

Preliminary communication

Structure and reactivity of (Dibenzo[b,e]fulvalene)Mo₂(CO)₆

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Received 9 October 1995; in revised form 27 November 1995

Abstract

The title compound **1** was prepared by a one pot double-deprotonation, migration, and oxidation sequence starting with ($\mu, \eta^6: \eta^6$ -2,2'-biindenyl)Mo₂(CO)₆ (**2**). An X-ray structure was determined, and the relevant structural features are compared with analogous fulvalene and dibenzo[a,d]fulvalene complexes. The reactions of **1** with 4-octyne and P(CH₃)₃ are described. Compound **1** is a more effective catalyst in the Kharasch reaction than other bimetallic molybdenum complexes.

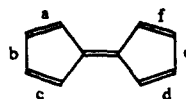
Keywords: Molybdenum; Fulvalene; Bimetallic; Kharasch reaction

1. Introduction

Bimetallic compounds have attracted attention in recent years based on the idea that the concerted effects of two metals in proximity should result in novel reactions useful in stoichiometric synthesis and in catalysis [1]. Fulvalene (bicyclopentadienylidene) has provided the foundation for many bimetallic complexes [2] for several reasons: (a) its cyclopentadienyl rings bond strongly to early and middle transition metals; (b) metal–metal bond cleavage can occur without fragmentation to mononuclear complexes, since metal–metal cooperativity may be maintained thru proximity and by communication through the π -bond system of the fulvalene ligand [3]; (c) the fulvalene ligand, whose ring centroids in an idealized planar conformation are separated by 4 Å [4], acquires a pyramidalized structure to accommodate M–M bond lengths of 2.8–3.5 Å: longer, and possibly more reactive, than those in the analogous cyclopentadienyl dimers [5].

On the downside, the η^5 -Cp ring occupies three coordination sites of the metal, leaving little room for additional ligands in the case of late transition metals, and it tends to disfavor associative reactions which require reduction in hapticity [6]. In contrast, (η^5 -indenyl)metal compounds often display enhanced reactivity—the “indenyl effect” [7]—in ligand substitution reactions. In an effort to enhance the reactivity of fulvalene bimetallic complexes, we have recently prepared [8] several Group 6 bimetallic complexes of dibenzo[a,d]fulvalene¹. We now report the synthesis, X-ray crystal structure, and novel reactivity of ($\mu, \eta^5: \eta^5$ -dibenzo[b,e]fulvalene)Mo₂(CO)₆ (**1**), the first neutral transition metal complex of the unknown hydrocarbon dibenzo[b,e]fulvalene. This hydrocarbon, because of its annulation pattern and resultant symmetry, is predicted to exist as a ground state triplet rather than as the diquinonoid singlet.

¹ The bonds in the parent fulvalene are labelled as shown. Dibenzo-fulvalenes are named according to which bonds are benzannulated.



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2. Results and discussion

Compound **1** was prepared as shown in Scheme 1². Details for the first step have been reported previously [8]. An ORTEP³ diagram for **1** is presented in Fig. 1. The bond length in **1** is 3.3485(6) Å, shorter than the 3.371(1) Å bond found in (fulvalene)dimolybdenum hexacarbonyl, FvMo₂(CO)₆ [9], but somewhat longer than the 3.3172(8) and 3.286(4) Å bonds found in (μ, η^5 : η^5 -dibenzo[a,d]fulvalene) Mo₂(CO)₅P(OMe)₃ and (μ, η^5 : η^5 -dibenzo[a,f]fulvalene)Mo₂(CO)₆, respectively [8]. The degree of ligand pyramidalization exhibited by all four compounds is comparable, the respective bend angles [8] being 6.7, 7.3, 6.9, and 9.0°, however, compound **1** twists much less about the C–C bond connecting the two five-membered rings than the other three compounds. Specifically, the average of the torsion angles C(2)C(3)C(8)C(7) and C(4)C(3)C(8)C(9)

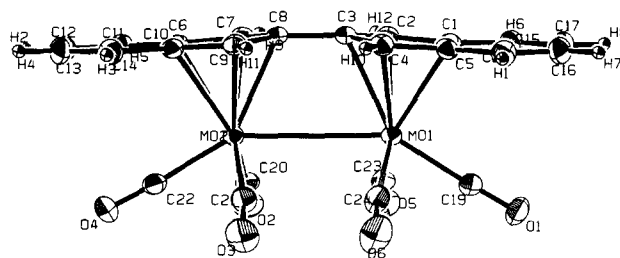


Fig. 1. ORTEP drawing of **1** showing the labeling scheme. Atoms are represented by thermal ellipsoids at the 30% level.

in **1** is 0.3°, while the analogous angle in the other three compounds ranges between 4 and 24°. Both metals are distorted towards an η^3 bonding mode; this tends to decrease the metal–metal bond length compared to the fulvalene analogue.

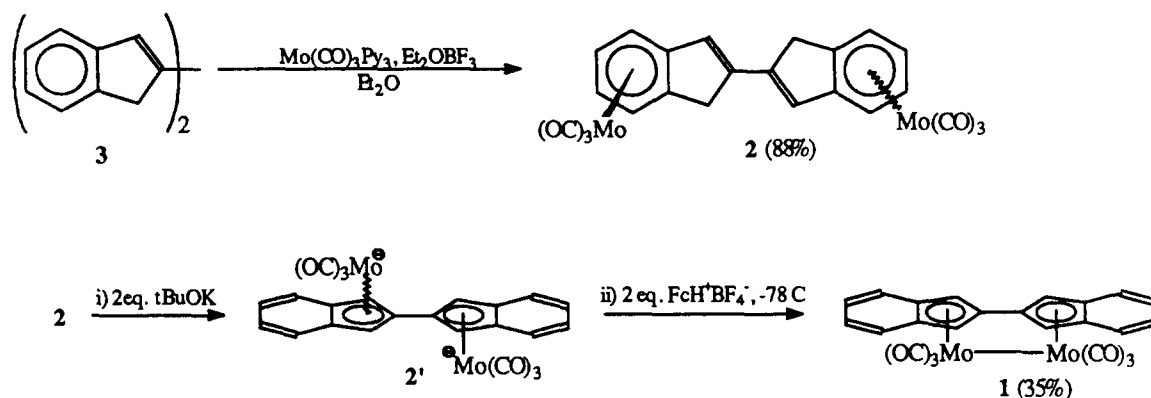
The visible spectrum of **1** in THF shows absorption maxima at 615, 528, and 402 nm, compared with 543 and 376 nm for FvMo₂(CO)₆ (Ref. [9] 558, 378 nm), and 607 and 374 nm for (μ, η^5 : η^5 -dibenzo[a,d]fulvalene)Mo₂(CO)₆. The two absorptions of FvMo₂(CO)₆ were assigned to $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions, respectively, associated with metal non-bonding electrons and metal–metal bonding electrons, however, the strong effect of ligand annulation suggests that the visible absorptions may be metal–ligand charge transfer bands. Both **1** and (μ, η^5 : η^5 -dibenzo[a,d]fulvalene)Mo₂(CO)₆ are green while FvMo₂(CO)₆ is violet.

Reaction of **1** with excess 4-octyne in refluxing toluene produced alkyne complex **4**,⁴ isolated in 53% yield after column chromatography. In addition, earlier fractions gave ¹H NMR and MS data consistent with the presence of the cyclotrimerization product, hexa-*n*-propyl-benzene. No evidence of cyclotrimerization was reported when FvMo₂(CO)₆ reacted with alkynes under either thermal or photochemical conditions [9]. The lack of symmetry seen in the ¹H NMR of **4** indicates that the bridging alkyne, although symmetrically placed relative to both metals and perpendicular to the Mo–Mo bond, leans to one side of the molecule like a pendulum frozen in its upswing, as was found to be the case in the crystal structures of two related compounds, FvMo₂(CO)₃(EC≡CE)₂ (E = CH₃O₂C) [9] and (μ, η^5 : η^5 -dibenzo[a,d]fulvalene)Mo₂(CO)₄(μ, η^2 : η^2 -PhC≡CPh)

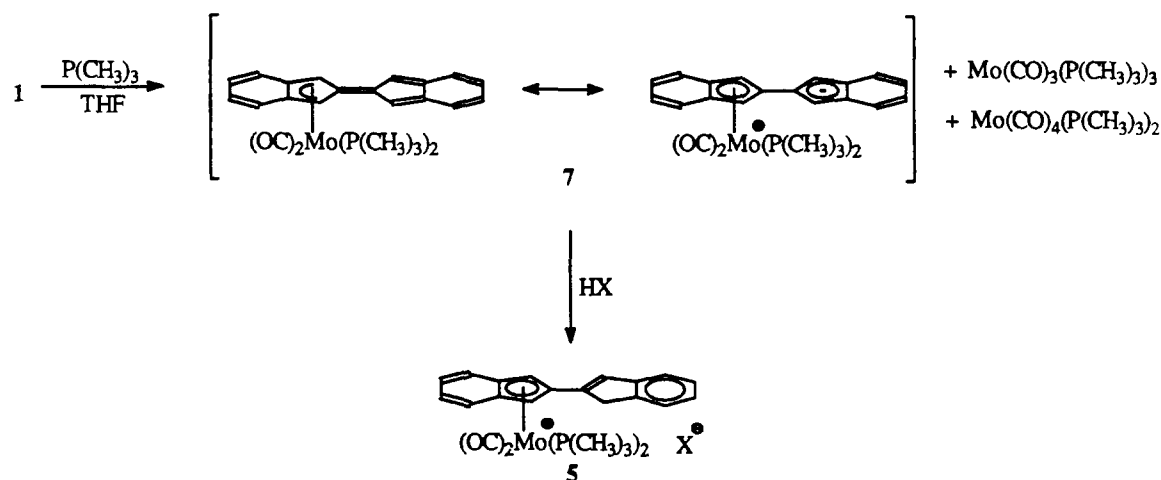
² Experimental: Into a stirring suspension of **2** (1.028 g, 1.74 mmol) in 50 ml Et₂O was syringed 3.7 ml (3.7 mmol) of a 1 M THF solution of *t*-BuOK. Within twenty-five minutes, a color change to yellow had occurred, and the reaction mixture was cooled to –78°C in a dry ice bath. Ferrocenium tetrafluoroborate (0.956 g, 3.50 mmol) was added quickly against a counterstream of dinitrogen. The dry ice was allowed to sublime, and stirring was continued for one hour after the reaction mixture had reached room temperature. The green reaction mixture was then filtered with suction through a medium frit funnel. The reaction vessel was washed with CH₂Cl₂ and these washings were also filtered until the filtrate was no longer green in color. All filtrates were combined and roto-evaporated. The residue was washed with hexane (2x) and toluene (3x) and the washings filtered. The filtrates contained mostly ferrocene and were discarded. The remaining green precipitate was dried in vacuo to give 0.360 g (35%) of spectroscopically pure **1**. ¹H NMR (250 MHz, CD₂Cl₂) δ 5.24 (s, 4H), δ 7.1 (AA'; 3.0 Hz, 6.8 Hz; 4H), δ 7.3 (BB'; 3.1 Hz, 6.8 Hz; 4H); ¹³C NMR (75.5 MHz, CDCl₃) δ 77.6, 93.7, 106.3, 124.6, 126.4, 229.8; MS (EI), *m/z* (based on ⁹⁶Mo) 588 (0.54) (M)⁺, 560 (5) (M–CO)⁺, 532 (12) (M–2CO)⁺, 504 (7) (M–3CO)⁺, 476 (34) (M–4CO)⁺, 448 (62) (M–5CO)⁺, 420 (77) (M–6CO)⁺, 228 (34) (C₁₈H₁₂)⁺, 210 (100) (C₉H₆Mo)⁺, 196 (57) (Mo₂)⁺; IR (KBr) 2012(s), 1962(s), 1911(s), 1870(m), 739(m) cm^{–1}; dec. > 230°C; Anal. Calc. for C₂₄H₁₂Mo₂O₆: C, 49.00; H, 2.06. Found: C, 48.60; H, 2.04.

³ X-ray data: C₂₄H₁₂Mo₂O₆, **1**, green crystals 0.1 × 0.2 × 0.5 mm. Monoclinic, P2₁/n, *a* = 13.978(2), *b* = 6.9523(5), *c* = 21.729(3) Å, β = 98.340(7)°, *V* = 2089.3(8) Å³, *Z* = 4, *D_c* = 1.870 g cm^{–3}, μ = 12.102 cm^{–1}, Mo K α (λ = 0.71073 Å), $0 < 2\theta < 50^\circ$; reflections: collected = 4273, independent = 4010, observed = 2915; min, max abs. = 0.952, 1.055; *R* = 2.6%, *R_w* = 3.4%. Data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature. Data collection began with a random search at low θ to yield 25 reflections which were indexed to give an initial unit cell. An accurate cell was obtained using higher angle (θ = 10–12°) reflections. Initial direct methods solution (SHELXS) revealed the metals. A difference Fourier map then yielded the remaining heavy atoms. After partial refinement, hydrogen atom positions were calculated, and the structure was subjected to full anisotropic refinement of the heavy atoms using full matrix least squares. A DIFABS absorption correction was applied, and the structure was refined with five more cycles of least squares.

⁴ ¹H NMR (300 MHz, CDCl₃) δ 0.92 (m, 6H), δ 1.2 (m, 2H), δ 1.5 (m, 2H), δ 2.3 (m, 2H), δ 3.2 (m, 2H), δ 4.47 (s, 2H), δ 4.77 (s, 2H), δ 6.91 (m, 2H), δ 7.21 (m, 4H), δ 7.37 (d, 8.7 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 14.7, 25.1, 25.4, 29.7, 38.5, 43.3, 56.9 (μ -carbon of alkyne, other carbon not found), 69.9, 75.9, 92.9, 103.7, 113.6, 121.9, 123.5, 127.2, 127.4, 223.2, 233.0; MS (EI), *m/z* (based on ⁹⁶Mo) 642 (1) (M)⁺, 586 (9) (M–2CO)⁺, 584 (9) (M–2CO–2H)⁺, 556 (11) (M–3CO–2H)⁺, 524 (85), 261 (100), 229 (60) (C₁₈H₁₃)⁺; IR (KBr) 1974, 1940, 1909, 1869 cm^{–1}; dec. > 210°C.



Scheme 1.



Scheme 2.

[8]. The room temperature ^1H NMR spectrum of the latter, in contrast to **4**, shows a time-averaged C_2 axis perpendicular to the dibenzo[*a,d*]fulvalene ligand, explainable by a rapid side-to-side pendular motion of the bridging alkyne. A similar pendular motion was postulated to explain the ^1H NMR temperature dependence of $\text{FvMo}_2(\text{CO})_4(\text{EC}\equiv\text{CE})$ [9], which exhibits coalescence near room temperature. A variable temperature ^1H NMR study of **4** shows coalescence by 85°C of all resonances formerly inequivalent as a result of the frozen nature of the alkyne at room temperature.

Compound **1** reacts almost instantly with slightly more than one equivalent of $\text{P}(\text{CH}_3)_3$ at 0°C in THF to give a tan-colored precipitate whose spectral data (^1H and ^{13}C NMR, IR, FAB MS)⁵ were consistent with

⁵ ^1H NMR (250 MHz, DMSO-d_6) δ 1.76 (quasi triplet, 18H), δ 3.65 (s, 2H), δ 6.71 (s, 2H), δ 7.18–7.35 (m, 4H), δ 7.42 (d, 6.8 Hz, 1H), δ 7.51 (d, 7.1 Hz, 1H), δ 7.76 (m, 2H); ^{13}C (62.9 MHz, DMSO-d_6) δ 18.7 (quintet), 84.0, 109.0, 111.5, 121.4, 123.9, 124.4, 125.6, 126.2, 126.8, 129.9, 138.5, 142.5, 143.8; MS (FAB), m/z 535 (100) (M^+), 507 (31) ($\text{M}-\text{CO}^+$); IR (KBr) 1946(m), 1857(s), 958(m) cm^{-1} ; dec. $> 163.5^\circ\text{C}$.

structure **5** (Scheme 2); the identity of X^- is unknown. The presence of *cis*- $\text{Mo}(\text{CO})_4(\text{P}(\text{CH}_3)_3)_2$ and *fac*- $\text{Mo}(\text{CO})_3(\text{P}(\text{CH}_3)_3)_3$ (identified by ^1H NMR, IR, and MS) in the soluble portion of the crude product reveals the fate of the other $\text{Mo}(\text{CO})_3$ moiety. The relative intensities of the carbonyl stretching frequencies in the IR of **5** are consistent with a *trans* arrangement of the two $\text{P}(\text{CH}_3)_3$ ligands [10]. Reaction of $\text{FvMo}_2(\text{CO})_6$ with two equivalents of $\text{P}(\text{CH}_3)_3$ under similar conditions [2a] resulted in the zwitterionic species $\mu, \eta^5: \eta^5\text{-Fv}[\text{Mo}(\text{CO})_3]^+[\textit{trans}\text{-Mo}(\text{CO})_2(\text{P}(\text{CH}_3)_3)_2]^-$ after three days. Moreover, conversion of the zwitterion to $[\eta^4\text{-fulvalene}]\text{Mo}(\text{CO})_2(\text{P}(\text{CH}_3)_3)_2$, **6**, required a six-fold excess of $\text{P}(\text{CH}_3)_3$ and two additional days reaction time in acetonitrile. The basicity of **6** was demonstrated by its H/D exchange with D_2O in acetonitrile- d_3 . Assuming a similar reaction mechanism starting with either **1** or $\text{FvMo}_2(\text{CO})_6$, the disparity in reaction rates is strong evidence for operation of the indenyl effect. Presumably, **5** resulted from protonation of precursor **7**, an analogue of **6**. The fact that this precursor was not isolated speaks to the destabilizing effect of the isobenzofulvene resonance structure on **7**.

Table 1
Addition of CCl₄ to 1-hexene catalyzed by di-molybdenum compounds^a

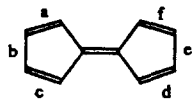
catalyst	% yield ^b	8 h % recovery ^c	turnover ^d	% yield	24 h % recovery	turnover
1	21	43	12.6	69	0	40.7
[CpMo(CO) ₃] ₂	5.6	75	3.1	11	71	5.8
(μ, η^5 : η^5 -dibenzo[a,d]fulvalene)Mo ₂ (CO) ₆ ^e	< 0.20 ^f	77	< 0.11	< 0.4 ^g	65	0.24
FvMo ₂ (CO) ₆	< 0.16 ^f	60	< 0.09	< 0.16 ^f	83	< 0.09

^a Reactions were run in 5 ml CCl₄ at 55°C employing 57 equiv. of 1-hexene per equiv. catalyst. Approximately 0.1 g catalyst used in all reactions. ^b Yield of 1,1,1,3-tetrachloroheptane calculated on 1-hexene. ^c Recovery of catalyst. ^d Calculated as: moles product/initial moles catalyst. ^e See Ref. [8]. ^f No product detected by ¹H NMR; the limit of detection was less than 4.5 mg product in 0.6 ml CDCl₃. ^g A trace of product was detected in ¹H NMR.

A comparative study of the efficacy of several di-molybdenum compounds in catalyzing the addition of CCl₄ to 1-hexene to give 1,1,1,3-tetrachloroheptane gave the results presented in Table 1. Compound **1** was found to be the most effective catalyst, while FvMo₂(CO)₆ proved to be inert. Attempts to catalyze other Kharasch-type reactions with **1** are underway. Kinetic studies by Bitterwolf et al. [11] on the addition on halogenocarbons to 1-octene in the presence of [Mo(CO)₃(η -C₃H₄)₂CH₂] suggest the involvement of free radical intermediates containing an intact metal-metal bond. Consistent with this, insertion products such as (μ, η^5 : η^5 -dibenzo[b,e]fulvalene)Mo₂(CO)₆Cl₂ or (μ, η^5 : η^5 -dibenzo[b,e]fulvalene)[Mo(CO)₃Cl][Mo(CO)₃CCl₃] could not be identified in the reaction mixtures involving **1**.

Several attempts to prepare non-metal-metal-bonded derivatives of **1** were unsuccessful. Reaction of **2'** with one equivalent of either NiCl₂(PPh₃)₂, thionyl chloride, malonyl dichloride, or 2,3-bis(bromomethyl)-1,3-butadiene resulted in **1** and **3**, with no signs of bridged metal-metal species. Deuteration of **2'** with excess CF₃COOD at room temperature in DMSO-d₆ resulted in a complex mixture that contained **1** and **8** (7.5%). The identity of **8** was confirmed by ²D NMR and MS.

In conclusion, we have prepared the first neutral transition metal complex of dibenzo[b,e]fulvalene and have provided examples of its enhanced reactivity compared with FvMo₂(CO)₆, consistent with operation of the indenyl effect. Bridged derivatives without metal-metal bonds remain elusive in the (dibenzo)fulvalene series.



Acknowledgements

We wish to thank Ms. HuaFen Hsu for mounting the crystals and acquiring the data sets.

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