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Synthesis and Reactivity of Doubly Bridged μ-η^5:η^7-Cyclopentadienylcycloheptatrienyl Dimolybdenum Complexes

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The reaction of tropylium tetrafluoroborate, $(C_7H_7)BF_4$, with lithium cyclopentadienides afforded isomeric mixtures of dihydrosesquifulvalenes ((1,3,5-cycloheptatrien-7-yl)cyclopentadienes) of the type $C_5H_3RR'{-}C_7H_7$ (**1a**, R = R′ = *tert*-butyl; **1b**, R = *tert*-butyl, R′ = H; **1c**, R = R′ = H). Lithiation of the hydrocarbons **1a**−**c** followed by reaction with $[(CH_3CN)_3Mo(CO)_3]$, oxidation with iodine, and hydride abstraction using triphenylcarbenium tetrafluoroborate, $(Ph_3C)BF_4$, resulted in the formation of the intensely colored sesquifulvalene complexes $[(\eta^5\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo(CO)_3I]BF_4$ (**2a**), $[(\eta^5\text{-}3\text{-}t\text{-}BuC_5H_3{-}C_7H_6)Mo(CO)_3I]BF_4$ (**2b**), and $[(\eta^5\text{-}C_5H_4{-}C_7H_6)Mo(CO)_3I]BF_4$ (**2c**). Because of the poor solubility and stability of **2c**, the arene exchange reaction with $[(\eta^6\text{-}p\text{-xylene})Mo(CO)_3]$ and complexation of the cycloheptatrienyl moiety could only be carried out with **2a**,**b**, giving bimetallic $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_6I]BF_4$ (**3a**) and $[(\mu\text{-}\eta^5{:}\eta^7\text{-}3\text{-}t\text{-}BuC_5H_3{-}C_7H_6)Mo_2(CO)_6I]BF_4$ (**3b**), in which the five- and seven-membered rings are coordinated in η^5 and η^7 modes, respectively. **3a**,**b** were thermally converted into *syn*-facial $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_5(\mu\text{-}I)]BF_4$ (**4a**) and $[(\mu\text{-}\eta^5{:}\eta^7\text{-}3\text{-}t\text{-}BuC_5H_3{-}C_7H_6)Mo_2(CO)_5(\mu\text{-}I)]BF_4$ (**4b**) by intramolecular CO substitution and formation of an additional Mo−I−Mo bridge. Reaction with triphenylphosphine lead to cleavage of the newly formed Mo−I bond and addition to the dicarbonylcycloheptatrienylmolybdenum unit to yield $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_5I(PPh_3)]BF_4$ (**5a**) and $[(\mu\text{-}\eta^5{:}\eta^7\text{-}3\text{-}t\text{-}BuC_5H_3{-}C_7H_6)Mo_2(CO)_5I(PPh_3)]BF_4$ (**5b**). Similarly, addition of NaI to **4a** gave neutrally charged $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_5I_2]$ (**5**). In addition, the dihydrosesquifulvalene **1a** has been employed in the syntheses of the methyl derivatives $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo(CO)_3(CH_3)]BF_4$ (**8**) and $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_6(CH_3)]BF_4$ (**9**) following a protocol similar to that described for complexes **2** and **3**. Attempts to convert **9** into a methyl-bridged complex via addition of NaI and $Ag(CF_3SO_3)$ unexpectedly gave the corresponding triflate $[(\mu\text{-}\eta^5{:}\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_6(CH_3)]CF_3SO_3$ (**10**) only. The X-ray crystal structures of **4a**·CH_2Cl_2, **5a**·CH_2Cl_2, and **10**·CH_2Cl_2 are reported. Attempts to obtain sesquifulvalene complexes containing Mo−Mo bonds proved to be unsuccessful.

Introduction

Sesquifulvalene **I** is highly reactive and not stable in the free state.[1] Although it can be described in terms of the two resonance structures **IA** and **IB**, its spectroscopic characterization at low temperature reveals that it behaves like a polyene with alternating bond lengths and that its ground-state electronic structure is best represented by the apolar resonance form **IA**.[2] In contrast, charge separation is observed upon complexation and stabilization of **I** and derivatives thereof by transition-metal fragments,[3−6] and heterobimetallic iron/chromium[4] and manganese/chromium[5] complexes

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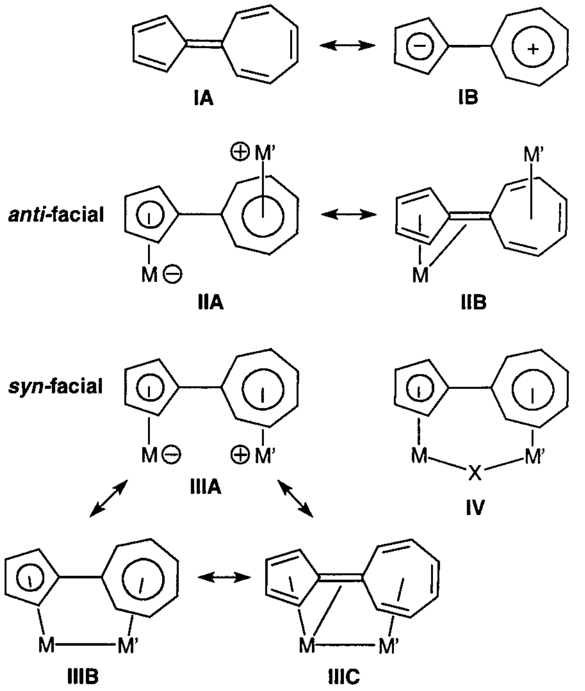
Scheme 1



of type **II** have been obtained. The spectroscopic and structural properties of the latter clearly indicate sesquifulvalene ligands coordinated in a dipolar μ-η^5:η^7 fashion (resonance structure **IIA**, Scheme 1). In these complexes the cyclopentadienyl and cycloheptatrienyl fragments act as strongly coupled electron-donating and -accepting groups, respectively, and therefore together meet the requirements for the classical construction of compounds with large SHG (second harmonic generation) efficiencies.[7] Consistently, it has been observed that sesquifulvalene complexes exhibit unusually large nonlinear optical (NLO) properties, and first molecular hyperpolarizabilities β have been determined[5b,6] which are among the highest values ever measured for organometallic NLO chromophores.[8]

All bimetallic sesquifulvalene complexes structurally characterized in the past[4,5] show an *anti*-facial arrangement of the transition-metal centers, only allowing indirect communication across the bridging ligand. To achieve "true" bimetallic reactivity with both metal centers participating in dinuclear organometallic transformations, however, the metal centers must coordinate to the same side of the sesquifulvalene ligand. Therefore, in view of the interesting properties of *syn*-facially oriented bimetallic complexes containing the related hydrocarbon fulvalene (or bicyclopentadienyl, respectively),[9,10] we have recently aimed toward the synthesis of *syn*-facial sesquifulvalene complexes of type **III** (Scheme 1). Although one has to expect a longer distance between the ring centers in planar sesquifulvalene than in planar μ-η^5:η^5-fulvalene,[10,11] which will inevitably cause a greater bending distortion of the π-ligand, we anticipated that the formation of metal−metal bonds should be possible due to the dipolar characteristics of coordinated sesquifulvalene (vide supra). Consequently, in neutrally charged complexes, this polarization should result in nucleophilic properties of the cyclopentadienyl complex fragment, whereas the cycloheptatrienyl complex fragment should react as an electrophile (**IIIA**, Scheme 1). An intramolecular dinuclear interaction of nucleophile and electrophile could thereby lead to the formation of a potentially dipolar metal−metal bond (**IIIB**). Contributions from resonance structure **IIIC**, which consists of a pentafulvene[12] and a heptafulvene[13] structural motif, could account for some shortening of the metal−metal bond distance.

Our first target molecules had been complexes of type **III** with M = Mo(CO)$_3$ and M′ = Mo(CO)$_2$, as Whiteley has reported the preparation of the corresponding unbridged complex [(η^5-C$_5$H$_5$)(CO)$_3$Mo−Mo(CO)$_2$(η^7-C$_7$H$_7$)] by the reaction of anionic, nucleophilic [(η^5-C$_5$H$_5$)(CO)$_3$Mo]$^-$ with cationic, electrophilic [(η^7-C$_7$H$_7$)Mo(CO)$_2$(CH$_3$CN)]$^+$.[14] Thus, in a continuation of our work on transition-metal complexes with dipolar cycloheptatrienyl ligands,[3,5,15] we wish to report on our attempts to prepare the corresponding dimolybdenum sesquifulvalene derivatives via *syn*-facial complexes of type **IV** (Scheme 1), which contain a second linkage to block rotation to the *anti* orientation and to place the

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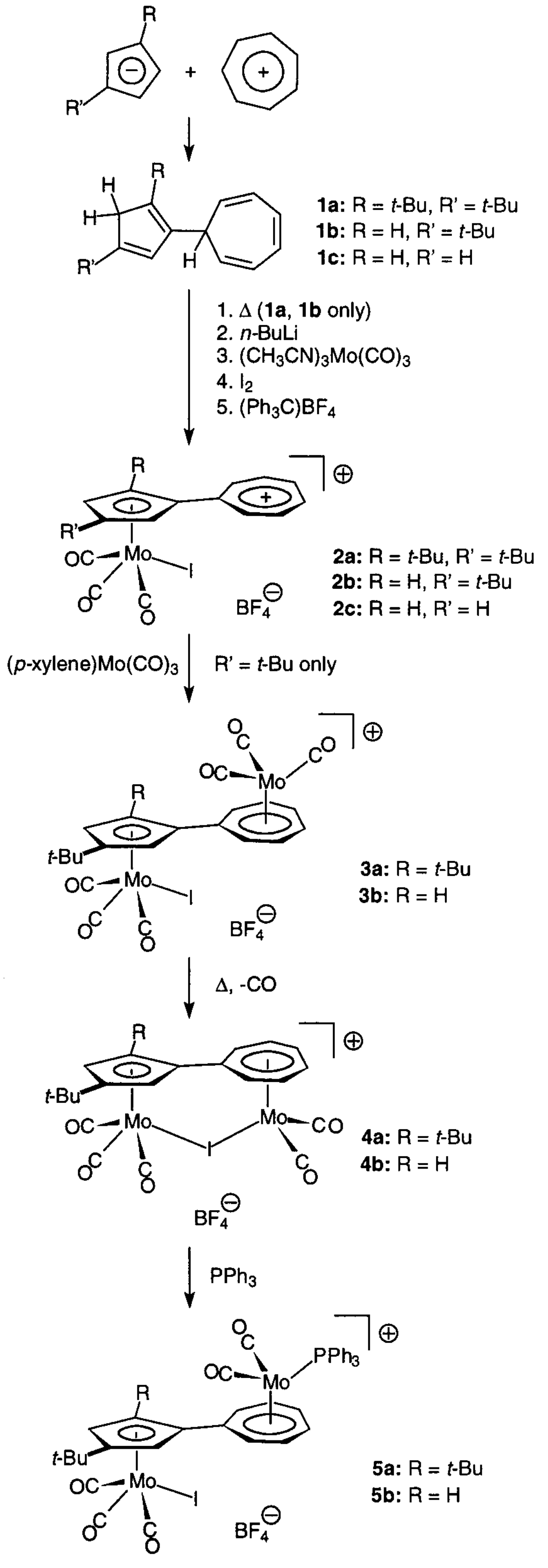
two metal centers in close proximity for subsequent reductive formation of a metal–metal bond.[16]

Results and Discussion

Preparation and Characterization of Iodo-Bridged Sesquifulvalene Complexes. Previously, the preparation of sesquifulvalene complexes has been accomplished by template syntheses which usually involve a C–C coupling reaction between a cyclopentadienyl complex and a cycloheptatrienyl derivative, followed by complexation of the cycloheptatrienyl unit and/or hydride abstraction.[3–6] This synthetic procedure is limited to cyclopentadienyl complexes which can readily be functionalized at the five-membered ring, e.g. by metalation and halogenation reactions.[17] To develop methods more widely applicable to the preparation of sesquifulvalene complexes, we became interested in employing dihydrosesquifulvalenes such as **1a**–**c** (Scheme 2), which can be deprotonated and transferred to metal centers like ordinary cyclopentadiene derivatives.[18] Thus, on reaction of lithium cyclopentadienides with $(C_7H_7)BF_4$ the nucleophilic cyclopentadienyl anion adds to the electrophilic tropylium cation, yielding 1,3,5-cycloheptatrienes **1a**–**c**, which bear the Cp residue in the allylic 7-position.[19]

Scheme 2



As the unsubstituted dihydrosesquifulvalene **1c** and its isomers are not stable in pure form and easily decompose to form polymeric material, presumably via intra- and intermolecular Diels–Alder additions, the reaction mixture obtained upon the addition of $(C_7H_7)BF_4$ to a thf solution of $Li(C_5H_5)$ was directly treated with another 1 equiv of *n*-butyllithium to generate the (1,3,5-cycloheptatrien-7-yl)cyclopentadienide, which could then be coordinated to a molybdenum tricarbonyl unit on reaction with $[(CH_3CN)_3Mo(CO)_3]$. The intermediate anionic complex was oxidized with iodine to give a cycloheptatrienyl-functionalized complex of the type $[(\eta^5\text{-}C_5H_4\text{–}C_7H_7)Mo(CO)_3I]$[20] in the form of red crystals after chromatographic purification. Subsequent hydride abstraction to form the cationic sesquifulvalene complex $[(\eta^5\text{-}C_5H_4\text{–}C_7H_6)Mo(CO)_3I]BF_4$ (**2c**) could then be accomplished with triphenylcarbenium tetrafluoroborate, $(Ph_3C)BF_4$ (Scheme 2). In principle, the analogous *tert*-butyl-substituted sesquifulvalene derivatives **2a**,**b** could be prepared in the same manner. In contrast to **1c**, however, the dihydrosesquifulvalenes **1a**,**b** could be isolated as stable yellow oils which can be further purified by Kugelrohr distillation and/or column chromatography. As we have observed that the bulky *tert*-butyl groups might hamper the ensuing hydride abstraction, these hydrocarbons were thermally rearranged in DMF at 150 °C through 1,5-sigmatropic hydrogen migration.[21] Lithiation followed by successive treatment with $[(CH_3CN)_3Mo(CO)_3]$ and I_2 gave isomeric mixtures of neutrally charged hydrosesquifulvalenyl complexes which after chromatographic purification underwent smooth hydride abstraction to yield red-purple $[(\eta^5\text{-}2,4\text{-}$

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t-Bu$_2$C$_5$H$_2$−C$_7$H$_6$)Mo(CO)$_3$I]BF$_4$ (**2a**) and purple [(η^5-3-*t*-BuC$_5$H$_3$−C$_7$H$_6$)Mo(CO)$_3$I]BF$_4$ (**2b**) (Scheme 2).

Similar to previously reported sesquifulvalene complexes, **2a**−**c** are intensely colored compounds. They show strong solvatochromic behavior, and their ultraviolet/visible spectra are markedly affected by varying the solvent. The lowest energy band $\lambda_{\max}$ centered at about 470−550 nm is most strongly shifted upon changing the solvent from dichloromethane to acetonitrile ($\Delta\tilde{\nu}$ ranging from 770 cm^{-1} in **2b** to 1800 cm^{-1} in **2a**, see Experimental Section). Because of these hypsochromic shifts (negative solvatochromism) the lowest energy transition in these systems can be assigned as being effectively the π to π^* CT transition, which can *approximately* (!) be represented by canonical forms similar to **IIA** (ground state) and **IIB** (excited state) depicted for bimetallic complexes in Scheme 1. For all complexes **2** the ^{1}H NMR resonances for the seven-membered-ring hydrogen atoms are observed as a single, unresolved multiplet at low field (9.18−8.84 ppm) typical of substituted tropylium salts,[22] supporting the conclusion that the ground-state electronic structures of complexes **2** are best described by the Lewis formulas shown in Scheme 2. Unfortunately, **2c** is only sparingly soluble in organic solvents and defied our efforts to characterize it by ^{13}C NMR spectroscopy. As it contains a C_s symmetric complex cation, one would have expected only two different resonances for the carbonyl carbon atoms, whereas the unsymmetric substitution pattern of the cyclopentadienyl rings in **2a** and **2b** gives rise to three separate signals, each with the CO group trans to iodine being identified at lowest field. The observation of only four ^{13}C NMR resonances for the cycloheptatrienyl carbon nuclei in **2a** and **2b** indicates that rotation around the C−C bond between the five- and seven-membered rings is fast on the NMR time scale, quickly interconverting the diastereotopic CH groups.

To use the monometallic complexes **2** for the preparation of the bimetallic dimolybdenum derivatives of type **3**, a high-yielding protocol for the direct complexation of the tropylium moieties in **2a**−**c** is required. Previously, Whiteley and co-workers have demonstrated that the reaction of monosubstituted cycloheptatrienyl cations with *fac*-[(MeCN)$_3$Mo(CO)$_3$] in the presence of a catalytic amount of the ferricenium cation results in the formation of [(η^7-C$_7$H$_6$R)Mo(CO)$_3$]$^+$ (R = alkyl, alkynyl, aryl), albeit in only moderate yield.[23] Stimulated by reports on the possibility of Mo(CO)$_3$ group transfer onto tropyne[24] and 1,2,4,6-cycloheptatetraene[25] complexes by using [(η^6-*p*-xylene)Mo(CO)$_3$],[26] we have recently been able to successfully apply this method for the preparation of sterically demanding cycloheptatrienyl complexes.[27] Accordingly, treatment of thf solutions of the monometallic tetrafluoroborate salts **2a**,**b** with a slight excess of [(η^6-*p*-xylene)Mo(CO)$_3$] leads to an instantaneous color change and furnishes the bimetallic cycloheptatrienyl complexes **3a**,**b** in about 60% yield after stirring for about 2 h (Scheme 2). The air-stable complexes **3a**,**b** are obtained as orange-brown, crystalline solids after precipitation with diethyl ether. In contrast, Mo(CO)$_3$ group transfer onto **2c** proved to be much more complicated. Although the spectroscopic data indicated the formation of a bimetallic compound, its complete spectroscopic characterization was hampered by its significantly reduced solubility and stability compared to **3a**,**b**. In addition, the use of this material for the preparation of a doubly bridged complex was of limited success, too, and therefore all experiments detailed below have been carried out with mono- or di-*tert*-butyl substituted derivatives only.

The orange-brown color of the complexes **3a**,**b** already indicates that the lowest energy UV/vis bands in these systems must have hypsochromically shifted relative to those of monometallic **2a**,**b**. In fact, no strong absorption maximum can be observed in the visible region, only a broad shoulder which merges into an intense band centered at about 300 nm. As described for other bimetallic sesquifulvalene complexes,[5,6] interaction of the Mo(CO)$_3$ group with the cycloheptatrienyl unit increases the HOMO/LUMO energy gap of the relevant π to π^* CT excitation, or, in other words, the [(C$_7$H$_6$R)-Mo(CO)$_3$ moiety has a stronger ability to effectively stabilize a positive charge than the “naked” tropylium system, which leads to an increase in the energy difference between the two limiting resonance structures **IIA** and **IIB** in Scheme 1. As another result of Mo(CO)$_3$ coordination, all ^{1}H and ^{13}C NMR resonances attributable to the cycloheptatrienyl rings in complexes **3** are strongly shielded with respect to those of monometallic **2a**,**b** and are typical of those observed for ring-substituted cycloheptatrienyl complexes of the type [(η^7-C$_7$H$_6$R)Mo(CO)$_3$]$^+$.[23,27] The unsymmetrically *tert*-butyl-substituted sesquifulvalene ligands in the chiral complexes [(μ-η^5:η^7-2,4-*t*-Bu$_2$C$_5$H$_2$−C$_7$H$_6$)Mo$_2$(CO)$_6$I]BF$_4$ (**3a**) and [(μ-η^5:η^7-3-*t*-BuC$_5$H$_3$−C$_7$H$_6$)Mo$_2$(CO)$_6$I]BF$_4$ (**3b**) give rise to six ^{1}H NMR resonances each for the diastereotopic cycloheptatrienyl protons in addition to the four resonances for the remaining cyclopentadienyl CH or *tert*-butyl CH$_3$ groups, respectively. In agreement with the ^{1}H NMR data, the ^{13}C NMR spectra of **3a**,**b** exhibit 12 signals attributable to the sesquifulvalene framework and four signals for the carbonyl groups (in **3a** two of these signals accidentally overlap). The three smaller, lower field signals arise from the tricarbonylcyclopentadienylmetal fragment (vide supra), while the high-field resonance can be assigned to the tricarbonylcycloheptatrienylmetal fragment.

The ^{13}C NMR measurements for complexes **3** must generally be performed at lower temperature (usually at −5 °C) in order to obtain spectra of the pure compounds only. Recording the data overnight at room temperature resulted in more complicated spectra and in the observation of additional resonances, which can be assigned to the doubly bridged complexes **4**. This indicates that intramolecular CO substitution can easily be achieved, and consequently, complete conversion of complexes **3** can be achieved by heating in dichloromethane at 40 °C to form the *syn*-facially oriented complexes **4** containing a bridging μ-iodo ligand. This

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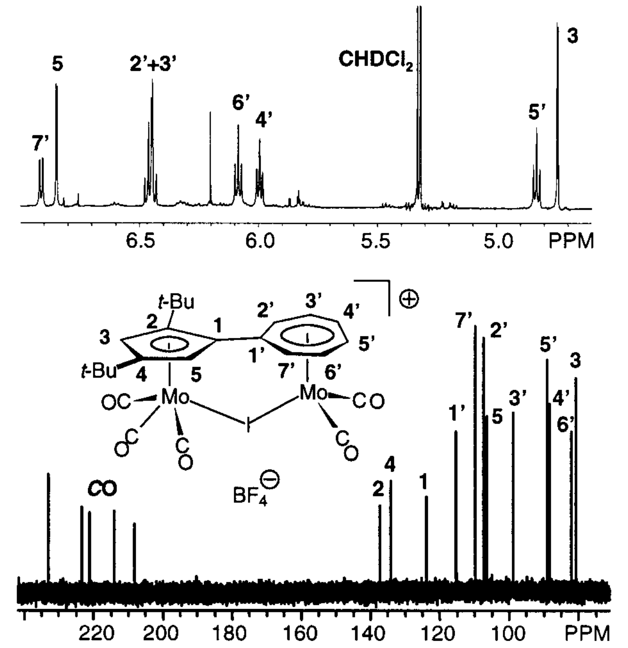

Figure 1. Selected parts of the ^{1}H NMR (600 MHz, CD_2Cl_2) and ^{13}C NMR spectra (150.9 MHz, CD_2Cl_2) of **4a**.

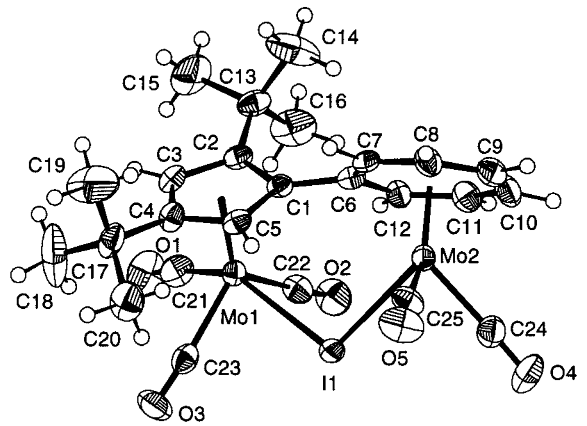

Figure 2. ORTEP drawing of one cation (molecule A) in **4a**·CH_2Cl_2 with thermal ellipsoids drawn at 50% probability.

reaction resembles the formation of the doubly bridged bicycloheptatrienyl complex $[(\mu\text{-}\eta^7:\eta^7\text{-}C_7H_6{-}C_7H_6)Mo_2(CO)_4(\mu\text{-}I)]PF_6$ containing a similar Mo−I−Mo unit.[28] The NMR resonances of the sesquifulvalene framework are strongly affected by the introduction of the second linkage, and as an illustrative example the well-resolved CH portion of the ^{1}H NMR spectrum of $[(\mu\text{-}\eta^5:\eta^7\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo_2(CO)_5(\mu\text{-}I)]BF_4$ (**4a**) is depicted in Figure 1 (top). The same holds true for comparison of the ^{13}C NMR spectra, and in the case of **4a** all 12 resonances attributable to the sesquifulvalene CH groups are strongly shifted in comparison with **3a**. The most striking difference in the spectra of complexes **3a** and **4a**, however, is the observation of five individual resonances for the five CO groups in **4a** in contrast to four resonances in **3a**, as the carbonyl groups of the cycloheptatrienyl-bound $Mo(CO)_2$ moiety also become diastereotopic upon introduction of the second linkage. The CO and CH portion of the ^{13}C NMR spectrum of **4a** is presented in Figure 1 (bottom). The assignment of all sesquifulvalene ^{1}H and ^{13}C resonances is supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). On the other hand, the mono-*tert*-butyl substituted derivative **4b** is much less soluble than **4a**, and satisfactory NMR measurements could only be performed in CD_3CN solution. Significant broadening of several CH resonances indicates dynamic behavior and partial cleavage of the Mo−I−Mo bridge by addition of nucleophilic acetonitrile and presumably formation of a $[(\mu\text{-}\eta^5:\eta^7\text{-}3\text{-}t\text{-}Bu_2C_5H_3{-}C_7H_6)Mo_2(CO)_5\text{-}I(CD_3CN)]BF_4$, in which the solvent molecule is most likely coordinated to the tricarbonylcyclopentadienylmetal fragment in analogy to the phosphine ligand in complexes **5** (vide infra).

To unambiguously confirm the formation of iodo-bridged species, a single-crystal of **4a**·CH_2Cl_2 was subjected to X-ray diffraction analysis. The asymmetric unit contains two independent, almost identical molecules **4a**, and the structure of cation A is shown in Figure 2. The sesquifulvalene ligand coordinates to the $Mo(CO)_3$ and $Mo(CO)_2$ fragments in η^5 and η^7 modes, respectively, and the inter-ring distances (molecule A, C1−C6 = 1.489(9) Å; molecule B, C1−C6 = 1.500(9) Å) clearly correspond to $C(sp^2){-}C(sp^2)$ single bonds. These structural features indicate that the cation in **4a** can be best regarded as being composed of (η^5-cyclopentadienyl)$Mo(CO)_3$ and (η^7-cycloheptatrienyl)$Mo(CO)_2$ moieties which are additionally linked by a μ-iodo ligand. The Mo−I−Mo angles in molecules A and B are 104.56(2) and 105.22(2)°, respectively, and are similar to those of other iodine-bridged species,[28,29] for which a relatively wide range of angles has been observed due to the general structural flexibility of halide bridges. Although the formation of the doubly bridged complexes **4** from precursors **3** might give the impression that the (η^5-cyclopentadienyl)$Mo(CO)_3I$ unit should be regarded as a hemilabile donor group only weakly coordinating to the (η^7-cycloheptatrienyl)$Mo(CO)_2$ fragment, this is not reflected by the molybdenum−iodine distances, as the newly formed I−$Mo(CO)_2$ bond is even shorter than the preexisting $(CO)_3Mo{-}I$ bond (2.8196(7) vs 2.8510(7) Å in molecule A and 2.8158(7) vs 2.8572(7) Å in molecule B). Another striking structural feature of **4a** is the twisted conformation of the sesquifulvalene ligand with bend angles between the best ring planes containing C1−C5 and C6−C12 of 48.5° (molecule A) and 41.9° (molecule B). On one hand, this twisted conformation can partially be attributed to the *tert*-butyl groups at C2, which prevents the five- and seven-membered rings from adopting a strictly coplanar orientation. On the other hand, such twisted conformations are a consistent structural feature in related doubly bridged bimetallics, and similar twist angles have been observed in the closely related bicycloheptatrienyl complex $[(\mu\text{-}\eta^7:\eta^7\text{-}C_7H_6{-}C_7H_6)Mo_2(CO)_4(\mu\text{-}I)]PF_6$ (two independent mol-

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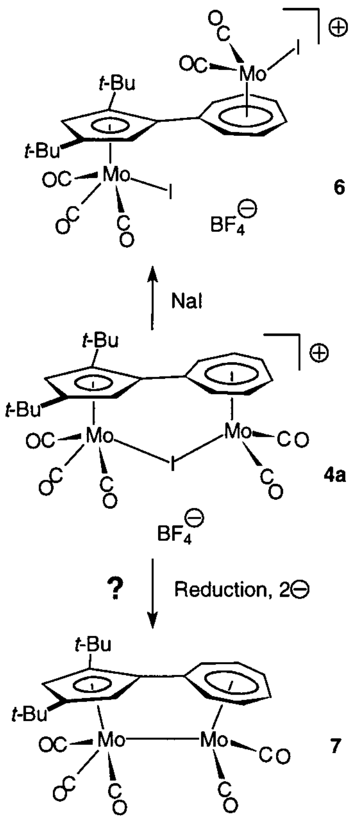
(28) Beddoes, R. L.; Davies, E. S.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1995**, 3231.

(29) For selected examples, see: (a) Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Cai, R.; Ackermann, K.; Neugebauer, D. *Chem. Ber.* **1982**, *115*, 3152. (b) Curtis, M. D.; Fotinos, N. A.; Han, K. R.; Butler, W. M. *J. Am. Chem. Soc.* **1983**, *105*, 2686. (c) Calderazzo, F.; Poli, R.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1988**, *118*, 583.

Scheme 3



ecules with interplanar angles of 39.8 and 35.5°)[28] as well as in diphosphine-bridged biphenyl complexes.[30]

Reactions of Iodo-Bridged Sesquifulvalene Complexes. The formation of complexes **4** from **3** represents an example of true bimetallic reactivity promoted by the sesquifulvalene ligand, which places the two metal centers in close proximity, allowing fast intramolecular CO substitution and formation of a stable iodo bridge. On reaction with nucleophiles such as triphenylphosphine or iodide (from NaI), however, rapid cleavage and addition is observed, and the triphenylphosphine complexes $[(\mu\text{-}\eta^5\text{:}\eta^7\text{-}2,4\text{-}t\text{-Bu}_2\text{C}_5\text{H}_2\text{-C}_7\text{H}_6)\text{Mo}_2(\text{CO})_5\text{I}(\text{PPh}_3)]\text{BF}_4$ (**5a**) and $[\text{-}(\mu\text{-}\eta^5\text{:}\eta^7 3\text{-}t\text{-BuC}_5\text{H}_3\text{-C}_7\text{H}_6)\text{Mo}_2(\text{CO})_5\text{I}(\text{PPh}_3)]\text{BF}_4$ (**5b**) (Scheme 2) as well as the diiodo complex $[(\mu\text{-}\eta^5\text{:}\eta^7\text{-}2,4\text{-}t\text{-Bu}_2\text{C}_5\text{H}_2\text{-C}_7\text{H}_6)\text{Mo}_2(\text{CO})_5\text{I}_2]$ (**6**) (Scheme 3) can be isolated in high yield. Whereas the diiodide **6** does not allow us to decide which of the two Mo−I bonds has formed, the nucleophilic addition of the triphenylphosphine ligand could lead to two different structural isomers. The NMR spectroscopic data of **5a** and **5b**, however, indicate that the addition proceeds in a regioselective manner and that complexes with linked $(\eta^7\text{-cycloheptatrienyl})\text{Mo}(\text{CO})_2(\text{PPh}_3)$ and $(\eta^5\text{-cyclopentadienyl})\text{Mo}(\text{CO})_3\text{I}$ units have formed. This structural assignment could be confirmed by an X-ray study of **5a**·CH$_2$Cl$_2$. Again, the asymmetric unit contains two independent, chemically identical molecules, and the structure of cation A is shown in Figure 3. In contrast to related *anti*-facially oriented bimetallic sesquifulvalene complexes, the five- and seven-membered rings are not coplanar but rather adopt an almost perfectly perpendicular orientation (dihedral angles 82.6° (molecule A) and 94.4° (molecule B)), which completely precludes any significant electronic π-interaction between the $(\eta^7\text{-cycloheptatrienyl})\text{Mo}(\text{CO})_2(\text{PPh}_3)$ and $(\eta^5\text{-cyclopentadienyl})\text{Mo}(\text{CO})_3\text{I}$ subunits. Again this can partially be attributed to steric hindrance caused by the *tert*-butyl group in the 2-position. In addition, however, one should also take into account that coordination of the PPh$_3$ ligand leaves the cycloheptatrienyl complex fragment more electron-rich, thus decreasing its π-accepting abilities and its urge to withdraw π-electron density from the cyclopentadienyl complex fragment. The remaining Mo−I bond length in **5a** is only slightly shorter than the corresponding distance in **4a** (2.8401(12) and 2.8450(10) Å vs 2.8510(7) and 2.8572(7) Å), and within experimental error, all comparable bond distances and angles fall in the same ranges observed for **4a** (vide supra, Table 1).

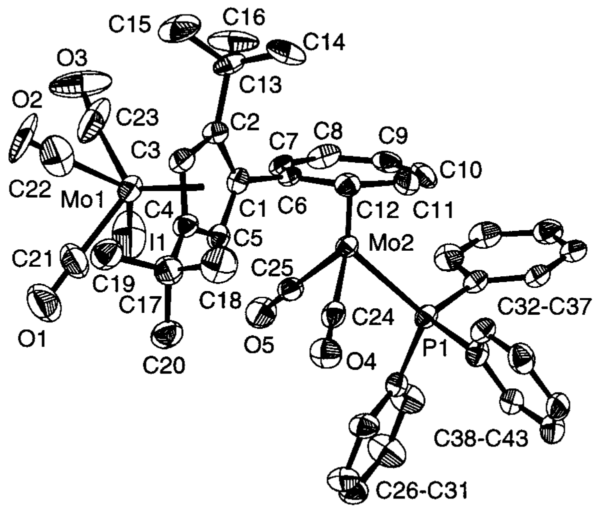


Figure 3. ORTEP drawing of one cation (molecule A) in **5a**·CH$_2$Cl$_2$ with thermal ellipsoids drawn at 50% probability.

Apart from addition reactions, the most important goal was the preparation of bimetallics of type **III** (Scheme 1) by two-electron reduction of complexes **4**, in which the second linkage places the two metal centers in close proximity for subsequent reductive formation of a metal−metal bond. Although the intermetallic molybdenum−molybdenum separations of 4.485 Å (molecule A) and 4.507 Å (molecule B) in **4a** seem to preclude the possibilty of metal−metal bond formation, our preliminary model studies suggested that a sesquifulvalene ligand bent in a similar manner as reported for fulvalene (or bicyclopentadienyl) systems should be able to bridge a metal−metal distance of 3−3.5 Å, which is the range observed for related dimolybdenum derivatives. For instance, the Mo−Mo distances in $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Mo-Mo}(\text{CO})_2(\eta^7\text{-C}_7\text{H}_7)]$,[14b] $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6]$,[31] and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\text{CO})_6]$,[32] which contain unsupported metal−metal bonds, are 3.160, 3.235, and 3.281 Å, respectively, whereas the corresponding bond

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(30) (a) Van Order, N., Jr.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680. (b) Geiger, W. E.; Van Order, N., Jr.; Pierce, D. T.; Bitterwolf, T. E.; Rheingold, A. L.; Chasteen, N. D. *Organometallics* **1991**, *10*, 2403.

(31) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

(32) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C. *Acta Crystallogr.* **1988**, *C44*, 568.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 4a·CH_2Cl_2, 5a·CH_2Cl_2, and 10·CH_2Cl_2

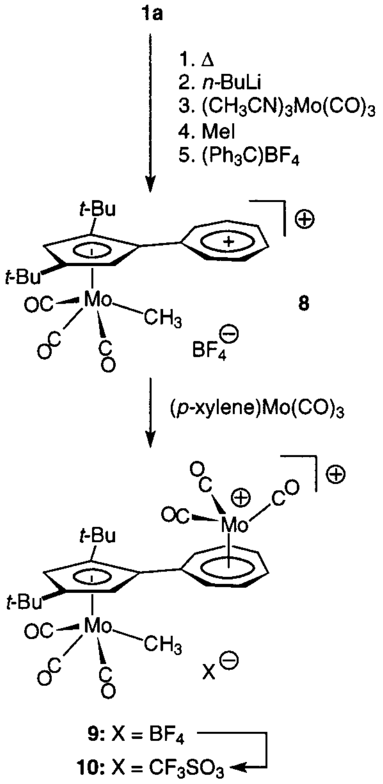
	4a·CH_2Cl_2		**5a**·CH_2Cl_2		
	molecule A	molecule B	molecule A	molecule B	**10**·CH_2Cl_2
C1−C2	1.441(8)	1.439(9)	1.418(11)	1.431(11)	1.443(6)
C1−C6	1.489(9)	1.500(9)	1.505(12)	1.537(12)	1.497(6)
C2−C3	1.440(9)	1.435(9)	1.433(13)	1.406(13)	1.424(6)
C3−C4	1.418(9)	1.410(10)	1.429(12)	1.430(12)	1.420(6)
C4−C5	1.390(9)	1.405(9)	1.414(12)	1.382(12)	1.413(6)
C6−C7	1.393(9)	1.398(9)	1.385(12)	1.390(13)	1.429(6)
C7−C8	1.421(9)	1.433(9)	1.408(13)	1.428(13)	1.408(6)
C8−C9	1.400(10)	1.399(10)	1.405(14)	1.389(13)	1.405(8)
C9−C10	1.411(10)	1.405(10)	1.395(15)	1.414(14)	1.411(8)
C10−C11	1.419(10)	1.405(10)	1.397(14)	1.376(14)	1.397(7)
C11−C12	1.383(9)	1.403(9)	1.399(13)	1.428(13)	1.430(6)
Mo1−C1	2.310(6)	2.281(6)	2.379(9)	2.309(8)	2.334(4)
Mo1−C2	2.346(6)	2.369(6)	2.397(9)	2.333(8)	2.360(4)
Mo1−C3	2.321(6)	2.326(6)	2.305(9)	2.282(9)	2.335(5)
Mo1−C4	2.374(7)	2.368(7)	2.333(9)	2.415(9)	2.394(5)
Mo1−C5	2.324(6)	2.310(6)	2.295(8)	2.353(9)	2.350(4)
Mo2−C6	2.328(6)	2.345(6)	2.339(8)	2.345(7)	2.381(4)
Mo2−C7	2.319(6)	2.340(6)	2.301(8)	2.303(8)	2.296(5)
Mo2−C8	2.264(7)	2.284(7)	2.336(10)	2.348(9)	2.329(5)
Mo2−C9	2.315(7)	2.295(6)	2.321(9)	2.358(10)	2.312(5)
Mo2−C10	2.280(7)	2.283(7)	2.299(9)	2.306(9)	2.331(5)
Mo2−C11	2.341(7)	2.321(7)	2.345(9)	2.348(9)	2.316(5)
Mo2−C12	2.303(7)	2.306(6)	2.294(8)	2.307(8)	2.333(4)
Mo1−I1	2.8510(7)	2.8572(7)	2.8401(12)	2.8450(10)	
Mo2−I1	2.8196(7)	2.8158(7)			
Mo2−P1			2.511(2)	2.511(2)	
Mo1−C21	2.003(8)	2.007(9)	2.003(12)	1.988(11)	2.012(5)
Mo1−C22	1.989(8)	2.024(9)	2.055(16)	2.010(12)	1.983(6)
Mo1−C23	2.008(8)	2.013(8)	2.068(17)	1.978(9)	1.985(5)
Mo2−C24	2.030(8)	2.058(9)	2.016(11)	2.009(11)	
Mo2−C25	2.031(8)	2.013(7)	2.039(10)	2.033(10)	2.037(6)
Mo2−C26					2.024(7)
Mo2−C27					2.021(5)
C21−O1	1.129(9)	1.122(9)	1.137(13)	1.169(12)	1.125(6)
C22−O2	1.149(9)	1.081(9)	0.977(15)	1.135(13)	1.138(7)
C23−O3	1.128(8)	1.130(9)	0.985(16)	1.136(11)	1.138(6)
C24−O4	1.130(9)	1.128(9)	1.135(12)	1.136(12)	
C25−O5	1.133(9)	1.131(8)	1.130(11)	1.126(11)	
C25−O4					1.126(7)
C26−O5					1.133(8)
C27−O6					1.125(7)
Mo1−I1−Mo2	104.56(2)	105.22(2)			
(C1−C5)−(C6−C12)[a]	48.5	41.9	82.6	94.4	73.6

[a] Interplanar angle.

length in the fulvalene complex [(μ-η^5:η-C_5H_4−C_5H_4)-$Mo_2(CO)_6$] is 3.371 Å.[33]

Nevertheless, we have to admit that our attempts to treat **4a** with a wide variety of reducing agents to form **7** (Scheme 3) have been completely unsuccessful, and on reaction with Na/K, Na/Hg, or Li(BEt_3H), we could only observe decomposition and/or formation of the known compounds **3a** and **6**, which must have formed by CO or iodine scrambling processes, respectively. During the reaction with hydride sources, we anticipated that in analogy to the diiodide **6** a dihydride containing linked (η^5-cyclopentadienyl)$Mo(CO)_3H$ and (η^7-cycloheptatrienyl)$Mo(CO)_2H$ moieties could form, which might then reductively eliminate dihydrogen.

Scheme 4



Attempted Preparation of Methyl-Bridged Sesquifulvalene Complexes. Similarly, a methyl hydride derivative could undergo methane elimination, and therefore we aimed toward the synthesis of the mono- and bimetallic methyl complexes **8** and **9**, which have been synthesized by following a procedure analogous to that described for the synthesis of the iodo complexes **2a** and **3a**. Hence, treatment of lithiated **1a** (and isomers thereof) with *fac*-[$(MeCN)_3Mo(CO)_3$] followed by reaction of the anionic intermediate with methyl iodide gives neutrally charged [(η^5-2,4-*t*-$Bu_2C_5H_2$−C_7H_7)Mo-$(CO)_3(CH_3)$], which is subsequently treated with $(Ph_3C)BF_4$ to yield the monometallic sesquifulvalene derivative [(η^5-2,4-*t*-$Bu_2C_5H_2$−C_7H_6)$Mo(CO)_3(CH_3)$]BF_4 (**8**) (Scheme 4). This was used directly for the reaction with [(η^6-*p*-xylene)$Mo(CO)_3$] to produce bimetallic [(μ-η^5:η^7-2,4-*t*-$Bu_2C_5H_2$−C_7H_6)$Mo_2(CO)_6CH_3$]BF_4 (**9**). As described for the corresponding iodide **3a**, the ^{13}C NMR spectrum exhibits three carbonyl resonances for the cyclopentadienyl bound $Mo(CO)_3(CH_3)$ group together with only one resonance for the cycloheptatrienyl-bound $Mo(CO)_3$ group. Furthermore, 12 different signals can be observed for the sesquifulvalene carbon framework and four signals for the quarternary and primary *tert*-butyl carbon atoms in addition to one signal at −18.2 ppm, which can be assigned to the metal-bound CH_3 group.

Preliminary results show that formation of a doubly bridged methyl complex containing a Mo−CH_3−Mo three-center−two-electron bond is not possible, as the reaction of **8** with sodium iodide followed by iodide abstraction with silver trifluoromethanesulfonate does not give the desired methyl-bridged derivative but [(μ-η^5:η^7-2,4-*t*-$Bu_2C_5H_2$−C_7H_6)$Mo_2(CO)_6CH_3$](CF_3SO_3) (**10**) as the only isolable compound, which must have formed by an intermolecular CO scrambling process leading to the same cation as in compound **9**. Consequently, the spectroscopic data are also virtually identical. In addition, single crystals of **10**·CH_2Cl_2 suitable for X-ray diffraction analysis could be grown, and Figure 4 shows a presentation of the respective cation. As observed for **4a** and **5a**, the sesquifulvalene ligand is strongly twisted, with an interplanar angle between the best

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(33) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 82.

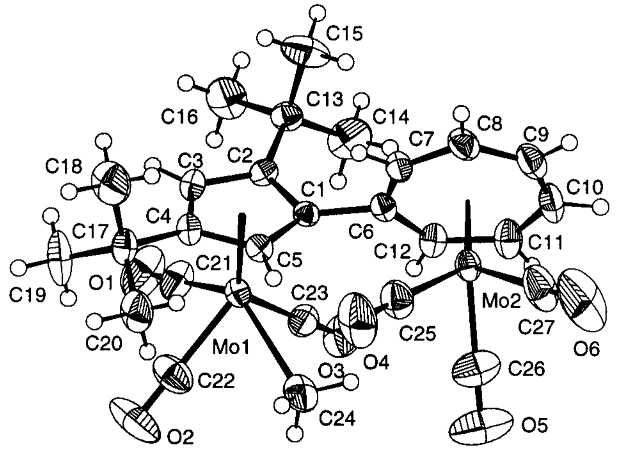

Figure 4. ORTEP drawing of one cation (molecule A) in **10**·CH_2Cl_2 with thermal ellipsoids drawn at 50% probability.

least-squares planes containing C1−C5 and C6−C12 of 73.6°, and the structural features indicate two noninteracting cyclopentadienyl and cycloheptatrienyl moieties. All other comparable bond lengths and angles resemble those of **4a** and **5a** and fall in the expected ranges (Table 1). In addition, the cyclopentadienyl part of the molecule is very similar to the structure of the tetra-*tert*-butylfulvalene complex $[(\mu\text{-}\eta^5{:}\eta^5\text{-}t\text{-}Bu_4C_{10}H_{10})Mo_2(CO)_6(CH_3)_2]$.[34]

Conclusion

In summary, we have presented a high-yielding protocol for the syntheses of doubly bridged bimetallic sesquifulvalene complexes. Attaching *tert*-butyl groups to the sesquifulvalene framework proved to be essential to sufficiently increase the stability and solubility of the resulting complexes. Although the use of these systems for the preparation of complexes containing metal−metal bonds has not been successful and indeed does not seem to be particularly encouraging on the basis of the results presented here, these complexes might become useful for the introduction of various bridging groups other than halides such as H, OH, O, S, Se, Te, alkynyl, etc. In addition, dihydrides containing linked (η^5-cyclopentadienyl)Mo(CO)$_3$H and (η^7-cycloheptatrienyl)Mo(CO)$_2$H moieties are interesting target molecules, as the dipolar nature of the coordinated sesquifulvalene ligand should also result in an opposite polarization of the metal−hydrogen bonds, resulting in a more "protic" and in a more "hydridic" hydrogen atom on the cyclopentadienyl and cycloheptatrienyl sides of the molecule, respectively, which is particularly interesting in view of applications directed toward the heterolytic cleavage of dihydrogen.[35] Proper substitution of the sesquifulvalene framework, the judicious choice of supporting ligands, and variation of the metal centers will allow us to adjust the properties of these systems to future challenges of that kind.

Experimental Section

All operations were performed under an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. Tropylium tetrafluoroborate,[22] triphenylcarbenium tetrafluoroborate,[36] $[(\eta^6\text{-}p\text{-xylene})Mo(CO)_3]$,[26] and $[(CH_3CN)_3Mo(CO)_3]$[37] were prepared according to published procedures.

Preparation of $[(\eta^5\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_6)Mo(CO)_3I]BF_4$ (2a). A solution of 1,3-di-*tert*-butylcyclopentadiene (2.75 g, 15.4 mmol) in thf (50 mL) was treated with *n*-butyllithium (6.5 mL, 2.5 M solution in hexane, 16.3 mmol) at −78 °C. After the mixture was stirred for 30 min, solid $(C_7H_7)BF_4$ (2.75 g, 15.4 mmol) was added at −78 °C, and the reaction mixture was slowly warmed to room temperature (3 h), whereupon saturated NH_4Cl solution (100 mL) was added. The resulting mixture was treated with diethyl ether (3 × 50 mL), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent and purification by flash chromatography on silica with petroleum ether/dichloromethane (3:1) as eluent afforded a stable orange oil. GC/MS showed that this oil contained the dihydrosesquifulvalene **1a** (and presumably isomers thereof) in 95% purity. Yield: 3.33 g (77% based on the purity observed by GC/MS).

Prior to the use of **1a** for complexation reactions, it was thermally rearranged by refluxing in *N*,*N*-dimethylformamide for 30 min. After evaporation of the solvent, the mixture was purified by flash chromatography as described above to give a mixture of isomers in more than 90% yield. A solution of this mixture (2.90 g, 10.8 mmol) in thf (50 mL) was treated with *n*-butyllithium (4.8 mL, 2.5 M solution in hexane, 12.0 mmol) at −78 °C. The reaction mixture was warmed to 0 °C within 1 h, whereupon solid $[(EtCN)_3Mo(CO)_3]$ (3.73 g, 10.8 mmol) was added. After it was stirred for 3 h at ambient temperature, the reaction mixture was cooled to −78 °C and carefully treated with a solution of iodine (2.60 g, 10.3 mmol) in thf (10 mL). Warming to room temperature afforded a dark solution, which was concentrated and transferred to an alumina−petroleum ether chromatography column. Elution with petroleum ether/dichloromethane (3:1) produced a red band which was collected to give a mixture of isomeric hydrosesquifulvalenyl complexes of the type $[(\eta^5\text{-}2,4\text{-}t\text{-}Bu_2C_5H_2{-}C_7H_7)Mo(CO)_3I]$ as a red, crystalline solid which was directly used for the subsequent hydride abstraction. Yield: 4.12 g (70% based on iodine).

A 4.12 g (7.2 mmol) portion of the mixture obtained as described above was dissolved in dichloromethane (70 mL) and was treated with $(Ph_3C)BF_4$ (2.13 g, 6.4 mmol) at 0 °C. After it was warmed to room temperature, the reaction mixture was heated to 40 °C for 30 min. The solution was reduced in volume to 20 mL and added to rapidly stirred diethyl ether (300 mL) at 0 °C to precipitate **2a** as an intensely colored, red-brown solid. Yield: 3.40 g (80% based on $(Ph_3C)BF_4$). ^{1}H NMR (200 MHz, CD_3CN): δ 9.18 (m, 6H, C_7 ring: C*H*), 5.83 (d, $^4J_{HH}$ = 2.8 Hz, 1H, C_5 ring: C*H*), 5.61 (d, $^4J_{H,H}$ = 2.8 Hz, 1H, C_5 ring: C*H*), 1.32 (s, 9H, CH_3), 1.16 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CD_3CN): δ 234.7 (*C*O), 221.3 (*C*O), 220.9 (*C*O), 162.9 (C_7 ring: *C*-1), 160.9, 156.4, 153.9 (C_7 ring: *C*H), 131.8, 131.3 (*C*−CMe$_3$), 112.8 (C_5 ring: *C*-1), 102.6, 88.2 (C_5 ring: *C*H), 35.4 (*C*Me$_3$), 33.2 (*C*H$_3$), 32.8 (*C*Me$_3$), 31.4 (*C*H$_3$). IR (KBr): ν(CO) 2033, 1956, 1938 cm^{-1}. MS (ESI): *m*/*z* (%) 575 (100) [(**2a** −

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$BF_4)^+$]. UV/vis (CH_2Cl_2): λ (log ϵ) 317 (3.55), 517 (2.86) nm. UV/vis (CH_3CN): λ (log ϵ) 314 (3.87), 473 (3.14) nm. Anal. Calcd for $C_{23}H_{26}BF_4IMoO_3$ ($M_r = 660.10$): C, 41.85; H, 3.97. Found: C, 43.58; H, 4.33.

Preparation of [(η^5-3-*t*-BuC$_5$H$_3$−C$_7$H$_6$)Mo(CO)$_3$I]BF$_4$ (2b). A solution of 6,6-dimethylfulvene (3.72 g, 35.0 mmol) in thf (120 mL) was treated with methyllithium (24.1 mL of a 1.6 M solution in hexane, 38.5 mmol) at −40 °C. The reaction mixture was warmed to 0 °C and stirred for an additional 30 min, whereupon it was cooled to −78 °C and treated with solid (C_7H_7)BF_4 (6.23 g, 35.0 mmol). After the mixture was stirred at ambient temperature for 2 h, saturated NH_4Cl solution (150 mL) was added. The resulting mixture was treated with diethyl ether (3 × 50 mL), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent and purification by flash chromatography on silica with petroleum ether/dichloromethane (2:1) as eluent afforded a stable orange oil. GC/MS showed that this oil exclusively contained the dihydrosesquifulvalene **1b** (and presumably isomers thereof). Yield: 6.23 g (84%).

A solution of **1b** (1.74 g, 8.2 mmol) in thf (80 mL) was treated with *n*-butyllithium (3.4 mL, 2.5 M solution in hexane, 8.6 mmol) at −78 °C. The reaction mixture was warmed to 0 °C within 1 h, whereupon solid [$(MeCN)_3Mo(CO)_3$] (2.48 g, 8.2 mmol) was added. After it was stirred for 3 h at ambient temperature, the reaction mixture was cooled to −78 °C and carefully treated with a solution of iodine (1.97 g, 7.8 mmol) in thf (10 mL). Warming to room temperature afforded a dark solution, which was concentrated and transferred to an alumina−petroleum ether chromatography column. Elution with petroleum ether/dichloromethane (3:1) produced a red band, which was collected to give the hydrosesquifulvalenyl complexes [(η^5-3-*t*-Bu$_2$C$_5$H$_3$−C$_7$H$_7$)Mo(CO)$_3$I] as a red, crystalline solid which was directly used for the subsequent hydride abstraction. Yield: 2.96 g (73% based on iodine).

A 2.86 g (5.5 mmol) portion of the complex obtained as described above was dissolved in dichloromethane (60 mL), and the solution was treated with (Ph_3C)BF_4 (1.63 g, 5.0 mmol) at 0 °C. After it was warmed to room temperature, the reaction mixture was heated to 40 °C for 30 min. The solution was reduced in volume to about 15 mL and added to rapidly stirred diethyl ether (200 mL) at 0 °C to precipitate **2b** as an intensely colored, red-purple solid. Yield: 1.32 g (44% based on (Ph_3C)-BF_4). ^1H NMR (200 MHz, CD_3CN): δ 8.86 (m, 6H, C_7 ring: C*H*), 6.52 (dd, 1H, C_5 ring: C*H*), 6.43 (dd, 1H, C_5 ring: C*H*), 5.87 (dd, 1H, C_5 ring: C*H*), 1.27 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CD_3CN): δ 230.2 (*C*O), 220.6 (*C*O), 219.8 (*C*O), 162.2 (C_7 ring: *C*-1), 153.2, 152.4, 148.5 (C_7 ring: *C*H), 135.6 (*C*−CMe$_3$), 105.6 (C_5 ring: *C*H), 102.4 (C_5 ring: *C*-1), 92.2, 91.3 (C_5 ring: *C*H), 32.9 (*C*Me$_3$), 31.4 (*C*H$_3$). IR (KBr): ν(CO) 2056, 2048, 1985, 1963 cm^{-1}. MS (ESI): *m/z* (%) 519 (100) [(**2b** − $BF_4)^+$]. UV/vis (CH_2Cl_2): λ (log ϵ) 362 (3.83), 507 (3.67) nm. UV/vis (CH_3CN): λ (log ϵ) 357 (3.97), 488 (3.62) nm. Anal. Calcd for $C_{19}H_{18}BF_4IMoO_3$ ($M_r = 603.99$): C, 37.78; H, 3.00. Found: C, 38.63; H, 3.20.

Preparation of [(η^5-C$_5$H$_4$−C$_7$H$_6$)Mo(CO)$_3$I]BF$_4$ (2c). A solution of freshly distilled cyclopentadiene (1.98 g, 30 mmol) in thf (90 mL) was treated with *n*-butyllithium (13.2 mL of a 2.5 M solution in hexane, 33 mmol) at −78 °C. The reaction mixture was warmed to room temperature and stirred for additional 30 min, whereupon it was cooled to −78 °C and treated with solid (C_7H_7)BF_4 (5.34 g, 33.0 mmol). After it was stirred at ambient temperature for 2 h, the resulting solution was treated again with *n*-butyllithium (12 mL of a 2.5 M solution in hexane, 30 mmol) at −78 °C. The reaction mixture was warmed to 0 °C within 1 h, whereupon solid [$(MeCN)_3Mo(CO)_3$] (10.36 g, 30 mmol) was added. After it was stirred for 3 h at ambient temperature, the reaction mixture was cooled to −78 °C and carefully treated with a solution of iodine (7.23 g, 28.5 mmol) in thf (25 mL). Warming to room temperature afforded a dark solution, which was concentrated and transferred to an alumina−petroleum ether chromatography column. Elution with petroleum ether/dichloromethane (3:1) produced a red band, which was collected to give the hydrosesquifulvalenyl complexes [(η^5-C$_5$H$_4$−C$_7$H$_7$)Mo(CO)$_3$I] as a red, crystalline solid. Yield: 8.94 g (68% based on iodine). ^1H NMR (200 MHz, $CDCl_3$): δ 6.70 (t, 2H, C_7 ring: C*H*), 6.27 (m, 2H, C_7 ring: C*H*), 5.55−5.60 (m, 4H, C_5 ring: C*H*), 5.29 (dd, 2H, C_7 ring: C*H*), 2.74 (t, 1H, C_7 ring: C*H*). ^{13}C NMR (50.3 MHz, CD_3CN): δ 240.4 (*C*O), 225.4 (2 × *C*O), 132.2, 126.3, 125.2 (C_7 ring: *C*H), 122.7 (C_5 ring: *C*-1), 98.0, 93.3 (C_5 ring: *C*H), 39.1 (C_7 ring: *C*-1). IR (KBr): ν(CO) 2036, 1942, 1910, 1879 cm^{-1}. MS (EI): *m/z* (%) 464 (6.2) [M$^+$], 408 (14) [(M − 2CO)$^+$], 380 (74) [(M − 3CO)$^+$], 380 (100) [M − 3CO − I)$^+$]. Anal. Calcd for $C_{15}H_{11}IMoO_3$ ($M_r = 462.09$): C, 38.99; H, 2.40. Found: C, 37.97; H, 2.61.

A 2.78 g (6.0 mmol) portion of the complex obtained as described above was dissolved in dichloromethane (90 mL), and the solution was treated with (Ph_3C)BF_4 (1.79 g, 5.4 mmol) at 0 °C. After it was warmed to room temperature, the reaction mixture was heated to 40 °C for 30 min. The solution was reduced in volume to about 20 mL and added to rapidly stirred diethyl ether (250 mL) at 0 °C to precipitate **2c** as an intensely colored, purple solid. Yield: 1.99 g (67% based on (Ph_3C)BF_4). ^1H NMR (200 MHz, CD_3CN): δ 8.84 (m, 6H, C_7 ring: C*H*), 6.51 (dd, 2H, C_5 ring: C*H*), 5.97 (dd, 2H, C_5 ring: C*H*). IR (KBr): ν(CO) 2047, 1969 cm^{-1}. MS (ESI): *m/z* (%) 463 (100) [(**2c**-$BF_4)^+$]. UV/vis (CH_2Cl_2): λ (log ϵ) 347 (4.00), 555 (3.61) nm. UV/vis (CH_3CN): λ (log ϵ) 312 (3.85), 517 (3.38) nm. Anal. Calcd for $C_{15}H_{10}BF_4IMoO_3$ ($M_r = 547.89$): C, 32.88; H, 1.84. Found: C, 32.30; H, 2.76.

Preparation of [(μ-η^5:η^7-2,4-*t*-Bu$_2$C$_5$H$_2$−C$_7$H$_6$)Mo$_2$(CO)$_6$I]-BF$_4$ (3a). A solution of **2a** (2.50 g, 3.8 mmol) in thf (75 mL) was treated with [(η^6-*p*-xylene)Mo(CO)$_3$] (1.08 g, 3.8 mmol), and the resulting mixture was stirred for 2 h. The solvent was removed in vacuo, and the residue was dissolved with a minimum amount of CH_2Cl_2 and carefully added to rapidly stirred diethyl ether (200 mL) at 0 °C to precipitate bimetallic **3a** as an orange, crystalline solid. Yield: 1.93 g (61%). ^1H NMR (200 MHz, CD_2Cl_2): δ 6.79−6.63 (m, 3H, C_7 ring: C*H*), 6.28 (dd, 1H, C_7 ring: C*H*), 6.14−5.99 (m, 2H, C_7 ring: C*H*), 5.81 (d, $^4J_{H,H} = 2.6$ Hz, 1H, C_5 ring: C*H*), 5.18 (d, $^4J_{H,H} = 2.6$ Hz, 1H, C_5 ring: C*H*), 1.33 (s, 9H, CH_3), 1.14 (s, 9H, CH_3). ^1H NMR (200 MHz, acetone-d_6): δ 7.19 (d, $^3J_{H,H} \approx 8$ Hz, 1H, C_7 ring: C*H*), 7.08 (t, $^3J_{H,H} \approx 8$ Hz, 1H, C_7 ring: C*H*), 6.85 (m, 2H, C_7 ring: C*H*), 6.47 (dt, $^3J_{H,H} \approx 8$ Hz, 1H, C_7 ring: C*H*), 6.22 (t, 1H, $^3J_{H,H} \approx 8$ Hz, C_7 ring: C*H*), 6.01 (d, $^4J_{H,H} = 2.5$ Hz, 1H, C_5 ring: C*H*), 5.90 (d, $^4J_{H,H} = 2.5$ Hz, 1H, C_5 ring: C*H*), 1.35 (s, 9H, CH_3), 1.22 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CD_2Cl_2, $T = 268$ K): δ 235.9 (*C*O), 221.2 (*C*O), 218.1 (*C*O), 205.6 (3 × *C*O), 128.7, 127.4, 114.3, 108.4, 108.0, 107.7, 103.3, 102.3, 98.3, 97.4, 96.0, 84.5 (C_5 ring + C_7 ring), 33.8 (*C*Me$_3$), 32.2 (*C*H$_3$), 32.1 (*C*Me$_3$), 31.2 (*C*H$_3$). IR (KBr): ν(CO) 2080, 2032, 1955 cm^{-1}. MS (ESI): *m/z* (%) 753 (100) [(**3a** − $BF_4)^+$]. Anal. Calcd for $C_{26}H_{26}BF_4IMo_2O_6$ ($M_r = 840.07$): C, 37.17; H, 3.12. Found: C, 36.93; H, 3.36.

Preparation of [(μ-η^5:η^7-3-*t*-BuC$_5$H$_3$−C$_7$H$_6$)Mo$_2$(CO)$_6$I]-BF$_4$ (3b). A solution of **2b** (0.69 g, 1.1 mmol) in thf (30 mL) was treated with [(η^6-*p*-xylene)Mo(CO)$_3$] (0.33 g, 1.1 mmol), and the resulting mixture was stirred for 2 h. The solvent was removed in vacuo, and the residue was dissolved with a minimum amount of CH_2Cl_2 and added dropwise to rapidly stirred diethyl ether (100 mL) at 0 °C to precipitate bimetallic **3b** as an ochre crystalline solid. Yield: 0.54 g (60%). ^1H NMR (200 MHz, acetone-d_6): δ 6.84−6.67 (m, 6H, C_7 ring: C*H*), 6.62−6.57 (m, 2H, C_5 ring: C*H*), 6.00 (dd, 1H, C_5 ring: C*H*), 1.34 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CD_2Cl_2, $T = 268$ K): δ 233.0 (*C*O), 219.7 (2 × *C*O), 206.8 (3 × *C*O), 132.8, 113.2, 103.4, 101.0, 100.7, 100.0, 99.8 (2 × C), 99.4, 95.4, 95.0, 89.2 (C_5 ring + C_7 ring), 32.5 (*C*Me$_3$), 31.4 (*C*H$_3$). IR (KBr): ν(CO) 2075, 2038, 1958 cm^{-1}. MS (ESI): *m/z* (%) 669 (100) [(**3b** −

$BF_4 - CO)^+$]. Anal. Calcd for $C_{22}H_{18}BF_4IMo_2O_6$ ($M_r = 783.96$): C, 33.71; H, 2.31. Found: C, 34.44; H, 2.65.

Preparation of [(μ-η^5:η^7-2,4-*t*-$Bu_2C_5H_2-C_7H_6$)$Mo_2(CO)_5$(μ-I)]BF_4 (4a). A solution of **3a** (0.36 g, 0.4 mmol) in dichloromethane (20 mL) was heated to reflux for 2 h. Filtration of the resulting green solution and evaporation of all volatiles afforded **4a** as a green crystalline solid. Yield: 0.35 g (100%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 6.91 (d, $^3J_{H,H} = 8.0$ Hz, 1H, 7′-C*H*), 6.85 (d, $^4J_{H,H} = 2.8$ Hz, 1H, 5-C*H*), 6.45 (m, 2H, 2′-C*H* + 3′-C*H*), 6.09 (t, $^3J_{H,H} = 8.1$ Hz, 1H, 6′-C*H*), 6.00 (t, $^3J_{H,H} = 7.7$ Hz, 1H, 4′-C*H*), 4.83 (t, $^3J_{H,H} = 8.3$ Hz, 1H, 5′-C*H*), 4.74 (d, $^4J_{H,H} = 2.8$ Hz, 1H, 3-C*H*), 1.43 (s, 9H, 2-CCH_3), 1.36 (s, 9H, 4-CCH_3). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.15 (m br, 2H, C_7 ring + C_5 ring: C*H*), 7.01 (t, $^3J_{H,H} = 8.5$ Hz, 1H, C_7 ring: C*H*), 6.71 (d, $^3J_{H,H} = 8.8$ Hz, 1H, C_7 ring: C*H*), 6.41 (t, 1H, $^3J_{H,H} = 8.0$ Hz, C_7 ring: C*H*), 6.17 (t, 1H, $^3J_{H,H} = 8.0$ Hz, C_7 ring: C*H*), 5.57 (d, $^4J_{H,H} = 2.7$ Hz, 1H, C_5 ring: C*H*), 5.16 (m br, 1H, C_7 ring: C*H*), 1.50 (s, 9H, CH_3), 1.39 (s, 9H, CH_3). ^{13}C NMR (150.9 MHz, CD_2Cl_2): δ 233.0, 223.4, 221.2, 213.9, 208.2 (5 × *C*O), 137.3 (2-*C*), 134.1 (4-*C*), 124.0 (1-*C*), 115.3 (1′-*C*), 109.8 (7′-*C*H), 107.3 (2′-*C*H), 106.5 (5-*C*H), 98.9 (3′-*C*H), 89.0 (5′-*C*H), 88.4 (4′-*C*H), 82.1 (6′-*C*H), 80.8 (3-*C*H), 35.0 (2-*C*Me$_3$), 33.9 (2-C*C*H$_3$), 32.6 (4-*C*Me$_3$), 31.1 (4-C*C*H$_3$). IR (KBr): ν(CO) 2043, 1996, 1984, 1945 cm^{-1}. MS (ESI): *m/z* (%) 725 (100) [(**4a** − $BF_4)^+$]. Anal. Calcd for $C_{25}H_{26}BF_4IMo_2O_5$ ($M_r = 812.06$): C, 36.98; H, 3.23. Found: C, 35.56; H, 3.37.

Preparation of [(μ-η^5:η^7-3-*t*-$BuC_5H_3-C_7H_6$)$Mo_2(CO)_5$(μ-I)]BF_4 (4b). A solution of **3b** (0.50 g, 0.6 mmol) in dichloromethane (30 mL) was heated to reflux for 2 h. When the solution was cooled, **4b** precipitated from the solution and was isolated as a dark green, crystalline solid by filtration of the reaction mixture. Yield: 0.46 g (95%). ^{1}H NMR (200 MHz, CD_3CN): δ 6.17 (d, $^3J_{H,H} = 8.8$ Hz, C_7 ring: C*H*), 5.95 (d, $^3J_{H,H} = 9.1$ Hz, 1H, C_7 ring: C*H*), 5.93 (dd, $^4J_{H,H} = 2.2$ Hz, 1H, C_5 ring: C*H*), 5.86 (t, $J_{H,H} = 2.5$ Hz 1H, C_5 ring: C*H*), 5.60 (dd, $J_{H,H} = 2.8$, 2.2 Hz, 1H, C_5 ring: C*H*), 5.26 (m br, 1H, C_7 ring: C*H*), 5.18 (m br, 1H, C_7 ring: C*H*), 5.11 (m br, 1H, C_7 ring: C*H*), 4.74 (m br, 1H, C_7 ring: C*H*), 1.23 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CD_3CN): δ 237.5, 224.2, 224.0, 223.8, 223.7 (*C*O), 130.5, 126.9, 126.3, 126.2, 116.3, 94.9, 91.3, 90.9 (C_5 ring + C_7 ring, several signals could not be observed presumably due to line broadening), 32.9 (*C*Me$_3$), 31.8 (*C*H$_3$). IR (KBr): ν(CO) 2042, 2017, 1984, 1974, 1950 cm^{-1}. MS (ESI): *m/z* (%) 669 (100) [(**4b** − $BF_4)^+$]. Anal. Calcd for $C_{21}H_{18}BF_4IMo_2O_5$ ($M_r = 755.96$): C, 33.37; H, 2.40. Found: C, 33.53; H, 2.53.

Preparation of [(μ-η^5:η^7-2,4-*t*-$Bu_2C_5H_2-C_7H_6$)$Mo_2(CO)_5I$(PPh_3)]BF_4 (5a). A solution of **4a** (0.12 g, 0.15 mmol) in CH_2Cl_2 (20 mL) was treated with triphenylphosphine (0.04 g, 0.16 mmol), and the reaction mixture was heated to 40 °C for 30 min. The solution was concentrated to about 5 mL and added to rapidly stirred diethyl ether (50 mL) at 0 °C to afford **5a** as an orange crystalline solid. Yield: 0.09 g (60%). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.63−7.45 (m, 15H, PC_6H_5), 6.79 (d, 1H, C_7 ring: C*H*), 6.52 (m, 2H, C_7 ring: C*H*), 6.03 (m, 1H, C_7 ring: C*H*), 5.94 (d, 1H, C_5 ring: C*H*), 5.91 (d, 1H, C_5 ring: C*H*), 5.66 (m, 2H, C_7 ring: C*H*), 1.33 (s, 9H, CH_3), 1.22 (s, 9H, CH_3). ^{31}P NMR (81 MHz): δ 40.6. IR (KBr): ν(CO) 2032, 1975, 1964, 1940 cm^{-1}. MS (ESI): *m/z* (%) 987 (100) [(**5** − $BF_4)^+$]. Anal. Calcd for $C_{43}H_{41}BF_4IMo_2O_5P$ ($M_r = 1074.36$): C, 48.07; H, 3.85. Found: C, 47.34; H, 3.79.

Preparation of [(μ-η^5:η^7-3-*t*-$BuC_5H_3-C_7H_6$)$Mo_2(CO)_5I$(PPh_3)]BF_4 (5b). A solution of **4b** (0.05 g, 0.07 mmol) in CH_2Cl_2 (20 mL) was treated with triphenylphosphine (0.02 g, 0.08 mmol), and the reaction mixture was heated to 40 °C for 30 min. The solution was concentrated to about 5 mL and added to rapidly stirred diethyl ether (50 mL) at 0 °C to afford **5b** as an orange-brown crystalline solid. Yield: 0.06 g (90%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.58 (m, 3H, PC_6H_5), 7.54 (m, 6H, PC_6H_5), 7.29 (m, 3H, PC_6H_5), 6.10 (d, $^3J_{H,H} = 8.9$ Hz, 1H, C_7 ring: C*H*), 6.06 (7, $^3J_{H,H} = 2.3$ Hz, 1H, C_5 ring: C*H*), 6.04 (d, $^3J_{H,H} = 8.9$ Hz, 1H, C_7 ring: C*H*), 5.97 (t, $^3J_{H,H} = 2.5$ Hz, 1H, C_7 ring: C*H*), 5.84 (td, $^3J_{H,H} = 8.6$ Hz, $^3J_{H,P} = 2.2$ Hz, 1H, C_7 ring: C*H*), 5.78 (td, $^3J_{H,H} = 8.5$ Hz, $^3J_{H,P} = 2.5$ Hz, 1H, C_7 ring: C*H*), 5.63 (td, $^3J_{H,H} = 8.1$ Hz, $^3J_{H,P} = 2.5$ Hz, 1H, C_7 ring: C*H*), 5.56 (td, $^3J_{H,H} = 8.1$ Hz, $^3J_{H,P} = 2.7$ Hz, 1H, C_7 ring: C*H*), 5.40 (dd, $J_{H,H} = 3.0$, 2.2 Hz, $^3J_{H,P} = 2.5$ Hz, 1H, C_7 ring: C*H*), 1.26 (s, 9H, CH_3). ^{31}P NMR (81 MHz): δ 45.2. IR (KBr): ν(CO) 2036, 2018, 1961 cm^{-1}. MS (ESI): *m/z* (%) 932 (100) [(**5** − $BF_4)^+$]. Anal. Calcd for $C_{39}H_{33}BF_4IMo_2O_5P$ ($M_r = 1018.25$): C, 46.00; H, 3.27. Found: C, 45.25; H, 3.34.

Preparation of [(μ-η^5:η^7-2,4-*t*-$Bu_2C_5H_2-C_7H_6$)$Mo_2(CO)_5I_2$] (6). A solution of **4a** (0.20 g, 0.2 mmol) in acetone (15 mL) was treated with NaI (0.18 g, 12.0 mmol). The resulting mixture was stirred for 12 h, and the solvent was evaporated. The residue was extracted with dichloromethane and the extract filtered through Celite. Evaporation afforded **6** as a red-brown crystalline solid. Yield: 0.19 g (90% based on **4a**). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 6.30 (d, $^4J_{H,H} = 2.7$ Hz, 1H, C_5 ring: C*H*), 6.17 (d, 1H, $^3J_{H,H} = 7.3$ Hz, 1H, C_7 ring: C*H*), 5.96 (d, $^3J_{H,H} = 8.3$ Hz, 1H, C_7 ring: C*H*), 5.86 (t, 1H, $^3J_{H,H} = 8.0$ Hz, C_7 ring: C*H*), 5.34 (d, $^4J_{H,H} = 2.7$ Hz, 1H, C_5 ring: C*H*), 5.35−5.31 (m, partially concealed by the $CHDCl_2$ signal, 3H, C_7 ring: C*H*), 1.32 (s, 9H, CH_3), 1.16 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 239.2 (*C*O), 221.9 (*C*O), 220.8 (*C*O), 212.7 (2 × *C*O), 126.5, 126.3, 112.8, 105.2, 104.1, 103.7, 101.5, 98.9, 91.1, 89.5, 89.4, 87.1 (C_5 ring + C_7 ring), 33.2, 32.3 (*C*Me$_3$), 32.1, 31.3 (*C*H$_3$). IR (KBr): ν(CO) 2030, 2017, 1968, 1960 cm^{-1}. MS (EI): *m/z* (%) 725 (15) [(M − I)$^+$], 669 (8) [(M − I − 2CO)$^+$]. Anal. Calcd for $C_{25}H_{26}I_2Mo_2O_5$ ($M_r = 852.17$): C, 35.24; H, 3.08. Found: C, 35.07; H, 3.04.

Preparation of [(η^5-2,4-*t*-$Bu_2C_5H_2-C_7H_6$)Mo$(CO)_3(CH_3)$]BF_4 (8). As described for the preparation of **2a**, dihydrosesquifulvalene **1a** was thermally rearranged. A solution of this isomeric mixture (5.37 g, 20.0 mmol) in thf (100 mL) was treated with *n*-butyllithium (8.4 mL, 2.5 M solution in hexane, 21.0 mmol) at −78 °C. The reaction mixture was warmed to 0 °C within 1 h, whereupon solid [$(MeCN)_3Mo(CO)_3$] (5.76 g, 19.0 mmol) was added. After it was stirred for 3 h at ambient temperature, the reaction mixture was cooled to −78 °C and carefully treated with MeI (2.55 g, 18.0 mmol). Warming to room temperature afforded a dark solution, which was concentrated and transferred to an alumina−petroleum ether chromatography column. Elution with petroleum ether/dichloromethane (3:1) produced a red band that was collected to give a mixture of isomeric hydrosesquifulvalenyl complexes of the type [(η^5-2,4-*t*-$Bu_2C_5H_2-C_7H_7$)Mo$(CO)_3(CH_3)$] as a red, crystalline solid, which was directly used for the subsequent hydride abstraction. Yield: 4.83 g (58% based on MeI).

A 4.01 g (8.7 mmol) amount of the mixture obtained as described above was dissolved in dichloromethane (90 mL) and treated with $(Ph_3C)BF_4$ (2.29 g, 6.94 mmol) at 0 °C. After it was warmed to room temperature, the reaction mixture was heated to 40 °C for 30 min. The solution was reduced in volume to 10 mL and added to rapidly stirred diethyl ether (200 mL) at 0 °C to precipitate **7** as an intensely colored, brick red solid. Yield: 1.49 g (40% based on $(Ph_3C)BF_4$). ^{1}H NMR (200 MHz, acetone-d_6): δ 9.11 (m, 6H, C_7 ring: C*H*), 5.55 (d, 1H, C_5 ring: C*H*), 5.40 (d, 1H, C_5 ring: C*H*), 1.30 (s, 9H, CH_3), 1.17 (s, 9H, CH_3), 0.48 (s, Mo−CH_3).

Preparation of [(μ-η^5:η^7-2,4-*t*-$Bu_2C_5H_2-C_7H_6$)$Mo_2(CO)_6$-CH_3]BF_4 (9). A solution of **8** (1.30 g, 2.4 mmol) in thf (40 mL) was treated with [(η^6-*p*-xylene)Mo$(CO)_3$] (0.68 g, 2.4 mmol), and the resulting mixture was stirred for 2 h. After evaporation of the solvent, the residue was dissolved with a minimum amount of CH_2Cl_2 and added dropwise to rapidly stirred diethyl ether (200 mL) at 0 °C to precipitate bimetallic **9** as a yellow-ochre crystalline solid. Yield: 1.34 g (78%). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.06−6.88 (m, 3H, C_7 ring: C*H*), 6.79 (t, $J_{HH} = 8.4$ Hz, 1H, C_7 ring: C*H*), 6.58 (t, $J_{HH} = 8.2$ Hz, 1H, C_7 ring: C*H*), 6.30 (t, $J_{HH} = 8.6$ Hz, 1H, C_7 ring: C*H*), 5.63 (d, $J_{HH} = 2.2$ Hz, 1H, C_5 ring: C*H*), 5.45 (d, $J_{HH} = 2.2$ Hz, 1H, C_5 ring: C*H*), 1.32 (s, 9H, CH_3), 1.24 (s, 9H, CH_3). ^{13}C NMR (50.3

MHz, acetone-d_6): δ 240.9 (*C*O), 227.3 (*C*O), 226.4 (*C*O), 207.7 (3 × *C*O), 127.0, 126.9, 117.7, 110.0, 108.1, 106.4, 103.7, 101.6, 99.4, 97.4, 95.8, 95.7 (C_5 ring + C_7 ring), 34.5 (*C*Me$_3$), 33.2 (*C*H$_3$), 32.8 (*C*Me$_3$), 31.6 (*C*H$_3$), −18.2 (Mo-*C*H$_3$). IR (KBr): ν(CO) 2073, 2012, 1945, 1928 cm^{-1}. MS (ESI): *m*/*z* (%) 642 (100) [(**9** − BF_4)$^+$]. Anal. Calcd for $C_{27}H_{29}BF_4Mo_2O_6$ (M_r = 728.20): C, 44.53; H, 4.01. Found: C, 43.78; H, 4.27.

Preparation of [(μ-η^5:η^7-2,4-*t*-Bu$_2$C$_5$H$_2$−C$_7$H$_6$)Mo$_2$(CO)$_6$CH$_3$](CF$_3$SO$_3$) (10). A solution of **8** (0.5 g, 0.7 mmol) in acetone (20 mL) was treated with NaI (0.63 g, 42.0 mmol). The resulting mixture was stirred for 3 h, and the solvent was evaporated. The residue was extracted with dichloromethane and filtered. Evaporation afforded [(μ-η^5:η^7-2,4-*t*-Bu$_2$C$_5$H$_2$−C$_7$H$_6$)Mo$_2$(CO)$_5$(CH$_3$)I] as a green solid, which was pure enough for further reaction, as shown by ^{1}H NMR. Treatment of a solution of this compound in dichloromethane (15 mL) with Ag(CF$_3$SO$_3$) resulted in the formation of a white precipitate (presumably AgI). After it was stirred for 2 h, the reaction mixture was filtered through Celite and concentrated and hexane was added. After this mixture stood in the refrigerator at 0 °C for 1 week, yellow crystals had deposited. The ^{1}H NMR spectroscopic characterization revealed that **10** must have formed, the cation of which is identical with that of compound **9**. Anal. Calcd for $C_{28}H_{29}F_3Mo_2O_9S$ (M_r = 790.47): C, 42.55; H, 3.70. Found: C, 40.77; H, 3.80.

X-ray Crystallography. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection, COLLECT (Nonius BV, 1998), Denzo-SMN;[38] absorption correction, SORTAV;[39] structure solution, SHELXS-97;[40] structure refinement, SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997); graphics, DIAMOND (K. Brandenburg, Universität Bonn, 1997).

Crystal data and refinement details for **4a**·CH$_2$Cl$_2$: formula $C_{26}H_{28}BCl_2F_4IMo_2O_5$, M_r = 896.98, red crystal 0.15 × 0.10 × 0.05 mm, $a = 10.563(1)$ Å, $b = 13.765(1)$ Å, $c = 43.561(1)$ Å, $\beta = 95.74(1)°$, $V = 6302.0(8)$ Å^3, $\rho_{calcd} = 1.891$ g cm^{-3}, $\mu = 20.03$ cm^{-1}, empirical absorption correction ($0.753 \le T \le 0.907$), $Z = 8$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 16 984 reflections collected (±*h*, ±*k*, ±*l*), (sin θ)/λ = 0.62 Å^{-1}, 10 428 independent ($R_{int} = 0.037$) and 8455 observed reflections ($I \ge 2\,\sigma(I)$), 761 refined parameters, R1 = 0.046, wR2 = 0.102, maximum residual electron density 1.39 (−0.68) e Å^{-3} close to Mo, two almost identical molecules in the asymmetric unit, one of the BF$_4$ molecules refined with positional disorder, hydrogens calculated and refined as riding atoms.

Crystal data and refinement details for **5a**·CH$_2$Cl$_2$: formula $C_{44}H_{43}BCl_2F_4IMo_2O_5P$, M_r = 1159.24, yellow crystal 0.15 × 0.10 × 0.05 mm, $a = 16.117(1)$ Å, $b = 20.437(1)$ Å, $c = 27.876(1)$ Å, $\beta = 92.79(1)°$, $V = 9171.0(8)$ Å^3, $\rho_{calcd} = 1.679$ g cm^{-3}, $\mu = 14.31$ cm^{-1}, empirical absorption correction ($0.814 \le T \le 0.932$), $Z = 8$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 52 624 reflections collected (±*h*, ±*k*, ±*l*), (sin θ)/λ = 0.62 Å^{-1}, 16 338 independent ($R_{int} = 0.077$) and 10 632 observed reflections ($I \ge 2\,\sigma(I)$), 1093 refined parameters, R1 = 0.074, wR2 = 0.193, maximum residual electron density 1.96 (−2.12) e Å^{-3} close to Mo, two almost identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

Crystal data and refinement details for **10**·CH$_2$Cl$_2$: formula $C_{29}H_{31}Cl_2F_3Mo_2O_9S$, M_r = 875.38, yellow crystal 0.20 × 0.15 × 0.05 mm, $a = 21.354(1)$ Å, $b = 8.556(1)$ Å, $c = 19.378(1)$ Å, $\beta = 98.95(1)°$, $V = 3497.3(5)$ Å^3, $\rho_{calcd} = 1.663$ g cm^{-3}, $\mu = 9.94$ cm^{-1}, empirical absorption correction ($0.826 \le T \le 0.952$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 24 434 reflections collected (±*h*, ±*k*, ±*l*), (sin θ)/λ = 0.65 Å^{-1}, 8025 independent ($R_{int} = 0.046$) and 5962 observed reflections ($I \ge 2\,\sigma(I)$), 422 refined parameters, R1 = 0.053, wR2 = 0.121, thermal parameters of the SO$_3$CF$_3$ indicate some disorder, which was not refined, maximum residual electron density 1.16 (−1.03) e Å^{-3}, hydrogens calculated and refined as riding atoms.

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Supporting Information Available: Tables giving details of the X-ray crystal structure analyses and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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