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Cooperative effects in π-ligand bridged dinuclear complexes XXII. New dinuclear bis(cyclopentadienediyl)ketone complexes containing molybdenum, tungsten, cobalt and iron[☆,☆☆]

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Abstract

Hydrolysis of the siloxyfulvene compounds $\{M\}[\eta^5\text{-}C_5H_4C(OTMS)(C_5Me_4)]$ ($\{M\} = Mo(CO)_3Me$: **1a**; $\{M\} = W(CO)_3Me$: **1b**) affords $\{M\}[\eta^5\text{-}C_5H_4C(O)(C_5Me_4H)]$ ($\{M\} = Mo(CO)_3Me$: **3a**; $\{M\} = W(CO)_3Me$: **3b**) which are suitable precursors for the synthesis of dinuclear complexes. The reactivity of the molybdenum and the tungsten compounds shows remarkable differences: heating of **3a** with $Co_2(CO)_8$ in the presence of 3,3-dimethylbut-1-ene reveals the heterodinuclear complex $Me(CO)_3Mo[(\eta^5(Mo){-}C_5H_4)C(O)(\eta^5(Co){-}C_5Me_4)]Co(CO)_2$ (**4a**) along with the homodinuclear complex $(CO)_2Co[(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5Me_4)]Co(CO)_2$ (**5**), the comparable reaction of **3b** with $Co_2(CO)_8$ results in the formation of the heterodinuclear complex $Me(CO)_3W[(\eta^5(W){-}C_5H_4)C(O)(\eta^5(Co){-}C_5Me_4)]Co(CO)_2$ (**4b**) only. The metal–metal bound complexes $[(\eta^5(M){-}C_5H_4)C(O)(\eta^5(M'){-}C_5Me_4)]MM'(CO)_6$ ($M{-}M'$) ($M = W$, $M' = Mo$: **8**; $M = M' = W$: **9**; $M = M' = Mo$: **10**) are synthesized from the reaction of **3a** or **3b** with $M'(CO)_3(EtCN)_3$ ($M' = Mo$, W). When $Mo(CO)_6$ is used in place of $Mo(CO)_3(EtCN)_3$ **10** can also be obtained in addition to $[(\eta^5\text{-}C_5H_3Me)C(O)(\eta^5\text{-}C_5Me_4)]Mo_2(CO)_6$ ($Mo{-}Mo$) (**12**) as an unexpected by-product. In complex **12** the cyclopentadienyl ligand is regioselectively methylated in the vicinal position to the bridge-head atom. The synthesis of $[(\eta^5(Mo){-}C_5H_4)C(O)(\eta^5(Fe){-}C_5Me_4)]MoFe(CO)_5$ ($Mo{-}Fe$) (**14**) is achieved by reaction of **3a** with $Fe(CO)_3(C_8H_{14})$. An X-ray diffraction study of the mononuclear siloxyfulvene $Me(CO)_3W[\eta^5\text{-}C_5H_4C(OSiMe_2t\text{-}Bu)(C_5Me_4)]$ (**2**) proves the fulvene-like structure of the uncoordinated tetramethylated *cyclo*-C_5-moiety. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Homo- and heterodinuclear complexes; Bis(cyclopentadiendiyl) bridged complexes; Tungsten; Molybdenum; Cobalt; Iron

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1. Introduction

Ligand-bridged dinuclear complexes, especially in combination with two different metal centers [1], still attract attention in synthetic chemistry because of their potential in new reactivity patterns [2] or new catalytic reactivity [3] due to co-operative effects of metal centers kept in close proximity. In particular, metal–metal bond containing congeners are prone to unique initial steps which can trigger new reactivity patterns: (i) homo- or heterolytic cleavage of the metal–metal bonds; (ii) regioselective oxidative additions of x–y or (iii) release of one ligand and stabilisation of the coordinatively unsaturated intermediate by an intermetallic dative bond (Scheme 1).

A prerequisite to exploitation of the co-operative effect is the prevention of the dissociation of the dinuclear complexes into mononuclear species which is fulfilled in bis(cyclopentadiendiyl) bridged dinuclear complexes [4–6].

Recently we reported a new strategy for the synthesis of homo- and heterodinuclear bis(cyclopentadienediyl) bridged complexes starting with the mononuclear siloxyfulvene complexes $\{M\}[\eta^5\text{-}C_5H_4C(OTMS)(C_5Me_4)]$ and $\{M\}[\eta^5\text{-}C_5H_4C(O)(C_5Me_4H)]$ with $\{M\} = W(CO)_3Me$, $Mn(CO)_3$. In this paper, we expand this

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[☆] 21st communication: J. Heck, G. Lange, M. Malessa, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 659.

[☆☆] Dedicated to Professor Christoph Elschenbroich on the occasion of his 60th birthday.

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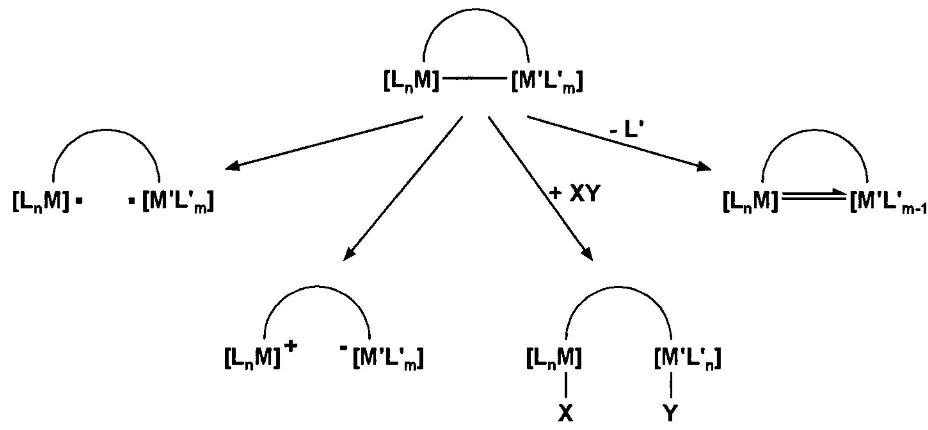


Scheme 1.

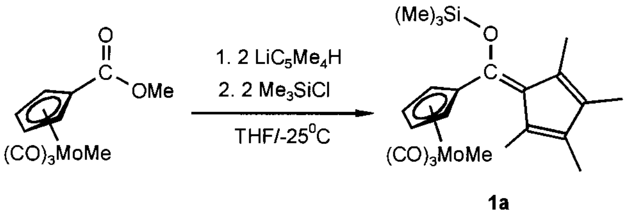
concept to synthesize complexes with the $Mo(CO)_3Me$ moiety, which exhibit remarkable differences in reactivity compared with the analogous tungsten compounds.

2. Results and discussion

The Mo-containing siloxyfulvene complex $Me(CO)_3Mo[\eta^5\text{-}C_5H_4C(OTMS)(C_5Me_4)]$ (**1a**) was synthesized in very good yield according to the procedure described recently for the preparation of the complexes $\{M\}[\eta^5\text{-}C_5H_4C(OTMS)(C_5Me_4)]$ ($\{M\} = W(CO)_3Me$: **1b**, $\{M\} = Mn(CO)_3$: **1c**. The complex **1a** was formed by the reaction of $Me(CO)_3Mo(\eta^5\text{-}C_5H_4COOMe)$ with two equivalents of tetramethylcyclopentadienyl lithium and a subsequent addition of an excess of Me_3SiCl (Scheme 2). To minimize the formation of by-products due to the sensitivity of the $Mo(CO)_3Me$ moiety towards basic reaction conditions, the synthesis of **1a** was performed at − 25°C, in contrast to the synthesis of the tungsten containing complex **1b,** which can be prepared at room temperature in good yields.

To confirm the formation of the siloxyfulvene complexes, in our recent publication [7] we reported the preliminary result of a molecular structure analysis of the corresponding manganese complex $(CO)_3Mn[\eta^5\text{-}C_5H_4C(OTMS)(C_5Me_4)]$ (**1c**). Unfortunately, the X-ray structure analysis of **1c** was hampered by the poor quality of the crystals and attempts to achieve suitable crystals of **1a** and **1b** were even less successful. Therefore, the derivative $Me(CO)_3W[\eta^5\text{-}C_5H_4C(OSiMe_2t\text{-}Bu)(C_5Me_4)]$ (**2**) has now been synthesized containing a *tert*-butyldimethylsilyl group instead of the trimethylsilyl group in **1a–c**. Beautiful orange–red crystals were obtained, and the molecular structure was resolved in very good quality (Table 1, Fig. 1).

The fulvene moiety of **2** displays a pronounced bond length alternation quite typical for this type of hydrocarbon [8] (Table 2). An interesting feature is the torsion along the *exo*-cyclic C=C double bond of the fulvene. Due to the large groups attached to this bond there is a high amount of strain which is partly relieved by twisting out of the planar shape by 26°. The η^5-$(C_5H_4)W(CO)_3Me$ moiety is quite regular and shows no significant deviations to related compounds.



Scheme 2. Synthesis of **1a**.

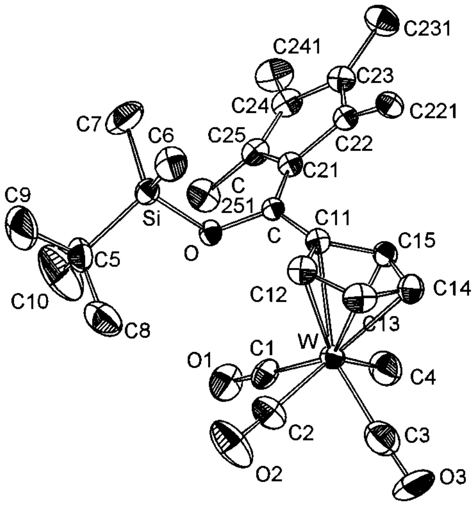


Fig. 1. Molecular structure of **2**. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 1
X-ray crystal structure, data collection and refinement data for **2**

Crystal parameters	
Formula	$C_{25}H_{34}O_4SiW$
Formula weight (g mol^{-1})	610.48
T (K)	173
λ (pm)	71.073 (Mo–K_α)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	847.0(2)
b (Å)	1207.9(4)
c (Å)	1353.3(7)
α (°)	85.02(3)
β (°)	82.74(3)
γ (°)	72.11(2)
V (nm^3)	1.304
Z	2
ρ_{calc} (g cm^{-3})	1.554
μ (Mo–K_α) (mm^{-1})	4.50
Crystal size (mm^3)	$0.2\times0.25\times0.4$
Crystal color	Orange–red
Data collection	
Diffractometer used	Hilger & Watts
Radiation	Mo–K_α ($\lambda=0.71073$ Å)
Monochromator	Graphite
$\theta_{min,max}$ (°)	2.5–25.0
Index ranges	$-2\le h\le 10$; $-16\le k\le 17$; $-19\le l\le 19$
Reflections collected	6624
Unique reflections	4583 (4422 $I>2\sigma(I)$)
R_{int}	0.0139
Refinement	
Parameters	294
GOF	1.086
R_1/wR_2	0.0451/0.1058
w^{-1} [a]	$\sigma^2(F_o^2)+(0.0458\ P)^2+12.91P$
max, min resd (10^{-6} e pm^{-3})	4110/−3060

The spectroscopic features of **2** very much resemble those of **1a**–**c** with the exception of the NMR signals of the Cp ligand and of the methyl groups of the silyl substituent: the ^{1}H-NMR spectrum of **2** reveals two singlets for the methyl groups of the silyl substituent, and four signals for the protons of the coordinated cyclopentadienyl ligand, while in the spectra of **1a**–**c** the corresponding protons display an AA′MM′ pattern with two pseudo-triplets. The number of the ^{13}C-NMR signals for **2** confirms the anisochrony of the two methyl substituents and four Cp positions.

Apparently, the steric influence of the *tert*-butyldimethylsilyl group hinders the free rotation of the η^5-cyclopentadienyl moiety around the C11–C single bond.

The siloxyfulvene complexes **1a** and **1b** were readily hydrolyzed to $\{M\}[\eta^5\text{-}C_5H_4C(O)(C_5Me_4H)]$ ($\{M\}=Mo(CO)_3Me$: **3a**; $\{M\}=W(CO)_3Me$: **3b**) (Scheme 3) which were isolated as a mixture of the two isomers **A** and **B**. The compounds **3a** and **3b** contain a non-coordinated tetramethylcyclopentadiene ring and are suitable precursors for dinuclear species.

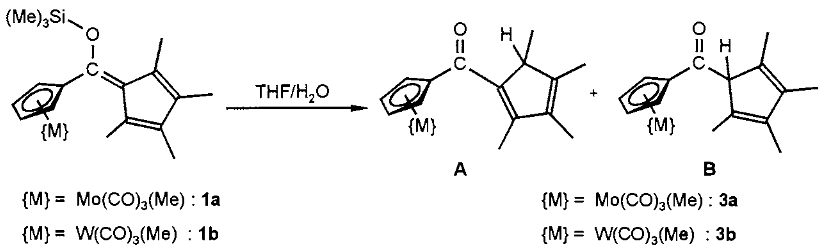
A rich chemistry of **3b** has been reported previously [7]. In comparison, the corresponding reactions of the molybdenum complex **3a** exhibit some surprising results.

Heating the tungsten complex **3b** with $Co_2(CO)_8$ in the presence of 3,3-dimethylbut-1-ene in THF afforded the dinuclear species $Me(CO)_3W[(\eta^5(W)\text{–}C_5H_4)C(O)(\eta^5(Co)\text{–}C_5Me_4)]Co(CO)_2$ (**4b**) in high yields. The same reaction with **3a** yielded the expected heterodinuclear complex $Me(CO)_3Mo[(\eta^5(Mo)\text{–}C_5H_4)C(O)(\eta^5\text{-}(Co)\text{–}C_5Me_4)]Co(CO)_2$ (**4a**) along with the homodinuclear derivative $(CO)_2Co[(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5Me_4)]Co(CO)_2$ (**5**) as a by-product (Scheme 4(a)). The yields of **4a** and **5** are approximately 40% each.

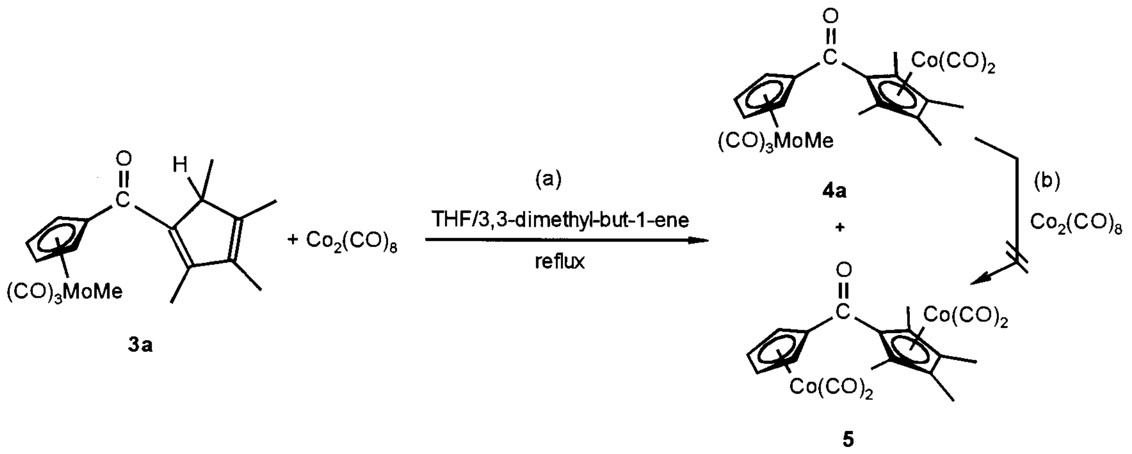
To prove whether the substitution of the $Mo(CO)_3Me$ moiety by $Co(CO)_2$ is associated with the coordination of $Co(CO)_2$ to the tetramethylcyclopenta-

Table 2
Selected bond lengths (Å), bond angles (°) and angles between planes for **2**

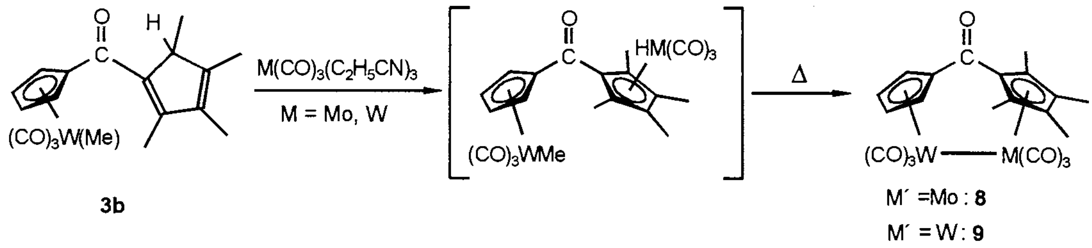
Bond lengths (Å)			
W–C11	237.1(7)	C–C11	146.8(9)
W–C12	231.2(7)	C–O	137.3(7)
W–C13	233.0(7)	O–Si	168.8(5)
W–C14	234.0(7)	C–C21	135.7(9)
W–C15	235.3(7)	C21–C22	148.1(9)
W–C1	196.6(10)	C22–C23	136.3(9)
W–C2	199.3(8)	C23–C24	147.6(10)
W–C3	199.6(8)	C24–C25	134.8(10)
W–C4	229.3(9)	C25–C21	148.4(9)
C1–O1	116.1(12)	C22–C221	150.5(9)
C2–O2	115.8(10)	C23–C231	149.1(10)
C3–O3	114.3(9)	C24–C241	151.0(9)
		C25–C251	150.1(10)
Bond angles (°)			
W–C1–O1	177.31(85)	C21–C22–C23	107.14(57)
W–C2–O2	178.59(88)	C22–C23–C24	108.88(58)
W–C3–O3	178.53(61)	C23–C24–C25	109.95(57)
C12–C11–C	127.24(59)	C24–C25–C21	107.12(59
C15–C11–C	126.07(58)	C21–C22–C221	126.87(56)
C11–C–O	113.16(52)	C221–C22–C23	124.79(60)
C–O–Si	124.36(38)	C22–C23–C231	127.48(66)
C21–C–C11	125.10(57)	C231–C23–C24	123.61(62)
C21–C–O	121.50(56)	C23–C24–C241	121.83(66)
C–C21–C22	127.49(57)	C241–C24–C25	128.14(69)
C–C21–C25	125.75(59)	C24–C25–C251	126.39(62)
		C251–C25–C21	125.44(61)
Angles between planes			
[Cp]: C11–15		[Cp]/[CO]	29.13(42)
[CO]: C11–C–O–C21		[CO]/[Cp″]	25.86(38)
[Cp″]: C21–25		[Cp]/[Cp″]	50.36(34)



Scheme 3. Synthesis of **3a** and **3b**.



Scheme 4. Products isolated from the reaction of **3a** and $Co_2(CO)_8$.



Scheme 5. Synthesis of the metal–metal bound complexes **8** and **9**.

dienyl ring in **4a**, a sample of **4a** was heated with $Co_2(CO)_8$ and 3,3-dimethylbut-1-ene in THF and the reaction was monitored by IR spectroscopy (Scheme 4(b)). However, neither substitution of the $Mo(CO)_3Me$ moiety by $Co(CO)_2$ nor decomposition of **4a** was observed. Apparently, **4a** is not a precursor for the formation of **5**, and **5** is formed in a quite different way requiring the initial reaction between **3a** and $Co_2(CO)_8$; the fate of the eliminated molybdenum fragment is yet uncertain.

A very interesting feature of the chemistry of the tungsten compound **3b** is the formation of metal–metal bound species in reactions with suitable metal carbonyls. Previously we reported the synthesis of the heterodinuclear pentacarbonyl complexes $[(\eta^5(W)-C_5H_4)C(O)(\eta^5(M)-C_5Me_4)]WM(CO)_5$ $(W-M)$ (M = Fe: **6**; M = Ru: **7**) by reaction of **3b** with $Fe(CO)_5$ and $Ru_3(CO)_{12}$, respectively [7]. Similarily it is possible to prepare the hexacarbonyl compounds $[(\eta^5(W)-C_5H_4)C(O)(\eta^5(M)-C_5Me_4)]WM(CO)_6$ $(W-M)$ (M = Mo: **8**, M = W: **9**) (Scheme 5). Treatment of **3b** with $M(CO)_3(C_2H_5CN)_3$ (M = Mo, W) in diglyme at room temperature first led to the formation of the complexes $Me(CO)_3W[(\eta^5(W) - C_5H_4)C(O)(\eta^5(M) - C_5Me_4)]M - (CO)_3H$ (M = Mo, W) without a metal–metal bond, which have not been isolated, but identified in the reaction mixture by means of IR and ^1H-NMR spectroscopy demonstrating the typical features of $Cp(CO)_3WMe$ and $Cp^*M(CO)_3H$ (M = W, H) entities. Upon heating the solutions of the intermediate hydrido complexes in diglyme the metal–metal bound species **8** and **9** were formed (Scheme 5). The yields in these reactions (23–39%) are limited due to the special mechanism of the metal–metal bond formation which is discussed by Bergman et al. [9] (vide infra).

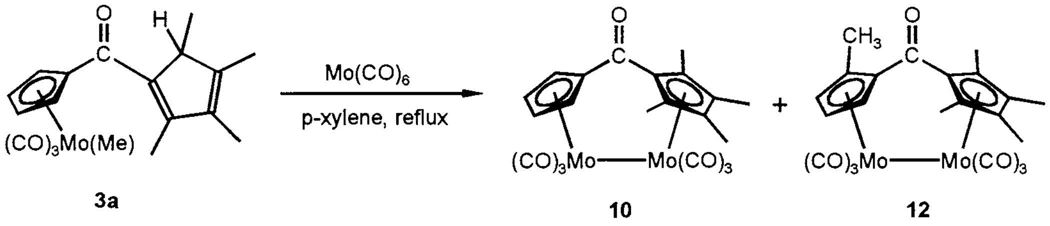
A quite similar chemistry of the molybdenum complex **3a** was expected, but in fact, there are considerable differences in reactivity and product formation compared to the reactions of **3b**. The reaction of **3a** with $Mo(CO)_3(C_2H_5CN)_3$ in THF at room temperature generates $Me(CO)_3Mo[(\eta^5(W)\text{-}C_5H_4)C(O)(\eta^5(M)\text{-}C_5Me_4)]\text{-}Mo(CO)_3H$ (**11**) which is identified *in situ* by IR and ^1H-NMR spectroscopy. Subsequent heating of the reaction mixture yielded $[(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5Me_4)]Mo_2(CO)_6$ (*Mo–Mo*) (**10**) which has been isolated in a yield of 28%. In this case, the reaction conditions are less strict than in the synthesis of **8** and **9** due to the higher reactivity of the $Mo(CO)_3Me$ and $Mo(CO)_3H$ moieties compared to the tungsten analogues.

Complex **10** can also be prepared by heating **3a** and $Mo(CO)_6$ in refluxing *p*-xylene (Scheme 6). From this reaction the new complex $[(\eta^5\text{-}C_5H_3Me)C(O)(\eta^5\text{-}C_5Me_4)]Mo_2(CO)_6$ (*Mo–Mo*) (**12**) was isolated as a remarkable side product which contains a monomethylated cyclopentadiendiyl ligand with the Me substituent in 2-position exclusively. **12** was unequivocally identified by means of IR, NMR and mass spectrometry, but unfortunately gave unsatisfactory elemental analysis only, probably due to solvent residues which could not be stripped off completely even when drying the oily material several days under reduced pressure. However, no indication was found for an acylated Cp ligand as observed in the complex $[(\eta^5\text{-}C_5H_3C(O)Me)CH_2(\eta^5\text{-}C_5H_4)]W_2(CO)_6$ (*W–W*) [10].

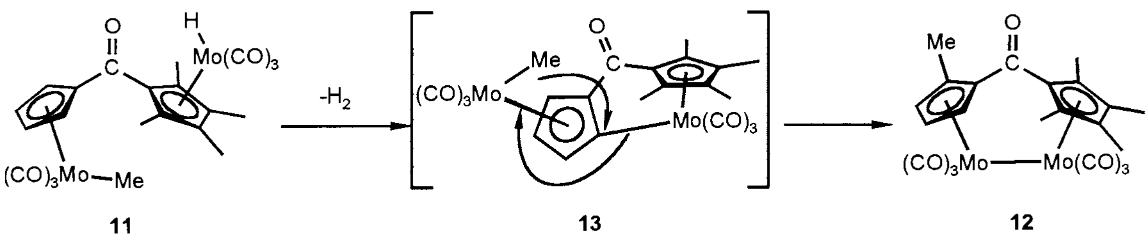
The new methyl substituent in **12** was formerly bound to the molybdenum center in **3a**. This has been proven by repeating the reaction with the deuterated derivative $(CD_3)(CO)_3Mo[\eta^5\text{-}C_5H_4C(O)(C_5Me_4H)]$ (**3a–CD₃**). The main product again is **10**, whereas $[\{\eta^5\text{-}C_5H_3(CD_3)\}C(O)(\eta^5\text{-}C_5Me_4)]Mo_2(CO)_6$ (**12–CD₃**) has been formed in small amounts (Scheme 6).

It is very likely that there are differences in the mechanism of the formation of the metal–metal bonds in the complexes **10** and **12**. However, it seems reasonable to assume complex **11** as the precursor in both cases. Complex **10** is probably formed in a similar manner as described for the formation of $Cp_2Mo_2(CO)_6$ from $CpMo(CO)_3Me$ and $CpMo(CO)_3H$ [9]. This mechanism includes CO insertion into the metal–methyl bond; the metal–metal bond is then generated under elimination of acetaldehyde from the metal–acyl intermediate. The CO deficiency in this reaction leads to the formation of $Cp_2Mo_2(CO)_4$ as a by-product having a metal–metal triple bond; corresponding complexes with a one-atom bridging unit between the two cyclopentadiendiyl moieties are not known, since for steric reasons this type of ligand does not allow the almost linear conformation of the Cp–Mo–Mo–Cp array as it is observed in $Cp_2Mo_2(CO)_4$ [5b,11].

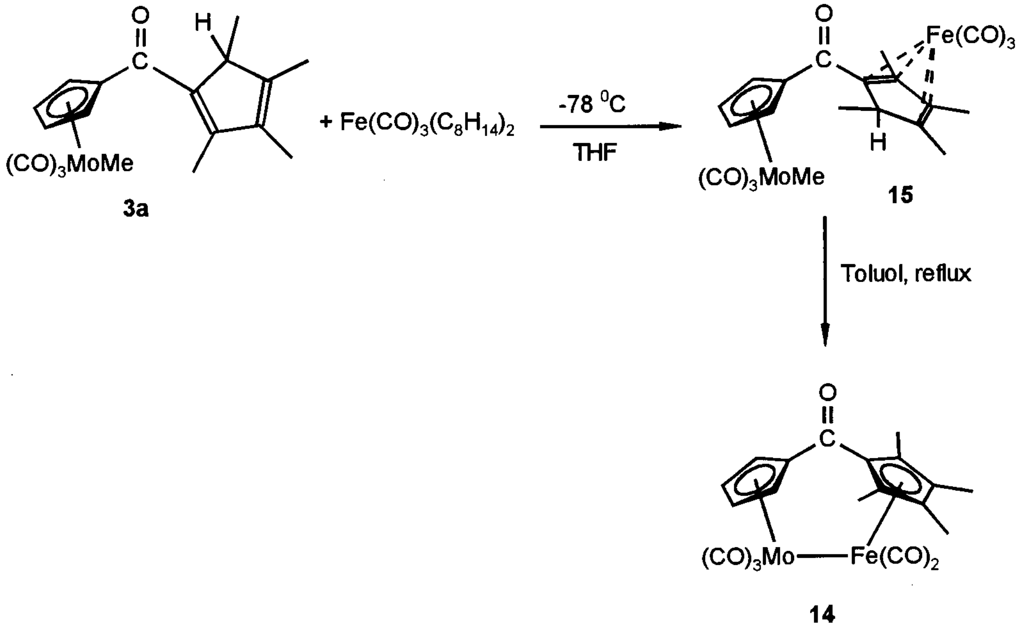
In the mechanism described above, the cyclopentadienyl ligands are spectator ligands, and apparently not directly involved in the conversion of the mononuclear compounds into the dinuclear molybdenum complexes. In contrast, it is quite obvious that the bis(cyclopentadiendiyl)ketone ligand is engaged in the formation of **12** from **11**. A possible pathway is depicted in Scheme 7. C–H activation and H_2 elimination would generate an intermediate **13** with a sigma bonded cyclopentadienediyl ligand. Analogous compounds to **13** have recently been described by Bitterwolf et al. [12]. The



Scheme 6. Products of the reaction of **3a** and $Mo(CO)_6$ in refluxing *p*-xylene.



Scheme 7. Possible pathway for the formation of **12** starting with **11**.



Scheme 8. Synthesis of the metal–metal bound heteronuclear compound **14**.

methyl migration from the Mo center to the 2-position of the C_5H_4-ligand together with the formation of the metal–metal bond should lead to the Cp methylated product **12**. Comparable anion-induced migration reactions of a hydrocarbyl ligand from a metal center to the deprotonated Cp ligand have already been investigated recently [13]. This pathway would explain the regioselectivity of methyl migration since only the 2-methylcyclopentadienediyl isomer has been formed.

Attempts to synthesize the heterodinuclear compound $[(\eta^5(\mathit{Mo})\text{-}C_5H_4)C(O)(\eta^5(\mathit{W})\text{-}C_5Me_4)]MoW(CO)_6$ (*Mo–W*) by the reaction of **3a** with $W(CO)_3(C_2H_5CN)_3$ at room temperature failed. However, at higher reaction temperature an inseparable mixture of the complexes $[(\eta^5(M)\text{-}C_5H_4)C(O)(\eta^5(M')\text{-}C_5Me_4)]M'M(CO)_6$ (*M′–M*) (M, M′ = Mo, W) was obtained. Apparently, in this reaction the $Mo(CO)_3Me$ moiety can be displaced by a tungsten carbonyl fragment similar to the reaction of $Co_2(CO)_8$ with **3a**. In addition, no evidence was found for a compound comparable to **12**.

The thermal instability of the $Mo(CO)_3Me$ moiety is also observed when **3a** is heated in refluxing *p*-xylene. This reaction condition mainly leads to the decomposition of the starting material and small amounts of $Mo(CO)_6$ and **10** could be isolated from the reaction mixture. Under the same conditions the tungsten compound **3b** is quite stable and shows only a slight tendency to decompose.

The instability of **3a** at elevated temperatures does not allow the synthesis of heterodinuclear complexes containing molybdenum–iron and molybdenum–ruthenium bonds by simply heating of **3a** with $Fe(CO)_5$ and $Ru_3(CO)_{12}$, respectively. The formation of the complex $[(\eta^5(\mathit{Mo})\text{-}C_5H_4)C(O)(\eta^5(\mathit{Fe})\text{-}C_5Me_4)]MoFe(CO)_5$ (*Mo–Fe*) (**14**) was achieved by utilizing $Fe(CO)_3(C_8H_{14})_2$ [14], which is an excellent transfer reagent for a $Fe(CO)_3$ unit to dienes at low temperatures. As an intermediate $Me(CO)_3Mo[(\eta^5(\mathit{Mo})\text{-}C_5H_4)C(O)(\eta^5(\mathit{Fe})\text{-}C_5Me_4H)]Fe(CO)_3$ (**15**) was formed which was identified by the characteristic carbonyl stretching bands of a (η^4-diene)$Fe(CO)_3$ entity when the course of the reaction was monitored by means of IR spectrocopy. Heating the intermediate **15** in refluxing toluene afforded the metal–metal bound heterodinuclear complex **14** which was isolated in a 30% yield (Scheme 8).

All attempts to synthesize the analogous molybdenum–ruthenium complex by using $Ru(CO)_3(C_2H_4)_2$ [15] as a synthon for a $Ru(CO)_3$ fragment failed. We have found no evidence that a $Ru(CO)_3$ fragment has been co-ordinated to the free cyclopentadiene ring in **3a**.

3. Experimental

All reactions were conducted under nitrogen using standard Schlenk techniques. Solvents were dried with the appropriate drying agents under nitrogen. Literature procedures were used to synthesize **3b** [7], $Me(CO)_3Mo[\eta^5\text{-}C_5H_4COOMe]$ [16] and $M(CO)_3(C_2H_5CN)_3$ (M = Mo, W) [17]. ^{1}H- and ^{13}C-NMR spectra were measured on a Varian Gemini 200 BB and referenced against tetramethylsilane. IR spectra were recorded on a Perkin–Elmer FT-IR 1720X using KBr cells. Elemental analysis (C, H) were carried out on a Heraeus CHN–O-Rapid, in the Institut für Anorganische und Angewandte Chemie, Universität Hamburg.

3.1. Synthesis of $Me(CO)_3Mo[\eta^5\text{-}C_5H_4C(OTMS)\text{-}(C_5Me_4)]$ (**1a**)

$Me(CO)_3Mo(\eta^5\text{-}C_5H_4COOMe)$ (4.05 g; 13 mmol) was dissolved in 100 ml of THF and cooled to −25°C. Tetramethylcyclopentadienyl lithium (3.7 g; 28.6 mmol) was added and the mixture was stirred at −25°C for 5 h. Subsequently, Me_3SiCl (4.5 ml, 35 mmol) was added. After stirring for an additional 30 min, the solvent was removed under reduced pressure. The resulting red residue was extracted with *n*-hexane. Evaporation of the solvent and drying in vacuo yielded **1a** (5.30 g; 85%) as a red oil.

Anal. Calc. for $C_{22}H_{28}MoO_4Si$ (480.49): C, 55.00; H, 5.87. Found: C, 54.63; H, 5.76. IR (THF, cm^{-1}): 2017 (s), 1931 (s), 1581 (m). ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.15 (s, 9H, $SiMe_3$), 0.54 (s, 3H, Mo–Me), 1.77 (s, 3H, C_5Me_4), 1.78 (s, 3H, C_5Me_4), 1.80 (s, 3H, C_5Me_4), 2.17 (s, 3H, C_5Me_4), 4.51 (t, 2H, C_5H_4), 5.03 (t, 2H, C_5H_4) (t = pseudo-triplet). ^{13}C-NMR (C_6D_6, 50 MHz): δ 19.9 (Mo–Me), 0.8 ($SiMe_3$), 11.3 ($C_5\mathit{Me}_4$), 11.8 ($C_5\mathit{Me}_4$), 13.8 ($C_5\mathit{Me}_4$), 14.2 ($C_5\mathit{Me}_4$), 92.7 (C_5H_4), 95 (b, C_5H_4), 112.0 (C_5H_4), 122.0 ($\mathbf{C}_5Me_4$), 123.9 (C_5Me_4), 137.2 (C_5Me_4), 137.4 (C_5Me_4), 139.0 (C_5Me_4), 147.2 (=C–O), 227.1 (Mo–CO), 240.1 (Mo–CO).

3.2. Synthesis of $Me(CO)_3W[\eta^5\text{-}C_5H_4C(OSiMe_2t\text{-}Bu)\text{-}(C_5Me_4)]$ (**2**)

3b (0.296 g; 0.6 mmol) was added to a suspension of NaH (0.10 g; 4 mmol) in THF. The mixture was stirred until the H_2 evolution ceased, and then filtered. Subsequently, *t*-$BuMe_2SiCl$ (0.90 g; 0.6 mmol) was added to the red solution and the reaction mixture was stirred for 30 min. After evaporation of the solvent, the residue was extracted with *n*-hexane. Removal of the solvent yielded **2** (0.327 g; 89%) as red crystals. F.p.: 163–164°C. Anal. Calc. for $C_{25}H_{34}O_4SiW$ (610.48): C, 49.19; H, 5.61. Found: C, 49.25; H, 5.78. IR (THF, cm^{-1}): 2014 (s), 1921 (s), 1574 (w). ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.02 (bs, 3H, Si–Me), 0.15 (bs, 3H, Si–Me), 0.59 (s, 3H, W–Me), 1.03 (s, 9H, tert-Butyl), 1.76 (s, 3H, C_5Me_4), 1.79 (s, 3H, C_5Me_4), 1.83 (s, 3H, C_5Me_4), 2.19 (s, 3H, C_5Me_4), 4.39 (bs, 1 H, C_5H_4), 4.58 (bs, 1 H, C_5H_4), 4.95 (bs, 1 H, C_5H_4), 5.22 (bs, 1 H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz): δ −31.5 (W–Me), −3.8 (Si–Me), −3.5 (Si–Me), 11.3 ($C_5\mathit{Me}_4$), 11.9 ($C_5\mathit{Me}_4$), 13.8 ($C_5\mathit{Me}_4$), 14.3 ($C_5\mathit{Me}_4$), 18.7 ($\mathit{C}(Me)_3$), 25.9 ($C(\mathit{Me})_3$), 87.5 (C_5H_4), 90.7 (C_5H_4), 103.2 (C_5H_4), 109.7 (C_5H_4), 121.4 (C_5Me_4), 124.7 (C_5Me_4), 137.7 (C_5Me_4), 138.3 (C_5Me_4), 140.0 (C_5Me_4), 147.9 (=C–O), 229.4 (W–CO).

3.3. Synthesis of $Me(CO)_3Mo[\eta^5\text{-}C_5H_4C(O)(C_5Me_4H)]$ (**3a**)

A solution of **1a** in THF was treated with a 10-fold excess of water. The solvent was evaporated and the resulting yellow–orange crystals were dried in vacuo to afford a quantitative yield of **3a**. F.p.: 85–90°C. Anal. Calc. for $C_{19}H_{20}MoO_4$ (408.31): C, 55.89; H, 4.94. Found: C, 55.92; H, 5.15. IR (THF, cm^{-1}): 2020 (s), 1932 (s), 1618 (m). ^{1}H-NMR (C_6D_6, 360 MHz), isomer **A**: δ 0.63 (s, 3H, Mo–Me); 1.06 (d, $J = 7.6$ Hz, 3H, $C_5\mathit{Me}_4H$), 1.51 (s, 3H, $C_5\mathit{Me}_4H$), 1.58 (s, 3H, $C_5\mathit{Me}_4H$), 1.88 (d, $J = 2.3$ Hz, 3H, $C_5\mathit{Me}_4H$), 3.22 (m, 1H, $C_5Me_4\mathit{H}$), 4.36 (m, 1H, C_5H_4), 4.52 (m, 1H, C_5H_4), 4.94 (m, 1H, C_5H_4), 5.50 (m, 1H, C_5H_4); isomer **B**: δ 0.47 (s, 3H, Mo–Me), 1.58 (s, 6H, $C_5Me_4\mathit{H}$), 1.81 (s, 6H, $C_5Me_4\mathit{H}$), 3.66 (m, 1H, $C_5Me_4\mathit{H}$), 4.31 (m, 2H, C_5H_4), 5.18 (m, 2H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz), isomer **A**: δ −19.1 (Mo–Me), 10.5 ($C_5\mathit{Me}_4H$), 11.9 ($C_5\mathit{Me}_4H$), 13.8 ($C_5\mathit{Me}_4H$), 14.8 ($C_5\mathit{Me}_4H$), 50.4 (C_5Me_4H), 92.3 (C_5H_4), 94.0 (C_5H_4), 94.1(C_5H_4), 96.9 (C_5H_4), 109.7 (C_5H_4), 135.6 (C_5Me_4H), 142.4 (C_5Me_4H), 148.2 (C_5Me_4H), 152.8 (C_5Me_4H), 185.6 (C_5H_4–C(O)–C_5Me_4H), 226.1 (Mo–CO), 226.2 (Mo–CO), 238.8 (Mo–CO); isomer **B**: δ −19.6 (Mo–Me), 11.2 ($C_5\mathit{Me}_4H$), 12.7 (C_5Me_4H), 70.0 (C_5Me_4H), 92.8 (C_5H_4), 96.0 (C_5H_4), 132.5 (C_5Me_4H), 139.7 (C_5Me_4H).

3.4. Synthesis of $Me(CO)_3Mo[(\eta^5(Mo)\text{-}C_5H_4)C(O)\text{-}(\eta^5(Co)\text{-}C_5Me_4)]Co(CO)_2$ (**4a**) and $(CO)_2Co[(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5Me_4)]Co(CO)_2$ (**5**)

3a (0.110 g; 0.27 mmol) and $Co_2(CO)_8$ (0.24 g; 0.7 mmol) were dissolved in a mixture of 30 ml THF and 5 ml 3,3-dimethylbut-1-ene. The course of the reaction was monitored by means of IR spectroscopy. The solution was refluxed until the stretching band of the organic CO bridging group in **3a** at 1618 cm^{-1} was no longer detected. After evaporation of the solvent, the residue was chromatographed on silica. Elution with toluene separated two dark red bands: the first fraction contained **4a**, the second **5**. The solvent was removed under reduced pressure. The resulting red solids were dried in vacuo. 0.058 g (41%) of **4a** and 0.044 g (37%) of **5** were isolated.

4a: F.p.: > 85°C (dec.). Anal. Calc. for $C_{21}H_{19}CoMoO_6$ (522.25): C, 48.30; H, 3.67. Found: C, 48.66; H, 3.96. IR (THF, cm^{-1}): 2024 (s), 2014 (s), 1957 (s), 1933 (s), 1637 (m). ^{1}H-NMR (C_6D_6, 360 MHz): δ 0.73 (s, 3H, Mo–Me), 1.46 (s, 6H, C_5Me_4), 1.67 (s, 6H, C_5Me_4), 4.46 (t, 2H, C_5H_4), 5.72 (t, 2H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz): δ −18.5 (Mo–Me), 10.0 ($C_5\mathit{Me}_4$), 11.5 ($C_5\mathit{Me}_4$), 94.1 (C_5H_4), 96.0 (C_5H_4), 97.2 (C_5Me_4), 98.3 (C_5H_4), 101.5 (C_5Me_4), 108.5 (C_5Me_4), 187.5 (C_5H_4–C(O)–C_5Me_4), 205.3 (Co–CO), 225.7 (Mo–CO), 238.1 (Mo–CO).

5: F.p.: 77–78°C. Anal. Calc. for $C_{21}H_{19}Co_2O_5$ (442.20): C, 51.61; H, 3.65. Found: C, 51.07; H, 3.78. IR (THF, cm^{-1}): 2033 (s), 2012 (s), 1973 (s), 1953 (s), 1633 (m). ^{1}H-NMR (C_6D_6, 360 MHz): δ 1.49 (s, 6H, C_5Me_4), 1.71 (s, 6H, C_5Me_4), 4.50 (t, 2H, C_5H_4), 5.59 (t, 2H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz): δ 10.1 ($C_5\mathit{Me}_4$), 11.5 ($C_5\mathit{Me}_4$), 86.2 (C_5H_4), 87.9 (C_5H_4), 97.0 (C_5Me_4), 99.3 (C_5H_4), 100.5 (C_5Me_4), 102.9 (C_5H_4), 186.9 (C_5H_4–C(O)–C_5H_4), 200–210 (broad, Co–CO).

3.5. Synthesis of [(η^5(W)-C_5H_4)C(O)(η^5(Mo)-C_5Me_4)]-WMo$(CO)_6$ (W–Mo) (**8**)

3b (0.530 g; 1.07 mmol) and $Mo(CO)_3(C_2H_5CN)_3$ (0.454 g; 1.31 mmol) were dissolved in diglyme (10 ml). The mixture was heated to 100°C for 20 min and then refluxed for 1 h. After evaporation of the solvent, the resulting residue was chromatographed on silica with toluene. Complex **8** was eluted as the last, dark red band. After removal of the solvent, **8** was obtained as dark red solid (0.270 g, 38%). F.p.: > 180°C (dec.). Anal. Calc. for $C_{21}H_{16}MoO_7W$ (660.15): C, 38.21; H, 2.44. Found: C, 38.29, H, 2.51. IR (THF, cm^{-1}): 2013 (s), 1962 (s), 1919 (s), 1908 (sh), 1895 (m), 1655 (m). ^{1}H-NMR (C_6D_6, 200 MHz, 20°C): δ 1.42 (s, 6H, C_5Me_4), 1.68 (bs, 6H, C_5Me_4), 4.33 (t, 2H, C_5H_4), 5.20 (t, 2H, C_5H_4). ^{1}H-NMR (toluene-d_8, 360 MHz, −40°C): δ 1.27 (s, 3H, C_5Me_4), 1.29 (s, 3H, C_5Me_4), 1.34 (s, 3H, C_5Me_4), 1.92 (s, 3H, C_5Me_4), 4.00 (m, 1H, C_5H_4), 4.24 (m, 1H, C_5H_4), 4.90 (m, 1H, C_5H_4), 5.19 (m, 1H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz, 20°C): δ 10.7 ($C_5\mathit{Me}_4$), 12.4 ($C_5\mathit{Me}_4$), 88.5 (broad, C_5H_4), 89.5 (C_5H_4), 102.2 (C_5H_4), 102.5 (C_5Me_4), 109.0 (C_5Me_4), 183.4 (C_5H_4–C(O)–C_5Me_4), 211.6 (W–CO), 218.8 (W–CO), 227.3 (Mo–CO), 236.8 (Mo–CO).

3.6. Synthesis of [(η^5-C_5H_4)C(O)(η^5-C_5Me_4)]$W_2(CO)_6$ (W–W) (**9**)

3b (0.460 g; 0.92 mmol) and $W(CO)_3(C_2H_5CN)_3$ (0.580 g; 1.34 mmol) were dissolved in diglyme (10 ml) and refluxed for 2 h. A second crop of $W(CO)_3(C_2H_5CN)_3$ (0.100 g; 0.23 mmol) was added. After refluxing the solution for additional 2 h and work-up of the reaction mixture as described above gave **9** (0.165 g; 23%) as a red solid. F.p.: 195–196°C. Anal. Calc. for $C_{21}H_{16}O_7W_2$ (748.06): C, 33.72; H, 2.16. Found: C, 34.14; H, 2.32. IR (THF, cm^{-1}): 2012 (s), 1960 (s), 1916 (s), 1900 (sh), 1880 (m), 1660 (w). ^{1}H-NMR (C_6D_6, 200 MHz): δ 1.53 (s, 6H, C_5Me_4), 1.75 (broad s, 6H, C_5Me_4), 4.31 (t, 2H, C_5H_4), 5.17 (broad s, 2H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz): δ 10.6 ($C_5\mathit{Me}_4$), 12.4 ($C_5\mathit{Me}_4$), 89.0 (b, C_5H_4), 90.1 (C_5H_4), 100.4 (C_5Me_4), 102 (b, $C_5\mathit{Me}_4$), 102.2 (C_5H_4), 105.2 ($C_5\mathit{Me}_4$), 183.7 (C_5H_4–C(O)–C_5Me_4), 219.1 (W–CO), 223.9 (W–CO).

3.7. Synthesis of [(η^5-C_5H_4)C(O)(η^5-C_5Me_4)]$Mo_2(CO)_6$-(Mo–Mo) (**10**) and [(η^5-C_5H_3Me)C(O)(η^5-C_5Me_4)]-$Mo_2(CO)_6$ (Mo–Mo) (**12**)

(a) **3a** (0.265g, 0.64 mmol) and $Mo(CO)_3(C_2H_5CN)_3$ (0.30 g; 0.87 mmol) were dissolved in THF (20 ml) and stirred at room temperature for 1 h. Subsequently, the solution was refluxed for 1.5 h. After removal of the solvent, the residue was chromatographed on silica with toluene. The last, dark red band was collected and after removal of the solvent, **10** was obtained as a dark red solid (0.101 g, 28%).

(b) **3a** (0.524 g; 1.28 mmol) and $Mo(CO)_6$ (0.340 g; 1.29 mmol) were dissolved in 10 ml *p*-xylene and refluxed for 2 h. Subsequently, the reaction mixture was separated by column chromatography as described above. The last two dark red fractions were collected, the first one contained **12** (0.080 g; 11%), followed by the main product **10** (0.230 g; 31%).

10: F.p.: > 160°C (dec.). Anal. Calc. for $C_{21}H_{16}Mo_2O_7$ (572.24): C, 44.08; H, 2.82. Found: C, 44.40; H, 3.08. IR (THF, cm^{-1}): 2015 (s), 1964 (s), 1922 (s), 1908 (sh), 1889 (m), 1654 (w). ^{1}H-NMR (C_6D_6, 200 MHz): δ 1.44 (s, 6H, C_5Me_4), 1.65 (s, 6H, C_5Me_4), 4.38 (broad s, 2H, C_5H_4), 5.17 (t, 2H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz): δ 10.6 ($C_5\mathit{Me}_4$), 12.4 ($C_5\mathit{Me}_4$), 90.0 (C_5H_4), 91.1 (C_5H_4), 102.6 (C_5Me_4), 103.4 (C_5H_4), 104.1 (C_5Me_4), 109.5 (C_5Me_4), 183.1 (C_5H_4–C(O)–C_5Me_4), 223.9 (Mo–CO), 228.0 (Mo–CO), 232.1 (Mo–CO), 236.8 (Mo–CO).

12: IR (THF, cm^{-1}): 2013 (s), 1962 (s), 1920 (s), 1906 (sh), 1887 (m), 1656 (w). ^{1}H-NMR (C_6D_6, 200 MHz): δ 1.40 (s, 3H, C_5Me_4), 1.44 (s, 3H, C_5Me_4), 1.47 (s, 3H, C_5Me_4), 1.90 (s, 3H, C_5Me_4), 2.01 (d, $J = 0.3$ Hz, 3H, $C_5H_3\mathit{Me}$,), 4.09 (dd, H, $C_5\mathit{H}_3Me$), 4.71 (m, H, $C_5\mathit{H}_3Me$), 5.28 (dd, H, $C_5\mathit{H}_3Me$). ^{13}C-NMR (C_6D_6, 50 MHz): δ 10.4 ($C_5\mathit{Me}_4$), 11.0 ($C_5\mathit{Me}_4$), 11.5 ($C_5\mathit{Me}_4$), 13.1 ($C_5\mathit{Me}_4$), 14.7 ($C_5H_3\mathit{Me}$), 87.1 (C_5H_3Me), 93.2 (C_5H_3Me), 93.4 (C_5H_3Me), 101.2, (C_5H_3Me) 102.1, (C_5Me_4), 102.3, (C_5Me_4), 104.7, (C_5Me_4), 106.4, (C_5Me_4), 111.3, (C_5Me_4), 186.0 (C_5H_3Me–C(O)–C_5Me_4), 224.2 (Mo–CO), 225.1 (Mo–CO), 227.0 (Mo–CO), 229.6 (Mo–CO), 233.3 (Mo–CO), 236.8 (Mo–CO).

3.8. Synthesis of [(η^5(Mo)-C_5H_4)C(O)(η^5(Fe)-C_5Me_4)]-MoFe$(CO)_5$ (Mo–Fe) (**14**)

Tricarbonyl[bis(cyclooctene)]iron (0.410 g; 1.1 mmol) was added to a solution of **3a** (0.450 g; 1.1 mmol) in THF (50 ml) at −78°C. The stirred solution was allowed to warm up to room temperature within 3 h. After removal of the solvent, the residue was dissolved in *p*-xylene (20 ml) and heated to 120°C for 1.5 h. Subsequently, the solvent was removed and the resulting residue chromatographed on silica with toluene.

The desired complex **14** was eluted as the last, red–brown band. The solvent was evaporated, and **14** (0.174 g; 30%) was isolated as black crystals.

14: F.p. 185°C. Anal. Calc. for $C_{20}H_{16}FeMoO_6$ (504.13): C, 47.65; H, 3.20. Found: C, 47.16; H, 3.59. IR (THF, cm^{-1}): 2011 (s), 1954 (s), 1908 (w), 1888 (s), 1660 (m). ^1H-NMR (C_6D_6, 200 MHz): δ 1.26 (s, 6H, C_5Me_4), 1.54 (s, 6H, C_5Me_4), 4.36 (t, 2H, C_5H_4), 5.14 (t, 2H, C_5H_4). ^{13}C-NMR (C_6D_6, 50 MHz): δ 9.7 ($C_5\mathit{Me}_4$), 10.9 ($C_5\mathit{Me}_4$), 87.9 (C_5H_4), 90.2 (C_5H_4), 91.4 (C_5Me_4), 95.3 (C_5Me_4), 97.1 (C_5H_4), 107.2 (C_5Me_4), 184.9 (C_5H_4–C(O)–C_5Me_4), 224.4 ($J_{C-W} = 49$ Hz, M–CO).

3.9. *X-ray structure analysis of* **2**

Suitable crystals for X-ray structure analysis were obtained by cooling down a *n*-hexane solution of **2** to −20°C. The data were recorded on a Hilger & Watts (Y290) at −120°C, applying monochromatic Mo–K_α rays. The structure was solved by direct methods using SHELXS-86 [18]. Refinement on F^2 was carried out by full matrix least square techniques (SHELXL-93) [19]. An empirical absorption correction was applied using DIFABS [20] from PLATON [21]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined at calculated positions with a fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic thermal parameter of their carrier atoms. Weights were optimized in the final refinement cycles.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 114932 for compound **2**. Copies of this information may be obtained free of charge from: The Director CCDC 12 Union Road Cambridge, CB2 1 EZ UK Fax. (int code = +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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