

Migratory-insertion of carbon monoxide into metal–acyl bonds

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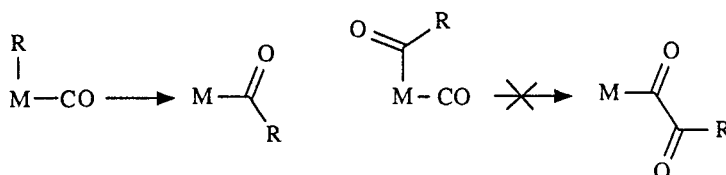
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Abstract - The α -ketoacyl complex $\text{Cp}'(\text{CO})(\text{NO})\text{Mn}-\text{C}(\text{O})\text{C}(\text{O})\text{Tol}$, **4** ($\text{Cp}'=\text{C}_5\text{H}_4\text{Me}$), has been prepared by two independent routes involving the oxidation of the carbyne ligand in $[\text{Cp}'(\text{CO})_2\text{Mn}\equiv\text{CTol}]^+$ with nitrite ion and oxidation of the anionic acyl complex $[\text{Cp}'(\text{CO})_2\text{Mn}-\text{C}(\text{O})\text{Tol}]^-$ followed by addition of NO gas. A common intermediate in both reactions is the $17e^-$ acyl complex $[\text{Cp}'(\text{CO})_2\text{Mn}-\text{C}(\text{O})\text{Tol}]^\bullet$ which undergoes migratory-insertion of CO into the metal-acyl bond upon addition of NO. Aspects of the reactivity of complex **4** and its PPh_3 substituted derivative **9** with electrophiles, nucleophiles, alkynes, and oxidizing agents are discussed. A surprisingly facile carbon-carbon bond cleavage of the α -ketoacyl ligand of complex **9** occurs upon either oxidation or protonation of the complex, and the α -ketoacyl ligand of complex **4** readily couples with alkynes to form metallacycles. Demetallation of the latter by treatment with acid releases vinyl- α -dione products.

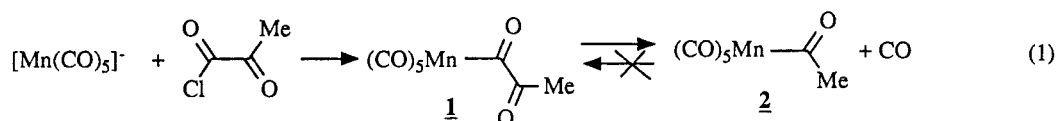
INTRODUCTION

Migratory insertion of CO into metal-alkyl bonds, Scheme 1, is a well-established reaction of fundamental importance in organometallic chemistry and is an essential step in many catalytic processes and stoichiometric reactions. In contrast, migratory-insertion of CO into metal-acyl bonds to form α -ketoacyl ligands has long been

Scheme 1

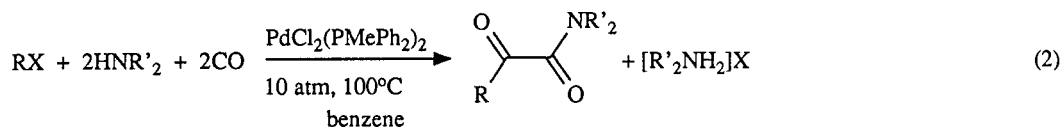


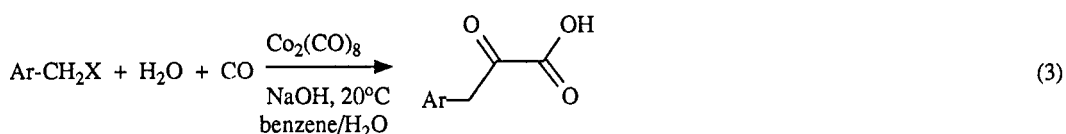
recognized as an unfavorable reaction and one with no definitive examples until the work summarized herein was first reported (ref. 1-2). It was Casey who first provided quantitative data illustrating the reluctance of CO to insert into a metal-acyl bond through a study of the α -ketoacyl complex **1**, eq. 1 (ref. 3). This species deinserts



CO to form the acyl complex **2**, but under no conditions examined (*e.g.*, 258 atm CO, 80°C, 9h) was any evidence obtained for the reverse insertion of CO into the metal-acyl bond. It was further shown that the α -ketoacyl complex **1** was kinetically 21 times more stable than **2** but thermodynamically 400 times less stable, indicating a highly unfavorable equilibrium for the $\mathbf{2} \rightleftharpoons \mathbf{1}$ reaction.

However, there are a number of reported catalytic "double-carbonylation" reactions which give products that could have been produced by the migratory-insertion of CO into a metal-acyl bond in some intermediate species. Two such reactions are illustrated in eqs. 2 (ref. 4) and 3 (ref. 5). The total lack of precedent for CO insertion into





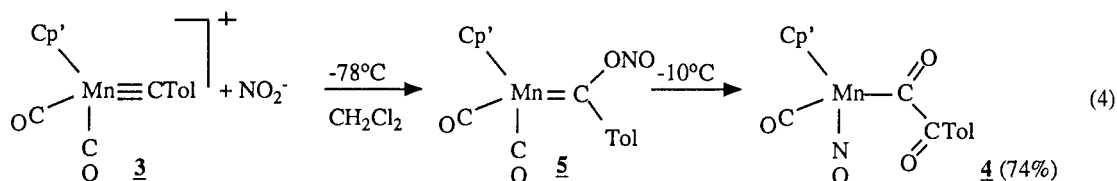
metal-acyl bonds has led to the suggestion of alternative mechanisms for these and related "double-carbonylation" processes. For example, there is now strong evidence that the Pd catalyzed reactions proceed by a mechanism involving addition of a nucleophile to an intermediate carbonyl-acyl complex to form a bis(acyl) species that then undergoes reductive coupling of these ligands to give the observed products (ref. 4). For the cobalt catalyzed reactions, which work well only with benzylic halides, mechanisms have been suggested in which a key step is tautomerization of an acyl intermediate to its enol form which is the species believed to undergo the second CO insertion (ref. 5).

During the course of our studies of the chemistry of the cationic carbyne complex $[\text{Cp}'(\text{CO})_2\text{Mn}\equiv\text{CTol}]^+$ (**3**, $\text{Cp}'=\text{C}_5\text{H}_4\text{Me}$), we unexpectedly prepared an α -ketoacyl complex by a process involving oxidation of the carbyne ligand and incorporation of one of the CO ligands into the α -ketoacyl moiety (ref. 1). Subsequent studies of the mechanism of this process showed that it occurs by initial oxidation of the carbyne to an acyl ligand which then undergoes migratory-insertion of CO to form the α -ketoacyl product (ref. 2). This reaction thus provided the first demonstrated example of the insertion of CO into a metal-acyl bond. This article summarizes our studies in this area and presents new results concerning the chemical properties of the resultant α -ketoacyl complexes.

RESULTS AND DISCUSSION

Nitrite induced transformation of the carbyne ligand in $[\text{Cp}'(\text{CO})_2\text{Mn}\equiv\text{CR}]^+$ into an α -ketoacyl ligand.

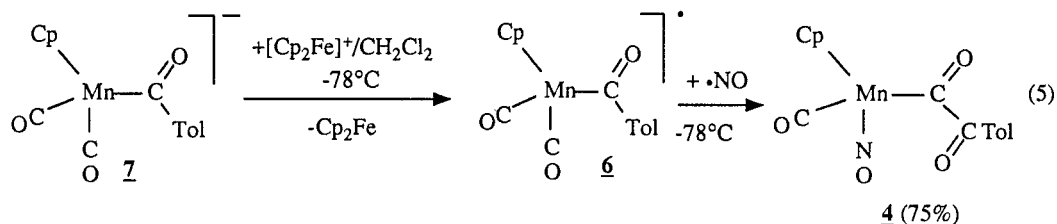
In the course of investigating the photochemical properties of the carbyne complex **3**, it was discovered that it readily reacts with $[\text{PPN}][\text{NO}_2]$ to form the α -ketoacyl complex **4**, eq. 4. This species was isolated in good yield



and was spectroscopically and crystallographically characterized (ref. 1). An unstable intermediate **5** that transformed into **4** upon warming to room temperature was observed by IR monitoring of the reaction at -78°C . This species shows two $\nu(\text{CO})$ bands at 1999 and 1939 cm^{-1} in the region characteristic of neutral $\text{Cp}'(\text{CO})_2\text{Mn}=\text{C}(\text{R})(\text{X})$ carbene complexes.¹¹ As illustrated in eq. 4, we believe it to be $\text{Cp}'(\text{CO})_2\text{Mn}=\text{C}(\text{ONO})\text{Tol}$ since a variety of related nucleophiles (CN^- , Cl^- , SCN^-) have been shown to add to **3** to give similar carbene derivatives (ref. 6). The mechanism by which this species decays to give **4** will be discussed shortly. First, an alternative preparation of **4** involving the migratory-insertion of CO into a metal-acyl bond will be described.

Migratory-insertion of CO into the metal-acyl bond of $[\text{Cp}'(\text{CO})_2\text{Mn}-\text{C}(\text{O})\text{Tol}]^-$.

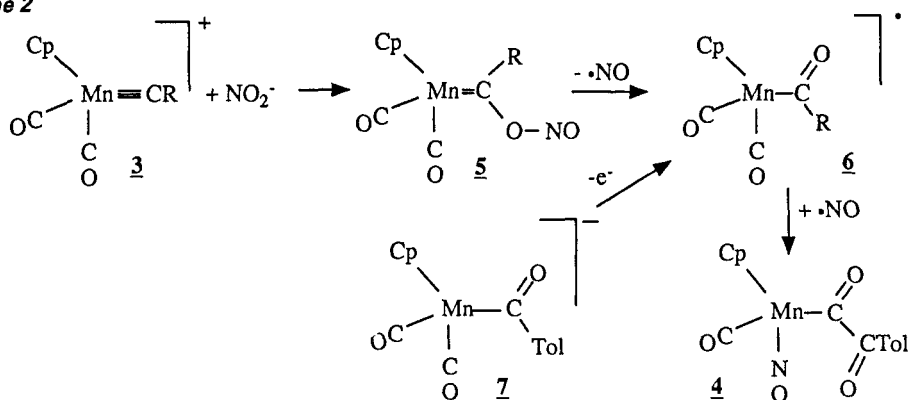
In the course of investigating the mechanism of the above reaction, the possibility that the intermediate **5** could decay to give NO and the $17e^-$ acyl complex $\text{Cp}'(\text{CO})_2\text{Mn}-\text{C}(\text{O})\text{Tol}$, **6**, was considered. The product **4** could then derive by recombination of these species (see below). To test this possibility, complex **6** was independently generated by oxidation of the known acyl complex $[\text{Cp}'(\text{CO})_2\text{Mn}-\text{C}(\text{O})\text{Tol}]^-$, **7**. Cyclic voltammetry (22°C , CH_2Cl_2 , $[\text{Bu}_4\text{N}]\text{PF}_6$, 100mV/sec) showed that acyl complex **7** undergoes a clean, reversible oxidation at -1.03 V vs. the $[\text{Cp}_2\text{Fe}]^+/\text{Cp}_2\text{Fe}$ couple to form the acyl radical **6**. The oxidation product **6** can be chemically prepared by treatment of CH_2Cl_2 solutions of **7** at -78°C with either $[\text{NO}]\text{BF}_4$ or $[\text{Cp}_2\text{Fe}]\text{PF}_6$, eq. 5. IR monitoring showed



that complex **6** survives warmup to room temperature, although it slowly decomposes to $\text{CpMn}(\text{CO})_3$ and other unidentified products over several hours at 22°C . Significantly, treatment of -78°C solutions of **6** with bubbling NO gas led immediately to formation of the α -ketoacyl complex, **4**, eq. 5. This reaction was quantitative by IR, and complex **4** was isolated in 75% recrystallized yield (ref. 2). Note that the overall conversion of **7** into **4** occurs by the migratory-insertion of CO into the metal-acyl bond.

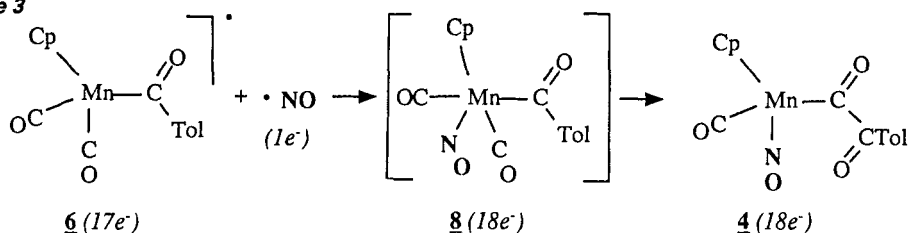
Mechanisms of formation of the α -ketoacyl complex 4 via reactions 4 and 5.

The overall mechanism which is proposed to account for reaction 4, the coupling of an oxidized carbyne ligand and CO to give an α -ketoacyl ligand, and reaction 5, the formation of an α -ketoacyl ligand by migration of an acyl ligand to a coordinated CO, is shown in Scheme 2. A key intermediate which connects these reactions is the 17e⁻

Scheme 2

acyl complex **6**. This species is proposed to form from the carbene complex **5** by cleavage of the oxygen-nitrogen bond, releasing NO in the process. Alternatively, **6** can be generated by oxidation of the 18e⁻ acyl complex **7**. The α -ketoacyl complex **4** then forms via addition of NO to **6**.

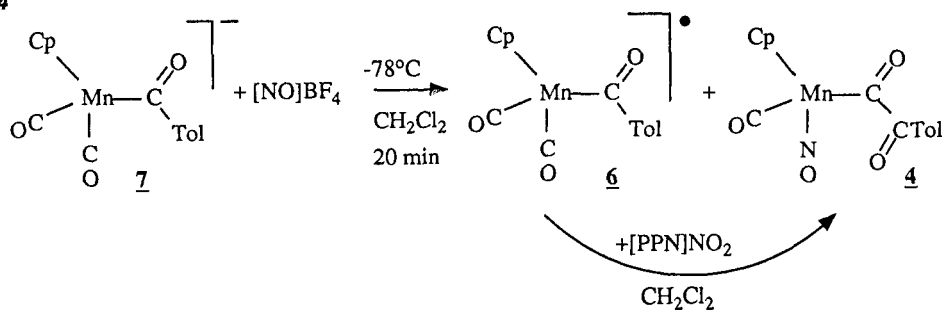
Nitric oxide clearly plays a pivotal role in the **6** to **4** conversion, and this process can be rationalized by assuming that the NO radical adds to the 17e⁻ complex **6** to give an 18e⁻ Cp(CO)₂(NO)Mn-C(O)R intermediate (**8**), having a bent, 1e⁻ donor NO ligand, Scheme 3. However, the more common bonding mode of a nitrosyl ligand in

Scheme 3

low-valent organometallic complexes such as these is as a linear 3e⁻ donor. In order to achieve this bonding form in a stable 18e⁻ product, either a CO ligand must be lost from **8** or a CO must insert into the metal-acyl bond. The latter reaction clearly occurs in the chemistry reported herein, with the energy gained in the bent to linear conversion of the NO ligand apparently providing the driving force for the acyl to CO migration.

Improved Synthesis of Cp*(CO)(NO)Mn-C(O)C(O)Tol using [NO]BF₄/[(PPH₃)₂N]NO₂.

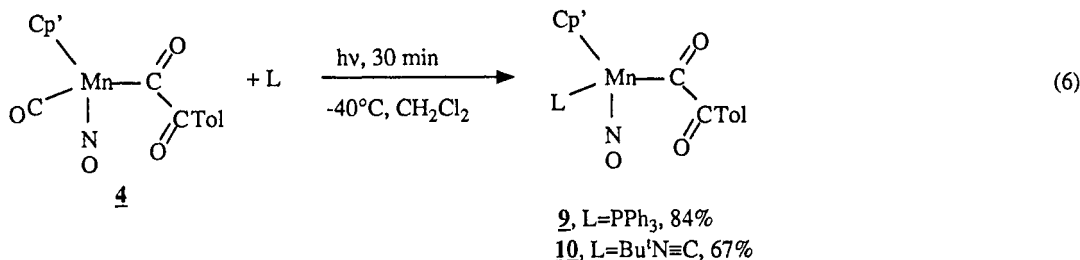
The synthesis of **4** described in eq. 5 used [Cp₂Fe]⁺ as the oxidizing agent and gave yields of 75% on a 100 mg scale (ref. 2). However, on larger scales (>2g) this method gave less than 20% yield of **4**, mainly due to difficulties in controlling the rate of addition of NO gas. A sufficient NO concentration must be maintained in solution for reaction to occur, but too high a concentration has been found to rapidly degrade the product. An improved preparatory scale procedure illustrated in Scheme 4 has since been developed (ref. 7). This method utilizes [NO]BF₄ as both the oxidizing agent and as one source of NO. Treatment of the anionic acyl complex **7** with 1 equiv of this reagent resulted in complete disappearance of **7** within 20 min at -78°C and formation of an approximate 4:1 ratio of the 17e⁻ complex **6** and the α -ketoacyl complex **4**. This reaction is believed to proceed

Scheme 4

by outer sphere electron transfer to form **6** and NO which then reacts with some **6** to form **4**. However, this latter reaction must be inefficient as the yield of **4** is low at this point. Addition of [PPN][NO₂] to this initial mixture of **6** and **4**, followed by warm-up to room temperature, gave quantitative conversion to **4** by IR. The salt [PPN][NO₂] has recently been shown to react with CH₂Cl₂, the solvent used in this reaction, to form the potent nitrosylating agent ClCH₂-ONO (ref. 8), and this is the species which apparently completes the **6** to **4** conversion. The method outlined in Scheme 4 has been reproducibly used on a 2.5 mmol scale to give **4** in 55-60% isolated yields.

Photoinduced ligand substitution in the α -ketoacyl complex **4**.

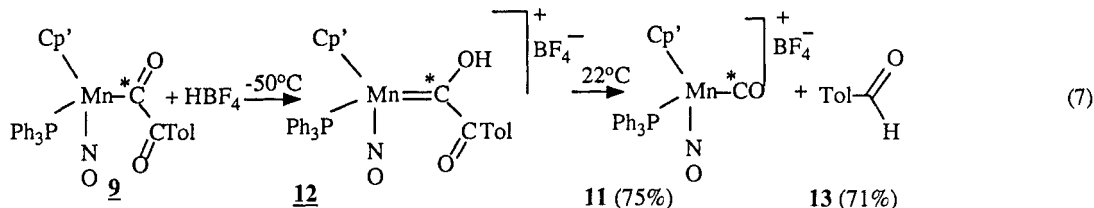
When complex **4** was heated in toluene (66°, 12h) in the presence of ~1 equivalent of PPh₃, the phosphine substituted complex **9** readily formed. This species was more conveniently prepared by photolyzing **4** with excess PPh₃, eq. 6. The BuⁿN≡C substituted derivative **10** was similarly prepared. These complexes were isolated in



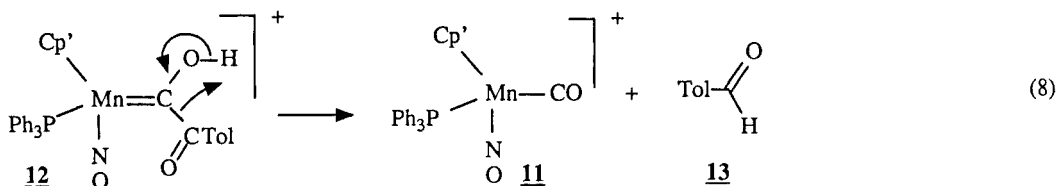
good yields and were spectroscopically characterized. Each shows the typical four band IR pattern in the α -ketoacyl region and characteristic ¹³C NMR resonances due to the α - and β -carbons of the α -ketoacyl ligand (e.g., **9**: δ 292.3 (d, J_{PC} = 25Hz, -C(O)C(O)Tol), 189.6 (d, J_{PC} = 5.5Hz, -C(O)C(O)Tol)).

Cleavage of the α -ketoacyl carbon-carbon bond upon protonation of complex **9**.

The unsubstituted α -ketoacyl complex **4** slowly decomposed to a mixture of products when protonated. However, the PPh₃ substituted derivative **9** gave rapid formation of the known complex [Cp'⁺Mn(CO)(NO)(PPh₃)]⁺, **11** (ref. 9), and 4-methylbenzaldehyde when treated with one equivalent of HBF₄·Et₂O at room temperature, eq. 7 (ref.7).

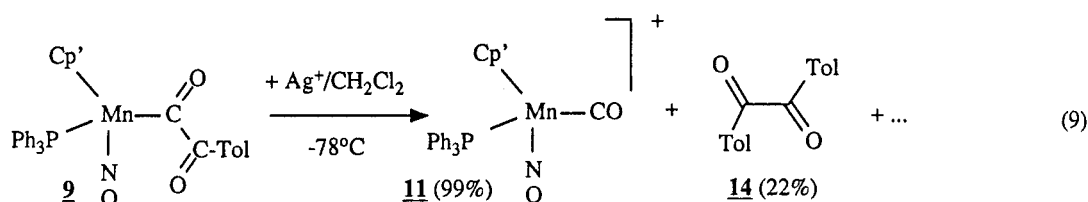


As indicated in the equation, a ¹³C labeling study using **9** exclusively enriched in ¹³C at the α -carbonyl carbon led to **11** with a ¹³C enriched CO ligand. This demonstrates that the metal coordinated CO in **11** derives from the α -carbonyl of the α -ketoacyl ligand, and thus protonation induces cleavage of the α -ketoacyl carbon-carbon bond. When reaction 7 was conducted at -78°C and monitored by IR, an intermediate formed ($\nu_{\text{NO}} = 1771 \text{ cm}^{-1}$) which then gave **7** upon warmup. Similar ¹³C NMR monitoring of the -50°C protonation of **9**, enriched at the α -carbon of the α -ketoacyl ligand, showed a resonance at δ 335.4 (d, J_{C,P} = 23 Hz) due to the intermediate species along with the δ 223.6 (d, J_{C,P} = 24 Hz) resonance of the product **11**. Upon warming to 0°C, the δ 335.4 resonance decreased in intensity as the δ 223.6 resonance of **11** grew in. These intermediate spectroscopic features are attributed to the hydroxycarbene complex **12** illustrated in eq. 7. Particularly indicative of this formulation is the downfield ¹³C NMR resonance in the region typical of metal carbene complexes. This is also the logical product of protonation since many acyl complexes have been shown to undergo protonation at the acyl carbonyl oxygen to give hydroxycarbene derivatives (ref. 10). The most likely mechanism for the **12**→**11**+**13** conversion is one involving an intramolecular hydrogen shift concomitant with cleavage of the carbon-carbon bond in the α -ketoacyl ligand, as outlined in eq. 8.



Oxidatively induced cleavage of the α -ketoacyl carbon-carbon bond in Cp'(PPh₃)(NO)-MnC(O)C(O)Tol.

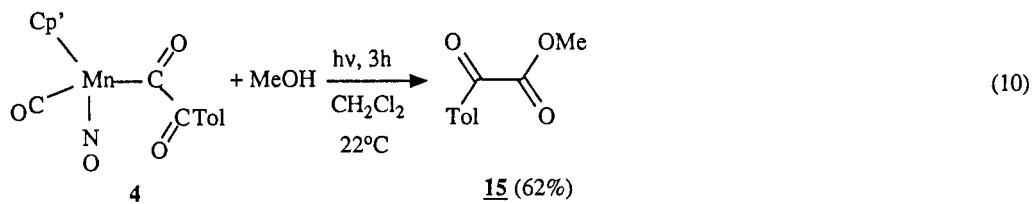
Treatment of a CH₂Cl₂ solution of **9** at -78°C with one equivalent of [Cp₂Fe]⁺ or Ag⁺ resulted in near instantaneous and quantitative conversion to the known cation **11**, along with a complex mixture of organic products, eq. 9 (ref. 7). The only organic formed in substantial yield and the only one confidently identified was



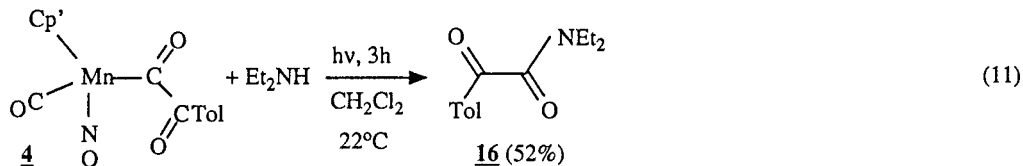
TolC(O)-C(O)Tol, **14**. The stoichiometry of this reaction indicates that oxidation induces cleavage of the carbon-carbon bond of the α -ketoacyl ligand to form **11** and Tol-C(O) \cdot radicals. A substantial fraction of the latter must couple to form the observed **14**, with the remainder decaying to other unidentified organic products. Unlike **9**, the unsubstituted α -ketoacyl complex **4** gave no reaction with either Ag⁺ or [Cp₂Fe]⁺.

Photoinduced Reaction of **1** with MeOH and Et₂NH.

Rapid reaction of MeOH with α -ketoacyl complex **4** occurred when the solution was irradiated, and the ester **15** was isolated in good yield, eq. 10 (ref. 7). Similarly, **1** reacted with NEt₂H under photochemical conditions to give



the corresponding α -ketoamide, **16**, eq. 11. During the course of these reactions, the IR bands of **4** progressively

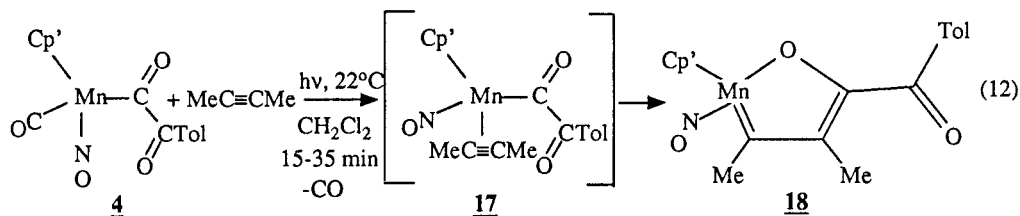


decreased in intensity and no new ν_{CO} bands were detected. No tractable organometallic products could be isolated after completion of the photolyses.

In contrast to the photochemical results, under thermal conditions complex **4** slowly decomposes when stirred at 22°C with excess MeOH over the course of 10 days, but no evidence was obtained for the formation of the α -ketoester. Since complex **4** has been established to readily lose CO upon photolysis, it appears that an open coordination site is necessary for reaction of **4** with methanol and diethylamine to occur. The PPh₃ substituted complex **9** is not photoactive, and accordingly we were unable to observe any reaction with methanol or with NEt₂H, under thermal or photochemical conditions.

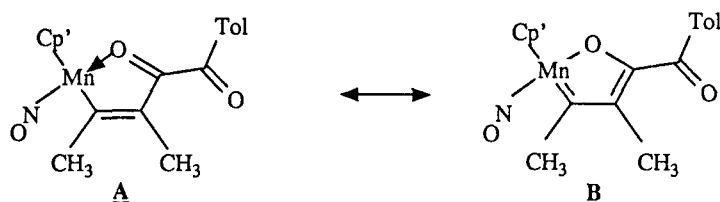
Coupling of alkyne and α -ketoacyl ligands to form metallacycles.

To explore the possibility of coordination and then interaction of small organic molecules with the α -ketoacyl ligand in complex **4**, this species was irradiated in the presence of alkynes in anticipation of photosubstitution of alkyne for CO. Rapid reaction occurred with small electron-rich alkynes to form metallacycles of the type depicted in eq. 12 for MeC \equiv CMe (ref. 7). The intermediate alkyne complex **17** was not detected, but it is the logical



species that would result upon photoinduced CO loss and coordination of alkyne. This reaction sequence is analogous to the *acyl*-alkyne coupling which has already been demonstrated to occur with (CO)₄Mn-C(O)R, generated at high pressure from (CO)₅Mn-R, to form the corresponding metallacycles (ref. 11).

Complex **18** was obtained as a very moisture-sensitive solid and was spectroscopically characterized. The complex showed a parent ion in its mass spectrum consistent with the indicated formulation and its ¹H NMR spectrum showed the usual Cp' ¹H NMR resonances and two additional resonances at δ 2.52 and 1.54, respectively attributed to the methyl groups on the α and β carbons of the metallacycle. Both of these are significantly downfield from the resonance of free 2-butyne at δ 1.10. The inequivalence of these resonances and their significantly different chemical shifts indicate that the compound is not the simple alkyne adduct **17**. Supporting the metallacycle structure is the ¹³C NMR spectrum of **18** which showed resonances at δ 275.9 and 140.6 assigned to the "alkyne" carbons along with resonances at δ 193.4 and 206.2 attributed to the α and β carbons of the α -ketoacyl moiety. The δ 275.9 resonance is in the region typical of carbene ligands, and it indicates the importance of the resonance form drawn above rather than the alternative resonance form depicted in **A** below. An X-ray diffraction study of the related (CO)₄Mn(OC[Me]C[H]C[Ph]) metallacycle prepared by

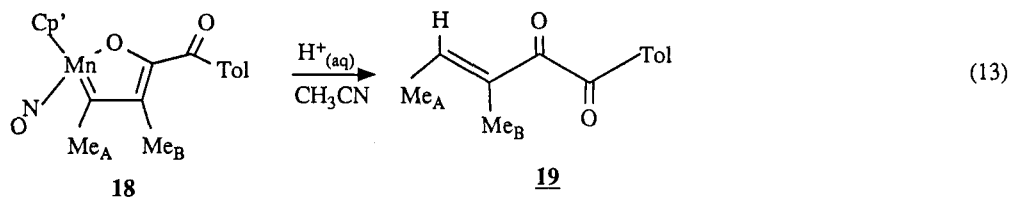


DeShong and co-workers also indicated the importance of the carbene resonance form (ref. 11). The nitrosyl infrared stretch of complex **18** is at 1700 cm^{-1} . This is 52 cm^{-1} lower in energy than the corresponding stretch in **4**, indicating a significant increase in electron density on the metal as a consequence of the alkyne incorporation.

Similar metallacycles were observed to form upon reaction of **4** with $\text{Bu}^t\text{C}\equiv\text{CH}$, $\text{MeC}\equiv\text{CEt}$, and $\text{MeC}\equiv\text{CPh}$ under photochemical conditions. These were not characterized as fully as **18**, but their similar chemical behavior, particularly their hydrolysis to give vinyl- α -diones as described below indicate that they have similar structures. Only the alkynes listed above gave relatively clean reactions. The less electron rich $\text{PhC}\equiv\text{CMe}$ and $\text{Me}_3\text{SiC}\equiv\text{CMe}$ reacted more slowly and less cleanly, the latter rapidly hydrolyzing upon metallacycle formation. The alkynes $\text{PhC}\equiv\text{CH}$, $\text{PhC}\equiv\text{CPh}$ and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ did not react at all with **4** nor did the electron rich but sterically bulky $\text{Bu}^t\text{C}\equiv\text{CMe}$.

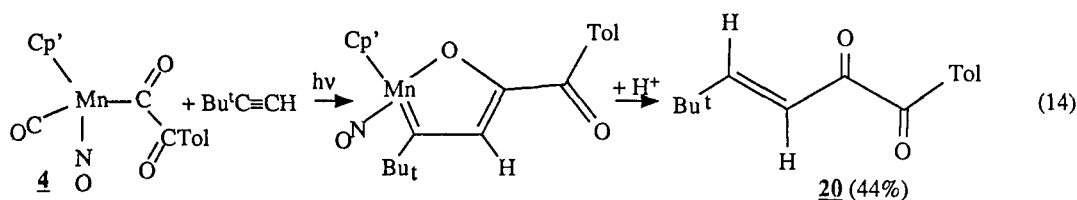
Hydrolysis of metallacycles **18** to form vinyl α -diones.

The metallacycles produced in the above reactions are extremely susceptible to hydrolysis, and the complexes can easily be demetallated by addition of aqueous HCl to a CH_3CN solution of the complex and also to a large extent upon chromatographic work-up. For example, an immediate brown to green-brown color change occurred upon addition of acid to complex **18**, and the vinyl α -dione product **19** was isolated in 46% overall yield from **4**, eq. 13.



The compound **19** was characterized by its mass spectrum and by NMR spectroscopy. The latter also showed the stereochemistry to be that depicted in eq. 13 with the α -ketoacyl and hydride substituents in a *cis* arrangement. The ^1H NMR spectrum of **19** shows a vinyl proton resonance at δ 6.64 (qd, $J_{\text{HH}}=6.8, 1.1\text{ Hz}$) and two methyl resonances at δ 1.93 (d, $J_{\text{HH}}=1.1\text{ Hz}$) and δ 1.92 (d, $J_{\text{HH}}=6.8\text{ Hz}$) along with the tolyl resonances. In a difference NOE experiment, irradiation of the vinyl multiplet gave enhancement of only the δ 1.92 methyl resonance which is then assigned to Me_A . The intensity of the δ 1.93 resonance was not enhanced and this methyl substituent must be *trans* to the hydrogen.

Alkyne- α -ketoacyl coupling also occurred with $\text{Bu}^t\text{C}\equiv\text{CH}$ to give a single regioisomer of the vinyl α -dione, eq. 14. The intermediate metallacycle was observed by IR ($\nu_{\text{NO}}=1701\text{ cm}^{-1}$) but was not otherwise characterized.



The vinyl α -dione **20** was isolated in modest overall yield from **4**, and its ^1H NMR spectrum showed two vinyl hydrogen resonances as doublets at δ 6.38 and 6.93 with a 76.4 Hz coupling between them. A coupling of this magnitude is consistent only with a *trans* arrangement of the hydrogens as depicted in eq. 14. Thus the overall coupling of the alkyne and α -ketoacyl ligands is highly regioselective.

CONCLUDING REMARKS

The most important aspect of the work described in this paper is the demonstration that α -ketoacyl ligands can be formed by the migratory-insertion of CO into metal-acyl bonds (eq. 5). Although it was necessary to use unusual methodologies to accomplish this transformation, the results described herein clearly show that this is a viable reaction step and one that must be considered in discussions of "double carbonylation" reactions. The experimental results indicate that both reactions 4 and 5 proceed via a common path involving formation of the $17e^-$ acyl complex $[\text{Cp}'(\text{CO})_2\text{Mn}-\text{C}(\text{O})\text{Tol}]^\bullet$ which undergoes the migratory-insertion step when treated with NO. A key element of the latter conversion is the proposed intermediate formation of the $18e^-$ species $\text{Cp}(\text{CO})_2(\text{NO})\text{Mn}-\text{C}(\text{O})\text{Tol}$ having a *bent, 1e^- donor nitrosyl ligand*. The isomerization of this ligand to the more common linear, $3e^-$ form is believed to provide the driving force for the acyl to CO migratory-insertion process.

Also important are the reactions of the α -ketoacyl complexes **4** and **9** that are described above since little was known about the chemical properties of α -ketoacyl ligands prior to this work. The facile photosubstitution reactions illustrated in eq. 6 show that the α -ketoacyl ligand in complex **4** is quite stable and does not readily undergo de-insertion to form an acyl species. This has allowed the formation of novel metallacycles (**18**) by photolysis of complex **4** in the presence of alkynes to induce photosubstitution of alkyne for CO followed by migration of the α -ketoacyl ligand to the alkyne. A surprising result is the facile cleavage of the carbon-carbon bond of the α -ketoacyl ligand upon both protonation and oxidation of complex **9**. While the reasons why these latter two reactions occur are not completely understood, one important factor must be the stability of the product $\text{Cp}(\text{CO})_2(\text{NO})\text{Mn}$ which forms in both processes.

Acknowledgements

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