Insertion of Imines and Carbon Monoxide into Manganese−Alkyl Bonds: Synthesis and Structure of a Manganese−α-Amino Acid Derivative

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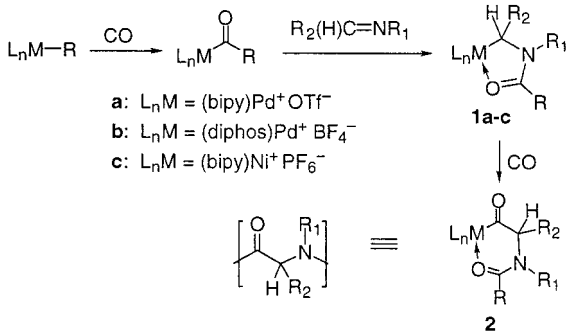
Two new routes have been developed to generate manganese-chelated amides from imine and carbon monoxide building blocks. The reaction of $(CO)_5MnR$ (R = CH_3, Ph) with (*p*-tolyl)(R^1)═NR^2 (R^1 = H, ^{t}Bu; R^2 = alkyl, H) results in the generation of the cyclometalated imine complexes $(CO)_4Mn[\eta^2$-4-CH_3-2-(C(R^1)═NR^2)-$C_6H_3]$ in 50−84% isolated yield. However, when the reaction of (*p*-tolyl)(H)C═NCH_3 with $(CO)_5MnCH_3$ is performed in the presence of $AlCl_3$, the product of sequential carbon monoxide and imine insertion is generated in 35% yield: $(CO)_4Mn[\eta^2$-C(H)(*p*-tolyl)N(CH_3)$COCH_3]$. The addition of PPh_3 to the latter complex results in replacement of a carbonyl ligand and formation of the isolable *fac*-$(CO)_3(PPh_3)$-$Mn[\eta^2$-C(H)(*p*-tolyl)N(CH_3)$COCH_3]$. In an alternative route to metal-bound amides, the oxidative addition of the N-acyl iminium salt (*p*-tolyl(H)C═N(CH_3)$COPh^+Cl^-$ to $(CO)_5Mn^-Na^+$ has been found to lead to the generation of the product of subsequent CO insertion, $(CO)_4Mn$-$[\eta^2$-COC(H)(*p*-tolyl)N(CH_3)COPh]. The latter represents the first example of a acyl-bound transition-metal-chelated α-amino acid complex and has been characterized by X-ray crystallography. Preliminary reactivity studies demonstrate that $(CO)_4Mn[\eta^2$-COC(H)(*p*-tolyl)N(CH_3)COPh] reacts with PPh_3 to generate the unchelated *cis*-$(CO)_4(PPh_3)$Mn[COC-(H)(*p*-tolyl)N(CH_3)COPh], while reaction with $NaBH_4$ leads to the liberation of the amide (*p*-tolyl)CH_2N(CH_3)COPh, rather than the amino acid residue.

Introduction

The sequential insertion of carbon monoxide and imines into metal−carbon bonds provides a potential method to generate metal-bound amides (**1**) and the related metalated α-amino acid (**2**) complexes (Scheme 1). These represent important intermediates in the development of metal-mediated routes to construct amino acid derivatives from simple and flexible imine/CO building blocks.[1] Indeed, complexes analogous to **2** have been postulated as intermediates in the cobalt- and palladium-catalyzed synthesis of α-amino acids from aldehydes, amides, and CO.[2] Nevertheless, while the insertion chemistry of olefins and carbon monoxide has been thoroughly explored,[3] much less is known about the analogous insertion of imines. Recently, we and others reported that the sequential insertion of carbon monoxide and imine can be achieved with palladium complexes of the form $L_2Pd(CH_3)(RN{=}C(H)R')^+X^-$

Scheme 1



(L_2 = bidentate ligand; R = alkyl, aryl; R′ = aryl; X = noncoordinating anion), providing the first well-defined examples of imine insertion into a late-metal−carbon bond.[1a,b] This process has since been elaborated to the analogous nickel complexes.[4] These reactions have allowed for the construction of metal-bound α-amides (**1**); however, the products were found to be completely inert to the subsequent insertion of CO. To our knowledge, metalated α-amino acid derivatives of the form of **2** have not been previously prepared via sequential imine/carbon monoxide insertion.[5]

A rationale put forward for the lack of CO insertion in the palladium and nickel versions of complex **1** was that strong chelation of the amide oxygen blocks the empty coordination site required for CO coordination.

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(3) (a) Drent. E.; Budzellar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (b) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746 and references therein. (c) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (d) Johnson, J. K.; Ittel, S. D.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(4) Davis, J. L.; Arndtsen, B. A. *Organometallics* **2000**, *19*, 4657.

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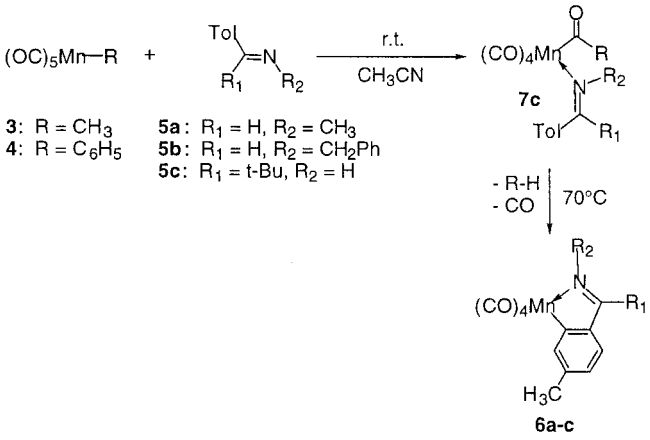
With this in mind, we reasoned that the use of metal−carbonyl complexes for sequential CO/imine insertion would result in the formation of the metal−α-amide complex with a cis-coordinated carbon monoxide ligand (**1**; L = CO), which may more readily undergo subsequent CO insertion. Manganese carbonyl complexes have been demonstrated to undergo the sequential insertion of carbon monoxide with olefins and alkynes to generate five-membered metallacycles analogous to **1a**−**c**.[6] In addition, imine insertion into the metal−acyl bonds of $(CO)_xMCOR$ (M = Mn, Co) has been postulated in several reports.[7] These suggest that $(CO)_5Mn-R$ (R = CH_3, C_6H_5) may be prime candidates to mediate the sequential insertion of carbon monoxide and imines to generate metal-bound α-amino acid products.

We report below the results of our investigation on the insertion of imines with manganese carbonyl complexes. These show an unusual discrimination between imine C−H bond activation and insertion that can be controlled by the addition of external Lewis acids. We also report a mild oxidative addition route to these products of CO/imine insertion. The latter has allowed the factors which affect the subsequent CO insertion chemistry to be explored and has ultimately led to the first crystallographic characterization of a manganese-bound α-amido-substituted acyl derivative (**2**).

Results

Reactivity of $(CO)_5Mn-R$ (R = CH_3, C_6H_5) with Imines. Manganese carbonyl complexes of the form $(CO)_5Mn-R$ (**3**, R = CH_3; **4**, R = Ph) are known to undergo facile insertion of carbon monoxide in the presence of added ligands to generate the corresponding manganese−acyl complexes.[8] Thus, our first attempts to achieve sequential CO/imine insertion involved the simple reaction of $(CO)_5Mn-R$ with imines. The addition of imines **5a**−**c** to $(CO)_5Mn-CH_3$ (**3**) in CH_3CN followed by warming to 70 °C leads to the formation of a new organometallic complex. However, rather than generating the product of imine insertion, the ortho-metalated products **6a**−**c** are isolated in 50−84% yield (Scheme 2). Identical products were observed upon the reaction of **5a**−**c** with $(CO)_5Mn-Ph$ (**4**).

Scheme 2



Complexes **6a**−**c** have been fully characterized in analogy to previously reported arene-metalated imine complexes.[9] Notably, three distinct aromatic resonances are observed in the ^1H NMR of these complexes (e.g., **6a**: δ 7.72 (s, 1H), δ 7.48 (d, 1H), δ 6.96 (d, 1H)), demonstrating that metalation of the *p*-tolyl aromatic ring has occurred. In addition, the imine hydrogen (=C*H*) is shifted downfield from that in the free imine (^1H NMR (CD_3CN): **6a**, δ 8.48 (s); **5a**, δ 8.20), consistent with chelation of the imine nitrogen to manganese.[10] The cis-substituted $Mn(CO)_4$ unit is observed in both the IR (**6a**: 2075 (m), 1966 (m), 1910 cm^{-1} (s)) and ^{13}C NMR (**6a**: δ 220.2, 214.6, 213.5).

The C−H activation of aromatic imines by alkylmanganese carbonyl complexes is not a new reaction. Bruce and co-workers have reported that the reaction of Ph(H)C=NPh with $(CO)_5MnCH_2Ph$ leads to the generation of a product analogous to **6**.[9] In these studies, arene metalation is postulated to occur via the initial displacement of CO and imine coordination to $(CO)_4MnCH_2Ph$, followed by C−H bond activation (either via a σ-bond metathesis or oxidative addition/reductive elimination mechanism) and elimination of alkane. An analogous process is likely active in the reaction of **3** and **4** with imines. Monitoring the reaction of $(CO)_5Mn-Ph$ (**4**) with **5a**−**c** by ^1H NMR (CD_3CN) reveals the quantitative formation of benzene in addition to **4a**−**c**.

In the case of the less sterically encumbered imine **5c**, monitoring its reaction with **3** by ^1H NMR reveals the quantitative formation of intermediate **7c** at ambient temperature, which has been characterized to be the σ-coordinated imine complex *cis*-$(CO)_4Mn(COCH_3)$-[HN=(Tol)^{t}Bu] (Scheme 2). The formation of the acyl ligand in **7c** can be clearly observed in the ^1H (δ 2.78 (s, 3H)) and ^{13}C NMR (δ 275.1), and the imine hydrogen is shifted downfield in the ^1H NMR (δ 10.76 (s, 1H)), consistent with imine σ-coordination. Warming of complex **7c** in CD_3CN to 70 °C for 20 h leads to the generation of **6c** in 84% isolated yield, presumably via the loss of CO followed by imine C−H activation.

(5) Complexes of this form have been previously generated via alternative routes: (a) Severin, K.; Bergs, R.; Beck, W. *Angew. Chem., Int. Ed.* **1998**, *37*, 1634 and references therein. (b) Nagy-Gergely, I.; Szalontai, G.; Ungvary, F.; Marko, L.; Moret, M.; Sironi, A.; Zucchi, C.; Sisak, A.; Tschoerner, M.; Martinelli, A.; Sorkau, A.; Palyi, G. *Organometallics* **1997**, *16*, 2740. (c) Petri, W.; Beck, W. *Chem. Ber.* **1984**, *117*, 3265. (d) Hungate, R. W.; Miller, F.; Goodman, M. S. *Tetrahedron Lett.* **1988**, *29*, 4273. (e) Amiens, C.; Balavoine, G.; Guibe, F. *J. Organomet. Chem.* **1993**, *443*, 207.

(6) (a) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575. (b) DeShong, P.; Slough, G. A.; Rheingold, A. L. *Tetrahedron Lett.* **1987**, *28*, 2229. (c) DeShong, P.; Slough, G. A. *Organometallics* **1984**, *3*, 636. (d) Booth, B. L.; Gardner, M.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1856. (e) DeShong, P.; Slough, G. A. *Tetrahedron Lett.* **1987**, *28*, 2233.

(7) (a) Reduto, A. C.; Hegedus, L. S. *Organometallics* **1995**, *14*, 1586. (b) Vaspallo, G.; Alper, H. *Tetrahedron Lett.* **1988**, *29*, 5113. (c) Alper, H.; Amaratunga, S. *J. Org. Chem.* **1982**, *47*, 3595. (d) Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Organometallics* **1989**, *8*, 33.

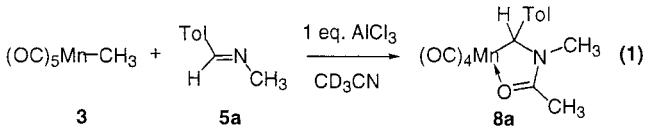
(8) (a) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806 and references therein. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (d) Flood, T. C. In *Topics in Organic and Organometallic Stereochemistry*; Goeffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12, p 83. (e) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

(9) (a) Bennett, R. L.; Bruce, M. I.; Goodall, B. L.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1787. (b) Bruce, M. I.; Goodall, B. L.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1971**, 1595. (c) Bennett, R. L.; Bruce, M. I.; Matsuda, I. *Aust. J. Chem.* **1975**, *28*, 1265.

(10) (a) Lenges, C. P.; Brookhart, M.; White, P. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 552. (b) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennet, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523.

Sequential CO/Imine Insertion vs Cyclometalation: Influence of Lewis Acids. Mechanistic studies on the insertion of imines into palladium−acyl bonds have demonstrated that this reaction proceeds via the initial σ-coordination of imine to the palladium center, followed by a migratory insertion reaction.[11] These studies also suggested that the nucleophilic attack of the imine on the acyl ligand carbon may lead to generation of the insertion product and that increasing the electrophilicity of the acyl ligand can facilitate this transformation. The observation of intermediate **7c** in the reaction of imine with complex **3** shows that a similar σ-coordination of imines cis to an acyl ligand can be obtained with manganese complexes. However, the decarbonylation of **7c** followed by C−H bond activation occurs at a faster rate than imine insertion into the manganese−acyl bond. Considering the mechanism of imine insertion with palladium complexes, it was reasoned that factors which increase the electrophilicity of the acyl ligand in these manganese complexes (i.e., **7c**) may make imine insertion more favorable than C−H bond activation. Since Lewis acids are well-known to interact with manganese−acyl ligands,[12] the influence of $AlCl_3$ on the reaction with imines was examined.

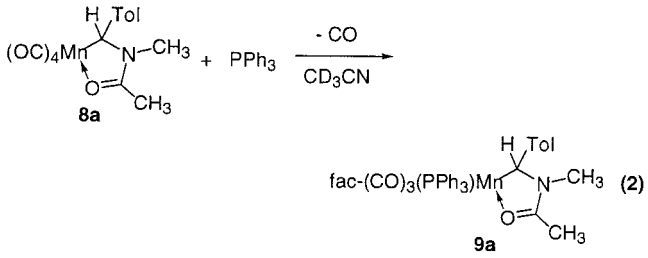
The addition of imine **5a** to complex **3** in the presence of 1 equiv of $AlCl_3$ in CD_3CN followed by monitoring the reaction by ^1H NMR reveals the formation of a new product (**8a**, 35% NMR yield) over the course of 24 h (eq 1). Of note, no evidence for the formation of the



(1)

cyclometalated product **6a** was observed. The reaction of imine **5b** with **3** and $AlCl_3$ also does not lead to imine C−H activation; however, this reaction yields a complex mixture of products.[13] The ^1H NMR of **8a** shows that the former imine hydrogen (=C*H*) shifted upfield to δ 5.09 (s, 1H), consistent with a reduction in the C=N bond, and the formation of new NCH_3 (δ 2.98 (s, 3H)), $COCH_3$ (δ 2.23 (s, 3H)) and $C_6H_4CH_3$ (δ 2.05 (s, 3H)) resonances. These data are directly analogous to those observed for the palladium-chelated α-amide complex (bipy)Pd[η^2-CH(Tol)N(CH_3)$COCH_3$]$^+$OTf$^-$[1a] and allow a preliminary structural assignment of **8a** as the product of carbon monoxide and imine insertion into the manganese−methyl bond of **3**.

Attempts to isolate complex **8a** were unsuccessful. However, the addition of 1 equiv of PPh_3 to the reaction mixture results in an immediate effervescence, due to CO loss, and the quantitative conversion of **8a** to its phosphine-substituted derivative **9a** (eq 2). The latter could be isolated upon crystallization at −30 °C from CH_3CN and has been characterized as *fac*-$(CO)_3(PPh_3)$-



(2)

Mn[η^2-C(H)TolN(CH_3)$COCH_3$]. The nonaromatic ^1H NMR resonances for **9a** are similar to those observed in **8a** (δ 4.60 (d, 1H, Mn−C*H*), δ 2.98 (s, 3H, NCH_3), δ 2.23 (s, 3H, $COCH_3$), δ 2.05 (s, 3H, $C_6H_4CH_3$)), with the three-bond coupling of the phosphine ligand to Mn−C*H* clearly evident ($^3J_{P-C}$ = 18.5 Hz). The IR of **9a** demonstrates the presence of the fac-substituted manganese center (ν_{CO} 1996 (s), 1904 (vs), 1873 cm^{-1} (vs)). In addition, the amide carbonyl vibration in **9a** is observed at 1600 cm^{-1}, which is a low frequency compared to that of free amides (ν_{CO} 1630−1680 cm^{-1}). The latter is a characteristic of chelation of the amide oxygen to the manganese center and is directly analogous to that previously observed for chelated amides in **1a**−**c**.[1,4] The structure of **9a** was further confirmed by X-ray structural analysis of a related derivative (vide infra).

The generation of manganese-chelated amide products upon addition of Tol(H)C=NMe (**5a**) to $(CO)_5Mn-CH_3$ (**3**) in the presence of $AlCl_3$ shows that the sequential insertion of CO and imine into manganese−carbon bonds is a viable reaction pathway. The role of $AlCl_3$ in this process will be discussed in a later section. Nevertheless, the product **8a** is formed in low yield and could only be isolated as triphenylphosphine derivative **9a**. This limited our ability to directly examine its subsequent insertion chemistry and its potential as an intermediate on the pathway towards manganese-bound α-amino acid derivatives (**2**; Scheme 1). Thus, we became interested in alternative, higher yield, routes to complexes analogous to **8**.

Oxidative Addition of N-Acyl Iminium Salts to $(CO)_5Mn^-$: Synthesis of α-Amido-Substituted Acyl Complexes. It is known that the carbonylmanganate anion, $(CO)_5Mn^-$, can be used to generate Mn−R bonds via the nucleophilic displacement of halides from RX.[14] This suggests an alternative route to complexes analogous to **8**, which could occur by reaction of $(CO)_5Mn^-Na^+$ (**11**) with N-acyl iminium chloride salts.[15] Iminium salt **12** can be easily prepared in situ by reaction of imine with the appropriate acid chloride, in analogy to literature procedures.[16] The addition of **12** to $(CO)_5Mn^-Na^+$ (**11**) in CH_3CN results in the immediate precipitation of NaCl and the clean formation of a new manganese-containing product. However, rather than generating a complex analogous to **8**, this reaction results in the formation of the new manganese-chelated α-amido acyl complex **13** (Scheme 3).

Complex **13** can be isolated by crystallization from acetonitrile at −30 °C. The ^1H NMR of **13** shows the

(11) Dghaym, R. D.; Dhawan, R.; Arndtsen, B. A. Submitted for publication.

(12) (a) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Strimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. (b) Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.; Strimson, R. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 5864. (c) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272.

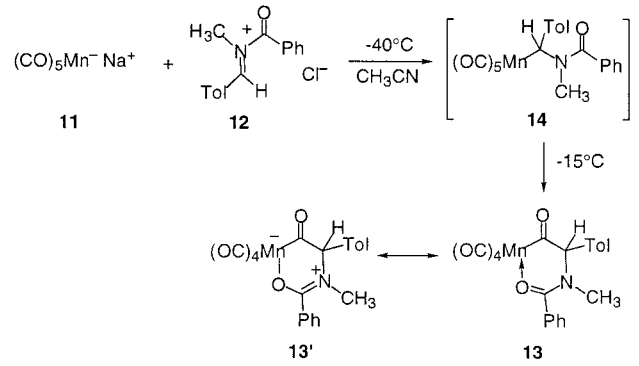
(13) A complex analogous to **8a** was detected in the ^1H NMR of the reaction mixture in ca. 10% yield but could not be isolated to allow complete characterization.

(14) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1995; p 50.

(15) The analogous oxidative addition of *N*-phthaloylmethyl choride to metal carbonyl complexes has been reported to yield complexes analogous to **8**.[5a−c]

(16) Ratts, K.; Chupp, J. *J. Org. Chem.* **1974**, *39*, 3745.

Scheme 3



formation of new NCH_3 (δ 3.16 (3H)) and $C_6H_4CH_3$ (δ 2.31 (3H)) resonances. In addition, a new signal at δ 4.54 (s, 1H) is observed, which is assigned to the former iminium hydrogen in **12**. This chemical shift is significantly upfield of that in **12** (7−8 ppm) and is similar to that observed in **8a**, suggesting that **13** may be simply the product of $(CO)_5Mn^-$ displacement of Cl^- in **12**. However, the ^{13}C NMR of **13** is quite diagnostic for the structure shown. This reveals four separate metal−carbonyl ligand resonances (δ 218.1, 213.1, 212.2, 210.1), demonstrating the presence of a cis-substituted $(CO)_4Mn$ fragment rather than a pentacarbonylmanganese center. A new amide resonance is observed at δ 178.0, once again consistent with chelation of the amide oxygen to the manganese center. The ^{13}C NMR also reveals the presence of a manganese−acyl ligand in **13** (δ 269.9 (s)). This acyl ligand would arise from the insertion of carbon monoxide into the manganese−carbon bond of the addition product.

The generation of complex **13** upon addition of N-acyl iminium salt **12** to **11** likely arises from the rapid insertion of carbon monoxide into the metal−carbon bond generated by nucleophilic displacement of Cl^- by $(CO)_5Mn^-$. To further probe the mechanism of this process, the reaction was examined by low-temperature NMR. The addition of **11** and **12** in CD_3CN at −40 °C followed by ^1H NMR analysis reveals the immediate formation of a reaction intermediate, which has been preliminarily assigned as complex **14** (Scheme 3). Notably, this product displays new NCH_3 (δ 3.02) and $C_6H_4CH_3$ (δ 2.35) resonances and the presence of a C*H*(Tol) resonance at δ 5.94. The upfield shift in the C*H* signal from **12** demonstrates that reduction of the C=N has occurred upon addition to $(CO)_5Mn^-$ and is in a region similar to that observed for complexes **8a** and **9a**. Complex **14** is the only intermediate observed and is rapidly converted to the product of CO insertion into the Mn−C bond (**13**) upon warming to −15 °C.

Crystallographic Characterization of Complex 13. Crystals of complex **13** suitable for X-ray diffraction can be grown from acetonitrile at −40 °C, and its formulation as illustrated in Scheme 4 is confirmed by X-ray crystallography. As shown in Figure 1, **13** has a pseudo-octahedral geometry about the metal center. The Mn−carbonyl bond lengths are similar for three of the carbonyl ligands (ca. 1.86 Å); however, the carbonyl ligand trans to the amide oxygen has a shortened Mn−C(2) bond (1.780(4) Å). This is accompanied by a slight lengthening of the C(2)−O(2) bond (1.149(4) Å), relative to the other carbonyl C−O bonds (ca. 1.13 Å). This can be attributed to the π-donor ability of the oxygen ligand, which increases back-bonding to the trans carbonyl ligand.

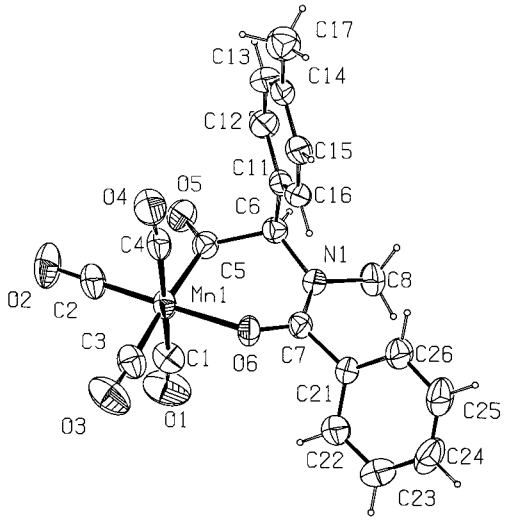
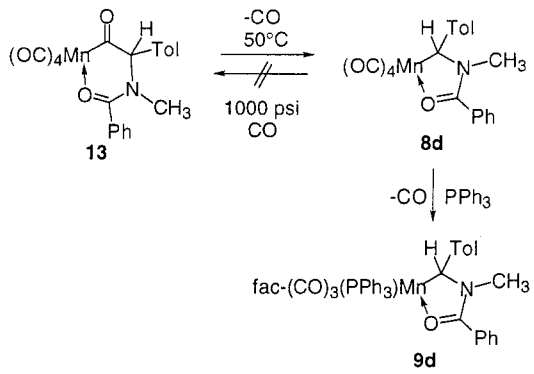


Figure 1. Crystal structure of $(CO)_4Mn[\eta^2$-COCH(Tol)N-(CH_3)COPh] (**13**). Selected bond lengths (Å) and angles (deg): Mn(1)−C(1), 1.854(5); Mn(1)−C(2), 1.780(4); Mn(1)−C(3), 1.860(5); Mn(1)−C(4), 1.862(4); Mn(1)−C(5), 2.017-(4); Mn(1)−O(6), 2.040(2); C(1)−O(1), 1.128(4); C(2)−O(2), 1.149(4); C(3)−O(3), 1.136(5); C(4)−O(4), 1.131(4); C(5)−O(5), 1.210(4); C(7)−O(6), 1.259(4); C(7)−N(1), 1.326(4); C(5)−Mn(1)−O(6), 88.30(13); C(7)−N(1)−C(8), 122.9(3); C(7)−N(1)−C(6), 122.4(3); C(8)−N(1)−C(6), 114.5(3).

Scheme 4



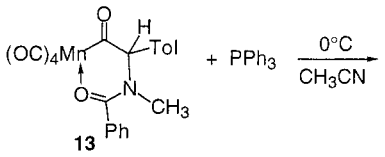
The chelation of the amide oxygen to the Mn center creates a six-membered metallacycle. Interestingly, the amide nitrogen is essentially planar (sum of bond angles 359.8°), and the N(1)−C(7) bond length of 1.326(4) Å is shorter than the C−N bond distance in formamide (C−N = 1.368 Å)[17] and closer in length to a typical carbon−nitrogen double bond (1.30 Å). In addition, the carbonyl bond length (C(7)−O(6) = 1.259(4) Å), is lengthened from that found in typical amides (formamide: C=O = 1.212 Å). These data are indicative of a significant contribution of resonance structure **13′** to the overall structure of the complex.

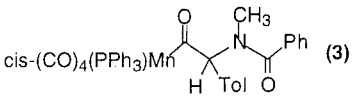
To our knowledge, complex **13** is the first example of a crystallographically characterized acyl-bound transition metal α-amino acid derivative.[5] Importantly, this complex can be generated from simple imine, carbon monoxide, and acid chloride building blocks. Therefore,

(17) *CRC Handbook of Chemistry and Physics*, 81th ed.; Kide, D. R., Ed.; CRC Press: Cleveland, OH, 2000; p 9-1.

a preliminary examination of the reactivity of **13** toward external substrates has been performed.

Dechelation of 13 with PPh_3. In contrast to the behavior of the five-membered metallacycle **8a**, the addition of 1 equiv of PPh_3 to complex **13** does not lead to displacement of a carbonyl ligand and instead leads to the formation of a new complex (**15**) in 70% NMR yield. Complex **15** can be isolated as a pale yellow solid and has been characterized as the product of dechelation of the amide ligand by coordination of PPh_3 (eq 3). The





(3)

15

formulation of **15** is supported by the ^{13}C NMR, which shows four separate metal−carbonyl resonances: δ 216.9 (d, $^2J_{P-C} = 32$ Hz), δ 216.2 (d, $^2J_{P-C} = 84$ Hz), δ 214.6 (d, $^2J_{P-C} = 76$ Hz), and δ 213.2 (d, $^2J_{P-C} = 59$ Hz), confirming that the $(CO)_4Mn$ fragment remains intact and phosphine is bound to the metal center. The final coordination site on manganese is occupied by the acyl ligand. This can be clearly observed in the ^{13}C NMR signal for the acyl carbon (δ 267.5 (d)), which has strong two-bond coupling to the phosphine ligand ($^2J_{P-C} = 50$ Hz). The dechelation of the amide ligand is also evident from ^{13}C NMR, in which the amide carbonyl resonance (δ 170.8) is shifted upfield from that in **7a** and **8a** and is instead similar to that observed in free amides (δ 171).

The facile dechelation of the amide oxygen from **13** is surprising when compared to the reactivity of complex **8a**, which does not undergo amide dechelation and instead loses carbon monoxide upon PPh_3 addition. Thus, while the chelation of the amide in the five-membered ring of **8a** is quite robust, the added flexibility of the six-membered chelate appears to result in a weaker Mn−O bond that can be broken by strong ligands.

Decarbonylation of Complex 13. Complex **13** has been found to be susceptible to CO deinsertion in the absence of strong ligands. The warming of complex **13** in CD_3CN to 50 °C for 15 min results in a rapid decarbonylation of the complex to form **8d** in 40% NMR yield (Scheme 4). Similarly, the reaction of imines **5a**−**c** with complex **13** in CD_3CN also results in the slow loss of carbon monoxide and generation of complex **8d**. Thus, it appears that the weaker coordinating imine cannot stabilize the dechelated version of complex **13** in analogy to PPh_3 (**15**) and, instead, leads to CO deinsertion and formation of the stable five-membered metallacycle. This process also occurs more rapidly than imine insertion into the Mn−acyl bond of **13**. The decarbonylation of **13** appears to be irreversible, and the addition of up to 1000 psi of CO to **8d** does not lead to the regeneration of complex **13**.

Complex **8d** can be partially isolated by extraction with pentane and has been characterized by multi-

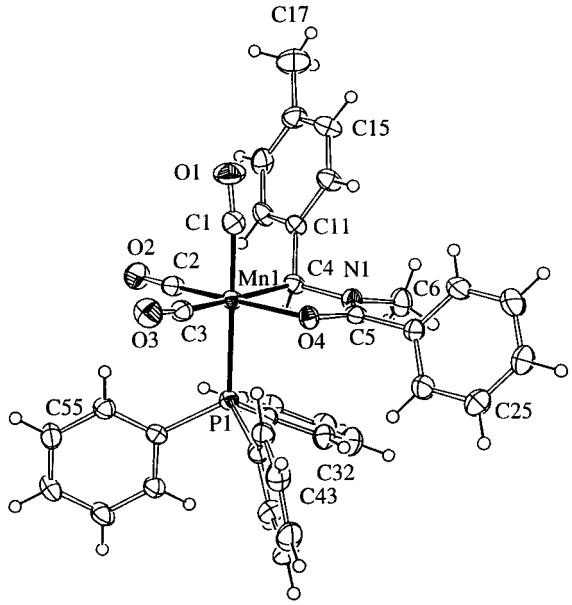


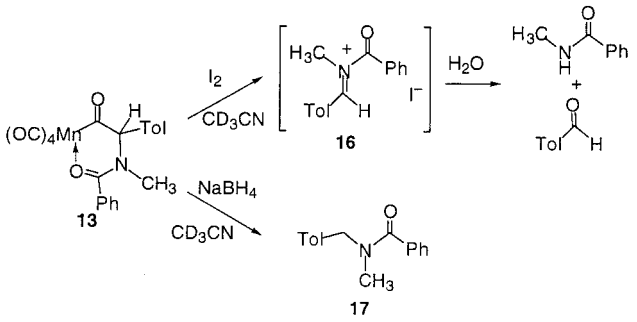
Figure 2. Crystal structure of *fac*-$(CO)_3(PPh_3)Mn[\eta^2$-CH(Tol)N(CH_3)COPh] (**9d**). Selected bond lengths (Å) and angles (deg): Mn(1)−C(1), 1.814(2); Mn(1)−C(2), 1.775(2); Mn(1)−C(3), 1.812(2); Mn(1)−C(4), 2.128(2); Mn(1)−P(1), 2.3690(9); Mn(1)−O(4), 2.0242(14); C(1)−O(1), 1.149(2); C(2)−O(2), 1.155(2); C(3)−O(3), 1.154(2); C(5)−O(4), 1.270(2); C(5)−N(1), 1.31(2); C(4)−Mn(1)−O(4), 80.12(7); C(5)−N(1)−C(6), 123.4(2); C(5)−N(1)−C(4), 115.59(12); C(6)−N(1)−C(4), 117.8(2).

nuclear NMR and IR. The NMR data for **8d** are almost identical with those of its methyl analogue **8a**, with the diagnostic Mn−C*H* resonance shifted upfield of free imine to δ 5.09 (s) (**8a**: δ 5.09). The ^{13}C NMR of **8d** reveals the disappearance of the manganese−acyl resonance at δ 269.9, confirming that decarbonylation has occurred. In addition, the amide resonance is once again downfield of the free amide (δ 179.9), demonstrating that the carbonyl oxygen remains chelated to the manganese center after CO loss. All other data are consistent with the structure as shown.

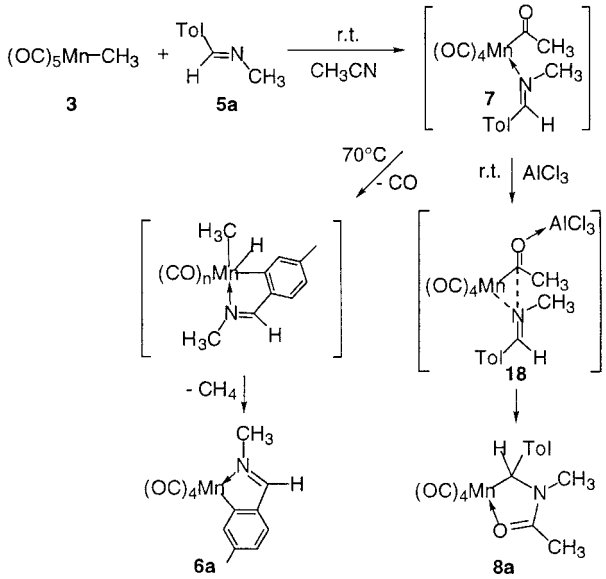
As with **8a**, the addition of PPh_3 to a CD_3CN solution of **8d** leads to an immediate displacement of carbon monoxide and the quantitative generation of the phosphine-substituted complex **9d**. Complex **9d** can be isolated as yellow crystals by crystallization from acetonitrile at −40 °C, and its structure as *fac*-$(CO)_3(PPh_3)Mn[\eta^2$-C(H)TolN(CH_3)COPh] has been confirmed by X-ray crystallography (Figure 2).

This structure demonstrates that carbon monoxide deinsertion has occurred from **13** to generate the five-membered amide-chelated complex. The geometry about manganese is near octahedral and clearly shows the *fac* orientation of the three carbonyl ligands about the metal center. As with complex **13**, the carbonyl ligand trans to the oxygen ligand displays a shortened Mn−C(2) bond (1.775(2) Å) relative to the other carbonyl ligands (M−C(1) = 1.814(2) Å; Mn−C(3) = 1.812(2) Å), suggestive of the stronger back-bonding with this CO ligand. The shortened amide N(1)−C(5) bond length (1.313(2) Å) and lengthened C(5)−O(4) bond (1.270(2) Å) are consistent with a strong chelation of the amide oxygen to the manganese center, in which a resonance structure similar to **13′** is strongly contributing to the overall structure of the complex.

Scheme 5



Scheme 6



Cleavage of the Mn−C Bond in Complex 13. Preliminary attempts to liberate the α-amino acid unit from the metal center in **13** show that decarbonylation to generate the five-membered chelate ring occurs prior to cleavage of the manganese−acyl bond. Thus, the oxidation of complex **13** with I_2 in CH_3CN, followed by workup under hydrolytic conditions, yields *p*-tolualdehyde and the amide $(CH_3)HNCOPh$. These products would arise from hydrolysis of the N-acyl iminium iodide salt **16** (Scheme 5). Considering that oxidation of the manganese center by I_2 likely causes the displacement of CO ligands, the generation of **16** presumably occurs via initial CO loss from the Mn center, followed by CO deinsertion and cleavage of the Mn−C bond. Similarly, the reduction of **13** with $NaBH_4$ leads to the formation of amide **17** (70% NMR yield). Once again, this product shows that CO deinsertion from **13** occurs prior to rupture of the Mn−C bond.

Discussion

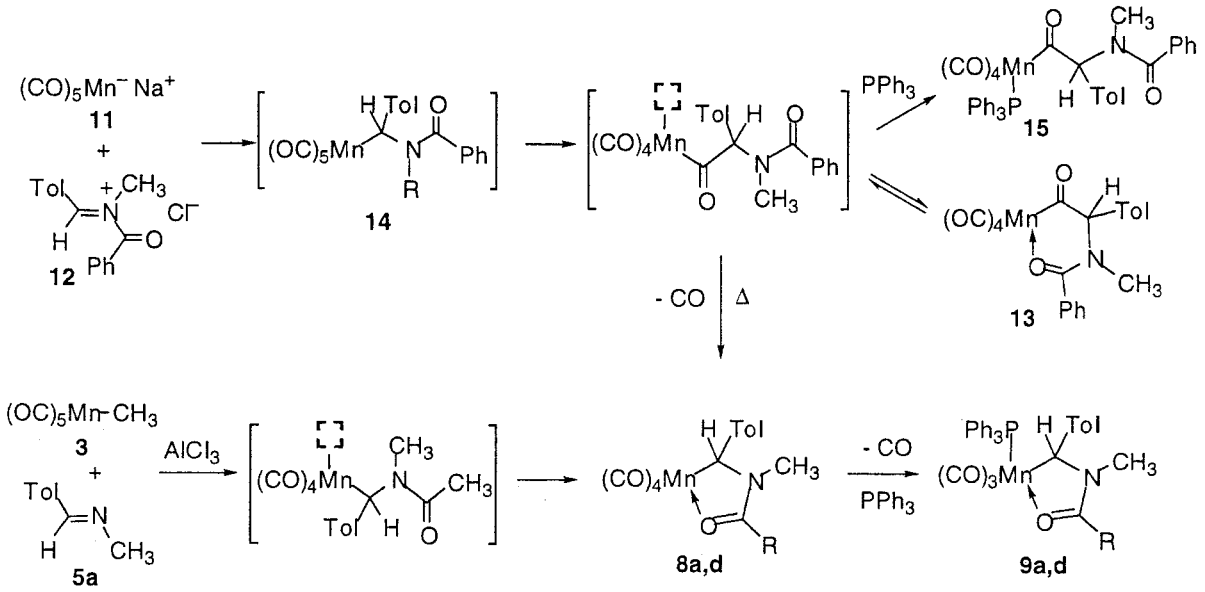
Sequential CO/Imine Insertion with $(CO)_5MnCH_3$. While olefins and alkynes have been previously examined for migratory insertion into the manganese−acyl bonds of $(CO)_5MnCOR$,[6] our observation of the formation of **8a** upon reaction of $Tol(H)C{=}NCH_3$ (**5a**) with $(CO)_5Mn{-}CH_3$ in the presence of $AlCl_3$ represents the first well-defined example of sequential carbon monoxide and imine insertion with a neutral metal complex. Structurally, this sequential insertion occurs to generate a manganese-chelated product that is directly analogous to those observed with alkenes and alkynes.[6] A similar amide chelation has also been noted in the only other reports of imine insertion reactions with cationic palladium and nickel complexes (Scheme 1).[1,4] As demonstrated by in the X-ray structure of **9d** (Figure 2), this chelation is strongly resonance stabilized, generating a robust and nearly planar five-membered metallacycle. This chelation undoubtedly provides a further thermodynamic driving force for imine insertion.

In contrast to the behavior of the cationic palladium and nickel complexes, imine insertion into the manganese−acyl bond of $(CO)_4Mn(COR)$ is only observed in the presence of $AlCl_3$. The ability of the Lewis acid to completely divert the reactivity of $Tol(H)C{=}NCH_3$ with methylmanganese pentacarbonyl (**3**) from cyclometalation to sequential insertion has, to our knowledge, not been previously noted. A reasonable rationale for this behavior is summarized in Scheme 6. The formation of intermediate **7c** upon reaction of imine **5c** with **3** demonstrates that the complex *cis*-$(CO)_4Mn(COCH_3)$(imine) can be generated both with and without Lewis acid present. Considering that the insertion of $Tol(H)C{=}NCH_3$ into the manganese−acyl bond occurs under much milder conditions (ambient temperature) than cyclometalation (70 °C), the influence of $AlCl_3$ likely occurs as anticipated: by lowering the barrier for imine insertion from intermediate **7**. This does not allow the higher barrier C−H activation chemistry to compete with insertion. The ability of $AlCl_3$ to lower the kinetic barrier to imine insertion likely arises from its ability to coordinate to the acyl ligand oxygen,[12] thereby creating a more electrophilic acyl ligand in **18**. Thus, it appears that, provided the acyl ligand is sufficiently electrophilic, these neutral manganese complexes behave in a fashion similar to cationic group 10 metals and undergo imine insertion into the metal−acyl bond under relatively mild conditions.

CO Insertion into $(CO)_nMnCH(Tol)N(CH_3)COR$ (8 and 14). The oxidative addition of N-acyl iminium chloride salts to $(CO)_5Mn^-Na^+$ provides an alternative route to generate manganese-bound amides similar to those obtained from sequential imine/CO insertion. In contrast to what has been observed from imine/CO insertion, this oxidative addition route results in the immediate insertion of carbon monoxide into the Mn−C bond, forming the six-membered metallacycle **13**. Thus, not only is CO insertion into the α-amido substituted manganese-alkyl complex possible but it occurs under very mild conditions. By way of comparison, CO insertion into the $Mn{-}CH_3$ bond of $(CO)_5MnCH_3$ (**3**) under 1 atm of CO is only 75% complete at 25 °C after 24 h.[18] Similarly, Beck and co-worker have reported that the less basic α-amide-substituted phthalimidomethyl−manganese complex requires high CO pressure to undergo carbonylation.[5c] The rapid insertion of CO at −15 °C in complex **14** is likely related to the ability of the amide oxygen to undergo rapid intramolecular chelation to the manganese center. This would allow for the rapid trapping of the product of CO insertion into the Mn−C bond of complex **14**.

(18) Determined by monitoring the reaction of methylmanganese carbonyl (27 mg, 0.12 mmol) in 0.5 mL of CD_3CN under 1 atm of CO by ^1H NMR.

Scheme 7



The difference in CO insertion propensity between the similar α-amido-substituted manganese complexes obtained from oxidative addition (**14**) and sequential imine/CO insertion (**8a**) likely arises from the structure of these complexes. The oxidative addition route generates the α-amido-substituted manganese−alkyl complex in a nonchelated form (**14**) and bound to a pentacarbonyl manganese center (Scheme 7). In order for the amide oxygen to chelate to the Mn center from **14**, carbon monoxide must first insert into the Mn−C bond, and this is subsequently trapped out as **13**. This contrasts with the imine insertion route, in which the migration of the *σ*-bound imine from *cis*-$(CO)_4Mn(COCH_3)(H_3CN{=}C(H)Tol)$ (**7a**) generates an unsaturated tetracarbonyl center, in which the amide oxygen can undergo rapid chelation to form a five-membered metallacycle. Considering the greater stability of the five-membered amide-chelated metallacycle (vide infra), these data strongly argues that efforts toward utilizing sequential imine/CO insertion to generate α-amino acid derivatives may be greatly facilitated by the generation of unchelated insertion products.

Relative Stability of the Five- and Six-Membered Metallacycles. Depending upon he synthetic route employed, either the five- (complex **8**) or six-membered (complex **13**) amide-chelated metallacycles can be generated as the initial isolated product. However, the five-membered metallacycle is the thermodynamically more stable form of the two complexes. This is clearly demonstrated in the thermal reactivity of **13**, which undergoes irreversible CO loss upon warming to generate complex **8d**. The greater stability of the five-membered metallacycles may be related to the ability of the five-membered ring to achieve amide chelation to the manganese center stronger than that of the more flexible six-membered metallacycle. This is not evident in the crystal structures of the complexes, which show similar Mn−O bond distances in both **13** and **9d** (**13**, 2.040(2) Å; **9d**, 2.0242(14) Å). However, it is revealed in their reactivity toward phosphine ligands. In contrast to the six-membered metallacycle in **13**, which undergoes reaction with PPh_3 to generate the nonchelated phosphine-substituted analogue **8d**, PPh_3 does not cleave the amide chelation from the five-membered metallacycles and, instead, results in the displacement of a CO ligand. The propensity of complex **13** to undergo rapid CO deinsertion is further demonstrated in our preliminary attempts to liberate the α-amino acid unit from the manganese center with I_2 and $NaBH_4$, which instead results in the decarbonylation of **13** prior to cleavage of the Mn−C bond (Scheme 5).

Conclusion

In conclusion, two new routes have been developed to generate manganese-chelated amides: the sequential insertion of carbon monoxide and imine into manganese−methyl bonds and the oxidative addition of N-acyl iminium salts to $(CO)_5Mn^-$. Structural characterizations of the products of both these reactions demonstrate the strong propensity of the amide ligand to coordinate to the manganese center to generate five- and six-membered metallacycles, respectively. In the case of oxidative addition, this chelation is accompanied by CO insertion, allowing the synthesis and structural characterization of a novel manganese-chelated α-amino acid derivative. The propensity of the latter complex to undergo CO deinsertion has hindered our preliminary attempts to liberate the organic amino acid fragment from the metal center. Nevertheless, the reactivity of this six-membered metallacycle with strong ligands implies it may be possible to stabilize this complex and selectively cleave the manganese−acyl bond. Considering that this would allow for the controlled synthesis of α-amino acids from simple imine, carbon monoxide, and acid chloride building blocks, efforts along these lines are currently being pursued in our laboratory.

Experimental Section

Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmosphere 553-2 drybox or by using standard Schlenk or vacuum-line techniques. NMR spectra were obtained on a 270 MHz JEOL NMR. IR spectra were obtained on a Bruker IFS-48 spectrometer. X-ray analyses were performed on either an Enraf-Nonius CAD4 with Cu Kα radiation (**9d**) or a Rigaku diffractometer

with Mo Kα radiation (**13**). Elemental analyses were performed by Laboratoire d'analyse elementaire de l'Universite de Montreal, Montreal, Quebec, Canada, or by QTI, Whitehouse, NJ.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Liquids were freeze−pump−thawed three times to degas before use. Diethyl ether was distilled from sodium benzophenone. Pentane, methylene chloride, and chlorobenzene were distilled from CaH_2. Deuterated solvents were dried as their protonated analogues but were vacuum-transferred from the drying agent. UHP grade carbon monoxide was obtained from Matheson. Manganese carbonyl was obtained from Strem Chemical Co. and used without further purification. Imines were prepared by reaction of *p*-tolualdehyde and the appropriate amine in diethyl ether at room temperature for 1 day in the presence of 4 Å molecular sieves. N-Acyl iminium salt **12** was generated in situ by the reaction of benzoyl chloride with MeN=C(H)Tol, in analogy to literature procedures.[16] $(CO)_5$MnR (R = CH_3, Ph)[19] and $(CO)_5MnNa$[19] were prepared by literature procedures.

Synthesis of $(CO)_4Mn[\eta^2$-2-$(CH{=}NCH_3)$-5-$(CH_3)C_6H_3]$ (6a). Methylmanganese pentacarbonyl (200 mg, 0.95 mmol) and Tol(H)C=NMe (127 mg, 0.95 mmol) were dissolved in 5 mL of acetonitrile, and the solution was heated to 70 °C for 24 h. The solution was concentrated in vacuo until the appearance of a solid and then cooled to −30 °C overnight. The yellow crystals formed were collected by filtration, washed with cold diethyl ether, and dried under vacuum, yielding **6a** (190 mg, 67% yield). Anal. Found: C, 52.16; H, 3.35; N, 4.63. Calcd: C, 52.19; H, 3.37; N, 4.68. IR (KBr): 2075 (m), 1966 (m), 1910 (s), 1614 (m), 1581 (m), 1431 (w), 1134 (m), 1033 (m), 808 (m), 633 (s), 546 (m) cm^{-1}. ^1H NMR (CD_3CN): δ 8.31 (s, 1H, HC=N), 7.72 (s, 1H), 7.48 (d, 1H), 6.96 (d, 1H), 3.60 (s, 3H, NCH_3), 2.36 (s, 3H, Tol). ^{13}C NMR (C_6D_6, 5 °C): δ 220.2, 21.6, 181.5, 176.1, 145.4, 142.1, 141.3, 128.6, 124.8, 51.4, 21.7.

Synthesis of $(CO)_4Mn[\eta^2$-2-$(CH{=}NCH_2Ph)$-5-$(CH_3)C_6H_3]$ (6b). Methylmanganese pentacarbonyl (200 mg, 0.95 mmol) and Tol(H)C=NCH_2Ph (197 mg, 0.95 mmol) were dissolved in 5 mL of acetonitrile, and the solution was heated to 70 °C for 72 h. The solution was removed in vacuo, and the residual oil was dissolved in 3 mL of pentane and cooled to −30 °C overnight. The yellow crystals formed were collected by filtration, washed with cold diethyl ether, and dried under vacuum, yielding **6b** (251 mg, 70% yield). Anal. Found: C, 60.72; H, 3.48; N, 3.71. Calcd: C, 60.81; H, 3.76; N, 3.73. IR (KBr): 2071 (s), 1994 (vs), 1974 (s), 1936 (s), 1604 (s), 1580 (s), 1545 (m), 1452 (m), 1345 (m), 1064 (m), 1032 (m), 742 (m), 640 (s), 546 (m) cm^{-1}. ^1H NMR (CD_3CN): δ 8.53 (s, 1H, HC=N), 7.71 (s, 1H), 7.58 (d, 1H), 7.28−7.44 (m, 5H, Ph), 6.99 (d, 1H), 4.92 (s, 2H, NCH_2Ph), 2.36 (s, 3H, Tol). ^{13}C NMR (C_6D_6, 5 °C): δ 220.3, 214.2, 182.5, 175.9, 145.2, 142.1, 141.9, 135,8, 129.4, 128.7, 128.5, 124.9, 67.8, 21.8.

Synthesis of $(CO)_4Mn[\eta^2$-2-$(C(^tBu){=}NH)$-5-$(CH_3)C_6H_3]$ (6c). Methylmanganese pentacarbonyl (180 mg, 0.86 mmol) and ^{t}Bu(Tol)C=NH (151 mg, 0.86 mmol) were dissolved in 10 mL of acetonitrile and stirred for 15 min. An aliquot of the solution was removed and analyzed by IR and NMR, revealing the quantitative formation of complex **7c**. Anal. Found: C, 56.54; H, 4.73; N, 4.00. Calcd: C, 56.32; H, 4.73; N, 4.10. IR (KBr): 3128 (w), 2971 (w), 2065 (m), 1954(vs), 1920 (vs), 1608 (s), 1476 (w), 1388 (w), 1242 (w), 1076 (m), 822 (m), 641 (s), 546 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 10.76 (s, 1H, NH), 6.91 (d, 2H), 6.67 (d, 2H), 2.78 (s, 3H, $COCH_3$), 2.06 (s, 3H, Tol), 0.86 (s, 9H). ^{13}C NMR (C_6D_6, 5 °C): δ 275.1, 220.1, 213.7, 211.2, 197.9, 188.7, 138.9, 136.4, 129.0, 126.6, 50.1, 43.1, 27.4, 20.9. The reaction solution was warmed to 70 °C for 20 h. The solvent was removed in vacuo, the residue was dissolved in diethyl ether, and this solution was filtered through Celite. The ether was removed in vacuo, and the crude product was recrystallized from 5 mL of pentane at −30 °C overnight. The light yellow crystals were collected by filtration, washed with cold pentane, and dried under vacuum, yielding **6c** (117 mg, 34% yield). IR (KBr): 3372 (s), 2970 (m), 2074 (s), 1983 (vs), 1898 (s), 1569 (s), 1449 (m), 1360 (m), 1189 (m), 1140 (m), 1041 (w), 962 (m), 852 (m), 646 (s), 544 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 8.13 (s, 1H), 7.66 (s, 1H, NH), 7.57 (d, 1H), 6.75 (d, 1H), 2.13 (s, 3H, Tol), 0.77 (s, 9H). ^{13}C NMR (C_6D_6, 5 °C): δ 220.0, 215.7, 214.5, 197.8, 183.0, 142.9, 141.8, 141.0, 130.0, 124.2, 39.6, 27.9, 21.3.

Synthesis of $(CO)_4Mn[\eta^2$-CH(Tol)N$(CH_3)COCH_3]$ (8a). Methylmanganese pentacarbonyl (200 mg, 0.95 mmol), Tol(H)C=NMe (127 mg, 0.95 mmol), and $AlCl_3$ (127 mg, 0.965 mmol) were dissolved in 20 mL of acetonitrile, and the solution was stirred at room temperature for 24 h. ^1H NMR of the reaction mixture reveals the formation of **8a** in 30% yield. Attempts to isolate **8a** were unsuccessful. ^1H NMR (CD_3CN): δ 7.04 (d, 2H), 6.89 (d, 2H), 5.09 (s, 1H, Mn−CH), 2.98 (s, 3H, NCH_3), 2.23 (s, 3H, $COCH_3$), 2.05 (s, 3H, Tol).

Synthesis of *fac*-$(CO)_3(PPh_3)Mn[\eta^2$-CH(Tol)N(CH_3)-$COCH_3]$ (9a). Methylmanganese pentacarbonyl (200 mg, 0.95 mmol), Tol(H)C=NMe (127 mg, 0.95 mmol) and $AlCl_3$ (127 mg, 0.965 mmol) were dissolved in 20 mL of acetonitrile, and the solution was stirred at room temperature for 24 h. A 3 mL acetonitrile solution of triphenylphosphine (250 mg, 0.95 mmol) was added to the reaction mixture, resulting in an immediate effervesence. After 15 min of stirring, the solution was concentrated in vacuo until the appearance of a solid precipitate, and the solution placed at −30 °C overnight. The pale yellow powder was collected, washed with cold diethyl ether, and dried under vacuum, yielding **9a** (122 mg, 22% yield). Anal. Found: C, 66.33; H, 5.14; N, 2.56. Calcd: C, 66.55; H, 5.06; N, 2.43. IR (KBr): 1996 (s), 1904 (vs), 1873 (vs), 1600 (m), 1505 (w), 1434 (w), 1089 (w), 679 (m), 520 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 7.69 (m, 8H), 6.9−7.5 (m, 11H), 4.60 (d, $^3J_{P-H}$ = 19 Hz, 1H), 2.22 (s, 3H, NCH_3), 1.85 (s, 3H, Tol), 1.09 (s, 3H, $COCH_3$). ^{31}P NMR (C_6D_6): δ 53.97.

Synthesis of $(CO)_4Mn[\eta^2$-COCH(Tol)N$(CH_3)COPh]$ (13). Sodium manganese pentacarbonyl (500 mg, 2.29 mmol) and Tol(H)CN$(CH_3)COPh^+Cl^-$ (630 mg, 2.29 mmol) were stirred in 10 mL of acetonitrile for 2 min, and the cloudy yellow solution was quickly filtered through Celite (to remove NaCl). The solution was concentrated in vacuo until the appearance of a yellow solid precipitate, and the cold solution was filtered through a fritted Buchner funnel. The pale yellow powder was collected, washed with cold diethyl ether, and dried under vacuum, yielding **13** (520 mg, 52% yield). Anal. Found: C, 58.07; H, 3.80; N, 3.18. Calcd: C, 58.21; H, 3.72; N, 3.23. IR (KBr): 2076 (m), 1987 (vs), 1630 (m), 1582 (s), 1494 (w), 1013 (m), 912 (w), 698 (m), 638 (m), 532 (m) cm^{-1}. ^1H NMR (CD_3CN): δ 7.57 (m, 5H, Ph), 7.21 (d, 2H, Tol), 7.07 (d, 2H, Tol), 4.54 (s, 1H, Mn−CH), 3.16 (s, 3H, NCH_3), 2.31 (s, 3H, Tol). ^{13}C NMR (C_6D_6, 5 °C): δ 269.9, 218.1, 213.1, 212.2, 210.1, 178.0, 137.7, 133.8, 131.2, 130.9, 129.7, 128.7, 127.5, 126.0, 83.0, 41.4, 20.8.

Synthesis of *cis*-$(CO)_4(PPh_3)Mn[\eta^2$-COCH(Tol)N(CH_3)-$COPh]$ (15). Sodium manganese pentacarbonyl (300 mg, 1.38 mmol) and Tol(H)CN$(CH_3)COPh^+Cl^-$ (378 mg, 1.38 mmol) were mixed in 10 mL of acetonitrile for 2 min, and the cloudy yellow solution was quickly filtered through Celite (to remove NaCl). A 10 mL acetonitrile solution of triphenylphosphine (362 mg, 1.28 mmol) was added to the reaction mixture, and the solution was stirred for 2 h at 0 °C. The pale yellow solid was collected by filtration, washed with cold diethyl ether, and dried under vacuum, yielding **15** (237 mg, 37% yield). Complex **15** proved too unstable for elemental analyses and was therefore characterized by spectroscopic methods. See the Supporting Information for ^1H and ^{13}C NMR spectra. IR (KBr): 2063 (m), 1962 (vs), 1939 (vs), 1624 (s), 1434 (m), 1389 (m), 1328 (m), 1063 (w), 997 (m), 633 (s), 520 (m) cm^{-1}. ^1H

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NMR (C_6D_6): δ 7.76−7.86 (m, 6H), 7.40−7.48 (m, 2H), 7.32 (s, 1H), 7.26 (d, 2H), 7.02−7.13 (m, 8H), 6.93−7.02 (m, 5H), 2.53 (s, 3H, NCH_3), 2.02 (s, 3H, Tol). ^{31}P NMR (C_6D_6): 52.05. ^{13}C NMR (C_6D_6, 5 °C): δ 267.6 (d, $^2J_{P-C}$ = 50 Hz), 216.9 (d, $^2J_{P-C}$ = 32 Hz), 216.2 (d, $^2J_{P-C}$ = 84 Hz), 214.6 (d, $^2J_{P-C}$ = 76 Hz), 213.3 (d, $^2J_{P-C}$ = 59 Hz), 170.7, 138.0 (d, J_{P-C} = 54 Hz), 135.2, 134.6, 134.0 (d, J_{P-C} = 38 Hz), 132.5, 130.5, 129.9 (d, J_{P-C} = 27 Hz), 129.7, 128.9, 128.4 (d, J_{P-C} = 27 Hz), 83.0 (d, $^3J_{P-C}$ = 10 Hz), 36.0, 20.9.

Synthesis of $(CO)_4Mn[\eta^2$-CH(Tol)N(CH_3)COPh] (8d). Sodium manganese pentacarbonyl (500 mg, 2.29 mmol) and Tol(H)CN(CH_3)COPh$^+$Cl$^-$ (400 mg, 1.46 mmol) were mixed in 10 mL of acetonitrile, and the solution was stirred at 50 °C for 15 min. The solvent was removed, and the residue was dissolved in 10 mL diethyl ether. The red solution was filtered through Celite, diluted with 20 mL of pentane, and allowed to stand at ambient temperature for 24 h. The solution was filtered (to remove a red impurity), the solvent was removed in vacuo, and the product was extracted with 20 mL of pentane. Evaporation of the pentane solution yielded **8d** as a yellow powder with approximately 95% purity by ^{1}H NMR (250 mg, 43% yield). See the Supporting Information for ^{1}H and ^{13}C NMR spectra. IR (KBr): 2014 (s), 1979 (vs), 1951 (vs), 1913 (s), 1589 (w), 1559 (m), 1508 (m), 1474 (w), 1070 (m), 710 (m), 639 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.09 (m, 2H), 7.01 (m, 5H), 6.90 (m, 2H), 5.04 (s, 1H, Mn−CH), 2.49 (s, 3H, NCH_3), 2.16 (s, 3H, Tol). ^{13}C NMR (C_6D_6): δ 220.8, 214.8, 212.8, 179.9, 148.8, 1233.1, 132.8, 130.6, 129.5, 128.3, 127.6, 67.5, 38.5, 20.8.

Synthesis of *fac*-$(CO)_3(PPh_3)Mn[\eta^2$-CH(Tol)N(CH_3)-COPh] (9d). Complex **15a** (200 mg, 0.50 mmol) and triphenylphosphine (132 mg, 0.50 mmol) were dissolved in 10 mL acetonitrile, and the mixture was stirred for 2 h at 0 °C. The pale yellow solid precipitate was collected by filtration and washed with cold diethyl ether to yield **9d** (140 mg, 52% yield). Complex **9d** proved too unstable for elemental analyses and was therefore characterized by spectroscopic methods. See the Supporting Information for ^{1}H and ^{13}C NMR spectra. IR (KBr): 3013 (w), 2002 (s), 1902 (vs), 1868 (vs, 1601 (s), 1504 (m), 1433 (m), 1162 (w), 1089 (m), 1016 (w), 820 (m), 755 (m), 699 (s), 518 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.70−7.88 (m, 6H), 7.22 (m, 3H), 6.85−7.08 (m, 15H), 4.59 (d, $^3J_{P-H}$ = 18 Hz, 1H, Mn−CH), 2.22 (s, 3H, NCH_3), 2.14 (s, 3H, Tol). ^{31}P NMR (C_6D_6): 55.57. ^{13}C NMR (C_6D_6, 5 °C): δ 226.8 (d, $^2J_{P-C}$ = 84 Hz), 220.6 (d, $^2J_{P-C}$ = 146 Hz), 217.9 (d, $^2J_{P-C}$ = 84 Hz), 150.0 (d, $^2J_{P-C}$ = 30 Hz), 133.8, 133.6, 133.1, 132.1, 130.2, 129.8, 129.1, 128.4 (d, $^1J_{P-C}$ = 35 Hz), 127.6, 74.8 (d, $^4J_{P-C}$ = 49 Hz), 38.6, 21.0.

X-ray Crystallographic Study of *fac*-$(CO)_3(PPh_3)Mn$-[CH(Tol)N(CH_3)COPh] (9d) and $(CO)_4Mn[\eta^2$-COCH(Tol)N-(CH_3)COPh] (13). Crystals of **9d** and **13** for diffraction analysis were grown by cooling an acetonitrile solution and mounted on a capillary. X-ray data for **9d** were collected at 230 K on a Enraf-Nonius CAD4 with Cu Kα radiation. X-ray data for **13** were collected at 293 K on a Rigaku diffractometer with Mo Kα radiation. The crystal, data collection, and refinement parameters are collected in Table 1. The space groups were confirmed by the PLATON program.[20] Data reduction was performed using NRCVAX.[21] The structures were solved with direct methods using SHELXS96[22] and difmap synthesis using SHELXL96.[23] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. Hydrogen atoms in **9d** were calculated at idealized positions using a riding model with different C−H distances for the types of hydrogens. Hydrogen atoms in **13** were constrained to the parent site using a riding model. The isotropic displacement factors were adjusted to a value 50% higher than that of the parent site (methyl) and 20% higher (others). A final verification of possible voids was performed using the VOID routine of the PLATON program.[20]

Table 1. Crystallographic Details for Complexes 9d and 13

	9d	**13**
empirical formula	$C_{37}H_{31}NMnNO_4P$	$C_{21}H_{16}NMnNO_6$
fw	639.57	433.29
temp, K	230(2)	293(2)
wavelength, Å	1.540 56	0.709 30
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	14.975(5)	10.309(5)
b (Å)	13.004(5)	10.518(3)
c (Å)	17.838(7)	11.002(4)
α (deg)		75.09(3)
β (deg)	111.76 (3)	62.73 (2)
γ (deg)		85.46 (4)
V (Å^3)	3226 (2)	1023.6 (7)
Z	4	2
d(calcd) (Mg m^{-3})	1.317	1.406
μ (mm^{-1})	4.129	0.681
F(000)	1328	444
no. of rflns collected	15 711	8042
no. of indep rflns	6114	4021
θ_{min}, θ_{max} (deg)	3.17, 69.87	2.00, 25.96
goodness of fit on F^2	0.860	1.040
R ($I > 2\sigma(I)$)	R1 = 0.0303, wR2 = 0.0669	R1 = 0.0601, wR2 = 0.1081
R (all data)	R1 = 0.0455, wR2 = 0.0692	R1 = 0.1122, wR2 = 0.1216
min, max $\Delta\rho$ (e/Å^3)	−0.350, 0.358	−0.381, 0.384

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Supporting Information Available: Tables giving X-ray structural data for complexes **9d** and **13** and figures giving NMR spectra of complexes **8d**, **9d**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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