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Notes

Carbon−Carbon Bond Rearrangements on Heterobimetallic Centers: Synthesis, Isomerization, and Molecular Structures of Flyover Complexes $\mathbf{CpMo(CO)_2(\mu{:}\eta^2,\eta^4\text{-}C_4R_2R'_2)Co(CO)_4}$ and $\mathbf{CpMo(CO)_2(\mu{:}\eta^2,\eta^4\text{-}C_4R_2R'_2)(\mu\text{-}CO)Fe(CO)_2}$ (R = Me, R′ = Ph; R = R′ = Ph)

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Summary: Reaction of $CpClMo(RC{\equiv}CR')_2$ *(R = Me, R′ = Ph; R = R′ = Ph) with* $Co_2(CO)_8$ *or* $Fe_2(CO)_9$ *gives good yields of the flyover complexes,* $Cp(CO)_2Mo(\mu{:}\ \eta^2,\eta^4\text{-}C_4R_2R'_2)Co(CO)_2$ *(**1** R = Me, R′ = Ph; **3** R = R′ = Ph) and* $Cp(CO)_2Mo(\mu\text{-}CO)(\mu{:}\ \eta^2,\eta^4\text{-}C_4R_2R'_2)Fe(CO)_2$*. The kinetically favored isomer of **1** has alternating Me and Ph substituents on the* C_4 *ring, whereas the thermodynamically favored isomer has Me substituents on the terminal carbon atoms and phenyl substituents on the internal carbon atoms of the* C_4 *ligand.*

Introduction

Reductive coupling of alkynes on mono- and polynuclear transition metal centers has led to a variety of products. Examples of mononuclear complexes include coordinated η^4-cyclobutadienes,[1,2] 1,3-metallacyclopentadienes,[3,4] 2,4-metallacyclopentadienes,[4,5] and 1,3,5-metallacyclopentatrienes.[4,6−8] Dinuclear complexes are known in which two coupled alkynes bridge a metal−metal bond nearly symmetrically (η^4-C_4R_4)[9−11] or form the more familiar "flyover" structure. Flyover structures are known for both homonuclear[12−15] and heteronuclear[16−19] metal−metal complexes. Stepwise coupling of three or four alkyne units on dimetal centers to form C_6 and C_8 carbon chains have also been reported.[20] Early transition metal complexes are promising catalysts for polymerization of internal alkynes.[21] The structures of discrete metal complexes containing coupled alkynes are of interest because they might shed light on the mechanism of polymerization. In this note we report an unusual isomerization of a dinuclear metallacyclopentadiene flyover complex that involves the reversible scission of a C−C bond. Similar isomerizations are known to occur in mononuclear metallacyclopentadienes;[22a] but, to our knowledge, there is only one other observation of this phenomenon on a dinuclear center.[22b]

Experimental Section

General Considerations. All manipulations and reactions were performed under a dinitrogen atmosphere with standard Schlenk techniques or in a drybox. Elemental analyses were performed by the University of Michigan microanalytical service located in the Department of Chemistry or by Oneida Research Services, Inc., Whitesboro, NY. NMR spectra were recorded on a Bruker AM-300 operating at 300 MHz for ^1H

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and at 75.5 MHz for ^{13}C. IR spectra were recorded on a Nicolet 5DXB spectrometer. Mass spectra were obtained on Finnigan Model 4021 GC−MS or VG 70-250s spectrometers. $Co_2(CO)_8$ and $Fe_2(CO)_9$ were purchased from Aldrich. The CpMoCl(alkyne)$_2$ complexes were prepared by modification of the procedure described earlier.[23]

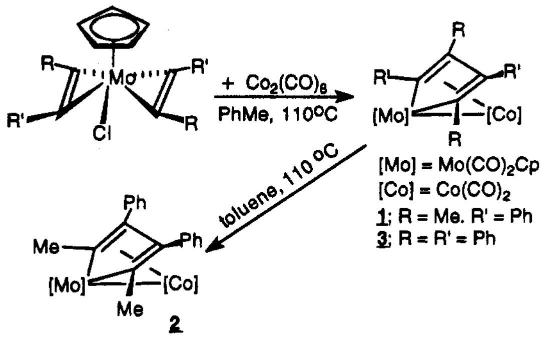
$CpMo(CO)_2Co(CO)_2(\mu,\eta^2,\eta^4$-C(Me)C(Ph)C(Me)C(Ph)), 1. A mixture of $CpMo(PhC_2Me)_2Cl$ (2 g, 4.6 mmol), and $Co_2(CO)_8$ (1.6 g, 4.6 mmol) in 30 mL of toluene was refluxed for 24 h. The solution was concentrated and chromatographed on alumina (4 × 10 cm). The first hexane eluate was collected and the solvent pumped off to obtain a yellow microcrystalline product. Yield: 1.8 g (69%) based on Mo. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39−7.08 (m, 10H, C_6H_5), 4.86 (s, 5H, C_5H_5), 1.98 (s, 3H, CH_3), 1.63 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 239, 235 (*C*O); 160.5, 152.1 (C_α, C_α'); 143.0, 138.6, 133.1, 131.5, 128.9, 128.7, 128.2, 127.7, 127.3, 124.7 (*C*$_6$H$_5$ and C_β, C_β'); 90.3 (*C*$_5$H$_5$); 33.4, 10.2 (*C*H$_3$). Mass spec (EI, 70 eV): m/z = 566, 538 (M^+ − CO), 510 (M^+ − 2CO), 482 (M^+ − 3CO), 454 (M^+ − 4CO). IR (KBr) (cm^{-1}): ν_{CO} 2011 (vs), 1950 (vs), 1898 (vs). Anal. Calcd for $C_{27}H_{21}CoMoO_4$: C, 57.46; H, 3.75. Found: C, 57.02; H, 3.61.

$CpMo(CO)_2Co(CO)_2(\mu:\eta^2,\eta^4$-C(Me)C(Ph)C(Ph)C(Me)), 2. $CpMo(CO)_2Co(CO)_2(\mu,\eta^2,\eta^4$-C(Me)C(Ph)C(Me)C(Ph)) (1) (0.05g, 0.09 mmol), was heated in toluene (20 mL) at 100 °C for 24 h. The solution was then concentrated to 0.5 mL and left at room temperature . Yellow orange crystals were collected after 24 h, yield 46 mg (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15−6.95 (m, 10H, C_6H_5); 5.00 (s, 5H, C_5H_5); 2.07 (s, 6H, CH_3). $^{13}C\{^1H\}$ (75.5 MHz, $CDCl_3$): δ 238.2 (*C*O); 166.2 (C_α) 143.6, 137.5, 130.7, 127.5, 126.7 (*C*$_6$H$_5$, C_β); 89.2 (*C*$_5$H$_5$); 33.5 (*C*H$_3$). IR (KBr) (cm^{-1}): ν_{CO} 2012 (vs), 1958 (vs), 1898 (vs). Mass spec (EI, 70 eV): m/z = 566, 538 (M^+ − CO); 510 (M^+ − 2CO); 482 (M^+ − 3CO), 454 (M^+ − 4CO). Anal. Calcd for $C_{27}H_{21}CoMoO_4$: C, 57.46; H, 3.75. Found: C, 56.26; H, 3.86.

$CpMo(CO)_2Co(CO)_2(\mu:\eta^2,\eta^4-C_4Ph_4)$, 3. In a 100-mL Schlenk flask, 2.0 g (3.62 mmol) of $CpMo(PhC_2Ph)_2Cl$ was dissolved in 30 mL of toluene and 1.3 g (3.8 mmol) of $Co_2(CO)_8$ added. The mixture was then refluxed for 24 h with continuous stirring. The solvent was pumped off under vacuum and the residue chromatographed on alumina (10 × 4 cm). The red orange CH_2Cl_2 eluate was collected, concentrated to 15 mL, and cooled to −10 °C for 8 h. Red brown microcrystals were obtained, yield 2.00 g, 80.4% based on Mo. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.01−6.89 (br m, 20 H, C_6H_5), 5.00 (br s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 235 (*C*O); 171 (C_α); 151.4, 140.5, 137.9, 131.5, 129.1, 128.9, 126.9, 126.2, 124.7 (*C*$_6$H$_5$ and C_β); 91.7 (*C*$_5$H$_5$). Anal. Calcd for $C_{38}H_{27}Cl_2CoMoO_4$ (methylene chloride solvate): C, 59.01; H, 3.52. Found: C, 59.08; H, 3.47. IR (KBr) (cm^{-1}): ν_{CO} 2017 (vs),1963 (vs),1910 (vs). Mass spec (EI, 70 eV): m/z = 689, 661 (M^+ − CO), 634 (M^+ − 2CO), 606 (M^+ − 3CO), 578 (M^+ − 4CO). This compound was prepared previously from the reaction of $CpMoCo(CO)_7$ with diphenylacetylene.[18]

$CpMo(CO)_2(\mu$-CO)$(\mu:\eta^2,\eta^4-C_4(Me)_2(Ph)_2)Fe(CO)_2$, 4. A mixture of $CpMo(PhC_2Me)_2Cl$ (0.5 g,1.17 mmol) and $Fe_2(CO)_9$ (0.42 g, 1.17 mmol), was refluxed in 20 mL of toluene for 24 h. The solvent was pumped off under vacuum, and the remaining greenish yellow residue was chromatographed on a 5 × 3 cm layer of alumina. The first yellow hexane eluate was discarded. The green band eluted with CH_2Cl_2 was collected and the solvent pumped off to obtain greenish microcrystals which gave no proton NMR signals at room temperature. ESR (CH_2Cl_2, 25 °C): g = 2.018, A_{Mo} = 12 G. IR (KBr) (cm^{-1}): ν_{CO} 2035, 1977, 1968, 1962, 1646. Anal. Calcd for $C_{28}H_{21}FeMoO_5$: C, 57.07; H, 3.59. Found: C, 55.62; H, 3.83. Mass spec (EI, 70 eV): m/z = 591, 507 (M^+ − 3CO), 479 (M^+ − 4CO), 451 (M^+ − 5CO). On the basis of these data the compound is formulated as $CpMo(CO)_2(\mu$-CO)$(\mu:\eta^2,\eta^4-C_4(Me)_2(Ph)_2)Fe(CO)_2$.

Scheme 1



2

Structure Determinations. Yellow crystals of **2** were recrystallized from toluene as rectangular plates, and a suitable crystal was mounted on a Syntex P2$_1$ diffractometer. The space group was uniquely determined by the systematic absences. Rust colored rectangular plates of **3** were grown from CH_2Cl_2/hexane and mounted on a Siemens R3m/V diffractometer. The choice of space group was based on counting statistics as well as the successful solution and refinement of the structure in the centric space group. All crystallographic computations were done with the SHELX[24] package of crystallographic programs running on a VAX 3500. Thermal ellipsoid plots were made with ORTEP.[25] Atomic scattering factors were taken from ref 26. Metal atoms were located by direct methods, and the remaining heavy atoms were located by Fourier difference maps. During refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight is given by $w = 1/(\sigma^2 + 0.0001F_o^2)$. After the heavy atom parameters had converged, hydrogen atoms were located and assigned a C−H distance of 0.96 Å, and the group isotropic temperature factor refined to values of 0.083 and 0.084, respectively, for **2** and **3**. All the crystallographic data are deposited as supplementary material.

Results and Discussion

The reaction of $Co_2(CO)_8$ with $CpClMo(PhC{\equiv}CR)_2$ (R = Ph, Me) in toluene solutions at 100−110 °C gave good yields of the bimetallic flyover complexes **1** (R = Me) and **3** (R = Ph), as shown in Scheme 1. The ^{1}H-NMR spectrum of **1** showed a signal at δ 4.86 ascribed to the Cp protons and broad multiplets in the region δ 7.39−7.08 due to the phenyl protons. The methyl group resonances were observed at δ 1.98 and 1.63 with relative areas of 3:3.

The ^{13}C-NMR spectrum of **1** showed two resonances assigned to the methyl carbon atoms at δ 33.4 and 10.2 and two lines at δ 238 and 235 that were assigned to the carbonyl carbon atoms bonded to the Mo atom. This assignment was made on the basis that the carbonyl carbon resonances in the compound $Cp(CO)_2Mo(\mu:\eta^2,\eta^4-C_4Et_4)Mo(CO)Cp$ occur at 247 and 236 ppm,[13] and because the signals of the carbonyl groups bonded to quadrupolar cobalt are often difficult to detect due to line broadening. The resonances of the terminal carbon atoms (C_α) of the C_4R_4 ligand appeared at δ 160 and 152 ppm. Ten lines due to inequivalent phenyl and C_β carbon atoms were also observed. These spectral prop-

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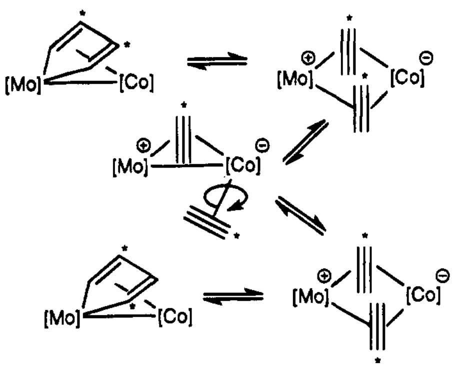
erties are consistent with an unsymmetric flyover complex that arises from head-to-tail coupling of two PhC≡CMe molecules, as shown in Scheme 1. In comparison, the ^{13}C-NMR spectrum of symmetric complex **3** shows only one resonance each for CO (δ 235) and C_α (δ 171), and nine resonances in the phenyl and C_β region: eight for the two inequivalent sets of phenyl groups and one for the two equivalent C_β carbon atoms.

Heating a toluene solution of **1** for 24 h afforded a new complex **2** whose mass spectrum was virtually identical to that of **1**. Hence, **1** and **2** appeared to be isomers, but the NMR spectra of **2** indicated it had a mirror symmetry. Thus, only one methyl group resonance was observed in the ^{1}H-NMR spectrum at δ 2.07 (relative area 6). In the ^{13}C-NMR spectrum, there was one resonance each for CO (δ 238) and C_α (δ 166); and the phenyl groups were now equivalent as were the C_β's (only five peaks in the Ph, C_β region). A crystal structure determination confirmed the head-to-head structure shown in Scheme 1 in which the carbon atoms bearing the methyl groups are both bonded to the molybdenum atom. The above results show that **1** is the kinetically favored isomer and **2** is the more thermodynamically stable isomer. The head-to-head isomer is disfavored by steric repulsion at the β-positions, but this orientation is favored by relief of steric congestion at the molybdenum center and possibly by stronger Mo—C bonds. Apparently, the latter effects are dominant. No evidence was seen for the existence of the third possible isomer with both phenyl groups attached to the terminal carbon atoms.

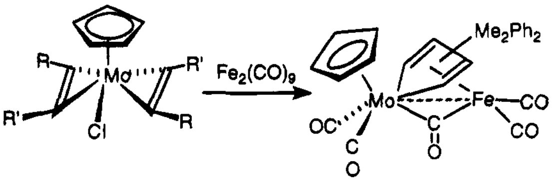
After 24 h, conversion of **1** to **2** was essentially quantitative and **1** was not detectable in the NMR spectrum of the reaction mixture. If one assumes that [**2**]:[**1**] $\geq$ 50:1 (i.e. that **1** would have been detected if it were present at 2% of **2**), then **2** is at least 3 kcal/mol more stable than **1**. Once the identity of **2** was known, several "impurity" peaks (ca. 5% of the intensity of the peaks due to **1**) in the NMR spectrum of the crude reaction mixture from the initial synthesis of **1** could be assigned as peaks due to **2**. If one assumes that this amount of **2** arises from a competitive reaction of $Co_2(CO)_8$ with $CpClMo(PhC{\equiv}CMe)_2$ rather than sequentially from **1**, then $k_2/k_1 \approx 0.05$ at 110 °C and the activation energy to form **2** must be at least ca. 2.5 kcal/mol greater than that for the pathway leading to **1**. The regioselectivity of this reaction cannot be caused by a preferential conformation of the starting bis(alkyne) complex, $CpClMo(PhC{\equiv}CMe)_2$. This molecule is fluxional at room temperature,[27] so that at the reaction temperature (110 °C) all the alkyne rotomers are sampled faster than the flyover complexes are formed. The kinetic preference is most likely expressed at the time of ring closure and is the result of a delicate balance of electronic and steric contributions in a bimetallic bis(alkyne) intermediate (see below).

The conversion of **1** to **2** appears to be intramolecular. An equimolar solution of **1** and bis(*p*-toyl)acetylene in toluene-d_8 was heated to 110 °C and the NMR spectrum recorded after 24 h. Conversion to **2** occurred and no free phenylmethylacetylene or metallacycles incorporating *p*-tolylacetylene were detected in the reaction mixture. We suggest the pathway shown in Scheme 2 to account for these observations. The intermediates in Scheme 2 are drawn to preserve the 18 electron count as far as possible. The first step is a ring opening to form a bimetallic bis(alkyne) complex. Further rearrangement may lead to a structure with a terminal alkyne ligand. The barrier to rotation of terminal acetylenes is known to be low,[27] and skeletal isomerization of mononuclear metallacyclopenta-dienes has been proposed to occur through ring opened intermediates.[22a] In one other example, isomerization of $Cp'_2W_2Cl_2(\mu{:}\eta^4,\eta^4\text{-}C_4Me_2Et_2)$ was effected by heating the solid compound to 250 °C.[22b]

Scheme 2



The reaction of $CpClMo(PhC{\equiv}CMe)_2$ with $Fe_2(CO)_9$ gave a green, paramagnetic compound formulated as $Cp(CO)_2Mo(\mu\text{-}CO)(\mu{:}\eta^2,\eta^4\text{-}C_4Me_2Ph_2)Fe(CO)_2$, **4** (eq 1).



(1)

This compound gave no NMR signal, but an ESR spectrum consisting of a six-line pattern with features similar to those of the paramagnetic Mo complex, $CpMo(\eta^4\text{-}C_4Ph_4)Cl_2$, **5**,[2] was recorded at room temperature. The value of the hyperfine splitting, A_{Mo}, for **4** was only 12 G, much smaller than the value of 36 G observed for the Mo complex **5**, indicating that the unpaired electron is not as localized on the Mo atom in the bimetallic complex.

Complex **4** gives a parent ion with *m/z* = 591 and peaks corresponding to the successive loss of five CO ligands. In its IR spectrum, **4** shows a strong band at 2035 cm^{-1} and a broad, strong band at 1977–1963 cm^{-1}. An important feature in the IR spectrum is a band at 1646 cm^{-1}, assigned to a bridging CO. This feature is absent in the spectra of the Mo—Co bimetallics **1**–**3**. A bridging CO implies a metal—metal interaction. If complex **4** contains a "normal" bridging carbonyl and a "normal" metal—metal bond, then the Fe would have an electron count of 18 and the molybdenum atom would have a formal electron count of 19. The low value of A_{Mo} (see above) and the very low CO stretching frequency for the bridging carbonyl suggest that the odd

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[27] A VT-NMR experiment with $CpClMo(ArC{\equiv}CAr)_2$ (Ar = *p*-tolyl) showed the alkyne rotation was frozen at ~63 °C, with a coalescence temperature of −13 °C, from which a free energy barrier of 13 kcal/mol was estimated (see supplementary material). Low barriers to alkyne rotation have been noted previously: see ref 23. See also: (a) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644. (b) Kreissel, F. R.; Sieber, W. J.; Hofmann, P.; Riedle, J.; Wolfgruber, M. *Organometallics* **1985**, *4*, 788. (c) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

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electron occupies a delocalized orbital with significant CO π^* character. Some metal—metal antibonding character is most likely also present, so the excess electron density is spread out over the Mo(μ-CO)Fe bridge. A related, 18-electron Mo—Fe flyover complex, $Cp(CO)_2Mo(\mu\text{-}CO)(\mu{:}\eta^2,\eta^4\text{-}C_4Me_2Ph_2)FeCp$, **6**, is known and structurally characterized.[16] This compound has head-to-tail coupled alkynes as in compound **1**.

Structural Results. During the course of this work, we had determined the crystal and molecular structures of **2** and **3** when Yanez et al. published their alternate synthesis and structure determination of **3**.[18] The structures of **2** and **3** are so similar to the published structures of **3** and **6**[16,18] that extensive discussion of them here is not warranted. The structural tables for **2** and **3** have been deposited as supplementary material (see below). The structure determination of **2** confirmed the head-to-head coupling of the alkynes and proved that the methyl groups were attached to the terminal carbon atoms of the C_4 fragment. As with the previous structures, the C—C bonds in the metallacycle all have about the same value (average 1.420 ± 0.005 Å). As discussed elsewhere,[6,28] the transition from a metallacyclopenta*di*ene with alternating short—long—short C—C bonds, through a delocalized structure with all C—C bonds having nearly equal lengths, to a metallacyclopenta*tri*ene with alternating long—short—long C—C bonds involves transfer of electron density from the butadiene-like π_2-HOMO of the C_4R_4 fragment to the π^*_3-LUMO. The flyover structures can be viewed as sandwich compounds with η^5-MC_4 ligands π-bonded to the second metal; and it appears that this structural motif enhances the transfer of electron density within the C_4 fragment when compared to most mononuclear MC_4 metallacycles.

Concluding Remarks. The present results show that, as in mononuclear metallacyclopentadienes, skeletal isomerization involving C—C bond cleavage is a facile process in binuclear compounds as well and that the thermodynamically less stable isomer may be kinetically favored.

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Supplementary Material Available: Tables of crystallographic data, fractional atomic coordinates, complete bond distances and angles, thermal parameters, and equations for C5—C8 plane, ORTEP plots with numbering schemes for **2** and **3**, and variable temperature ^1H-NMR spectra for CpMo(ArC≡CAr)$_2$Cl (Ar = *p*-tolyl) (28 pages). Ordering information is given on any current masthead page.

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