Communications

The Unexpected Formation of an $Fe_2(CO)_6$ Complex Containing a μ_2-Bridging Carbyne Ligand: Structure and Reactivity

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Summary: The reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with $Hg(C{\equiv}CCH_2OCH_3)_2$ gave a bridging carbyne complex, $(\mu\text{-}CH_3OCH{=}CHC)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$. Acid hydrolysis of this product produced $(\mu\text{-}CH{=}CHCH{=}O)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$, while reactions with activated acetylenes gave insertion products. The structures of the carbyne complex and of one of the insertion products have been determined by X-ray diffraction.

Previous work at M.I.T. has shown that reactions of dialkynylmercury compounds with the triethylammonium salts of the $[(\mu\text{-}CO)(\mu\text{-}SR)Fe_2(CO)_6]^-$ anions gave as the sole new organometallic products the alkynyl-bridged species $(\mu\text{-}\sigma,\pi\text{-}R'C{\equiv}C)(\mu\text{-}SR)Fe_2(CO)_6$.[1,2] We were therefore surprised when the analogous reaction of a functional dialkynylmercurial, $Hg(C{\equiv}CCH_2OCH_3)_2$, gave a completely different type of product. In one such experiment, 3.11 mmol of $Hg(C{\equiv}CCH_2OCH_3)_2$[3] was added (under nitrogen) to a solution of 2.98 mmol of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$[4] in 30 mL of THF. An immediate reaction occurred, causing gas evolution and a color change from brown-red to deep red. After 30 min of stirring at room temperature, solvent evaporation in vacuo and filtration chromatography (silicic acid, 9/1 by volume pentane/CH_2Cl_2) gave 0.35 g of an air-stable, orange-red solid (27%), mp 85–87 °C (recrystallized from pentane).[5] This was not the expected product, $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CCH_2OCH_3)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$,[6] rather, on the basis of its spectroscopic properties and, ultimately, its structure determination by X-ray diffraction, it was identified as $(\mu\text{-}trans\text{-}CH_3OCH{=}CHC)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (1), i.e. an $Fe_2(CO)_6$ complex with a bridging carbyne ligand. The presence of the latter was indicated by a signal far downfield in the ^{13}C NMR spectrum at 360.47 ppm, in agreement with δ_C of the bridging carbyne ligand of other bridging carbyne complexes reported earlier by other workers.[7] The proton and ^{13}C NMR spectra of 1 clearly

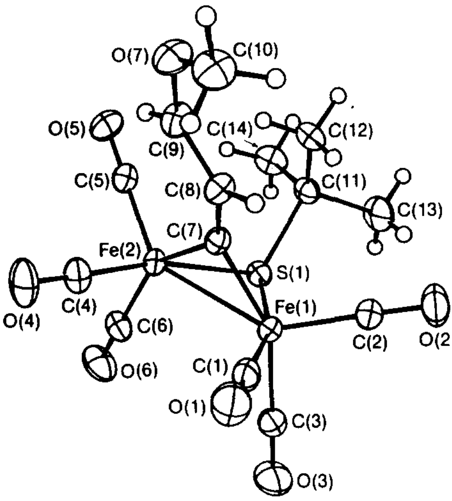
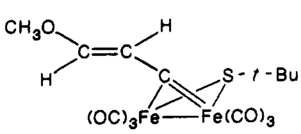
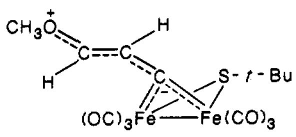


Figure 1. ORTEP diagram of $(\mu\text{-}CH_3OCH{=}CHC)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$, molecule 1, showing the atom-labeling scheme. Pertinent bond lengths (Å) for the two independent molecules are as follows: Fe(1)–Fe(2) = 2.5214 (6), 2.5035 (7); Fe(1)–S(1) = 2.265 (1), 2.257 (1); Fe(2)–S(1) = 2.263 (1), 2.261 (1); Fe(1)–C(7) = 1.860 (3), 1.843 (3); Fe(2)–C(7) = 1.881 (3), 1.879 (3); C(7)–C(8) = 1.416 (5), 1.468 (6); C(8)–C(9) = 1.317 (5), 1.241 (7); C(9)–O(7) = 1.335 (5), 1.406 (6); O(7)–C(10) = 1.411 (5), 1.394 (7). Pertinent bond angles (deg) are as follows: Fe(1)–C(7)–Fe(2) = 84.7 (1), 84.5 (2); Fe(1)–C(7)–C(8) = 134.5 (2), 130.0 (3); Fe(2)–C(7)–C(8) = 139.5 (2), 143.9 (3); C(7)–C(8)–C(9) = 122.7 (3), 117.3 (5); C(8)–C(9)–O(7) = 129.3 (3), 124.4 (6).



1a



1b

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(1) Seyferth, D.; Archer, C. M. *Organometallics* **1986**, *5*, 2572.

(2) Archer, C. M. Ph.D. Thesis, Massachusetts Institute of Technology, 1986.

(3) Prepared by the procedure in *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Academic Press: New York, 1981; Vol. 2, p 114. Mp: 106–107 °C, ^{13}C NMR ($CDCl_3$): δ_C 57.58 (q, J = 141.7 Hz, OCH_3), 60.16 (t, J = 146.8 Hz, CH_2OCH_3), 102.78 (s, $C{\equiv}CCH_2$), 116.98 (s, $HC{\equiv}C$). Anal. Calcd for $C_8H_{10}O_2Hg$: C, 28.36; H, 2.98. Found: C, 28.37; H, 3.23.

(4) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

(5) (a) Another major product, a deep red-black solid which contains mercury, also was formed but has not been isolated in good purity so that it has not yet been identified. (b) Characterizing data for 1: ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H, $SC(CH_3)_3$), 4.00 (s, 3 H, OCH_3), 7.74 and 8.08 (AB quartet, J = 11.52 Hz, 2 H, CH=CH); ^{13}C NMR ($CDCl_3$) δ_C 32.92 (q, J = 127.4 Hz, $SC(CH_3)_3$), 49.57 (s, $SC(CH_3)_3$), 59.91 (q, J = 148.5 Hz, OCH_3), 132.72 (d, J = 159.5 Hz, $CC(H){=}C(H)OCH_3$), 165.85 (d, J = 181.5 Hz, $CC(H){=}C(H)OCH_3$), 209.92 and 211.12 (both s, FeCO), 360.47 (s, carbyne C). Calcd for $C_{14}H_{14}O_7SFe_2$: C, 38.39; H, 3.22. Found: C, 38.65; H, 3.30. The 70-eV EI mass spectrum showed M^+ and $[M - nCO]^+$ (n = 1–6).

(6) This complex, a red oil, could be prepared in 62% yield by the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with $BrC{\equiv}CCH_2OCH_3$. The ^1H NMR spectrum indicated the presence of two isomers. Compound 1 also was produced in this reaction in 22% yield.

(7) A selection: (a) Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 51 (μ_2-$COCH_3$, neutral δ_C 361.3; μ_3-$COCH_3$, δ_C 342.6). (b) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621 (μ_3-$COCH_3$, anionic, δ_C 357.0, 362.9). (c) Keister, J. B. *J. Chem. Soc., Chem. Commun.* **1979**, 214 (μ_2-$COCH_3$, neutral, δ_C 360). (d) Reference 1, μ_2-$COCH_3$, neutral, δ_C 383.3. (e) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620 (μ_2-CR, cationic, δ_C 448.27, 443.65, 432.7). (f) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134 (μ_2-CH, cationic, δ_C 490.2). (g) Ros, J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1087 (μ_2-COEt,s δ_C 383.8).

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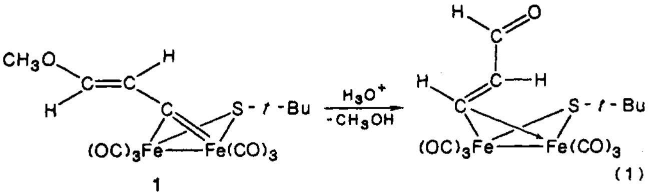
demonstrated the presence of the methoxy-substituted vinyl group,[5] but the spin–spin coupling constant of the vinyl AB quartet of 11.5 Hz did not allow us to distinguish between a cis and trans configuration. A single-crystal X-ray diffraction study of 1 was carried out.[8] The complex crystallized in the space group $P\bar{1}$ (No. 2) with two independent molecules per asymmetric unit. Figure 1 shows an ORTEP plot for one of these molecules. Noteworthy in this structure is the presence of an Fe–Fe single bond (average Fe(1)–Fe(2) = 2.513 Å) and a symmetrical thiolate bridge, with the *tert*-butyl group of this ligand occupying an axial position.

The slightly asymmetric carbyne bridge (average Fe(1)–C(7) = 1.825 Å; average Fe(2)–C(7) = 1.880 Å) may suggest that the bonding in 1 can be described in localized valence bond terms, as diagrammed in **1a**. However, it appears more likely that this bonding is better described as being delocalized over the entire metal ligand framework with a dipolar vinylidene structure (**1b**) contributing to the ground state. Such a view is consistent with the observed shortening of the C(7)–C(8) (average 1.44 Å) and C(8)–O(7) (average 1.37 Å) bond lengths from the values expected from a localized bonding model and with the bonding descriptions for a series of related cationic μ_2-carbyne complexes reported by Casey et al.[9] The observed asymmetry would then appear to result from nonbonded interactions between Fe(2) and the vinyl moiety, which is bent toward this metal. It is noteworthy that the two independent molecules of 1 display significantly different parameters for the bridging hydrocarbyl moiety. These differences appear to be real since parameters involving the rest of the two molecules are in excellent agreement. It may be that one molecule is closer to the carbyne form and the other to the vinylidene form, with the packing forces favoring each in the respective environments.

The reactivity of these neutral carbyne complexes should provide an interesting comparison with the chemistry of cationic carbyne complexes of type 2, as developed by Casey and his co-workers, and, in fact, we observe interesting reactivity both at the vinyl ether function and at the carbyne carbon. As expected, the former group can be hydrolyzed under acidic conditions to yield a metallo-olefin moiety having an aldehyde function trans to the σ-bound iron center, as shown in eq 1.[10] An experiment in which DCl/D_2O was used to hydrolyze 1 established that the entering proton became bonded exclusively to the α-carbon atom. However, more noteworthy is the reactivity of our carbyne complex with acetylenes. Casey had demonstrated[11g] that the cationic carbynes 2 inserted acetylenes to yield products of type 3. Similarly we find that activated acetylenes ($CH_3O_2CC{\equiv}CCO_2CH_3$, HC≡C-



(1)

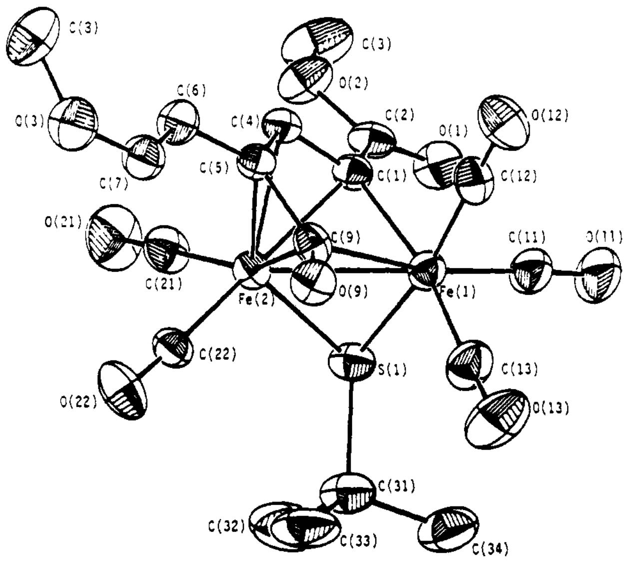
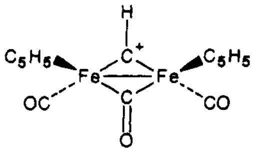


Figure 2. ORTEP diagram of [μ-C(O)C(CH=CHOCH$_3$)C(H)C(CO$_2$CH$_3$)](μ-*t*-BuS)Fe$_2$(CO)$_5$ (**4b**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) are as follows: Fe(1)–Fe(2) = 2.498 (2), Fe(1)–S(1) = 2.291 (2), Fe(2)–S(1) = 2.189 (2), Fe(1)–C(1) = 1.983 (6), C(1)–C(4) = 1.405 (7), C(4)–C(5) = 1.407 (7), C(5)–C(6) = 1.458 (8), C(6)–C(7) = 1.302 (9), C(5)–C(9) = 1.463 (8), C(9)–Fe(1) = 2.180 (6), Fe(2)–C(1) = 2.028 (5), Fe(2)–C(4) = 2.109 (5), Fe(2)–C(5) = 2.164 (5), Fe(2)–C(9) = 2.138 (6), C(9)–O(9) = 1.221 (6), FeC–O(mean) = 1.135, Fe–CO(Mean) = 1.801. Pertinent bond angles (deg) are as follows: Fe(1)–C(1)–C(4) = 116.8 (4), C(1)–C(4)–C(5) = 118.1 (5), C(4)–C(5)–C(9) = 113.7 (5), C(5)–C(9)–Fe(1) = 110.6 (4).



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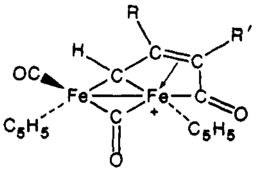

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(8) Crystal data for 1: a = 15.064 (3) Å, b = 15.154 (4) Å, c = 8.479 (1) Å, α = 100.11 (2)°, β = 99.30 (1)°, γ = 83.62 (2)°, V = 1873.7 Å^3, space group $P\bar{1}$ (No. 2), Z = 4, μ = 16.831 cm^{-1}. Data in the range $1.0 \le 2\theta \le 53°$ were collected at 22 °C using Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. The structure was solved by Patterson and difference Fourier syntheses and refined by full-matrix least-squares techniques. All hydrogen atoms were located but were not refined; they were input to the least-squares program as fixed contributions in their idealized positions (d_{C-H} = 0.95 Å). All other atoms were refined anisotropically. Absorption corrections were applied by using the method of N. Walker and D. Stuart (*Acta Crystallogr.* **1983**, *A39*, 1581). Final R = 0.038 and R_w = 0.053 for 5338 observed reflections (h, $\pm k$, $\pm l$) [$F_0^2 \ge 3\sigma(F_0^2)$] and 433 variables. The largest peak on the final difference Fourier map was 0.74 e/Å^3. Cell reductions failed to locate a higher symmetry cell, and a consideration of the largest correlation coefficients in the least-squares refinement indicated that no significant correlations were present between the two independent molecules, arguing that the molecules are indeed independent and that there is no hidden higher symmetry cell.

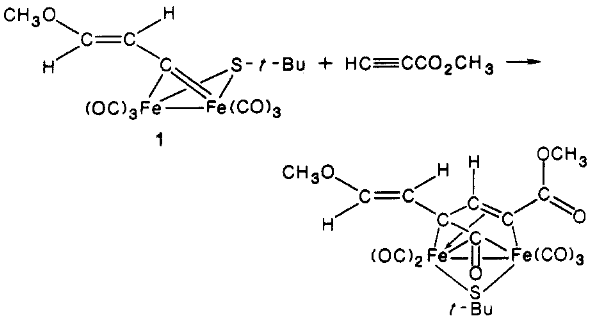
(9) Casey, C. P.; Konings, M. S.; Marder, S. R. *Polyhedron* **1988**, *7*, 881.

(10) (a) Hydrolysis with aqueous HCl in THF at room temperature; product (97% yield) (μ,η^1,η^2-CH=CHCH=O)(μ-*t*-BuS)Fe$_2$(CO)$_6$: mp 96–98 °C; IR (CCl$_4$) ν(C=O) 1692 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.39 (s, 9 H, SC(CH$_3$)$_3$), 3.80 (dd, J = 5.37 Hz, J = 12.21 Hz, 1 H, C(*H*)=C(*H*)C(O)H), 8.84 (d, J = 12.21 Hz, 1 H, C(*H*)=C(H)C(O)H), 9.10 (d, J = 5.38 Hz, 1 H, C(H)=C(H)C(O)*H*); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ 32.98 (q, J = 127.8 Hz, SC(CH$_3$)$_3$), 48.74 (s, SC(CH$_3$)$_3$), 84.71 (dd, J = 163.2 Hz, J = 26.8 Hz, C(H)*C*(H)C(O)H, 163.03 (d, J = 152.5 Hz, *C*(H)=C(H)C(O)H), 193.95 (d, J = 171.8 Hz, C(H)=C(H)*C*(O)H), 207.49 and 208.20 (both s, FeCO); mass spectrum (EI, 70 eV) shows (M$^+$ – nCO) (n = 1–6). (b) A similar complex, (μ,η^1,η^2-PhC=CHCH=O)(μ-EtS)Fe$_2$(CO)$_6$ [ν(C=O) 1682 cm^{-1}], was prepared by the reaction of [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] with PhC≡CCHO.

(11) (a) Casey, C. P.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1986**, *5*, 196. (b) Casey, C. P.; Meszaros, M. W.; Colborn, R. E.; Roddick, D. M.; Miles, W. H.; Gohdes, M. A. *Organometallics* **1986**, *5*, 1879. (c) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Bly, R. K.; Fagan, P. J. *Organometallics* **1986**, *5*, 1873. (d) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053. (e) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043. (f) Casey, C. P.; Woo, L. K. *J. Organomet. Chem.* **1986**, *328*, 161. (g) Casey, C. P.; Woo, K. L.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447. (h) Casey, C. P.; Konings, M. S.; Marder, S. G. *J. Organomet. Chem.* **1988**, *345*, 125.

CO_2CH_3, $HC\equiv CC(O)CH_3$, $CH_3C\equiv CCO_2CH_3$) react with **1** to give brown-black solids, **4**, in yields of 32–76%, depending on the electron-withdrawing ability of the two acetylene substituents.[12] The mass spectra of the products showed peaks due to molecular ions having m/e ratios equivalent to the sum of the mole masses of the two reactants, speaking for an insertion process. Assignment of structure on the basis of IR and ^1H and ^{13}C NMR spectra was not obvious. Noteworthy in the ^{13}C NMR spectra was the loss of the carbyne carbon resonance on going from **1** to the insertion products, the appearance of three new C resonances in the vinyl region, and a singlet at approximately δ_C 235 and the presence of five distinct singlet C signals in the terminal CO region. Also, the IR spectra of the products showed strong bands at about 1630 cm^{-1} which could not be assigned to the carbonyl stretches of the ketone and ester substituents of the originally acetylenic carbon atoms.

In order to determine unambiguously the identity of these insertion products, an X-ray diffraction study[13] was performed on the crystalline product obtained in the reaction of **1** with methyl propiolate, $HC\equiv CCO_2CH_3$. The resulting molecular structure is shown in Figure 2, and the transformation of **1** to **4b** is diagrammed in eq 2. The observed structure contains an Fe–Fe single bond (Fe(1)–Fe(2) = 2.498 (2) Å) with three terminal CO ligands on Fe(1) and two on Fe(2). The thiolate ligand bridges the Fe_2 unit unsymmetrically (Fe(1)–S(1) = 2.291 (2) Å; Fe(2)–S(1) = 2.189 (2) Å). The organic ligand framework consists of a five-membered metallacycle that is comprised of the original carbyne carbon atom [C(5)], the two acetylenic carbon atoms [C(1), C(4)], an inserted carbonyl carbon atom [C(9)], and one Fe atom [Fe(1)]. The ring containing these five atoms is slightly puckered, with the mean deviation from planarity equal to 0.06 Å. The atoms C(1), C(4), and C(5) form an asymmetric σ,π-allyl unit. The bond lengths C(1)–C(4) = 1.405 (7) Å and C(4)–C(5) = 1.407 (7) Å are identical and lie between the values reported for C–C single and double bonds.[14] In addition, the C(1)–C(4)–C(5) angle of 118.1 (5)° very nearly equals the ideal value of 120.0°. Finally, the metallacycle also contains a carbonyl group which presumably was derived from a terminal CO ligand on Fe(2) but which now bridges both iron atoms and the former carbyne carbon atom. The C(9)–O(9) bond distance of this carbonyl group (1.221 (6) Å) is typical for that involving organic ketones[14] and is significantly longer than a terminal FeC–O bond (mean = 1.135 Å). This inserted CO explains the ambiguities in the ^{13}C NMR and IR spectra. The singlets observed at approximately δ_C 235 correspond to this carbonyl C atom and the strong bands in the IR spectra at about 1630 cm^{-1} can be assigned to the ν(C=O) stretch of this carbonyl.



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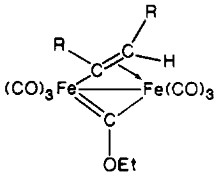
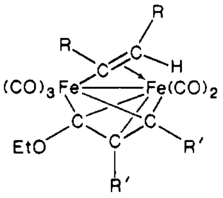
(2)

It is of interest that Mathieu and his co-workers have reported that complexes **5** react with dimethyl acetylenedicarboxylate and hexafluorobutyne to give insertion products of type **6**.[7g] It will be noted that the structure of the newly formed organic ligand is different from that of ours, so it may be that in (μ_2-carbyne)$Fe_2(CO)_6$ complexes of type (μ-ZC)(μ-ligand)$Fe_2(CO)_6$ the nature of the substituent on the carbyne carbon atom and especially of the other bridging ligand play important roles in determining the course of such insertion reactions.



5a, R = Ph
b, R = H



6a, R′ = C(O)OMe
b, R′ = CF_3

The mechanisms of the reactions reported in this communication are of interest, but at this point any discussion would be speculation. It is hoped that further studies will shed light on these unexpected processes.

Acknowledgment. We are grateful to the National Science Foundation for generous support of the work carried out at M.I.T. and to the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for support of the structural study carried out at U. of A. Thanks also are due to the Biomedical Research Support-Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (N.I.H. Grant RR02243) and the M.I.T Mass Spectrometry Facility (supported by N.I.H. Division of Research Resources, Grant No. RR 00317, K. Biemann, principal investigator) for mass spectra. In addition M.C. thanks NSERC for partial funding of the diffractometer at U. of A. and A.D.H. thanks NSERC and the Izaak Walton Killam Foundation for postdoctoral fellowships.

Registry No. **1a**, 118576-54-8; **4a**, 118576-58-2; **4b**, 118576-60-6; **4c**, 118597-22-1; **4d**, 118576-59-3; $Hg(C\equiv CCH_2OCH_3)_2$, 118576-

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[12] In a typical experiment, the apparatus of ref 4 was used in the reaction of 1.5 mmol each of **1** and $HC\equiv CCO_2CH_3$ in 25 mL of THF for 20 h at room temperature under nitrogen. A color change from red to brown-black was observed. Removal of solvent left a brown-black, oily solid which was purified by medium-pressure chromatography (silica gel, 1:1 and then 1:2 pentane/dichloromethane) to give a 43% yield of an air-stable, black solid, **4b**: mp 93.5–95.5 °C (from pentane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.39 (s, 9 H, $SC(CH_3)_3$), 3.67 (s, 3 H, CO_2CH_3), 3.86 (s, 3 H, OCH_3), 5.66 (d, J = 12.21 Hz, 1 H, $C(H)=C(H)OCH_3$), 5.87 (s, 1 H, C(H)), 7.67 (d, J = 12.24 Hz, 1 H, $C(H)=C(H)OCH_3$); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 32.14 (q, J = 129.4 Hz, $SC(CH_3)_3$), 51.29 (s, $SC(CH_3)_3$), 52.81 (q, J = 146.8 Hz, CO_2CH_3), 57.18 (q, J = 144.9 Hz, OCH_3) 69.07 (s, $CC(H)=C(H)OCH_3$), 95.43 (d, J = 155.8 Hz, $CC(H)=C(H)OCH_3$), 117.67 (d, J = 169.6 Hz, CH), 118.51 (s, CCO_2CH_3), 156.87 (d, J = 179.4 Hz, $CC(H)=C(H)OCH_3$), 165.93 (s, CO_2CH_3), 199.89, 204.46, 204.59, 209.96, and 210.53 (all s, FeCO), 235.29 (s, inserted CO); IR (CCl_4, cm^{-1}) 1628 vs (inserted C=O); IR (terminal carbonyl region, CCl_4, cm^{-1}) 2080 s, 2025 vs, 1983 s, 1950 w; mass spectrum (EI, 70 eV); M^+ and ($M^+ - n$CO) (n = 1–6). Anal. Calcd for $C_{18}H_{18}O_9SFe_2$: C, 41.41; H, 3.48. Found: C, 41.73; H, 3.60. Also prepared in this manner were **4a**, **4c**, and **4d**. Full characterizing data are provided as supplementary material.

[13] Crystal data for **4b**: a = 17.442 (6) Å, b = 10.218 (2) Å, c = 13.700 (3) Å, β = 113.10 (2)°, V = 2246 (1) Å^3, space group $P2_1/a$ (No. 14), Z = 4, μ = 14.60 cm^{-1}. Data in the range of $1.0° \leq 2\theta \leq 55.0°$ were collected at ambient temperature by using Mo Kα radiation on a Rigaku AFC6R diffractometer. The structure was solved by Patterson and difference Fourier syntheses and refined by full-matrix least-squares techniques. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å). All other atoms were refined anisotropically. An empirical absorption correction was applied. Final R = 0.052 and R_w = 0.064 for 2733 observed reflections ($h0l$, $h \neq 2n$, and $0k0$, $k \neq 2n$) [$4F_o^2/\sigma^2(F_o)^2$] and 271 variables. The largest peak in the final difference Fourier map was 0.36 e/Å^3.

[14] MacGillavry, C. H.; Rieck, G. D., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. III, p 276.

61-7; $[Et_3NH][\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$, 105040-77-5; $BrC{\equiv}CCH_2OCH_3$, 54339-94-5; $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CCH_2OCH_3)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$, 118576-55-9; $(\mu,\eta^1,\eta^2\text{-}CH{=}CHCH{=}O)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$, 118576-56-0; $(\mu,\eta^1,\eta^2\text{-}PhC{=}CHCH{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$, 118576-57-1; $[Et_3NH][\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$, 93530-38-2; $PhC{\equiv}CCHO$, 2579-22-8; $CH_3O_2CC{\equiv}CCO_2CH_3$, 762-42-5; $HC{\equiv}CCO_2CH_3$, 922-67-8; $HC{\equiv}CC(O)CH_3$, 1423-60-5; $CH_3C{\equiv}CCO_2CH_3$, 23326-27-4.

Supplementary Material Available: A table of spectroscopic and analytical data and tables of positional parameters, anisotropic thermal parameters, and bond lengths and angles (16 pages); listings of observed and calculated structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

Reactive Mono- and Dinuclear Bis(diphenylphosphino)methane Derivatives of Ruthenium Carbonyls: $Ru(CO)_4(\eta^1\text{-dppm})$ and $Ru_2(CO)_7(\mu\text{-dppm})$

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Summary: Reaction of bis(diphenylphosphino)methane with in situ generated $Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3)$ gives $Ru(CO)_4(\eta^1\text{-dppm})$ (**1**). Photolysis of **1** and $Ru(CO)_5$ or that of $Ru_3(CO)_{10}(\mu\text{-dppm})$ in the presence of CO yields $Ru_2(CO)_7(\mu\text{-dppm})$ (**2**). Evidence for high reactivity of these complexes is presented by the reaction of **2** with CH_2N_2 and HCCH and that of **1** with $[Rh(CO)_2(solv)_2]^+$ and $[Rh(CO)_2Cl]_2$, all occurring below 0 °C.

Recent, investigations by Shaw et al.[1] and Knox et al.[2] have established that $Fe(CO)_4(\eta^1\text{-dppm})$ and $Fe_2(CO)_7(\mu\text{-dppm})$ (dppm = bis(diphenylphosphino)methane) have a very rich derivative chemistry. The mononuclear iron complex, containing a monodentate diphosphine ligand, is a versatile building block for the synthesis of heterobimetallic complexes while the diiron compound exhibits interesting phosphorus–carbon bond cleavage reactions[2a] and its stepwise reaction with acetylene serves as a realistic model for the iron carbonyl mediated synthesis of tropone. Although the analogous ruthenium derivatives are expected to be even more reactive,[3] their synthesis so far remained elusive. Here we report the successful synthesis of $Ru(CO)_4(\eta^1\text{-dppm})$ (1) and $Ru_2(CO)_7(\mu\text{-dppm})$ (2) and divulge some preliminary reactivity studies which bear out these expectations.

In our hands, reaction of dppm with the commonly used "$Ru(CO)_4$" transfer reagents such as $Ru(CO)_5$,[4a] $Ru(CO)_4(\eta^2\text{-}C_2H_4)$,[4a] and $Ru(CO)_4(\eta^2\text{-}CH_2CHCO_2CH_3)$[4b] led to mixtures of products with one of the components being 1. However, successful preparation of 1 was achieved by the use of the in situ generated, very labile $Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3)$[5] (eq 1). Compound 1[6] is moderately stable at room temperature, but it must be protected from light since it slowly converts to $Ru(CO)_3(\eta^2\text{-dppm})$. As expected from the behavior of related $M(CO)_4L$ types of compounds[7]

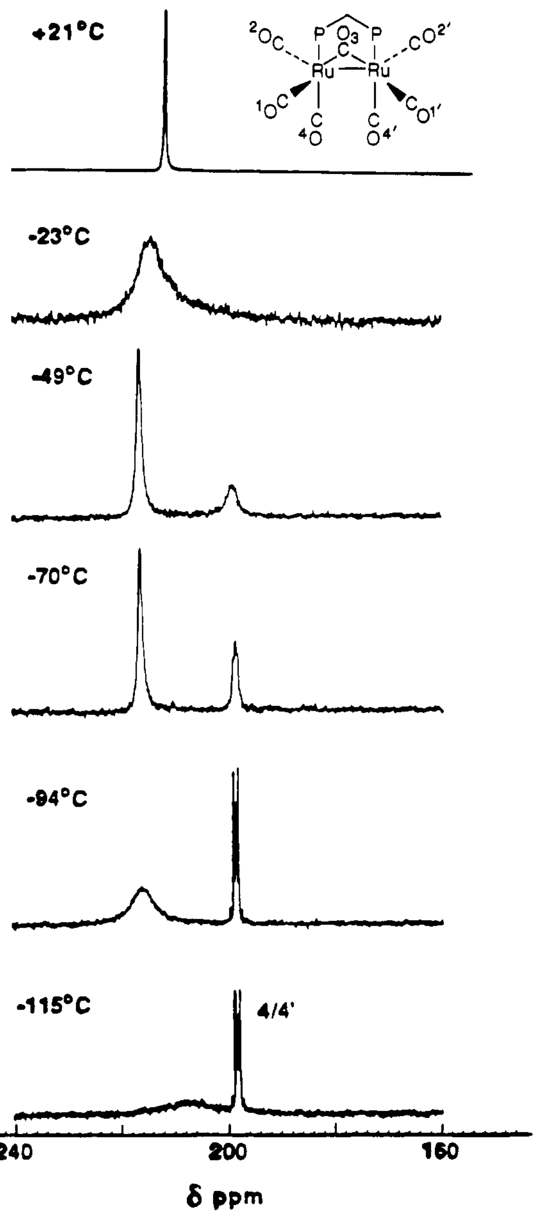

Figure 1. Variable-temperature ^{13}C NMR spectra of 2.

$$Ru(CO)_5 + CH_2CHCH_3 \xrightarrow[\text{pentane, }-20\ ^\circ\text{C}]{h\nu,\ \lambda > 370\text{ nm}} Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3)$$

$$Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3) + 1\text{dppm} \xrightarrow[0\ ^\circ\text{C, dark}]{\text{pentane/toluene}} \underset{\mathbf{1}\ (70\%\ \text{yield})}{Ru(CO)_4(\eta^1\text{-dppm})} \quad (1)$$

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[1] Fontaine, X. L.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741 and references therein.

[2] (a) Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; Macpherson, K. A.; Melchior, F.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, *540*. (b) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358.

[3] Basolo, F. *Isr. J. Chem.* **1986**, *27*, 233.

[4] (a) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974**, *67*, C75; *J. Chem. Soc., Dalton Trans.* **1975**, 1876. (b) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *Inorg. Synth.* **1986**, *24*, 176.

[5] The lability of this compound has so far prevented its isolation. It was identified in solution by IR spectroscopy (cm^{-1}, pentane, −20 °C); ν_{CO} 2101 w, 2019 vs, 1993 s.

[6] 1: yellow solid; IR (ν_{CO}, pentane, cm^{-1}) 2061 s, 1989 m, 1957 s, 1944 s. NMR (δ, ppm, CD_2Cl_2): ^1H, 3.33 (dd, CH_2); ^{31}P, 38.3 (d, Ru–P), −26.2 (d, free P). Anal. Calcd for $C_{29}H_{22}O_4P_2Ru$: C, 58.30; H, 3.71. Found: C, 57.60; H, 4.02.

[7] Martin, L. R.; Einstein, W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777 and references therein.

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