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A New Metal–Metal Bond-Forming Reaction: Synthesis, Structure, and Mechanism of Formation of $(\eta\text{-}C_5H_5)(CO)Fe(\mu\text{-}C(O)\text{-}p\text{-tolyl})(\mu\text{-}CO)Mo(NO)(\eta\text{-}C_5H_5)$, a Rare π-Bound μ-Acyl Compound

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We are presently developing synthetic methods for the stepwise incorporation of simple σ-bound organic functional groups into heteronuclear transition-metal clusters.[2] The use of two or more different metal atoms in a cluster[3] can provide mechanistic markers in studying the basic reactivity of any bound organic fragments. We report here (1) the novel synthesis, from two readily available mononuclear starting materials, of isomeric cis and trans iron–molybdenum complexes possessing a bridging toluoyl ligand, (2) the X-ray crystal structures of these acyl complexes, revealing a rare π-bonding mode, and (3) mechanistic details of the reaction that are revealed due to the use of the different metal atoms.

Addition of p-tolyllithium to $CpMo(CO)_2(NO)$ (**1**) (Cp = η-C_5H_5) gave the anionic "acyl" $Cp(CO)(NO)Mo{=}C(OLi)(Tol)$ (Tol = p-tolyl) (**2**) in 45–60% yield as an ether solvate.[4] The carbene resonance structure (Scheme I) was suggested by the low-field position (311.2 ppm) of the "acyl" carbon.[5] Reaction of **2** and $Cp(CO)_2Fe(THF)^+BF_4^-$ (**3**) in a 20:1 ether/CH_2Cl_2 solution at −78 °C followed by warming to room temperature gave rise to the new heterodinuclear acyls **4c** and **4t** in 40% combined isolated yield in a 1:1.15 ratio;[4] byproducts $CpMo(CO)_2(NO)$ (**1**) (4%), $Cp(CO)_2FeTol$ (**5**) (2%),[4] and $[CpFe(CO)_2]_2$ (**6**) (17%) were also isolated (Scheme I). Following chromatographic separation of **4c** and **4t** using 9:1:1 ether/hexanes/benzene on silica, ^{13}C NMR data,[4] including two peaks between 278.8 and 284.0 ppm consistent with both a μ-acyl carbonyl[6] and a μ-CO, indicated that both isomers were the desired μ-acyl compounds.

Single-crystal X-ray diffraction studies[4] on **4c** and **4t** not only confirmed that they were μ-acyls (Figure 1, **4c** shown) but also revealed that *the acyl ligand had migrated from molybdenum to iron.* No less surprising was the observation of a rare *π-bond*[7] between the acyl carbonyl and the molybdenum center. Most X-ray studies on μ-acyl compounds[6c–e,7g,8] reveal the presence of an essentially planar M—O═C(R)—M′ moiety with a 180° M—O—C—R dihedral angle, indicating a M—O *σ-bond* involving the oxygen sp^2 lone pair and a nonbonding M—C distance that is typically very close to the M—M′ distance.[9] In **4c** and **4t**, Mo–O–C–C(tolyl) dihedral angles of 128.1° and 135.7° are observed, and *bonding* Mo–C(1) distances of 2.39 and 2.46 Å, much shorter than the 2.72 and 2.73 Å Mo–Fe bond lengths, are seen.

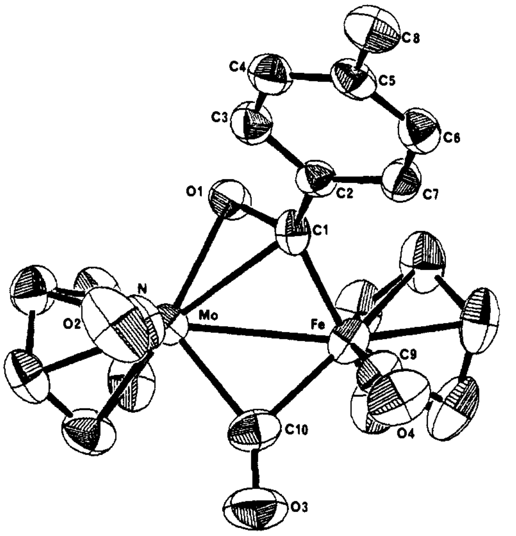
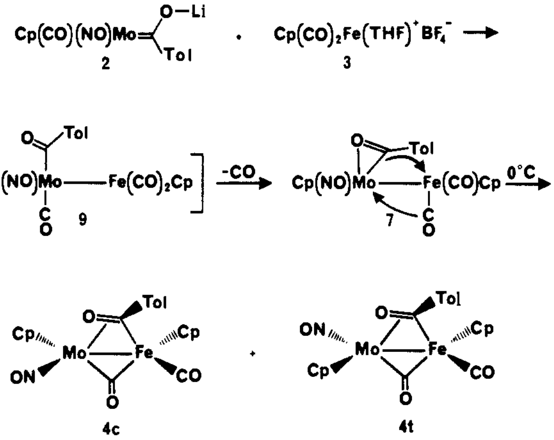


Figure 1. ORTEP drawing of **4c**. Selected bond distances (Å) and angles (deg): Mo–Fe, 2.717 (1); Mo–O(1), 2.115 (3); Mo–C(1), 2.394 (5); Mo–C(10), 2.065 (6); Fe–C(1), 1.923 (5); Fe–C(10), 1.972 (6); C(1)–O(1), 1.289 (6); Mo–O(1)–C(1), 85.72 (28); Mo–C(1)–Fe, 77.16 (18); Fe–C(1)–O(1), 118.90 (36); Fe–C(1)–C(2), 126.22 (35); C(2)–C(1)–O(1), 114.82 (45).

Scheme I



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[4] Data for new compounds and details of the X-ray diffraction studies are available in the supplementary material.

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[9] See for instance 8g, 8j, and 6c, where M–M′ is 2.65, 2.88, and 2.93 Å and M–C is 2.61, 2.79, and 2.81 Å, respectively.

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Mechanistic information about the formation of **4c** and **4t** was obtained by mixing **2** and **3** at −35 °C in CD_2Cl_2: a single new product (**7**) was obtained, along with the byproducts **1**, **5**, and **6**.[10] Warming **7** to 0 °C resulted in slow conversion to **4c** and **4t**. A structure for **7** consistent with the spectroscopic data[4] is shown in Scheme I. The lack of any splitting of the *Cp*Mo and *Cp*Fe signals in the ^1H and ^{13}C NMR spectra down to −70 °C is consistent with the presence of an unbridged Mo–Fe bond, particularly since the isomers **4c** and **4t** exhibit substantial cyclopentadienyl chemical shift differences (0.50 and 0.10 ppm in the ^1H NMR and both 1.8 ppm in the ^{13}C NMR for *Cp*Mo and *Cp*Fe, respectively). The acyl resonance at 265.0 ppm is consistent with both η^1-coordination[5b] and η^2-coordination,[11] but the latter is more likely based on the effective atomic number rule and the absence of other coordinating ligands.[12] Finally, the ^{13}C peaks at 220.3 and 218.2 ppm are consistent with the presence of diastereotopic carbonyl ligands on iron.[5] In order to confirm this point we combined $Cp(^{13}CO)_2Fe(THF)^+BF_4^-$ (**3**-$^{13}C_2$)[13] with **2** to give **7** *in which the only labeled carbons were the diastereotopic carbonyl ligands*. However, an unexpected *singlet* was observed at the center of each doublet, the intensity of which indicated the presence of a 0.75:1 ratio of **7**-$(^{13}CO)(^{12}CO)$/**7**-$(^{13}CO)_2$. The ^{13}C–^{13}C coupling constant in **7**-$(^{13}CO)_2$ was 11.4 Hz; evidence that this is indeed a *geminal* coupling constant is its similarity to the value of 10.2 Hz observed in $Cp(^{13}CO)_2Fe(Ph(CH_3)NH)^+BF_4^-$ (**8**-$^{13}C_2$), prepared by reaction of $Ph(CH_3)NH$ with **3**-$^{13}C_2$.[4]

A mechanism for the formation of **4c** and **4t** consistent with the above data is presented in Scheme I. Initial reaction of **2** and **3** could occur to directly give the dinuclear intermediate **9**. The ^{13}CO-labeling experiment requires rapid exchange of CO between the metal centers in order to account for the partial[14] loss of ^{13}CO label in **7**, and we propose that such a process occurs in **9**.[15] Formation of **7** from **9** is proposed to occur by dissociation of CO *from molybdenum*, since the 16-electron center that would remain should be particularly stable both due to the possibility of η^2-coordination of the acyl and by analogy to the stable 16-electron compounds $Cp(NO)MoR_2$ (R = CH_2SiMe_3, SPh).[16] Finally, conversion of **7** to **4c** and **4t** can readily occur by acyl carbon migration to iron with concomitant formation of the μ-CO interaction.

In conclusion, the synthesis of **4c** and **4t** represents a novel and potentially general synthesis of heterodinuclear μ-acyls. The acyl migration may be related to those previously observed during syntheses of other μ-acyls,[7h,8b,c,e,i,m,17] but in only one other case has a metal–metal-bonded[18] intermediate—actually a stable isomer—been isolated.[6b] Based on that example, Kaesz suggested that reversible acyl flipping might be analogous to that of fluctional μ-σ,π-vinyl complexes.[19] Based on the observed conversion of **7** to **4c** and **4t**, however, it is tempting to suggest that acyl migrations may also involve *stepwise* interconversion of bridging and *nonbridging* η^2-acyls. Further work on the synthetic and mechanistic chemistry of the acyls described herein is in progress.

Acknowledgment. We thank Perry Geue for working out the synthesis and isolation of **2**. The 500-MHz NMR spectrometer used in this work was purchased through funds provided in part by the National Science Foundation. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, the UCLA Committee on Research, and the Universitywide Energy Research Group is gratefully acknowledged.

Supplementary Material Available: Spectroscopic data for **2**, **4c**, **4t**, **5**, **7**, **8**, and **10** and tables of crystallographic data for **4c** and **4t** and details of the solution (23 pages); tables of observed and calculated structure factors for **4c** and **4t** (26 pages). Ordering information is given on any current masthead page.

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[10] Intermediate **7** can be isolated in 35–45% yield by carrying out the reaction at −78 °C and collecting the resultant orange precipitate.

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[14] Complete scrambling prior to CO loss would give a 2:1 ratio of **7**-$(^{13}CO)(^{12}CO)$/**7**-$(^{13}CO)_2$, so the scrambling is less than 40% complete.

[15] We observe fast exchange (on the NMR time scale) of CO in the model compounds $Cp(CO)_2Fe$–$M(CO)_3Cp$ (M = Mo, W) down to −90 °C.

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Length of the Ethane Bond in Hexaphenylethane and Its Derivatives

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The length of the central carbon–carbon bond (r_c) in hexaphenylethane and its derivatives has been the subject of some dispute. It was originally predicted, by the use of empirical force field calculations, that r_c in hexaphenylethane is 1.64 Å.[1] This prediction was challenged by an announcement of the X-ray structure of hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane (**1a**), in which it was claimed that far from being lengthened relative to the standard value of 1.54 Å, r_c is appreciably *shortened*, to 1.47 (2) Å.[2] A subsequent and more elaborate computational study[3] not only confirmed the original conclusions[1] in all essential details but predicted r_c = 1.64 Å (MM2) for **1a** as well,[4] thus discounting the possibility that the substituents on the benzene

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