

New heterodimetallic cyclopentadienyl carbonyl complexes: crystal structure of $(C_5Me_4Et)W(\mu-CO)_3Ru(C_5Me_5)^1$

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Abstract

A series of heterodimetallic complexes of general formula $(C_5R_5)M(\mu-CO)_3RuC_5Me_5$ ($M = Cr, Mo, W$; $R = Me, Et$) has been prepared in good yields by the reaction of $[C_5R_5M(CO)_3]^-$ with $[C_5Me_5Ru(CH_3CN)_3]^+$. $(C_5Me_4Et)W(\mu-CO)_3Ru(C_5Me_5)$ was characterized by a crystal structure determination. The W–Ru bond length of 2.41 Å is consistent with the formulation of a metal–metal triple bond, while the unsymmetrical bonding mode of the three bridging carbonyl groups reflects the inherent non-equivalence of the two different C_5R_5M -units. Using $[CpRu(CH_3CN)_3]^+$ or $[CpRu(CO)_2(CH_3CN)]^+$ as the cationic precursor leads to the formation of dimetallic species $(C_5R_5)M(CO)_3RuC_5H_5$ with both bridging and terminal carbonyl groups.

Keywords: Chromium; Molybdenum; Tungsten; Ruthenium; Carbonyl; Cyclopentadienyl; Metal–metal bond; Crystal structure

1. Introduction

The synthesis and reactivity of complexes with multiple bonds between two metal atoms remains a research subject of topical interest. The most common classes of compounds exhibit metal–metal bonding between the same element, the examples involving two different metals still being relatively rare. This is to some extent due to difficulties of synthesis, since there are few reliable routes to such complexes.

We have in the past devised synthetic routes to heterodimetallic complexes with bridging carbocyclic rings such as C_8H_8 and C_7H_7 , and described their structure and fluxional behaviour [1–4]. In most of these complexes, the different electron count of the two non-equivalent organometallic units was offset by either an unsymmetrical bonding mode of the bridging ligand or by a donor–acceptor bond between the two metal centres involved.

An important class of dimetallic compounds consists of those with general formula $Cp_2M_2(CO)_x$, with $Cp = C_5H_5$. In this series, complexes involving unsaturation and therefore metal–metal multiple bonding most often

concern the pentamethylcyclopentadienyl ligand C_5Me_5 , rather than C_5H_5 . The chemistry of these species was reviewed some time ago [5].

Complexes involving heterodimetallic bonds may exhibit unusual redox properties or interesting non-linear optical properties. Their inherent low symmetry can also be useful in elucidating specific sites of reactivity. Metal–cluster compounds with heteronuclear bonds between transition metals have been used to synthesize heterogeneous catalysts [6].

In continuation of the previously mentioned work on dimetallic complexes, as well as some related studies on triple-deckers and metallabenzenes [7,8], we decided to investigate the reactivity of the $[C_5R_5M(CO)_3]^-$ anion [$M = Cr, Mo, W$] as a useful building block for the formation of heterodimetallic compounds. Theoretical work by Hofmann and Schmidt [9] had shown that the $CpM(CO)_3^-$ fragment can be regarded as isolobal with the $C_5H_5^-$ ligand, and that by virtue of this isolobal relationship these two units could function as interchangeable moieties to potential bonding partners. Fig. 1 shows a qualitative representation of the three highest occupied MOs of $CpM(CO)_3^-$ in the plane of the carbonyl C-atoms and the three occupied MOs of the Cp^- ligand. The shape and nodal properties of the three MOs are very similar, and the five-membered ring and the

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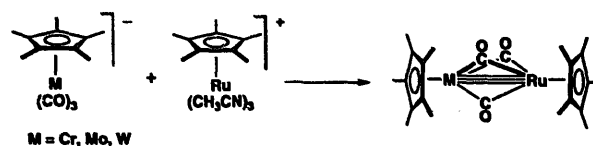
¹ Dedicated to the memory of Professor H. Takaya.

C_3 -triangle of the carbonyl C-atoms have similar dimensions.

Since the orbitals of the $CpM(CO)_3^-$ fragment available for bonding are linear combinations of metal and ligand orbitals, any interaction, and consequently any overlap, with a second metal fragment $M'L_n$ must by necessity involve $M-M'$ interactions [9] which may, but need not, lead to $M-M'$ bonding. Depending on the symmetry and number of MOs of the bonding partner $M'L_n$, the $CpM(CO)_3^-$ fragment may formally contribute two, four or six electrons. Since the $1a_1$ and $1e$ orbitals are almost degenerate, the geometry of interaction with acceptor fragments demanding less than six electrons (e.g. $Rh(PR_3)_2^+$ and $Cu(PR_3)_2^+$) will be quite flexible. This has been confirmed by structural and spectroscopic studies on dimetallic compounds involving these metals [10]. For pure σ -acceptors such as H^+ and CH_3^+ , direct σ -bonding is expected and found. For $M'L$ -fragments with three acceptor MOs (e.g. $Mn(CO)_3^+$, $C_4H_4Co^+$, $C_5H_5Fe^+$ or $C_6H_6Mn^+$), a symmetrical sandwich-type formation may be anticipated. This provides a direct link between multi-decker sandwich complexes and the class of compounds presently under discussion [11]. The validity of this general concept has been confirmed by the synthesis of $C_5H_5Mo(\mu-CO)_3CoC_4Me_4$ [12]. We now wish to report that one C_5R_5 -ligand in Group 8 metallocenes can also isolobally be replaced by the $C_5R_5M(CO)_3^-$ moiety.

2. Results and discussion

The cationic 12e-precursor $[C_5Me_5Ru(CH_3CN)_3]^+$ is easily generated photolytically from the corresponding benzene cation [13], while the anionic moieties $[C_5Me_5M(CO)_3]^-$ were prepared in situ as their Li-salts by the reaction of lithium pentamethylcyclopentadienide with the respective metal hexacarbonyls. Cation and anions were joined in THF at $-40^\circ C$. After stirring the mixture for several hours at room temperature, we were



Scheme 1.

able to isolate a number of dimetallic compounds in generally over 60% yields as dark red to violet crystals (Scheme 1). They are easily recrystallized from methanol or toluene/hexane. The dimetallic compounds appear to be air-stable for at least several days and are soluble in most organic compounds without decomposition.

Similar reactions were performed with the ethyltetramethylcyclopentadienide ligand and its respective Group 6 complexes $Li[C_5Me_4EtM(CO)_3]^-$ (Tables 1–3).

The IR and NMR data of complexes 1–6 were in full agreement with the formulation of these complexes as dimetallic species with terminal cyclopentadienyl ligands and three bridging carbonyl groups, although the very low IR frequencies (1765 – 1780 cm^{-1}) suggested an unusual type of coordination.

Attempts to perform a crystal structure determination of complex 2 failed to give a satisfactory result, possibly due to the fact that the dimetallic molecules were disordered in the unit cell in such a way that the C_5Me_5Ru - and C_5Me_5Mo -units could not be distinguished unequivocally. We therefore performed a structural analysis of complex 6 instead, where the C_5Me_5 ligand at tungsten had been replaced with the C_5Me_4Et equivalent, thereby labelling both metals with two different cyclopentadienyl ligands and making them crystallographically unique.

Dark red crystals of $(C_5Me_4Et)W(\mu-CO)_3Ru(C_5Me_5)$ (6) were grown from a hot saturated methanolic solution. The molecular structure of 6 is shown in Fig. 2, atomic coordinates are listed in Table 4, selected

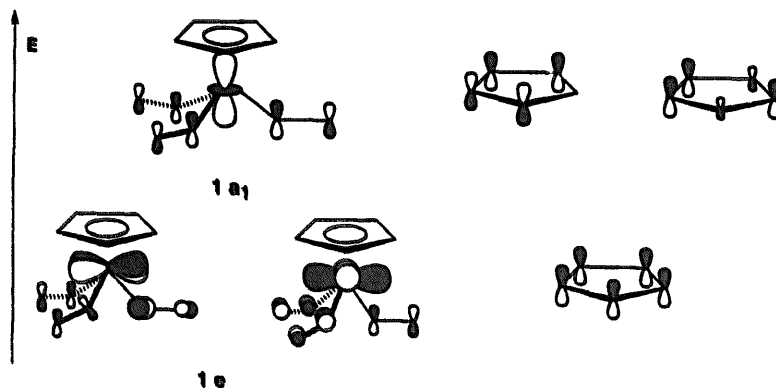


Fig. 1. The HOMOs for $CpM(CO)_3^-$ and $C_5H_5^+$.

Table 1
Yield and carbonyl IR frequencies for complexes 1–6

Compound	Yield (%)	IR (cm ⁻¹ , hexane)
1 C ₅ Me ₅ Cr(CO) ₃ RuC ₅ Me ₅	45	1780
2 C ₅ Me ₅ Mo(CO) ₃ RuC ₅ Me ₅	63	1776
3 C ₅ Me ₅ W(CO) ₃ RuC ₅ Me ₅	65	1766
4 C ₅ Me ₄ EtCr(CO) ₃ RuC ₅ Me ₅	62	1780
5 C ₅ Me ₄ EtMo(CO) ₃ RuC ₅ Me ₅	64	1777
6 C ₅ Me ₄ WCr(CO) ₃ RuC ₅ Me ₅	65	1765

Table 2
¹H-NMR chemical shifts δ (ppm) for 1–6 (C₆D₆)

	1	2	3
C ₅ Me ₅ -M	1.73 (s, 15H)	1.84 (s, 15H)	1.90 (s, 15H)
C ₅ Me ₅ -Ru	1.57 (s, 15H)	1.58 (s, 15H)	1.51 (s, 15H)
	4	5	6
C ₅ Me ₄ Et-M	1.81 (s, 6H) 1.75 (s, 6H) 2.25 (q, 2H) 0.83 (t, 3H)	1.90 (s, 6H) 1.89 (s, 6H) 2.33 (q, 2H) 0.89 (t, 3H)	1.97 (s, 6H) 1.90 (s, 6H) 2.31 (q, 2H) 0.83 (t, 3H)
C ₅ Me ₅ Ru	1.60 (s, 15H)	1.58 (s, 15H)	1.51 (s, 15H)

bond lengths and angles in Table 5, X-ray data collection parameters in Table 6.

In complex 6, the two metal atoms and their three bridging carbonyl groups (inter-ligand angles 85–96.5°) form a slightly distorted trigonal-bipyramidal core, very similar to the isoelectronic complexes (C₅Me₅)₂Re₂(CO)₃ [14], (C₅Me₅)₂Mn₂(CO)₃ [15] as well as (C₅Me₅)₂Fe₂(CO)₃ [16]. The W–Ru bond length of 2.410(1) Å is practically identical to that in the Re–Re complex (Re≡Re = 2.411(1) Å), thereby supporting the assignment of a formal W≡Ru triple bond. However, in molecular orbital schemes, specific metal–metal bonds are not readily assigned [11], as the three bridging groups are heavily implicated in the bonding and therefore make a simple assignment of metal–metal bonding orbitals unrealistic. If four extra electrons were to be placed into this 30-electron compound, they would have to be placed in an e^{*} level that is antibonding with respect to metal–metal bonding. The fact that these four

Table 4
Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (Å² × 10³) and 6

Atom	x	y	z	U _{eq} ^a
W(1)	1198(1)	750(1)	2396(1)	35(1)
Ru(1)	-906(1)	1014(1)	2671(1)	31(1)
C(1)	-157(12)	-181(8)	2360(9)	45(3)
O(1)	-575(10)	-846(5)	2259(8)	60(3)
C(2)	1142(10)	1188(7)	3691(7)	35(3)
O(2)	1623(9)	1432(6)	4492(6)	56(3)
C(3)	-184(12)	1523(8)	1540(9)	49(3)
O(3)	-611(11)	2005(8)	890(8)	80(4)
C(4)	-2043(10)	1899(6)	3269(8)	36(3)
C(5)	-2811(10)	1758(7)	2266(8)	36(3)
C(6)	-3170(11)	905(7)	2155(8)	40(3)
C(7)	-2610(11)	517(7)	3091(9)	41(3)
C(8)	-1923(11)	1117(7)	3783(8)	36(3)
C(9)	-1524(13)	2709(7)	3749(10)	50(4)
C(10)	-3202(12)	2404(8)	1485(9)	48(3)
C(11)	-4017(12)	483(8)	1216(10)	51(4)
C(12)	-2841(14)	375(7)	3281(11)	52(4)
C(13)	-1262(13)	1018(9)	4867(8)	51(4)
C(14)	2551(11)	-178(8)	1896(9)	43(3)
C(15)	3300(10)	57(8)	2890(9)	41(3)
C(16)	3560(10)	921(8)	2887(9)	44(3)
C(17)	2969(11)	1236(6)	1911(9)	38(3)
C(18)	2364(10)	530(7)	1287(8)	39(3)
C(19)	2170(13)	-1044(7)	1569(11)	50(4)
C(20)	3343(17)	-1502(9)	1441(15)	79(4)
C(21)	3745(14)	-517(10)	3770(10)	63(4)
C(22)	4386(12)	1430(10)	3767(10)	56(4)
C(23)	3092(14)	2087(8)	1555(11)	53(4)
C(24)	1743(12)	571(9)	202(8)	48(3)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

electrons are not there helps to account for the short metal–metal distance [5]. It is significant that the Cp–W–Ru–Cp axis is linear and the two cyclopentadienyl ligands are parallel to each other, within experimental error. The overall structure therefore resembles that of a triple-decker sandwich, the middle deck being formed by the three carbons of the bridging carbonyl groups. It is noteworthy that molecules such as 6 have been listed in Hoffmann and coworkers classical paper [11] on triple-decker sandwiches as “missing molecules”. It

Table 3
¹³C-NMR chemical shifts δ (ppm) for complexes 1–6 (C₆D₆)

	1	2	3
CO	268.4	259.7	258.7
C ₅ Me ₅ -M	100.5, 9.3	104.9, 9.8	103.9, 9.8
C ₅ Me ₅ -Ru	97.5, 8.9	95.4, 8.8	94.8, 9.1
	4	5	6
CO	268.2	259.6	258.7
C ₅ Me ₄ Et-M	106.0, 100.7, 97.5 18.4, 14.8 9.3, 9.1	110.6, 105.1, 104.6 18.4, 15.3 9.8, 9.6	109.2, 103.8, 103.4 18.5, 15.7 9.8, 9.6
C ₅ Me ₅ Ru	97.5, 8.9	95.4, 8.8	94.8, 9.1

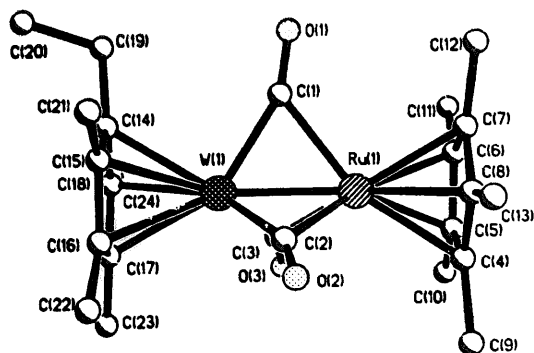


Fig. 2. The molecular structure of $(C_5Me_4Et)W(\mu-CO)_3Ru(C_5Me_5)$ (**6**).

seems, however, equally appropriate, in view of the isolobal analogy shown in Fig. 1, to consider **6** as a structural variation of a sandwich complex, e.g. of ruthenocene. There is therefore a close analogy between **6** and a similar heterodimetallic compound with a C_4Me_4Co -unit prepared by Härter et al. [12].

Complexes **1–6** cannot be directly compared with the symmetrical molecules $(C_5Me_5)_2M_2(CO)_3$ ($M = Mn, Re, Fe$) mentioned above, as they have an inherent asymmetry based on the different electron count in the units C_5R_5M ($M = Cr, Mo, W$) and C_5R_5Ru . The

Table 6
Crystal data for **6**, collection, solution and refinement

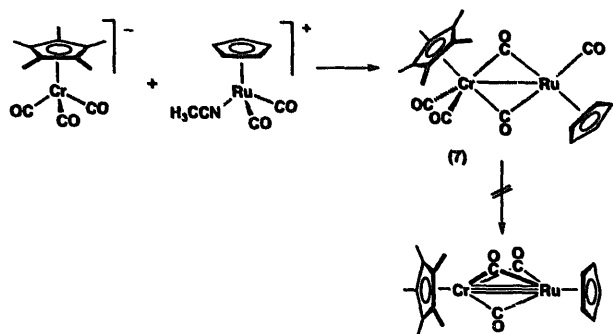
Empirical formula	$C_{24}H_{32}O_3RuW$, 653.4 amu
Colour; habit	dark red cube, from methanol
Crystal size (mm^3)	$0.4 \times 0.3 \times 0.2$
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	$a = 10.478(3)$, $b = 16.217(3)$, $c = 14.549(4)$ Å $\beta = 110.09(2)^\circ$
Volume	$2321.8(10)$ Å ³ , $Z = 4$
Density (calc.)	1.869 Mg m ⁻³
Absorption coefficient	5.718 mm ⁻¹
$F(000)$	1272
Index range	$-7 \leq h \leq 14$, $-22 \leq k \leq 22$, $-19 \leq l \leq 19$
Reflexes collected	7316
Independent reflexes	6215 ($R_{int} = 1.71\%$)
Observed reflexes	5917 ($F \leq 6.0 \sigma(F)$)
Weighting scheme	unit weights
Solution	direct methods
Refinement method	full-matrix least-squares
Hydrogen atoms	riding model, fixed isotropic U
Final R indices (obs. data)	$R = 7.86\%$, $wR = 7.82\%$
Largest difference peak	$6.82 e \text{ \AA}^{-3}$
Largest difference hole	$-3.78 e \text{ \AA}^{-3}$

triangular faces spanned by the $M-CO$ vector pairs (i.e. $CO-M-CO$) are all irregular and mutually dissimilar. The structure of the $M-M$ core reflects some polar character of the complex, in that the $C_5R_5M(CO)_3$ ($M = Cr, Mo, W$) fragment functions as a six-electron donor and the C_5Me_5Ru fragment as an electron acceptor. This is signified by the fact that the $Ru-CO$ bonds in **6**, with distances of 2.196(13), 2.168(9) and 2.195(15) Å, are generally longer than the corresponding $W-CO$ bonds, 2.060(13), 2.033(11) and 1.995(12) Å. Such differences are well in accord with trends observed for analogous complexes [12]. There are also marked differences in the angles $W-C-O$ and $Ru-C-O$, of 156.6, 156.3 and 154.7° for the former and 134.8, 135.3 and 135.5° for the latter, indicative of the qualitatively different nature of the two $M-CO$ interactions. The CO -groups could also be labelled 'semi-bridging' [5], although this expression is somewhat vague and has been used for a variety of bonding situations.

Efforts to extend the scope of this reaction to complexes with non-substituted cyclopentadienyl rings either failed or led to different products. We were unable to isolate similar compounds on reaction of $[C_5Me_5Ru]^+$ fragments with the corresponding $[C_5H_5M(CO)_3]^-$ anions. The only products isolable in very low yields were the known dimetallic species $[Cp_2M_2(CO)_6]$ ($M = Cr, Mo, W$). Similarly, reaction of the anion $[C_5Me_4EtMo(CO)_3]^-$ with the $[C_5H_5Ru]^+$ fragment gave rise to $(C_5Me_4Et)_2Mo_2(CO)_4$ (characterized by a crystal structure determination [14]) as well as a dimetallic species of formula $C_5Me_4EtMo(CO)_5RuC_5H_5$. The two dimetallic complexes could be separated by column

Table 5
Bond lengths (Å) and angles (deg) for **6**

W(1)–Ru(1)	2.410(1)	C(4)–C(8)	1.456(15)
W(1)–C(1)	2.060(13)	C(4)–C(9)	1.499(15)
W(1)–C(2)	2.033(11)	C(5)–C(6)	1.427(16)
W(1)–C(14)	2.348(13)	C(6)–C(7)	1.430(16)
W(1)–C(15)	2.355(11)	C(6)–C(11)	1.514(16)
W(1)–C(16)	2.345(10)	C(7)–C(8)	1.407(15)
W(1)–C(17)	2.338(13)	C(7)–C(12)	1.508(17)
W(1)–C(18)	2.363(13)	C(8)–C(13)	1.497(15)
Ru(1)–C(1)	2.196(13)	C(14)–C(15)	1.439(16)
Ru(1)–C(2)	2.168(9)	C(14)–C(18)	1.423(17)
Ru(1)–C(3)	2.195(15)	C(14)–C(19)	1.493(17)
Ru(1)–C(4)	2.224(12)	C(15)–C(16)	1.429(18)
Ru(1)–C(5)	2.231(10)	C(15)–C(21)	1.521(19)
Ru(1)–C(6)	2.235(11)	C(16)–C(17)	1.434(16)
Ru(1)–C(7)	2.227(13)	C(16)–C(22)	1.520(17)
Ru(1)–C(8)	2.228(13)	C(17)–C(18)	1.463(15)
C(1)–O(1)	1.154(15)	C(17)–C(23)	1.494(17)
C(2)–O(2)	1.169(13)	C(18)–C(24)	1.488(15)
C(3)–O(3)	1.189(17)	C(19)–C(20)	1.502(24)
C(4)–C(5)	1.422(14)		
Ru(1)–W(1)–C(1)	58.2(4)	W(1)–Ru(1)–C(2)	52.4(3)
Ru(1)–W(1)–C(2)	57.7(3)	W(1)–Ru(1)–C(3)	51.1(3)
Ru(1)–W(1)–C(3)	58.9(4)	W(1)–C(1)–Ru(1)	68.9(4)
C(1)–W(1)–C(2)	92.4(5)	W(1)–C(2)–Ru(1)	69.9(3)
C(1)–W(1)–C(3)	95.7(5)	W(1)–C(3)–Ru(1)	70.0(4)
C(2)–W(1)–C(3)	96.5(5)	W(1)–C(1)–O(1)	156.3(12)
C(1)–Ru(1)–C(2)	85.2(4)	W(1)–C(2)–O(2)	154.6(10)
C(1)–Ru(1)–C(3)	86.4(5)	W(1)–C(3)–O(3)	154.7(12)
C(2)–Ru(1)–C(3)	87.1(4)	Ru(1)–C(1)–O(1)	134.8(11)
W(1)–Ru(1)–C(1)	52.9(3)	Ru(1)–C(2)–O(2)	135.5(10)
		Ru(1)–C(3)–O(3)	135.3(11)



Scheme 2.

chromatography, but were obtained only in very low yields, not surprisingly as their formation requires redox reactions between the two metals as well as extensive carbonyl scrambling.

It was possible to prepare such pentacarbonyl dimers by a more rational route, namely the reaction between $[\text{C}_5\text{Me}_4\text{EtMo}(\text{CO})_3]^-$ or $[\text{C}_5\text{Me}_5\text{Cr}(\text{CO})_3]^-$ with $[\text{CpRu}(\text{CO})_2(\text{CH}_3\text{CN})]^+$, where the starting materials already contain the requisite number of carbonyl groups and the formation of a dimetallic complex could therefore be formulated in a stoichiometric manner. This did indeed lead to a considerable increase in yield and the dimetallic complexes $\text{C}_5\text{Me}_5\text{Cr}(\text{CO})_3\text{RuC}_5\text{H}_5$ (**7**) and $\text{C}_5\text{Me}_4\text{EtMo}(\text{CO})_3\text{RuC}_5\text{H}_5$ (**8**) could be isolated as red crystalline material. Their structure, according to spectroscopic data, was similar to previously prepared compounds [12], in that the carbonyl groups were both terminal and bridging (Scheme 2).

The resonances for the bridging carbonyls in the IR spectra appeared in the expected range, almost 100 cm^{-1} higher than those for complexes 1–6. We were unable to convert complexes **7** and **8** into unsaturated complexes similar to **1** and **5** by thermal or photochemical loss of two carbon monoxide ligands. This is somewhat surprising as, in analogous complexes with the $\text{C}_4\text{Me}_4\text{Co}$ -moiety, two carbonyl groups were reversibly abstractable [12]. It is, however, an illustration of the fact that the differing steric and electronic requirements of the C_5H_5 - and C_5Me_5 -ligands can have quite dramatic effects on the reactivity of the metal atom to which they are bound. The presence of two peralkylated ring ligands seems to be almost a prerequisite for the existence of dimetallic species such as 1–6.

1–6 were also inert to carbon monoxide. Work currently in progress will show whether 1–6 will react with other Lewis-bases under substitution of ligands or opening of the bridge structure.

3. Experimental

All experiments were performed under an atmosphere of purified nitrogen in solvents purified and dried by standard methods, using Schlenk-type glass-

ware. $[\text{C}_5\text{H}_5\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ and $[\text{C}_5\text{Me}_5\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ were prepared by the method of Mann and coworkers [13,18], $[\text{C}_5\text{H}_5\text{Ru}(\text{CH}_3\text{CN})-(\text{CO})_2]\text{BF}_4$ by the procedure of Crocker et al. [19]. NMR spectra were recorded on a Varian Gemini 200, IR spectra on a Bio-Rad FTS 45, and mass spectra on a Finnigan MAT 8230 spectrometer. Elemental analyses were performed by the organic laboratory of the University of Zurich. The X-ray diffraction structural analysis was performed on a Siemens R3m/V diffractometer with Mo K α radiation ($\lambda = 0.71073\text{ \AA}$). Data were collected at 202 K. Three standard reflexes were measured every 97 reflections. For solution and refinement, the Siemens SHELXTL-PLUS system (MicroVAXII) was used.

3.1. $\text{Li}[\text{C}_5\text{R}_5\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $\text{R} = \text{H}, \text{Me}$) and $\text{Li}[\text{C}_5\text{R}_4\text{R}'\text{M}(\text{CO})_3]$ ($\text{R} = \text{Me}, \text{R}' = \text{Et}$)

A 100 ml flask was charged with 5.6 mmol of $\text{C}_5\text{R}_5\text{H}$ and 50 ml of THF. The solution was cooled to $-78\text{ }^\circ\text{C}$ and an equimolar amount of *n*-butyllithium in hexane was syringed into it. The solution was allowed to warm to room temperature and stirred over night. An equimolar amount of $\text{M}(\text{CO})_6$ was added to the white suspension formed, upon which the colour changed from white to yellow. The solution was refluxed for 12 h for molybdenum, 24 h for chromium and 56 h for tungsten with the help of a Strohmeier condenser. The dark brownish-red solution was used directly without further purification.

3.2. General procedure for complexes 1–6

The solutions of the anionic complexes $\text{Li}[\text{C}_5\text{R}_5\text{M}(\text{CO})_3]$, obtained as described above, were used directly, assuming 100% conversion, and treated at $-40\text{ }^\circ\text{C}$ with an equimolar amount of $[\text{C}_5\text{Me}_5\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$. The cooling bath was removed and the dark red solutions were stirred for 2 h at room temperature. Silica gel (2 g) was added to the reaction mixture and the solvent removed completely in vacuo. The dark red residue was placed directly on a chromatography column (silica gel, Merck Silica 60) and eluted with a mixture of hexane/methylene chloride/chloroform 7:2:2. After eluting an initial yellow band, which was discarded, a dark red or violet zone was collected. Solvent was removed from this fraction and the residue recrystallized from toluene/hexane or methanol. Yield and IR data: Table 1. NMR data: Tables 2 and 3.

$\text{C}_5\text{Me}_5\text{Cr}(\text{CO})_3\text{RuC}_5\text{Me}_5$ (**1**). Anal. Found: C, 54.28; H, 5.87. $\text{C}_{23}\text{H}_{30}\text{O}_3\text{CrRu}$ Calc.: C, 54.43, H, 5.96%.

$\text{C}_5\text{Me}_5\text{Mo}(\text{CO})_3\text{RuC}_5\text{Me}_5$ (**2**). Anal. Found: C, 50.12; H, 5.44. $\text{C}_{23}\text{H}_{30}\text{O}_3\text{MoRu}$ Calc.: C, 50.08; H, 5.48%.

$\text{C}_5\text{Me}_5\text{W}(\text{CO})_3\text{RuC}_5\text{Me}_5$ (**3**). Anal. Found: C, 43.13; H, 4.75. $\text{C}_{23}\text{H}_{30}\text{O}_3\text{RuW}$ Calc.: C, 43.20; H, 4.72%.

$C_5Me_4EtCr(CO)_3RuC_5Me_5$ (4). Anal. Found: C, 55.35; H, 6.24. $C_{24}H_{32}O_3CrRu$ Calc.: C, 55.26; H, 6.18%.

$C_5Me_4EtMo(CO)_3RuC_5Me_5$ (5). Anal. Found: C, 50.88; H, 5.66. $C_{24}H_{32}O_3MoRu$ Calc.: C, 50.97; H, 5.70%.

$C_5Me_4EtW(CO)_3RuC_5Me_5$ (6). Anal. Found: C, 44.19; H, 4.98. $C_{24}H_{32}O_3WRu$ Calc.: C, 44.11; H, 4.93%.

3.3. Synthesis of $C_5Me_5Cr(CO)_5RuC_5H_5$ (7) and $C_5Me_4EtMo(CO)_5RuC_5H_5$ (8)

To a solution of 2 mmol of the respective Li-anion, prepared as described above in 50 ml of THF, was added 0.7 g (2 mmol) of $[(C_5H_5Ru(CO)_2(CH_3CN)]BF_4$ at $-40^\circ C$. After removing the cooling bath, the reaction mixture was stirred for 3 h at room temperature. Silica (2 g) was added to the mixture and the solvent removed in vacuo. The dark powdery mixture was purified by column chromatography (Silica 60, Merck). After eluting a yellow fraction which was discarded (toluene/hexane 1:3), a deep red zone was eluted with toluene/hexane 1:1 and collected. This solution was evaporated under vacuum and the residue recrystallized from methanol to yield 0.57 g (66%) of 7 and 0.72 g (72%) of 8 as dark red crystals.

$C_5Me_5(CO)_2Cr(\mu-CO)_2Ru(CO)C_5H_5$ (7). IR: 2005, 1945, 1923, 1860 cm^{-1} (hexane). 1H -NMR: 4.61(s), 1.74(s) ppm (C_6D_6). ^{13}C -NMR: 232.7, 100.3, 90.0, 10.4 ppm ($-60^\circ C$, CD_2Cl_2). MS (EI): 494 (M^+), 438 (M^+-2CO), 410 (M^+-3CO). Anal. Found: C, 49.51; H, 4.68. $C_{18}H_{20}O_3CrRu$ Calc.: C, 49.42, H, 4.61%.

$C_5Me_4Et(CO)_2Mo(\mu-CO)_2Ru(CO)C_5H_5$ (8). IR: 1984, 1945, 1927, 1873 cm^{-1} (hexane). 1H -NMR: 2.37 (q, 2H, $^3J = 7.6$ Hz), 1.93 (s, 6H), 1.89 (s, 6H), 1.81 (s, 5H), 0.96 (t, $^3J = 7.6$ Hz) ppm (C_6D_6). ^{13}C -NMR:

239.6, 108.3, 103.8, 102.5, 88.5, 18.2, 14.7, 9.34, 9.14 ppm ($25^\circ C$, C_6D_6). Anal. Found: C, 46.12; H, 4.50. $C_{19}H_{22}O_3MoRu$ Calc.: C, 46.06; H, 4.47%.

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