THE REACTIVITY OF COMPLEXED CARBOCYCLES

XII *. NEUTRAL DIMETALLIC COMPLEXES WITH BRIDGING CYCLOOCTATETRAENE. X-RAY STRUCTURE OF μ-[1—4:5—8η-CYCLOOCTATETRAENE]CYCLOPENTADIENYLCOBALT-TRICARBONYLMOLYBDENUM (*Co—Mo*)

A. SALZER *, T. EGOLF,

Anorganisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (Switzerland)

L. LINOWSKY and W. PETTER

Institut für Kristallographie und Petrographie der ETHZ, Sonneggstrasse 5, CH-8092 Zürich (Switzerland)

(Received June 15th, 1981)

Summary

The reaction of $CpCoC_8H_8$ with $(diglyme)Mo(CO)_3$, $(CH_3CN)_3Cr(CO)_3$ and $(DMF)_3W(CO)_3$ yields dimetallic complexes $CpCoC_8H_8M(CO)_3$ which contain bridging fluctional cyclooctatetraene. The electron deficiency of the $Mo(CO)_3$ groups relative to CpCo is believed to be balanced by a π-donor metal—metal bond. This is indicated by an unusually low absorption band in the IR spectrum, and by the X-ray structure of the Co—Mo dimer, which shows a shortened Mo—CO bond *trans* to the metal—metal bond. A further product is the nonfluctional dimer $CpCoC_8H_8Mo(CO)_4$, in which cyclooctatetraene retains a rigid "tub" conformation. Reaction of $C_8H_8Fe(CO)_3$ with $(diglyme)Mo(CO)_3$ also yields a dimeric product $(CO)_3FeC_8H_8Mo(CO)_3$ with a fluctional bridge ligand.

Introduction

A large number of dimeric compounds containing two metal centers are known [2]. The most common class involves metal—metal bonding between the same element, and there are few complexes with two different metal centers. This is largely due to difficulties of synthesis, since reliable routes to such com-

---

* For part XI see ref. 1.

pounds are rare. The most common methods produce mixtures of products or reduced yields due to competitive redox reactions between the two metals involved.

Our approach was based on the reaction of low-valent olefin complexes containing uncoordinated double bonds with unsaturated zero-valent organometallic groups. As starting compounds we chose the cyclooctatetraene complexes $CpCoC_8H_8$ [Cp = C_5H_5] and $C_8H_8Fe(CO)_3$, both having two uncoordinated double bonds. The cobalt complex exists in two forms in a dynamic equilibrium [3]. These 18 + 4e precursors, when treated with unsaturated 12e moieties like $M(CO)_3$ [M = Cr, Mo, W], should yield 34e dimers having metal—metal bonds and bridging ligands.

A further possibility was the formation of triple-decker species, since such structures with a central planar cyclooctatetraene ring have recently been proposed for $[(C_8H_8)_3Ti]^{2-}$ [4] and $[(C_8H_8)_3Co_2]^{2+}$ [5]. Our own synthesis of the first 34e triple-decker sandwich $[(C_5H_5)_3Ni_2]^+$ utilised in fact the same approach, namely reaction of the 20e compound $Ni(Cp)_2$ with the unsaturated fragment $[CpNi]^+$ [6].

Results and discussion

Treatment of $CpCoC_8H_8$ with (diglyme)$Mo(CO)_3$ in THF results in a slow darkening of the mixture within two hours. After work-up, two products were isolated in good yields, a dark red, almost black complex I, soluble in toluene, and a light red, hexane-soluble complex II. Elemental analyses indicated a composition $C_{17}H_{13}CoMoO_4$ for II, suggesting a complex $C_5H_5CoC_8H_8Mo(CO)_4$. The IR spectrum of II supported this assumption, since it showed four strong absorptions in the carbonyl region typical of a $Mo(CO)_4$ moiety.

The ^{13}C NMR revealed three signals in the oleginic region in an approximate ratio of 4 : 5 : 4. This suggested a dimeric structure for II, in which cyclooctatetraene retains its "tub" conformation and acts as a bridging ligand coordinating to both metals with two double bonds each. The 18e rule is satisfied for both metals and there is no interaction between them. Because of the different chemical environments, there is a large difference in chemical shifts between cyclooctatetraene carbons coordinated to Co (66.6 ppm) and those coordinated to Mo (105.1 ppm). The overall structure, which might be called a pseudo triple-decker, is similar to the dimer $CpCoC_8H_8CoCp$ [5].

The dark red compound I, having an analytical composition of $C_{16}H_{13}CoMoO_3$, showed IR absorptions at 1837, 1882 and 1951 cm^{-1}. In the ^{13}C as well as the ^1H NMR only two sharp singlets were obtserved in the olefinic region in the ratio of 5 : 8. These data suggested a complex $CpCoC_8H_8Mo$-$(CO)_3$. Although we considered the IR absorption at 1837 cm^{-1} to be too low for a terminal carbonyl group, no reasonable structure with bridging carbonyls could be suggested. We, therefore, assigned this absorption to a terminal carbonyl group, influenced by a strong electron-donating *trans* effect.

Two alternative structures were consistent with the spectroscopic data, namely
a) a triple-decker complex with a planar cyclooctatetraene ligand sandwiched between both metals.
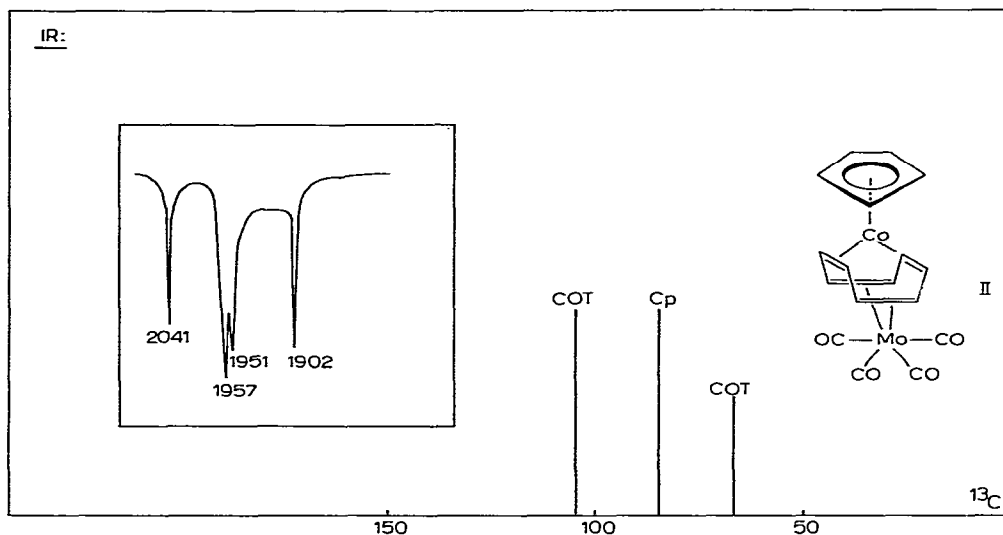
Fig. 1. ^{13}C NMR (noise decoupled, schematic C_6D_6) and IR spectrum (hexane) of II

b) a metal—metal bonded compound with a bridging fluctional cyclooctatetraene
ring, similar to the complexes $C_8H_8Fe_2(CO)_5$ [7] and $C_8H_8Mn_2(CO)_6$ [8].

As no other method allowed distinction between these two isomeric struc-
tures, a single crystal X-ray diffraction study was performed. A perspective
view of the molecule $C_5H_5CoC_8H_8Mo(CO)_3$ is shown in Fig. 2. Final positional
and thermal parameters, bond lengths and bond angles for two crystallographic-
ally different molecules are given in Tables 1, 2 and 3.

Fig. 2. A side view of the $CpCoC_8H_8Mo(CO)_3$ molecule with appropriate numbering scheme.

TABLE 1

FINAL POSITIONAL AND THERMAL ^{a} PARAMETERS FOR $C_5H_5CoC_8H_8Mo(CO)_3$
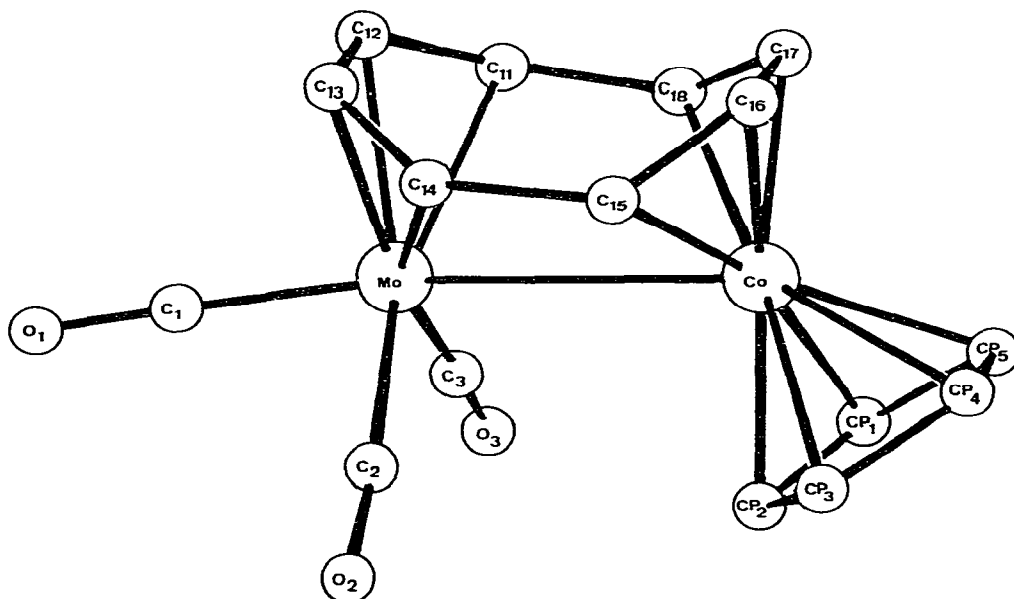
(a) Molecule 1

	x/a	y/b	z/c	U_{iso}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	0.10112(5)	0.60083(4)	0.71735(4)	4.43(2)	4.44(3)	3.78(3)	5.01(4)	0.20(3)	0.25(3)	0.04(3)
Co(1)	-0.082228(8)	0.48883(6)	0.76810(6)	4.32(4)	4.49(6)	2.86(5)	5.96(7)	-0.01(4)	1.23(5)	-0.39(5)
C(1)	0.2241(6)	0.6717(5)	0.6930(5)	5.3(3)	5.5(5)	4.6(6)	5.7(5)	-0.6(4)	1.2(4)	-0.6(4)
O(1)	0.2983(5)	0.7137(4)	0.6799(4)	8.1(3)	6.9(4)	7.7(4)	10.7(5)	-3.2(4)	3.7(4)	-1.0(4)
C(2)	0.0964(6)	0.6789(5)	0.8135(5)	5.5(3)	5.6(5)	3.7(4)	7.0(5)	-1.1(4)	1.4(4)	-0.9(4)
O(2)	0.0964(6)	0.7244(4)	0.8667(4)	8.3(3)	11.5(6)	5.5(4)	9.0(5)	-1.3(4)	3.3(4)	-3.0(3)
C(3)	0.2267(7)	0.4665(5)	0.7826(5)	6.0(4)	6.9(6)	4.4(5)	5.7(5)	0.1(4)	-1.6(4)	-0.9(4)
O(3)	0.3025(6)	0.4965(4)	0.8184(4)	9.6(3)	10.6(5)	7.1(4)	11.9(6)	2.5(4)	-5.4(5)	-1.0(4)
C(11)	0.0634(6)	0.4836(5)	0.6222(4)	4.9(3)	4.4(5)	6.0(5)	4.1(4)	0.1(4)	-0.5(4)	1.2(4)
C(12)	0.0557(6)	0.5611(5)	0.5784(4)	5.5(3)	5.5(5)	6.8(5)	3.7(4)	-0.8(4)	0.0(4)	-0.4(4)
C(13)	-0.0084(7)	0.6362(5)	0.5905(5)	5.9(3)	5.5(5)	6.3(5)	4.8(5)	-0.8(4)	-1.0(4)	1.8(4)
C(14)	-0.0777(7)	0.6519(5)	0.6496(5)	5.3(3)	4.5(5)	4.4(5)	6.7(5)	0.6(4)	-0.4(4)	1.4(4)
C(15)	-0.1481(6)	0.5952(5)	0.6919(5)	5.6(3)	3.8(4)	5.2(5)	8.1(6)	1.1(4)	0.0(4)	0.9(4)
C(16)	-0.1996(6)	0.5145(5)	0.6681(5)	6.2(4)	3.3(4)	6.2(6)	8.8(6)	-0.5(4)	-0.2(4)	1.1(5)
C(17)	-0.1378(6)	0.4413(5)	0.6650(5)	5.5(3)	4.4(5)	5.0(5)	7.4(6)	1.5(4)	-0.5(4)	0.5(4)
C(18)	-0.0179(6)	0.4377(4)	0.6642(4)	4.4(3)	5.4(5)	3.5(4)	5.1(5)	0.2(4)	-0.4(4)	1.3(3)
CP(1)	-0.001(1)	0.4138(9)	0.8643(6)	8.9(5)	13.0(1)	10.5(9)	4.8(6)	-5.4(8)	3.3(6)	-3.9(6)
CP(2)	0.006(1)	0.501(1)	0.3890(6)	8.9(5)	17.1(1)	11.1(1)	3.9(6)	6.0(1)	0.4(7)	-2.6(6)
CP(3)	-0.103(2)	0.5299(9)	0.8847(8)	10.6(6)	26.0(2)	10.0(1)	6.1(8)	6.0(1)	9.0(1)	2.1(7)
CP(4)	-0.178(1)	0.465(1)	0.8603(8)	11.2(6)	9.0(1)	22.0(2)	11.0(1)	1.0(1)	5.9(8)	7.0(1)
CP(5)	-0.117(2)	0.3919(7)	0.8477(6)	9.6(5)	16.0(1)	7.2(8)	7.4(7)	4.4(9)	1.7(8)	-2.8(6)

(b) Molecule 2

(b) Molecule 2

	x/a	y/b	z/c	U_{iso}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(2)	0.36593(5)	0.20675(4)	0.13231(4)	4.44(2)	4.46(3)	4.23(3)	4.66(3)	0.31(3)	0.70(3)	−0.47(3)
Co(2)	0.50740(9)	0.25878(6)	0.00507(6)	4.10(4)	4.90(6)	4.32(6)	3.30(5)	0.58(5)	0.65(4)	0.04(4)
C(1)	0.2650(6)	0.1908(4)	0.2134(4)	4.9(3)	5.4(5)	4.0(4)	5.0(5)	−0.3(4)	1.2(4)	−0.6(4)
O(1)	0.2019(5)	0.1870(3)	0.2605(3)	6.7(3)	6.8(4)	7.0(4)	7.6(4)	−1.4(3)	3.8(3)	−1.0(3)
C(2)	0.2316(7)	0.2613(5)	0.0627(5)	5.5(3)	5.5(5)	4.8(5)	5.7(5)	0.7(4)	−0.2(4)	−1.7(4)
O(2)	0.1537(5)	0.2897(4)	0.0222(4)	9.0(3)	7.7(5)	8.8(5)	10.7(5)	3.5(4)	−3.8(4)	−2.8(4)
C(3)	0.4067(6)	0.3137(5)	0.1973(4)	5.1(3)	5.0(5)	4.9(5)	5.1(5)	0.2(4)	1.3(4)	−0.3(4)
O(3)	0.4286(5)	0.3737(4)	0.2361(3)	7.5(3)	9.2(3)	6.3(4)	8.1(4)	−1.4(3)	0.9(4)	−3.3(3)
C(11)	0.3524(6)	0.0977(4)	0.0285(5)	5.3(3)	6.1(5)	4.1(4)	5.9(5)	0.1(4)	1.0(4)	−2.0(4)
C(12)	0.3863(7)	0.0607(4)	0.1071(5)	5.3(3)	6.3(6)	3.2(4)	7.5(6)	0.2(4)	2.4(5)	−1.2(4)
C(13)	0.4764(7)	0.0867(5)	0.1723(5)	4.9(3)	7.0(6)	5.4(5)	5.5(5)	2.9(5)	2.1(5)	1.2(4)
C(14)	0.5544(6)	0.1535(5)	0.1733(4)	4.5(3)	3.5(4)	6.1(5)	4.5(4)	1.2(4)	0.5(4)	0.8(4)
C(15)	0.6044(6)	0.1942(5)	0.1063(5)	5.3(3)	3.6(4)	6.2(5)	5.7(5)	0.9(4)	−0.2(4)	0.8(4)
C(16)	0.6216(6)	0.1634(5)	0.0255(5)	5.5(3)	5.0(5)	6.7(5)	5.6(5).	1.8(4)	1.8(4)	0.8(4)
C(17)	0.5323(7)	0.1406(5)	−0.0371(4)	5.9(4)	8.0(6)	5.4(5)	4.1(5)	−1.5(5)	2.1(4)	0.6(4)
C(18)	0.4137(7)	0.1429(5)	−0.0168(4)	4.9(3)	6.8(6)	4.9(5)	4.2(4)	0.5(4)	0.4(4)	1.9(4)
CP(1)	0.556(1)	0.3860(6)	0.0316(7)	9.9(5)	15.1(1)	4.6(6)	9.5(8)	−3.7(7)	−2.5(9)	1.75(5)
CP(2)	0.437(1)	0.3809(5)	0.0111(7)	7.3(4)	15.0(1)	3.0(6)	8.7(8)	1.9(6)	5.3(8)	1.7(5)
CP(3)	0.406(1)	0.1524(6)	0.4307(7)	8.6(5)	12.0(1)	6.4(7)	7.7(7)	−3.2(6)	0.4(7)	−2.8(5)
CP(4)	0.505(1)	0.1673(6)	0.3993(6)	8.3(5)	17.0(1)	6.6(7)	6.5(7)	−2.2(8)	5.4(8)	−2.7(5)
CP(5)	0.600(1)	0.1460(7)	0.458(1)	9.2(5)	10.0(1)	6.1(7)	16.0(1)	1.3(7)	5.8(9)	−4.0(8)

^{a} ×10^2 (Å^2).

TABLE 2

DISTANCES IN THE TWO CRYSTALLOGRAPHICALLY DIFFERENT MOLECULES $C_5H_5CoC_8H_8Mo(CO)_3$ (IN Å)

(a) Molecule 1

Mo(1)—Co(1)	2.998(1)	Co(1)—C(15)	2.131(8)
Mo(1)—C(1)	1.925(8)	Co(1)—C(16)	1.997(7)
Mo(1)—C(2)	1.982(8)	Co(1)—C(17)	1.982(7)
Mo(1)—C(3)	1.977(8)	Co(1)—C(18)	2.108(7)
Mo(1)—C(11)	2.371(7)	Co(1)—CP(1)	2.06(1)
Mo(1)—C(12)	2.302(7)	Co(1)—CP(2)	2.07(1)
Mo(1)—C(13)	2.312(7)	Co(1)—CP(3)	2.04(1)
Mo(1)—C(14)	2.369(7)	Co(1)—CP(4)	2.05(1)
C(1)—O(1)	1.14(1)	Co(1)—CP(5)	2.06(1)
C(2)—O(2)	1.14(1)	CP(1)—CP(2)	1.41(2)
C(3)—O(3)	1.14(1)	CP(2)—CP(3)	1.37(3)
C(11)—C(12)	1.39(1)	CP(3)—CP(4)	1.36(3)
C(12)—C(13)	1.43(1)	CP(4)—CP(5)	1.38(3)
C(13)—C(14)	1.38(1)	CP(5)—CP(1)	1.41(2)
C(14)—C(15)	1.46(1)		
C(15)—C(16)	1.42(1)		
C(16)—C(17)	1.39(1)		
C(17)—C(18)	1.41(1)		
C(18)—C(11)	1.45(1)		

(b) Molecule 2

Mo(2)—Co(2)	2.969(1)	Co(2)—C(15)	2.098(7)
Mo(2)—C(1)	1.929(8)	Co(2)—C(16)	2.000(8)
Mo(2)—C(2)	1.988(7)	Co(2)—C(17)	1.995(7)
Mo(2)—C(3)	1.981(7)	Co(2)—C(18)	2.134(7)
Mo(2)—C(11)	2.368(7)	Co(2)—CP(1)	2.08(1)
Mo(2)—C(12)	2.322(7)	Co(2)—CP(2)	2.08(1)
Mo(2)—C(13)	2.310(8)	Co(2)—CP(3)	2.08(1)
Mo(2)—C(14)	2.380(7)	Co(2)—CP(4)	2.05(1)
C(1)—O(1)	1.15(1)	Co(2)—CP(5)	2.06(1)
C(2)—O(2)	1.13(1)	CP(1)—CP(2)	1.41(2)
C(3)—O(3)	1.13(1)	CP(2)—CP(3)	1.39(2)
C(11)—C(12)	1.39(1)	CP(3)—CP(4)	1.38(2)
C(12)—C(13)	1.43(1)	CP(4)—CP(5)	1.39(2)
C(13)—C(14)	1.40(1)	CP(5)—CP(1)	1.46(2)
C(14)—C(15)	1.46(1)		
C(15)—C(16)	1.43(1)		
C(16)—C(17)	1.39(1)		
C(17)—C(18)	1.45(1)		
C(18)—C(11)	1.42(1)		

It is immediately obvious that reaction between $CpCoC_8H_8$ and $Mo(CO)_3$ does not produce a triple-decker species, but a complex with a bridging cyclooctatetraene ligand with *cisoid* arrangement of the CpCo and $Mo(CO)_3$ moieties.

Both metal groups are each within bonding distance of four carbon atoms of cyclooctatetraene, the ring having a flattened boat shape. Some angles within the ring are significantly larger than in free cyclooctatetraene, where all angles are 126.5° [9].

The cobalt—molybdenum bond lengths, 2.969 and 2.998 Å respectively, are rather long even for single bonds. The cause of this lengthening is most likely due to the presence of the bridging C_8H_8 moiety and the resulting balance between metal—metal bond length and optimum overlap between ligand and

TABLE 3

BOND ANGLES (deg.) IN MOLECULES 1 AND 2

(a) Molecule 1

Co(1)—Mo(1)—C(1)	175.9(2)	C(18)—C(11)—C(12)	132.7(7)
Co(1)—Mo(1)—C(2)	91.5(2)	C(11)—C(12)—C(13)	128.0(7)
Co(1)—Mo(1)—C(3)	94.1(2)	C(12)—C(13)—C(14)	129.7(7)
Co(1)—Mo(1)—C(11)	70.5(2)	C(13)—C(14)—C(15)	132.0(7)
Co(1)—Mo(1)—C(12)	93.1(2)	C(14)—C(15)—C(16)	131.3(7)
Co(1)—Mo(1)—C(13)	92.9(2)	C(15)—C(16)—C(17)	123.2(7)
Co(1)—Mo(1)—C(14)	71.5(2)	C(16)—C(17)—C(18)	124.6(7)
C(1)—Mo(1)—C(3)	83.0(3)	C(17)—C(18)—C(11)	131.9(6)
C(1)—Mo(1)—C(11)	112.2(3)		
C(1)—Mo(1)—C(12)	90.7(3)		
C(1)—Mo(1)—C(13)	91.1(3)	Average angles in C_5H_5: 108.0(1)	
C(1)—Mo(1)—C(14)	111.5(3)		
C(2)—Mo(1)—C(1)	85.7(3)	Torsion angles:	
C(2)—Mo(1)—C(3)	91.1(3)		
C(2)—Mo(1)—C(11)	162.1(3)	C(18)—C(11)—C(12)—C(13)	31.2
C(2)—Mo(1)—C(12)	153.6(3)	C(11)—C(12)—C(13)—C(14)	1.2
C(2)—Mo(1)—C(13)	117.6(3)	C(12)—C(13)—C(14)—C(15)	−31.1
C(2)—Mo(1)—C(14)	91.0(3)	C(13)—C(14)—C(15)—C(16)	−24.9
C(3)—Mo(1)—C(11)	89.6(3)	C(14)—C(15)—C(16)—C(17)	61.8
C(3)—Mo(1)—C(12)	114.4(3)	C(15)—C(16)—C(17)—C(18)	0.5
C(3)—Mo(1)—C(13)	150.2(3)	C(16)—C(17)—C(18)—C(11)	−60.6
C(3)—Mo(1)—C(14)	165.5(3)	C(17)—C(18)—C(11)—C(12)	21.4
Mo(1)—Co(1)—C(15)	67.1(2)	CP(1)—CP(2)—CP(3)—CP(4)	1.3
Mo(1)—Co(1)—C(16)	96.2(2)	CP(2)—CP(3)—CP(4)—CP(5)	−0.5
Mo(1)—Co(1)—C(17)	96.4(2)	CP(3)—CP(4)—CP(5)—CP(1)	−0.5
Mo(1)—Co(1)—C(18)	68.1(2)	CP(4)—CP(5)—CP(1)—CP(2)	1.3
Mo(1)—C(1)—O(1)	178.7(6)	CP(5)—CP(1)—CP(2)—CP(3)	−1.6
Mo(1)—C(2)—O(2)	178.4(7)		
Mo(1)—C(3)—O(3)	177.1(8)		

(b) Molecule 2

Co(2)—Mo(2)—C(1)	171.2(2)	C(18)—C(11)—C(12)	132.2(7)
Co(2)—Mo(2)—C(2)	89.2(2)	C(11)—C(12)—C(13)	128.7(7)
Co(2)—Mo(2)—C(3)	91.2(2)	C(12)—C(13)—C(14)	129.6(7)
Co(2)—Mo(2)—C(11)	71.7(2)	C(13)—C(14)—C(15)	131.7(6)
Co(2)—Mo(2)—C(12)	93.3(2)	C(14)—C(15)—C(16)	131.7(7)
Co(2)—Mo(2)—C(13)	93.0(2)	C(15)—C(16)—C(17)	122.9(7)
Co(2)—Mo(2)—C(14)	71.0(2)	C(16)—C(17)—C(18)	123.8(7)
C(1)—Mo(2)—C(3)	82.7(3)	C(17)—C(18)—C(11)	131.8(7)
C(1)—Mo(2)—C(11)	114.2(3)		
C(1)-Mo(2)—C(12)	95.1(3)		
C(1)—Mo(2)—C(13)	95.4(3)	Average angles in C_5H_5: 108.0(2)	
C(1)—Mo(2)—C(14)	117.3(3)		
C(2)—Mo(2)—C(1)	84.7(3)	Torsion angles:	
C(2)—Mo(2)—C(3)	92.8(3)		
C(2)—Mo(2)—C(11)	87.0(3)	C(18)—C(11)—C(12)—C(13)	31.0
C(2)—Mo(2)—C(12)	114.4(3)	C(11)—C(12)—C(13)—C(14)	−1.9
C(2)—Mo(2)—C(13)	150.5(3)	C(12)—C(13)—C(14)—C(15)	−29.5
C(2)—Mo(2)—C(14)	160.0(3)	C(13)—C(14)—C(15)—C(16)	−24.3
C(3)—Mo(2)—C(11)	163.0(3)	C(14)—C(15)—C(16)—C(17)	62.8
C(3)—Mo(2)—C(12)	152.4(3)	C(15)—C(16)—C(17)—C(18)	−1.8
C(3)—Mo(2)—C(13)	116.5(3)	C(16)—C(17)—C(18)—C(11)	−61.9
C(3)—Mo(2)—C(14)	90.2(3)	C(17)—C(18)—C(11)—C(12)	25.5
Mo(2)—Co(2)—C(15)	68.4(2)	CP(1)—CP(2)—CP(3)—CP(4)	−0.9
Mo(2)—Co(2)—C(16)	97.4(2)	CP(2)—CP(3)—CP(4)—CP(5)	1.1
Mo(2)—Co(2)—C(17)	96.8(2)	CP(3)—CP(4)—CP(5)—CP(1)	−0.8
Mo(2)—Co(2)—C(18)	66.8(2)	CP(4)—CP(5)—CP(1)—CP(2)	0.2
Mo(2)—C(1)—O(1)	175.3(6)	CP(5)—CP(1)—CP(2)—CP(3)	0.5
Mo(2)—C(2)—O(2)	177.7(6)		
Mo(2)—C(3)—O(3)	178.0(7)		

metal orbitals. This could also be the reason for the distortion of the C_8H_8 ring, which is clearly separated in two diene units. The organic ligand, although fluctional in solution, is far from planar in the solid state, and so complete delocalization of π-electrons and equal bond distances are not expected and are not found. The longest bond lengths, of 1.45—1.46 Å, are observed for the C—C bonds separating the two diene units bound to Co and Mo.

A related structure has been found for $C_8H_8Mn_2(CO)_6$ [8] with a similarly long Mn—Mn distance of 3.045 Å, while the bridging cyclooctatetraene ring in $C_8H_8Fe_2(CO)_5$ adopts a different orientation in relation to the metal—metal bond [7].

A noteworthy difference is evident in the Mo—CO bond lengths in the molecule. While the two carbonyl groups *trans* to cyclooctatetraene have normal Mo—C bond lengths of 1.97—1.98 Å (the same bond lengths are found, for instance, in $C_8H_8Mo(CO)_3$ [10], a significantly shorter Mo—C bond length is found for the carbonyl group *trans* to cobalt, with values of 1.92 and 1.93 Å, respectively. An explanation of the short M—CO distance of the carbonyl group *trans* to the metal—metal bond (and the unusual IR frequency at 1837 cm^{-1}) can be found by careful "electron counting". In contrast to the two previously mentioned dimers, $C_8H_8Fe_2(CO)_5$ [7] and $C_8H_8Mn_2(CO)_6$ [8], complex I has an inherently unsymmetrical electronic structure. The d^8 Co^I atom achieves a noble gas configuration by the donation of six electrons from the cyclopentadienyl ring and four electrons from the *cis* diene system. Cobalt therefore does not need to form a metal—metal bond. The d^6 Mo^0 atom on the other hand, receiving two electrons from each of the three carbonyl groups and four electrons from the cyclooctatetraene ring, is short of a noble gas configuration by two electrons. Within the structural frame that has emerged from the X-ray analysis this electronic imbalance between the two metal centers can only be compensated by a two-electron donor metal—metal bond, with the CpCo unit acting as a Lewis base and Mo(CO)$_3$ as a Lewis acid.

This donor effect is clearly reflected in the structural and spectroscopic properties of the CO group *trans* to the metal—metal bond. The back-bonding ability of molybdenum is greatly enhanced in this direction, leading to a stronger Mo—C bond (as shown by the X-ray structure) with concurrent weakening of the C—O bond (as evident from the unusually low frequency IR band). The C—O bond is only slightly elongated in one molecule but this effect is, as expected, not large. The interaction between cobalt and molybdenum is most likely a π-donor bond, with the donor orbital of cobalt lying in the same plane as the π^*-orbital of the CO group. This would explain the sharp increase in back-bonding to the CO group.

Further experiments showed that similar complexes can be prepared by reaction of CpCoC$_8$H$_8$ with (CH$_3$CN)$_3$Cr(CO)$_3$ and (DMF)$_3$W(CO)$_3$, no tetracarbonyl complexes like II being formed in either reaction.

CpCoC$_8$H$_8$Cr(CO)$_3$ (III) also forms dark red crystals with almost identical IR absorptions as I. In the ^{13}C NMR spectrum we observed two sharp signals of the fluctional C$_5$H$_5$ and C$_8$H$_8$ ligands and a weak signal at 239 ppm from the Cr(CO)$_3$ group. This signal remained unchanged on cooling to —50°C. Further cooling was not possible due to the low solubility of this complex. This ^{13}C signal indicated rapid exchange of the carbonyl groups, as two signals should be

observed in a non-fluctional configuration. The chemical shift is also unusual, the signal appearing at a lower field than normal $Cr(CO)_3$ groups.

Preliminary results of an X-ray structure analysis of III show that this complex has a completely analogous structure to I, with a Cr—Co bond length of 2.92 Å and a significantly shorter Cr—CO bond *trans* to Co [11].

A low yield of $CpCoC_8H_8W(CO)_3$ (IV) was obtained after prolonged reaction between $CpCoC_8H_8$ and $(DMF)_3W(CO)_3$. This dark red complex showed IR absorptions at 1836, 1889 and 1947 cm^{-1} and two signals at 3.50 and 4.61 ppm in the ^1H NMR in the ratio of 8 : 5.

We were not able to induce a similar reaction between the analogous rhodium complex $CpRhC_8H_8$ and the reagents mentioned above. Prolonged reaction of $C_8H_8Fe(CO)_3$ with (diglyme)$Mo(CO)_3$, however, also produced a dimeric complex in moderate yields having the analytical composition $C_8H_8FeMo(CO)_6$ (V). The IR spectrum revealed three strong and broad absorptions at 1921, 1985 and 2043 cm^{-1}, while ^1H and ^{13}C spectra showed one sharp signal only at 4.4 and 73.8 ppm, respectively, in the olefinic region, indicating again a fluctional C_8H_8 ring. In addition, two ^{13}C signals were observed, at 212.4 and 210.6 ppm, attributed to two different tricarbonyl units. This spectrum remained unchanged on cooling to —70°C. Complex V although apparently similar to I, III and IV in having a metal—metal bond and a fluctional bridging C_8H_8 ring, does not show the unusually low carbonyl absorptions in the infrared. As the $Fe(CO)_3$ and $Mo(CO)_3$ groups again differ by two electrons, a totally symmetrical structure as in $C_8H_8Mn_2(CO)_6$ can be excluded. Electronic equilibrium and noble gas configuration for both metals can be theoretically achieved, in several ways:

a) through bridging carbonyls (this can be excluded from the IR),
b) through a donor metal—metal bond as in I (unlikely from the IR),
c) through an unsymmetrical bonding mode of the C_8H_8 ring.

The last, most likely arrangement, is shown in Fig. 3 as well as the arrangement of compound I for comparison. The cyclooctatetraene ring would coordinate with three carbons to iron and with five to molybdenum, each metal achieving a noble gas configuration through a normal metal—metal bond. A similar arrangement was observed in the analogous complex $(CO)_3FeC_7H_7Rh(CO)_2$, where ion is bound to three carbons of a bridging tropylium ring, while the $Rh(CO)_2$ moiety, having one electron less, coordinates to four carbons [12].

No reaction, however, occurred even under more rigorous conditions between $C_8H_8Fe(CO)_3$ and $(CH_3CN)_3Cr(CO)_3$ or $(DMF)_3W(CO)_3$.
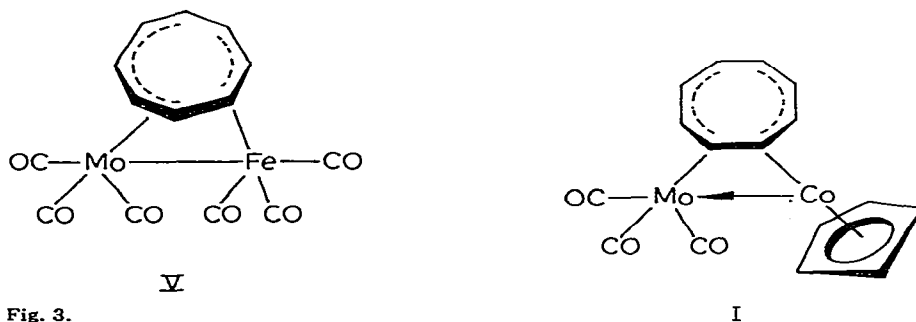

Fig. 3.

V

I

Conclusion

The present study was undertaken to demonstrate the possibility of using electron-rich olefin complexes as starting materials toward the synthesis of dimetallic compounds. No true triple-decker species are formed in these reactions, but in some of the product complexes a remarkable type of π-donor bond between two different metals is observed, through which both metals can achieve an eighteen electron valence shell.

A further series of cationic dimetallic complexes with bridging fluctional cyclooctatetraene, obtained by a similar method, is discussed in the following paper [15].

Experimental

All experiments were carried out under nitrogen, using solvents purified under nitrogen by standard procedures. NMR measurements were performed on a Varian XL-100 or a JEOL C 60 HL spectrometer and IR spectra were recorded on a Beckman IR 12 spectrometer. References to the preparation of the Cr, Mo and W precursors are given in ref. 13.

(a) X-Ray study of I

Crystals were grown from a mixture of CH_2Cl_2, toluene, and hexane. Weissenberg and precession photographs revealed that the crystals belonged to the monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14). Cell parameters are: $a = 11.889(2)$ Å, $b = 15.512(3)$ Å, $c = 16.153(3)$ Å, $\beta = 99.25(2)°$, $d_{obs} = 1.82$ g cm^{-3}, $d_{calc.} = 1.84$ g cm^{-3}, $Z = 8$ with two crystallographically different molecules. Intensity data to $2\theta < 48°$ (Mo-K_α radiation) were collected with a Syntex $P2_1$ automated diffractometer and corrected for absorption ($\mu = 20.1$ cm^{-1}). The 4614 reflexes within $2\theta < 48°$ were reduced in the usual manner, giving 3853 observed reflexes with $I > 3\sigma(I)$. The structure was solved by a combination of Patterson, Fourier and least squares refinement techniques using the XRAY system [14], the final R value being 4.67% based on the observed reflexes. A table of final values of the observed and calculated structure factors has been deposited at the British Lending Library.

(b) Synthesis of I and II

0.50 g (2.2 mmol) of $C_5H_5CoC_8H_8$ in 30 ml THF is treated with 0.75 g (2.4 mmol) of (diglyme)$Mo(CO)_3$ and stirred for two hours. After removal of the solvent under vacuum the residue is extracted with acetone. At $-80°C$ a mixture of I and II crystallizes and is filtered off. Repeated extraction of this mixture with hexane leaves dark crystals of I, while II precipitates from the combined hexane fractions at $-30°C$. Complex I can be recrystallized from toluene/hexane at $-30°C$. Yield of I: 0.44 g (55% based on CpCoC$_8$H$_8$), yield of II: 0.32 g (34%).

(I) Found: C, 47.00; H, 3.14; Co, 14.28; Mo, 23.38. $C_{16}H_{13}CoMoO_3$ calcd.: C, 47.03; H, 3.21; Co, 14.44; Mo, 23.50%. IR (CH_2Cl_2): 1837, 1882, 1951 cm^{-1}. ^{1}H NMR (C_6D_6): 3.55 (s, 8 H), 4.60 (s, 5 H) ppm. ^{13}C NMR (CDCl$_3$, noise decoupled): 68.4, 81.7 ppm.

(II) Found: C, 46.81; H, 3.00; Co, 13.46; Mo, 22.07. $C_{17}H_{13}CoMoO_4$ calcd.: C, 46.81; H, 3.03; Co, 13.51; Mo, 21.99%. IR (hexane): 1902, 1951, 1957, 2041 cm^{-1}. ^{13}C NMR (acetone-d_6), noise decoupled): 66.6, 85.2, 105.1 ppm.

(c) Synthesis of III and IV

To a solution of 0.50 g (2.2 mmol) of $C_5H_5CoC_8H_8$ in 30 ml THF is added 0.70 g (2.4 mmol) of $(CH_3CN)_3Cr(CO)_3$, and the mixture is stirred for 8 hours. After evaporation of the solvent, the residue is taken up in toluene and the solution filtered. After addition of hexane to this solution the complex crystallizes at −30°C, yield 0.33 g (42%). (III) Found: C, 51.36; H, 3.67. $C_{16}H_{13}CrCoO_3$ calcd.: C, 51.65; H 3.5%. IR (CH_2Cl_2): 1836, 1879, 1942 cm^{-1}. ^1H NMR (acetone-d_6): 3.55 (s, 8 H), 4.60 (s, 5 H) ppm. ^{13}C NMR (acetone-d_6): 69.3, 83.9, 239.0 ppm.

The procedure for IV is the same, but with use of 1.15 g (2.4 mmol) $(DMF)_3W(CO)_3$ and with a reaction time of 16 hours. IR (CH_2Cl_2):1836, 1889, 1947 cm^{-1}. ^1H NMR (acetone-d_6): 3.50 (s, 8 H), 4.61 (s, 5 H) ppm.

(d) Synthesis of V

The method is the same as above, using 0.50 g $(CO)_3FeC_8H_8$ (2 mmol) and 0.70 g (diglyme)$Mo(CO)_3$ (2.2 mmol) and a reaction time of 16 hours, yield 0.33 (40%). (V) Found: C, 39.78; H, 1.87; Fe, 13.07; Mo, 22.45. $C_{14}H_8FeMoO_6$ calcd.: C, 39.65; H, 1.90; Fe, 12.99; Mo, 22.62%. IR (CH_2Cl_2): 1921, 1985, 2043 cm^{-1}. ^1H NMR (acetone-d_6): 4.4 (s) ppm. ^{13}C NMR ($CDCl_3$): 73.8, 210.6, 212.4 ppm.

Acknowledgement

References

1 A. Salzer and P. Bigler, Inorg. Chim. Acta, 48 (1981) 199.
2 D.L. Kepert and K. Vrieze, Compounds of the Transition Elements involving metal—metal bonds, Pergamon Press, Oxford, 1973.
3 J. Moraczewski and W.F. Geiger Jr., J. Amer. Chem. Soc., 101 (1979) 3407.
4 S.P. Kolesnikov, J.E. Dobson and P.S. Skell, J. Amer. Chem. Soc., 100 (1978) 999.
5 J. Moraczewski and W.F. Geiger Jr., J. Amer. Chem. Soc., 100 (1978) 7429.
6 H. Werner and A. Salzer, Synth. Inorg. Met.-Org. Chem., 2 (1972) 239.
7 E.B. Feischer, A.L. Stone, R.B.K. Dewar, J.D. Wright, C.E. Keller and R. Pettit, J. Amer. Chem. Soc., 88 (1966) 3158.
8 M.R. Churchill, F.J. Rotella, R.B. King and M. Ackermann, J. Organometal. Chem., 99 (1975) C15.
9 H. Kaufmann, I. Fankuchen and H. Mark, Nature, 182 (1958) 391.
10 J.S. McKechnie and I.C. Paul, J. Amer. Chem. Soc., 88 (1966) 5927.
11 C. Krüger and R. Goddard, personal communication.
12 M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. LiShingMan and J. Takats, J. Amer. Chem. Soc., 98 (1976) 4810.
13 A. Salzer, J. Organometal. Chem., 117 (1976) 245.
14 J.M. Stewart, F.A. Kundell and J.C. Baldwin, XRAY-SYSTEM, Computer Science Center, Univ. of Maryland (1972).
15 A. Salzer, T. Egolf and W. von Philipsborn, J. Organometal. Chem., 221 (1981) 351.