α-Ketoacyl Complexes of Manganese Formed by Insertion of CO into a Manganese–Acyl Bond and by Nitrite Addition to a Manganese Carbyne Complex

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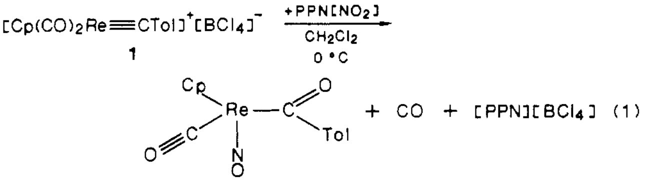
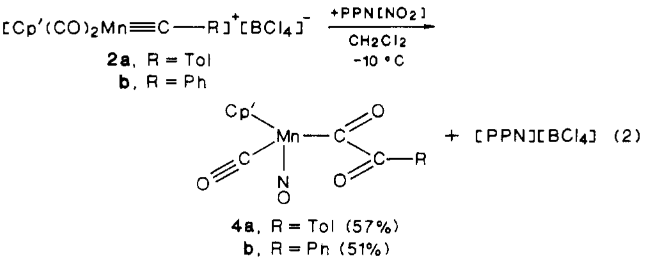
The carbyne complex $[Cp'(CO)_2Mn{\equiv}CR]^+$ ($Cp' = C_5H_4Me$; R = Ph, Tol) cleanly reacts with NO_2^- to form the α-ketoacyl complex $Cp'(CO)(NO)Mn{-}C\{O\}C\{O\}R$ (**4**). A similar reaction of $[Cp(CO)_2Re{\equiv}CTol]^+$ with NO_2^- gives the acyl complex $Cp(CO)(NO)Re{-}C\{O\}Tol$ (**3**). α-Ketoacyl complex **4** has also been prepared by oxidation of $[Cp'(CO)_2Mn{-}C\{O\}R]^-$ to form the 17e complex $Cp'(CO)_2Mn{-}C\{O\}R$ (**8**) followed by its reaction with NO gas. The latter reaction is the first demonstration of the insertion of CO into a metal–acyl bond. A mechanism is proposed for this process involving the addition of NO to **8** to give $Cp'(CO)_2(NO)Mn{-}C\{O\}R$ with a bent, 1e nitrosyl ligand which then inserts CO into the Mn–acyl bond as the nitrosyl relaxes to the more common linear, 3e form. The proposed intermediate **8** can also be obtained from the carbene complex $Cp'(CO)_2Mn{=}C(ONO)R$, which forms by addition of NO_2^- to $[Cp'(CO)_2Mn{\equiv}CR]^+$, and accounts for the formation of **4** in this latter reaction. Complex **4a** (R = Tol) has been crystallographically characterized: $P\bar{1}$, $a = 6.928$ (3), $b = 7.425$ (3), $c = 16.153$ (6) Å, $\alpha = 94.32$ (3), $\beta = 97.70$ (3), $\gamma = 110.73$ (3)°, $V = 763.3$ (5) Å^3, $Z = 2$, $R(F) = 4.74\%$, $R(wF) = 5.25\%$ for 1855 reflections with $F_o > 3\sigma(F_o)$. The molecule has the usual three-legged piano-stool geometry characteristic of $CpMnL_3$ complexes, and the α-ketoacyl ligand is bound in an η^1 fashion. The α-ketoacyl ligand adopts an s-trans configuration with a dihedral angle of 78° between the planes defined by the two carbonyl groups and their substituents. Complex **4** readily undergoes substitution reactions with L = PPh_3 and $C{\equiv}N$-t-Bu to form the α-ketoacyl complexes $Cp'(NO)(L)Mn{-}C\{O\}C\{O\}R$, but no deinsertion of CO from the α-ketoacyl ligand to form an acyl complex was observed for **4** nor its substituted derivatives under any conditions examined. The rhenium–acyl complex **3** was alkylated to form the cationic carbene complex $[Cp(CO)(NO)Re{=}C(OMe)Tol]^+$ which readily re-forms **3** upon reaction with H_2O.

Introduction

The chemistry of transition-metal carbyne complexes has been extensively studied,[1] but one important aspect that had not been investigated prior to this work involves their reactions ith potential oxygen atom donors such as Me_3NO, PhIO, and NO_2^-. Following our photochemical studies of $Cp(CO)_2W{\equiv}CTol$, $[Cp(CO)_2Re{\equiv}CTol]^+$ (**1**), and $[Cp'(CO)_2Mn{\equiv}CR]^+$ ($Cp' = C_5H_4Me$; R = Tol (**2a**), R = Ph (**2b**)),[2] we reacted the latter Re and Mn complexes with nitrite ion and observed the remarkable transformation of the carbyne ligand into acyl and α-ketoacyl ligands (eq 1 and 2).[3a] There is no precedent for either reaction, although the reverse transformation of eq 1 involving oxygen atom abstraction from an acyl ligand is a useful synthetic method for carbyne complexes.[4] Carbynes have been previously converted into acyl ligands, but in all cases these have involved formation of an alkyl ligand which then inserted CO.[5]



3 (73%)



4a, R = Tol (57%)
b, R = Ph (51%)

Relatively few complexes with α-ketoacyl ligands have been prepared,[6] although such species have been of interest because of their use to probe the feasibility of acyl to CO migratory insertion and the possible intermediacy of α-ketoacyl ligands in the Pd-catalyzed double carbonylation

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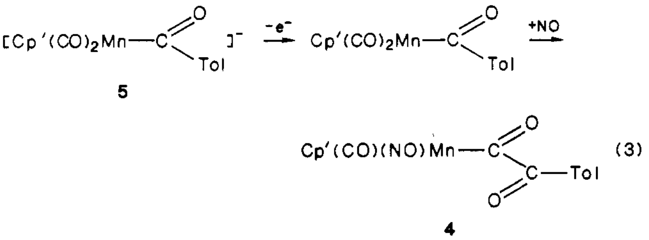
of aryl halides.[6b–e] All previous syntheses of complexes of these ligands have involved the addition of preformed α-ketoacyl halides to the appropriate metal precursors,[6] and never before had this ligand been assembled from coordinated ligands as observed in the reaction of eq 2. The concensus of opinion had been that acyl to CO migratory insertion does not occur.[6]

While conducting these studies we discovered that *direct migration* of an acyl ligand to a coordinated CO could be induced by reactions like that in eq 3, involving oxidation of the anionic acyl complex **5** followed by reaction with nitric oxide.[3b] This reaction represents the *first example of the direct insertion of CO into a metal–acyl bond*, and an important question that must be addressed is how the α-ketoacyl ligand in complex 4 forms in reaction 3, as well as in reaction 2.



Herein we present full details of our studies, including a description of experiments that address these mechanistic issues and also the crystallographic characterization of complex **4a**.[3] Also described are selected reactions of the acyl and α-ketoacyl complexes **3** and **4**, and especially interesting is the resistance of the α-ketoacyl ligand in **4** to deinsertion of CO under both photochemical and thermal conditions.

Results and Discussion

Nitrite-Induced Transformation of the Carbyne Ligand in $[Cp(CO)_2Re{\equiv}CTol]^+$ into an Acyl Ligand. The carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$ (**1**)[7] cleanly reacts with 1 equiv of [PPN][NO$_2$] to yield the new acyl complex **3** (eq 1). This reaction proceeds in near quantitative yield, and **3** was isolated as an air stable orange crystalline solid. It was characterized from its analytical and spectroscopic data. Noteworthy are IR bands at 1993 and 1717 cm^{-1}, respectively due to the carbonyl and nitrosyl ligands, and the presence of two bands at 1578 and 1561 cm^{-1} in the acyl region. These are attributed to rotational isomers of the acyl ligand, as previously proposed for other acyl complexes which show two acyl CO absorptions.[8] Complex **3**, although simple in composition, has not been previously reported although its PPh$_3$ analogue Cp(PPh$_3$)(NO)Re–C{O}R has been well studied.[9]

The formation of an intermediate in the reaction of **1** with [PPN][NO$_2$] was indicated by the initial color change from yellow to dark red when the reagents were combined at −78 °C, followed by a further change to the red-orange color of the acyl complex **3** upon warmup to room temperature. However, all attempts to spectroscopically characterize this intermediate failed due to its rapid conversion to **3**.

Two experiments were conducted in an attempted to form a Re α-ketoacyl complex analogous to that which resulted when $[Cp'(CO)_2Mn{\equiv}CR]^+$ was treated with NO$_2^-$ (eq 2). First, the rhenium acyl complex **3** was subjected to high CO pressure (1500 psi, 22 °C) to try to force CO insertion into the Re–acyl bond, but no reaction occurred. Secondly, the Re carbyne complex **1** was treated with [PPN][NO$_2$] *under 6 atm of CO*, but only acyl complex **3** was formed with no evidence for an α-ketoacyl ligand.

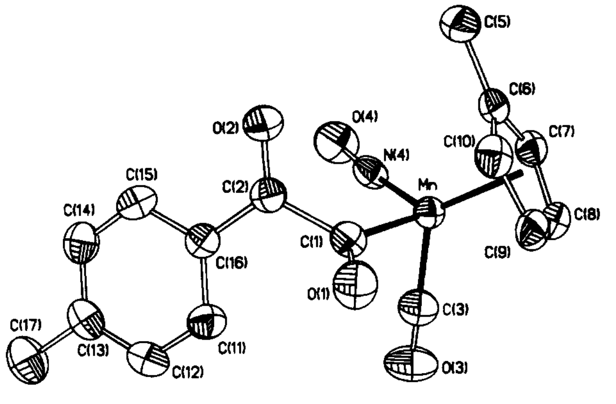
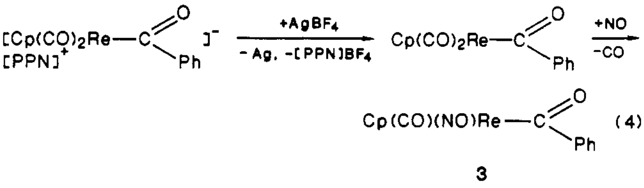


Figure 1. An ORTEP drawing of Cp'(CO)(NO)Mn–C{O}C{O}Tol (**4a**). Thermal ellipsoids are drawn at the 40% probability level.

Formation of Cp(CO)(NO)Re–C{O}Tol by Oxidation and NO Addition to $[Cp(CO)_2Re–C\{O\}Tol]^-$. It was also found that the acyl complex **3** could be formed from $[Cp(CO)_2Re–C\{O\}Tol]^-$ by an oxidation/NO addition reaction sequence. Treatment of CH$_2$Cl$_2$ solutions of the latter complex with AgBF$_4$ at −78 °C led rapidly to the formation of the oxidized complex Cp(CO)$_2$Re–C{O}Tol, which shows ν(CO) bands at 1956 and 1875 cm^{-1}. These are ~80 cm^{-1} higher in energy than those of $[Cp(CO)_2Re–C\{O\}Tol]^-$ (ν(CO) 1876, 1795 cm^{-1}), indicative of an oxidized species. Addition of NO gas to the cold solution of this oxidized complex led to its rapid and quantitative (by IR) conversion to complex **3** (eq 4).



Nitrite-Induced Transformation of the Carbyne Ligand in $[Cp'(CO)_2Mn{\equiv}CR]^+$ into an α-Ketoacyl Ligand. The manganese carbyne complexes $[Cp'(CO)_2Mn{\equiv}CR]^+$ (**2a,b**)[10] react with [PPN][NO$_2$] to form the novel α-ketoacyl complexes **4a** and **4b** (eq 2). Both complexes were isolated in 50–60% yields as thermally and air-stable orange crystalline solids. They were spectroscopically characterized, and **4a** was fully defined by an X-ray crystallographic study (Figure 1). They each show IR bands due to the CO and NO ligands and four bands which can be assigned to the α-ketoacyl ligands (e.g., **4a**: 1665, 1615, 1607, 1590 cm^{-1}). A four-band pattern is common for α-ketoacyl ligands and arises from the existence of *s-cis* and *s-trans* rotational isomers.[6e] The ^{13}C NMR spectra of **2a** and **2b** show resonances assigned to the α- and β-carbons of the α-ketoacyl ligand (e.g., **4a**: δ 273.2 (α), 189.2 (β)) on the basis of similar spectral assignments for *trans*-Pd(C{O}C{O}R)Cl(PMePh$_2$)$_2$ (R = Me, δ 233.2 (α), 193.8 (β); R = Ph, δ 236.2 (α), 185.4 (β)).[6c] Supporting this assignment is the ^{13}C–^{31}P coupling pattern observed in Cp'(PPh$_3$)(NO)Mn–C{O}C{O}Tol (see below), where the downfield resonance shows the largest coupling

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[10] Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140.

to phosphorus. When **4a** was prepared from ^{13}CO-enriched **2a**, its' ^{13}C NMR spectrum showed that only the α-carbon was enriched in ^{13}C, implying that this carbonyl was an original CO ligand.

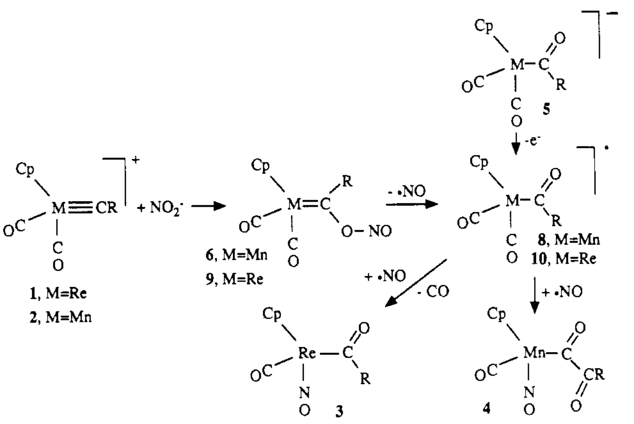
An unstable intermediate, **6**, that transformed into **4a** upon warming to room temperature was observed by IR monitoring of the reaction of $[Cp'(CO)_2Mn{\equiv}CTol]^+$ with $[PPN][NO_2]$ at -78 °C. This intermediate has two ν(CO) bands at 1999 and 1939 cm^{-1} in the region characteristic of neutral $Cp'(CO)_2Mn{=}CR(X)$ complexes.[11] (e.g., $Cp(CO)_2Mn{=}C(CN)Ph$: ν(CO) 1994, 1932 cm^{-1} [11b]). We assume it to be $Cp'(CO)_2Mn{=}C(ONO)Tol$ since a variety of related nucleophiles (CN$^-$, Cl$^-$, SCN$^-$) related to NO_2^- have been shown to add to **2** to give similar carbene derivatives.[1a,11]

The spectroscopic data do not allow us to determine whether the nitrite moiety in the intermediate **6** is oxygen or nitrogen bound to the carbene carbon. We assume it to be oxygen bound, because it leads to a better rationalization of the observed chemistry (see below). Such an assignment is also reasonable based on the organic literature. For example, it is known that the reaction of $AgNO_2$ with alkyl halides leads to both nitroalkanes and alkyl nitrites with the yield of the latter increasing as the carbonium ion character increases during the reaction.[12] The established carbonium ion character of $[Cp'(CO)_2Mn{\equiv}CTol]^+$ [1a,11] would thus lead to the prediction of an O-bound nitrite.

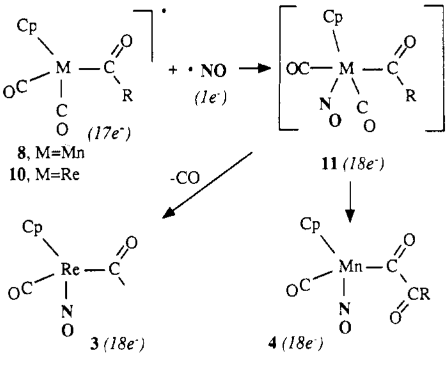
Curiously, the yield of **4a** from **1** proved to be markedly dependent on the amount of NO_2^- used. With only *1* equiv of nitrite, the only product observed was $[Cp'Mn(CO)_2(NO)]^+$ (**7**),[13] but when 1.2–1.4 equiv of NO_2^- were used a near quantitative yield of **4** was obtained (by IR). A slight excess of NO_2^- repeatedly proved necessary to obtain good isolated yields of **4a** and **4b**, although this was not necessary for the preparation of the rhenium acyl complex **3**. A discussion of the reasons for the necessity of using excess NO_2^- will be given in the mechanistic discussion that follows.

Migratory Insertion of CO into the Metal–Acyl Bond of $[Cp'(CO)_2Mn{-}C\{O\}Tol]^-$ Induced by an Oxidation/NO Addition Reaction Sequence. In the course of the above experiments, α-ketoacyl complex **4a** was also prepared from the acyl complex $[Cp'(CO)_2Mn{-}C\{O\}Tol]^-$ (**5**) in what is the first example of migratory insertion of a coordinated CO into a metal–acyl bond (eq 3). Cyclic voltammetry (22 °C, CH_2Cl_2, $[Bu_4N]PF_6$, 100 mV/s) showed that the acyl complex **5** undergoes reversible oxidation at -1.03 V vs the $[Cp_2Fe]^+/Cp_2Fe$ couple. The oxidation product $Cp'(CO)_2Mn{-}C\{O\}Tol$ (**8**) can be chemically prepared by treatment of CH_2Cl_2 solutions of **5** at -78 °C with either of the one-electron oxidants $[NO]BF_4$ or $[Cp_2Fe]PF_6$. It shows two ν(CO) bands at 1997 and 1913 cm^{-1} that are ~120 cm^{-1} higher in energy than the 1878 and 1797 cm^{-1} bands of **5**, consistent with an oxidized species. IR monitoring showed that complex **8** survives warmup to room temperature, although it slowly decomposes to $Cp'Mn(CO)_3$ and other unidentified products over a several hour period at 22 °C. Treatment of -78 °C solutions of **8** with bubbling NO gas led immediately to formation of the α-ketoacyl complex **4a**. This species was isolated in 75% recrystallized yield, although IR monitoring showed the reaction to be quantitative. Use of $[NO]BF_4$ as the oxidant of **5** initially gave a ~1:2 mixture of **4a** and **8** over a 20-min period at -78 °C, with the former presumably deriving from the NO formed in the oxidation process. In the presence of added ligand (L = PPh_3, CH_3CN, or CO), the oxidized complex **8** rapidly transformed (<30 s, 22 °C) into $Cp'(CO)_2Mn{-}L$, but the fate of the acyl ligand was not determined.

Scheme I



Scheme II



Mechanisms of Reactions 1–3. Reactions 1–3 involving (i) the conversion of a carbyne ligand into an acyl ligand by an oxygen atom transfer process, (ii) the coupling of an oxidized carbyne ligand and CO to give an α-ketoacyl ligand, and (iii) the formation of an α-ketoacyl ligand by migration of an acyl ligand to a coordinated CO are transformations without precedent in organometallic chemistry. It is thus important to address the mechanisms of these reactions. Spectroscopic evidence indicates that the first step in the reaction of $[Cp(CO)_2M{\equiv}CR]^+$ with nitrite is addition of the nitrite ion to the carbyne carbon to form a carbene derivative (**6**, M = Mn; **9**, M = Re; Scheme I). This species was observed for M = Mn but not for M = Re, in which the intermediate **9** must have a very short lifetime since the formation of **3** from **1** is rapid even at -78 °C. In the latter case, this species **9** must decompose by transfer of the NO group from the carbene ligand to the metal, with loss of CO, to form the observed acyl product. As shown in Scheme I, this transformation could occur in a concerted intramolecular process or, alternatively, via homolytic cleavage of the O–NO bond to form free NO and the 17e acyl complex $Cp(CO)_2Re{-}C\{O\}Ph$ (**10**). This latter species could then react with the released NO to form the observed product **3**.

For M = Mn, a variant of this latter route can explain the formation of the α-ketoacyl complex **4** from both the carbyne + nitrite and the acyl oxidation/NO addition routes, since the proposed intermediate **8** can be accessed by either reaction (Scheme I). Indeed, IR monitoring showed that **8** forms upon oxidation of $[Cp'(CO)_2Mn{-}C{-}$

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[11] (a) Fischer, E. O.; Chen, J.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231. (b) Fischer, E. O.; Stueckler, P.; Kreissl, F. R. *J. Organomet. Chem.* **1977**, *129*, 197.

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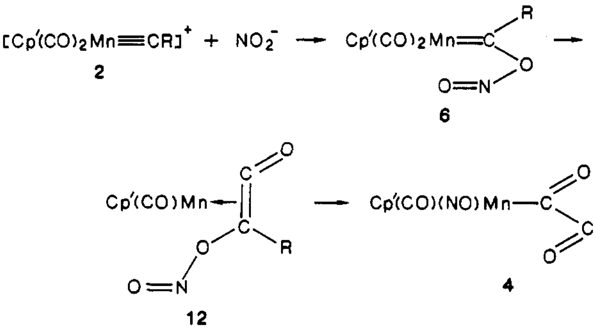
Scheme III



{O}Tol]$^-$ and then rapidly transforms into the α-ketoacyl complex **4a** upon exposure to NO gas.

Nitric oxide clearly plays a pivotal role in these transformations. We suggest that the NO radical adds to the 17e complexes **8** and **10** to give 18e $Cp(CO)_2(NO)M$–C{O}R intermediates, *having a bent, 1e donor NO ligand as in* **11** (Scheme II). However, the more common bonding mode of a nitrosyl ligand in low-valent organometallic complexes such as these is as a linear 3e donor.[14] In order to achieve this bonding form a stable 18e product, either a CO ligand must be lost or a CO must insert into the metal–acyl bond. The former must occur with rhenium, but the latter path must dominate with manganese. The energy gained in the bent to linear conversion of the NO ligand must then provide the driving force for the acyl to CO migration.

An alternative mechanism for the formation of **4** from nitrite addition to the carbyne complex **2**, and one that was suggested in our original communication,[3a] is outlined in Scheme III. This mechanism invokes CO migration to the carbene ligand in **6** to yield a coordinatively unsaturated ketene intermediate **12**. Migration of NO from this species to the vacant manganese coordination site would then give **4** directly. The formation of ketene ligands from carbene and carbonyl ligands has precedent,[15] particularly for manganese.[16] While we cannot exclude this possibility, this mechanism is difficult to reconcile with the separate formation of the α-ketoacyl complex **4** by the oxidation/NO addition reaction sequence, unless we invoke the unlikely possibility that two completely different paths are involved in the two reactions.

It should be pointed out that an alternative pathway to **4** involving acyl to CO migratory insertion in an intermediate such as Cp'(NO)(CO)Mn–C{O}R, analogous to **3**, is unlikely since the original preparation of this latter complex involved the high-pressure carbonylation of Cp(NO)(PPh_3)Mn-C{O}Ph, and no **4** was reported to form.[17] Similarly, complex **3** did not insert CO to form an α-ketoacyl ligand when subjected to 1500 psi of CO nor when the synthesis of **3** was conducted under 6 atm of CO.

Still to be addressed is the reason why a slight excess of [PPN][NO_2] is consistently necessary to achieve high-yield conversion of [Cp'$(CO)_2$Mn≡CR]$^+$ to Cp'(CO)(NO)Mn–C{O}C{O}R. One important point is that all of these reactions were conducted in CH_2Cl_2 solutions since [Cp'$(CO)_2$Mn≡CR]$^+$ is not sufficiently stable in other viable solvents such as THF. It has been recently reported that NO_2^- slowly reacts with CH_2Cl_2 at 22 °C to form $ClCH_2$-ONO which is a potent nitrosylating agent.[18]

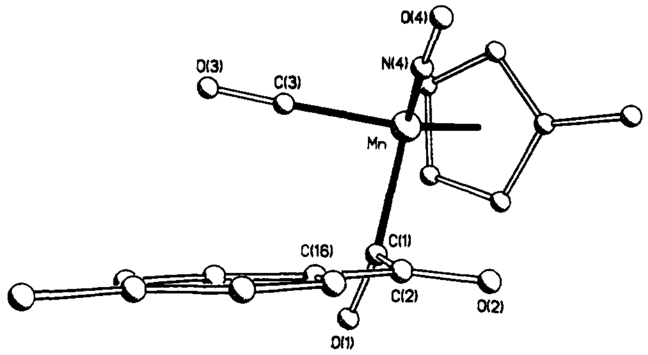


Figure 2. An ORTEP drawing of Cp'(CO)(NO)Mn–C{O}C{O}Tol (**4a**), viewed down the C(1)–C(2) bond.

However, at the low temperature used in the initial addition of [PPN][NO_2] to the carbyne complex, addition of nitrite to the carbyne carbon to form the carbene complex **6** should be far more rapid than the reaction of nitrite with CH_2Cl_2.[18] As suggested in Scheme I, the initially formed carbene complex **6** can decay by loss of NO to form the 17e complex Cp$(CO)_2$Mn–C{O}R (**8**) which could then *react with the released NO to form the α-ketoacyl complex* **4**. However, **8** can also decay to other products if insufficient NO is present to efficiently capture it. We suggest that the excess NO_2^- reacts with the CH_2Cl_2 solvent to form $ClCH_2$–ONO which in turn is an effective nitrosolating agent for **8**. Supporting this assumption is the observation that addition of [PPN][NO_2] to CH_2Cl_2 solutions of **8**, generated by [Cp_2Fe]$^+$ oxidation of [Cp'$(CO)_2$Mn–C{O}Tol]$^-$, gave formation of **4** in good yield.

Crystallographic Characterization of Cp'(CO)(NO)Mn–C{O}C{O}Tol (4a). An ORTEP drawing of complex **4a** is shown in Figure 1, and important bond distances and angles are set out in Table III. The complex has the usual three-legged piano-stool geometry typical of this family of complexes with the α-ketoacyl ligand bound in an η^1 fashion. This ligand has an approximate *s-trans* configuration with a dihedral angle of 78° between the planes defined by the two carbonyl groups and their substituents as illustrated in Figure 2. The other two structurally characterized α-ketoacyl complexes $(CO)_5$Mn–C{O}C{O}CH_3[6a] and $(PPh_3)_2$ClPt–C{O}C{O}-*p*-FC_6H_4[6c] have near planar α-ketoacyl ligands with corresponding dihedral angles of 10.4° and 3.3°, respectively. However, there appears to be no electronic requirement for planarity in α-ketoacyl complexes since a search of the Cambridge Crystallographic Database showed significant variation in the corresponding dihedral angles for organic α-ketoacyl derivatives. This is particularly well illustrated by the compounds *p*-$MeOC_6H_4$–C{O}C{O}-*p*-C_6H_4X where the dihedral angle varies significantly with the nature of X: 52° (X = OMe),[19a] 81° (X = OEt),[19a] 111° (X = NO_2).[19b] All other geometric parameters within the α-ketoacyl ligand of **4a** fall within established ranges.

Alkylation of the Acyl Ligand in 3 To Give a Carbene Derivative. Acyl complex **3** rapidly reacts with [Me_3O][BF_4] to yield the carbene complex **13** (eq 5, which was isolated in near quantitative yield as a yellow microcrystalline solid. This species was spectroscopically characterized; particularly indicative of its formulation is the δ 289.2 ^{13}C NMR resonance for the carbene carbon.

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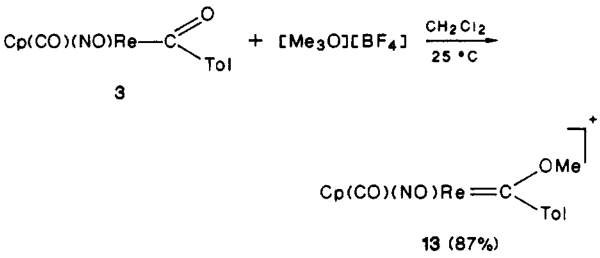
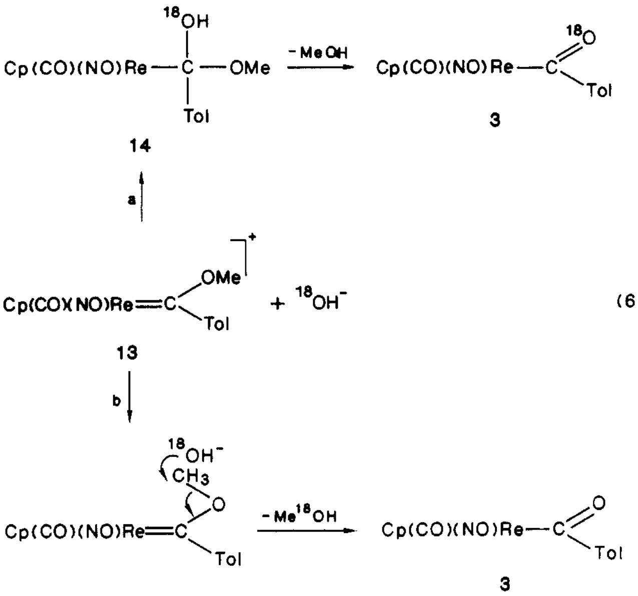


(5)

An interesting feature of carbene complex **13** is its facile hydrolysis, both in solution and in the solid state to give methanol and the acyl complex **3**. ^{1}H NMR monitoring showed this reaction with excess H_2O to be complete within 1 h at 22 °C. Cationic iron carbene complexes have been previously noted to undergo similar hydrolyses to generate acyl complexes, although the mechanisms of such reactions have never been determined.[20] Possible mechanisms for the hydrolysis involve (a) nucleophilic addition of OH^- on the carbene carbon to give an alkyl complex such as **14** (a hemiacetal) followed by MeOH loss and (b) S_N2 nucleophilic displacement of the acyl ligand by backside attack of OH^- on the methoxy carbon (eq 6).

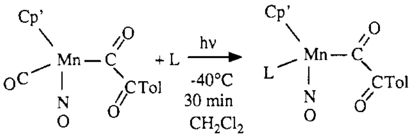


(6)

Note that these two mechanisms predict different results for hydrolysis with $H_2{}^{18}O$. That mechanism a is correct was indicated by the reaction of **13** with >95% enriched $H_2{}^{18}O$ in CH_2Cl_2. This gave **3** with an ^{18}O-labeled acyl ligand ($\nu(C^{18}O)$ 1538 (br) cm^{-1}), but absolutely no unlabeled **3** (ν(CO) 1578, 1561 cm^{-1}) was detected.

Ligand Substitution in α-Ketoacyl Complexes 4a and 4b. The previously characterized α-ketoacyl complex $(CO)_5Mn\text{–}C\{O\}C\{O\}Me$ was shown to undergo CO loss upon heating to give the acetyl complex $(CO)_5Mn\text{–}C\{O\}Me$ in the absence of added ligand and substituted complexes $L\text{-}(CO)_4Mn\text{–}C\{O\}C\{O\}Me$ in the presence of added L.[6a] However, when the complexes **4a** of **4b** described herein were heated or irradited in CH_2Cl_2 solution under an inert atmosphere in the absence of added ligand, only slow decomposition occured as evidenced by the gradual disappearance of all IR bands in the 1600–2200 cm^{-1} region. This result is expected since the product of CO loss and deinsertion is $Cp'(CO)(NO)Mn\text{–}C\{O\}Tol$ which is known to be both thermally and photochemically unstable.[17]

However, when complexes **4a** and **4b** were heated in toluene (65 °C, 12 h) in the presence of ~1 equiv of PPh_3, the phosphine-substituted complexes $Cp'(PPh_3)(NO)Mn\text{–}C\{O\}C\{O\}R$ (**16a,b**) were readily formed. These species were more conveniently prepared by photolyzing **4a,b** with excess PPh_3 in CH_2Cl_2 solution for 30 min (eq 7). The



(7)

16a, R=Tol, L=PPh$_3$ (57%)
16b, R=Ph, L=PPh$_3$ (84%)
17, R=Tol, L=*t*-BuNC (67%)

^{t}BuNC-substituted derivative **17** was similarly prepared. These complexes were spectroscopically characterized, and each shows the typical four band IR pattern in the α-ketoacyl region and ^{13}C NMR resonances due to the α- and β-carbons of the α-ketoacyl ligand (e.g., **16a**: δ 292.3 (d, $J_{^{31}PC}$ = 25 Hz, *C*{O}C{O}Tol), 189.6 (d, $J_{^{31}PC}$ = 5.5 Hz, C{O}*C*{O}Tol)).

Summary

This paper describes three reactions which had no precedent before the preliminary communication of these results. These are (1) the conversion of a carbyne ligand into an acyl ligand by an oxygen atom transfer process in forming **3**, (2) the coupling of an oxidized carbyne ligand with CO to give an α-ketoacyl ligand, and (3) the formation of an α-ketoacyl ligand by migration of an acyl ligand to a coordinated CO. The latter reaction is particularly important because this process has long been regarded as an unlikely reaction.[6] Yet there are a number of catalytic "double carbonylation" reactions of considerable practical importance that could proceed via such a process, although mechanisms for these have generally been invoked which avoid suggesting an acyl to CO migratory-insertion step. The results described herein show that this reaction step can now be considered viable, although certainly it would be difficult to develop a catalytic process based on the stoichiometric chemistry described herein.

The experimental results indicate that all of the reactions 1–3 proceed via a common path involving formation of the 17e complex $Cp'(CO)_2M\text{–}C\{O\}R$. With M = Re, this species substitutes NO for CO to give the observed acyl complex $Cp(CO)(NO)Re\text{–}C\{O\}Ph$ (**3**). However, for M = Mn, we suggest that NO adds to the 17e complex to form the 18e species $Cp'(CO)_2(NO)Mn\text{–}C\{O\}R$ with a bent, 1e donor nitrosyl ligand, and the isomerization of this ligand to the more common linear, 3e form is suggested to provide the driving force for the acyl to CO migratory-insertion process.

Experimental Section

The complexes $[Cp(CO)_2Re{\equiv}CTol][BCl_4]$ and $[Cp'(CO)_2Mn{\equiv}CR][BCl_4]$ (R = Tol, Ph) were prepared by the literature procedure.[7,10] Solvents were dried by stirring over Na/benzophenone (THF, Et_2O) or CaH_2 (CH_2Cl_2, pentane, hexane, toluene) and were freshly distilled prior to use. [PPN][NO_2], PPh_3, and ^{t}BuNC were purchased from the Aldrich Chemical Co., [Me_3O][BF_4] was purchased from Alfa Chemicals, and 95–99% enriched $H_2{}^{18}O$ was purchased from MSD isotopes. All manipulations were performed by using standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the transmittance mode, NMR spectra were obtained on a Brucker WP 200 FT NMR spectrometer, and electron-impact (EI) mass spectra were recorded on an AEI-MS9 mass spectrometer. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY. Photolyses were conducted in Pyrex Schlenk glassware with broad-band irradiation from a 450-W medium-pressure Hg lamp (Hanovia). ^{13}CO-enriched (~20%) $[Cp'(CO)_2Mn{\equiv}CR][BCl_4]$ was

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[20] Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237.

prepared from ^{13}CO-enriched Cp′(CO)$_2$Mn=C(OMe)R which was in turn prepared by photolysis of the carbene complex under 1 atm of ^{13}CO for 30 min in CH$_2$Cl$_2$ at 22 °C.

Preparation of Cp(CO)(NO)Re–C{O}Tol (3). Method A. To a cold (−10 °C) solution of [Cp(CO)$_2$Re≡CTol][BCl$_4$] (0.056 g, 0.099 mmol) in CH$_2$Cl$_2$ (5 mL) was added [PPN][NO$_2$] (0.058 g, 0.1 mmol) which gave an immediate color change from yellow to red. Warmup to room temperature and removal of CH$_2$Cl$_2$ in vacuo gave an orange residue. Chromatography on a neutral alumina column (2 × 10 cm), eluting with 60% CH$_2$Cl$_2$/hexane, gave Cp(CO)(NO)Re–C{O}Tol (**3**) as a light orange microcrystalline solid on removal of the solvent (73%, 0.031 g, 0.072 mmol).

Method B. The salt [PPN][Cp(CO)$_2$Re–C{O}Tol)][21] (0.20 g, 0.21 mmol) and Ag[BF$_4$] (0.04 g, 0.21 mmol) were weighed directly into a 40-mL Schlenk flask. Cold (−78 °C) CH$_2$Cl$_2$ (15 mL) was added and the mixture stirred for 5 min at −78 °C. IR monitoring showed complete oxidation to form Cp(CO)$_2$Re–C{O}Tol (ν(CO) 1956, 1875 cm^{-1}). Nitric oxide gas was then slowly bubbled through the cold solution giving **3** in essentially quantitative yield by IR.

3 (from method A): IR (CH$_2$Cl$_2$) ν(CO) 1993 (s), ν(NO) 1717 (s), ν(acyl) 1578 (w), 1561 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.36 (3 H, s, Me), 5.78 (5 H, s, Cp), 7.21 (2 H, d, *J* = 8 Hz, Tol), 7.45 (2 H, d, *J* = 8 Hz, Tol); ^{13}C NMR (CDCl$_3$) δ 21.3 (Me), 93.9 (Cp), 126.6, 128.7, 140.7, 152.3 (Tol), 201.7 (CO), 238.5 (acyl CO); MS, *m/z* 429 (M$^+$, ^{187}Re). Anal. Calcd for C$_{14}$H$_{12}$NO$_3$Re: C, 39.23; H, 2.80; N, 2.90. Found: C, 39.00; H, 2.80; N, 2.70.

Preparation of Cp′(CO)(NO)Mn–C{O}C{O}R (4). Method A. To a cold (−78 °C) solution of [Cp′(CO)$_2$Mn≡CPh][BCl$_4$] (**2b**, 1.2 g, 2.80 mmol) in CH$_2$Cl$_2$ (100 mL) was added [PPN][NO$_2$] (1.9 g, 3.25 mmol) which gave an immediate color change from orange to very dark green. After being stirred for 1 h, the reaction was warmed to room temperature over 30 min resulting in a color change to red. The solvent was removed in vacuo to give a brown residue. This was dissolved in CH$_2$Cl$_2$ (10 mL) and placed on a neutral alumina chromatography column (3 × 30 cm). Elution with 45% CH$_2$Cl$_2$/hexane gave an orange band from which orange crystals of Cp′(CO)(NO)Mn–C{O}C{O}Ph (**4b**) were obtained upon removal of solvent (0.46 g, 1.42 mmol, 51%). Complex **4a** was prepared in a similar manner from **2a** in isolated yields ranging from 45 to 57%.

Method B. A cold (−78 °C) CH$_2$Cl$_2$ (10 mL) solution of [PPN][Cp′(CO)$_2$Mn–C{O}Tol] (0.10 g, 0.12 mmol) was treated with [Cp$_2$Fe][PF$_6$] (0.04 g, 0.12 mmol). An IR spectrum of the dark reaction mixture showed the only species present to be Cp′(CO)$_2$Mn–C{O}Tol (ν(CO) 1997, 1913 cm^{-1}). After the solution was stirred for 10–15 min, a few milliliters of NO gas were bubbled through the solution, followed by slow warmup to room temperature. The solution changed to a red color during the warmup. IR analysis of this solution showed the only species present to be **4a**. Evaporation of solvent in vacuo and workup as above gave **4a** as orange crystals in 75% yield (0.03 g, 0.09 mmol).

Method C. A cold (−78 °C) solution of Cp′(CO)$_2$MnC{O}Tol in CH$_2$Cl$_2$ (10 cm^3) was prepared as in B above from [PPN]{Cp′(CO)$_2$MnC{O}Tol] (0.11 g, 0.13 mmol) and [FeCp$_2$][PF$_6$] (0.043 g, 0.13 mmol). [PPN][NO$_2$] (0.076 g, 0.13 mmol) was added resulting in an immediate color change to clear orange/red. Workup of the reaction mixture as above gave **4a** as orange microcrystals (0.041 g, 0.12 mmol, 93%).

4a (R = Tol) (from method A): IR (CH$_2$Cl$_2$) ν(CO) 2016 (s), ν(NO) 1759 (s), ν(α-ketoacyl) 1665 (w), 1615 (m), 1607 (m), 1590 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.99 (3 H, s, MeCp), 2.41 (3 H, s, MeTol), 4.97 (2 H, s, Cp′), 5.08 (1 H, s, Cp′), 5.16 (1 H, s, Cp′), 7.29 (2 H, d, *J* = 7 Hz, Tol), 7.82 (2 H, d, *J* = 7 Hz, Tol); ^{13}C NMR (CDCl$_3$) δ 12.8 (MeCp), 21.7 (MeTol), 92.4, 93.5, 93.9, 94.5, 110.2 (Cp′), 128.0, 129.6, 130.1, 144.6 (Tol), 189.2 (COCOR), 226.7 (CO), 273.2 (COCOR); MS, *m/z* 339 (M$^+$). Anal. Calcd for C$_{16}$H$_{14}$MnNO$_4$: C, 56.63; H, 4.13; N, 4.13. Found: C, 56.54; H, 4.01; N, 3.88.

4b (R = Ph) (from method A): IR (CH$_2$Cl$_2$) ν(CO) 2016 (s), ν(NO) 1759 (s)8 ν(α-ketoacyl) 1673 (w), 1622 (m), 1605 (m), 1593 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.99 (3 H, s, MeCp), 4.98 (2 H, s, Cp′), 5.09 (1 H, s, Cp′), 5.16 (1 H, s, Cp), 7.52–7.92 (5 H, m, Ph); ^{13}C NMR (CDCl$_3$) δ 12.8 (MeCp) , 92.5, 93.6, 93.9, 94.5, 110.3 (Cp′), 128.8, 130.0, 130.8, 133.6 (Ph), 189.2 (COCOR)8 226.5 (CO), 273.4 (COCOR). Anal. Calcd for C$_{15}$H$_{12}$MnNO$_4$: C, 55.38; H, 3.69; N, 4.31. Found: C, 55.20; H, 3.47; N, 4.04.

One-Pot Synthesis of 4a from Cp′(CO)$_2$Mn=C{OMe}Tol. Gaseous BCl$_3$ was bubbled through a cold (−40 °C) *n*-pentane (130 mL) solution of Cp′(CO)$_2$Mn=C{OMe}Tol[22] (0.835 g, 2.58 mmol) until the pentane became clear (~1 min). The resulting yellow precipitate of **2a** {ν(CO) 2081, 2043 cm^{-1} (CH$_2$Cl$_2$)} was cooled to −78 °C and washed with −78 °C pentane (2 × 50 mL) and dried in vacuo for 1 h. Addition of −78 °C CH$_2$Cl$_2$ (30 mL) and [PPN][NO$_2$] (2.055 g, 3.50 mmol) gave a deep red-green solution of intermediate **6** which was stirred at −78 °C for 15 min and allowed to slowly warmup to room temperature over 30 min. The clear orange solution was then worked up as above to give **4a** in 57% yield as orange microcrystals (0.499 g, 1.47 mmol).

Low-Temperature IR Monitoring of the Reaction of 2a with [PPN][NO$_2$]. To a −78 °C solution of **2a** (0.248 g, 0.56 mmole was added 1 equiv of [PPN][NO$_2$] (0.327 g, 0.56 mmol). The IR spectrum of this cold solution showed ν(CO) bands at 1999 and 1939 cm^{-1} assigned to Cp′(CO)$_2$Mn=C(ONO)Tol (**6**) and weak bands indicating the formation of a small amount of α-ketoacyl complex **4a**. A small sample was withdrawn and placed in an IR cell, and spectra were recorded at ~20-s intervals as the solution in the IR cell warmed to 22 °C. These showed the gradual conversion of **6** into [Cp′(CO)$_2$(NO)Mn]$^+$ (**7**) (ν(CO) 2118, 2070 cm^{-1}; ν(NO) 1835 cm^{-1}).[13] To the remainder of the cold reaction solution was added a further 0.25 equiv of [PPN][NO$_2$] (0.085 g, 0.14 mmol), and a sample was withdrawn and placed in an IR cell. IR monitoring as above showed that intermediate **6** converted quantitatively to **4a** upon warmup. Another experiment revealed that the yield of **4a** from the intermediate **6** was directly proportional to the amount of excess NO$_2^-$ aded, with 0.1 and 0.2 excess equiv of NO$_2^-$ giving **4a** and **7** in ~3:1 and ~10:1 ratios, respectively. An optimum excess of NO$_2^-$ of 0.25–0.35 equiv gave complex **4a** in 45–57% isolated yields.

Reaction of Cp(CO)(NO)Re–C{O}Tol with [Me$_3$O][BF$_4$]. A solution of Cp(CO)(NO)ReC{O}Tol (0.1 g, 0.23 mmol) and [Me$_3$O][BF$_4$] (0.05 g, 3.4 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred for 3 h at room temperature. Filtration of the yellow solution and addition of Et$_2$O gave a yellow solid which was recrystallized from CH$_2$Cl$_2$/Et$_2$O to yield [Cp(CO)(NO)Re=C{OMe}Tol][BF$_4$] (**13**) as yellow microcrystals in 87% yield (0.105 g, 0.20 mmol).

13: IR (CH$_2$Cl$_2$) ν(CO) 2039 (s), ν(NO) 1763 (s) cm^{-1}; ^{1}H NMR ([^{2}H$_6$]acetone) δ 2.42 (3 H, s, MeTol), 4.80 (3 H, s, OC*H*$_3$), 6.38 (5 H, s, Cp), 7.38 (2 H, d, *J* = 8 Hz, Tol), 7.57 (2 H, d, *J* = 8 Hz, Tol); ^{13}C NMR ([^{2}H$_6$]acetone) δ 21.6 (MeTol), 71.7 (MeO), 97.5 (Cp), 129.3, 129.6, 130.2, 146.2 (Tol), 205.7 (CO), 289.2 (Re=*C*). Anal. Calcd for C$_{15}$H$_{15}$BF$_4$NO$_3$Re: C, 33.96; H, 2.83; N, 2.64. Found: C, 33.80; H, 2.92; N, 2.90.

Reaction of 13 with H$_2$O and H$_2{}^{18}$O. To a solution of **13** (0.05 g, 0.09 mmol) in CH$_2$Cl$_2$ (5 mL) was added 1 drop of distilled H$_2$O. After the solution was stirred for 1 h, the IR spectrum showed complete conversion to **3**, and workup as above gave pure **3** in 68% yield (0.026 g, 0.06 mmol). ^{1}H NMR monitoring of a similar reaction in acetone-*d*$_6$ showed the gradual decrease in intensity of the MeO resonance of **13** at δ 4.80 along with a corresponding intensity increase in the MeOH resonance at δ 3.16. The use of H$_2{}^{18}$O in this reaction gave **3** with a broad acyl IR absorption at 1537 cm^{-1}.

Preparation of Cp′(PPh$_3$)(NO)Mn–C{O}C{O}R (16). Method A. A toluene (30 mL) solution of Cp′(CO)(NO)Mn–C{O}C{O}Ph (0.08 g, 0.25 mmol) and PPh$_3$ (0.085 g, 0.32 mmol) was heated at 65 °C for 12 h during which time the color changed from orange to purple. The resulting solution was evaporated to dryness in vacuo followed by chromatography of the residue on alumina. Elution with 10% acetone/CH$_2$Cl$_2$ gave a deep red band from which red/purple microcrystals of Cp′(PPh$_3$)(NO)MnC{O}C{O}Ph (**16b**) precipitated upon removal of solvent (0.077 g, 0.14 mmol, 56%).

Method B: A CH$_2$Cl$_2$ (10 mL) solution of Cp′(CO)(NO)MnC{O}C{O}Ph (0.08 g, 0.25 mmol) and PPh$_3$ (0.072 g, 0.27 mmol)

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[21] [PPN][Cp(CO)$_2$Re–C{O}Tol)] was prepared by metathesis of [PPN]Cl with the Li$^+$ salt of this complex, the latter prepared according to the recipe for the Mn derivative given in ref 22.

[22] Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445.

Table I. Crystallographic Data for Cp′(CO)(NO)Mn–C{O}C{O}Tol (4a)

	(a) Crystal Parameters		
formula	$C_{16}H_{14}MnNO_4$	γ, deg	110.73 (3)
cryst system	triclinic	V, Å^3	763.3 (5)
space group	$P\bar{1}$	Z	2
a, Å	6.928 (3)[a]	D(calcd), g cm^{-3}	1.476
b, Å	7.425 (3)	μ(Mo Kα) cm^{-1}	8.45
c, Å	16.153 (6)	temp, K	294
α, deg	94.32 (3)	cryst size, mm	0.21 × 0.22 × 0.23
β, deg	97.07 (3)	cryst color	orange
	(b) Data Collection		
diffractometer	Nicolet R3m/u	rflns collected	2367
radiation	Mo Kα	unique rflns	2263
wavelength, Å	0.71073	unique ($3\sigma(F_o)$)	1855
monochromator	graphite	R(int), %	2.28
scan method	Wyckoff	std rflns	3 std/97 rflns
scan limits, deg	$4 \le \theta \le 47$	decay	(<1%)
scan speed, deg min^{-1}	var 5–20	T_{max}/T_{min}	1/0.93
	(c) Refinement		
$R(F)$, $R(wF)$, %	4.74, 5.25	Δ/σ	0.06
GOF	1.118	$\Delta(\rho)$, e Å^{-3}	0.30
N_o/N_v	8.03	g; $w^{-1} = \sigma^2(F_o + gF_o^2)$	0.0007

[a] Least-squares refinement of the angular settings of 25 reflections (19° ≤ 2θ ≤ 27°).

was irradiated with Pyrex-filtered UV light for 30 min. Workup of the purple solution as in method A gave **16b** in 84% yield (0.115 g, 0.21 mmol). The tolyl derivative **16a** was similarly prepared in 57% yield.

16a (R = Tol): IR (CH_2Cl_2) ν(NO) 1713 (s), ν(α-ketoacyl) 1659 (w), 1574 (m), 1568 (m), 1554 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.89 (3 H, s, MeCp), 2.34 (3 H, s, MeTol), 4.11, 4.45, 4.71, 4.81 (4 H, s, MeCp), 7.02 (2 H, d, J = 8 Hz, tolyl), 7.35–7.55 (17 H, m, Tol and PPh_3); ^{13}C NMR ($CDCl_3$) δ 12.4 (MeCp), 21.5 (MeTol), 90.9, 93.9, 94.7, 96.1, 105.6 (MeCp), 128.1, 128.3, 128.7, 129.9, 130.0, 130.4, 133.1, 133.4, 134.6, 135.5, 142.5 (PPh_3, Tol), 189.6 (d, $J_{^{31}PC}$ = 5.5 Hz, CO*C*OTol), 292.3 (d, $J_{^{31}PC}$ = 25 Hz, *C*OCOTol). Anal. Calcd for $C_{33}H_{29}NO_3PMn$: C, 69.10; H, 5.06; N, 2.44. Found: C, 68.80; H, 4.79; N, 2.21.

16b (R = Ph): IR (CH_2Cl_2) ν(NO) 1713 (s), ν(α-ketoacyl) 1659 (w), 1574 (m), 1568 (m), 1554 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.87 (3 H, s, MeCp), 4.10, 4.45, 4.70, 4.79 (4 H, s, MeCp), 7.15–7.57 (20 H, m, Ph and PPh_3); ^{13}C NMR ($CDCl_3$) δ 12.4 (MeCp), 90.9, 93.9, 94.7, 96.2, 105.7 (MeCp), 127.9, 128.1, 128.3, 129.8, 130.0, 130.1, 131.8, 133.1, 133.2, 133.3, 134.5, 135.4 (PPh_3, Ph), 189.7 (d, $J_{^{31}PC}$ = 5.5 Hz, CO*C*OPh), 292.4 (d, $J_{^{31}PC}$ = 25 Hz, *C*OCOPh). Anal. Calcd for $C_{32}H_{27}NO_3PMn$: C, 68.69; H, 4.83; N, 2.50. Found: C, 68.08; H, 4.77; N, 2.53.

Preparation of Cp′(^{t}BuNC)(NO)Mn–C{O}C{O}Tol (17). A −40 °C CH_2Cl_2 (10 mL) solution of Cp′(CO)(NO)Mn–C{O}C{O}Tol (0.105 g, 0.31 mmol) and ^{t}BuNC (0.06 mL, 0.60 mmol) was irradiated with Pyrex-filtered UV light for 90 min. Removal of the solvent in vacuo and chromatography on neutral alumina with 5% acetone/CH_2Cl_2 as eluant gave a single red band from which 17 was isolated as a red oil (0.084 g, 0.21 mmol, 67%). Complex 17 is moderately air-sensitive and was characterized from its IR, ^{1}H NMR, and ^{13}C NMR Data, but a suitable elemental analysis was not obtained.

17: IR (CH_2Cl_2) ν(^{t}BuNC) 2147 (s), ν(NO) 1726 (s), ν(α-ketoacyl) 1659 (w), 1595 (m), 1580 (m), 1570 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (9 H, s, ^{t}BuNC), 1.93 (3 H, s, MeCp), 2.42 (3 H, s, MeTol), 4.77, 4.84, 5.01, (4 H, s, MeCp), 7.27 (2 H, d, J = 7 Hz, Tol), 7.86 (2 H, d, J = 7 Hz, Tol); ^{13}C NMR ($CDCl_3$) δ 13.0 (MeCp), 21.6 (MeTol), 30.6 ($\mathrm{C\{\mathit{C}H_3\}_3}$), 58.4 ($\mathit{C}\mathrm{\{CH_3\}_3}$), 92.2, 92.7, 92.9, 93.7, 108.9 (MeCp), 129.1, 129.6, 130.0, 143.4 (Tol), 168.6 (^{t}BuNC), 189.6 (CO*C*OTol), 288.2 (*C*OCOTol).

X-ray Diffraction Study of Cp′(CO)(NO)Mn–C{O}C{O}Tol (4a). Crystals suitable for diffraction studies were obtained by recrystallization from CH_2Cl_2/hexane at −10 °C and fixed to glass fibers with epoxy cement. Crystal, data collection, and refinement parameters are collected in Table I. Photographic characterization showed no symmetry higher than triclinic. The centrosymmetric alternative, $P\bar{1}$, was initially assumed and proved correct from the well-behaved solution and refinement of the structure. Data collection 2θ limits were determined by the availability of data. No correction for absorption was required (small crystal, uniform dimensions, and μ = 8.45 cm^{-1}).

Table II. Atomic Positional Parameters for Cp′(CO)(NO)Mn–C{O}C{O}Tol (4a)

	x	y	z	U,[a] Å^2
Mn	956 (1)	2484.4 (9)	3009.4 (4)	38.5 (3)
O(1)	2002 (5)	6668 (4)	3209 (2)	67 (2)
O(2)	6086 (4)	5677 (4)	3464 (2)	60 (1)
O(3)	−1584 (6)	2514 (6)	1387 (2)	88 (2)
O(4)	3716 (6)	992 (5)	2318 (2)	81 (2)
N(4)	2594 (5)	1682 (5)	2583 (2)	48 (2)
C(1)	2559 (7)	5338 (6)	3051 (3)	46 (2)
C(2)	4803 (7)	5788 (6)	2902 (3)	44 (2)
C(3)	−614 (7)	2530 (7)	2019 (3)	56 (2)
C(5)	3503 (7)	1372 (8)	4612 (3)	69 (2)
C(6)	1538 (6)	1638 (6)	4246 (3)	46 (2)
C(7)	−262 (7)	176 (6)	3757 (3)	51 (2)
C(8)	−1772 (7)	949 (7)	3526 (3)	56 (2)
C(9)	−935 (7)	2932 (7)	3871 (3)	56 (2)
C(10)	1080 (7)	3347 (6)	4319 (3)	52 (2)
C(11)	3913 (7)	6722 (7)	1476 (3)	55 (2)
C(12)	4448 (8)	7262 (7)	713 (3)	60 (2)
C(13)	6399 (8)	7479 (6)	528 (3)	55 (2)
C(14)	7801 (7)	7140 (7)	1121 (3)	61 (2)
C(15)	7298 (7)	6607 (7)	1885 (3)	56 (2)
C(16)	5337 (6)	6382 (5)	2077 (3)	42 (2)
C(17)	6949 (9)	8082 (8)	−309 (3)	80 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Important Bond Lengths (Å) and Angles (deg) for Cp′(CO)(NO)Mn–C{O}C{O}Tol (4a)

	(a) Bond Distances		
Mn–CNT[a]	1.785 (5)	C(2)–O(2)	1.212 (5)
Mn–C(1)	2.005 (4)	C(1)–C(2)	1.527 (7)
Mn–C(3)	1.820 (5)	C(3)–O(3)	1.141 (6)
Mn–N(4)	1.656 (4)	N(4)–O(4)	1.178 (6)
C(1)–O(1)	1.203 (6)		
	(b) Bond Angles		
CNT–Mn–C(1)	114.4 (2)	Mn–C(1)–C(2)	112.6 (3)
CNT–Mn–C(3)	124.5 (2)	Mn–C(3)–O(3)	178.0 (5)
CNT–Mn–N(4)	126.3 (2)	Mn–N(4)–O(4)	174.7 (3)
C(1)–Mn–C(3)	89.0 (2)	O(1)–C(1)–C(2)	118.8 (3)
C(1)–Mn–N(4)	98.0 (2)	C(1)–C(2)–O(2)	118.8 (4)
C(3)–Mn–N(4)	96.2 (2)	C(1)–C(2)–C(16)	118.6 (4)
Mn–C(1)–O(1)	128.5 (3)	O(2)–C(2)–C(16)	122.6 (4)
	(c) Torsion Angles (deg)		
O(1)–C(1)–C(2)–O(2)	101.7	Mn–C(1)–C(2)–O(2)	−75.3
O(1)–C(1)–C(2)–C(16)	−77.2	Mn–C(1)–C(2)–C(16)	105.9

[a] CNT = centoid of C(6) to C(10).

The Mn atom coordinates were obtained from a sharpened Patterson synthesis, and the structure was developed by difference Fourier syntheses. All hydrogen atoms were placed in idealized locations; the methyl group rotational orientations are based on a partial list of found hydrogen atom locations. All non-hydrogen atoms were refined with anisotropic parameters. The assignment of the Mn-bonded NO and CO groups was unambiguous based on the observed thermal parameters and the Mn–N and Mn–C distances.

All calculations used the SHELXTL program library (Nicolet Corp., Madison, WI). Table II gives the atomic coordinates and Table III selected bond distances and angles. Additional crystallographic data are available (see supplementary material paragraph).

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Registry No. **1**, 106865-70-7; **2a**, 106865-74-1; **2b**, 93756-36-6; **3**, 106865-71-8; **4a**, 106865-75-2; **4b**, 106865-72-9; **5**·PPN, 111583-10-9; **6**, 116184-62-4; **7**, 46134-83-2; **13**, 116184-67-9; **16a**, 116184-68-0; **16b**, 116184-70-4; **17**, 116184-69-1; [PPN][Cp-(CO)$_2$Re—C{O}Tol], 116184-64-6; Cp′(CO)$_2$Mn=C{OMe}Tol, 116184-65-7; CO, 630-08-0.

Supplementary Material Available: Tables of anisotropic temperature factors, complete bond lengths and bond angles, and calculated hydrogen atom positions (4 pages); a list of structure factors (11 pages). Ordering information is given on any current masthead page.

Formation of Indolenine Derivatives from Dicobalt Octaisocyanide and Carbon Polyhalide[1]

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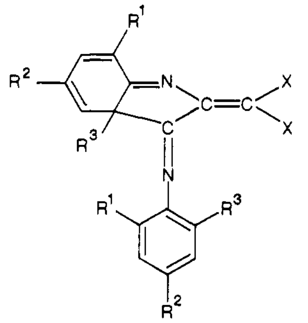
Reactions of dicobalt octaisocyanide with carbon tetrahalides (CCl_4 or CBr_4) gave indolenine derivatives and $CoX_2(RNC)_4$ (R = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,6-Me_2-4-BrC_6H_2, 2,4-*t*-Bu_2-6-MeC_6H_2; X = Cl, Br). Benzyl bromide reacted with dicobalt octakis(2,6-xylyl isocyanide) to afford 1,6-diphenyl-2,3,4,5-tetrakis(*N*-2,6-xylylimino)hexane and $CoBr_2$(2,6-$Me_2C_6H_3NC)_4$. The reaction path for formation of indolenine derivatives is discussed.

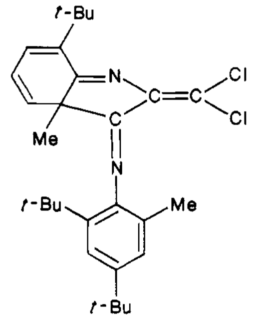
Dicobalt octacarbonyl has been widely used as a catalyst or precursor of a stoichiometric reagent in organic synthesis.[2] Dicobalt octaisocyanide also can be used in analogy to $Co_2(CO)_8$.[3] Previously we reported that $Co_2(RNC)_8$ behaves as a catalyst for the preparation of diiminoindazoles and indazolines from azo compounds and isocyanides.[4] In this paper, we describe the formation of indolenine derivatives from $Co_2(RNC)_8$ and carbon tetrahalides.

When carbon tetrachloride was added to a mixture of dicobalt octakis(2,6-xylyl isocyanide) and 2,6-xylyl isocyanide in benzene at room temperature, the reaction proceeded readily to give a green precipitate, identified as $CoCl_2$(2,6-$Me_2C_6H_3NC)_4$ (**2a**). Chromatography of the yellow solution gave indolenine derivative **1a**, identified by comparison with the melting point and infrared and ^{1}H NMR spectra of the authentic compound.[5]

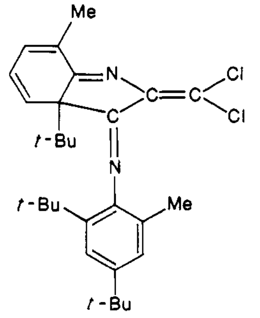
Similar reactions occurred to give the corresponding indolenine derivatives when Co_2(2,4,6-$Me_3C_6H_2NC)_8$ and Co_2(2,6-Me_2-4-$BrC_6H_2NC)_8$ were used. Carbon tetrabromide was also employed in the reaction with Co_2(2,6-$Me_2C_6H_3NC)_8$ in place of carbon tetrachloride. In the case of the reaction of dicobalt octakis(2,4-di-*tert*-butyl-6-methylphenyl isocyanide) with CCl_4, the cyclization is expected to occur in either ipso position occupied by the 2-*tert*-butyl or the 6-methyl group (1e-A or 1e-B). The ^{1}H NMR spectrum showed two peaks at δ 1.28 and 2.13, each corresponding to three protons of the methyl groups. The resonance at δ 1.28 falls in the range of chemical shifts of methyl protons bound to a sp^3 carbon atom, suggesting the structure 1e-A. Thus, the position of cyclization seems to be controlled by steric factors.



1a: $R^1 = R^3 = \text{Me}$, $R^2 = \text{H}$, X = Cl
b: $R^1 = R^2 = R^3 = \text{Me}$, X = Cl
c: $R^1 = R^3 = \text{Me}$, $R^2 = \text{Br}$, X = Cl
d: $R^1 = R^3 = \text{Me}$, $R^2 = \text{H}$, X = Br
e: $R^1 = R^2 = t\text{-Bu}$, $R^3 = \text{Me}$, X = Cl



1e-A



1e-B

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