Synthesis and characterization of ring-coupled cyclopentadienyl and indenyl bimetallic derivatives of Cr, Mo and W

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Abstract

A series of new ring-coupled bimetallic complexes $M_2(CO)_6[\eta^5,\eta^5-C_5H_4-C(CH_3)_2-C_5H_4]$, where M = Cr, Mo, W, was synthesized by reaction of the dianion of the ligand 2,2-bis(cyclopentadienyl)propane and $M(CO)_3(CH_3CN)_3$, M = Cr, Mo, W. Oxidation with acetic acid–Fe(III) produced the bimetallic complexes in moderate yields. Using the same strategy, reactions of $Mo(CO)_3(CH_3CN)_3$ with the dianion of 2-cyclopentadienyl-2-indenylpropane produced only the dimer $[Mo(CO)_3[\eta^5-C_5H_4-C(CH_3)_2-C_9H_7]_2$ in which the indenyl ring was unmetallated. Subsequent detailed studies revealed that the desired dimetalloanion was initially formed, but that the indenyl bound metal was lost upon protonation. Evidence for the mechanism of this demetallation process is presented. The dimetalloanion could be intercepted by methyl iodide to form $[Mo(CO)_3CH_3]_2[\eta^5,\eta^5-C_5H_4-C(CH_3)_2-(C_9H_6)]$. Synthesis of $Mo_2(CO)_6[\eta^5,\eta^5-C_5H_4-C(CH_3)_2-(3-RC_9H_5)]$, where R = H, CH_3, was achieved by aprotic oxidation of the intermediate dimetalloanion by ferricinium tetraphenylborate. The molecular structures of two compounds are reported:
$Mo_2(CO)_6[\eta^5,\eta^5-C_5H_4-C(CH_3)_2-(3-CH_3C_9H_5)]$: triclinic, $P\bar{1}$, $a = 8.777(3)$ Å, $b = 9.428(4)$ Å, $c = 14.915(4)$ Å, $\alpha = 91.42(3)°$, $\beta = 102.04(3)°$, $\gamma = 114.69(3)°$, $V = 1087.9(8)$ Å³, $Z = 2$, $R(F) = 3.03\%$.$[Mo(CO)_3CH_3]_2[\eta^5,\eta^5-C_5H_4-C(CH_3)_2-(C_9H_6)]$: triclinic, $P\bar{1}$, $a = 8.298(6)$ Å, $b = 11.662(6)$ Å, $c = 13.241(8)$ Å, $\alpha = 100.28(1)°$, $\beta = 93.02(1)°$, $\gamma = 99.72(1)°$, $V = 1238(1)$ Å³, $Z = 2$, $R(F) = 3.99\%$.

Keywords: Group 6; Ring-coupled; Tungsten; Bimetallic compounds; Cyclopentadienyl; Indenyl

1. Introduction

Bimetallic complexes have attracted attention because of the belief that molecules containing two closely adjacent metal atoms may permit cooperative effects resulting in unique catalytic applications [1]. Coupling cyclopentadienyl rings is one strategy to maintain metal centers within close range. Our previous work with ring-coupled rhodium complexes showed the ease of formation of derivatives with ligands bridging the two metals [2]. Another example of the special reactivity of bridged bimetallic systems was observed by Lilga and Hubler [3] who found that the reaction of Cr_2-$(CO)_6[\eta^5,\eta^5-C_5H_4-CH_2-C_5H_4]$ and dihydrogen is smoothly second order. The analogous reaction between the non-ring-coupled $Cr_2(CO)_6(\eta^5-C_5H_5)_2$ and dihydrogen follows a more complex kinetics. Ring-coupled systems have the potential to produce fixed stereochemistry (cisoid for the two Cp rings) and chiral derivatives may be formed by using asymmetric ligands. Such fixed stereochemistry has been crucial in applications like Group 4 metallocene Ziegler–Natta olefin polymerization catalysis [4].

Several examples of ring-coupled derivatives of Group VI metals have been reported involving fulvalene [5,6], bis(cyclopentadienyl)-*m*-xylene [7], bis(cyclopentadienyl)dimethylsilane [8], and bis(tetramethylcyclopentadienyl)dimethylsilane [9].

The chemistry of $M_2(CO)_6[\eta^5,\eta^5-C_5H_4-CH_2-C_5H_4]$, where Cr [10,11], Mo [11,12] and W [11,12],

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have been reported. Inert gas matrix photochemical studies of the Mo and W derivatives have been described [13].

The recent interest in ring-coupled bis(cyclopentadienyl) derivatives of the Group IV metals has yielded a bounty of syntheses for new ring-coupled ligands. In the present work we describe the preparation of Group VI derivatives of 2,2-bis(cyclopentadienyl)propane, 1, 2-cyclopentadienyl-2-indenylpropane, 2, and 2-cyclopentadienyl-2-(3-methyl-indenyl)propane, 3. These compounds, together with the earlier derivatives of bis(cyclopentadienyl)methane allow us to compare the electronic and structural effects of substitutions on the bridge, as well as begin to explore the chemistry of the indenyl ring in the context of bimetallic chemistry. In particular, we are interested in determining whether carbonyl exchange reactions will be enhanced at the indenyl-bound metal as has been observed for mononuclear compounds [14,15]. Alt and coworkers have previously examined the chemistry of molybdenum and tungsten derivatives of 2 in which only the cyclopentadienyl ring is pentahapto-bound to the metal [16,17].

The present paper will describe the synthesis and characterization of new bimetallic compounds M_2-$(CO)_6[\eta^5,\eta^5$-C_5H_4-$C(CH_3)_2$-$C_5H_4]$, where $M = Cr$ (4), Mo (5), and W (6), as well as $Mo_2(CO)_6[\eta^5,\eta^5$-

C_5H_4-$C(CH_3)_2$-$(3$-$RC_9H_5)]$, where $R = H$ (14) and CH_3 (15), and some of their derivatives. The synthesis of 14 and 15 were complicated by a side reaction that led to loss of the indenyl-bound metal atom during work-up. Evidence for the mechanism of this decomposition and a strategy for avoiding it are described. Variable-temperature NMR studies for the M–M derivatives are presented. The reaction chemistry of 14 and 15 will be presented elsewhere [18].

2. Results and discussion

2.1. Synthesis of 2,2-bis(cyclopentadienyl)propane derivatives

Following the method of King [19] as modified by Curtis and Hay [20] reaction of 1 with two equivalents of $Mo(CO)_3(CH_3CN)_3$ in refluxing THF yielded 5 after chromatographic purification. Alternatively, $Cr(CO)_3$-$(CH_3CN)_3$ and $Mo(CO)_3(CH_3CN)_3$ react with the lithium salt of the dianion of 1 to give dimetalloanion intermediates $[M(CO)_3]_2[\eta^5,\eta^5$-$C_5H_4$-$C(CH_3)_2$-$C_5H_4]^{2-}$ that may be oxidized to the final products, 4 and 5, by a solution of acetic acid and iron(III)chloride [21]. Synthesis of 6 was optimized by reaction of the
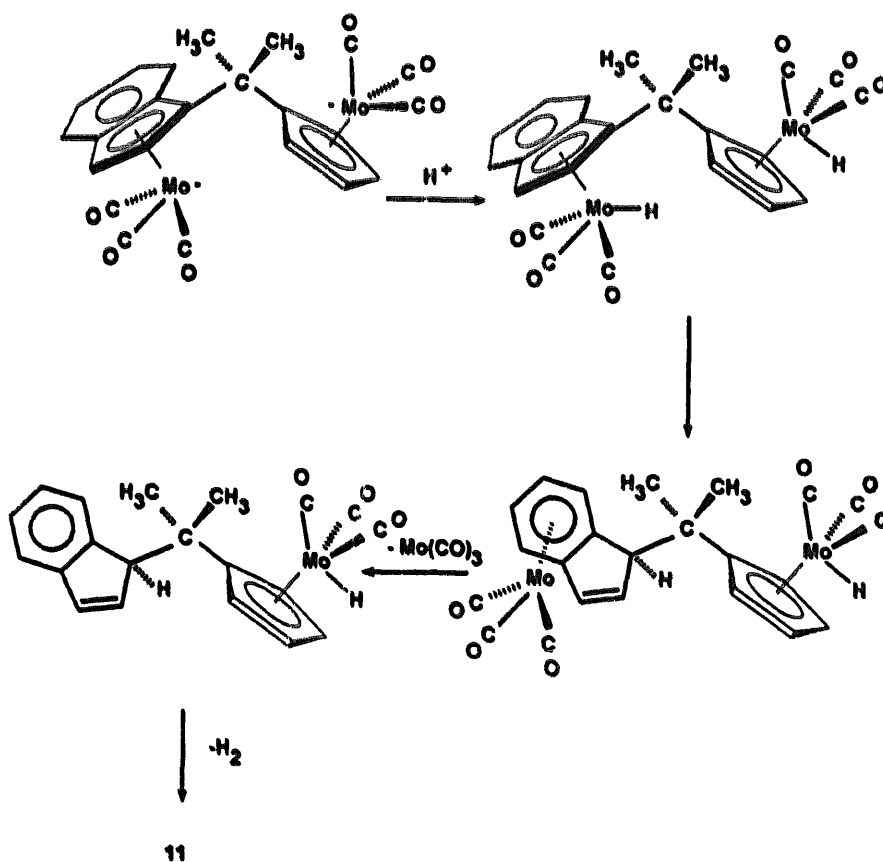
Structure 4, 5, 6.

potassium salt of **1** with W(CO)$_3$(CH$_3$CN)$_3$ followed by oxidation. As we have previously observed for analogous tungsten derivatives of bis(cyclopentadienyl)methane, **6** is formed along with its 2-acetyl derivative, **7** [12]. It is likely that the acetyl group arises from intermediate reactions with acetonitrile followed by hydrolysis [22].

The metal–methyl derivative, [Mo(CO)$_3$CH$_3$]$_2$-[η^5,η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_5$H$_4$] (**8**), may be prepared by reaction of the dimetalloanion with methyl iodide. The corresponding metal-hydride, [Mo(CO)$_3$H]$_2$-[η^5,η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_5$H$_4$] (**9**) may be conveniently prepared by reaction of the dimetalloanion with powdered KHSO$_4$, although this compound is unstable to loss of H$_2$ and reforms **5** in solution over a period of several hours.

2.2. Synthesis of molybdenum derivatives of 2-cyclopentadienyl-2-indenylpropane and 2-cyclopentadienyl-2-(3-methylindenyl)propane

Reaction of **2** with Mo(CO)$_3$(CH$_3$CN)$_3$ in refluxing THF produced exclusively the red dimer, Mo(CO)$_3$[η^5-C$_5$H$_4$-C(CH$_3$)$_2$-(3-H-C$_9$H$_7$)]$_2$, **10**, in which the indenyl ring is unbound. NMR analysis of this compound revealed that the indenyl fragment is exclusively present as the more thermodynamically stable 3-H isomer. Reported syntheses [23] for Mo(CO)$_3$(η^5-C$_9$H$_7$) call for reaction between indene and Mo(CO)$_6$ in high boiling-point solvents; thus, it is possible that the reaction in refluxing THF was not sufficiently vigorous to lead to metallation of the relatively unreactive indenyl ring.

Reaction of the lithium salt of the dimetalloanion of **2** with Mo(CO)$_3$(CH$_3$CN)$_3$ followed by oxidative work-up as described for **5** above, yielded a small quantity of **10** accompanied by a larger amount of a second, red product, **11**, whose IR spectrum was identical to that of **10**. NMR spectra of **11** established that it was the, less thermodynamically stable, 1-H isomer of **10**. No product was isolated in which the indenyl ring was metallated.

The dimers **10** and **11** showed typical absorptions in dimolybdenum hexacarbonyl species. At least four signals are observed in the terminal carbonyl region of the IR spectra. Both ^{1}H and ^{13}C NMR establish that the cyclopentadienyl ring is pentahapto-bound to the molybdenum in both compounds. The cyclopentadienyl ring proton resonances appear as a set of two signals (AA'BB') in the case of **10** and four in **11**. The proton resonances of the C$_5$ ring of the indenyl moiety of **10** appear as broad multiplets at 3.27 δ (2-H) and 6.19 δ (1-H) that could be assigned to a CH$_2$ in the 3-position and CH in the 2-position respectively. In contrast, compound **11** displays a broad singlet at 3.4 δ that could be assigned to a proton in the 1-position and two doublets at 6.35 δ and 6.72 δ for the protons on the 2- and 3-positions respectively. The bridge methyl resonances of **10** appear as a singlet at room temperature (1.68 δ), consistent with a planar symmetric indenyl group (3-H). In contrast, there are two bridge methyl resonances (1.25 δ and 1.41 δ) in the spectrum of **11**, consistent with an asymmetric indenyl moiety (1-H).

To further characterize the structure of **11**, a sample of the compound was reduced with K-Selectride and

M = Cr (4), Mo (5), W (6)   R = H (14), Me (15)

10   11
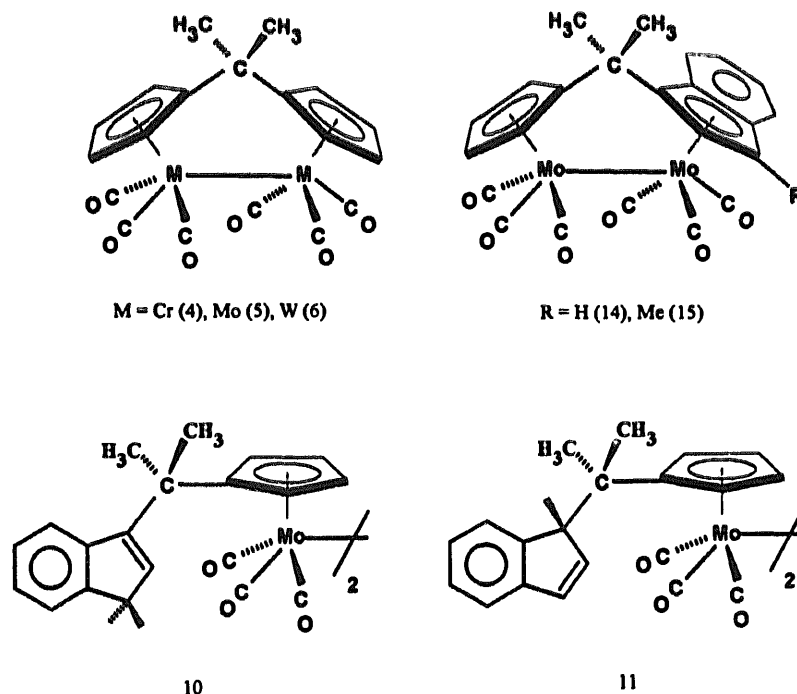
Structure 10.

Table 1
^{1}H Chemical shifts (δ/ppm) for bimetallic complexes 4–6, 14, 15

Complex	δ CH$_3$ bridge	δ Cp–H				δ Ind-H	
		H-α		H-β		H-2	H-3
4 [a]	0.83	3.39	4.96	3.88	4.00	–	–
5 [b]	1.49	5.03	5.63	5.18	5.28	–	–
6 [c]	1.54	5.06	5.71	5.21	5.40	–	–
14 [d]	1.64/1.53	5.06/4.96	5.37/5.43	5.30/5.25	5.90/5.80	6.46	5.53
	1.78/1.84						
15 [d]	1.62/1.52	4.98/4.95	5.51/5.56	5.28/5.28	5.32/5.39	6.46	–
	1.76/1.82						

[a] Toluene-d^8, −40°C. [b] CDCl$_3$, −20°C. [c] CDCl$_3$, −5°C. [d] CDCl$_3$, −30°C.

treated with an excess of methyl iodide. Column chromatography of the reaction mixture yielded a yellow compound, 12, whose IR and NMR spectra were consistent with its assignment as Mo(CO)$_3$CH$_3$[η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_9$H$_7$]. The ^{1}H NMR spectrum of 12 revealed that the indenyl portion of the molecule had been transformed to the more stable 3-H-indenyl isomer in the course of the reaction or work-up. 12 has previously been reported by Alt et al. [16a].

In order to establish whether the indenyl ring was being metallated during the course of the reaction, the dilithium salt of 2 was again reacted with Mo(CO)$_3$(CH$_3$CN)$_3$ followed by addition of methyl iodide to the reaction mixture to trap the metalloanion intermediate species. Chromatography of the reaction mixture isolated a small amount of 12 as well as a yellow compound which was shown spectroscopically and by X-ray analysis (vide infra) to be [Mo(CO)$_3$-CH$_3$]$_2$[η^5,η^5-C$_5$H$_3$-C(CH$_3$)$_2$-C$_9$H$_6$], 13.

The isolation of 13 established unequivocally that both the cyclopentadienyl and indenyl rings undergo metallation in the initial reaction; thus, we postulated that the indenyl bound molybdenum group was being lost under the conditions of the acetic acid–Fe(III)chloride oxidative work-up. In order to avoid the protic acid requirements of the conventional work-up, we repeated

the synthesis using ferricinium tetraphenylborate as the oxidant. Reaction of the dilithium salt of 2 and its methyl derivative, 3, with Mo(CO)$_3$(CH$_3$CN)$_3$ followed by direct oxidation of the dimetalloanions with ferricinium produced modest yields of red crystalline products, 14 and 15, that were found to have IR spectra similar to that of 5. ^{1}H and ^{13}C NMR spectra confirmed that both the cyclopentadienyl and indenyl rings were metallated. Finally, an X-ray structure (vide infra) of 15 confirmed the structure to be that of the expected ring-coupled bimetallic.

2.3. Spectroscopic properties of the M–M bonded compounds

The dinuclear compounds 4, 5, 6, and 7 have similar spectroscopic characteristics to the previously reported methylene-bridged analogs [3,10–12]. The IR spectra of these compounds show four terminal carbonyl bands with the highest energy, symmetric stretch being very intense consistent with the cis orientation of the metals and carbonyl groups. In contrast, the highest energy, symmetric stretching band of 10 and 11 are weak, reflecting the preference for the trans orientation of these compounds.

Table 2
T_c and ΔG‡ values for ring-linked bimetallic complexes

Complex	Bridge	T_c/K (ΔG‡/kJ mol^{-1}) Cp–αH		T_c/K (ΔG‡/kJ mol^{-1}) Cp–βH		Reference
4 (Cr)	C(CH$_3$)$_2$	256(47.6)		236(48.7)		This work
5 (Mo)	C(CH$_3$)$_2$	284(55.3)		266(55.6)		This work
6 (W)	C(CH$_3$)$_2$	– [c]		ca. 294 [c]		This work
(Cr) [a]	CH$_2$	257(47.7)		243(48.6)		[3]
(Mo) [a]	CH$_2$	287(55.9)		279(55.9)		[12]
(W) [a]	CH$_2$	300(59.2)		296(59.2)		[12]
(Cr) [b]	Si(CH$_3$)$_2$	–		240(47.7)		[8]
(Mo) [b]	Si(CH$_3$)$_2$	–		308(60.6)		[8]
(W) [b]	Si(CH$_3$)$_2$	–		340(67.8)		[8]
14 (Mo)	C(CH$_3$)$_2$	285(60.0)	281(60.1)	275(57.6)	–	This work
15 (Mo)	C(CH$_3$)$_2$	273(59.9)	273(58.7)	277(58.8)	–	This work

[a] CH$_2$[(C$_5$H$_4$)M(CO)$_3$]$_2$. [b] Si(CH$_3$)$_2$[(C$_5$H$_4$)M(CO)$_3$]$_2$. [c] Could not be determined with accuracy due to the overlapping of the signals.
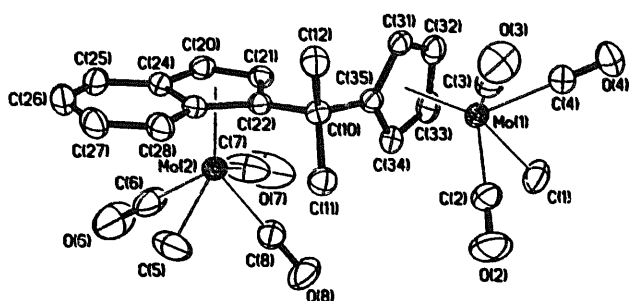
Fig. 1. Molecular structure of 13.

The acetyl derivative, 7, has a pattern of terminal carbonyl stretching bands that is characteristic of a cis orientation plus a ketonic absorption at 1685 cm^{-1}. The ^{1}H NMR spectrum shows two signals at 1.55 δ and 1.61 δ for the non-equivalent bridge-methyl groups, and the acetyl resonance at 2.34 δ. The molecule is asymmetric and all the seven ring protons are resolved at −5 °C. The structural assignment is further supported by ^{13}C NMR and MS.

The low-temperature ^{13}C NMR spectra of 4–6 show three distinct resonances for the carbonyl groups and five resonances for the ring carbons, consistent with the C_2 symmetry expected of these molecules on the basis of earlier molecular structures of the CH$_2$ and Si(CH$_3$)$_2$ ring-coupled derivatives. At room temperature these carbonyl groups average into one signal consistent with a turnstile averaging mechanism. Additionally, the ring carbon resonances coalesce into three resonances, C-2, C-5; C-3, C-4; and ipso-C, at room temperature. The room temperature ^{1}NMR spectra for 4 and 5 show two broad singlets for the ring protons, and a sharp signal for the isopropylidene bridge (Table 1). Upon cooling, the ring proton resonances decoalesce to give four

resonances at the low temperature limit, again consistent with the C_2 symmetry observed in the solid state. The tungsten derivative, 6, behaves in a similar manner although its higher coalescence temperatures could not be determined with accuracy owing to the overlapping of the ring proton resonances. The Gibbs free energies of activation ΔG‡s) were calculated (Table 2) using the Eyring equation. The exchange of the ring proton pairs were treated as simple uncoupled, two-site exchanges. The rate expression, $k = \pi \delta \nu/(2)^{1/2}$ was used without correction [24]. ΔG‡ for compounds 4–6, increase in the order Cr < Mo < W, and are very similar to those previously reported for the CH$_2$ ring-coupled derivatives [12]. The ΔG‡ values for 4 and 5 are slightly lower than the values observed for the Si(CH$_3$)$_2$-bridged compound.

Compounds 14 and 15 possess C_1, not C_2 symmetry, although like 4–6 they do undergo a torsional motion about a pseudo C_2 axis that runs through the C(CH$_3$)$_2$ bridge and the midpoint of the Mo–Mo bond. An averaging behavior of the cyclopentadienyl ring resonances was observed similar to that of 4–6, and the coalescence temperatures and chemical shift values were used to calculate an approximate value for the ΔG‡. These values (Table 2) are similar to those calculated for 5, suggesting that the indenyl ring has surprisingly little effect on the energy barrier of the torsional twist.

An examination of the ^{13}C NMR spectra of 14 and 15 at −30 °C indicates that the two torsional conformers exist in a 70:30 ratio for the former and a 55:45 ratio for the latter. This distribution may be explained by noting that the conformers of 14 differ by presenting either an indenyl hydrogen or the benzo ring to the cyclopentadienyl ring, whereas the conformers of 15 present either a methyl group or the benzo ring. The contrast in non-bonded interactions between the two
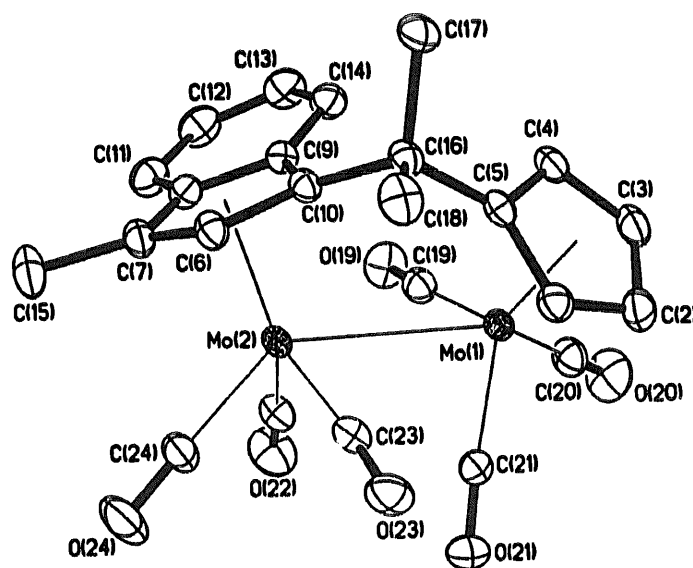

Fig. 2. Molecular structure of 15.

torsional conformers in **14** is greater than that in **15**, thus a greater population difference would be expected in the former.

The dimethyl derivatives **8** and **13** were fully characterized by IR, NMR, MS and elemental analysis, and the molecular structure of **13** was determined. The IR spectra for **8** and **13** have two carbonyl bands in the terminal region almost identical in position to those of $Mo(CO)_3CH_3(\eta^5\text{-}C_5H_5)$. Molybdenum-methyl resonances in the ^1H NMR spectra were observed at 0.35 δ for **8** and 0.37 δ and -0.64 δ for **13**. The high field methyl resonance in the spectrum of **13** is assigned to the (indenyl)$Mo(CO)_3CH_3$ group which is shielded relative to the (cyclopentadienyl)$Mo(CO)_3CH_3$ by the anisotropy of the benzo group. The ^{13}C NMR spectrum of **8** showed two carbonyl resonances and the asymmetric derivative **13** displayed all six carbonyl signals.

2.4. Molecular structures of 13 and 15

The structures of **13** and **15** are shown in Figs. 1 and 2. Crystal, data collection and refinement parameters are given in Table 3. Selected bond lengths and angles are presented in Tables 4 and 5. The structure of compound **15** is consistent with the structures of $W_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}C_5H_4]$ and its acetyl derivative previously reported [12]. The molecule has a pseudo C_2 twist axis about a line intersecting the $C(CH_1)_2$ bridge and the midpoint of the Mo=Mo bond resulting in the $Mo(CO)_3$ groups being staggered slightly relative to one another. The Mo=Mo distance in **15**, 3.149 Å, is almost identical to the bond length of $Mo_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}C_5H_4]$, 3.1406 Å [25], and shorter than that of the non-ring-coupled analog $Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, 3.235 Å [26] and of the strained, fulvalene complex, $Mo_2(CO)_6(\eta^5,\eta^5\text{-}C_{10}H_8)$, for which the Mo=Mo distance is 3.371 Å [6e]. A similar compression of the M=M bond distance by single carbon-bridged ligands has been previously observed for CH_2-bridged bis-cyclopentadienyl derivatives of Cr [11] and W [12]. The indenyl-bound molybdenum atom displays a slight slippage towards C(6) in the indenyl group; however, the Mo–C(Ind) distances are very similar to those of the $Mo_2(CO)_6(\eta^5\text{-}C_9H_7)_2$ [27] and the bonding is best regarded as pentahapto.

The structure of **13** shows the two metallic centers coordinated to the cyclopentadienyl and indenyl fragments. The Mo–C(Cp) distances (2.353–2.384 Å) are slightly greater than those reported by Alt et al. [16a] for **10** (2.334–2.347 Å). The same applies for the Mo–Me distances (2.340 vs. 2.310 Å).

Crabtree and coworkers [28] have studied the slippage of various metal–indenyl complexes. In general it was found that the metal slips away from the benzo-aromatic carbons in the five-membered ring. A similar observation is found in **15**. The Mo-ring C bond dis-

tances suggest that the metal rests slightly closer to the C–H carbons C(20) and C(21) than to the benzo or bridge head carbons. This effect may be entirely steric rather than electronic. The Mo bonding to the indenyl moiety is certainly pentahapto.

2.5. Discussion

Substitution of an indenyl group for a cyclopentadienyl group has made possible the synthesis of a new class of ring-coupled bimetallic compounds in which 'indene effects' may play a role in the chemistry of one of the metal atoms. The structures and physical properties of **14** and **15** are very similar to those of **5**, suggesting that the indenyl group has only a modest

Table 3
X-ray crystal structure, data collection and refinement data

	13	15
Crystal parameters		
Formula	$C_{25}H_{22}Mo_2O_6$	$C_{24}H_{18}Mo_2O_6$
Formula weight	610.3	594.3
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.298(6)	8.777(3)
b (Å)	11.662(6)	9.428(4)
c (Å)	13.241(8)	14.915(4)
α (deg)	100.28(1)	91.42(3)
β (deg)	93.02(1)	102.04(3)
γ (deg)	99.72(1)	114.69(3)
V (Å^3)	1238(1)	1087.9(8)
Z	2	2
Crystal dimensions (mm)	$0.4 \times 0.4 \times 0.4$	$0.2 \times 0.3 \times 0.3$
crystal color	yellow	red
D(calc) (g cm^{-3})	1.637	1.798
μ(Mo Kα) (cm^{-1})	10.49	11.81
Temp (K)	296	296
T(max)/T(min)	1.2	1.1
Data collection		
Diffractometer		Siemens P4
Monochromator		graphite
Radiation		Mo Kα ($\lambda = 0.71073$ Å)
2Θ scan range (deg)	4.0–62.0	4.0–60.0
Data collected (h,k,l)	12, 16, 19	12, 13, 21
Rflns. collected	7601	6609
Indpt. rflns	7364	6382
Indpt. obsvd. rflns $F_o \geq n\sigma(F_o)$	5218 ($n = 4$)	4925 ($n = 5$)
Refinement [a]		
$R(F)$ (%)	3.99 (5.84) [b]	3.03 (4.33) [b]
$R(wF)$ (%)	5.23 (6.02) [b]	4.20 (4.69) [b]
Δ/σ (max)	0.01	0.00
$\Delta(\rho)$, (e Å^{-3})	0.50	0.56
N_o/N_v	17.5	17.0
GOF	1.13	1.00

[a] Quantity minimized $= \Sigma w \Delta^2$; $R = \Sigma \Delta / \Sigma (F_o)$; $R(w) = \Sigma \Delta w^{1/2}/\Sigma(F_o \cdot w^{1/2})$, $\Delta = |(F_o - F_c)|$.
[b] Based on all data.

Table 4
Selected bond lengths (Å) and angles (deg) for 13

Bond lengths (Å)			
Mo(1)-C(1)	2.341(5)	Mo(1)-C(2)	1.986(5)
Mo(1)-C(3)	2.008(5)	Mo(1)-C(4)	2.001(4)
Mo(2)-C(5)	2.322(6)	Mo(2)-C(6)	1.991(7)
Mo(2)-C(7)	1.971(6)	Mo(2)-C(8)	1.980(5)
C(2)-O(2)	1.161(6)	C(3)-O(3)	1.152(6)
C(4)-O(4)	1.145(5)	C(6)-O(6)	1.143(9)
C(7)-O(7)	1.145(7)	C(8)-O(8)	1.158(6)
Bond angles (°)			
Mo(1)-C(2)-O(1)	178.0(4)	Mo(1)-C(3)-O(3)	178.7(3)
Mo(1)-C(4)-O(4)	179.6(4)	Mo(2)-C(6)-O(6)	178.7(7)
Mo(2)-C(7)-O(7)	178.1(7)	Mo(2)-C(8)-O(8)	179.7(4)
C(1)-Mo(1)-C(2)	73.7(2)	C(2)-Mo(1)-C(3)	79.0(2)
C(3)-Mo(1)-C(4)	77.8(2)	C(4)-Mo(1)-C(1)	71.4(2)
C(1)-Mo(1)-C(3)	131.2(2)	C(2)-Mo(1)-C(4)	105.1(2)
C(5)-Mo(2)-C(6)	70.9(2)	C(6)-Mo(2)-C(7)	80.1(3)
C(7)-Mo(2)-C(8)	78.2(2)	C(8)-Mo(2)-C(5)	71.3(2)
C(5)-Mo(2)-C(7)	131.3(3)	C(6)-Mo(2)-C(8)	102.3(2)
C(22)-C(10)-C(35)	106.8(3)	C(11)-C(10)-C(12)	109.3(3)

effect on the ground state properties of these compounds.

The remaining question then has to do with the demetallation of the indenyl ring upon work-up of the dimetalloanion with acetic acid–Fe(III)chloride. As described above, reaction of the ligand, 2-cyclopentadienyl-2-indenylpropane with Mo(CO)$_3$(CH$_3$CN)$_3$ in refluxing THF yields **10** in which the unbound indenyl ring is in the thermodynamically stable 3-H isomer, whereas acidic oxidation of the dimetalloanion yields predominantly the less stable 1-H isomer, **11**.

It is well known that Group VI derivatives of indenyl and fluorenyl undergo haptotropic rearrangements in which the η^6-arene ring is preferred for neutral (indene or fluorene) species and the η^5-cyclopentadienyl ring is preferred for anionic species [29,30]. Ceccon et al. [30]

have established the mechanism for the reaction of [Cr(CO)$_3$(η^5-C$_9$H$_7$)]$^-$ with protons as proceeding via initial formation of a metal hydride. The metal-bound proton is transferred to the ring, followed by a haptotropic shift of the metal to the arene ring via a lowest energy pathway that follows one edge of the indene group. Importantly, if the five-membered ring of the indenyl carries an alkyl group in the 1-position, the metal-bound proton is transferred to this position so that the metal may move along the less sterically encumbered edge of the molecule. In the case of the acidic oxidative work-up of the dimetalloanions of the compounds described here, it appears that the initially formed molybdenum hydride follows exactly the same pattern, Scheme 1, depositing its proton to the 1-position and then undergoing a haptotropic shift to the arene

Table 5
Selected bond lengths (Å) and angles (deg) for 15

Bond lengths (Å)			
Mo(1)-Mo(2)	3.149(1)	Mo(1)-C(19)	1.976(3)
Mo(1)-C(20)	1.957(3)	Mo(1)-C(21)	1.969(4)
Mo(2)-C(22)	2.007(4)	Mo(2)-C(23)	1.956(3)
Mo(2)-C(24)	1.958(5)	C(19)-O(19)	1.156(4)
C(20)-O(20)	1.140(4)	C(21)-O(21)	1.153(5)
C(22)-O(22)	1.142(5)	C(23)-O(23)	1.146(4)
C(24)-O(24)	1.140(6)		
Bond angles (°)			
Mo(1)-C(19)-O(19)	172.4(3)	Mo(1)-C(20)-O(20)	179.1(3)
Mo(1)-C(21)-O(21)	176.0(3)	Mo(2)-C(22)-O(22)	176.1(4)
Mo(2)-C(23)-O(23)	171.7(3)	Mo(2)-C(24)-O(24)	177.3(3)
C(19)-Mo(1)-C(20)	77.0(1)	C(20)-Mo(1)-C(21)	78.9(2)
C(19)-Mo(1)-C(21)	98.3(2)	Mo(2)-Mo(1)-C(20)	137.4(1)
C(22)-Mo(2)-C(24)	78.6(2)	C(23)-Mo(2)-C(24)	76.3(2)
C(22)-Mo(2)-C(23)	103.7(1)	Mo(1)-Mo(2)-C(24)	136.3(1)
C(5)-C(16)-C(10)	112.2(2)	C(17)-C(16)-C(18)	107.3(3)

ring. It is well known that areneMo(CO)$_3$ compounds are sensitive to metal loss, thus it is likely that demetallation occurs either during the reaction or under subsequent purification. Oxidation of the dimetalloanion with ferricinium avoids the protonated intermediate and thus the Mo–Mo bound product is readily formed.

3. Experimental

All reactions were conducted under nitrogen, and solvents were freshly distilled from the appropriate drying agents under nitrogen. Literature procedures were used to synthesize 2,2-bis(cyclopentadienyl)propane (1) [31], 2-cyclopentadienyl-2-indenyl-propane (2) [32], 2-cyclopentadienyl-2-(3-methyl-1-indenyl)-propane (3) [32] and (CH$_3$CN)$_3$M(CO)$_3$ [33]. Molybdenum, chromium and tungsten hexacarbonyls were purchased from Strem. Ferrocene, sodium tetraphenylborate and K-Selectride were from Aldrich.

IR spectra were recorded on a Digi Lab Qualimatic FTIR. NMR spectra were recorded on IBM 200 and 300 MHz spectrometers. Mass spectra were recorded on a Finningan Model 4610 mass spectrometer operating in the electron-impact mode. Elemental analyses were conducted by Desert Analyticals, Tucson, Arizona.

3.1. Synthesis of Cr$_2$(CO)$_6$[η^5,η^5-C$_5$H$_4$–C(CH$_3$)$_2$–C$_5$H$_4$] (4)

1, 1.0 g, 5.8 mmol, was allowed to react at 0 °C in THF with 7.25 ml of 1.6 M n-butyllithium. The reaction mixture was stirred for 4 h and heated at 50 °C for another hour to produce a dark yellow-brown solution. After cooling to room temperature Cr(CO)$_3$(CH$_3$CN)$_3$, 3.00 g, 11.6 mmol, was added and the reaction mixture was stirred for 10 h, then refluxed for another hour. The resulting dark brown solution was then treated with an aqueous solution of FeCl$_3$–CH$_3$COOH. The color turned dark green and the layers were separated. The organic phase was evaporated under reduced pressure and the dark residue chromatographed on an alumina column. Elution with pet. ether–CH$_2$Cl$_2$ 1:1 afforded a dark green band. After solvent removal, the residue was recrystallized from toluene at −78 °C to afford 1.03 g of 4 (40%) as a dark green crystalline solid.

Elemental analysis: Calc.: C, 51.60; H, 3.19. Found: C, 51.38; H, 3.01%.

IR (CH$_2$Cl$_2$): 2008 (s); 1946 (s); 1918 (m); 1882 (sh).

^{1}H NMR (CD$_3$C$_6$D$_5$, −40 °C): 0.83 (s, 6 H, C(CH$_3$)$_2$); 3.39 (bs, 2 H, C$_5$H$_4$); 3.88 (bs, 2 H, C$_5$H$_4$); 4.00 (bs, 2 H, C$_5$H$_4$); 4.96 (bs, 2 H, C$_5$H$_4$).

^{13}C NMR (CD$_3$C$_6$D$_5$, −40 °C): 30.11 (C(CH$_3$)$_2$); 35.17 (C(CH$_3$)$_2$); 82.21 (C$_5$H$_4$); 84.64 (C$_5$H$_4$); 85.14 (C$_5$H$_4$); 92.80 (C$_5$H$_4$); 116.45 (ipso-C$_5$H$_4$); 239.46 (CO); 247.11 (CO); 248.19 (CO).

MS: m/e 444 (M + 2H)$^+$; 358 (M − 3CO)$^+$; 330 (M − 4CO)$^+$; 332 (M − 5CO)$^+$; 274 (M − 6CO)$^+$; 222 (M − 6CO − Cr)$^+$; 207 (M − 6CO − Cr − CH$_3$)$^+$; 155 ((CH$_3$)$_2$C(C$_5$H$_4$)$_2$)$^+$.

3.2. Synthesis of Mo$_2$(CO)$_6$[η^5,η^5-C$_5$H$_4$–C(CH$_3$)$_2$–C$_5$H$_4$] (5)

The lithium salt of the dimetalloanion of 1 was prepared as described above. After cooling to room temperature, Mo(CO)$_3$(CH$_3$CN)$_3$, 3.52 g, 11.6 mmol, was added and after stirring for 10 h the reaction mixture was refluxed for 1 h. The resulting dark brown solution was treated with an aqueous solution of FeCl$_3$–CH$_3$COOH. The color turned dark red and the layers were separated. The organic phase was evaporated under reduced pressure and the oily dark residue was chromatographed on an alumina column. Eluting with pet. ether–CH$_2$Cl$_2$ 5:1 afforded a dark red band. The solvent was evaporated and the residue was recrystallized from pet. ether–CH$_2$Cl$_2$ at −78 °C to afford 1.05 g of 5 (34%) as dark red crystals.

5 can also be obtained by refluxing 1.0 g of ligand and 3.52 g of Mo(CO)$_3$(CH$_3$CN)$_3$ in THF for 15 h. Evaporation of the solvent and chromatography affords 0.90 g (29%) of product.

Elemental analysis: Calc.: C, 43.04; H, 2.66. Found: C, 42.92; H, 2.54%.

IR (CH$_2$Cl$_2$): 2015(s); 1962 (s); 1912 (m); 1880 (sh).

^{1}H NMR (CDCl$_3$, −20 °C): 1.49 (s, 6 H, C(CH$_3$)$_2$); 5.03 (bs, 2 H, C$_5$H$_4$); 5.18 (bs, 2 H, C$_5$H$_4$); 5.28 (bs, 2 H, C$_5$H$_4$); 5.63 (bs, 2 H, C$_5$H$_4$).

^{13}C NMR (CDCl$_3$, −30 °C): 31.1 (C(CH$_3$)$_2$); 36.0 (C(CH$_3$)$_2$); 84.71 (C$_5$H$_4$); 86.35 (C$_5$H$_4$); 88.20 (C$_5$H$_4$); 97.10 (C$_5$H$_4$); 122.9 (ipso-C$_5$H$_4$); 223.9 (CO); 229.7 (CO); 234.3 (CO).

MS: m/e 530 (M)$^+$; 502 (M − CO)$^+$; 574 (M − 2CO)$^+$; 446 (M − 3CO)$^+$; 418 (M − 4CO)$^+$; 390 (M − 5CO)$^+$; 362 (M − 6CO)$^+$; 265 (M − 6CO − Mo)$^+$; 170 (M − 6CO − 2Mo)$^+$.

3.3. Synthesis of W$_2$(CO)$_6$[η^5,η^5-C$_5$H$_4$–C(CH$_3$)$_2$–C$_5$H$_4$] (6) and W$_2$(CO)$_6$[η^5,η^5-(2-CH$_3$CO–C$_5$H$_3$)–C(CH$_3$)$_2$–C$_5$H$_4$] (7)

1, 1.0 g, 5.8 mmol, was allowed to react at 0 °C in THF with 0.46 g (11.8 mmol) of potassium metal. The reaction mixture was stirred for 12 h and heated at 50 °C for another hour to produce a yellow-cream suspension. After cooling to room temperature, W(CO)$_3$(CH$_3$CN)$_3$, 4.54 g, 11.6 mmol, was added and after stirring for 10 h the reaction mixture was refluxed for another 1 h. The resulting dark brown solution was then treated with an aqueous solution of FeCl$_3$–CH$_3$COOH. The color turned dark purple and the layers were separated. The organic phase was evaporated un-

der reduced pressure and the oily dark residue was chromatographed on an alumina column. Eluting with pet. ether–CH$_2$Cl$_2$ 5:1 afforded a wide red-burgundy band. HPLC and IR analysis revealed the presence of two compounds. After evaporation of the solvent, the residue was purified by medium pressure chromatography on a 35 × 2 cm silica gel column. Elution with heptane–benzene 10:3 separated two bands. The first band was collected, the solvent evaporated and the residue recrystallized from pet. ether–CH$_2$Cl$_2$ to afford 0.61 g of **6** (15%).

Elemental analysis: Calc.: C, 32.32; H, 2.00. Found: C, 32.54; H, 2.06%.

IR (CH$_2$Cl$_2$): 2011 (s); 1959 (s); 1905 (m); 1870 (sh).

^{1}H NMR (CDCl$_3$, −5 °C): 1.54 (s, 6 H, C(CH$_3$)$_2$); 5.06 (bs, 2 H, C$_5$H$_4$); 5.21 (bs, 2 H, C$_5$H$_4$); 5.40 (bs, 2 H, C$_5$H$_4$); 5.71 (bs, 2 H, C$_5$H$_4$).

^{13}C NMR (CDCl$_3$, −5 °C): 31.5 (C(CH$_3$)$_2$); 36.1 (C(CH$_3$)$_2$); 84.1 (C$_5$H$_4$); 84.2 (C$_5$H$_4$); 86.9 (C$_5$H$_4$); 94.7 (C$_5$H$_4$); 122.5 (ipso-C$_5$H$_4$); 213.2 (CO); 217.1 (CO); 221.0 (CO).

MS: m/e 706 (M)$^+$; 678 (M − CO)$^+$; 650 (M − 2CO)$^+$; 622 (M − 3CO)$^+$; 594 (M − 4CO)$^+$; 566 (M − 5CO)$^+$; 538 (M − 6CO)$^+$; 508 (M − 6CO − 2Me)$^+$.

Continued elution with benzene produced a second, red band in the medium pressure chromatography. A dark red fraction was collected. The solvent was removed and the residue recrystallized from pet. ether–CH$_2$Cl$_2$ to afford 0.43 g (10%) of **7** as a burgundy crystalline solid.

Elemental analysis: Calc.: C, 33.72; H, 2.16. Found: C, 33.54; H, 2.07%.

IR (CH$_2$Cl$_2$): 2016 (s); 1966 (s); 1912 (s); 1877 (sh); 1685 (m).

^{1}H NMR (CDCl$_3$, −5 °C): 1.55 (s, 3 H, C(CH$_3$)$_2$); 1.61 (s, 3 H, C(CH$_3$)$_2$); 2.34 (s, 3 H, COCH$_3$); 5.06 (bs, 1 H, Cp); 5.12 (bs, 1 H, Cp); 5.47 (bs, 1 H, Cp); 5.53 (bs, 1 H, Cp); 5.60 (bs, 1 H, Cp); 5.74 (bs, 1 H, Cp); 5.96 (bs, 1 H, Cp).

^{13}C NMR (CDCl$_3$, −5 °C): 26.4 (C(CH$_3$)$_2$); 27.26 (C(CH$_3$)$_2$); 35.2 (COCH$_3$); 36.2 (C(CH$_3$)$_2$); 80.8 (Cp); 83.9 (Cp); 84.1 (Cp); 89.6 (Cp); 90.6 (Cp); 90.7 (Cp); 98.1 (ipso-Cp); 100.25 (Cp); 117.0 (ipso-Cp); 129.3 (ipso-Cp); 193.7 (COCH$_3$) 211.1 (CO); 212.7 (CO); 214.5 (CO); 216.9 (CO); 217.5 (CO); 220.1 (CO).

MS: m/e 748 (M)$^+$; 720 (M − CO)$^+$; 692 (M − 2CO)$^+$; 580 (M − 6CO)$^+$.

3.4. Synthesis of [Mo(CO)$_3$CH$_3$]$_2$[η,η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_5$H$_4$]. (8)

1, 1.0 g, 5.8 mmol, was allowed to react at 0 °C in THF with 7.25 ml of 1.6 M n-butyllithium. The reaction mixture was stirred for 4 h and heated at 50 °C for another hour to produce a dark yellow-brown solution. After cooling to room temperature, 3.52 g (11.6 mmol)

of Mo(CO)$_3$(CH$_3$CN)$_3$ was added and after stirring for 10 h the reaction mixture was refluxed for another 1 h. The resulting dark brown solution was then cooled to 0 °C and treated with 0.5 ml of methyl iodide. The pale yellow solution darkened and was stirred at room temperature for 1 h. After removal of solvent by trap-to-trap transfer, the oily dark residue was chromatographed on an alumina column. Eluting with pet. ether afforded a single bright yellow band. The solvent was evaporated and the residue was recrystallized from pet. ether at −78 °C to afford 1.80 g **8** (55%) as yellow needles.

Elemental analysis: Calc.: C, 45.02; H, 3.60. Found: C, 45.40; H, 3.57%.

IR (CH$_2$Cl$_2$): 2016 (s); 1925 (s).

^{1}H NMR (CDCl$_3$, 20 °C): 0.35 (s, 6 H, Mo–CH$_3$); 1.45 (s, 6 H, C(CH$_3$)$_2$); 5.10 (t, 4 H, C$_5$H$_4$); 5.20 (bs, 4 H, C$_5$H$_4$).

^{13}C NMR (CDCl$_3$, 20 °C): −21.0 (Mo–CH$_3$); 31.7 (C(CH$_3$)$_2$); 35.2 (C(CH$_3$)$_2$); 91.45 (C$_5$H$_4$); 91.49 (C$_5$H$_4$); 126.4 (ipso-C$_5$H$_4$); 226.6 (CO); 239.9 (CO).

MS: m/e 560 (M)$^+$; 476 (M − 3CO)$^+$; 448 (M − 4CO)$^+$; 420 (M − 5CO)$^+$; 405 (M − 5CO − CH$_3$)$^+$; 377 (M − 6CO − CH$_3$)$^+$; 281 (M − 6CO − Mo − CH$_3$)$^+$.

3.5. Synthesis of [Mo(CO)$_3$H]$_2$[η,η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_5$H$_4$]. (9)

5, 0.050 g, 90 μmol, was taken up in THF and reacted at room temperature with an excess of sodium–potassium alloy, 0.100 g, for 4 h. During this time the color of the reaction mixture turned from deep red to yellow. The reaction mixture was filtered through Celite using Schlenk techniques. An IR spectrum of the reaction mixture revealed stretching bands at 1897, 1792, and 1743 cm^{-1}, consistent with the formation of the dimetalloanion of **5**. An excess of KHSO$_4$, 0.4 g, was added to the solution of the dimetalloanion and the reaction mixture stirred for 3 h. An IR of the reaction mixture contained bands at 2019 and 1933 cm^{-1}, characteristic of CpMo(CO)$_3$H species. After filtration of the reaction mixture through Celite, THF was removed by trap-to-trap transfer. The solution color changed from yellow to red during solvent removal, suggesting that Mo–Mo bonds were reforming through loss of dihydrogen. The red-orange product was left under vacuum overnight whereupon it was taken up on degassed benzene-d_6 and the NMR spectrum recorded. ^{1}H NMR: (C$_6$D$_6$) −5.38 (Mo–H), 1.00 (s, CH$_3$), 4.9–4.5 (m, Cp).

3.6. Synthesis of {Mo(CO)$_3$[η^5-C$_5$H$_4$-C(CH$_3$)$_2$-(3-H-C$_9$H$_7$)]}$_2$. (10)

2, 1.0 g, 4.5 mmol, was refluxed in THF with 2.73 g (9.0 mmol) of Mo(CO)$_3$(CH$_3$CN)$_3$ for 24 h. The resulting reaction mixture turned dark brown. After solvent

removal under reduced pressure, the dark oily residue was chromatographed on a column of alumina. Elution with pet. ether–CH$_2$Cl$_2$ 1:10 afforded a dark yellow band followed by a wide dark red band. The red fraction was evaporated under reduced pressure and the residue was recrystallized from CH$_2$Cl$_2$ at −78 °C to afford 0.70 g (19%) of **10** as a bright red powder.

IR (CH$_2$Cl$_2$): 2008 (m); 1950 (s); 1938 (s); 1912 (s). ^{1}H NMR (CDCl$_3$): 1.68 (s, 6 H, C(CH$_3$)$_2$); 3.27 (m, 2 H, 1-CH$_2$-indene); 5.09 (m, 2 H, C$_5$H$_4$); 5.36 (m, 2 H, C$_5$H$_4$); 6.19 (m, 1 H, 3-CH-indene); 7.1–7.5 (bm, 4 H, aromatic).

3.7. Synthesis of {Mo(CO)$_3$[η^5-C$_5$H$_4$-C(CH$_3$)$_2$-(1-H-C$_9$H$_7$)]}$_2$ (11)

2, 1.0 g, 4.5 mmol, was reacted at 0 °C in THF with 3.6 ml of n-butyllithium (2.5 M). The solution turned dark yellow and after stirring at room temperature for 4 h appeared brown red. The reaction mixture was then heated at 50 °C for another hour. Mo(CO)$_3$(CH$_3$CN)$_3$, 2.73 g, 9.0 mmol, was then added and the reaction mixture was stirred for 10 h at room temperature and heated to reflux for another hour. After cooling to room temperature, the dark brown solution was treated with an aqueous solution of FeCl$_3$–CH$_3$COOH. With the first addition the reaction mixture turned red and by the end of the addition appeared red-brown. The layers were separated and the organic phase was evaporated under reduced pressure. The dark residue was chromatographed on an alumina column. Eluting with pet. ether–CH$_2$Cl$_2$ 1:1 afforded first a yellow-brown band followed by a wide red band. The red fraction was collected, the solvent evaporated under reduced pressure and the resulting solid was recrystallized twice from toluene at −78 °C to afford 1.80 g (50%) of **11** as a bright red solid.

Elemental analysis: Calc.: C, 59.86; H, 4.27. Found: C, 60.08; H, 4.35%.

IR (CH$_2$Cl$_2$): 2008 (m); 1950 (s); 1913 (s); 1897 (sh).

^{1}H NMR (CDCl$_3$): 1.25 (s, 3 H, CH$_3$); 1.41 (s, 3 H, CH$_3$); 3.40 (m, 1 H, 1H-indene); 5.02 (m, 1 H, C$_5$H$_4$); 5.05 (m, 1 H, C$_5$H$_4$); 5.08 (m, 1 H, C$_5$H$_4$); 5.21 (m, 1 H, C$_5$H$_4$); 6.35 (d, 6 Hz, 1 H, 2H-indene); 6.72 (d, 6 Hz, 1 H, 2H-indene); 7.0–7.30 (m, 4 H, aromatic).

^{13}C NMR (CDCl$_3$): 26.1 (CH$_3$); 29.1 (CH$_3$); 38.0 (C(CH$_3$)$_2$); 62.8 (C1-indene); 89.8; 90.0; 93.2; 94.8 (C$_5$H$_4$); 121.1; 124.8; 124.5; 127.0 (aromatic); 129.1 (ipso-C$_5$H$_4$); 132.6 (C2-indene); 136.9 (C3-indene); 144.2; 145.3 (ipso-indene); no CO resonances could be observed owing to limited solubility.

3.8. Synthesis of Mo(CO)$_3$CH$_3$[η^5-C$_5$H$_4$-C(CH$_3$)$_2$-(3-H-C$_9$H$_7$)] (12)

11, 0.30 g, 0.37 mmol, was treated at −20 °C with 1.0 ml of a 1.0 M solution of KB[CH(CH$_3$)C$_2$H$_5$]$_3$H

(K-Selectride) in 50 ml of THF. Upon warming to room temperature the color changed from red to brown. After stirring for 2 h, the reaction was quenched with 20 ml of methyl iodide. The solvent was evaporated under reduced pressure and the dark residue was chromatographed on alumina. Eluting with pet. ether a bright yellow band was obtained. The solvent was evaporated and **12** was isolated as a yellow solid, 0.05 g, (33%). The spectral properties of this material were identical to those reported by Alt et al. [16a].

3.9. Synthesis of [Mo(CO)$_3$CH$_3$]$_2$[η^5,η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_9$H$_6$]. (13)

2, 1.0 g, 4.5 mmol, was treated with 3.6 ml of 2.5 M n-butyllithium in THF at 0 °C. After stirring for 4 h at room temperature and 1 h at 50 °C, Mo(CO)$_3$(CH$_3$CN)$_3$, 2.73 g, 9.0 mmol, was added and the reaction mixture was stirred at room temperature for 12 h followed by reflux for an additional hour. The resulting dark brown mixture was cooled to 0 °C and treated with 0.60 ml of CH$_3$I and stirred at room temperature for 2 h. The solvent was evaporated and the dark brown oily residue chromatographed on an alumina column. Elution with pet. ether afforded a yellow band that was spectroscopically shown to be **12**, 0.20 g, (11%). Continued elution with pet. ether–CH$_2$Cl$_2$ 5:1 afforded a slightly darker yellow band. Evaporation of the solvent and recrystallization from pet. ether–CH$_2$Cl$_2$ at −78 °C yielded 1.18 g of **13** (43%) as a dark yellow solid.

Elemental analysis: Calc.: C, 49.20; H, 3.63. Found: C, 49.26; H, 3.58%.

IR (CH$_2$Cl$_2$): 2016 (s); 1933 (s).

^{1}H NMR (CDCl$_3$): −0.64 (s, 3 H, CH$_3$); 0.37 (s, 3 H, CH$_3$); 1.68 (s, 3 H, C(CH$_3$)$_2$); 1.74 (s, 3 H, C(CH$_3$)$_2$); 5.16 (d, 3 Hz, 1 H, 2H-indene); 5.61 (dd, 3 Hz, 0.5 Hz, 1 H, 3H-indene); 5..11 (dd, 5 Hz, 2 Hz, 1 H, C$_5$H$_4$); 5.19 (dd, 5 Hz, 2 Hz, 1 H, C$_5$H$_4$); 5.20 (dd, 5 Hz, 2 Hz, 1 H, C$_5$H$_4$); 5.27 (dd, 5 Hz, 2 Hz, 1 H, C$_5$H$_4$); 7.04–7.09 (m, 1 H, aromatic); 7.13–7.19 (m, 2 H, aromatic); 7.35 (dd, 9 Hz, 2 Hz, 1 H, aromatic).

^{13}C NMR (CDCl$_3$): −21.0 (CH$_3$); −6.0 (CH$_3$); 31.9 (C(CH$_3$)$_2$); 32.1 (C(CH$_3$)$_2$); 36.4 (C(CH$_3$)$_2$); 91.1/91.2; 91.4; 91.7; 92.6 (C$_5$H$_4$); 111.2 (C2-indene); 112.0 (ipso-indene); 114.7 (C3-indene); 126.1 (ipso-C$_5$H$_4$); 123.6; 125.0; 125.5; 126.2 (aromatic); 225.9; 226.5; 226.6; 227.2; 239.9; 240.9 (CO).

MS: m/e 610 (M)$^+$; 582 (M − CO)$^+$; 554 (M − 2CO)$^+$; 526 (M − 3CO)$^+$; 511 (M − 3CO − CH$_3$)$^+$; 496 (M − 3CO − 2CH$_3$)$^+$; 427 (M − 6CO − CH$_3$)$^+$.

3.10. Synthesis of [Mo(CO)$_3$]$_2$[η^5,η^5-C$_5$H$_4$-C(CH$_3$)$_2$-C$_9$H$_6$]. Mo–Mo. (14)

2, 0.60 g, 2.7 mmol, was treated with 3.4 ml of 1.6 M n-butyllithium in THF at 0 °C. After stirring for 4 h

at room temperature and 1 h at 50 °C, Mo-$(CO)_3(CH_3CN)_3$, 1.64 g, 5.4 mmol, was added and the reaction mixture stirred at room temperature for 12 h followed by reflux for an additional hour. The resulting dark brown mixture was then treated with 2.73 g (5.4 mmol) of $Fc(BPh_4)$ [34] and stirred for 1 h during which the reaction mixture turned dark red. The solvent was removed under reduced pressure and the dark residue was washed twice with 100 ml of pet. ether in order to eliminate ferrocene. The residue was chromatographed on alumina. Elution with pet. ether–CH_2Cl_2 1:1 afforded a dark red band. The solvent was evaporated and the remaining red solid was recrystallized from pet. ether–CH_2Cl_2 at −78 °C to produce 14 as a red solid, 0.70 g (45%).

Elemental analysis: Calc.: C, 47.61; H, 2.78. Found: C, 47.48; H, 2.73%.

IR (CH_2Cl_2): 2013 (s); 1960 (s); 1910 (m); 1878 (sh).

^1H NMR $(CDCl_3$, −20 °C). Two conformers are observed: **A**, 1.64 (s, 3 H, CH_3); 1.78 (s, 3 H, CH_3); 5.06 (bs, 1 H, C_5H_4); 5.30 (bs, 1 H, C_5H_4); 5.37 (bs, 1 H, C_5H_4); 5.90 (bs, 1 H, C_5H_4); 5.53 (bs, 1 H, 2H-indene); 6.46 (bs, 1 H, 3H-indene); 7.1–7.4; 7.5–7.7; 7.9 (m, 4 H, aromatic); **B**, 1.53 (s, 3 H, CH_3); 1.84 (s, 3 H, CH_3); 4.96 (bs, 1 H, C_5H_4); 5.25 (bs, 1 H, C_5H_4); 5.43 (bs, 1 H, C_5H_4); 5.80 (bs, 1 H, C_5H_4); 5.53 (bs, 1 H, 2H-indene); 6.46 (bs, 1 H, 3H-indene); 7.1–7.4; 7.5–7.7; 7.9 (m, 4 H, aromatic).

MS: m/e 580 $(M)^+$; 552 $(M - CO)^+$; 524 $(M - 2CO)^+$; 496 $(M - 3CO)^+$; 468 $(M - 4CO)^+$; 440 $(M - 5CO)^+$; 412 $(M - 6CO)^+$; 316 $(M - 6CO - Mo)^+$; 156 $(M - 6CO - 2Mo - C_5H_4)^+$.

3.11. Synthesis of $[Mo(CO)_3]_2[\eta^5, \eta^5-C_5H_4-C(CH_3)_2-(3-CH_3-C_9H_5)]$, Mo=Mo, (15)

3, 0.45 g, 1.9 mmol, was treated with 2.5 ml of 1.6 M n-butyllithium in THF at 0 °C. After stirring for 4 h at room temperature and 1 h at 50 °C, Mo-$(CO)_3(CH_3CN)_3$, 1.212 g, 4.0 mmol, was added and the reaction mixture was stirred at room temperature for 12 h followed by reflux for an additional hour. The resulting dark brown mixture was then treated with 2.02 g (4.0 mmol) of $Fc(BPh_4)$ [34] and stirred for 1 h. The reaction mixture turned dark red. The solvent was removed under reduced pressure and the dark residue was washed twice with 100 ml of pet. ether in order to eliminate ferrocene. The residue was then chromatographed on alumina. Eluting with pet. ether–CH_2Cl_2 1:1 afforded a dark red band. The solvent was evaporated and the remaining red solid was recrystallized from pet. ether–CH_2Cl_2 at −78 °C to produce 15 as a dark red crystalline solid, 0.45 g (40%)..

Elemental analysis: Calc.: C, 48.51; H, 3.05. Found: C, 48.40; H, 2.98%.

IR (CH_2Cl_2): 2010 (s); 1957 (s); 1909 (m); 1877 (sh).

^1H NMR $(CDCl_3$, −20 °C). Two conformers are observed: **A**, 1.62 (s, 3 H, CH_3); 1.76 (s, 3 H, CH_3); 2.52 (s, 3 H, CH_3-indene); 4.98 (bs, 1 H, C_5H_4); 5.28 (bs, 1 H, C_5H_4); 5.32 (bs, 1 H, C_5H_4); 5.51 (bs, 1 H, C_5H_4); 6.46 (bs, 1 H, 3H-indene); 7.10–7.35 (m, 2 H, aromatic); 7.54 (d, 12 Hz, 1 H, aromatic); 7.62 (d, 12 Hz, 1 H, aromatic); **B**, 1.52 (s, 3 H, CH_3); 1.82 (s, 3 H, CH_3); 2.47 (s, 3 H, CH_3-indene); 4.95 (bs, 1 H, C_5H_4); 5.28 (bs, 1 H, C_5H_4); 5.39 (bs, 1 H, C_5H_4); 5.56 (bs, 1 H, C_5H_4); 6.46 (bs, 1 H, 3H-indene); 7 10–7.35 (m, 2 H, aromatic); 7.67 (d, 12 Hz, 1 H, aromatic); 7.92 (d, 12 Hz, 1 H, aromatic).

MS: m/e 594 $(M)^+$; 566 $(M - CO)^+$; 538 $(M - 2CO)^+$; 510 $(M - 3CO)^+$; 482 $(M - 4CO)^+$; 454 $(M - 5CO)^+$; 426 $(M - 6CO)^+$; 330 $(M - 6CO - Mo)^+$; 170 $(M - 6CO - 2Mo - C_5H_4)^+$.

3.12. X-ray structure determinations

Crystal, data collection and refinement parameters are given in Table 3. Satisfactory crystals of 12 and 15 were obtained by recrystallization from dichloromethane and pet. ether at −30 °C. Suitable crystals for single-crystal X-ray diffraction were selected and mounted with epoxy cement on thin glass fibers. The unit cell parameters were obtained by the least squares refinement of the angular setting of 24 reflections ($2\Theta \leq 2\Theta \leq 25°$).

No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for 13 and 15. The E-statistics suggested a centrosymmetric space group and $P\bar{1}$ was chosen. The space group choice was subsequently verified by chemically reasonable results of refinement. The structures were solved by automated Patterson methods, completed by subsequent difference Fourier synthesis and refined by least squares procedures. Semi-empirical ellipsoid absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in SHELXTL PLUS (4.2) program library (Sheldrick, Siemens XRD, Madison, WI).

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