Synthesis and Characterization of Bimetallic Complexes with the Bridging η²(σ,σ)-1,3-Butadiyne-1,4-diyl Ligand[1]

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Summary: The complex $(\eta^5\text{-}C_5H_5)(CO)_2FeC\equiv CC\equiv CH$ was prepared by sequential treatment of $LiC\equiv CC\equiv C\text{-}Si(CH_3)_3$ with $(\eta^5\text{-}C_5H_5)(CO)_2FeCl$ and tetrabutylammonium fluoride. The monometallic complexes $(\eta^5\text{-}C_5H_5)(CO)\text{-}LFeC\equiv CC\equiv CH$ (L = CO, PPh₃) were deprotonated with *sec*-BuLi, and the resulting anions were trapped with $(\eta^5\text{-}C_5H_5)M(CO)_nCl$ to form $(\eta^5\text{-}C_5H_5)(CO)LFeC\equiv CC\equiv CM\text{-}(CO)_n(\eta^5\text{-}C_5H_5)$ (n = 2, M = Fe, L = CO, PPh₃; n = 3, M = Mo, L = CO, PPh₃; n = 3, M = W, L = CO, PPh₃) in 55–86% isolated yield. IR data suggest that the butadiynediyl ligand is effective in conveying electronic information between the two metal centers of the bimetallic molecules.

Organometallic polymers whose metal centers are joined by organic ligands with delocalized π-systems have been investigated extensively over the last several years.[2] Such species are of interest due to their potential usefulness in the areas of electronics and material science.[3] One particular type of organometallic polymer, with transition metals linked by a 1,3-butadiyne-1,4-diyl ligand, is known to have a rigid, rodlike structure and exhibits unusual properties both in solution and in the solid state.[4] Furthermore, the magnetic anisotropy of these polymers may be systematically controlled by incorporating different transition-metal atoms in the polymer structure.[4] Our research is focused on the development of the synthetic methodology required to produce bimetallic complexes with a bridging 1,3-butadiyne-1,4-diyl linkage, since they may serve as model subunits of the polymer $-[-M'C\equiv CC\equiv CMC\equiv CC\equiv C-]_n-$. By systematically varying the metals involved, we hope to gain a fundamental understanding of the nature and extent of the electronic interaction between adjacent metal centers. Here we report the synthesis and characterization of several complexes containing the η²(σ,σ)-1,3-butadiyne ligand, including the first examples of heterobimetallic analogues.[5] It appears that, in these species, the butadiynediyl ligand is effective in conveying electronic information between the two metal centers.

The dilithiated butadiynediyl anion 1 may be prepared by treatment of (Z)-1-methoxy-but-1-en-3-yne with 3 equiv of *n*-BuLi at -25 °C in THF.[6] Trapping of 1 with 2 equiv of $(\eta^5\text{-}C_5H_5)(CO)_2FeCl$ resulted in the isolation of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2(\mu\text{-}C\equiv CC\equiv C)$ (4a) in 40% yield. Complex 4a had been reported previously but was characterized solely by IR spectroscopy.[7] Our initial attempts to unsymmetrically substitute 1 were disappointing. Dropwise addition of 1.0 equiv of $(\eta^5\text{-}C_5H_5)(CO)_2FeCl$ in 10 mL of THF to a solution of 1 at -78 °C was followed by quenching with $(CH_3)_3SiCl$ or H_2O. This resulted in the isolation of only low yields of the corresponding products $(\eta^5\text{-}C_5H_5)(CO)_2FeC\equiv CC\equiv CSi(CH_3)_3$ (2a, 5%) and $(\eta^5\text{-}C_5H_5)(CO)_2FeC\equiv CC\equiv CH$ (3a, 4%). Fortunately, we were able to obtain a higher yield of 2a by first converting 1 to 1,4-bis(trimethylsilyl)-1,3-butadiyne, followed by reaction with CH_3Li–LiBr (1 equiv) to form $LiC\equiv CC\equiv CSi(CH_3)_3$ (5),[8] and the reaction between 5 and $(\eta^5\text{-}C_5H_5)(CO)_2FeCl$ (1 equiv) resulted in the formation of 2a,[9] which may be isolated in 85% yield (Scheme I).

Interestingly, attempts to desilylate 2a with CH_3Li–LiBr were unsuccessful. However, the use of tetrabutylammonium fluoride in THF at room temperature resulted in the rapid transformation of 2a into 3a. Similarly, $(\eta^5\text{-}C_5H_5)PPh_3(CO)FeC\equiv CC\equiv CH$ (3b)[10] may be prepared from $(\eta^5\text{-}C_5H_5)PPh_3(CO)FeC\equiv CC\equiv CSi(CH_3)_3$ (2b) by treatment with tetrabutylammonium fluoride. It should be noted that these reactions were not stoichiometric, and the highest yields of 3a (70%) and 3b (84%) were obtained when ca. 0.2 equiv of tetrabutylammonium fluoride was used.

Complexes 2 and 3 were fully characterized by spectroscopy and by elemental analysis. The IR spectra of complexes 3 exhibited sharp medium ν_{C-H} bands (3306 cm⁻¹ for 3a, 3300 cm⁻¹ for 3b). Only one $\nu_{C\equiv C}$ band was observed in each case; the terminal $\nu_{C\equiv C}$ band may be obscured by ν_{CO}. Proton resonances of the alkynyl proton of 3a and 3b appeared unusually upfield at 1.44 and 1.27 ppm, respectively. In the case of 3b, it appeared as a doublet with $^6J_{^1H-^{31}P}$ = 0.8 Hz. The butadiynediyl carbons C(1)–C(4) in complexes 3a and 3b were unequivocally assigned on the basis of C–H coupling constants obtained from proton-coupled ¹³C NMR experiments.[11] In accord

(1) Presented in part by A.W.: *Abstracts of Papers*, 198 National Meeting of the American Chemical Society, Miami Beach, FL, Sept 1989; American Chemical Society: Washington, DC, 1989; INOR 40.

(2) See for example: (a) Hunter, A. D. *Organometallics* **1989**, *8*, 1118. (b) Maatta, E. A.; Devore, D. D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 569. (c) Gross, R.; Kaim, W. *J. Organomet. Chem.* **1987**, *333*, 347. (d) Collman, J. P.; McDevitt, J. T.; Leidner, C. R.; Yee, G. T.; Torrance, J. B.; Little, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 4606.

(3) (a) *Metal-Containing Polymeric Systems*; Sheets, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds.; Plenum: New York, 1985. (b) *Electrical Properties of Polymers*; Seanor, D. A., Ed.; Academic: New York, 1982; Vols. 1–3. (c) *Ultrastructure Processing of Ceramics, Glasses, and Composites*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1984.

(4) (a) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101. (b) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *Ibid.* **1978**, *160*, 319. (c) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1980**, *41*, 149. (d) Takahashi, S.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 661. (e) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237.

(5) Several heterobimetallic polymers containing the η²(σ,σ)-1,3-butadiyne-1,4-diyl ligand have been reported.[4b,e]

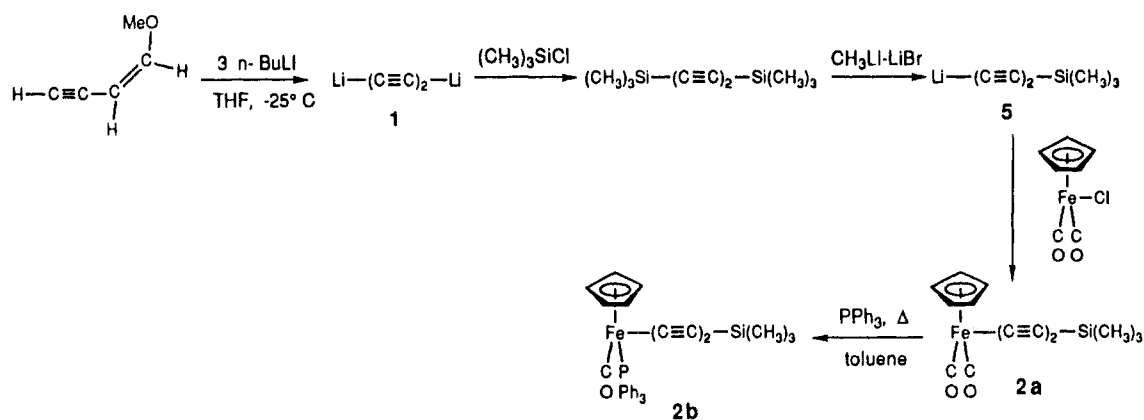(6) Zweifel, G.; Rajagopalan, S. *J. Am. Chem. Soc.* **1985**, *107*, 700.

(7) Kim, P. J.; Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181. This paper also described the preparation and characterization of several other homobimetallic complexes containing the η²(σ,σ)-1,3-butadiyne-1,4-diyl ligand.

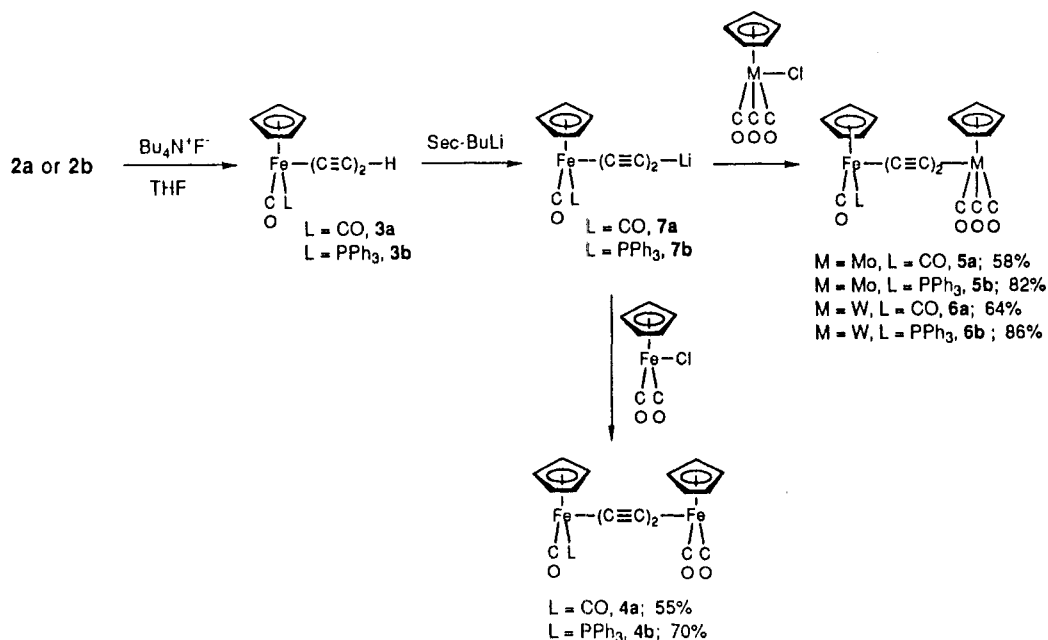(8) Holms, A. B.; Jennings-White, C. L. D.; Schulthess, A. H. *J. Chem. Soc., Chem. Commun.* **1979**, 840.

(9) Compound 2a: IR (CH₂Cl₂, cm⁻¹) $\nu_{C\equiv C}$ 2156 (w), 2124 (w), ν_{CO} 2054 (s), 2006 (s); ¹H NMR (200 MHz, CDCl₃, 23 °C) δ 5.04 (s, 5 H, Cp), 0.15 (s, 9 H, Si(CH₃)₃); ¹³C NMR (50 MHz, CDCl₃, 23 °C) δ 210.9 (MCO), 98.14, 91.9, 91.1, 71.0 (≡C), 85.34 (Cp), 0.15 (Si(CH₃)₃). Anal. Calcd for C₁₄H₁₄FeO₂Si: C, 56.37; H, 4.70. Found: C, 56.29; H, 4.64.

(10) Complex 3b was prepared by refluxing 3a with PPh₃ in toluene. Compound 3b: IR (CH₂Cl₂, cm⁻¹) $\nu_{\equiv CH}$ 3306 (m), $\nu_{C\equiv C}$ 2170 (w), ν_{CO} 1958 (s); ¹H NMR (200 MHz, CDCl₃, 23 °C) δ 7.32–7.64 (m, 15 H, PPh₃), 4.50 (d, J = 1.2 Hz, 5 H, Cp), 1.27 (d, J = 0.8 Hz, 1 H, ≡CH); ¹³C NMR (50 MHz, CDCl₃, 23 °C) δ 218.3 (d, J = 30.4, MCO), 135.5 (d, J = 45.0 Hz, i), 133.3 (d, J = 9.8 Hz, o), 130.1 (d, J = 2.5 Hz, p), 128.2 (d, J = 9.8 Hz, m) (all PPh₃), 109.4 (d, J = 39.4 Hz, C(1)), 99.1 (s, C(2)), 72.1 (s, C(3)), 54.3 (s, C(4)),[11] (all ≡C), 84.5 (d, J = 6.6 Hz, Cp). Anal. Calcd for C₂₈H₂₁FeOP: C, 73.06; H, 4.60. Found: C, 72.61; H, 4.66.

Scheme I

Scheme II

M = Mo, L = CO, 5a; 58%
M = Mo, L = PPh$_3$, 5b; 82%
M = W, L = CO, 6a; 64%
M = W, L = PPh$_3$, 6b ; 86%

L = CO, 4a; 55%
L = PPh$_3$, 4b; 70%

with the proton data, C(4) resonances for **3a** and **3b** also appeared upfield at 54.3 and 52.0 ppm, respectively. These unusual upfield shifts may possibly be due to resonance charge transfer or an increase in the diamagnetic anisotropy effect resulting from a coupling between the metal fragment and triple-bond ring currents. A similar argument was used to explain the upfield shift observed in the NMR spectra of fluoroacetylene.[12]

Complex **3a** may be deprotonated by n-BuLi at -78 °C and the resulting anion (**7a**) trapped by (CH$_3$)$_3$SiCl to form **2a** in 38% yield. The reaction was sluggish and appeared to be complicated by side reactions. A much cleaner reaction was observed between n-BuLi and **3b**. Reactions between **3a** or **3b** and sec-BuLi also appeared clean. Anions **7a** and **7b** generated in these latter cases may be trapped by (CH$_3$)$_3$SiCl to regenerate **2a** and **2b** in 80–90% yield. Although the acidity of alkynyl protons is well established, no data are available on the acidity of the alkynyl protons of transition-metal alkynyl complexes. We believe the reactions described above represent the first examples in which the terminal proton of a transition-metal alkynyl complex is deprotonated with a base.

Anions **7a** and **7b** generated in situ also react with transition-metal chlorides readily. Thus, reaction between

(η^5-C$_5$H$_5$)(CO)$_n$MCl (n = 3, M = Mo, W; n = 2, M = Fe) and **7a** or **7b** resulted in the formation of (η^5-C$_5$H$_5$)(CO)-LFeC≡CC≡CM(CO)$_n$(η^5-C$_5$H$_5$) in 55–86% yield (n = 2, M = Fe, L = CO, **4a**; n = 2, M = Fe, L = PPh$_3$, **4b**; n = 3, M = Mo, L = CO, **5a**; n = 3, M = Mo, L = PPh$_3$, **5b**; n = 3, M = W, L = CO, **6a**; n = 3, M = W, L = PPh$_3$, **6b**)[13] (Scheme II). Complexes **5** and **6**, to the best of our knowledge, are the first examples of heterobimetallic complexes containing the $\eta^2(\sigma,\sigma)$-1,3-butadiyne-1,4-diyl ligand. These bridging butadiynediyl complexes may be isolated as yellow to orange solids that are moderately stable to air and heat in the solid state. Complexes with L = PPh$_3$ are generally more stable and may be isolated in higher yields. They have been characterized by spectroscopy and by elemental analysis. Of particular interest are the IR spectra of **4a** and **4b**. Upon substitution of one CO by PPh$_3$, ν_{CO} of the CO on the other iron fragment was reduced significantly (ν_{CO} of **4a** at 2048 and 2000 cm^{-1}; ν_{CO} of **4b** at 2037, 1988, and 1949 cm^{-1}). This suggests that

(11) C(1) is bound to Fe.
(12) Rosenberg, D.; Drenth, W. *Tetrahedron* **1971**, *27*, 3893.

(13) Compound **6b**: IR (CH$_2$Cl$_2$, cm^{-1}) $\nu_{C≡C}$ 2127 (w), ν_{CO} 2030 (s), 1947 (vs, b), 1930 (sh); ^{1}H NMR (200 MHz, CDCl$_3$, 23 °C) δ 7.37–7.69 (m, 15 H, PPh$_3$), 5.54 (s, 5 H, Cp(W)), 4.45 (d, J = 1.2 Hz, 5 H, Cp(Fe)); ^{13}C NMR (50 MHz, CDCl$_3$, 23 °C) δ 232.6 (s, WCO), 218.9 (d, J = 30.5, FeCO), 210.8 (s, WCO), 136.0 (d, J = 44.1 Hz, i), 133.5 (d, J = 9.7 Hz, o), 129.8 (d, J = 2.1 Hz, p), 128.0 (d, J = 9.7 Hz, m) (all PPh$_3$), 117.6 (s), 105.1 (s), 98.1 (d, J = 41.3 Hz), 52.0 (s) (all ≡C), 91.6 (s), 84.5 (d, J = 41.3 Hz) (all Cp). Anal. Calcd for C$_{36}$H$_{25}$FeO$_4$PW: C, 54.58; H, 3.16. Found: C, 54.27; H, 3.10.

the butadiynediyl ligand is effective in conveying electronic information between the two metal centers in the same molecule. Work is underway to determine the extent of this interaction by studying other heterobimetallic complexes containing carbon–carbon triple bonds.

Supplementary Material Available: Listings of spectroscopic data (IR, ¹H NMR, ¹³C NMR) and analytical data for **2–6** (4 pages). Ordering information is given on any current masthead page.

# Organometallic Synthesis via "Surface-Mediated" Reactions: High-Yield Route to HOs₃(CO)₁₀(OH)

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Summary: The silica-anchored hydrido cluster HOs₃(CO)₁₀(OSi<) is easily prepared from physisorbed Os₃(CO)₁₂. Chemical displacement from the surface with HF leads to the isolation of pure HOs₃(CO)₁₀(OH). This approach is far simpler and gives much higher yields than the conventional syntheses in solution.

The surface organometallic chemistry originating from the interaction of Os₃(CO)₁₂ with the surface of silica has been investigated over the last few years.[1] In particular, the oxidative addition of a silanol group of the surface into an osmium–osmium bond of the cluster takes place easily on thermal treatment in argon or under vacuum at 373 K:

$$Os_3(CO)_{12} + HO-Si< \rightarrow HOs_3(CO)_{10}(OSi<) + 2CO$$
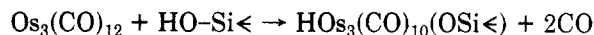
The surface reaction is stoichiometric;[1] the surface hydride is selectively formed and is stable up to 423 K.

Solvent extraction of the surface species with CH₂Cl₂ or THF was unsuccessful. However, we have found that dissolution of the silica support with HF leads to destruction of the Os–O–Si bonds, and by protonation, pure HOs₃(CO)₁₀(OH) is recovered:

$$HOs_3(CO)_{10}(OSi<) \xrightarrow{HF/H_2O} HOs_3(CO)_{10}(OH) + H_2SiF_6$$
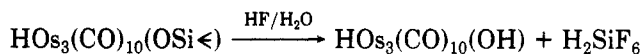
The proposed chemical displacement with HF thus may provide a general method for the characterization of silica-supported metal clusters. In addition, a novel "surface-mediated" route to the high-yield synthesis of HOs₃(CO)₁₀(OH) now is available.

In a typical experiment, the anchored osmium cluster HOs₃(CO)₁₀(OSi<) (2.0 wt % Os) was prepared from Os₃(CO)₁₂ (160 mg) and SiO₂ (Aerosil 200 Degussa, 5.0 g) by following two different procedures: (A) Os₃(CO)₁₂ was first physisorbed on silica, and then the mixture was heated under argon between 373 and 413 K.[2] (B) The support was suspended in a degassed n-octane solution of Os₃(CO)₁₂ and refluxed under argon until the solvent was decolorized.[3] Once dried, HOs₃(CO)₁₀(OSi<) is stable in air and

Table I. Chemical Extraction Data from Different Samples of HOs₃(CO)₁₀(OSi<)

support[a]	technique of impregnation[b]	thermal treatment		¹H NMR, ppm[c]
		T, K	t, h	
Aerosil 200	A	420	12	−12.60
	B	398	20	−12.60
Cab-O-Sil M5	A	373	40	−12.65
Akzo F6	B	398	6	−12.58
Carlo Erba GC	B	398	6	−12.60
Porasil 80-100	B	398	14	−12.57
HOs₃(CO)₁₀(OH)[d]				−12.58

[a] All supports used as received. [b] See text. [c] In CD₂Cl₂ at 300 K. [d] Reference 4.

can be handled without special precautions. It then was protonated at 195 K with 200 mL of degassed 20% hydrofluoric acid. In the process the solid dissolved completely. After it was warmed to room temperature, the aqueous solution was extracted three times with 100-mL portions of CH₂Cl₂. The yellow organic solution thus obtained was found by thin-layer chromatography to contain HOs₃(CO)₁₀(OH) as the only product.

The ¹H NMR spectrum of the solution showed a strong high-field signal at −12.60 ppm from TMS, in good agreement with the reported value for HOs₃(CO)₁₀(OH).[4] In the mass spectrum, the parent ion was observed at m/z = 868, with several other fragments corresponding to the successive loss of the 10 carbonyl groups. The FT-IR spectrum in n-pentane showed six bands in the ν(CO) region, at 2110 vw, 2069 vs, 2062 s, 2023 vs, 2000 s and 1984 m cm⁻¹. The yellow CH₂Cl₂ solution then was evaporated in vacuo. HOs₃(CO)₁₀(OH) was recovered as air-stable orange crystals after recrystallization from n-pentane at 273 K (85.6 mg, 56% yield based on Os₃(CO)₁₂).

Different types of silica were used to prepare the grafted hydride. In all cases, pure HOs₃(CO)₁₀(OH) was obtained after the chemical displacement with HF (see Table I). The insensitivity of the "surface-mediated" synthesis to the nature of the silica surface and/or to the preparation method is thus demonstrated.

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(1) Dossi, C.; Fusi, A.; Grilli, E.; Ugo, R.; Zanoni, R. *Catal. Today* **1988**, 2, 585 and references cited therein.
(2) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Basset, J. M. *J. Organomet. Chem.* **1981**, 213, 215.
(3) Barth, R.; Gates, B. C.; Knözinger, H.; Hulse, J. *J. Catal.* **1983**, 82, 147.
(4) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1976**, 838.