A New Metal-Metal Bond-Forming Reaction: Synthesis, Structure, and Mechanism of Formation of $(\eta$ -C₅H₅)(CO)Fe(μ -C(O)-*p*-tolyl)(μ -CO)Mo(NO)- $(\eta$ -C₅H₅), 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 cluster³ 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 ironmolybdenum 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 -C₅H₅) 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" earbon.⁵ Reaction of 2 and $Cp(CO)_2Fe(THF)^+BF_4^-$ (3) in a 20:1 ether/CH₂Cl₂ 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, ¹³C NMR data,⁴ including two peaks between 278.8 and 284.0 ppm consistent with both a μ -acyl carbonyl⁶ and a μ -CO, indicated that both isomers were the desired μ -acyl compounds.

Single-crystal X-ray diffraction studies⁴ 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 -bond⁷ between the acyl carbonyl and the molybdenum center. Most X-ray studies on μ -acyl compounds^{6c-e,7g,8} reveal the presence of

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

(5) The carbene carbon of Cp(CO)(NO)Mo=C(OCH₃)Tol is seen at 324.9 ppm,^{5a} while molybdenum acetyl carbonyls are seen near 265 ppm;^{5b}
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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



an essentially planar M - O = C(R) - M' moiety with a 180° M - O - C - R dihedral angle, indicating a $M - O \sigma$ -bond involving the oxygen sp² 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.

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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 CD₂Cl₂: 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 data⁴ is shown in Scheme I. The lack of any splitting of the CpMo and CpFesignals in the ¹H and ¹³C 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 ¹³C NMR for CpMo and CpFe, 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 ¹³C 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-(¹³CO)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(CH₃)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 ¹³CO-labeling experiment requires rapid exchange of CO between the metal centers in order to account for the partial¹⁴ loss of ¹³CO 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)MoR₂ (R = CH₂SiMe₃, 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-bonded¹⁸ 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

model compounds $Cp(CO)_2Fe-M(CO)_3Cp$ (M = Mo, W) down to -90 °C.

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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.

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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.

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 study³ not only confirmed the original conclusions¹ 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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