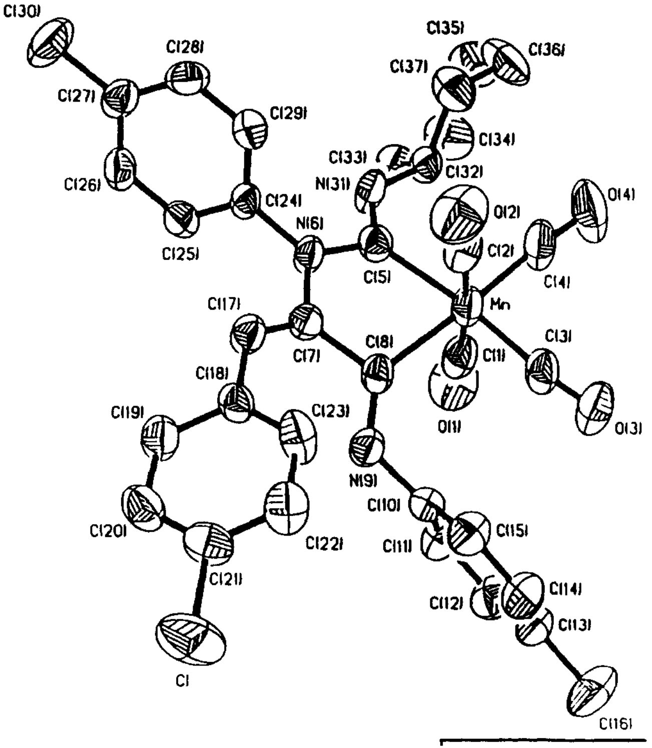

Figure 5. Molecular structure of $(CO)_4Mn[C(=N\text{-}p\text{-tolyl})C\{=CH(C_6H_4\text{-}p\text{-Cl})\}N(p\text{-tolyl})C(NHC_6H_{11})]$ (4c).

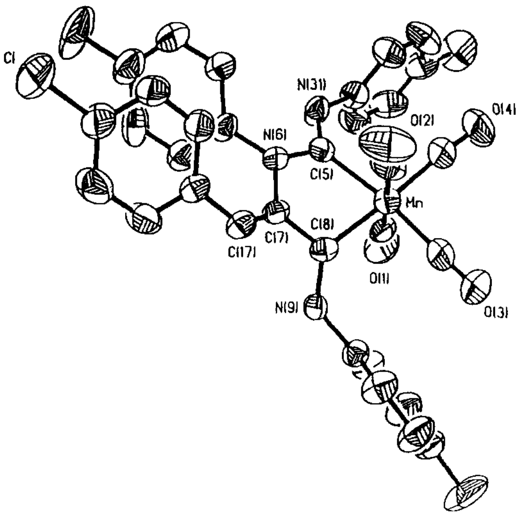

Figure 6. Molecular structure of $[(CO)_4Mn[C(NH\text{-}p\text{-tolyl})C\{=CH(C_6H_4\text{-}p\text{-Cl})\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]]^+$ (6a).

about 0.5 and 0.6 Å, respectively, on the side toward C(2).

The four terminal CO's are all linear and unremarkable in their bond distances and angles. The range of Mn–C distances, Mn–C_{av}, the range of C–O distances, and the C–O_{av} are as follows: for **4a**, 1.820 (6)–1.836 (7), 1.831, 1.141 (6)–1.150 (6), 1.145 Å; for **4b**, 1.811 (7)–1.846 (7), 1.831, 1.136 (6)–1.159 (6), 1.149 Å; for **4c**, 1.811 (4)–1.855 (5), 1.835, 1.126 (4)–1.152 (4), 1.141 Å.

The location of the cyclohexyl ring attached to C(5) in **4b** is evidence that the isocyanide allowed to react with **2** is indeed the one which is converted into a carbene. In both **4b** and **4c** the cyclohexyl rings adopt the chair conformation.

Molecular Structure of $[(CO)_4Mn[C(NH\text{-}p\text{-tolyl})C\{=CH(C_6H_4\text{-}p\text{-Cl})\}N(p\text{-tolyl})C(NH\text{-}p\text{-tolyl})]]BF_4$ (6a). Table X gives atomic coordinates, and Table XI gives pertinent bond distances and bond angles for **6a**. Figure 6 depicts the molecular geometry of the cation. The structure of **6a** is almost superimposable with that of **4a**. One major difference is that the

Table X. Atomic Coordinates (×10^4) and Their Estimated Standard Deviations for Non-Hydrogen Atoms in [(CO)$_4$Mn[C(NH-*p*-tolyl)C{═CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)]]BF$_4$ (6a)

atom	*x*	*y*	*z*
Mn	1722 (1)	1632 (1)	3102 (1)
Cl	−5061 (2)	3586 (2)	3397 (2)
O(1)	2252 (5)	−189 (4)	2902 (3)
O(2)	1063 (6)	3429 (4)	3231 (3)
O(3)	3753 (4)	1956 (4)	4267 (3)
O(4)	2937 (5)	2118 (4)	1964 (3)
C(1)	2036 (6)	502 (6)	2991 (4)
C(2)	1327 (7)	2747 (6)	3164 (4)
C(3)	2956 (6)	1819 (5)	3835 (4)
C(4)	2416 (6)	1929 (5)	2366 (5)
C(5)	248 (6)	1407 (4)	2406 (4)
N(6)	−557 (4)	1530 (4)	2753 (3)
C(7)	−233 (5)	1613 (5)	3577 (4)
C(8)	891 (5)	1356 (4)	3862 (4)
N(9)	1130 (5)	1025 (4)	4559 (3)
C(10)	2178 (6)	774 (5)	5010 (4)
C(11)	2638 (6)	44 (5)	4848 (4)
C(12)	3621 (6)	−198 (5)	5305 (5)
C(13)	4154 (6)	293 (7)	5932 (5)
C(14)	3647 (7)	1006 (7)	6075 (5)
C(15)	2679 (7)	1273 (5)	5624 (5)
C(16)	5216 (6)	12 (6)	6431 (5)
C(17)	−796 (6)	1950 (5)	4031 (4)
C(18)	−1836 (6)	2365 (5)	3854 (4)
C(19)	−2498 (7)	2217 (5)	4332 (5)
C(20)	−3491 (7)	2584 (6)	4191 (5)
C(21)	−3815 (6)	3125 (5)	3580 (5)
C(22)	−3145 (7)	3325 (5)	3121 (5)
C(23)	−2164 (6)	2942 (5)	3263 (4)
C(24)	−1656 (6)	1388 (5)	2365 (4)
C(25)	−2221 (7)	746 (5)	2587 (4)
C(26)	−3284 (7)	648 (6)	2220 (6)
C(27)	−3794 (7)	1176 (7)	1631 (5)
C(28)	−3214 (7)	1803 (6)	1400 (5)
C(29)	−2152 (6)	1923 (5)	1759 (4)
C(30)	−4971 (7)	1075 (7)	1220 (6)
N(31)	−51 (5)	1146 (4)	1673 (4)
C(32)	599 (6)	936 (6)	1171 (4)
C(33)	889 (7)	114 (7)	1107 (5)
C(34)	1505 (7)	−100 (6)	601 (6)
C(35)	1829 (7)	491 (7)	160 (5)
C(36)	1514 (7)	1320 (6)	226 (4)
C(37)	907 (6)	1542 (6)	726 (5)
C(38)	2542 (6)	251 (6)	−372 (5)
B	−15 (9)	1044 (8)	6331 (6)
F(1)	−45 (4)	436 (3)	6853 (3)
F(2)	−37 (4)	656 (3)	5641 (3)
F(3)	871 (5)	1527 (3)	6547 (3)
F(4)	−877 (5)	1522 (4)	6227 (4)

Mn–C(8) distance is shortened from 2.067 (5) Å in **4a** to 1.986 (7) Å in **6a**. This is consistent with the formal conversion of an iminoacyl group to an aminocarbene by protonation of N and the consequent increase in Mn–C bond order. In addition, the *p*-chlorophenyl ring attached to C(17) is trans instead of cis to C(8) so that H(9) and H(17) point toward each other instead of H(9) pointing toward the phenyl ring.

Experimental Section

General Comments. All infrared solution spectra were recorded with a Perkin-Elmer Model 599 spectrophotometer using either potassium bromide (0.1 mm) or sodium chloride (0.1 mm) cells. Band positions were determined relative to the 1601 cm^{-1} peak in polystyrene. For spectral intensities, the abbreviations w, m, s, br, and sh refer to weak, medium, strong, broad, and shoulder, respectively.

Proton nuclear magnetic resonance spectra were obtained on an IBM NR-80 instrument in Fourier transform mode. Positive chemical shifts are given in ppm downfield from tetramethylsilane as an internal standard. Spectral multiplicities are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Table XI. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for [(CO)$_4$Mn[C(NH-*p*-tolyl)C{═CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)]]BF$_4$ (6a)

Bond Distances			
Mn–C(1)	1.844 (9)	C(5)–N(6)	1.362 (7)
Mn–C(2)	1.840 (9)	C(5)–N(31)	1.329 (8)
Mn–C(3)	1.819 (8)	N(6)–C(7)	1.425 (7)
Mn–C(4)	1.833 (8)	N(6)–C(24)	1.442 (8)
Mn–C(5)	2.036 (7)	C(7)–C(17)	1.333 (9)
Mn–C(8)	1.986 (7)	C(7)–C(8)	1.482 (8)
C(1)–O(1)	1.144 (8)	C(8)–N(9)	1.308 (7)
C(2)–O(2)	1.141 (8)	N(9)–H(9)	0.94 (6)
C(3)–O(3)	1.146 (8)	N(31)–H(31)	0.83 (6)
C(4)–O(4)	1.145 (7)		
Bond Angles			
C(1)–Mn–C(2)	176.2 (4)	C(5)–N(6)–C(7)	114.8 (6)
C(1)–Mn–C(3)	93.0 (4)	C(5)–N(6)–C(24)	123.4 (5)
C(1)–Mn–C(4)	90.3 (3)	C(7)–N(6)–C(24)	120.3 (6)
C(2)–Mn–C(3)	90.8 (4)	N(6)–C(7)–C(8)	109.5 (6)
C(2)–Mn–C(4)	89.8 (4)	N(6)–C(7)–C(17)	126.6 (6)
C(3)–Mn–C(4)	87.9 (3)	C(8)–C(7)–C(17)	123.5 (6)
C(1)–Mn–C(5)	88.3 (3)	C(7)–C(8)–Mn	111.9 (5)
C(1)–Mn–C(8)	92.2 (3)	C(7)–C(8)–N(9)	114.1 (6)
C(2)–Mn–C(5)	88.0 (3)	Mn–C(8)–N(9)	134.0 (5)
C(2)–Mn–C(8)	87.5 (3)	C(5)–N(31)–C(32)	128.2 (6)
C(3)–Mn–C(5)	172.1 (3)	C(7)–C(17)–C(18)	132.0 (7)
C(3)–Mn–C(8)	94.9 (3)	C(8)–N(9)–C(10)	126.5 (6)
C(4)–Mn–C(5)	99.9 (3)	F(1)–B–F(2)	107.9 (9)
C(4)–Mn–C(8)	176.2 (3)	F(1)–B–F(3)	112.2 (9)
C(5)–Mn–C(8)	77.3 (3)	F(1)–B–F(4)	109.1 (9)
Mn–C(5)–N(6)	114.8 (5)	F(2)–B–F(3)	109.1 (8)
Mn–C(5)–N(31)	130.2 (6)	F(2)–B–F(4)	107.8 (9)
N(6)–C(5)–N(31)	115.0 (6)	F(3)–B–F(4)	110.7 (9)

Analytical thin-layer chromatography was conducted by using E. Merck silica gel 60-PF254 precoated plates. Compounds were made visible by UV light (254 nm) and by I$_2$ vapor. Preparative chromatographic separations were conducted by column chromatography using neutral or acidic alumina, 80–200 mesh, or using E. Merck silica gel, finer than 220 mesh.

Melting points were determined on a Mel-Temp apparatus, using open end capillaries, and are uncorrected. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard 5995A quadrupolar GC/MS system by means of direct inlet. High-resolution mass spectra (HRMS) were obtained on a Kratos MS801-DS55 spectrometer. Elemental analysis was performed by Galbraith Laboratories, Inc. Knoxville, TN.

Benzylmanganese pentacarbonyl[79] and cyclohexyl isocyanide[80] were prepared by standard literature methods. Dimanganese decacarbonyl was purchased from the Pressure Chemical Co., and *tert*-butyl isocyanide was purchased from Aldrich. All other laboratory chemicals were reagent grade and were used as received.

Tetrahydrofuran, THF, was dried by distillation from benzophenone ketyl. Toluene and benzene were dried with sodium ribbon. Reagent grade dichloromethane, chloroform, hexane, and petroleum ether (bp 60–80 °C) were freshly distilled before use. All other solvents were reagent grade and were used as received.

Preparation of *p*-Tolyl Isocyanide. This isocyanide was prepared in a manner similar to that for other aromatic isocyanides.[81] A solution of *p*-tolyl formamide (45.1 g, 0.333 mol), triphenylphosphine (104 g, 0.397 mol), triethylamine (55.0 mL, 0.345 mol), carbon tetrachloride (34.0 mL, 0.351 mol), and 350 mL of chloroform was stirred in a three-neck 1000-mL flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser topped with a drying tube. The reaction mixture was heated with a heating mantle to 65 °C over a period of 75 min and the temperature maintained between 60 and 65 °C for an

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[80] Ugi, I.; Meyr, R.; Lipinski, M.; Bodesheim, F.; Rosendahl, F. *Organic Syntheses*; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Coll. Vol. V, p 300.

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additional 4 h. The solvent was removed at reduced pressure, and the resulting brown residue was extracted with 5 × 200 mL portions of warm petroleum ether. The ether fractions were combined, the solvent was removed at reduced pressure, and the crude isocyanide was distilled under reduced pressure: yield 26.0 g (66.6%).

Preparation of (*p*-Chlorobenzyl)pentacarbonylmanganese (1a) and (*p*-Methoxybenzyl)pentacarbonylmanganese (1b). A diethyl ether (30 mL) solution of *p*-chlorobenzyl chloride (9.14 g, 56.9 mmol) at 0 °C was treated with a diethyl ether (80 mL) solution of Na[Mn(CO)$_5$] made by Na/Hg reduction of dimanganese decacarbonyl (11.1 g, 28.4 mmol). The reaction mixture was stirred at 0 °C for 5 h, hexane (50 mL) was added to complete the precipitation of sodium chloride, and the mixture was filtered through 2 in. of neutral grade I alumina. Reduction in volume by rotary evaporation gave the desired compound as yellow crystals (11.1 g), which were collected on a glass frit, washed with 2 × 5 mL portions of ice cold hexane, and air-dried. The remaining filtrate was reduced to approximately 10 mL in volume and chromatographed on 18 g of silica gel by using hexane as the eluent. After removal of unreacted dimanganese decacarbonyl, the pale yellow band was isolated and taken to dryness (1.25 g); yield 12.4 g (68%). Spectral values matched those reported in the literature.[58] **1b** was prepared similarly in 62% yield. Spectral values matched those reported in the literature.[82]

Preparation of (CO)$_4$Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)-CH$_2$C$_6$H$_4$-*p*-Cl] (2a) and (CO)$_4$Mn[C{=CH(C$_6$H$_4$-*p*-Cl)}N-(*p*-tolyl)C(NH-*p*-tolyl)] (3a). A toluene (20 mL) solution of (*p*-chlorobenzyl)pentacarbonylmanganese (1.40 g, 4.37 mmol), *p*-tolyl isocyanide (0.974 g, 1.00 mL, 8.31 mmol), and anhydrous PdO (0.023 g, 0.19 mmol) was stirred under nitrogen for 18 h at room temperature. After the solvent was removed at reduced pressure, the remaining residue was taken up in a minimum amount of chloroform and eluted through a silica gel column (200 g, 33 cm in length by 4 cm wide). Elution with 1:9 ethyl acetate/hexane removed, in order, small amounts of Mn$_2$(CO)$_{10}$, unreacted *p*-ClC$_6$H$_4$CH$_2$Mn(CO)$_5$, an unidentified red oil (0.023 g), an unidentified yellow oil (0.060 g), and **2a** (1.226 g, 53%). Elution with 1:4 ethyl acetate/hexane removed colorless **3a** (0.200 g, 9%), a yellow oil, **4a** (0.032 g, 1.8%), and an orange solid, **5a** (0.067 g, 3.8%). Crystals of **3a** suitable for X-ray analysis were grown by slow evaporation from dichloromethane/hexane solution at 0 °C.

2a: Low-resolution mass spectrum: *m/e* (relative intensity) 526 (M$^+$, 2), 414 (20), 359 (16), 297 (33), 242 (19), 180 (50), 125 (70), 91 (38), 55 (100). Anal. Calcd for C$_{27}$H$_{20}$ClMnN$_2$O$_4$: C, 61.65; H, 3.83; N, 5.33. Found: C, 61.55; H, 3.83; N, 5.32.

3a: mp 118–125 °C dec; turns red at high temperature. Low-resolution mass spectrum: *m/e* (relative intensity) 526 (M$^+$, 1), 470 (8), 442 (7), 415 (16), 278 (100), 243 (35), 207 (18), 161 (71), 118 (64), 106 (74), 91 (52), 65 (30), 55 (73).

Preparation of (CO)$_4$Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)-CH$_2$C$_6$H$_4$-*p*-OMe] (2b). A toluene solution (20 mL) solution of [(*p*-methoxy)benzyl]pentacarbonylmanganese (0.660 g, 2.1 mmol), *p*-tolyl isocyanide (0.487 g, 0.50 mL, 4.2 mmol), and anhydrous PdO (0.023 g, 0.19 mmol) was refluxed under nitrogen for 20 min. After the solvent was removed at reduced pressure, the remaining residue was taken up in a minimum amount of chloroform and eluted through a silica gel column (200 g, 33 cm in length and 4 cm wide). Elution with 3:17 ethyl acetate/hexane removed **2b** as a red band (0.200 g, 18.3%). Crystals suitable for X-ray analysis were grown by slow evaporation of a dichloromethane/hexane solution at 0 °C. Running the reaction at room temperature gave many products. At reflux in toluene only **2b** was isolated, any **3b** present having been thermally decomposed. High-resolution mass spectrum: *m/e* (relative intensity) 522 (M$^+$, not observed), 410 (22), 356 (40), 239 (64), 292 (23), 176 (15), 121 (32), 117 (100), 91 (32), 55 (10). Anal. Calcd for C$_{28}$H$_{23}$MnN$_2$O$_5$: C, 64.37; H, 4.44; N, 5.36. Found: C, 64.38; H, 4.47; N, 5.22.

Preparation of (CO)$_4$Mn[C(=N-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)] (4a) and (CO)$_4$Mn[C(=N-*p*-tolyl)C(NH-*p*-tolyl)C(C$_6$H$_4$-*p*-X)C(NH-*p*-tolyl)] (5a). *p*-Tolyl isocyanide (0.116 g, 0.120 mL, 0.990 mmol) and **2a** (0.465 g, 0.884 mmol) were stirred under argon in dry toluene (30 mL) at ambient temperature for 24 h, during which time the color of the reaction mixture changed from deep red to black. The reaction mixture was passed through a 2-in. silica gel column, and the column was then washed with 20 mL of 1:3 ethyl acetate/hexane. The fractions were combined, and the solvent was removed under reduced pressure. The resulting orange residue was chromatographed on silica gel (column 25 cm in length and 2.5 cm wide) by using 3:17 ethyl acetate/hexane as eluent. Two yellow bands were collected. Removal of the solvent under reduced pressure gave **5a** as a yellow oil and **4a** as an orange solid. Crystals of **4a** suitable for X-ray analysis were grown by slow evaporation of a dichloromethane/hexane solution at 0 °C.

4a: yield 0.275 g (43%); mp 170–175 °C. Low-resolution mass spectrum: *m/e* (relative intensity) 644 (M$^+$, not observed), 532 (3), 477 (13), 414 (11), 359 (59), 242 (65), 125 (42), 118 (34), 106 (57, 91 (32), 55 (8). Anal. Calcd for C$_{35}$H$_{27}$ClMnN$_3$O$_4$: C, 65.28; H, 4.23; N, 6.52. Found: C, 64.57; H, 4.51; N, 6.19.

5a: yield 0.107 g (17%). This compound underwent isomerization to form **4a**, and therefore elemental analysis was not possible.

4b, **5b**, and **4c** were prepared similarly. Data for **4b** and **5b** are given below.

4b: yield 0.089 g (18%); mp 145–150 °C. Low-resolution mass spectrum: *m/e* (relative intensity) 631 (M$^+$, not observed), 519 (8), 410 (63), 355 (100), 239 (36), 121 (36), 118 (19), 91 (8), 55 (10). Anal. Calcd for C$_{35}$H$_{34}$MnN$_3$O$_5$: C, 66.59; H, 5.43; N, 6.66. Found: C, 66.56; H, 5.67; N, 6.43.

5b: yield 0.080 g (16%); mp 145–150 °C. Low-resolution mass spectrum: *m/e* (relative intensity) 631 (M$^+$, 1), 603 (1), 575 (1), 547 (1), 519 (11), 411 (65), 239 (52), 121 (26), 117 (30), 110 (6), 91 (26), 81 (13), 76 (18), 55 (35). This compound underwent isomerization to **4b** making elemental analysis impossible.

Preparation of [(CO)$_4$Mn[C(NH-*p*-tolyl)C{=CH(C$_6$H$_4$-*p*-Cl)}N(*p*-tolyl)C(NH-*p*-tolyl)]]BF$_4$ (6a). A freshly chromatographed sample of **4a** (0.2 g, 0.3 mmol) was stirred for 2 h with 2 mL of 42% HBF$_4$ and 15 mL of benzene at room temperature. Yellow crystals separated that were dissolved by adding dichloromethane. The organic layer was washed with water and dried over MgSO$_4$. Solvent was removed in vacuo, and the residue was crystallized from dichloromethane/hexane at 0 °C to give X-ray quality crystals.

Preparation of (CO)$_4$(*t*-BuNC)Mn[C(=N-*p*-tolyl)C(=N-*p*-tolyl)CH$_2$C$_6$H$_4$-*p*-Cl] (7a) and (CO)$_3$(*t*-BuNC)Mn[C-(=N-*p*-tolyl)C(=N-*p*-tolyl)CH$_2$C$_6$H$_4$-*p*-Cl] (8a). *tert*-Butyl isocyanide (0.172 mL, 0.126 g, 1.521 mmol) and **2a** (0.800 g, 1.521 mmol) were stirred under argon in dry toluene (9 mL) for 24 h. The reaction mixture was diluted with 50 mL of hexane, cooled to 0 °C for 2 h, and filtered through a sintered glass frit to remove an unknown green byproduct. The solvent was removed from the filtrate, and the resulting red residue was chromatographed on silica gel (25 cm in length by 2.5 cm wide) by using 1:4 ethyl acetate/hexane as the eluent. Two red fractions were collected. Removal of the solvent under reduced pressure gave **7a** as a red oil and **8a** as a red solid.

7a: yield 0.375 g (40%). Compound **7a** converts to compound **8a**, making an elemental analysis impossible.

8a: yield 0.240 g (27%); mp 130–136 °C. High-resolution mass spectrum: *m/e* (relative intensity) 582 (M$^+$, not observed), 526 (4), 414 (87), 360 (100), 297 (85), 242 (54), 180 (34), 125 (35). Anal. Calcd for C$_{31}$H$_{29}$ClMnN$_3$O$_3$: C, 63.98; H, 5.02; N, 7.22. Found: C, 64.09; H, 5.67; N, 6.98.

Attempted Cyclization of 7a. (i) A solution of the "dangling" bis(imino) complex **7a** (0.100 g, 0.164 mmol) in benzene (20 mL) was stirred under argon at ambient temperature for 24 h. Thin-layer chromatography (silica gel, 1:4 ethyl acetate/hexane) revealed approximately equal amounts of **7a** and **8a**.

(ii) A solution of complex **7a** (0.100 g, 0.164 mmol) in benzene (20 mL) was stirred under carbon monoxide (2 atm) in a Paar Shaker for 24 h. Thin-layer chromatography revealed only compound **7a**.

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(82) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

Table XII. Structure Determination Summary for 2b, 3a, and 6a

	2b	3a	6a
		Crystal Data	
empirical formula	$C_{28}H_{23}MnN_2O_5$	$C_{27}H_{20}ClMnN_2O_4$	$C_{35}H_{28}BClF_4MnN_3O_4$
color and habit	red-orange plates	pink-yellow rectangular prisms	yellow prisms
size, mm	0.10 × 0.38 × 0.52	0.12 × 0.22 × 0.28	0.15 × 0.25 × 0.25
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
unit-cell dimens (*a*, *b*, *c*, Å) (angles, deg)	a = 19.616 (2) b = 12.287 (2) c = 11.368 (2) β = 103.13 (1)	a = 6.611 (1) b = 18.937 (2) c = 20.510 (2) β = 90.111 (8)	a = 13.054 (2) b = 15.721 (2) c = 17. 798 (3) β = 104.79 (1)
V, Å^3	2668.4 (6)	2567.8 (4)	3531.5 (8)
Z, molecules/cell	4	4	4
mol wt	522.44	526.86	731.82
D (calcd), g/cm^3	1.30	1.36	1.38
F(000), e	1080	1080	1496
		Data Collection	
hkl limits	±22,0–15,0–14	±8,0–21,0–23	±16,0–18,0–20
reflctns collected	3931 total (3281 independent)	3612 total (3363 independent)	5028 total (4627 independent)
reflctns obsd	1985; $F > 6\sigma(F)$	2119; $F > 3\sigma(F)$	2026; $F > 6\sigma(F)$
min/max transmissn	0.830/0.939	N/A	N/A
		Refinement	
R	0.0349	0.0643	0.0473
R_w	0.0379	0.0407	0.0392
no. of variables	327	344	453
data-to-parameter ratio	6.1:1	6.2:1	4.5:1

Table XIII. Structure Determination Summary for 4a–c

	4a	4b	4c
		Crystal Data	
empirical formula	$C_{35}H_{27}ClMnN_3O_4$	$C_{35}H_{34}MnN_3O_5$	$C_{34}H_{31}ClMnN_3O_4$
color and habit	orange plates	yellow prisms	orange-yellow prisms
size, mm	0.10 × 0.30 × 0.50	0.25 × 0.25 × 0.30	0.35 × 0.35 × 0.35
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
unit-cell dimens (*a*, *b*, *c*, Å) (angles, deg)	a = 16.354 (5) b = 13.273 (2) c = 15.513 (4) β = 108.96 (2)	a = 15.986 (2) b = 13.748 (2) c = 15.681 (2) β = 108.01 (1)	a = 15.915 (2) b = 13.550 (2) c = 15.611 (2) β = 108.723 (9)
V, Å^3	3185 (1)	3277.3 (8)	3188.3 (6)
Z, molecules/cell	4	4	4
mol wt	644.01	631.61	636.03
D (calcd), g/cm^3	1.34	1.28	1.32
F(000), e	1328	1320	1320
		Data Collection	
hkl limits	±19,0–16,0–18	±18,0–16,0–18	±21,0–18,0–21
reflctns collected	4498 total (4179 independent)	4726 total (4308 independent)	7956 total (7358 independent)
reflctns obsd	2292; $F > 6\sigma(F)$	2033; $F > 6\sigma(F)$	3303; $F > 6\sigma(F)$
min/max transmissn	0.833/0.954	0.815/0.849	N/A
		Refinement	
R	0.0402	0.0448	0.0434
R_w	0.0388	0.0370	0.0382
no. of variables	405	406	426
data-to-parameter ratio	5.7:1	5.0:1	7.8:1

(iii) A solution of complex **7a** (0.200 g, 0.328 mmol) dissolved in benzene (40 mL) was charged in an autoclave with 1200 psi of carbon monoxide and heated to 70 °C. After 24 h under these conditions, thin-layer chromatography revealed only decomposition of the original manganese complex.

Crystal Structure Determinations for 2b, 3a, 4a, 4b, 4c, and 6a. Summaries of the crystal structure determination parameters are provided in Tables XII and XIII. Suitable crystals were isolated, mounted on the tips of glass fibers with epoxy cement, and transferred to a Nicolet R3m/v four-circle diffractometer for characterization and data collection at ambient temperature. Axial photographs and a limited search of reciprocal space for all six compounds revealed systematic absences and symmetry consistent with their having crystallized in the monoclinic space group $P2_1/c$ (No. 14) or its nonstandard setting $P2_1/n$.

Data collections were carried out in the θ–2θ scan mode employing variable scan speeds and with three standards monitored for every 37 reflections measured. Corrections for Lorentz and polarization effects were made, and in the case of **2b**, **4a**, and **4b**, absorption corrections using empirical scan data were also applied. Structures were solved by standard methods and refined by full-matrix least squares. The least-squares refinements included a weighting scheme based on $\sigma(F)$, anisotropic temperature parameters for the non-hydrogen atoms, and hydrogens riding on their respective carbons. The positional parameters for the amino and olefinic H atoms were free to vary.

Registry No. **1a**, 65982-69-6; **1b**, 80105-78-8; **2a**, 120496-17-5; **2b**, 120474-75-1; **3a**, 122923-92-6; **4a**, 122923-94-8; **4b**, 122923-93-7; **4c**, 122923-95-9; **5a**, 122923-88-0; **5b**, 122923-90-4; **6a**, 123048-29-3; **7a**, 122923-91-5; **8a**, 122923-89-1; dimanganese decacarbonyl, 10170-69-1; *p*-chlorobenzyl chloride, 104-83-6; *p*-methoxybenzyl chloride, 824-94-2; *p*-tolyl isocyanide, 7175-47-5; *p*-tolylformamide, 3085-54-9; cyclohexyl isocyanide, 931-53-3; *tert*-butyl isocyanide, 7188-38-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, H-atom coordinates and isotropic displacement parameters, and least-squares planes (20 pages); listings of observed and calculated structure factors for **2b**, **3a**, **4a**, **4b**, **4c**, and **6a** (57 pages). Ordering information is given on any current masthead page.