Reactivity and Structure of a Cationic Allenyl Complex, (μ-η^2,η^3-Allenyl)bis(methylcyclopentadienyl)tetracarbonyldimolybdenum Tetrafluoroborate, and Its Reductive Coupling Product, $[Cp_2(CO)_4Mo_2]_2$-μ-(μ-$HC{\equiv}CCH_2$–$)_2$

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Bis(methylcyclopentadienyl)tetracarbonyldimolybdenum, 1′, reacts with methoxyallene to give the complex $M_2(\mu\text{-}CH_2{=}C{=}CHOMe)$ (3) and with methyl propargyl ether to give the isomeric complex $M_2(\mu\text{-}HC{\equiv}CCH_2OMe)$ (4) ($M = Mo(CO)_2Cp'$). Complexes 3 and 4 react with HBF_4 with loss of MeOH to produce the cationic allenyl complex $M_2(\mu\text{-}\eta^2,\eta^3\text{-}HCCCH_2)^+BF_4^-$ ($2{\cdot}BF_4$). The cation 2 reacts with a variety of nucleophiles (Nu) to form the substituted alkyne adducts $M_2(\mu\text{-}HC{\equiv}CCH_2Nu)$. With $CpFe(CO)_2^-$, the dimer $[M_2(\mu\text{-}HC{\equiv}CCH_2\text{–})]_2$ (11) is formed. Spectroscopic properties (^1H and ^{13}C NMR, IR, etc.) are reported. The structures of $2{\cdot}BF_4$ and 11 were determined by single-crystal X-ray diffraction: for $2{\cdot}BF_4$, $a = 8.663$ (2) Å, $b = 35.652$ (10) Å, $c = 13.746$ (3) Å, $\beta = 92.92$ (2)°, $V = 4240$ (2) Å^3, $Z = 8$, $\rho_{calcd} = 1.842$ g cm^{-3}, $\rho_{obsd} = 1.843$ g cm^{-3}, space group $P2_1/n$, $R_1 = 0.054$, and $R_2 = 0.059$ on 2589 reflections with $I > 3\sigma(I)$; for 11, $a = 8.897$ (2) Å, $b = 18.643$ (11) Å, $c = 11.457$ (4) Å, $\beta = 108.72$ (2)°, $V = 1800$ (1) Å^3, $Z = 2$, $\rho_{calcd} = 1.850$ g cm^{-3}, space group $P2_1/n$, $R_1 = 0.025$, and $R_2 = 0.024$ on 2062 reflections with $I > 3\sigma(I)$.

Introduction

The reactivity displayed by metal–metal multiply bonded compounds has provided new synthetic routes to a wide variety of organometallic complexes.[1] In particular, the reactions of $Cp_2Mo_2(CO)_4$ (1) with alkynes,[2] allenes,[3] diolefins,[4] and diazoalkanes[5] have allowed the isolation of novel complexes of hydrocarbyl ligands bonded to a dimetal framework.

Transformations of hydrocarbon fragments on multimetal sites are of interest from the standpoint of understanding bonding and reactivity modes of hydrocarbons on metal surfaces. We are especially interested in the chemistry of hydrogen-poor, carbon-rich fragments, C_nH_x ($n \geq 2$, $x < 2n$), which are formed on metal catalyst surfaces in the course of hydrogenations of olefins[6] and CO.[7] The mechanism of formation, the structures of these surface "carbides" (i.e. partially hydrogenated carbon species), and the role they play in product formation and/or catalyst deactivation ("coke" formation) are largely unknown and are a matter of some controversy.[7-11]

It is in this vein that we here report the synthesis and structure of $Cp'_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}C_3H_3)^+$ (2: $Cp' = C_5H_4Me$) and its reactions with various bases. Cation 2 is formed from the loss of MeOH from either $Cp'_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}H_2C{=}C{=}CHOMe)$ (3) or $Cp'_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}HC{\equiv}CCH_2OMe)$ (4) following protonation by HBF_4.

Experimental Section

Manipulation of all reactants and anhydrous solvents were carried out under an inert atmosphere of dry N_2 using standard Schlenk techniques. Solvents were dried and purged of molecular oxygen by distillation from sodium (potassium) benzophenone ketyl (toluene, benzene, THF). Hexane was dried by using CaH_2. CH_2Cl_2 and CH_3CN were distilled from P_4O_{10} and thoroughly degassed prior to use. $Cp'_2(CO)_4Mo_2$ was synthesized by the established method.[12] Organic reagents were purchased from Aldrich and purified by standard methods. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer (compensation method). Multinuclear NMR spectra were recorded on a Bruker WM360 FT spectrometer with a low-temperature probe. Temperatures were calibrated by using methanol. X-ray diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of $HC{\equiv}CCH_2OCH_3$. Synthesis of methyl propargyl ether was accomplished by the literature method of Reppe.[13] The colorless liquid was dried over Na_2SO_4 and distilled (60–65 °C, 1 atm); yield 33%.

Preparation of $CH_2{=}C{=}CHOCH_3$. Methoxyallene was prepared by the literature procedure.[14] Methyl propargyl ether (37.14 g, 0.53 mol) was added to 7.32 g (0.065 mol) potassium *tert*-butoxide. The mixture was refluxed for 2 h and distilled (50–51 °C, 1 atm).

Preparation of $Cp'_2(CO)_4Mo_2(CH_2{=}C{=}CHOMe)$ (3). Methoxyallene (0.30 g, 4.32 mmol) was slowly added via syringe to a solution of $Cp'_2(CO)_4Mo_2$ (2.0 g, 4.32 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 0.5 h at room temperature. Hexane (15 mL) was then added, and CH_2Cl_2 was removed in vacuo until a precipitate of 3 formed. The solution was filtered and the precipitate washed with hexane (3 × 5 mL) and dried in vacuo. The red solid (1.6 g, 70%) is soluble in toluene, CH_2Cl_2,

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[1] Review: Curtis, M. D. *Polyhedron* **1987**, *0*, 000.

[2] (a) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *17*, 2324. (b) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (c) Beck, J. A.; Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc. Dalton Trans.* **1982**, 195. (d) Gerlach, R. F.; Duffy, D. N.; Curtis, M. D. *Organometallics* **1983**, *2*, 1172.

[3] Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 802.

[4] (a) Goddard, R.; Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 147. (b) Griffiths, M.; Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *Ibid.* **1982**, 159.

[5] (a) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283. (b) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 0000.

[6] Thompson, S. J.; Webb, G. *J. Chem. Soc., Chem. Commun.* **1976**, 526.

[7] Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.

[8] Nijs, H. H.; Jacobs, P. A. *J. Catal.* **1980**, *65*, 328; **1980**, *66*, 401.

[9] Henrici-Olive, G.; Olive, S. *J. Mol. Catal.* **1983**, *18*, 367.

[10] Gibson, E. J.; Clarke, R. W. *J. Appl. Chem.* **1961**, *11*, 293.

[11] Hofer, L. J. E.; Sterling, E.; McCartney, J. T. *J. Phys. Chem.* **1955**, *59*, 1153.

[12] Curtis, M. D.; Fotinos, N. A.; Messerle, L.; Sattelberger, A. P. *Inorg. Chem.* **1983**, *22*, 1559.

[13] Reppe, W. *Justus Liebigs Ann. Chem.* **1955**, *596*, 74.

[14] (a) Ghalamkar-Moazzam, M.; Jacobs, T. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 615. (b) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1986**, *87*, 1179.

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and $CHCl_3$: mp 127–129 °C (sealed capillary); molecular mass calcd *m/e* 534, found *m/e* 534 (^{98}Mo, mass spectrum); IR (C_6H_{14}) 1958 m, 1924 vs, 1880 s, 1860 w, cm^{-1}; ^1H NMR (benzene-d_6) δ 5.67 (dd, $J = 1.8$ Hz, $J = 1.2$ Hz, $=C\mathit{H}OMe$), 4.69 (m, $MeC_5\mathit{H}_4$), 3.55 (dd, $J = 1.2$ Hz, $J = 2.4$ Hz, $=CH_2$), 3.45 (s, $-OCH_3$), 2.32 (dd, $J = 1.8$ Hz, $J = 2.4$ Hz, $=CH_2$), 1.72, 1.55 (s, CH_3Cp); ^{13}C NMR (benzene-d_6) δ 242.51, 236.56, 234.03, 232.47 (CO), 176.34 ($=C=$, $J = 11.4$ Hz), 108.67, 108.29 (ipso-C), 101.19 ($=\mathit{C}HOMe$, $J = 201$ Hz), 94.86, 94.64, 94.05, 93.36, 93.16, 91.85, 81.60, 91.39 ($Me\mathit{C}_5H_4$), 57.79 (OCH_3, $J = 142$ Hz), 38.33 ($=CH_2$, $J = 157$ Hz, $J = 171$ Hz), 13.69, 13.14 ($\mathit{C}H_3Cp$, $J = 128$ Hz). Anal. Calcd for $C_{20}H_{20}Mo_2O_5$: C, 45.13; H, 3.79; Mo, 36.05. Found: C, 44.79; H, 3.79; Mo, 35.66.

Preparation of $Cp'_2(CO)_4Mo_2(CH\equiv CCH_2OCH_3)$ (4). Propargyl methyl ether (0.160 g, 2.34 mmol) was added via syringe to a solution of $Cp'_2(CO)_4Mo_2$ (1.0 g, 2.34 mmol) in 20 mL of CH_2Cl_2. The solution was stirred for 15 min at room temperature. The solvent was removed in vacuo to yield the dark red solid, **4**, which was recrystallized from hexane at −78 °C (0.820 g, 71%). The product is soluble in toluene, CH_2Cl_2, and CH_3CN: mp 84–85 °C (sealed capillary); molecular mass calcd *m/e* 534, found *m/e* 534 (^{98}Mo, mass spectrum); IR (C_6H_{14}) 1990 s, 1963 m, 1918 vs, 1864 s cm^{-1}; ^1H NMR (benzene-d_6) δ 5.47 (t, $J = 0.72$ Hz, $\equiv CH$), 4.88 (m, $MeC_5\mathit{H}_4$), 4.42 (d, $J = 0.72$ Hz, $C\mathit{H}_2OMe$), 3.16 (s, $-OCH_3$), 1.78 (s, $C\mathit{H}_3Cp$); ^{13}C NMR (benzene-d_6) δ 233.53, 229.03 (CO), 107.0 (ipso-C), 91.91, 91.26, 91.04, 90.68 ($Me\mathit{C}_5H_4$), 85.55 ($\equiv\mathit{C}H$), 76.39 ($-\mathit{C}H_2OCH_3$), 58.22 ($-O\mathit{C}H_3$), 56.02 ($\equiv C-$), 13.99 ($\mathit{C}H_3Cp$). Anal. Calcd for $C_{20}H_{20}MoO_5$: C, 45.13; H, 3.78. Found: C, 45.36; H, 3.82.

Preparation of $[Cp'_2(CO)_4Mo_2(C_3H_3)]BF_4$ (2·BF_4). Method A. $Cp'_2(CO)_4Mo_2(CH_2=C=CHOCH_3)$ (**1**) (1.00 g, 1.88 mmol) was dissolved in 40 mL of CH_2Cl_2 and combined with an equivalent amount of $HBF_4·OEt_2$ (0.304 g, 1.88 mmol) at room temperature. The color of the solution immediately changed from red to yellow. After the solution was stirred for 10 min, 40 mL of Et_2O was slowly added. Bright yellow crystals of **2**·BF_4 were filtered, washed with Et_2O (1 × 5 mL), and dried in vacuo (1.06 g, 96%). The product is soluble in CH_2Cl_2, CH_3CN, and acetone. This material is spectroscopically identical with that described in method B below.

Method B. At room temperature $HBF_4·OEt_2$ (0.130 g, 0.81 mmol) was added to a solution of $Cp'_2(CO)_4Mo_2(CH\equiv CCH_2OMe)$ (**4**) (0.400 g, 0.81 mmol) in 20 mL of CH_2Cl_2. The mixture was stirred for 15 min, during which time the solution turned yellow. The workup followed as in method A: mp 124–126 °C (sealed capillary); largest *m/e* 504 ($M^+ - BF_4$, ^{98}Mo); $\Lambda_M = 169\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($c = 6.485 \times 10^{-4}$ M); IR (CH_2Cl_2) 2080 s, 2000 vs, 1906 m (ν_{str}(CO)), 1115 s (ν(BF)) cm^{-1}; ^1H NMR (acetone-d_6, −50 °C) δ 6.76 (d, $^4J_{HH} = 1.7$ Hz, $=CH$), 5.78 (m, $MeC_5\mathit{H}_4$), 5.33 (d, $^4J_{HH} = 1.7$ Hz, $-CH_2$), 5.05 (s, $-CH_2$), 2.16, 2.04 (s, $C\mathit{H}_3Cp$); $^{13}C\{^1H\text{-gated}\}$ NMR (acetone-d_6, 25 °C) 229.78, 228.06, 221.14, 218.31 (CO), 118.38 ($=C\overline{\cdot\cdot}$), 112.39, 111.48 (ipso-C), 96.91, 95.83, 95.04, 93.63, 93.30, 92.87, 92.23 ($Me\mathit{C}_5H_4$), 80.77 ($=CH$, $^1J_{CH} = 226.7$ Hz, $^3J_{CH} = 8.8$ Hz), 76.35 ($\overline{\cdot\cdot}CH_2$, $^1J_{CH} = 162.7$ Hz, $^1J_{CH} = 170.1$ Hz), 13.61, 13.45 ($\mathit{C}H_3Cp$, $^1J_{CH} = 129.4$ Hz). Anal. Calcd for $C_{19}H_{17}BF_4Mo_2O_4$: C, 38.81; H, 2.91; F, 12.92. Found: C, 39.12; H, 2.90; F, 12.68.

Preparation of $[Cp'_2(CO)_4Mo_2(CHCCH_2)]_2$ (11). Method A. A suspension of $[Cp'_2(CO)_4Mo_2C_3H_3]BF_4$ (**2**·BF_4) (0.500 g, 0.85 mmol) in 50 mL of THF was slowly added to a solution of Na[$Fe(CO)_2Cp$] (0.170 g, 0.85 mmol) in 30 mL of THF. The solution immediately changed from yellow to red. The solvent was removed in vacuo to yield a red solid. The solid was dissolved in CH_2Cl_2 (15 mL) and the solution filtered to remove $NaBF_4$. The filtrate was evaporated in vacuo and the red solid recrystallized from CH_2Cl_2/CH_3OH (1:1) (0.370 g, 87%). The same reaction was found to occur in benzene. The crystalline solid is soluble in THF, CH_2Cl_2, toluene, and hexane and is spectroscopically identical with the sample prepared by method B below.

Method B. To a 2% Na/Hg amalgam prepared from 31 mg (1.35 mmol) of Na and 13.54 g (67.50 mmol) of Hg was added a solution of 200 mg (0.34 mmol) of **2**·BF_4 in 10 mL of THF. The mixture was stirred at room temperature for 10 min, during which time the reaction mixture turned red. The solution was transferred to another flask by means of a cannula and worked up as described in method A: highest *m/e* 543 $\{[Cp'(CO)_2Mo]_2[CH\equiv CCH_2CH_2C\equiv CH]\}^+$; IR ($C_6H_6$) 1975 s, 1900 vs, br, 1825 s cm^{-1}; IR (KBr) 1980 s, 1920 s, 1900 s, 1820 s cm^{-1}; ^1H NMR (C_6D_6) δ 5.55 (s, $\equiv CH$), 4.96 (m, $MeC_5\mathit{H}_4$), 2.67 (s, $-CH_2-$), 1.84 (s, $C\mathit{H}_3C_5H_4$); ^{13}C NMR (C_6D_6) δ 234.6, 228.8 (CO), 108.0 (ipso-C), 92.1, 91.3 ($Me\mathit{C}_5H_4$), 87.2 ($\equiv CH$, $J = 209.0$ Hz), 59.5 ($\equiv C-$), 39.2 ($-CH_2$, $J = 132.7$ Hz), 14.80 ($\mathit{C}H_3Cp$, $J = 128.2$ Hz). Anal. Calcd for $C_{38}H_{34}Mo_4O_8$: C, 45.52; H, 3.41. Found: C, 45.44; H, 3.49. Needle-shaped crystals of **11** suitable for diffraction were grown from a saturated solution of 11 in a 1:1 mixture of CH_2Cl_2 and methanol.

Reactions of $[Cp'_2(CO)_4Mo_2(C_3H_3)]BF_4$ (2·BF_4) with Nucleophiles. With NaOMe. A solution of NaOMe (0.6 mL, 1.56 M) in methanol was added via syringe to a solution of **2**·BF_4 (0.55 g, 0.85 mmol) in 15 mL of CH_2Cl_2. The solution was stirred for 0.5 h, during which time the solution turned red. The solvent was evaporated in vacuo and the red solid extracted with 10 mL of hot hexane and filtered. The filtrate was cooled to −78 °C precipitating solid $Cp'_2(CO)_4Mo_2(CH\equiv CCH_2OCH_3)$ (**4**).

With *i*-Pr_2NLi. A solution of **2**·BF_4 (0.500 g, 0.85 mmol) in 15 mL of toluene was allowed to react with a hexane solution of *i*-Pr_2NLi (1.73 mL, 0.5 M) at 0 °C. The solution immediately changed from yellow to red. The reaction was stirred for 2 h, and $LiBF_4$ was removed by filtration (Celite). The filtrate was evaporated in vacuo to yield a pure red oil, $Cp'_2(CO)_4Mo_2(CH\equiv CCH_2N(i\text{-}Pr)_2)$: IR (toluene) 1977 s, 1905 vs, 1840 s cm^{-1}; ^1H NMR (acetone-d_6) δ 6.32 (s, $\equiv CH$), 5.45 (m, $MeC_5\mathit{H}_4$), 3.92 (s, $-CH_2$), 3.32 (quintet, $J = 7.0$ Hz, $C\mathit{H}Me_2$), 2.30 (s, $C\mathit{H}_3C_5H_4$), 1.16 (d, $J = 7.0$ Hz, $CHC\mathit{H}_3$).

With Pyridine. A solution of **2**·BF_4 (0.200 g, 0.34 mmol) in 10 mL of CH_2Cl_2 was combined with a solution of pyridine (0.027 g, 0.34 mmol) in 2.7 mL of CH_2Cl_2 at room temperature and stirred for 20 min. Diethyl ether (40 mL) was added to the red solution to precipitate $[Cp'_2(CO)_4Mo_2CH\equiv CCH_2(NC_5H_5)BF_4$ (**6**). The solid was filtered, washed with Et_2O (3 × 3 mL), and dried in vacuo (0.600 g, 72%). The red crystals are soluble in CH_2Cl_2, CH_3CN, and acetone: mp 138–139 °C (sealed capillary); largest *m/e* 504 (M^+ − py − BF_4, ^{98}Mo); IR (CH_2Cl_2) 1963 a, 1924 vs, 1855 s cm^{-1}; ^1H NMR (acetone-d_6) δ 9.0, 8.75, 8.22 (ABB′XX′, NC_5H_5), 6.04 (s, $\equiv C\mathit{H}$), 5.83 (s, $-C\mathit{H}_2$), 5.32 (m, $MeC_5\mathit{H}_4$), 2.07 (s, CH_3Cp); ^{13}C NMR (CD_3CN) δ 232.87, 228.40 (CO), 146.89, 144.74, 129.40 (NC_5H_5), 109.93 (ipso-C), 92.62, 92.43, 92.34, 91.91 ($Me\mathit{C}_5H_4$), 85.23 ($\equiv CH$, $J = 210.5$ Hz), 67.47 ($-CH_2$, $J = 150$ Hz), 52.57 ($\equiv C-$), 14.31 ($\mathit{C}H_3Cp$, $J = 128.3$ Hz). Anal. Calcd for $C_{24}H_{22}BF_4Mo_2NO_4$: C, 43.21; H, 3.32; N, 2.09; Mo, 28.65. Found: C, 43.03; H, 3.34; N, 1.98; Mo, 28.49.

With Dimethylphenylphosphine. Freshly distilled PMe_2Ph (0.564 g, 0.41 mmol) was added to a CH_2Cl_2 (5 mL) solution containing 0.240 g (0.41 mmol) of **2**·BF_4 at room temperature. The solution immediately turned red. After the solution was stirred for 10 min, 10 mL of hexane was slowly added to form a precipitate. The solid was filtered, washed with hexane (2 × 5 mL), and dried in vacuo (0.180 g, 61%). The product $[Cp'_2(CO)_4Mo_2(CH\equiv CCH_2PMe_2Ph)]BF_4$ (**8**) is a pale red crystalline solid soluble in CH_2Cl_2, CH_3CN, and acetone: mp 140–142 °C (sealed capillary); largest *m/e* 641 ($M^+ - BF_4$, ^{98}Mo); $\Lambda_M = 139\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($c = 6.646 \times 10^{-4}$ M); IR (CH_2Cl_2) 1994 s, 1915 vs, 1840 s cm^{-1}; ^1H NMR (acetone-d_6, −60 °C) δ 7.94 (m, Ph), 5.96 (dt, $J_{PH} = 1.9$ Hz, $J_{HH} = 0.7$ Hz, $\equiv CH$), 5.13 (m, $MeC_5\mathit{H}_4$), 4.29 (dd, $J_{PH} = 13.1$ Hz, $J_{HH} = 0.7$ Hz, $-CH_2$), 2.46 (d, $J_{PH} = 14.4$ Hz, $PC\mathit{H}_3$), 2.25 (d, $J_{PH} = 14.3$ Hz, $PC\mathit{H}_3$), 1.81 (s, $C\mathit{H}_3Cp$); ^{13}C NMR (acetone-d_6, −60 °C) δ 235.59, 232.96, 232,74, 224.43 (CO), 135.08, 132.49, 130.29, 120.85 ($J_{PC} = 9.6$, 12.1, 81.8 Hz, Ph), 111.94, 107.19 (ipso-C), 96.64, 94.70, 93.69, 92.99, 92.40, 91.39, 90.67, 88.44 (MeC_5H_4), 85.79 ($J = 212.7$ Hz, $\equiv CH$), 43.68 ($J = 11.9$ Hz, $\equiv C$), 31.39 ($J_{PC} = 39.6$ Hz, $-CH_2$) [in the low-temperature NMR, this signal was obscured by the CD_3CN signal; J and δ were taken from the room temperature spectrum], 14.11, 13.67 ($J = 128$ Hz, $C\mathit{H}_3Cp$), 8.16 ($J_{PC} = 52.1$ Hz, $J_{CH} = 136.5$ Hz, $P\mathit{C}H$), 6.64 ($J_{PC} = 54.10$, $J_{CH} = 136.5$ Hz, $P\mathit{C}H_3$); $^{31}P\{^1H\}$ NMR (acetone-d_6) 40.02 ppm. Anal. Calcd for $C_{27}H_{28}BF_4Mo_2O_4P$: C, 44.53; H, 4.15; F, 10.44. Found: C, 44.42; H, 4.02; F, 10.22.

With Trimethyl Phosphite. A solution of $P(OCH_3)_3$ (0.228 g, 1.84 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **2**·BF_4 (1.08 g, 1.84 mmol) in 25 mL of CH_2Cl_2. The red solution was stirred for 45 min at room temperature. The solution was then concentrated to a volume of 2 mL and chromatographed on Florisil

Table I. Crystal and Data Statistics

	$2\cdot BF_4$	11
chem formula	$C_{19}H_{17}BF_4Mo_2O_4$	$C_{38}H_{34}Mo_4O_8$
a, Å	8.663 (2)	8.897 (2)
b, Å	35.652 (10)	18.643 (11)
C, Å	13.746 (3)	11.457 (4)
β, deg	92.92 (2)	108.72 (2)
V, Å^3	4240 (2)	1800 (1)
Z	8	2
ρ_{obsd}, g cm^{-3}	1.843	
ρ_{calcd}, g cm^{-3}	1.842	1.850
space group	$P2_1/n$	$P2_1/n$
cryst dimens, mm	0.20 × 0.06 × 0.25	0.1 × 0.15 × 0.49
radiatn	Mo Kα (graphite)	Mo Kα (graphite)
abs coeff (μ), cm^{-1}	12.106	13.80
scan speed, deg min^{-1}	2.5–12	2.5–12
scan range	Mo Kα_1 − 0.8 to Mo Kα_2 + 0.8	Mo Kα_1 − 0.8 to Mo Kα_2 + 0.8
bkgd ratio	0.8	0.8
2θ limit, deg	40	45
reflctn collected	4318	2805
reflctns with $I > 3\sigma(I)$	2589	2062
R_1	0.054	0.025
R_2	0.059	0.024
$w = k/(\sigma^2(F_o) + pF_o^2)$ (last cycle)	$p = 0.003$ (refined each cycle, k = scale factor)	$p = 0.001$
largest peak in final diff map, e/Å^3	0.65	0.39

with CH_2Cl_2 as the eluent. Three bands developed. The red one was collected by elution with CH_3CN. After removal of the solvent and drying the red residue for 24 h in vacuo, $Cp'_2(CO)_4Mo_2(CH{\equiv}CCH_2P(O)(OMe)_2)$ (**10**) was obtained in 30% yield (380 mg) as a dark red crystalline solid, soluble in toluene, CH_2Cl_2 and CH_3CN: mp 65–67 °C (sealed capillary); largest m/e 612 (M^+, ^{98}Mo); $\Lambda_M = 5.74\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($c = 1.55 \times 10^{-3}$ M); IR (hexane) 1989 s, 1928 sh, 1915 vs, 1845 s cm^{-1} (ν(CO)); IR (KBr) 1249 m (ν(PO)), 1016 m (P–O–C) cm^{-1}; ^1H NMR (CD_3CN, room temp) 60.2 (dt, $J_{PH} = 2.1$ Hz, $J_{HH} = 0.8$ Hz, $\equiv$CH), 5.25 (m, MeC_5H_4), 3.62 (d, $J_{PH} = 10.8$ Hz, $POCH_3$), 3.11 (dd, $J_{PH} = 18.8$ Hz, $J_{HH} = 0.8$ Hz, $-CH_2$), 2.04 (s, CH_3Cp); ^1H NMR (acetone-d_6, −78 °C) 6.18 ($\equiv$CH), 5.34 (m, MeC_5H_4), 3.62 (t, $J_{PH} = 11.0$ Hz, $POCH_3$), 3.17 (m, $-CH_2$), 2.03, 2.00 (s, CH_3Cp); ^{13}C NMR (CD_3CN) 234, 230 (CO), 109.48 (ipso-C), 93.47, 92.18 (MeC_5H_4), 89.87 ($J = 214.3$ Hz, $\equiv$CH), 52.73 ($J_{PC} = 6.6$ Hz, $J_{CH} = 147.3$ Hz, $POCH_3$), 31.30 ($J_{PC} = 129.1$ Hz, $J_{CH} = 129.1$ Hz, $-CH_2$), 14.36 ($J = 127.9$ Hz, CH_3Cp); $^{31}P\{^1H\}$ NMR (CD_3CN) 29.86 ppm. Anal. Calcd for $C_{21}H_{25}Mo_2O_7P$: C, 41.19; H, 4.11; P, 5.06. Found: C, 41.28; H, 3.98; P, 5.01.

A reptition of the reaction with 500 mg (0.85 mmol) of $\mathbf{2}\cdot BF_4$ and 105 mg (0.85 mmol) of $P(OMe)_3$ in 20 mL of CH_2Cl_2 showed that initially $[Cp'_2(CO)_4Mo_2(CH{\equiv}CCH_2P(OMe)_3)]BF_4$ (**9**) was formed. This compound was isolated as follows: The solution was filtered and 35 mL of Et_2O added very slowly with stirring to the filtrate, yielding a red crystalline precipitate which was separated, washed with 2 × 5 mL portions of hexane, and dried in vacuo: yield 480 mg (80%) of $[Cp'_2(CO)_4Mo_2(CH{\equiv}CCH_2P(OMe)_3)]BF_4$ (**9**), soluble in CH_2Cl_2 and CH_3CN; mp 96–98 °C (sealed capillary); largest m/e 612 ($M^+ - Me - BF_4$, ^{98}Mo); $\Lambda_M = 155\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($c = 7.62 \times 10^{-4}$ M). The product was unstable in solution, so that no satisfactory NMR spectra could be obtained. IR (KBr): 1978 s, 1900 vs, 1824 s cm^{-1}. Anal. Calcd for $C_{22}H_{26}BF_4Mo_2O_7P$: C, 37.10; H, 3.67; P, 4.35; F, 10.67. Found: C, 36.02; H, 3.99; P, 5.22; F, 11.96. Treatment of $[Cp'_2(CO)_4Mo_2(CH{\equiv}CCH_2P(OMe)_3)]BF_4$ in acetone-d_6 with MeI formed $Cp'_2(CO)_4Mo_2(CH{\equiv}CCH_2P(O)(OMe)_2)$ (**10**) as shown by the NMR spectrum.

With *t*-BuNC. A CH_2Cl_2 solution (10 mL) containing 0.770 g (1.31 mmol) of $\mathbf{2}\cdot BF_4$ and 0.545 g (6.55 mmol) t-BuNC was stirred for 24 h at room temperature. The solvent was removed in vacuo to yield a red residue. Diethyl ether (30 mL) was added, and a yellow solid was filtered from the red solution. The solid was washed with Et_2O (3 × 10 mL) and dried in vacuo. The yellow solid has no absorbances assignable to ν_{str}(CO) and no resonances due to Cp′ in the NMR. The red filtrate was taken to dryness, washed with hexane (3 × 5 mL), and dried in vacuo: yield 300 mg (43%) of $Cp'_2(CO)_2Mo_2(CH{\equiv}CCH_2CN)$ (**7**) as a red powder, soluble in toluene, Et_2O, and CH_2Cl_2; mp 86–88 °C (sealed capillary); largest m/e 529 (M^+, ^{98}Mo); IR (hexane) 1996 s, 1933 s, 1920 vs, 1851 s cm^{-1}; ^1H NMR (benzene-d_6) δ 5.24 (t, $J = 0.8$ Hz, $\equiv$CH), 4.79 (m, MeC_5H_4), 3.01 (d, $J = 0.8$ Hz, $-CH_2$), 1.70 (s, CH_3Cp); ^{13}C NMR (acetone-d_6) δ 233.28, 229.09 (CO), 120.00 ($C{\equiv}N$), 109.46 (ipso-C), 92.99, 92.76, 91.98, 91.78 (MeC_5H_5), 88.40 ($\equiv$C—), 86.69 ($J = 209.2$ Hz, $\equiv$CH), 24.64 ($J = 138.0$ Hz, $-CH_2$), 14.33 ($J = 128.3$ Hz, CH_3Cp). Anal. Calcd for $C_{20}H_{17}Mo_2NO_4$: C, 45.56; H, 3.25; N, 2.65. Found: C, 45.38; H, 3.49; N, 2.73.

With NaCN. Purified 15-crown-5 (0.131 g, 0.60 mmol) was added to a solution of $\mathbf{2}\cdot BF_4$ (0.350 g, 0.60 mmol) in 10 mL of CH_2Cl_2, followed by addition of 0.030 g (0.61 mmol) of NaCN at room temperature. The mixture was stirred for 2 days at room temperature, during which time the NaCN gradually dissolved. The reaction mixture was poured into a separatory funnel containing 15 mL of H_2O and 10 mL of CH_2Cl_2. The organic layer was collected and the water layer washed with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$. The solution was concentrated to a volume of 2 mL and chromatographed on Al_2O_3 with CH_2Cl_2 as the eluent. Evaporation of the solvent in vacuo gave a product identical with that formed from the reaction of $\mathbf{2}\cdot BF_4$ with t-BuNC as described above.

Structure Determination of $\mathbf{2}\cdot BF_4$. Crystals of $\mathbf{2}\cdot BF_4$ were grown from CH_2Cl_2/Et_2O at room temperature. A crystal was mounted on a Syntex $P2_1$ diffractometer (see Table I for relevant statistics). Initial rotation photographs and counter data indicated that crystal to be monoclinic, space group $P2_1/n$ (No. 14),[15] and the measured density gave $Z = 8$. Thus, there are two independent molecules in the asymmetric unit. The positions of the four Mo atoms were obtained by MULTAN-78.[16] All other non-hydrogen atoms were located in subsequent different Fourier maps. Refinement of all positional and isotropic parameters (full matrix) leads to convergence at $R = 0.103$. The two BF_4^- anions were found to be disordered. A suitable model of the BF_4 disorder is represented by intermeshing two tetrahedrons with the same central boron. The occupancy factors for the fluorines were set to 0.7 and 0.3 for one BF_4^- and to 0.6 and 0.4 for the other. A refinement was carried out in which x, y, z, U, and the occupancy factor were allowed to vary. This model refined satisfactorily. A full-matrix refinement in blocks on 59 atoms with anisotropic

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(15) *The International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2 and Table 2.3.1.

(16) Computations were carried out on an Amdahl 5860 computer. Computer programs used during the structural analysis were from the SHELX program package by George Sheldrick, Institute fur Anorganische Chemie der Universitate Gottingen, Federal Republic of Germany. Other programs used include ORTEP, a thermal ellipsoidal drawing program by C. K. Johnson, and the direct methods program MULTAN78 by P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson.

temperature factors, one C atom (C32) isotropic, and both BF_4 groups isotropic gave the final R values shown in Table I. The occupancy factors for the fluorine atoms converged to 0.48, 0.52 and 0.53, 0.47 for the two BF_4^-, respectively. The anisotropic temperature factors for C32 would not refine properly (went nonpositive definite) so C32 was refined isotropically.

Structure Determination of 11. Single crystals of **11** were grown from a methylene chloride/methanol solution and mounted on a Syntex $P2_1$ diffractometer. Table I contains a summary of data collection conditions and results. Lattice parameters were determined from a least-squares refinement of 15 reflection settings obtained from an automatic centering routine.

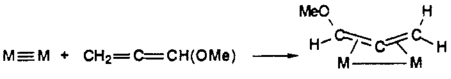
Intensity data were obtained by using Mo Kα radiation monochromatized from a graphite crystal whose diffraction vector was in the same plane as the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The data were reduced by procedures previously described.[16] An absorption correction was unnecessary.

The structure was solved by using MULTAN.[16] In the subsequent refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were used to evaluate the results. The atomic scattering factors are from ref 15. Hydrogen positions were located from a difference Fourier map and their positions refined. All hydrogens were given fixed U values (isotropic temperature factors) of 0.05.

Figure 2 shows the structure of **11**. Final positional parameters with estimated standard deviations are shown in Table IV. Anisotropic thermal parameters with their estimated standard deviations are available in the supplementary material. Table V lists the crystallographically determined bond distances and angles. Listings of observed and calculated structure factor amplitudes are available as supplementary material.

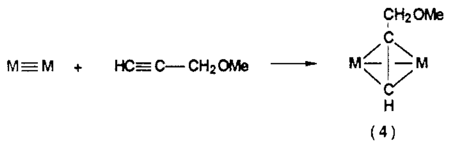
Results and Discussion

Our synthetic strategy for forming the hydrogen-poor, carbon-rich C_3H_2 fragment involved the removal of the elements HX from a C_3H_3X ligand. Two C_3H_3X ligands were chosen: methoxyallene, $CH_2{=}C{=}CH(OMe)$, and methyl propargyl ether, $HC{\equiv}CCH_2OMe$. These ligands readily formed adducts with $Cp'_2Mo_2(CO)_4$ (**1'**, Cp' = C_5H_4Me) according to eq 1 and 2, respectively (M = Mo$(CO)_2$Cp').



(3)

(1)



(4)

(2)

The allene adduct **3** is a deep red, crystalline solid and has spectral properties similar to those of the known compound $Cp_2Mo_2(CO)_4(H_2C{=}C{=}CHMe)$.[3] Five absorptions are observed in the range 2000–1800 cm^{-1} in the IR spectrum of **3**. There is a maximum of four ν_{CO} bands for **3** if only one isomer is present in solution, as is indicated by the NMR spectrum of **3**. Therefore, one of the bands may be tentatively assigned to a ν_{CCC} mode of the coordinated allene, but in the absence of isotopic labeling, a definite assignment cannot be made. The $^{13}C\{^1H\}$NMR spectrum of **3** reveals four carbonyl resonances at room temperature. Four ^{13}CO resonances were also observed in the spectra of $Cp_2(CO)_4Mo_2(HRC{=}C{=}CR'H)$ when the allene ligand was unsymmetric (R ≠ R').[3]

Spectroscopic data for **4** suggest a tetrahedrane structure as shown in eq 2. Four absorption bands assigned to ν_{CO}, in the 2000–1800 cm^{-1} region, are observed in the solution infrared spectrum of **4**. The lowest frequency band (1864 cm^{-1}) has been attributed to a semibridging carbonyl ligand.[2b] At room temperature, the ^1H NMR spectrum displays a singlet for the two sets of methyl protons on the methylcyclopentadienyl ligands, an observation consistent with the known fluxionality of this type of complex.[2]

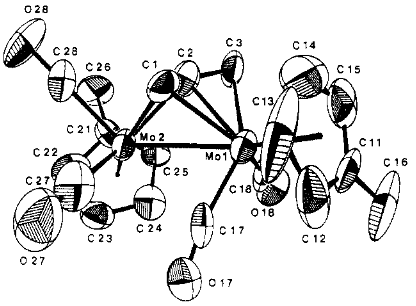
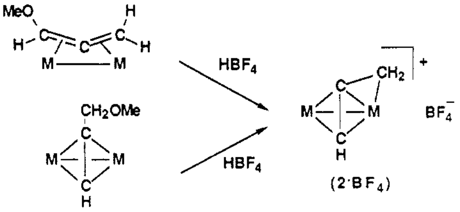


Figure 1. ORTEP plot of the cation $M_2(\mu\text{-}\eta^2,\eta^3\text{-}HCCCH_2)$ (**2**, M = $Mo(CO)_2Cp'$).

Complexes **3** and **4** both react with $HBF_4{\cdot}OEt_2$ to give the same product: a $(\mu\text{-}\eta^2,\eta^3\text{-}$allenyl)dimolybdenum cation (**2**) resulting from loss of methanol from the parent compounds (eq 3).



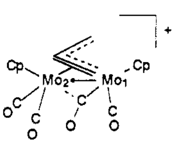
(2·BF4)

(3)

The composition of **2**·BF_4 is supported by elemental analysis ^1H NMR, ^{13}C NMR, and infrared spectroscopies, mass spectroscopy, and conductivity measurements. The structure was verified by single-crystal X-ray diffraction analysis, the results of which are presented in Figure 1 and in Tables I–III. The Cp-containing analogues of **2**-BF_4 have been prepared (but not characterized) previously.[17]

The key features to emerge from the crystal structure determination are (a) a Mo1–Mo2 distance of 3.015 ± 0.003 Å, (average for the two independent molecules) consistent with a single bond, (b) a semibridging carbonyl group of the charge-accepting type, and (c) all carbon atoms of the C_3H_3 linkage are bound to molybdenum: C1 and C2 are attached to both Mo1 and Mo2, whereas C3 interacts with Mo1 exclusively.

Complex **2** can be regarded as a cationic $\mu\text{-}\eta^2,\eta^3$-allenyl complex. In this model, the bonding of the three carbon atoms to Mo1 resembles that in a π-allyl complex (Figure 1). The second, orthogonal π-component of the C1–C2 bond in the allenyl fragment is available for bonding to Mo2:



A

If each Mo is assigned a formal 2+ oxidation state, this model requires a formal dative bond from Mo1 to Mo2 to attain an 18e count at each metal atom. The dative bond places more negative charge on Mo2. The observation of a charge-accepting, semibriding CO interaction with Mo2

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[17] Sokolov, V. I.; Barinov, I. V.; Reutov, O. A. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1992.

Table II. Fractional Atomic Coordinates for 2•BF_4

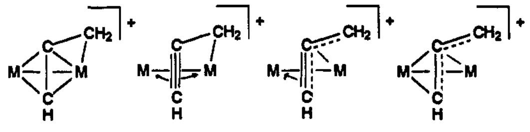
atom	*x*	*y*	*z*	*U*, Å^2
Mo1	0.1447 (2)	0.5912 (1)	0.0924 (1)	0.0496
Mo2	0.3769 (2)	0.6419 (0)	0.1962 (1)	0.0503
C1	0.3933 (18)	0.5883 (5)	0.1280 (13)	0.0602
C2	0.3789 (20)	0.6139 (5)	0.0559 (15)	0.0645
C3	0.3077 (20)	0.6173 (6)	−0.0329 (13)	0.0726
C11	−0.0618 (20)	0.5531 (5)	0.0419 (20)	0.0655
C12	−0.0105 (37)	0.5413 (7)	0.1334 (17)	0.1007
C13	0.1408 (40)	0.5291 (7)	0.1216 (35)	0.1535
C14	0.1714 (41)	0.5328 (8)	0.0260 (32)	0.1227
C15	0.0498 (39)	0.5492 (7)	−0.0268 (16)	0.0897
C16	−0.2203 (30)	0.5673 (8)	0.0062 (25)	0.1687
C17	0.0867 (20)	0.6092 (5)	0.2177 (14)	0.0557
O17	0.0316 (16)	0.6158 (4)	0.2926 (10)	0.0911
C18	0.0237 (22)	0.6346 (6)	0.0437 (13)	0.0700
O18	−0.0506 (16)	0.6601 (4)	0.0140 (11)	0.0905
C21	0.4595 (23)	0.7035 (5)	0.1566 (13)	0.0624
C22	0.4534 (23)	0.6987 (5)	0.2631 (16)	0.0776
C23	0.2968 (23)	0.6935 (5)	0.2905 (13)	0.0679
C24	0.2060 (23)	0.6925 (5)	0.2004 (16)	0.0726
C25	0.2977 (22)	0.6982 (4)	0.1182 (13)	0.0579
C26	0.5971 (24)	0.7126 (6)	0.1052 (15)	0.0955
C27	0.3773 (24)	0.6106 (6)	0.3142 (16)	0.0810
O27	0.3711 (17)	0.5917 (5)	0.3839 (11)	0.1151
C28	0.6054 (26)	0.6336 (5)	0.2038 (13)	0.0717
O28	0.7337 (18)	0.6299 (6)	0.2064 (13)	0.1521
Mo3	−0.0769 (2)	0.5965 (0)	0.5911 (1)	0.0495
Mo4	−0.2591 (2)	0.6545 (0)	0.6972 (1)	0.0478
C4	−0.2073 (21)	0.5969 (5)	0.7289 (11)	0.0553
C5	−0.0791 (22)	0.6188 (5)	0.7471 (10)	0.0506
C6	0.0844 (21)	0.6161 (5)	0.7354 (11)	0.0586
C31	−0.1638 (40)	0.5454 (9)	0.5035 (32)	0.1401
C32	−0.0197 (53)	0.5576 (7)	0.4722 (20)	0.0378
C33	0.0930 (25)	0.5499 (8)	0.5484 (38)	0.1472
C34	0.0145 (53)	0.5365 (7)	0.6235 (21)	0.1121
C35	−0.1323 (44)	0.5322 (6)	0.5971 (37)	0.1349
C36	−0.3336 (35)	0.5374 (8)	0.4718 (34)	0.2400
C37	0.0562 (22)	0.6380 (5)	0.5406 (12)	0.0534
O37	0.1354 (16)	0.6595 (4)	0.5091 (10)	0.0868
C38	−0.2365 (20)	0.6226 (4)	0.5102 (12)	0.0533
O38	−0.3189 (16)	0.6345 (4)	0.4478 (9)	0.0878
C41	−0.3467 (20)	0.7107 (4)	0.6242 (14)	0.0559
C42	−0.1950 (21)	0.7040 (4)	0.5904 (13)	0.0602
C43	−0.0923 (22)	0.7032 (5)	0.6802 (14)	0.0650
C44	−0.1772 (24)	0.7107 (5)	0.7629 (13)	0.0700
C45	−0.3320 (23)	0.7151 (4)	0.7269 (15)	0.0636
C46	−0.4821 (24)	0.7165 (5)	0.5555 (14)	0.0779
C47	−0.4634 (24)	0.6315 (5)	0.6515 (15)	0.0731
D47	−0.5777 (17)	0.6192 (4)	0.6256 (11)	0.0994
C48	−0.3368 (19)	0.6478 (5)	0.8301 (13)	0.0589
D48	−0.3735 (16)	0.6450 (4)	0.9071 (10)	0.0923
B1	0.2243 (35)	0.2274 (9)	0.6588 (21)	0.0295
F11	0.2319 (28)	0.2215 (10)	0.7521 (19)	0.0315
F12	0.1240 (38)	0.2036 (12)	0.6147 (21)	0.0425
F13	0.2186 (46)	0.2650 (11)	0.6466 (34)	0.0567
F14	0.3551 (31)	0.2103 (11)	0.6120 (18)	0.0364
F11′	0.1984 (53)	0.2563 (14)	0.7060 (43)	0.0642
F12′	0.3501 (34)	0.2341 (11)	0.6168 (19)	0.0368
F13′	0.2235 (34)	0.1982 (12)	0.7334 (22)	0.0410
F14′	0.0845 (27)	0.2247 (8)	0.6012 (15)	0.0240
B2	0.5656 (70)	0.4810 (19)	0.2202 (41)	0.0559
F21	0.7094 (38)	0.4703 (10)	0.2098 (20)	0.0444
F22	0.6250 (50)	0.5151 (13)	0.2401 (33)	0.0640
F23	0.5216 (39)	0.4888 (10)	0.1148 (26)	0.0520
F24	0.4393 (46)	0.4877 (10)	0.2482 (26)	0.0556
F21′	0.6300 (73)	0.4451 (17)	0.2126 (37)	0.0743
F22′	0.5482 (59)	0.4656 (15)	0.3093 (39)	0.0749
F23′	0.4597 (62)	0.4545 (17)	0.1734 (38)	0.0769
F24′	0.5661 (76)	0.5108 (18)	0.1703 (50)	0.0827

is consistent with this interpretation. However, the metrical parameters associated with the semibridging carbonyl suggest that its interaction with Mo2 is very weak,[18] and the lack of a ν_{CO} band below 1900 cm^{-1}, typical of semibridging carbonyls, also suggests a very weak interaction. Formation of the bonds to Mo2 causes the C1–C2–C3 angle in 2 to open up to 139° compared to 120° in unstrained η^3-allyl complexes.[19] This large angle is indicative of the sp-hybrid character made to the electronic structure by the resonance extreme (II) shown below.

Table III. Selected Bond Distances (Å) and Angles (deg) in the Two Independent Molecules of 2•BF_4[a]

	molecule 1	molecule 2
Bond Distances (Å)		
Mo1–Mo2	3.01 (1)	3.02 (1)
Mo1–C1	2.19 (2)	2.26 (2)
Mo1–C2	2.27 (2)	2.29 (2)
Mo1–C3	2.47 (2)	2.47 (2)
Mo1–C17	1.93 (2)	1.96 (2)
Mo1–C18	1.97 (2)	2.02 (2)
Mo1–C(Cp′ av)	2.3 [4]	2.3 [4]
Mo2–C1	2.14 (2)	2.14 (2)
Mo2–C2	2.17 (2)	2.10 (2)
Mo2–C27	1.97 (2)	2.02 (2)
Mo2–C28	2.00 (2)	1.99 (2)
Mo2–C(Cp′ av)	2.4 [6]	2.3 [4]
C1–C2	1.35 (3)	1.37 (3)
C2–C3	1.35 (3)	1.44 (3)
C17–O17	1.18 (2)	1.13 (2)
C18–O18	1.18 (2)	1.17 (2)
C27–O27	1.17 (3)	1.12 (3)
C28–O28	1.12 (3)	1.12 (3)
B–F (av)	1.4 [9]	1.3 [10]
Bond Angles (deg)		
Mo2–Mo1–C1	45.2 (5)	45.1 (4)
Mo2–Mo1–C2	46.0 (5)	44.0 (4)
Mo2–Mo1–C3	73.2 (4)	73.0 (4)
Mo1–Mo2–C1	46.6 (4)	48.2 (4)
Mo1–Mo2–C2	48.6 (5)	49.1 (4)
Mo1–C1–Mo2	88.2 (6)	86.7 (6)
Mo1–C2–Mo2	85.4 (7)	86.9 (5)
Mo1–C3–C2	65.0 (10)	65.7 (8)
Mo1–C1–C2	76.0 (10)	74.0 (10)
Mo2–C1–C2	73.0 (10)	70.0 (10)
C1–C2–C3	139 (2)	137 (2)
Mo1–C17–O17	169 (2)	167 (2)
Mo1–C18–O18	179 (2)	176 (2)
Mo2–C27–O27	177 (2)	179 (2)
Mo2–C28–O28	178 (2)	176 (2)
Mo2–Mo1–C17	64.9 (5)	65.1 (5)
F–B–F(av)	109 (2)	106 (3)

[a] In this table, the atom numbering scheme for molecule 2 has been transposed to follow that of molecule 1 to facilitate comparison.



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Further support for formulating the bonding of the C_3H_3 ligand in 2 as an unsymmetric π-allylic interaction comes from a comparison of the bond lengths determined in 2 (averaged for the two crystallographically independent molecules), Mo1–C1 = 2.22 (2) Å, Mo1–C2 = 2.28 (2) Å, and Mo1–C3 = 2.47 (3) Å, with the bridging alkylidene complex $[Cp_2(CO)_4Mo_2(\mu\text{-}C(C_6H_4CH_3)_2)]$,[5b,20] the η^3-benzyl complex $Cp(CO)_2Mo(CH_2C_6H_4CH_3)$,[21] the η^3-allyl complex

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[18] (a) Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034. (b) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096. (c) Horwitz, D. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

[19] Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227 and references therein.

[20] Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789.

[21] (a) King, R. B.; Fronzaglia, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 709. (b) Cotton, F. A.; LaPrade, M. D. *Ibid.* **1968**, *90*, 5418.

$Cp(CO)_2Mo(C_3H_5)$,[19] and the μ-vinyl complex $[Cp_2Mo_2(CO)_4(\mu\text{-}CHCHPh)(H_2)^+][BF_4^-]$.[2d] The Mo2–C1 and Mo2–C2 distances, both 2.14 (3) Å, are in the range expected for sp^2 C–Mo bonds.[22]

In solution, **2** is fluxional on the ^1H NMR time scale ($\Delta G^{\ddagger}$ = 16.9 kcal/mol at 338 K). At –60 °C, the spectrum of **2** is consistent with the solid-state structure and consists of two singlets (CH_3), two overlapping sets of ABCD multiplets ($C_5H_4CH_3$), two sets of doublets (H_c and H_a), and a singlet (H_b) (see below). The difference in coupling constants ($^4J_{HH}$) observed between the methylene protons and the methine proton may be geometry related, much like the dependence of $^3J_{HH}$ of vicinal protons on the dihedral angle.[23] At higher temperatures, the signals for $-CH_3$ and $C_5H_4CH_3$ broaden and coalesce. The $-CH_3$ resonances appear as a single, sharp line at 75 °C. The lines due to the $CHCCH_2$ protons (H_a, H_b, H_c) do not alter their shape or position with temperature.

The observed temperature dependence of the ^1H NMR spectra may be rationalized by the dynamical process shown below which interconverts enantiomers **2a** and **2b** via intermediate **2c** (Scheme I). In this scheme, the plane of the $CHCCH_2$ group in **2c** is perpendicular to the Mo–Mo bond. The proposed process time averages the $C_5H_4CH_3$ groups but not the methylenic (H_a and H_b) protons.

The variable-temperature ^{13}C NMR spectra are also consistent with this proposed fluxional process. At 25 °C, four carbonyl resonances are observed which collapse to two singlets at elevated temperature. Similarly, ten resonances are observed for the $C_5H_4CH_3$ carbon atoms at 25 °C (nine reported due to apparent overlap at 95.83 ppm) which coalesce to five peaks at elevated temperature. This behavior is similar to the high-energy fluxional process proposed for acetylene adducts, $M_2(\mu\text{-}RCCR)$,[2b] and μ-vinyl complexes, $M_2(\mu\text{-}CH{=}CHR)$.[2d,24]

The $^{13}C\{^1H\}$ NMR chemical shifts of the carbon atoms in the complexed C_3 fragment show interesting variations among compounds **2**, **3**, and **4**. If we label the carbons in the CH_3O-containing ligands as α, β, and γ (α being the carbon bearing the methoxide), then Cα of **4** becomes C3 (i.e. $-CH_2$) in **2** upon loss of CH_3OH, but Cγ of **3** is transformed into C3 in **2**. The list of corresponding carbons and their chemical shifts is

3		2		4
38 (Cγ)	→	76 (C3)	←	76 (Cα)
176 (Cβ)	→	118 (C2)	←	56 (Cβ)
101 (Cα)	→	81 (C1)	←	86 (Cγ)

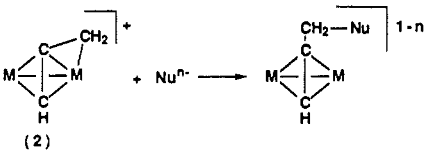
It can be seen that the chemical shift of C2 (**2**) is near the average (116 ppm) of the Cβ's of **3** and **4**. The chemical shift of C1 (**2**) is very near to Cγ of **4**, and both are considerably shielded with respect to Cα of **3**. Finally Cγ (**3**) is deshielded by 38 ppm upon formation of the cation.

Insofar as these ^{13}C chemical shifts can be correlated with charge density, it would appear that the positive charge is transferred from Cα to Cγ when the methoxyallyl complex **3** is converted into the cation **2** and that the charge distribution in **2** more closely resembles that in **4** than in **3**. The pattern of ^{13}C NMR chemical shifts observed here is very similar to that observed in $Co_2(CO)_6(\mu\text{-}RCC\text{-}CRR')^+$ cations.[25]

A comparison of the ^{13}C chemical shifts of the C_3H_3 fragment in **2** with π-allyl complexes is also useful in describing the bonding mode of the hydrocarbyl ligand. The chemical shifts of terminal carbons of unsubstituted π-allyl ligands typically fall in the range δ 40–55 and those of the central carbons in the range δ 90–115.[26] In particular, the terminal carbons of $Mo(\pi\text{-}allyl)_4$ resonate at δ 48.8 and 66.4 and the central carbon resonates at δ 102.9.[26] The chemical shifts of C_1, C_2, and C_3 in **2**, 81, 118, and 76 ppm, respectively, are thus similar to those of π-allyl complexes. The resonance for C1 (81 ppm) also falls in the range observed for molybdenum alkyne complexes, $M_2(\mu\text{-}RCCR)$.[1,2]

The $^1J_{CH}$ coupling constants are also helpful in assessing the hybridization state of the carbon atoms in the bridging hydrocarbyl ligand. The $^1J_{CH}$ coupling constants for the CH_2 bonds in **2** are 163 and 170 Hz, values similar to those in π-allyl complexes.[26] The value of $^1J_{CH}$ for the methine group (CH) in **2** is 227 Hz, however. This large value may be compared to the values of 250 Hz in C_2H_2[27] and 216 Hz in $M_2(\mu\text{-}HCCH)$.[2b] Thus, C1 in **2** appears to have a hybridization state very similar to that in μ-alkyne adducts. All these data are consistent with the formulation of the bonding as depicted above, with some positive charge localized on the CH_2 group.

The observed reactivity of the cation **2** with a variety of nucleophiles is entirely consistent with the proposed electronic structure of the complex. In all cases in which adducts were formed, the nucleophile displaced the C_3–Mo bond and formed substituted alkyne adducts according to eq 4. No evidence for nucleophilic attack at C_1 or C_2 was observed. In this respect, the reactivity of **2** resembles that of the cobalt-stabilized cations $Co_2(CO)_6(\mu\text{-}RCCCRR')^+$.[25,28,29]



(4)

An EHMO analysis has shown that nucleophilic attack on metal π-allyl complexes is frontier orbital controlled and that the usual model of attack is at a terminal carbon of the π-allyl.[30] The regioselectivity shown in eq 4 is undoubtedly determined not only by the preference for attack on a terminal carbon but also by the stability of the μ-alkyne adduct formed when the nucleophile attacks C_3.

The μ-alkyne adducts formed from **2** and various nucleophiles are listed in Table VI. Further physical characterization data of the complexes are found in the Experimental Section. The phosphite adduct **9** underwent the Michaelis–Arbuzov rearrangement[31] on attempted chromatography on silica gel. This rearrangement to complex **10** was also readily induced by the addition of MeI to a solution of **9**. The reaction of **2** with $[Bu_4N]Br$ or MeLi led to intractable mixtures of products.

The C_3H_3 ligand in **2** is extremely resistant to deprotonation. The cation **2** failed to react with "proton sponge" (1,8-bis(dimethylamino)naphthalene), and the hindered base $i\text{-}Pr_2N^-$ underwent simple nucleophilic addition.

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[22] Lupan, S.; Kapon, M.; Cais, M.; Herbstein, F. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1025.

[23] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; p 209.

[24] Beck, J. A.; Knox, S. A. R.; Riding, G. H.; Taylor, G. E.; Winter, M. J. *J. Organomet. Chem.* **1980**, *202*, C49.

[25] Pradmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23.

[26] Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257–304.

[27] Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980; p 376.

[28] Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.

[29] Nicholas, K. M.; Pettit, R. *J. Organomet. Chem.* **1972**, *44*, C21.

[30] Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

[31] Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976; p 117.

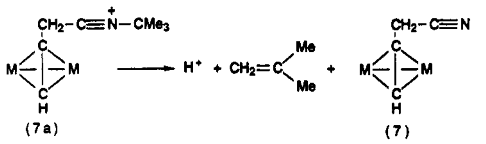
Table IV. Fractional Atomic Coordinates for 11

atom	x	y	z	U, Å^2
Mo1	−0.08754 (4)	0.11664 (2)	0.71713 (3)	0.0215
Mo2	0.17900 (4)	0.18866 (2)	0.65900 (3)	0.0244
C1	−0.2913 (6)	0.0949 (2)	0.5865 (5)	0.0357
O1	−0.4102 (4)	0.0836 (2)	0.5128 (4)	0.0596
C2	−0.1751 (5)	0.2155 (2)	0.7032 (4)	0.0314
O2	−0.2264 (5)	0.2723 (2)	0.6981 (3)	0.0546
C3	0.1604 (6)	0.2181 (3)	0.8185 (5)	0.0376
O3	0.1659 (5)	0.2446 (2)	0.9114 (3)	0.0642
C4	0.3140 (6)	0.1085 (3)	0.7376 (5)	0.0394
O4	0.3945 (5)	0.0606 (2)	0.7818 (4)	0.0647
C5	−0.0421 (5)	0.1469 (2)	0.5459 (4)	0.0249
C6	0.0442 (5)	0.0884 (2)	0.5908 (4)	0.0236
C7	0.0759 (5)	0.0188 (2)	0.5384 (5)	0.0308
C8	−0.2556 (12)	−0.0481 (4)	0.7441 (7)	0.0807
C9	−0.1447 (6)	0.0109 (2)	0.8072 (4)	0.0402
C10	−0.1873 (6)	0.0717 (3)	0.8652 (4)	0.0433
C11	−0.0479 (7)	0.1094 (3)	0.9260 (4)	0.0417
C12	0.0802 (6)	0.0731 (3)	0.9079 (4)	0.0423
C13	0.0197 (7)	0.0131 (3)	0.8334 (5)	0.0457
C14	0.1079 (11)	0.3722 (3)	0.6532 (9)	0.0983
C15	0.1871 (6)	0.3129 (2)	0.6083 (5)	0.0410
C16	0.3422 (6)	0.2874 (3)	0.6656 (5)	0.0452
C17	0.3731 (8)	0.2350 (3)	0.5869 (8)	0.0746
C18	0.2410 (10)	0.2275 (3)	0.4854 (6)	0.0755
C19	0.1265 (8)	0.2750 (3)	0.4976 (5)	0.0518

Table V. Selected Bond Distances (Å) and Angles (deg) for 11

Bond Distances			
Mo1–Mo2	2.981 (1)	Mo2–C3	1.965 (5)
Mo1–C5	2.200 (4)	Mo2–C4	1.947 (5)
Mo1–C6	2.198 (4)	C1–O1	1.141 (5)
Mo2–C5	2.126 (4)	C2–O2	1.146 (5)
Mo2–C6	2.222 (4)	C3–O3	1.160 (6)
C5–C6	1.337 (6)	C4–O4	1.156 (6)
C6–C7	1.495 (6)	Mo1–C(Cp′ av)	2.34 [1]
C7–C7′	1.520 (8)	Mo2–C(Cp′ av)	2.35 [1]
Mo1–C1	1.987 (5)		
Mo1–C2	1.987 (5)		
Bond Angles (deg)			
C5–Mo1–C6	35.4 (2)	C5–C6–C7	135.4 (4)
C5–Mo2–C6	35.7 (2)	Mo1–C1–O1	178.3 (4)
Mo1–C5–Mo2	87.1 (2)	Mo1–C2–O2	178.2 (4)
Mo1–C6–Mo2	84.8 (1)	Mo2–C3–O3	168.7 (4)
Mo1–C5–C6	72.2 (2)	Mo2–C4–O4	178.5 (5)
Mo1–C6–C5	72.4 (2)	Mo1–Mo2–C3	66.9 (1)
Mo2–C5–C6	76.1 (3)		
Mo2–C6–C5	68.2 (3)		

The reaction of **2** with *t*-BuNC gave the cyanide adduct **7**. Presumably, the isocyanide coordinates to form the adduct **7a**, which loses isobutene and H$^+$ (eq 5).


(5)

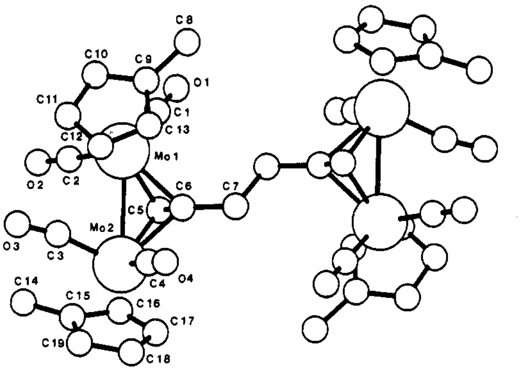
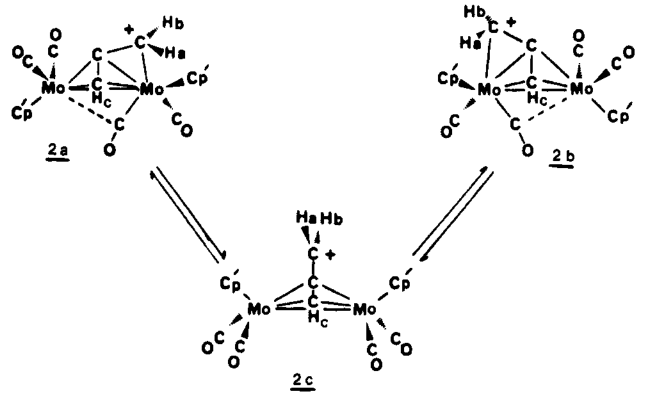
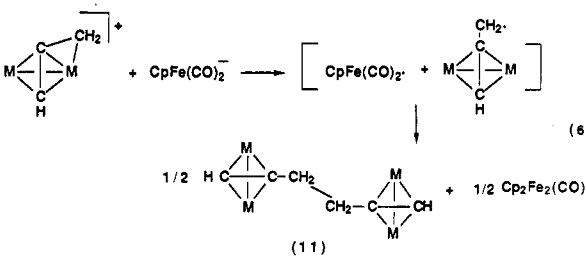


Figure 2. PLUTO drawing of the structure of the dimer **11**.

Scheme I



We were especially interested in the reactions of **2** with metal carbonyl anions since the resulting metal-substituted alkyne complexes could be precursors to interesting bimetallic clusters. However, $Co(CO)_4^-$ reacted with **2** to give a complex mixture of products, while $CpFe(CO)_2^-$ reacted in a redox manner according to eq 6. Complex **11** was also obtained by reduction of **2** with sodium amalgam.


(6)

The structure of complex **11** was established by a single-crystal X-ray determination. The dimer **11** lies on an inversion center in the solid state so the two halves of the molecule are identical. Figure 2 is a PLUTO drawing of the molecule. Atomic coordinates and selected bond distances and angles for **11** are in Tables IV and V, respectively.

The bond distances in the M_2C_2 core are virtually identical with those obtained in previous studies of $M_2(\mu\text{-}RCCR')$ complexes.[2b,c] The Mo–Mo distance 2.981 (1) Å is indicative of a Mo–Mo single bond. Three of the Mo–C (alkyne) distances are close to 2.2 Å, while the fourth is shorter, 2.126 (4) Å. Similar distortions have been noted

Table VI. Reactions of 2 with Various Nucleophiles (M = $(\eta\text{-}CH_3C_5H_4)(CO)_2Mo$)

	nucleophile	conditns	product (selected phys consts)
1	MeO^-	$MeOH/CH_2Cl_2$, 25 °C, 30 min	$M_2(\mu\text{-}HC{\equiv}CCH_2OMe)$ (**4**)
2	*i*-Pr_2NLi	toluene, 0 °C, 5 min	$M_2(\mu\text{-}HC{\equiv}CCH_2N\text{-}i\text{-}Pr_2)$ (**5**)
3	C_5H_5N	CH_2Cl_2, 0 °C, 5 min, 72%	$[\mu_2(\mu\text{-}HC{\equiv}CCH_2NC_5H_5)]BF_4$ (**6**) (mp 138–139 °C)
4	CN^-	NaCN, [15]-crown-5, CH_2Cl_2, 2 days, 68%	$M_2(\mu\text{-}HC{\equiv}CCH_2CN)$ (**7**) (mp 86–88 °C; $\delta(^{13}CN)$ 120)
5	*t*-BuNC (5 equiv)	CH_2Cl_2, 25 °C, 3 h	**7** (as above)
6	$PhMe_2P$	CH_2Cl_2, 25 °C, 10 min, 61%	$[M_2(HC{\equiv}CCH_2PMe_2Ph)]BF_4$ (**8**) (mp 140–142 °C; Λ = 139 Ω^{-1} cm^2 mol^{-1}; $\delta(^{31}P)$ 40.0)
7	$P(OMe)_3$	CH_2Cl_2, 25 °C, 5 min	$[M_2(HC{\equiv}CCH_2P(OMe)_3)]BF_4$ (**9**) (mp 96–98 °C, Λ = 155 Ω^{-1} cm^2 mol^{-1}; $\delta(^{31}P)$ 96.5)
8	**9**	[MeI] or SiO_2	$M_2(CH{\equiv}CCH_2P(O)(OMe)_2)$ (**10**) (mp 65–67 °C; Λ = 5.7 Ω^{-1} cm^2 mol^{-1}; $\delta(^{31}P)$ 29.6)

previously and have been ascribed to steric crowding in the M_2C_2 core.[2b] The C5–C6–C7 angle 135.4 (4)° is consistent with a change in the hybridization of the alkyne carbons from sp toward sp^2 as a result of bonding to the metal atoms. It is interesting to note that this angle is close to the central C–C–C angle (139°) in cation **2**. The low-frequency IR band at 1820 cm^{-1} observed for **11** shows that the semibridging carbonyl (C3–O3) is maintained in solution.

^1H and ^{13}C NMR of **11** demonstrate that complex **11** is fluxional as are all the μ-alkyne adducts of **1** investigated to date.[2] At room temperature, all four Cp′ environments are identical, and the eight carbonyls give rise to only two ^{13}C NMR resonances. Similar behavior has been noted previously for $M_2(\mu\text{-RC}{\equiv}\text{CR}')$ adducts ($R \neq R'$).[2]

Further investigations of carbon-rich hydrocarbyl ligands are in progress.

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Supplementary Material Available: Tables of thermal parameters and complete bond distances and angles (8 pages); lists of F_o vs. F_c for 2·BF_4 and 11 (21 pages). Ordering information is given on any current masthead page.

Organometallic Compounds. 41.[1]
[2]Metacyclo[2](1,1′)ferrocenophane

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[2]Metacyclo[2](1,1′)ferrocenophane (1), a standard organometallic system, was synthesized, and its crystal structure was determined by X-ray diffraction. Compound 1 crystallizes in the monoclinic system, space group $P2_1/a$, with unit-cell parameters $a = 17.547$ (9) Å, $b = 5.914$ (3) Å, $c = 14.499$ (7) Å, $\beta = 92.3$ (5)°, and $Z = 4$. The bond lengths and angles of the aromatic rings and methylene chains are normal. However, the two cyclopentadienyl (Cp) rings are tilted (dihedral angle 9.0°), and the bridge-carbon atoms linked directly to the Cp rings deviate considerably from the planes of the Cp rings (0.288 (9), 0.151 (9) Å) in the direction opposite to the iron atom. The benzene ring is situated to the side of the ferrocene nucleus, and the 9-hydrogen atom of the benzene ring is close to the iron atom of the ferrocene. The 9-proton signal in the ^1H NMR spectrum appears unusually downfield (δ 8.80) due to an anisotropic effect of the ferrocene nucleus. The electronic spectrum exhibits a large bathochromic shift of the d–d absorption band of the iron atom ($\lambda_{max} = 470$ nm). Attempted synthesis of [2]paracyclo[2](1,1′)ferrocenophane, which is more strained than 1, was unsuccessful.

Introduction

A large number of monobridged (1,1′)ferrocenophanes[2,3] have been studied[4-6] since the discovery of ferrocene. Most of these are [*m*](1,1′)ferrocenophanes[4-6] which are intramolecularly linked with a carbon chain and [*m.n*](1,1′)-ferrocenohanes[4-10] which are intermolecularly bridged between two ferrocene nuclei. Recently, several (1,1′)-ferrocenophanes containing aromatic rings in the bridge were synthesized,[11,12] but there has been no report on [2]meta- and [2]paracyclo[2](1,1′)ferrocenophanes (**1** and **2**). By inspection of a Dreiding molecular model, the benzene ring of **1** is situated to the side of the ferrocene nucleus and the 9-hydrogen of the ring is unusually close to the iron atom of the ferrocene (ca. 2.4 Å). A space-filling (CPK) molecular model reveals that the 9-hydrogen and the ferrocene nucleus repel each other. This situation should cause a high strain and/or some distortion in the molecule. The ^1H NMR spectrum and the d–d absorption band in the electronic spectrum of **1** should reflect such an unusual molecular structure and show characteristic shifts. The magnetic anisotropy of ferrocene nucleus was

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[1] Part 40: Hisatome, M.; Watanabe, J.; Yamakawa, K.; Kozawa, K.; Uchida, T. *Nippon Kagaku Kaishi* **1985**, 572.

[2] The nomenclature of ferrocenophanes in this paper is according to that presented by Vögtle and Neumann.[3]

[3] Vögtle, F.; Neumann, P. *Tetrahedron* **1970**, *26*, 5847.

[4] Watts, W. E. *Organomet. Chem. Rev.* **1967**, *2*, 231.

[5] Kasahara, A. *Kagaku* **1983**, *38*, 859.

[6] Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

[7] Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058.

[8] Barr, T. H.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1969**, *25*, 6001.

[9] (a) Rosenblum, M.; Brawn, N. M.; Clappenelli, D.; Tancrede, J. *J. Organomet. Chem.* **1970**, *24*, 469. (b) Kasahara, A.; Izumi, T. *Chem. Lett.* **1978**, 21. (c) Kasahara, A.; Izumi, T.; Shimizu, I. *Ibid.* **1979**, 1317.

[10] (a) Biernat, J. F.; Wilczewski, T. *Tetrahedron* **1980**, 36, 2521. (b) Sato, M.; Kubo, M.; Ebine, S.; Akabori, S. *Tetrahedron Lett.* **1982**, *23*, 185. (c) Czech, B.; Ratajczak, A.; Nagraba, K. *Monatsch. Chem.* **1982**, *113*, 965. (d) Izumi, T.; Tezuka, T.; Yusa, S.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2435.

[11] (a) Tanner, D.; Wennerstrom, O. *Acta Chem. Scand.* **1980**, *B34*, 529. (b) Kauffmann, K.; Ennen, J.; Lhotak, H.; Rensing, A.; Steinseifer, F.; Woltermann, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 328. (c) Shimizu, I.; Umezawa, H.; Kanno, T.; Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2023.

[12] (a) Tanaka, S.; Sato, M.; Ebine, S.; Morinaga, K.; Akabori, S. 16th Symposium on Structural Organic Chemistry, Urawa, Japan, 1983; The Symposium Papers, p 289. (b) Sato, M.; Tanaka, T.; Ebine, S.; Morinaga, K.; Akabori, S. *J. Organomet. Chem.* **1985**, *289*, 91.

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