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Reactivity of the α-Ketoacyl Ligand in Cp′(L)(NO)Mn–C{O}C{O}Tol with Electrophiles, Nucleophiles, and Alkynes

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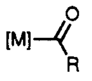
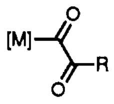
The reactivity of the α-ketoacyl complexes Cp′(L)(NO)Mn–C{O}C{O}Tol (Cp′ = C_5H_4Me; **1**, L = CO; **2**, L = PPh_3) with a variety of electrophiles, nucleophiles, and alkynes has been explored. Complex **2** undergoes protonation at the α-carbonyl oxygen at low temperature to produce a hydroxy–carbene complex. This species rearranges upon warmup by breaking the carbon–carbon bond of the α-ketoacyl ligand to give 4-methylbenzaldehyde and $[Cp'Mn(PPh_3)(NO)(CO)]^+$ (**6**). Oxidation of complex **2** with either $[Cp_2Fe]^+$ or Ag^+ also results in the formation of complex **6** along with a mixture of organic products in which TolC{O}C{O}Tol dominates. These products indicate that oxidation induces cleavage of the α-ketoacyl carbon–carbon bond to form **6** and TolC{O}$^\bullet$ radicals. Complex **1** reacts with NEt_2H under photochemical conditions to give the α-ketoamide TolC{O}C{O}NEt_2. Upon photolysis, complex **1** reacts with alkynes RC≡CR′ to form metallacycles of the type Cp(CO)(NO)$\overline{\mathrm{Mn{=}CR{-}CR'{=}C(C\{O\}Tol)O}}$ that result from coupling of the alkyne and the α-ketoacyl ligand. The metallacycles can be demetalated by treatment with HCl to give vinyl α-diones that are the net result of cis addition of the α-ketoacyl ligand and a proton across the alkyne triple bond.

Introduction

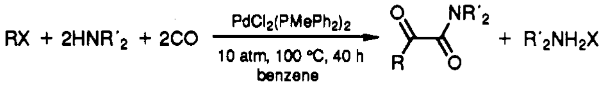
The acyl ligand (I) is an important functionality in organo-transition-metal chemistry due to its involvement in many catalytic and stoichiometric reactions. Its chemistry has accordingly been thoroughly investigated and is relatively well understood.[1] In contrast, only a few α-ketoacyl complexes (II) have been synthesized,[2,3] and little is known about the chemical properties of this ligand. Such ligand systems are of interest because of their possible intermediacy in catalytic reactions which give 1,2-dione products,[4] e.g. eq 1[4a,b,g] and 2,[4c–e] and the potential use of such products as starting materials in organic synthesis.[5]



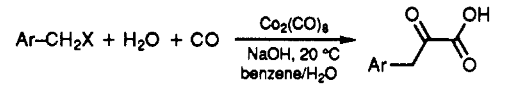
I



II

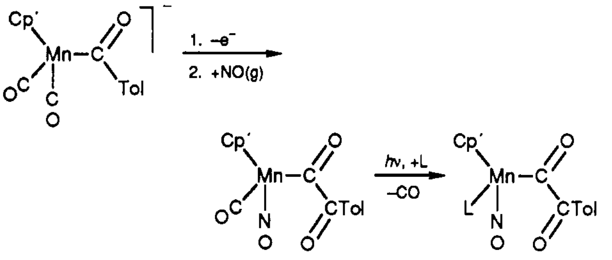


(1)



(2)

We previously showed that the α-ketoacyl complex **1** can be formed by the oxidation/NO addition reaction sequence shown in eq 3[3] and that this species undergoes clean photosubstitution of PPh_3 and $^tBuN{\equiv}C$ for CO to give complexes **2** and **3**. In order to more fully define the chemical properties of the α-ketoacyl ligand we have since undertaken a study of the reactivity of these species. These latter complexes are ideally suited for such studies since unlike most α-ketoacyl complexes which readily decarbonylate, complexes **1** and **2** have been shown to be relatively stable toward CO deinsertion.[3b] Herein are described aspects of the reactivity of **1** and **2** with electrophiles, nucleophiles, and alkynes, as well as a surprisingly facile carbon–carbon bond cleavage of the α-ketoacyl ligand upon oxidation. The reactions with alkynes are particularly interesting since the α-ketoacyl ligand regiospecifically couples with alkynes to form metallacycles that can be removed from the metal as vinyl α-diones.



(3)

1

2, L = PPh_3

3, L = $^tBuN{\equiv}C$

Cp′ = C_5H_4Me

Results and Discussion

Improved Synthesis of Cp′(CO)(NO)Mn–C{O}C{O}Tol (1). The original synthesis of the α-ketoacyl complex **1** described in eq 3 used $[Cp_2Fe]^+$ as the oxidizing

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[1] Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Oxford, 1980.

[2] (a) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166. (b) Chen, J.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506. (c) Sen, A.; Chen, J.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148. (d) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683. (e) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 692. (f) Fayos, J.; Dobrzynski, E.; Angelici, R. J.; Clardy, J. *J. Organomet. Chem.* **1973**, *59*, C33. (g) Blake, D. M.; Vinson, A.; Dye, R. *J. Organomet. Chem.* **1981**, *204*, 257. (h) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405. (i) Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 4077. (j) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553. (k) Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1455. (l) Dobrzynski, E. D.; Angelici, R. J. *Inorg. Chem.* **1975**, *14*, 59.

[3] (a) Sheridan, J. B.; Han, S. H.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 8097. (b) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2404.

[4] (a) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383. (b) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64. (c) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* **1977**, *134*, C11. (d) des Abbayes, H.; Buloup, A. *J. Chem. Soc., Chem. Commun.* **1978**, 1090. (e) des Abbayes, H. *Nouv. J. Chem.* **1987**, *11*, 535. (f) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701. (g) See refs 2c–e for a discussion of the mechanism of reaction 1.

[5] (a) Valentine, D., Jr., Scott, J. W. *Synthesis* **1978**, 329. (b) Ojima, I.; Tanaka, T.; Kogure, T. *Chem. Lett.* **1981**, 823. (c) Tani, K.; Suwa, K.; Otsuka, S. *ACS Symp. Ser.* **1982**, *No. 185*, 283. (d) Harada, K.; Munegumi, T.; Nomoto, S. *Tetrahedron Lett.* **1981**, *22*, 111.

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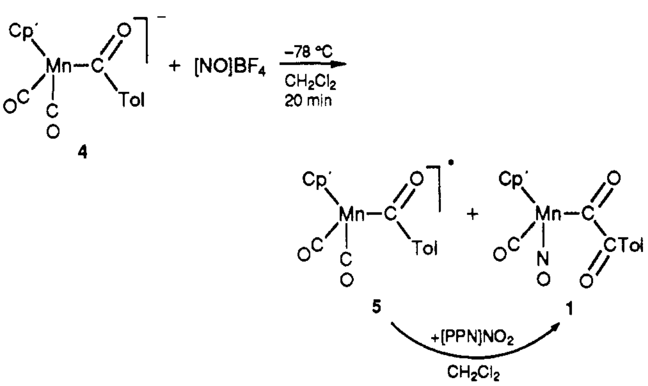
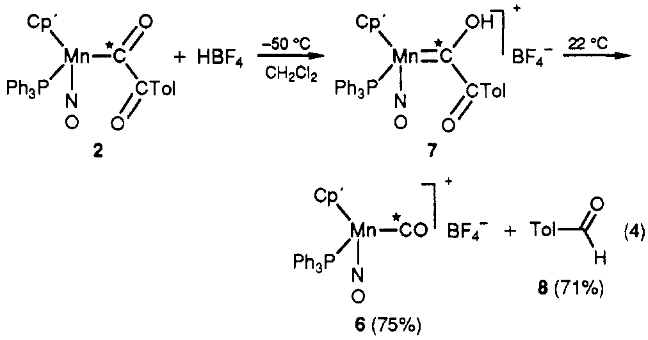
Scheme I

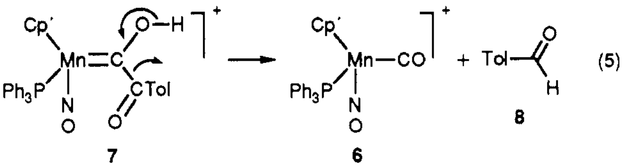


agent, and addition of NO(g) gave yields of 75% on a 100-mg scale.[3] However, on larger scales (>2 g) this method gave less than 20% yield of 1, mainly due to difficulties in controlling the NO addition. A sufficient NO concentration must be maintained in solution for reaction to occur, but too high a concentration has been found to rapidly degrade the product.

An improved preparatory scale procedure for 1 has since been developed and is illustrated in Scheme I and detailed in the Experimental Section. This method utilizes $[NO]BF_4$ both as the oxidizing agent and as one source of NO. Treatment of the anionic acyl complex 4 with 1 equiv of this reagent resulted in complete disappearance of 4 within 20 min at -78 °C and formation of an approximate 4:1 ratio of the previously described[3b] 17e complex 5 (ν_{CO} = 1977 (s), 1913 (s) cm^{-1}) and the α-ketoacyl complex 1. This reaction is believed to proceed by outer-sphere electron transfer to generate 5 and NO and then reaction of some of the NO with 5 to form 1. However, this latter step must be inefficient as the yield of 1 is low at this point. Addition of $[PPN][NO_2]$ to this initial mixture of 5 and 1, followed by warmup to room temperature, gave quantitative conversion of 5 to 1 by IR. Under similar room-temperature conditions, the salt $[PPN][NO_2]$ has recently been shown to react with CH_2Cl_2, the solvent used in this reaction, to form the potent nitrosylating agent $ClCH_2$–ONO,[6] and this is the species that apparently completes the 5 to 1 conversion. The method outlined in Scheme I has been reproducibly used on a 2-g scale to give 1 in 55–60% isolated yields.

Cleavage of the α-Ketoacyl Carbon–Carbon Bond of 2 upon Protonation. The α-ketoacyl complex 1 slowly decomposed to a mixture of products when treated with $HBF_4{\cdot}Et_2O$. However, the PPh_3-substituted derivative 2 gave rapid formation of the known complex $[Cp'Mn(CO)(NO)(PPh_3)]^+$ (6)[7] and 4-methylbenzaldehyde when 1 equiv of $HBF_4{\cdot}Et_2O$ was added at room temperature (eq 4). As indicated in the equation, a ^{13}C-labeled study using 2 exclusively enriched in ^{13}C at the α-carbonyl carbon (see Experimental Section) led to 6 with a ^{13}C enriched CO ligand. This demonstrates that the metal-coordinated CO in 6 derives from the α-carbonyl of the α-ketoacyl ligand, and thus protonation induces cleavage of the α-ketoacyl carbon–carbon bond. When reaction 4 was conducted at -78 °C and monitored by IR, an intermediate formed (ν_{NO} = 1771 cm^{-1}) which then gave 6 upon warmup. ^{13}C NMR monitoring of the -50 °C protonation of 2 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 6. Upon warming to 0 °C, the δ 335.4 resonance decreased in intensity as the δ 223.6 resonance of 6 grew in. We attribute these intermediate spectroscopic features to the hydroxycarbene complex 7 illustrated in eq 4. Particularly indicative of this formulation is the downfield ^{13}C NMR resonance in the region typical of metal carbene complexes.[8] For comparison, the known hydroxycarbene complex $Re(CO)_3Cl\{=C(OH)Me\}_2$ shows a carbene ^{13}C NMR resonance at δ 322.3.[9] 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.[10] Details of how the intermediate hydroxycarbene complex 7 decays to give complex 6 and the aldehyde 8 are not known, although one likely path involves an intramolecular hydrogen shift concomitant with cleavage of the carbon–carbon bond in the α-ketoacyl ligand, as outlined in eq 5.





Two alternative mechanisms for decay of the hydroxycarbene complex 7 into the observed products are outlined in Scheme II. Both involve the initial migration of the hydrogen atom to Mn to give the hydride intermediate 9. This species could decay by reductive elimination to give the α-ketoaldehyde 10 and a coordinatively unsaturated manganese complex. The latter species could extrude CO to form the observed aldehyde product, and recombination of the released CO and the Mn fragment would give 6. However, this pathway was ruled out by the observation that when reaction 4 was conducted by using unlabeled α-ketoacyl complex 2 under an atmosphere of ^{13}CO, there was no ^{13}CO incorporated into the product $[Cp'Mn(CO)(NO)(PPh_3)]^+$, indicating that the reaction is strictly intramolecular. Also, the related α-ketoaldehyde $PhC\{O\}CHO$ is a commercially available[11] and stable molecule that does not decarbonylate under the mild conditions used in reaction 4.

It is also possible that the intermediate 9 shown in Scheme II could undergo deinsertion of CO to form an acyl

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(7) (a) Brunner, H.; Langer, M. *J. Organomet. Chem.* **1973**, *54*, 221. (b) Reger, D. L.; Fauth, D. J.; Dukes, M. D. *J. Organomet. Chem.* **1979**, *170*, 217.

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(9) Darst, K. P.; Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *J. Organomet. Chem.* **1980**, *195*, 317.

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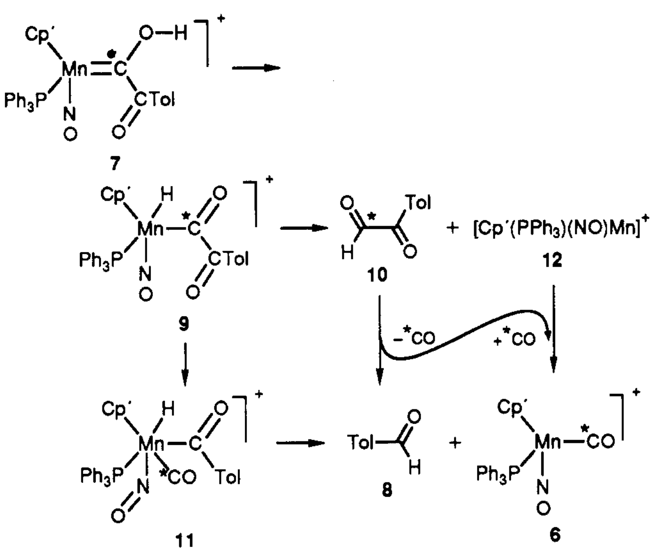
(11) Aldrich Chemical Co.

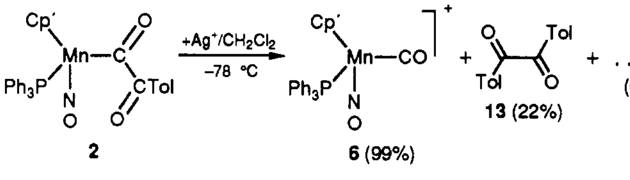
Scheme II



species if a coordination site were opened by the nitrosyl ligand bending (as in 11) or the cyclopentadienyl ligand slipping to an η^3-coordination mode. Reductive elimination of the aldehyde would then give the products 6 and 8 directly. It should be recalled that a change in coordination mode of the NO ligand from bent to linear is believed to be the key step in the α-ketoacyl complex synthesis that was illustrated in eq 3.[3] While this path cannot be eliminated from consideration, we believe it unlikely on the basis of the observation that the α-ketoacyl ligand of complex 1 does not readily undergo deinsertion of CO when a coordination site is opened by photolysis, and thus it does not seem likely that deinsertion would readily occur here. Also, an eight-coordinate intermediate such as 11 seems highly unlikely for steric reasons.

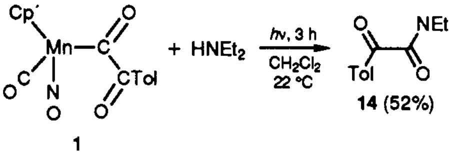
Whereas protonation of 2 readily occurs at the α-carbonyl oxygen, alkylation does not. Treatment of a −78 °C solution of 2 with 1 equiv of $CH_3OSO_2CF_3$ gave no change in the IR spectrum of 2 over a period of several hours. Upon warming to room temperature, slow decomposition of the α-ketoacyl complex occurred over the course of 3 days to give the cation 6 (97%), but no 4-methylacetophenone was detected.

Oxidatively Induced Cleavage of the α-Ketoacyl Carbon–Carbon Bond in Complex 2. Treatment of a CH_2Cl_2 solution of 2 at −78 °C with 1 equiv of $[Cp_2Fe]^+$ or Ag^+ resulted in rapid and quantitative conversion to the known cation 6,[7] along with a complex mixture of organic products (eq 6). The only organic product formed in substantial yield, and the only one confidently identified was TolC{O}C{O}Tol (13). The stoichiometry of this reaction indicates that oxidation induces cleavage of the carbon–carbon bond of the α-ketoacyl ligand to form 6 and Tol–C{O}$^\bullet$ radicals. A substantial fraction of the latter must couple to form the observed 13, with the remainder decaying to other unidentified organic products. Unlike 2, the unsubstituted α-ketoacyl complex 1 was not oxidized by $[Cp_2Fe]^+$, consistent with a decreased electron density at the metal center due to the electron-withdrawing carbonyl ligand. Consistent with the observed chemistry, the cyclic voltamogram of complex 2 showed a broad, irreversible oxidation wave at 347 mV (platinum disk electrode vs SCE; 100 mV/s; ferrocene couple = 560 mV).



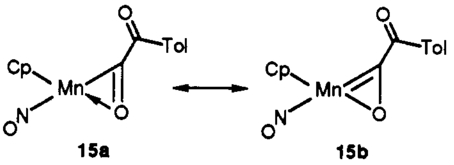
(6)

Photoinduced Reaction of the α-Ketoacyl Complex 1 with Et_2NH. Rapid reaction of complex 1 with NEt_2H occurred under photochemical conditions to give the α-ketoamide 14 (eq 7). During the course of this reaction, the IR bands of 1 progressively decreased in intensity and no new metal carbonyl IR bands appeared. No tractable organometallic products could be isolated after completion of the photolyses.

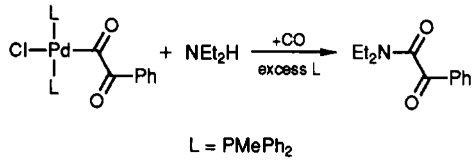


(7)

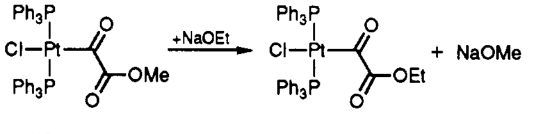
Since complex 1 does not react with Et_2NH under mild thermal conditions and since 1 has been established to readily lose CO upon photolysis,[3b] it appears that an open coordination site is necessary for reaction to occur between 1 and diethylamine. The PPh_3-substituted complex 2 is not photoactive, and accordingly we were unable to observe any reaction of 2 with NEt_2H under thermal or photochemical conditions. We believe that photolysis may induce CO loss and formation of an intermediate with an η^2-coordinated acyl ligand such as 15 and that this is the species that is rapidly attacked by Et_2NH. The oxycarbene resonance form **15b** would seem especially susceptible to nucleophilic attack at the carbene carbon since Fischer-type carbene complexes readily undergo trans-amination reactions by similar nucleophilic addition to the carbene carbon.



Reaction 8 illustrates the only other example of nucleophilic cleavage of an α-ketoacyl ligand from a metal,[2e] although two reactions have been reported that apparently involve nucleophilic attack at the *β-carbon* of α-ketoacyl ligands. Angelici and co-workers[21] showed that trans-esterification of the α-ketoacyl complex shown in eq 9 results upon addition of ethoxide, and Gladsyz and co-workers[2k] reported that hydride adds to the β-carbonyl of Mn and Re α-ketoacyl complexes to ultimately yield the metallacycles shown in eq 10.

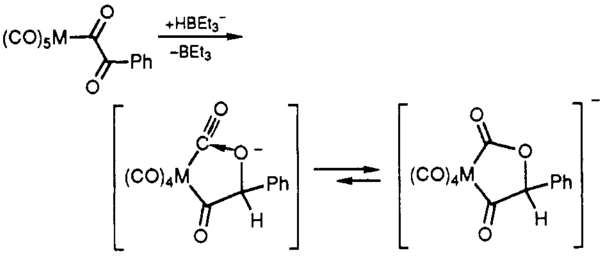


(8)



(9)

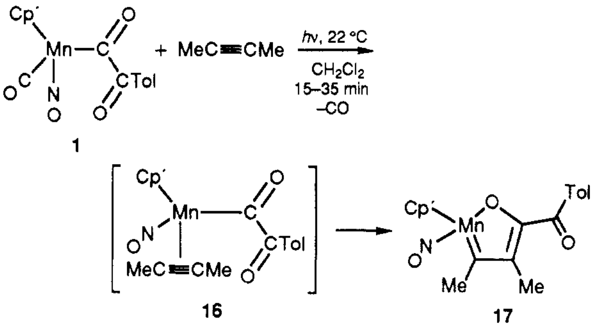
Coupling of Alkyne and α-Ketoacyl Ligands To Form Metallafuran Derivatives. Since complex 1 has been established to readily lose CO upon photolysis,[3b] it was anticipated that irradiation in the presence of alkynes would give photosubstitution of alkyne for CO and perhaps coupling of the alkyne and α-ketoacyl ligands. Indeed, rapid photoreaction occurred with small electron-rich



(10)

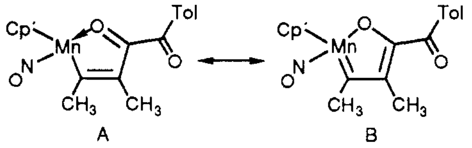
M = Mn, Re

alkynes to form metallacycles of the type depicted in eq 11 for reaction with MeC≡CMe. The intermediate alkyne complex **16** was not detected, but it is the logical species that would result from photoinduced CO loss and coordination of alkyne. This overall reaction sequence is analogous to the *acyl*–alkyne coupling to form metallacycles that has been demonstrated to occur with $(CO)_4Mn{-}C\{O\}R$[12a] and $Cp(CO)_2W{-}C(O)R$[12b] which formed in situ from $(CO)_5Mn{-}R$ and $Cp(CO)_3W{-}R$, respectively.



(11)

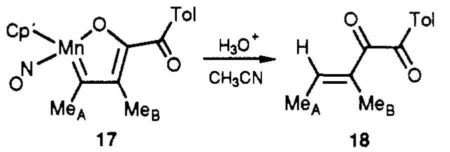
Complex **17** was obtained as a very moisture-sensitive solid and has been spectroscopically characterized. It shows a parent ion in its mass spectrum consistent with the given formulation, and its ^1H NMR spectrum shows two resonances at δ 2.52 and 1.54 that are respectively attributed to the methyl groups on the α- and β-carbons of the metallacycle. Both of these are significantly downfield from the δ 1.10 resonance of free 2-butyne. The inequivalence of these resonances and their significantly different chemical shifts indicate that the compound is not the simple alkyne adduct **16**. Supporting the metallacycle structure of **17** is its ^{13}C NMR spectrum which shows 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. These assignments are based on similar assignments for analogous metallacycles such as $Cp(CO)_2W\{CHCHC(Me)O\}$ [δ 237.7 (C_α), 131.7 (C_β), 200.0 (C_γ)].[12b] In the latter compounds, unambiguous assignments of the α-, β-, and γ-carbons of the metallacycle was made possible by the observation of $^{13}C{-}^1H$ coupling in the ^{13}C NMR spectra. The δ 275.9 resonance of our complex **17** is in the region typical of carbene ligands,[8] and it indicates the importance of the resonance form drawn above rather than the alternative resonance form A depicted below. The carbene resonance form has also been shown to be dominant in the related metallafuran $(CO)_4Mn\{OC(Me)CHC(Ph)\}$ by an X-ray diffraction study.[12a] The ν_{NO} stretch of complex **17** is at 1700 cm^{-1}, 52 cm^{-1} lower in energy than the corresponding stretch in complex **1**, indicating a significant increase in electron density on the metal as a consequence of the alkyne incorporation.



A B

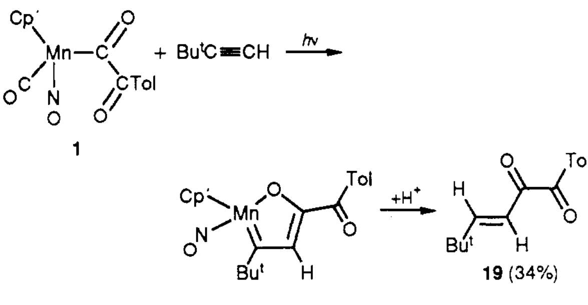
Similar metallacycles were observed to form upon reaction of **1** with Bu^{t}C≡CH, MeC≡CEt, and MeC≡CPh under photochemical conditions. These were not as fully characterized as **17**, but their chemical behavior, particularly their hydrolysis to give vinyl α-diones (see below), indicates that they have similar structures. Also indicative is the ν_{NO} stretch that each shows in the same 1689–1701 cm^{-1} region. The alkynes PhC≡CH, PhC≡CPh, $MeO_2CC{\equiv}CCO_2Me$, and Bu^{t}C≡CMe did not react with **1**.

Hydrolysis of the Metallafurans To Form Vinyl α-Diones. The metallacycles produced in the above reactions are extremely susceptible to hydrolysis as indicated by their extensive decomposition upon chromatographic workup. The hydrolysis is more conveniently carried out by addition of aqueous HCl to a CH_3CN solution of the complex to induce a demetalation reaction. For example, an immediate brown to green-brown color change occurred upon addition of acid to complex **17**, and the vinyl α-dione product **18** was isolated in 46% overall yield from **1** (eq 12). The vinyl α-dione **18** was characterized by its mass spectrum and by NMR spectroscopy with the latter indicating that the α-ketoacyl and hydride substituents are in a cis arrangement. This was shown by an NOE experiment in which irradiation of the vinyl multiplet at δ 6.64 (qd, J_{HH} = 1.1, 6.8 Hz) gave enhancement of the δ 1.92 (d, J_{HH} = 6.8 Hz) methyl resonance, but no change was observed in the δ 1.93 (d, J_{HH} = 1.1 Hz) methyl resonance. Only the cis structure depicted in eq 12 is consistent with this data with the enhanced methyl resonance at δ 1.92 assigned to Me_A.



(12)

A similar reaction occurred with Bu^{t}C≡CH to give a single regioisomer of the vinyl α-dione **19** (eq 13). The intermediate metallacycle was observed by IR (ν_{NO} = 1701 cm^{-1}) but was not otherwise characterized. The vinyl α-dione **19** was isolated in modest overall yield from **1**, and its ^1H NMR spectrum showed two doublets at δ 6.38 and 6.93 assigned to the vinyl hydrogens. The 16.4 Hz coupling between these hydrogens implies that they are in trans positions, and the geometry of **19** must be that given in eq 13.



(13)

Concluding Remarks

The objective of the work described herein was to define the chemistry of complexes **1** and **2** so as to further our

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(12) (a) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575. (b) Alt, H. G.; Engelhardt, H. E.; Thewalt, U.; Riede, J. *J. Organomet. Chem.* **1985**, *288*, 165.

understanding of the properties of this little-studied ligand. In this study we have shown that the α-ketoacyl ligand can be cleaved from the metal by nucleophiles under photochemical conditions, that the α-ketoacyl ligand is capable of coupling with alkynes to form metallafurans, and that the α-ketoacyl ligand undergoes a surprisingly facile cleavage of the carbon–carbon bond upon oxidation and protonation. The results summarized in eq 7 show that the α-ketoacyl ligand in complex **1** can be demetalated through nucleophilic attack at the α-carbon to form α-ketoamides. This type of reaction may be important in catalytic double-carbonylation reactions like those illustrated in the Introduction. Although mechanistic studies have indicated that this reaction step does not occur during the catalytic chemistry of eq 1,[2c] a similar nucleophilic attack of hydroxide on an α-ketoacyl ligand has been previously postulated, but not proven, as the reaction which leads to the α-ketoacid product of eq 2.[4e] The curious feature in the reaction of α-ketoacyl complex **1** with Et$_2$NH is the necessity of using photochemical initiation. While this phenomenon is not yet understood, we believe that it implies the formation of an η^2-α-ketoacyl ligand which is the actual species that undergoes attack by the nucleophiles.

Another interesting feature of the results described herein is the formation of metallafurans upon reaction of the α-ketoacyl complex **1** with alkynes. Metallafurans have been previously shown to form upon reaction of alkynes with the acyl complexes [(CO)$_4$Mn–C{O}R] and [Cp(CO)$_2$W–C{O}R], generated as intermediates from the corresponding alkyl complexes.[12] The results described in eq 11–13 show that α-ketoacyl complexes are also capable of undergoing this chemistry, and the subsequent demetallation reactions with HCl provide an interesting way to prepare vinyl α-diones.

Whereas the above reactions have analogies in metal–acyl chemistry, the facile cleavage of the α-ketoacyl carbon–carbon bond upon protonation and oxidation do not. While it is not yet understood why these reactions occur, the fact that they do indicates that the α-ketoacyl carbon–carbon bond in complex **2** must be relatively weak. An important feature of both reactions is the high-yield formation of [CpMn(CO)(NO)(PPh$_3$)]$^+$ as the organometallic product. We have observed this complex to form in much of the chemistry of this family of compounds, and its obvious thermodynamic stability must provide part of the driving force for the above-mentioned reactions.

Experimental Section

General Data. The complexes [Cp$_2$Fe][PF$_6$][13] and Cp′(PPh$_3$)(NO)Mn–C{O}C{O}Tol (**2**)[3] were prepared by published procedures. Solvents were dried by stirring over CaH$_2$ and were freshly distilled prior to use. All other reagents were used as received without further purification. All manipulations were performed by using standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode, NMR spectra were obtained on Brucker AM-300 and AM-500 FT NMR spectrometers, and electron-impact (EI) mass spectra were recorded on an AEI-MS9 mass spectrometer. Photolyses were conducted under N$_2$ in Pyrex Schlenk glassware using unfiltered, broad-band irradiation from a 450-W medium-pressure Hg lamp (Hanovia). Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY. The electrochemical experiments were performed in dried, degassed CH$_2$Cl$_2$ solutions using a disk-shaped platinum electrode sealed in a Teflon collar as the working electrode, a sodium saturated calomel electrode as the reference electrode, and a platinum wire as the auxiliary electrode (ferrocene couple = 560 mV). Solutions were approximately 10^{-3} M in metal complex and 0.1 M in tetra-*n*-hexylammonium perchlorate (Alfa) of supporting electrolyte.

Preparation of [PPN][Cp′(CO)$_2$Mn–C{O}Tol]. The salt [Li(OEt$_2$)$_x$][Cp′(CO)$_2$Mn–C{O}Tol] was prepared in Et$_2$O following the literature procedure[14] using Cp′Mn(CO)$_3$ (Strem, 2 mL, 12 mmol) and TolLi (24 mmol) that was prepared from lithium wire and *p*-bromotoluene in Et$_2$O. The solvent was removed, and the solid residue was dissolved in deoxygenated H$_2$O to give an orange solution. Addition of 1 equiv of solid [PPN]Cl (6.88 g, 12 mmol) gave immediate precipitation of yellow [PPN][Cp′(CO)$_2$Mn–C{O}Tol] which was isolated by filtering under N$_2$, washing with H$_2$O and Et$_2$O, and drying overnight under dynamic vacuum (65% yield, 6.66 g, 7.85 mmol). Anal. Calcd for C$_{52}$H$_{44}$MnNO$_3$P$_2$·CH$_2$Cl$_2$: C, 68.17; H, 5.07. Found: C, 68.75; H, 5.00. The spectroscopic data for this salt (IR (CH$_2$Cl$_2$) ν_{CO} = 1877 (s), 1800 (s) cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 7.60–6.90 (Tol), 4.24, 4.13 (C$_5$*H*$_4$CH$_3$), 2.19 (C$_5$H$_4$C*H*$_3$), 1.80 (TolC*H*$_3$)) compare well to literature values for the closely related compound [NMe$_4$][Cp(CO)$_2$Mn–C{O}Ph] (IR (Nujol) ν_{CO} = 1887 (s), 1792 (s) cm^{-1}; ^{1}H NMR (CH$_2$Cl$_2$) δ 7.12 (Ph), 4.32 (Cp)).[14]

Improved Synthesis of Cp′(CO)(NO)Mn–C{O}C{O}Tol (1).[3] The salt [PPN][Cp′(CO)$_2$Mn–C{O}Tol] (2.0131 g, 2.38 mmol), prepared as described above, was placed in a 250-mL Schlenk flask and dissolved in approximately 100 mL of CH$_2$Cl$_2$. The mixture was cooled to −78 °C, and 1 equiv of solid [NO][BF$_4$] (0.278 g) was added. IR monitoring of the reaction showed the disappearance of bands due to the acyl complex at 1878 (s) and 1797 (s) cm^{-1} and the appearance of bands of the intermediate **5** (1977 (s), 1913 (s) cm^{-1}) along with ~20% of **1** (2016 (s), 1759 (s), 1665 (w), 1615 (m), 1607 (m), 1590 (w) cm^{-1}). When no further change was detected by IR, approximately 1 equiv of solid [PPN]NO$_2$ (1.388 g) was added and the reaction mixture was allowed to warm to room temperature. IR analysis indicated the formation of **1** as the only organometallic product. Chromatography on an activated alumina (Alcoa F-20, 80–200 mesh) column with 50/50 CH$_2$Cl$_2$/hexane eluted first a trace of light orange Cp′Mn(CO)$_3$, followed by an orange band of **1**, and then a small purple band of an unidentified compound. Evaporation of solvent from the second band gave **1**[3] as an orange, microcrystalline solid in 55% yield (0.4468 g).

Reaction of Cp′(PPh$_3$)(NO)Mn–C{O}C{O}Tol (2) with HBF$_4$·Et$_2$O. To a cold −78 °C solution of complex **2** (0.25 g, 0.4 mmol) in CH$_2$Cl$_2$ (10 mL) was added HBF$_4$·Et$_2$O (80 μL, 0.6 mmol). At this point the IR spectrum showed the presence of **2**, the product [Cp′Mn(CO)(NO)(PPh$_3$)]$^+$ (**6**)[7] (ν_{CO} = 2036 cm^{-1}, ν_{NO} = 1795 cm^{-1}), and the intermediate species **7** (ν_{NO} = 1771 cm^{-1}). Warming to room temperature resulted in the complete conversion of **2** to **6** via **7**. Reduction of the solution volume to ca. 5 mL and addition of Et$_2$O (20 mL) gave **6** as a yellow-orange precipitate. This was washed with Et$_2$O (2 × 10 mL) and dried in vacuo to yield the BF$_4$$^-$ salt of the known anion **6**[7] as a microcrystalline solid in 75% yield (0.16, 0.3 mmol). [Anal. Calcd for C$_{25}$H$_{22}$BF$_4$MnNO$_2$P·$^1/_2$CH$_2$Cl$_2$: C, 52.48; H, 3.97. Found: C, 52.28; H, 4.76. IR (CH$_2$Cl$_2$): ν_{CO} = 2036 cm^{-1}, ν_{NO} = 1795 cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 7.88–7.24 (Ph), 5.41 (d, *J* = 18.6 Hz, C$_5$*H*$_4$CH$_3$), 5.04 (d, C$_5$*H*$_4$CH$_3$), 2.04 (C$_5$H$_4$C*H*$_3$), 1.50 (TolC*H*$_3$). ^{13}C NMR (acetone-*d*$_6$): δ 12.95 (C$_5$H$_4$*C*H$_3$), 92.9, 93.8, 95.0, 97.7, 114.9 (*C*$_5$H$_4$CH$_3$), 130.1, 130.5, 131.2, 132.6, 132.9, 135.8 (Ph's), 223.4 (*C*O). Literature values for the PF$_6$$^-$ salt of **6**:[7b] IR (acetone) ν_{CO} = 2039 cm^{-1}, ν_{NO} = 1794 cm^{-1}; ^{13}C NMR (CH$_2$Cl$_2$) δ 12.65 (C$_5$H$_4$*C*H$_3$), 92.74, 93.46, 95.80, 97.38, 114.64 (*C*$_5$H$_4$CH$_3$), 129.92, 130.68, 132.40, 132.83 (Ph's), 223.58 (*C*O).] Concentration of the mother liquors and washings followed by thin-layer chromatography of the oily residue on a silica TLC plate (Fischer 06-601A) with CH$_2$Cl$_2$/pentane (7/3) gave TolCHO (R_f = 0.45) as a clear colorless liquid (ν_{CO} = 1703 cm^{-1}) in 71% yield (0.034 g, 0.28 mmol). This product was readily converted by air oxidation into white crystalline 4-methylbenzoic acid which was characterized by IR (ν_{CO} = 1680 cm^{-1}) and mass spectral (*m/z* = 136 (M$^+$)) analysis.

Reaction of Cp′(PPh$_3$)(NO)Mn(^{13}C{O}C{O}Tol) with HBF$_4$·Et$_2$O. Complex **1** was prepared according to ref 3b from

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^{13}CO-enriched [Cp′(^{13}CO)$_2$Mn≡CTol]BCl$_4$ by oxidation with [PPN][NO$_2$]. Photosubstitution of PPh$_3$ for CO following the procedure given in ref 3b gave **2** exclusively enriched in ^{13}C at the α-carbon of the α-ketoacyl ligand. Protonation of this species with HBF$_4$·Et$_2$O was conducted as described above at −50 °C in CD$_2$Cl$_2$ and monitored by ^{13}C NMR. Immediately after addition of the acid the spectrum showed a resonance at δ 335.4 (d, J_{CP} = 23 Hz) assigned to **7** along with the CO resonance of [Cp′Mn(CO)(NO)(PPh$_3$)]$^+$ at δ 223.6 (d, J_{CP} = 24 Hz). Upon warmup to 22 °C, the δ 335.4 resonance decreased in intensity as the δ 223.6 resonance grew in.

Attempted Alkylation of Cp′(PPh$_3$)(NO)Mn–C{O}C{O}Tol (2) with CH$_3$OSO$_2$CF$_3$. To a cold −78 °C solution of **2** (54.3 mg, 0.0948 mmol) was added 1 equiv of CH$_3$OSO$_2$CF$_3$ (11 μL). The reaction was stirred at −78 °C for 3 h, but no change was detected in the IR spectrum. The solution was allowed to warm to room temperature, and over a 3-day period IR monitoring showed the replacement of the bands of **2** by those of **6**. Reduction of the solution volume to ~1 mL and addition of Et$_2$O (10 mL) gave **6** as a yellow orange precipitate. This was washed with Et$_2$O (3 × 5 mL) and dried in vacuo to give the known compound **6**[7] which was characterized as described above in 97% yield (50.1 mg, 0.0926 mmol).

Cleavage of the Carbon–Carbon Bond of Cp′(PPh$_3$)(NO)Mn–C{O}C{O}Tol (2) upon Oxidation. Complex **2** (58.5 mg, 0.102 mmol) was added as a solid to a −78 °C CH$_2$Cl$_2$ solution (20 mL) of AgBF$_4$ (28 mg, 0.144 mmol) in a 50-mL Schlenk flask. The solution was stirred and slowly warmed to room temperature. After 10 min, IR analysis showed only the presence of the known compound **6**[7] (ν_{CO} = 2036 (m), ν_{NO} = 1795 (s) cm^{-1}). The mixture was concentrated under vacuum, and Et$_2$O (10 mL) and water (10 mL) were added. The ether layer was removed, and the water layer was washed three times with Et$_2$O. The combined ether extracts were dried over MgSO$_4$ followed by removal of solvent by rotary evaporation. Chromatography of the yellow oil on a silica gel TLC plate (Fischer 06-601A) using 50/50 CH$_2$Cl$_2$/hexane as eluant gave one principal band ($R_f \approx 0.75$) and several minor bands in such low yield that they could not be confidently identified. The major band was removed from the plate and shown to be TolC{O}–C{O}Tol (**13**, 2.7 mg, 0.011 mmol, 22%) by the following spectral data: IR (CH$_2$Cl$_2$) ν_{CO} = 1669 (s), 1604 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.8 (d, 4 H, Tol), 7.3 (d, 4 H, Tol), 2.44 (s, 6 H, TolC*H*$_3$); MS (EI) *m/z* = 238 (M$^+$). In a separate experiment, 51.1 mg (0.089 mmol) of complex **2** was oxidized with AgBF$_4$ as described above. Addition of Et$_2$O to the concentrated reaction mixture precipitated the known compound **6** as an orange-yellow solid. This was recrystallized from CH$_2$Cl$_2$/ether to give **6**, characterized as described above, in 98.8% yield (50.3 mg).

Reaction of Cp′(CO)(NO)Mn–C{O}C{O}Tol (1) with NEt$_2$H. Excess NEt$_2$H (~0.4 mL) was added to a CH$_2$Cl$_2$ (35 mL) solution of complex **1** (48.0 mg, 0.142 mmol) in a 50-mL Schlenk flask. The reaction mixture was irradiated under N$_2$ in a closed Schlenk flask using the above-described lamp until IR analysis indicated loss of all the ν_{CO} bands of **1** (40 min). The solution was filtered in air through a plug of Celite, and the solvent was removed by rotary evaporation to yield a brown residue. This was dissolved in THF and filtered through a plug of silica gel. Evaporation of solvent from the filtrate left the α-ketoamide Et$_2$NC{O}–C{O}Tol (**14**) as a yellow/brown oil (51.8%, 16.1 mg, 0.074 mmol).

14: IR (CH$_2$Cl$_2$) ν_{CO} = 1677 (s), 1639 (s), 1607 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.85 (2 H, Tol), 7.23 (2 H, Tol), 3.64 (q, 2 H, Et-C*H*$_2$), 3.20 (q, 2 H Et-C*H*$_2$), 2.38 (s, 3 H, Tol-C*H*$_3$), 1.22 (t, 3 H, Et-C*H*$_3$), 1.18 (t, 3 H, Et-C*H*$_3$); MS EI) *m/z* = 219.1243 (M$^+$), calcd 219.1259.

General Method for the Reaction of Cp′(CO)(NO)Mn–C{O}C{O}Tol (1) with Alkynes. Approximately 50 mg of **1** was placed in a 50-mL Schlenk flask to which was added ~30 mL of CH$_2$Cl$_2$. A 6–9-fold excess of alkyne was added, and the solution was irradiated under N$_2$ in a closed Schlenk flask using the above-described lamp for 15–35 min until IR analysis showed the complete disappearance of complex **1**. The reaction mixture was concentrated in vacuo, and the residue was dissolved in 10 mL of CH$_3$CN. Approximately 250 μL of 3.7% aqueous HCl was added via syringe, and the mixture was left to stir overnight, during which time a brown to greenish brown color change occurred. The mixture was concentrated in vacuo, diluted with Et$_2$O, and extracted with water. The water layer was washed three times with Et$_2$O, and the combined Et$_2$O extracts were dried over MgSO$_4$. After solvent removal by rotary evaporation, the residue was subjected to TLC on silica plates (Fischer 06-601A) with 50/50 CH$_2$Cl$_2$/hexane as eluant. The vinyl α-dione products **18** and **19** appeared at an R_f of ~0.5. The specific yields and spectroscopic data are given below.

18, (*E*)-(CH$_3$)CH=C(CH$_3$)C{O}C{O}Tol: 43.5% yield; IR CH$_2$Cl$_2$) 1672 (sh), 1662 (s), 1638 (m), 1605 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.75 (d, 2 H, Tol), 7.28 (d, 2 H, Tol), 6.64 (qd, 1 H, =C*H*, J_{HH} = 6.8 Hz, 1.1 Hz), 2.43 (s, 3 H, TolC*H*$_3$), 1.93 (d, 3 H, Me, J_{HH} = 1.1 Hz), 1.92 (d, 3 H, Me, J_{HH} = 6.8 Hz); MS (EI) *m/z* = 202.0988 (M$^+$), calcd 202.0994.

19, (*E*)-(Bu^t)CH=CHC{O}C{O}Tol: 34% yield; IR (CH$_2$Cl$_2$) 1669 (s), 1659 (sh), 1630 (s), 1571 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.85 (d, 2 H, Tol), 7.30 (d, 2 H, Tol), 6.96 (d, 1 H, =C*H*, J_{HH} = 16.4 Hz), 6.38 (d, 1 H, =C*H*), 2.43 (s, 3 H, TolC*H*$_3$), 1.11 (s, 9 H, Bu^t); MS (EI) *m/z* = 230.1319, calcd 230.1307.

Preparation of the Metallafuran 17. Complex **1** (46.6 mg, 0.137 mmol) was irradiated in the presence of excess 2-butyne as described above for 25 min. The solution was then chromatographed on activated alumina (Alcoa F-20, 80–200 mesh) using acetone as eluent. A single orange-yellow band eluted from which **17** was obtained by solvent evaporation as a microcrystalline solid containing $^1/_2$ equiv of hexane (11.0 mg, 0.030 mmol, 22%).

Anal. Calcd for C$_{19}$H$_{20}$MnNO$_3$·$^1/_2$C$_6$H$_{14}$ (**17**): C, 64.69; H, 6.68. Found: C, 64.36; H, 5.47. **17**: IR (CH$_2$Cl$_2$) ν_{NO} = 1700 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.71 (d, 2 H, Tol), 7.32 (d, 2 H, Tol), 5.02 (s, 1 H, Cp′), 4.68 (s, 1 H, Cp′), 4.60 (s, 2 H, Cp′), 2.52 (s, 3 H, α-CH$_3$), 2.42 (s, 3 H, TolCH$_3$), 1.89 (s, 3 H, CpCH$_3$), 1.54 (s, 3 H, β-CH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 273.9 (α-*C*), 206.2, 193.4 (γ-*C*, –*C*{O}Tol), 146.4 (Tol), 140.6 (β-*C*), 129.9, 129.8 (Tol), 114.9, 94.5, 92.5, 90.0, 87.6 (Cp′), 32.5 (α-*C*H$_3$), 21.9 (Tol*C*H$_3$), 12.8 (Cp′*C*H$_3$), 11.5 (β-*C*H$_3$).

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Registry No. **1**, 106865-75-2; **2**, 116184-68-0; **2**(α-^{13}CO), 121393-62-2; **5**, 111583-12-1; **6**(BF$_4$), 121393-59-7; **6**(CF$_3$SO$_3$), 121393-63-3; **7**(BF$_4$), 121393-61-1; **8**, 104-87-0; **13**, 3457-48-5; **14**, 80120-40-7; **17**, 121393-64-4; **18**, 121393-56-4; **19**, 121393-57-5; [PPN][Cp′(CO)$_2$MnC{O}Tol], 111583-10-9; Li[Cp′(CO)$_2$MnC{O}Tol], 121393-58-6; [NO][BF$_4$], 14635-75-7; HBF$_4$·Et$_2$O, 67969-82-8; CH$_3$OSO$_2$CF$_3$, 333-27-7; AgBF$_4$, 14104-20-2; NEt$_2$H, 109-89-7; MeC≡CMe, 503-17-3; Bu^{t}C≡CH, 917-92-0; 4-methylbenzoic acid, 99-94-5.