cyclopentamer, the only known stable methyl-substituted cyclooligomer, and requires a ring-expansion step. In reactions of *cyclo*-$(PhAs)_6$ with (arene)$Mo(CO)_3$ compounds under even milder conditions, the formation of {*cyclo*-$(PhAs)_9[Mo(CO)_3]_2$}, containing a nine-membered ring, proceeds in high yield.[7] The presence of six-membered rings in both I and its precursor is likely more coincidental than mechanistically informative.

Acknowledgment. The National Science Foundation provided assistance in the purchase of the diffractometer.

Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (4 pages); a listing of observed and calculated structure factors (24 pages); Ordering information is given on any current masthead page.

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[7] Rheingold, A. L.; Fountain, M. E.; DiMaio, A.-J. *J. Am. Chem. Soc.*, in press.

The Reactivity of Complexed Carbocycles. 16.[1,2] Structural and NMR Spectroscopic Studies of Cyclooctatetraene as a Bridging Ligand: Five Different Bonding Modes in Dimetallic Complexes

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A series of dimetallic complexes have been prepared with cyclooctatetraene as a bridging ligand. An X-ray crystallographic analysis of $[C_5H_5Rh(C_8H_8)RhC_7H_8]BF_4$ (1) (C_7H_8 = norbornadiene), which crystallizes from acetone in the orthorhombic space group *Pnma* with $a = 18.611$ (2) Å, $b = 9.865$ (1) Å, $c = 9.899$ (1) Å, and $Z = 4$, reveals a cisoid η^4:η^4-bonding mode of the bridging ligand, similar to previously prepared compounds. On the other hand, $[(CO)_3Fe(C_8H_8)RhC_7H_8]BF_4$ (2), which crystallizes from acetone in the orthorhombic space group $P2_12_12_1$ with $a = 11.264$ (1) Å, $b = 11.681$ (1) Å, $c = 13.898$ (1) Å, and $Z = 4$, shows a different geometry for the bridging cyclooctatetraene with η^3(Fe)- and η^5(Rh)-coordination to the two metals. This difference is explained by two different modes of obtaining a closed shell for both metal atoms. A further series of cisoid complexes of general structure $[C_5H_5M_1(C_8H_8)M_2C_5R_5]^{n+}$ was prepared with n = 0–2 and R = H or CH_3. All complexes are fluxional on the ^{13}C NMR time scale. Complex 8 with $M_1 = M_2$ = Rh, R = H, and $n = 0$ was shown by X-ray structure analysis to contain a 1,2,6-η:3–5-η-bridging ligand with one uncoordinated double bond. This complex crystallizes from methylene chloride in the orthorhombic space group $P2_12_12_1$ with $a = 7.563$ (1) Å, $b = 11.239$ (2) Å, $c = 16.776$ (2) Å, and $Z = 4$. A general route to transoid dimetallic complexes having a pseudo-triple-decker structure has been developed. $C_5H_5Rh(C_8H_8)RhC_5H_5$ (11), an isomer of 8, crystallizes from chloroform/benzene in the monoclinic space group $P2_1/c$ with $a = 11.420$ (1) Å, $b = 28.410$ (3) Å, $c = 13.360$ (1) Å, $\beta = 92.76$ (1)°, and $Z = 12$. It shows a 1,2,5,6-η–3,4,7,8-η-coordination of tub-shaped C_8H_8 to the two rhodium centers; other complexes of this general type have indenyl or hexamethylbenzene ligands instead of cyclopentadienyl. A fifth type of coordination is found in $[C_5Me_5Rh(C_8H_8)CoC_5Me_5]^{2+}$ as well as $C_5H_5Ru(C_8H_8)RuC_5H_5$. These complexes have a slipped triple-decker structure with 1–5-η:4–8-η-transoid coordination in which two carbons of the bridging ring are simultaneously coordinated to both metal atoms. The ^{13}C NMR data of all complexes are reported, and the ^{103}Rh chemical shifts of selected mono- and dinuclear complexes are discussed.

Introduction

A large number of transition-metal complexes containing two metal centers are known.[4] The most common class involves metal–metal bonding between the same element, and complexes with two different metal centers are still relatively rare. This is largely due to difficulties in synthesis, since there are few reliable routes to such compounds. The most common methods produce mixtures of products or reduced yields due to competitive redox reactions between the two metals involved.

We had previously demonstrated that the low-valent, electron-rich cyclooctatetraene complexes CpM(COT) [Cp = cyclopentadienyl; COT = cyclooctatetraene; M = Co, Rh] and (COT)$Fe(CO)_3$ with two uncoordinated double bonds can be used as versatile starting materials for the synthesis of heterodimetallic complexes.[5a,b] This principle has also been extended to the preparation of dimetallic cycloheptatrienyl complexes.[6] On reaction with unsaturated 12e organometallic groups, these precursors yielded 34e species in high yields, in which both metals achieve a noble gas configuration through a metal–metal bond and a bridging fluxional carbocyclic ligand.

As the two metal moieties in our previously described dimetallic complexes, e.g., CpCo(COT)$Mo(CO)_3$ always differed by two electrons (CpCo, 14e; $Mo(CO)_3$, 12e), a closed-shell configuration for both metal centers could only

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[1] Part 15: Salzer, A.; Täschler, C. *J. Organomet. Chem.* **1985**, *294*, 261.

[2] Transition-Metal NMR Spectroscopy. 7.

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[4] Kepert, D. L.; Vrieze, K. *Compounds of the Transition Elements Involving Metal-Metal Bonds*; Pergamon Press: Oxford, 1973.

[5] (a) Salzer, A.; Egolf, T.; Linowsky, L.; Petter, W.; *J. Organomet. Chem.* **1981**, *221*, 339. (b) Salzer, A.; Egolf, T.; von Philipsborn, W. *J. Organomet. Chem.* **1981**, *221*, 351.

[6] Salzer, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 1145.

0276-7333/86/2305-2413$01.50/0

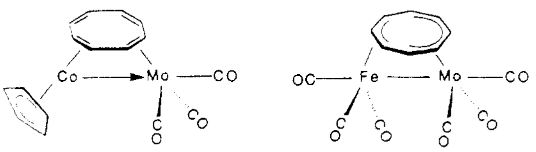
Table I. Crystallographic Data

	$[C_5H_5Rh(C_8H_8)Rh(nor-C_7H_8)]BF_4$ (1)	$[(CO)_3Fe(C_8H_8)Rh(nor-C_7H_8)]BF_4$ (2)	$[C_5H_5Rh(C_8H_8)RhC_5H_5]$ (8)	$[C_5H_5Rh(C_8H_8)RhC_5H_5]$ (11)
fw	554.00	525.88	440.15	440.15
crystallized from	acetone	acetone	methylene chloride	chloroform/benzene
cryst color	ruby colored	red	red	dark orange-red
temp, °C	ca. 20	ca. 20	ca. −140	ca. 20
space group	*Pnma*	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
cell const				
a, Å	18.611 (2)	11.264 (1)	7.563 (1)	11.420 (1)
b, Å	9.865 (1)	11.681 (1)	11.239 (2)	28.410 (3)
c, Å	9.899 (1)	13.898 (1)	16.776 (2)	13.360 (1)
β, deg				92.76 (1)
V, Å^3	1817.4	1828.6	1425.9	4329.5
reflctns centered, no., range (2θ)	25, $40 < 2\theta < 49°$	110, $34 < \lvert 2\theta \rvert < 45$	25, $35 < 2\theta < 40$	52, $35 < \lvert 2\theta \rvert < 39$
Z	4	4	4	12
D(calcd), g·cm^{-3}	2.02	1.91	2.05	2.03
cryst size, mm	0.6 × 0.6 × 0.5	0.3 × 0.4 × 0.4	0.1 × 0.2 × 0.4	0.4 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	18.3	17.4	22.2	22.4
2θ range, deg	≤55	≤70	≤60	≤50
no. of unique reflctns	2206	4471	2280	7634
no. of parameters varied	137	318	181	705
R	0.037	0.056	0.099	0.028
R_w	0.044	0.047	0.064	0.032
rec weighting scheme,[a] $1/w$	$(\sigma^2(F) + 0.0008F^2)/(1 - e^{-5s^2})$	$\sigma^2(F) + 0.0006F^2$	$\sigma^2(F) + 0.0005F^2$	$\sigma^2(F) + 0.0002F^2$

[a] s = (sin θ)/λ.

be achieved: (a) via a donor (metal–metal) bond and (b) by an unsymmetrical bonding mode of the bridging cyclooctatetraene ring. The first type has been realized in complexes like the Co–Mo complex mentioned above, where evidence had been found for a metal–metal donor bond in the spectroscopic as well as structural data.[5a] The corresponding Co–Cr complex has been the subject of an extensive electron density study based on a combination of high-resolution X-ray structure analysis and neutron diffraction.[7]

Bonding of type b was postulated by us to occur in other systems, e.g., $(CO)_3Fe(C_8H_8)Mo(CO)_3$ but had not yet been proved definitely by a structural analysis. It was, therefore, considered worthwhile to fully characterize such a compound with an unsymmetrical bridging ligand. A further aim of our work was to extend the series of examples to other organometallic groups and to further probe the spectroscopic and chemical properties of heterodimetallic systems with fluxional bridging ligands. Depending on the electronic as well as steric requirements of the organometallic moieties involved, we expected to find still further modes of bonding for the highly flexible cyclooctatetraene ligand, including transoid structures, possibly genuine triple-decker species, in extension of our previous work in this field.[8]



Results and Discussion

Crystallographic Study of $[C_5H_5Rh(C_8H_8)RhC_7H_8]BF_4$ (1) and $[(CO)_3Fe(C_8H_8)RhC_7H_8]BF_4$ (2). Two of the previously described dimetallic complexes (1 and 2)[5b] were selected for an X-ray crystallographic study. These are monocationic species prepared by the reaction of CpRh(COT) and $(CO)_3Fe(COT)$ with the unsaturated 12e norbornadiene species $[(C_7H_8)Rh]BF_4$.[9] Apart from the coordination of the bridging ring ligand which we presumed to be different in both compounds, we were interested in the orientation of the norbornadiene ligand in respect to cyclooctatetraene and the metal–metal bond. In solution at room temperature the diolefinic ligand in 1 and 2 exhibits fluxionality on the ^{13}C NMR time scale, while at low temperatures the ligand was shown[5b] to have two sets of nonequivalent coordinated carbon atoms. The COT ^{13}C signals remain in the fast-exchange limit even at −90 °C (50 MHz).

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $[C_5H_5Rh(C_8H_8)RhC_7H_8]BF_4$ (1)

atom	x/a	y/b	z/c	U_{eq}[a]
Rh(1)	1649 (1)	2500	2007 (1)	29 (1)
Rh(2)	225 (1)	2500	3345 (1)	32 (1)
C(1)	2308 (2)	1788 (4)	3734 (4)	44 (1)
C(2)	1700 (2)	926 (4)	3580 (4)	41 (1)
C(3)	992 (2)	955 (4)	4165 (3)	40 (1)
C(4)	673 (2)	1780 (4)	5184 (3)	43 (1)
C(5)	−296 (3)	2500	1363 (6)	91 (4)
C(6)	−533 (3)	3657 (6)	2104 (6)	77 (2)
C(7)	−894 (2)	3204 (5)	3231 (5)	57 (1)
C(8)	1869 (3)	2500	−1621 (6)	58 (2)
C(9)	1195 (3)	2500	−702 (5)	48 (2)
C(10)	1370 (2)	1297 (4)	240 (4)	45 (1)
C(11)	2117 (2)	1323 (4)	410 (4)	46 (1)
C(12)	2395 (3)	2500	−424 (6)	53 (2)
B	−877 (3)	2500	−2070 (6)	42 (2)
F(1)	−480 (2)	3631 (3)	−1709 (4)	78 (1)
F(2)	−946 (2)	2500	−3466 (4)	70 (1)
F(3)	−1525 (3)	2500	−1485 (7)	129 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensor.

Tables I–V list data collection and unit cell parameters, atomic positions, and bond distances for 1 and 2. Other data are available as supplementary material.[10] Figures 1 and 2 depict the molecular structure of the dimetallic cations. It is immediately apparent that the coordination of the bridging C_8H_8 ring is different in both compounds.

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(7) Goddard, R.; Krüger, C. In *Electron Distributions and the Chemical Bond*; Coppens, P.; Hall, M. B., Eds.; Plenum Press: New York, 1982.

(8) Salzer, A.; Werner, H. *Angew. Chem.* **1972**, *84*, 949; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 930.

(9) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

(10) See paragraph at the end of paper regarding supplementary material.

Table III. Bond Lengths (Å) for 1

Rh(1)–Rh(2)	2.962 (1)	Rh(1)–C(1)	2.219 (4)
Rh(1)–C(2)	2.201 (4)	Rh(1)–C(10)	2.177 (4)
Rh(1)–C(11)	2.147 (4)	Rh(2)–C(3)	2.239 (3)
Rh(2)–C(4)	2.124 (3)	Rh(2)–C(5)	2.189 (6)
Rh(2)–C(6)	2.192 (6)	Rh(2)–C(7)	2.199 (4)
C(1)–C(2)	1.423 (5)	C(1)–C(1′)	1.405 (8)
C(2)–C(3)	1.441 (5)	C(3)–C(4)	1.425 (5)
C(4)–C(4′)	1.420 (8)	C(5)–C(6)	1.427 (7)
C(6)–C(7)	1.377 (7)	C(7)–C(7′)	1.388 (10)
C(8)–C(9)	1.550 (8)	C(8)–C(12)	1.537 (8)
C(9)–C(10)	1.544 (5)	C(10)–C(11)	1.401 (5)
C(11)–C(12)	1.516 (5)	C(12)–C(11′)	1.516 (5)
B–F(1)	1.385 (5)	B–F(2)	1.388 (7)
B–F(3)	1.337 (8)		

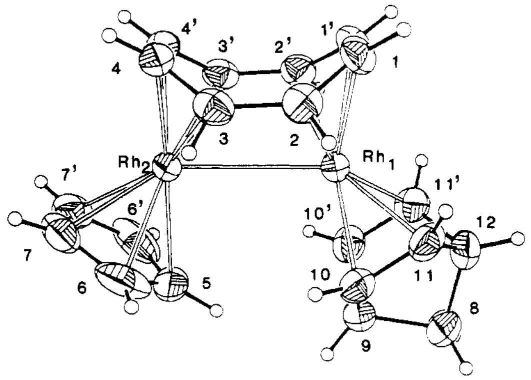

Figure 1. Molecular drawing of the $[C_5H_5Rh(C_8H_8)RhC_7H_8]^+$ cation 1. Thermal ellipsoids are represented at 50% probability, except for hydrogen atoms, which are artificially small.

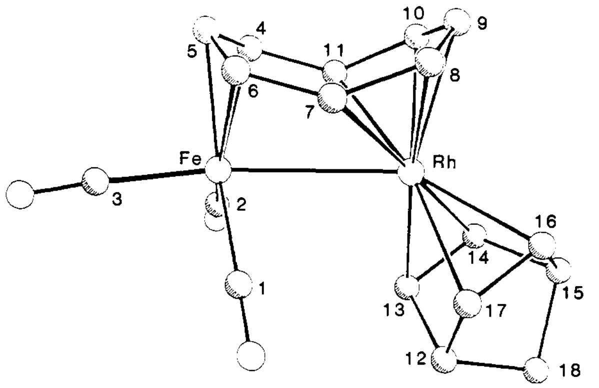

Figure 2. The molecular structure and crystallographic numbering scheme for $[(CO)_3Fe(C_8H_8)RhC_7H_8]BF_4$ (2) (BF_4^- anion not shown).

Table IV. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for $[(CO)_3Fe(C_8H_8)RhC_7H_8]BF_4$ (2)

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Rh	2074 (1)	3486 (1)	2134 (1)	38 (1)
Fe	3085 (1)	1933 (1)	3548 (1)	39 (1)
C(1)	3987 (5)	1017 (4)	4267 (4)	55 (1)
O(1)	4579 (4)	395 (4)	4673 (3)	87 (2)
C(2)	1874 (4)	923 (4)	3483 (4)	56 (1)
O(2)	1102 (4)	320 (3)	3510 (3)	86 (2)
C(3)	3898 (4)	1551 (4)	2472 (3)	48 (1)
O(3)	4446 (3)	1294 (3)	1827 (3)	67 (1)
C(4)	1924 (4)	2932 (4)	4381 (3)	54 (1)
C(5)	3124 (5)	3177 (4)	4590 (4)	58 (1)
C(6)	3955 (4)	3463 (4)	3886 (4)	57 (1)
C(7)	3816 (4)	4071 (4)	3012 (4)	59 (2)
C(8)	3051 (5)	4956 (4)	2708 (4)	67 (2)
C(9)	1838 (5)	5212 (4)	2911 (4)	69 (2)
C(10)	1006 (5)	4443 (4)	3227 (4)	60 (1)
C(11)	1173 (4)	3313 (4)	3593 (3)	51 (1)
C(12)	2249 (5)	2113 (5)	467 (4)	63 (2)
C(13)	1396 (5)	2026 (4)	1317 (4)	53 (1)
C(14)	613 (4)	2952 (5)	1217 (4)	55 (1)
C(15)	991 (5)	3574 (5)	306 (4)	67 (2)
C(16)	2167 (6)	4083 (5)	657 (4)	67 (2)
C(17)	2944 (4)	3166 (5)	770 (4)	60 (1)
C(18)	1427 (6)	2589 (6)	–319 (4)	69 (2)
B	2288 (5)	1613 (5)	6934 (4)	57 (2)
F(1)	3377 (3)	2021 (5)	7134 (5)	135 (2)
F(2)	1598 (4)	2544 (3)	6682 (3)	88 (1)
F(3)	2317 (6)	910 (4)	6170 (3)	141 (2)
F(4)	1751 (4)	1077 (4)	7696 (3)	102 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U** tensor.

Table V. Bond Lengths (Å) for 2

Rh–Fe	2.907 (1)	Rh–C(7)	2.410 (5)
Rh–C(8)	2.190 (5)	Rh–C(9)	2.302 (5)
Rh–C(10)	2.236 (5)	Rh–C(11)	2.277 (5)
Rh–C(13)	2.187 (5)	Rh–C(14)	2.173 (5)
Rh–C(16)	2.170 (5)	Rh–C(17)	2.167 (5)
Fe–C(1)	1.782 (5)	Fe–C(2)	1.806 (5)
Fe–C(3)	1.810 (5)	Fe–C(4)	2.101 (5)
Fe–C(5)	2.052 (5)	Fe–C(6)	2.092 (5)
C(1)–O(1)	1.137 (7)	C(2)–O(2)	1.119 (6)
C(3)–O(3)	1.129 (6)	C(4)–C(5)	1.411 (7)
C(4)–C(11)	1.454 (6)	C(5)–C(6)	1.394 (7)
C(6)–C(7)	1.416 (8)	C(7)–C(8)	1.411 (7)
C(8)–C(9)	1.426 (8)	C(9)–C(10)	1.370 (7)
C(10)–C(11)	1.428 (7)	C(12)–C(13)	1.526 (7)
C(12)–C(17)	1.518 (8)	C(12)–C(18)	1.536 (8)
C(13)–C(14)	1.403 (7)	C(14)–C(15)	1.520 (7)
C(15)–C(16)	1.531 (8)	C(15)–C(18)	1.523 (9)
C(16)–C(17)	1.392 (8)	B–F(1)	1.345 (7)
B–F(2)	1.381 (7)	B–F(3)	1.343 (7)
B–F(4)	1.372 (7)		

In 1, which has a crystallographic mirror plane passing the two rhodium atoms, the ring is symmetrically bound in an η^4–η^4 fashion as we observed in $CpCo(C_8H_8)Cr(CO)_3$[7] and $CpCo(C_8H_8)Mo(CO)_3$.[5a] Both metal groups are each within the 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 cyclooctatraene where all angles are 126.9°.[11]

The rhodium–rhodium bond length with 2.962 Å is rather long even for a single bond. The length of this bond is most likely determined by the bridging C_8H_8 moiety and the resulting balance between metal–metal bond length and optimum overlap between ligand and metal orbitals. This could also be the reason for the particular conformation of the C_8H_8 ring, which is clearly separated in two diene units. The organic ligand, although fluxional in solution, is far from planar in the solid state, and, thus, complete delocalization of π-electrons and equal bond distances are not expected and are not found, although the variations are smaller than in previous cases.[5a] A related structure had also been observed for $C_8H_8Mn_2(CO)_6$[12] with Mn–Mn = 3.045 Å. In contrast to this compound, however, complex 1 has an unsymmetrical electronic structure that is revealed by formal "electron counting". One d^8 Rh(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. [In another notation, only the metal atom in the cationic $(COT)Rh(C_7H_8)$ moiety is assigned the Rh(I) oxidation state, whereas the (COT)RhCp unit is assigned the Rh(0) state,[13] taking account of the very different Rh chemical shifts.] This

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(11) Kaufmann, H.; Fankuchen, I.; Mark, H. *Nature (London)* **1958**, *182*, 391.

(12) Churchill, M. R.; Rotella, F. J.; King, R. B.; Ackermann, M. *J. Organomet. Chem.* **1975**, *99* C15.

(13) Maurer, E.; Rieker, S.; Schollbach, M.; Schwenk, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 26.

rhodium center, therefore, does not need to form a metal–metal bond at all. The other d^8 Rh(I) atom receives four electrons from the norbornadiene and four from cyclooctatetraene, two short of a noble gas shell. Within the structural frame that has emerged from the X-ray analysis, this electronic imbalance between the two metal centers can only be reduced by a two-electron donor metal–metal bond with the CpRh unit acting as a Lewis base and $[C_7H_8Rh]^+$ acting as a Lewis acid. This donor effect could also be responsible for the slight shortening of the Rh–C(11) (2.147 Å) bond, compared to the Rh–C(10) (2.177 Å) bond, as the back-bonding ability of rhodium is enhanced in this direction, although the effect is not as pronounced as in $CpCo(C_8H_8)Mo(CO)_3$.[5a] In this context, the ^{103}Rh chemical shifts of 1 are of interest since they illustrate the different electronic environment of the two metal centers. Whereas the CpRh moiety (−1802.1 ppm, CH_2Cl_2) shows the typical high shielding of CpRh(diene) systems,[13] the cationic nature of the 16e metal center (−82.5 ppm) is reflected in a large deshielding effect, which was also observed in other dinuclear complexes.

In complex **2** we find a different coordination and conformation of the bridging cyclooctatraene ring, basically similar to the geometry found in $C_8H_8Fe_2(CO)_5$,[14] $C_8H_8(VCp)_2$,[15] and $C_8H_8(CrCp)_2$.[16] The bridging C_8H_8 ring consists of two virtually planar moieties that are inclined along the axis C_7–C_{11} at a dihedral angle of 128.9° and 133.8°, respectively. In contrast to the above molecules, **2** shows, however, an unsymmetrical bonding mode of the two metals to the bridging ligand, which is immediately apparent from the bond lengths (Table V). Rh–C distances to five carbons range from 2.19 (Rh–C(8)) to 2.41 Å (Rh–C(7)), a relative large variation for which we can offer no explanation, especially as there is a considerable difference in bond length from rhodium to the two carbons C(7) and C(11), which are directly above the metal–metal bond. This distance in the symmetrical complexes $C_8H_8(VCp)_2$ and $C_8H_8(CrCp)_2$[15,16] is 2.24–2.26 Å. The iron atom is only within bonding distance of three carbons of C_8H_8 with bond lengths ranging from 2.05 to 2.10 Å. As the distance between Fe and C(7) and C(11) is 2.733 and 2.691 Å, respectively, this cannot be regarded as an (even weak) bond. The bridging ring, therefore, adopts a η^3–η^5 coordination, fully in agreement with the "electron count", which gives both metal atoms a closed shell in this arrangement when the metal–metal bond is considered as a "normal" bond to which both metals contribute one electron each. This arrangement is to some extent comparable to the bonding in $(CO)_3Fe(C_7H_7)Rh(CO)_2$,[17] where the bridging cycloheptatrienyl ring adopts a η^3(Fe)–η^4(Rh) coordination to satisfy the 18e rule for both metals. The ^{103}Rh chemical shift of **2** (−67.5 ppm, CH_2Cl_2) is close to the shielding values of the corresponding $Rh(C_7H_8)$ unit of the Rh,Rh complex **1** (−82.5 ppm, CH_2Cl_2) and the cycloheptatrienyl complex $(CO)_3Fe(C_7H_7)Rh(C_7H_8)$ (−86.5 ppm, C_6H_6),[13] thus indicating a similar electronic structure of the $Rh(C_7H_8)$ moieties in the three dimetallic complexes. The Fe–Rh bond in **2** with 2.90 Å is within the expected range for complexes with C_8H_8 bridges. The cycloheptatrienyl complex mentioned above shows a bond length of 2.76 Å,[17] possibly a consequence of the smaller bridging ring. The structures of **1** and **2**, therefore, clearly reveal the two different modes by which the dimetallic complexes described so far with an inherent electronic imbalance achieve closed shells for both metal centers. The difference is possibly due to the lower "metal basicity" of the $Fe(CO)_3$ unit compared to CpCo or CpRh moieties,[18] which stabilize a different bonding ground state in both cases. In solution, however, both types of complexes show the same fluxionality for the bridging ligand, which cannot be slowed down sufficiently to observe the slow-exchange limit spectrum.[5b]

The orientation of the norbornadiene ligand in both molecules merits a further comment. The low-temperature ^{13}C NMR spectra had already revealed that this ligand as well as 1,5-cyclooctadiene in related complexes[5b] show two sets of olefinic resonances. The structure analysis now reveals that in both cases the norbornadiene adopts a "side-on" orientation, making the two double bonds themselves equivalent but not the two carbons of each C=C bond (nor the aliphatic bridgehead carbons). For this mode of coordination five ^{13}C resonances are expected for the norbornadiene ligand in the slow-exchange limit. In fact, two olefinic CH, only one aliphatic CH, and the CH_2 resonance are observed for **1**, **2**, and the Rh,Co analogue.[5b] The equivalence of the bridgehead carbons and hydrogens is also found in the 100-MHz ^{13}C spectrum and the 400-MHz ^1H spectrum of **2**, respectively. The observed ^{13}C NMR pattern would be consistent with an arrangement of the norbornadiene ligand orthogonal to the solid-state orientation. However, we do not yet have an unequivocal proof for this alternative structure in solution since the diastereotropic methylene protons are not split even at 400 MHz.

Cisoid Dimetallic Complexes of General Composition $[C_5H_5M_1(C_8H_8)M_2C_5R_5]^{n+}$ Starting from the same basic principle for the construction of dimetallic complexes with bridging ligands, we searched for further unsaturated 12e organometallic moieties that could be employed as building blocks. Isolable species are most often found in the late transition metals of the 4d and 5d series. Generally, weakly coordinated solvent molecules serve to stabilize these highly unsaturated groups. Systems that we tried to react with our COT precursors were of the general type $[C_6Me_6Ru(solv)_3]^{2+}$,[19] $[C_5Me_5M(solv)_3]^{2+}$ (M = Rh, Ir),[20] and $[CpRu(solv)_3]^+$.[21]

Reactions were only successful starting from CpMCOT, not from $COTFe(CO)_3$, where unidentifiable products were obtained. Likewise no reaction seemed to occur on the treatment of $[C_6Me_6Ru(acetone)_3]^{2+}$ with CpRhCOT so that this unsaturated moiety, whose stability appears to be very low,[19] was not further employed.

Reaction of yellow solutions of $[C_5Me_5Rh(acetone)_3](BF_4)_2$ with CpCoCOT or CpRhCOT immediately gave dark brown crystalline precipitates. They were insoluble in ether but readily dissolved in polar solvents like nitromethane. Elemental analyses confirmed the expected composition $[C_5H_5Co(C_8H_8)RhC_5Me_5](BF_4)_2$ (**3**) and $[C_5H_5Rh(C_8H_8)RhC_5Me_5](BF_4)_2$ (**4**). An analogous reaction between $[C_5Me_5Ir(acetone)_3]^{2+}$ and CpRhCOT produced $[C_5H_5Rh(C_8H_8)IrC_5Me_5](BF_4)_2$ (**5**). All reactions are virtually quantitative.

In the noise-decoupled ^{13}C NMR spectra (Table VI) these complexes show the expected resonances for C_5H_5

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[16] Elschenbroich, C.; Heck, J.; Massa, W.; Schmidt, R.; Angew. Chem. **1983**, *95*, 319; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 330.

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Table VI. ^{13}C NMR Data of Cis Dimetallic Complexes

		$\delta_C{}^b$ ($J_{Rh,C}$)^c			
compd	solv^a	COT		Cp	C_5Me_5
[CpCo(COT)RhC$_5$Me$_5$](BF$_4$)$_2$ (**3**)	N	73.5 (d, 3.2)		87.8	109.2 (d, 7.1), 10.5
[CpRh(COT)RhC$_5$Me$_5$](BF$_4$)$_2$ (**4**)	N	74.6 (t, 3.2)		92.1 (d, 6.2)	108.3 (d, 7.0), 10.8
[CpRh(COT)IrC$_5$Me$_5$](BF$_4$)$_2$ (**5**)	N	69.2 (d, 3.2)		92.2 (d, 6.0)	103.0, 10.2
[CpCo(COT)RuCp]PF$_6$ (**6**)	N	62.0		83.6, 83.0	
[CpRh(COT)RuCp]PF$_6$ (**7**)	N	63.6 (d, 3.2)		87.5 (d, 6.1)	
				81.4	
CpRh(COT)RhCp^d (**8**)	C	139.5		87.4 (d, 3.5)	
		60.9 (d, 7.7)		83.6 (d, 5.0)	
		52.9 (dd, 5.4, 2.7)			
		38.0 (m^e)			
CpRh(COT)RhCp^d (**8**)	C^{f,g}	147.4, 131.1, C-7,8		86.8^e (CpRh(2))	
		68.8,^{e} 51.2,^{e} C-3,4		83.3^e (CpRh(1))	
		55.3,^{e} 49.4,^{e} C-2,5			
		58.7,^{e} 14.2,^{e} C-1,C-6			
[CpRh(COT)RhCp](BF$_4$)$_2$ (**9**)	N	73.0 (t, 3.2)		93.4 (m^e)	
CpRh(COT)RhC$_5$Me$_5$ (**10**)	B	140.0	(A) C-7,8	87.1 (d, 3.4) (A)	94.0 (d, 5.6), 10.4 (A)
		138.6	(B)	83.6 (d, 4.8) (B)	96.9 (d, 4.0), 10.0 (B)
		68.2 (d, 8.0)	(A) C-3,4		
		58.8 (d, 8.6)	(B)		
		54.3 (dd, 5.7, 2.2)	(A) C-2,5		
		56.1 (dd, 5.4, 2.9)	(B)		
		36.1 (d, 17.8)	(A) C-1,6		
		49.3 (d, 17.6)	(B)		
[C$_5$Me$_5$Co(COT)Rh(CO)$_2$] (**19**)	N	73.1 (d, 2.2)			97.2, 11.5

^{a}Key: N, nitromethane-d_3; C, chloroform-d_1; B, benzene-d_6. ^{b}Ppm relative to Si(CH$_3$)$_4$. ^{c}Hertz; d = doublet; dd = double doublet; t = triplet; m = multiplet. ^{d}50.3 MHz. ^{e}J not resolved due to exchange broadening. ^{f}100.6 MHz. ^{g}203 K.

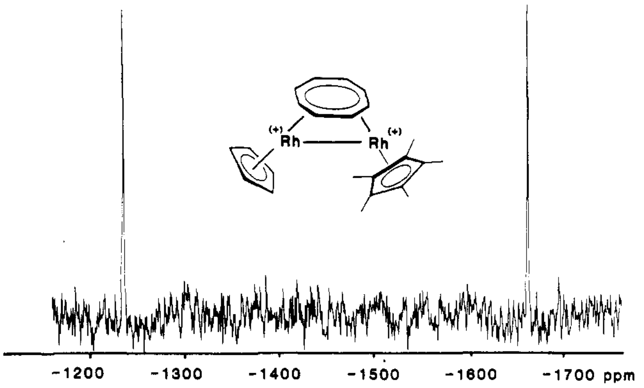

Figure 3. ^{103}Rh NMR spectrum of [(C$_5$H$_5$RhC$_8$H$_8$C$_5$Me$_5$)(BF$_4$)$_2$ (**4**) in CD$_3$NO$_2$ (12.6 MHz).

and C$_5$Me$_5$ groups and one sharp signal for the fluxional bridging C$_8$H$_8$ ring, which in **3** and **5** is a doublet by coupling to one ^{103}Rh nucleus while in **4** this resonance is a triplet by coupling to two ^{103}Rh nuclei. This complex was additionally characterized by ^{103}Rh NMR, which shows two resonances for two distinct Rh nuclei at −1240 and −1665 ppm, respectively (Figure 3; Table VII). The high shielding of the Rh nuclei in **4** and **9** is noteworthy since it is atypical for cationic complexes. Cisoid and transoid mono- and dicationic complexes are known to give a Rh resonance in the range from −85 to +135 ppm (cf. compounds **1**, **2**, **14**, **17**). The δ(Rh) values of **4** are reminiscent of the corresponding data reported[13] for the cycloheptatrienyl complex CpRhC$_7$H$_7$RhCpCl (−1394.8 ppm, CH$_3$OH). If charge density is responsible for the chemical shift differences discussed here, a possible explanation might be that positive charge is delocalized to a large extent into the bridging ligand, thereby satisfying the Hückel rule (C$_7$H$_7{}^+$ and C$_8$H$_8{}^{2+}$, respectively). Alternatively, a change in the (ΔE)$^{-1}$ term of the paramagnetic shielding expression may lead to the unusual shielding in these cationic complexes. These spectra are consistent with a cisoid coordination of the two metal moieties as in the previous examples. The difference in chemical shifts for the two ^{103}Rh nuclei seems too large to be solely due to the different shielding effects or back-bonding properties of the pentamethylcyclopentadienyl vs. the cyclopentadienyl ligand (according to our own observations generally in the order of −100 to −180 ppm for otherwise identical diolefin complexes),[22] much too small on the other hand to assign two different oxidation states to the rhodium atoms (cf. **1**, where a difference of ~1700 ppm was observed for the two Rh nuclei).[13] At present, we cannot determine the nature of the metal–metal bond in these complexes and the mechanism of electron exchange, although they appear to be largely symmetrical.

Table VII. ^{103}Rh Chemical Shifts of Selected Mono- and Dimetallic Complexes

compd	solv^a	ν_0/MHz	T/K	δ(Rh)^b
CpRh(COT)	A	2.8	300	−347.6 ± 12
(Ind)Rh(COT)	M			−17.9 ± 1.7
[(Hmbz)Rh-(COT)]BF$_4$	M			−51.9 ± 1.2
4	N	12.6	296	−1240 ± 1, −1665 ± 1
7	A			−1209 ± 1
8	C			−736 ± 1^c, −1077 ± 1^c
9	N			−1607 ± 1
11	M	2.8	300	−218.1 ± 0.6
12	M			−189.4 ± 0.8
				+86.6 ± 0.7
14	M			−233.4 ± 0.9
				+33.1 ± 0.6
15	M			+114.6 ± 0.6
16	M			−255.8 ± 1.8
17	M			+11.9 ± 0.9

^{a}Key: A, acetone-d_6; C, chloroform-d_1; M, methylene chloride; N, nitromethane-d_3. ^{b}Ppm relative to the arbitrary standard ν_{Rh}(ref)/ν_H(Me$_4$Si) = 0.316.[20] ^{c}δ values in benzene at 2.8 MHz: −733.8 ± 2.1; −1080.5 ± 0.4.

A related series of complexes can be prepared from the precursor [CpRu(CH$_3$CN)$_3$]PF$_6$. This molecule possesses three highly labile acetonitrile ligands that are easily

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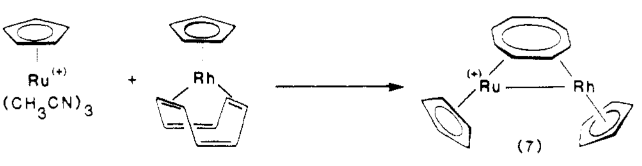
[22] (a) Buchmann, B.; Hafner, A.; von Philipsborn, W., unpublished results. (b) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R.; von Philipsborn, W.; Egolf, T. *J. Organomet. Chem.* **1984**, *272*, 231.

Scheme I



displaced by olefins and Lewis bases.[21] They are also readily substituted by our electron-rich metal complexes leading to the dimetallic complexes [CpCo(C_8H_8)RuCp]-PF_6 (**6**) and [CpRh(C_8H_8)RuCp]PF_6 (**7**) in high yields. These complexes have also a cisoid structure and, in addition, Co–Ru and Rh–Ru bonds. They show two resonances in the ^{13}C NMR for nonequivalent cyclopentadienyl rings as well as sharp signals for the bridging C_8H_8 with a ^{103}Rh coupling of the expected magnitude for **7** (Table VI).

Synthesis, Reactivity, and Molecular Structure of *cis*-(CpRh)$_2$C$_8$H$_8$ (8). A dimetallic rhodium complex $(CpRh)_2C_8H_8$ had been described in the literature[23] and assigned a trans pseudo-triple-decker structure analogous to $(CpCo)_2C_8H_8$. This has recently been confirmed by its reactivity (see later).[24] The published method was complicated and gave only low yields so that we tried to develop other routes to complexes of this general transoid structure. A rational route involved the displacement of ethylene from $[(C_2H_4)_2RhCl]_2$ with CpRh(COT) to form $[CpRh(C_8H_8)RhCl]_2$ with preformed *trans*-Rh(C_8H_8)Rh units and treatment of this rhodium tetramer with TlCp to displace the chloride bridges. While this reaction at room temperature indeed produced the desired yellow trans complex in satisfactory yields (see later), the same reaction at −78 °C led to the exclusive formation of a dark red complex of the analytical composition $(C_5H_5Rh)_2C_8H_8$ (**8**), not identical with the trans complex but obviously a structural isomer of it.

The noise-decoupled ^{13}C NMR spectrum of this complex at room temperature showed six resonance lines, two doublets for cyclopentadienyl ligands, one singlet (139.5 ppm) in the region for noncoordinated olefins, a doublet at 60.9 ppm, a broad resonance at 38 ppm, and a four-line multiplet at 52.9 ppm (X part of an AMX spectrum, J(Rh,C) = 5.4, 2.7 Hz). The ^{103}Rh NMR again gave two lines (Table VII) indicating the presence of two nonequivalent rhodium nuclei. At lower temperatures, the four ^{13}C lines due to C_8H_8 broadened and appeared in the slow-exchange limit (−70 °C)) as eight new resonances, pairwise equidistant to the previous signals, two in the region for noncoordinated olefins and all other assigned to metal-coordinated carbons (Table VI). This suggested a cisoid bonding mode similar to $(CpRh)_2C_8H_{10}$, described by Evans et al.,[25] in which one rhodium atom coordinates in a 1–3-η-allyl and the other rhodium in a $\pi + \sigma$ bonding mode, although it remained unclear why the method employed here should produce a cis dimetallic unit at all.

An X-ray structure analysis of complex **8** was undertaken to confirm this assignment. Table I lists data collection and unit cell parameters, and Tables VIII and IX list atomic positions and bond distances. Figure 4 depicts the molecular structure of this complex. The rhodium–rhodium distance in this complex (2.69 Å) is considerably shorter than in **1** and **2**, not surprising as only six carbons of the bridging ring are coordinated and a confirmation of our assumption that the ring size of the bridge exerts a considerable influence on this parameter. One cyclopentadienylrhodium unit coordinates to carbons 3, 4, and 5 in an η^3-allyl fashion, while the other metal, within bonding distance of carbons 1, 2, and 6, forms a π- and σ-bond, respectively. A similar type of bonding has also

Table VIII. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $C_5H_5Rh(C_8H_8)RhC_5H_5$ (8)

atom	x–a	y/b	z/c	U_{eq}[a]
Rh(1)	4279 (1)	5008 (1)	4843 (1)	13 (1)
Rh(2)	3652 (1)	4862 (1)	6418 (1)	15 (1)
C(1)	6758 (12)	5133 (10)	4105 (5)	27 (3)
C(2)	5366 (15)	4737 (9)	3605 (5)	29 (3)
C(3)	4774 (16)	3610 (10)	3904 (5)	30 (3)
C(4)	5727 (17)	3345 (8)	4593 (6)	30 (3)
C(5)	6996 (15)	4288 (10)	4735 (6)	31 (3)
C(6)	3652 (15)	6775 (7)	5232 (5)	19 (2)
C(7)	2261 (14)	6256 (8)	4787 (5)	21 (3)
C(8)	1502 (12)	5131 (8)	5039 (4)	20 (2)
C(9)	1132 (12)	4861 (8)	5894 (4)	19 (2)
C(10)	38 (15)	5846 (9)	6257 (5)	25 (3)
C(11)	882 (17)	6703 (8)	6649 (5)	29 (3)
C(12)	2856 (17)	6610 (8)	6739 (5)	25 (3)
C(13)	4055 (14)	6683 (7)	6107 (5)	20 (3)
C(14)	5906 (20)	3611 (11)	6654 (6)	42 (4)
C(15)	4349 (19)	2979 (9)	6643 (7)	36 (4)
C(16)	3295 (16)	3382 (12)	7287 (8)	44 (4)
C(17)	4217 (21)	4297 (11)	7685 (6)	44 (4)
C(18)	5857 (18)	4425 (10)	7297 (7)	40 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensor.

Table IX. Bond Lengths (Å) for 8

Rh(1)–Rh(2)	2.689 (1)	Rh(1)–C(1)	2.251 (9)
Rh(1)–C(2)	2.255 (9)	Rh(1)–C(3)	2.257 (10)
Rh(1)–C(4)	2.207 (10)	Rh(1)–C(5)	2.216 (12)
Rh(1)–C(6)	2.143 (8)	Rh(1)–C(7)	2.075 (10)
Rh(1)–C(8)	2.130 (9)	Rh(2)–C(9)	2.099 (9)
Rh(2)–C(12)	2.124 (9)	Rh(2)–C(13)	2.133 (8)
Rh(2)–C(14)	2.245 (14)	Rh(2)–C(15)	2.214 (10)
Rh(2)–C(16)	2.230 (13)	Rh(2)–C(17)	2.260 (11)
Rh(2)–C(18)	2.280 (13)	C(1)–C(2)	1.418 (14)
C(1)–C(5)	1.431 (14)	C(2)–C(3)	1.435 (15)
C(3)–C(4)	1.395 (15)	C(4)–C(5)	1.450 (16)
C(6)–C(7)	1.415 (14)	C(6)–C(13)	1.503 (12)
C(7)–C(8)	1.451 (13)	C(8)–C(9)	1.492 (11)
C(9)–C(10)	1.511 (13)	C(10)–C(11)	1.329 (14)
C(11)–C(12)	1.504 (18)	C(12)–C(13)	1.398 (14)
C(14)–C(15)	1.376 (20)	C(14)–C(18)	1.415 (17)
C(15)–C(16)	1.417 (17)	C(16)–C(17)	1.411 (18)
C(17)–C(18)	1.408 (20)		

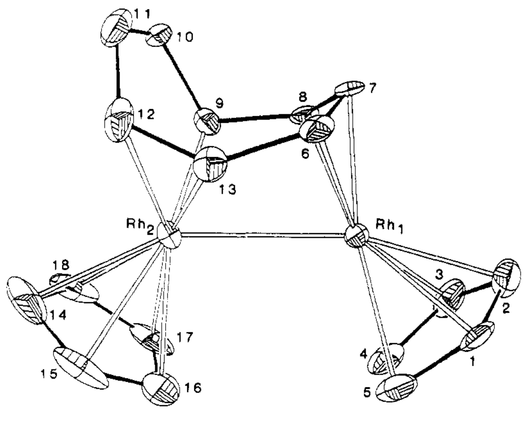


Figure 4. Molecular drawing for $C_5H_5Rh(C_8H_8)RhC_5H_5$ (**8**). Thermal ellipsoids are represented at 50% probability. The crystallographic labeling scheme is arbitrary and different from the numbering used for assignment of ^{13}C NMR spectra (Table VI).

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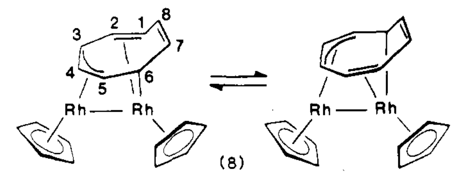
(23) Brenner, K. S.; Fischer, E. O.; Fritz, H. P.; Kreiter, C. G. *Chem. Ber.* **1963**, *96*, 2632.

(24) Edwin, J.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 3052.

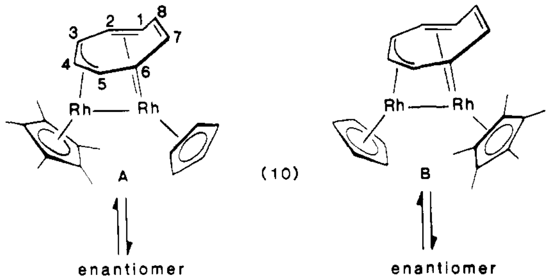
(25) Evans, J.; Johnson, B. F. G.; Lewis, J.; Watt, R. *J. Chem. Soc., Dalton Trans.* **1974**, 2368.

Scheme II



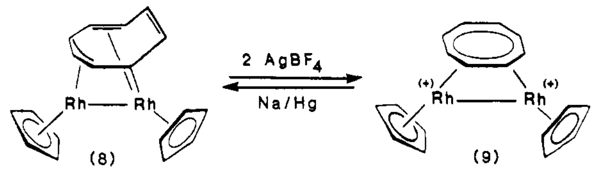
been observed in the dimetallic ruthenium cyclooctatraene complex $C_8H_8Ru_2(CO)_6$.[26a,b] The six coordinated carbons show approximately equal distances (1.44 ± 0.05 Å) to each other while the lone noncoordinated double bond is substantially shorter (1.32 Å) and separated from the other six carbon atoms by two longer bonds (1.51 Å). Electron counting reveals the reason for the unusually distorted geometry of the bridging ligand, and the removal of one double bond from the coordination sphere of both metals. Complex **8** has in contrast to all previous examples 36 valence electrons; by inclusion of all π-electrons of C_8H_8 *and* a metal–metal bond this would give both Rh atoms a 19e configuration, so that either a metal–metal bond has to be absent or two olefinic carbons removed from the electron count to obtain a closed-shell configuration. The latter case is realized in **8**. The dynamic behavior in solution is similar to that of a number of dimetallic cyclooctatriene complexes. It involves the interconversion of two energetically equivalent enantiomers which, in the fast-exchange limit, leads to the pairwise equivalence of carbons and a virtual symmetry in the ring carbon region[26b] (Scheme II).

Removal of two electrons from **8** would give a 34e dimetallic dication that should have a structure similar to **4**. This is indeed the case as low-temperature oxidation of **8** with 2 molar equiv of $AgBF_4$ gave a dark red solution in acetone, from which silver was separated by filtration and complex **9** precipitated by addition of ether. It had the expected analytical composition $[(C_5H_5Rh)_2C_8H_8](BF_4)_2$ and showed a symmetrical ^{13}C NMR spectrum with a fully fluxional C_8H_8 ring where all carbons are now coordinated to rhodium, similar to **4**. The C_8H_8 resonance is a triplet due to coupling to two equivalent rhodium nuclei, and only one ^{103}Rh resonance line is observed (Table VII). The reaction is easily reversible by sodium amalgam reduction of **9** which recovers **8** in good yields. A similar reduction of **4** gives the neutral species $(C_5H_5)Rh(C_8H_8)Rh(C_5Me_5)$ (**10**) which has, as **8**, an uncoordinated double bond. This complex, due to the nonequivalence of the two C_5 rings, is an inseparable mixture of two diastereomers A and B in an approximate ratio of 40/60, giving two sets of signals in the ^{13}C NMR at room temperature which can be assigned as listed in Table VI. On the NMR time scale at room temperature, these diastereomers interconvert rapidly into their enantiomers, but not into each other.

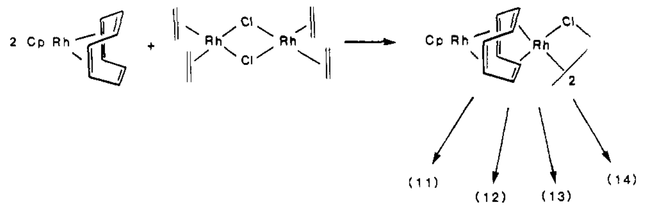


(10)

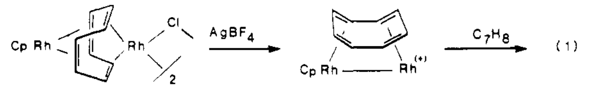
Scheme III



Scheme IV



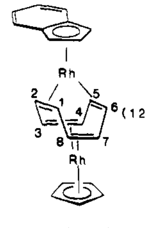
Scheme V



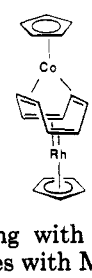
This redox behavior of cisoid dimetallic complexes, in which the bridging ligand can adapt to the electronic requirements of the two metal centers, is quite unusual although it finds its equivalence in the behavior of the isomeric trans complex discussed below.

Preparation of Pseudo-Triple-Decker Complexes—The X-ray Structure of *trans*-CpRh(C_8H_8)RhCp (11). It has already been mentioned that a rational general route to transoid dimetallic complexes had been developed by us to gain insight into the reactivity and spectroscopic properties of this type of dimetallic complexes. The key step in this synthesis is the ready replacement of ethylene from $[(C_2H_4)_2RhCl]_2$ for a cyclooctatetraene complex with a 1,2,5,6-η-coordination, e.g., CpCo(COT), CpRh(COT), or (indenyl)Rh(COT). In this manner, tetranuclear complexes are formed in which the four independent metal atoms retain their chelating trans coordination to C_8H_8, thus preforming the desired trans geometry. Replacement of the chloride bridges by a π-ligand should generally be possible, and this proved to be true.

Starting from CpRh(COT) and reacting first with $[(C_2H_4)_2RhCl]_2$ which formed an insoluble precipitate $[CpRh(C_8H_8)RhCl]_2$ with evolution of ethylene and subsequent treatment with TlCp or $Mg(Ind)_2$ (Ind = indenyl) at room temperature gave *trans*-$(CpRh)_2C_8H_8$ (**11**) and *trans*-(Ind)Rh(C_8H_8)RhCp (**12**) in high yields. A similar reaction with K_2CO_3 and acetylacetone (acac) generated (acac)Rh(C_8H_8)RhCp (**13**) and treatment with hexamethylbenzene (Hmbz) and CPh_3BF_4 as halide abstractor produced $[CpRh(C_8H_8)Rh(Hmbz)]BF_4$ (**14**). The same reaction principle, but starting with IndRhCOT and treating the tetranuclear species with $Mg(Ind)_2$ gave the symmetrical indenyl triple-decker *trans*-$(IndRh)_2C_8H_8$ (**15**). Using $CpCoC_8H_8$ initially gave the mixed-metal complex *trans*-CpCo(C_8H_8)RhCp (**16**).



(12)



(16)

It is interesting to note that reaction of the insoluble precipitate $[CpRh(C_8H_8)RhCl]_2$ with $AgBF_4$ in acetone at once gave a dark red solution of an unsaturated interme-

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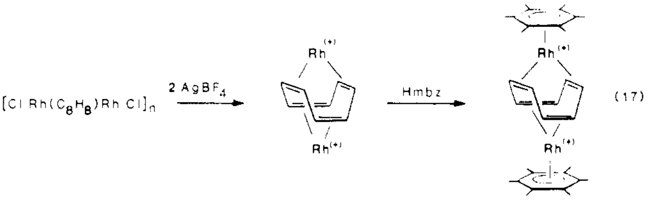
(26) (a) Cotton, F. A.; Edwards, F. T. *J. Am. Chem. Soc.* **1968**, *90*, 5412. (b) Deganello, G. "*Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: London, 1979.

Table X. ^{13}C NMR Data of Trans Dimetallic Complexes

compd	solv[a]	δ_C[b] $(J_{Rh,C})$[c]		
		COT	Cp	other ligands
CpRh(COT)RhCp (**11**)	C	72.0 (sm)	86.8 (sm)	
CpRh(COT)Rh(Ind) (**12**)	C	77.7 (dd, 11.8, 0.4), C-1,2,5,6 71.4 (dd, 12.1, 0.4), C-3,4,7,8	86.8 (d, 3.6)	123.1, 119.1, 114.2 (d, 1.7) 92.8 (d, 4.9), 76.2 (d, 4.3)
CpRh(COT)Rh(acac) (**13**)	C	85.8 (dd, 12.4, 0.5), C-1,2,5,6 71.0 (d, 12.4), C-3,4,7,8	87.2 (d, 3.5)	186.2, 100.0, 27.2
[CpRh(COT)Rh(Hmbz)]BF_4 (**14**)	C	90.8 (dd, 11.0, 0.6), C-1,2,5,6 70.8 (dd, 12.3, 0.4), C-3,4,7,8	87.7 (d, 3.7)	115.3 (d, 2.7), 15.6
(Ind)Rh(COT)Rh(Ind) (**15**)	C	77.4 (sm)		123.5, 119.3, 114.7 (sm), 93.0 (sm), 76.8 (sm)
CpRh(COT)CoCp (**16**)	C	72.4 (d, 12.4), C-3,4,7,8 72.8, C-1,2,5,6	86.6 (d, 3.5) 84.2	
[(Hmbz)Rh(COT)Rh(Hmbz)]$(BF_4)_2$ (**17**)	C	89.9 (sm)		118.4 (sm), 16.1
[C_5Me_5Co(COT)RhC_5Me_5]$(BF_4)_2$ (**18**)	A[d]	100.7, 97.6 (d, 5.8) 96.8 (d, 9.9), 93.4 (m)[e] 66.0 (d, 4.7), 57.9 (d, 11.9)		105.6 (d, 6.3), 9.3 101.7, 9.2
CpRu(COT)RuCp (**20**)	C[f]	87.7, 71.2, 66.1, 41.9	76.5	

[a] Key: C, chloroform-d_1; A, acetone-d_6. [b] Ppm relative to $Si(CH_3)_4$. [c] Hertz; d = doublet; dd = double doublet; sm = six-line multiplet (cf. Figure 5b). [d] 233 K. [e] Not resolved, three carbons. [f] 253 K.

Scheme VI



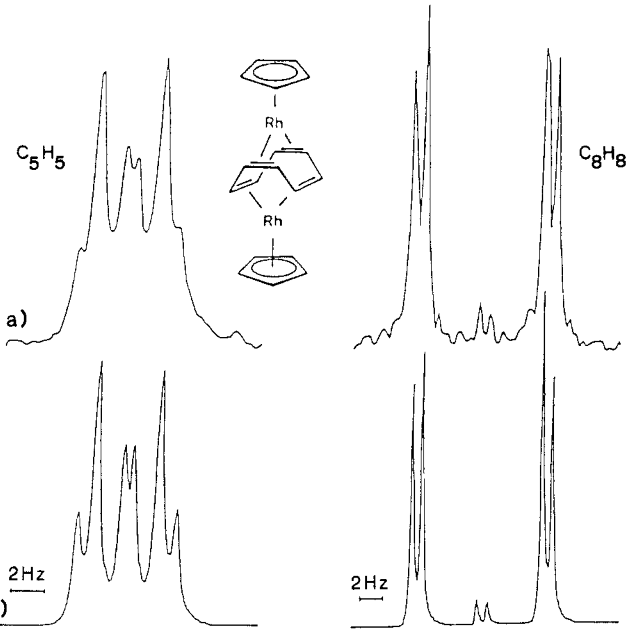


Figure 5. ^{13}C NMR spectra of $C_5H_5Rh(C_8H_8)RhC_5H_5$ (**11**) in $CDCl_3$ (proton noise decoupled, 25.2 MHz): (a) experimental spectra of the C_5H_5 and C_8H_8 signals; (b) simulated spectra (for parameters, see Table XI).

diate with precipitation of AgCl. Addition of C_7H_8 to this solution led to the quantitative formation of cisoid **1**; it was not important whether C_7H_8 was added before or after halide abstraction. This proves that rapid interconversion of the unsaturated intermediate $[CpRh(C_8H_8)Rh(solv)_x]^+$ from trans to cis is possible and facile. This also provides a likely explanation for the low-temperature formation of *cis*-$(CpRh)_2C_8H_8$ (**8**) as described earlier, if one assumes that Cl^- abstraction with Tl^+ occurs fast, formation of **8**, however, is slow at low temperatures to allow previous rearrangement of the unsaturated intermediate.

A variation of the general method described above employs the presumably polymeric intermediate $[ClRh(C_8H_8)RhCl]_n$.[27] On treatment with $Mg(Ind)_2$ a high yield of **15** can be isolated. Reacting the polymer with 1 equiv of $AgBF_4$ per chloride ion leads to an immediate precipitate of AgCl and a yellow solution of unsaturated $[Rh(C_8H_8)Rh](BF_4)_2$, stabilized by solvent molecules. Addition of hexamethylbenzene to this solution gave *trans*-$[((Hmbz)Rh)_2C_8H_8]BF_4)_2$ (**17**).

While analytical data confirmed the overall composition of all complexes, the *transoid* structures were apparent from their spectroscopic data (Tables VII and X). A characteristic feature in the ^{13}C NMR spectra of the symmetrical complexes **11**, **15**, and **17** was the appearance of multiplets for the COT ligand as well as the carbons of Cp, Ind, and Hmbz bonded directly to rhodium. In high-resolution, noise-decoupled spectra they appear as six-line multiplets (Figure 5) due to ^{103}Rh coupling. This typical six-line X pattern of an ABX spin system can only be rationalized if the two rhodium nuclei are spin-coupled via the π-system of the common COT ligand. The coupling pattern is independent of temperature and points to a slight inequivalence of the two rhodium atoms due to a $^{13}C/^{12}C$ isotope effect in the ^{13}C isotopomers. The ^{103}Rh spectra of these complexes reveal only one resonance in the expected chemical shift range (Table VII). We had encountered this phenomenon earlier in the complex $[CpRh(C_7H_7)RhCp]Cl$[6] and also in **9** (Table VI). Simulation of the Cp signal of **11** shows that only one rhodium atom is coupled to the Cp carbons ($^1J(Rh^A,C) = 3.6$ Hz, $^4J(Rh^B,C) = 0$ Hz). The first value is typical for Rh–Cp coupling. For C_8H_8, simulations gave the best fit with $^1J(Rh^A,C) = 12.1$ Hz and $^2J(Rh^B,C) = 0.6$ Hz. These values correspond closely to the couplings observed in monomeric $CpRhC_8H_8$, with $^1J(Rh,C) = 13.0$ Hz and $^2J(Rh,C) = 0.5$ Hz. Simulation of both signals of **11** additionally provides a $J(Rh,Rh)$ value of 2.1 Hz and a chemical shift difference of 0.5 Hz for the two ^{103}Rh resonance lines. This extremely small difference for Rh^A and Rh^B is a typical $^{13}C/^{12}C$ isotope effect. Due to the low natural abundance of ^{13}C, only one ^{103}Rh nucleus is coordinated to a ^{13}C, the other only to ^{12}C carbons. The parameters obtained by simulation of the C_8H_8 signal for several symmetrical complexes are listed in Table XI.

For the unsymmetrical complexes, two signals are observed in the ^{103}Rh NMR (Table VII). The ^{13}C resonances of C_8H_8 now appear as four-line multiplets as the typical X part of an AMX spectrum with the expected large and

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[27] Bennett, M. A.; Saxby, J. D. *Inorg. Chem.* **1968**, *7*, 321.

Table XI. Rh,C and Rh,Rh Coupling Constants (Hz) from Simulation of ^{13}C COT Multiplets in Symmetrical Trans Compounds

compd	J(Rh^A,X)	J(Rh^B,X)	J(Rh^A,Rh^B)	$\Delta\nu$(Rh^A,Rh^B),[a] Hz
CpRh(COT)RhCp (**11**)	12.1	0.6	2.1	0.5
(Ind)Rh(COT)Rh(Ind) (**15**)	11.5	1.0	1.5	0.35
[(Hmbz)Rh(COT)Rh(Hmbz)](BF$_4$)$_2$ (**17**)	12.0	0.8	1.7	0.5

[a] $\Delta\nu$(Rh,Rh) values are valid for ν_0 = 25.2 MHz.

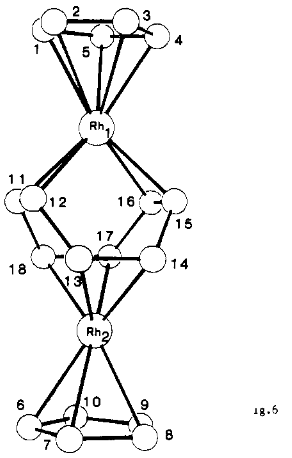

Figure 6. Crystal structure of $C_5H_5Rh(C_8H_8)RhC_5H_5$ (**11**): molecular geometry and atomic numbering scheme. The crystallographic labeling scheme is arbitrary and different from the numbering used for assignment of ^{13}C NMR spectra (Table X).

small couplings of Rh^A and Rh^M to the ring carbons. The Cp signals are doublets due to the fact that coupling to the remote rhodium (^4J(Rh,C)) is smaller than the digital resolution (cf. complex **11**). ^{103}Rh NMR spectra are also in agreement with the proposed trans geometry for these complexes (Table VII), in which both metals have virtually no interaction with each other. The signals are only moderately shifted to higher frequencies in comparison to the mononuclear complexes CpRh(COT), (Ind)Rh(COT), and [(Hmbz)Rh(COT)]BF$_4$. This slight *deshielding* is probably due to the coordination of the double bonds which are uncomplexed in the monomers. A strong *shielding* effect on the ^{103}Rh resonances, however, has been observed in all cis dimetallic complexes and has been discussed elsewhere.[13] To additionally confirm the trans assignment for this class of dimetallic complexes, an X-ray structure analysis of **11** was also performed. Figure 6 shows the structure of one dimetallic unit, the complex crystallizing with three different molecules per asymmetric unit. Table I lists data collection and unit cell parameters; Tables XII and XIII list atomic positions and bond parameters of selected distances for the three molecules in the unit cell.

The molecular structure, which need not be discussed in detail here, confirms the previous assignment of a trans arrangement of the two CpRh units bonded to a tub-shaped C_8H_8 ring, both rhodium atoms having their favored chelating coordination. This type of coordination has been called a "pseudo-triple-decker". The overall features of the structure are very similar to those of the isostructural compound $(CpCo)_2C_8H_8$,[28] and it is beyond doubt that all other complexes (**12**–**17**) show the same general bonding mode.

Table XII. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $C_5H_5Rh(C_8H_8)RhC_5H_5$ (11)

atom	x/a	y/b	z/c	U_{eq}[a]
Rh(1)	5020 (1)	3083 (1)	6604 (1)	41 (1)
Rh(2)	7096 (1)	2047 (1)	5642 (1)	40 (1)
C(1)	3345 (4)	3279 (2)	7230 (4)	92 (2)
C(2)	4189 (4)	3492 (2)	7862 (3)	82 (2)
C(3)	4762 (4)	3806 (2)	7323 (4)	73 (2)
C(4)	4308 (4)	3815 (1)	6381 (3)	70 (2)
C(5)	3392 (4)	3509 (2)	6272 (4)	85 (2)
C(6)	8891 (3)	1841 (1)	5112 (3)	64 (1)
C(7)	8619 (4)	1576 (1)	5941 (3)	65 (1)
C(8)	7690 (4)	1276 (1)	5670 (4)	71 (2)
C(9)	7303 (4)	1384 (2)	4703 (4)	78 (2)
C(10)	8045 (4)	1743 (2)	4354 (3)	74 (2)
C(11)	4689 (3)	2380 (1)	6156 (3)	49 (1)
C(12)	5307 (3)	2378 (1)	7082 (3)	46 (1)
C(13)	6580 (3)	2243 (1)	7087 (2)	45 (1)
C(14)	7356 (3)	2580 (1)	6736 (3)	50 (1)
C(15)	6857 (3)	3042 (1)	6394 (3)	56 (1)
C(16)	6247 (4)	3048 (1)	5476 (3)	59 (1)
C(17)	6121 (3)	2591 (1)	4899 (3)	57 (1)
C(18)	5347 (3)	2259 (1)	5250 (3)	53 (1)
Rh(1′)	4081 (1)	620 (1)	6941 (1)	38 (1)
Rh(2′)	1889 (1)	574 (1)	4504 (1)	36 (1)
C(1′)	5921 (3)	512 (2)	7612 (3)	64 (1)
C(2′)	5570 (4)	976 (1)	7757 (3)	61 (1)
C(3′)	4633 (4)	977 (2)	8412 (3)	63 (1)
C(4′)	4358 (4)	507 (2)	8591 (3)	69 (2)
C(5′)	5168 (4)	224 (2)	8118 (4)	75 (2)
C(6′)	230 (4)	806 (2)	3766 (3)	81 (2)
C(7′)	193 (4)	310 (2)	3778 (3)	74 (2)
C(8′)	1116 (5)	177 (2)	3204 (3)	89 (2)
C(9′)	1609 (4)	561 (2)	2828 (3)	101 (2)
C(10′)	1104 (4)	934 (2)	3140 (3)	96 (2)
C(11′)	4316 (3)	739 (2)	5396 (3)	58 (1)
C(12′)	3669 (4)	1107 (1)	5779 (3)	59 (1)
C(13′)	2385 (4)	1116 (1)	5518 (3)	53 (1)
C(14′)	1681 (3)	791 (1)	5994 (2)	47 (1)
C(15′)	2276 (3)	463 (1)	6735 (2)	46 (1)
C(16′)	2924 (3)	98 (1)	6348 (2)	45 (1)
C(17′)	2966 (3)	60 (1)	5226 (3)	47 (1)
C(18′)	3673 (3)	382 (2)	4745 (3)	53 (1)
R(1″)	8820 (1)	855 (1)	10111 (1)	32 (1)
Rh(2″)	10769 (1)	1848 (1)	8837 (1)	39 (1)
C(1″)	8487 (4)	433 (2)	11457 (3)	62 (1)
C(2″)	7419 (4)	663 (1)	11182 (3)	61 (1)
C(3″)	7076 (4)	504 (2)	10242 (3)	66 (1)
C(4″)	7844 (4)	159 (1)	9962 (3)	66 (1)
C(5″)	8688 (3)	106 (1)	10697 (3)	61 (1)
C(6″)	11722 (5)	2550 (2)	8959 (4)	78 (2)
C(7″)	12544 (4)	2213 (2)	8780 (3)	64 (2)
C(8″)	12237 (4)	2001 (2)	7859 (3)	63 (1)
C(9″)	11262 (4)	2242 (2)	7440 (3)	78 (2)
C(10″)	10917 (4)	2563 (2)	8123 (4)	84 (2)
C(11″)	9923 (3)	1394 (1)	10713 (2)	41 (1)
C(12″)	10607 (3)	1045 (1)	10297 (2)	41 (1)
C(13″)	11116 (3)	1147 (1)	9302 (3)	45 (1)
C(14″)	10354 (3)	1140 (1)	8450 (2)	45 (1)
C(15″)	9096 (3)	1030 (1)	8597 (2)	42 (1)
C(16″)	8418 (3)	1380 (1)	9012 (2)	42 (1)
C(17″)	8998 (3)	1839 (1)	9282 (3)	42 (1)
C(18″)	9762 (3)	1847 (1)	10137 (3)	44 (1)

[q] Equivalent isotropic U defined as one-third of the trace of the orthogonalized **U** tensor.

Dimetallic Complexes with a "Slipped" Triple-Decker Structure. $(CpCo)_2C_8H_8$ and its rhodium analogue (**11**) have 18 valence electrons around each metal for a total of 36 electrons and have been categorized as a "near miss" to the genuine triple-decker class.[29] Electrochemical investigations on the oxidation of the cobalt dimer had

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(28) Paulus, E.; Hoppe, W.; Huber, R. *Naturwissenschaften* **1967**, *54*, 67.

(29) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

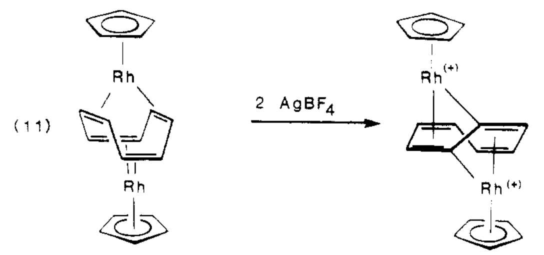
Table XIII. Bond Lengths (Å) for 11

Rh(1)–C(1)	2.196 (5)	Rh(1)–C(2)	2.286 (4)
Rh(1)–C(3)	2.293 (5)	Rh(1)–C(4)	2.247 (4)
Rh(1)–C(5)	2.245 (5)	Rh(1)–C(11)	2.116 (4)
Rh(1)–C(12)	2.125 (3)	Rh(1)–C(15)	2.133 (4)
Rh(1)–C(16)	2.109 (4)	Rh(2)–C(6)	2.277 (4)
Rh(2)–C(7)	2.216 (4)	Rh(2)–C(8)	2.294 (4)
Rh(2)–C(9)	2.281 (5)	Rh(2)–C(10)	2.250 (4)
Rh(2)–C(13)	2.119 (3)	Rh(2)–C(14)	2.116 (4)
Rh(2)–C(17)	2.123 (4)	Rh(2)–C(18)	2.127 (4)
C(1)–C(2)	1.389 (7)	C(1)–C(5)	1.440 (7)
C(2)–C(3)	1.338 (7)	C(3)–C(4)	1.339 (7)
C(4)–C(5)	1.362 (6)	C(6)–C(7)	1.387 (6)
C(6)–C(10)	1.393 (6)	C(7)–C(8)	1.396 (6)
C(8)–C(9)	1.380 (7)	C(9)–C(10)	1.420 (6)
C(11)–C(12)	1.395 (5)	C(11)–C(18)	1.495 (5)
C(12)–C(13)	1.502 (5)	C(13)–C(14)	1.402 (5)
C(14)–C(15)	1.492 (5)	C(15)–C(16)	1.381 (6)
C(16)–C(17)	1.513 (5)	C(17)–C(18)	1.390 (5)
Rh(1′)–C(1′)	2.265 (4)	Rh(1′)–C(2′)	2.219 (4)
Rh(1′)–C(3′)	2.275 (4)	Rh(1′)–C(4′)	2.235 (4)
Rh(1′)–C(5′)	2.256 (5)	Rh(1′)–C(11′)	2.121 (4)
Rh(1′)–C(12′)	2.115 (4)	Rh(1′)–C(15′)	2.115 (3)
Rh(1′)–C(16′)	2.113 (3)	Rh(2′)–C(6′)	2.195 (4)
Rh(2′)–C(7′)	2.253 (4)	Rh(2′)–C(8′)	2.218 (5)
Rh(2′)–C(9′)	2.247 (4)	Rh(2′)–C(10′)	2.240 (5)
Rh(2′)–C(13′)	2.109 (3)	Rh(2′)–C(14′)	2.108 (3)
Rh(2′)–C(17′)	2.111 (3)	Rh(2′)–C(18′)	2.118 (3)
C(1′)–C(2′)	1.392 (6)	C(1′)–C(5′)	1.389 (6)
C(2′)–C(3′)	1.415 (6)	C(3′)–C(4′)	1.394 (6)
C(4′)–C(5′)	1.400 (6)	C(6′)–C(7′)	1.412 (7)
C(6′)–C(10′)	1.381 (7)	C(7′)–C(8′)	1.385 (7)
C(8′)–C(9′)	1.337 (8)	C(9′)–C(10′)	1.285 (8)
C(11′)–C(12′)	1.390 (6)	C(11′)–C(18′)	1.505 (5)
C(12′)–C(13′)	1.491 (6)	C(13′)–C(14′)	1.398 (5)
C(14′)–C(15′)	1.498 (5)	C(15′)–C(16′)	1.386 (5)
C(16′)–C(17′)	1.507 (5)	C(17′)–C(18′)	1.396 (5)
Rh(1″)–C(1″)	2.210 (4)	Rh(1″)–C(2″)	2.264 (5)
Rh(1″)–C(3″)	2.242 (4)	Rh(1″)–C(4″)	2.274 (4)
Rh(1″)–C(5″)	2.276 (4)	Rh(1″)–C(11″)	2.116 (3)
Rh(1″)–C(12″)	2.115 (3)	Rh(1″)–C(15″)	2.120 (3)
Rh(1″)–C(16″)	2.128 (3)	Rh(2″)–C(6″)	2.272 (5)
Rh(2″)–C(7″)	2.281 (4)	Rh(2″)–C(8″)	2.218 (4)
Rh(2″)–C(9″)	2.269 (4)	Rh(2″)–C(10″)	2.253 (4)
Rh(2″)–C(13″)	2.121 (3)	Rh(2″)–C(14″)	2.124 (3)
Rh(2″)–C(17″)	2.135 (3)	Rh(2″)–C(18″)	2.129 (3)
C(1″)–C(2″)	1.417 (6)	C(1″)–C(5″)	1.404 (6)
C(2″)–C(3″)	1.374 (6)	C(3″)–C(4″)	1.379 (6)
C(4″)–C(5″)	1.350 (6)	C(6″)–C(7″)	1.369 (7)
C(6″)–C(10″)	1.412 (7)	C(7″)–C(8″)	1.400 (6)
C(8″)–C(9″)	1.401 (6)	C(9″)–C(10″)	1.362 (7)
C(11″)–C(12″)	1.393 (5)	C(11″)–C(18″)	1.508 (4)
C(12″)–C(13″)	1.504 (5)	C(13″)–C(14″)	1.400 (5)
C(14″)–C(15″)	1.493 (5)	C(15″)–C(16″)	1.393 (5)
C(16″)–C(17″)	1.497 (5)	C(17″)–C(18″)	1.404 (5)

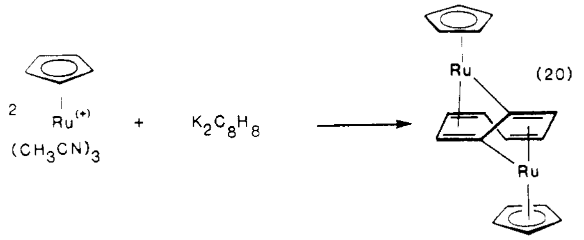
shown that a dicationic 34e species could easily be generated, to which a genuine triple-decker structure had been assigned.[30] This complex $[(CpCo)_2C_8H_8)]^{2+}$ was, however, too unstable to be structurally characterized. Recent cyclic voltammetry investigations on the oxidation of 11 (from a sample originally supplied by us) as well as the pentamethylcyclopentadienyl derivative $(C_5Me_5Co)_2C_8H_8$ showed that stable dications could be obtained for these molecules, also by bulk chemical oxidation with $AgPF_6$.[24] The rhodium dication $[CpRh(C_8H_8)RhCp](PF_6)_2$, a structural isomer of the cisoid dication **9**, was also characterized by an X-ray structure analysis.[24]

The key feature of the structure is that the metal atoms are slipped to the side of the C_8 ring which has two nearly planar C_4 fragments twisted by 34.8°. Each rhodium is formally bonded to five carbons, requiring two carbons to be bridging between two metals to give a 34-electron structure. This was also confirmed by the ^1H NMR spectrum at reduced temperatures (four sets of resonances for the C_8 ring) with fluxional behavior observed on warming up. This type of structure can be regarded as a "slipped" triple-decker.

Scheme VII



Scheme VIII



We now find that similar 34e complexes can also be generated by another route. Treatment of $C_5Me_5Co(COT)$ with the unsaturated moiety $[C_5Me_5Rh](BF_4)_2$ leads to the formation of a dark red salt, analyzed as $[C_5Me_5Co(C_8H_8)RhC_5Me_5](BF_4)_2$ (**18**). This complex is also fluxional on the ^{13}C NMR time scale at room temperature; however, at −40 °C the slow-exchange limit is reached, showing eight resonances for the central C_8 ring (Table X) as well as resonances for the two different C_5Me_5 ligands coordinated to Co and Rh. This spectrum is in good agreement with a slipped triple-decker structure for **18**, as two resonances of the C_8 ring are shifted to lower frequency due to coordination to two metals simultaneously. At elevated temperatures (+60 °C), all eight signals merge into a broad line at 87.5–88.5 ppm, the highest temperature we could reach before decomposition sets in. This suggests a fluxional movement of both metal units around the central ring as observed before for this type of coordination.[24]

It is not surprising that complexes with two bulky pentamethylcyclopentadienyl rings no longer favor a cisoid arrangement. Molecular models suggest that strong steric hindrance between the methyl groups of the two rings must occur, preventing interaction between the two metals and optimum overlap with C_8H_8 orbitals. A transoid arrangement, therefore, becomes more favorable. This steric argument is supported by the fact that reaction of $C_5Me_5Co(COT)$ with a less bulky unsaturated moiety, e.g., $[Rh(CO)_2]^+$, gives a cisoid dimetallic complex $[C_5Me_5Co(C_8H_8)Rh(CO)_2]^+$ (**19**) with the usual fluxional C_8H_8 bridge (Table VI).

Unpublished results by Siebert et al. had shown that other 34e dimetallic complexes of COT can also have slipped triple-decker structures as evidenced by the X-ray structure of $CpFe(C_8H_8)FeCp$ isoelectronic to **18**. The synthesis of this complex, unfortunately, was not reproducible.[31]

We have developed a repeatable route to the analogous complex of ruthenium. Treatment of the previously mentioned $[CpRu(CH_3CN)_3]PF_6$ (2 equiv) with $K_2C_8H_8$ in THF at low temperatures generated a dark red solution

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(30) Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7429.

(31) Siebert, W.; Krüger, C., personal communication.

from which a neutral dimetallic complex of analytical composition $(C_5H_5Ru)_2C_8H_8$ (**20**) could be isolated as orange crystals. This complex has a sharp resonance line assigned to a cyclopentadienyl group in the ^{13}C NMR at ambient temperatures as well as four broad signals in the region for coordinated olefinic carbons. These four lines sharpen on moderate cooling to −20 °C (Table X). The overall feature of this spectrum is in good agreement with a "slipped" triple-decker structure for **20**, with one signal attributed to the two carbons coordinated to two metals appearing at distinctly lower frequency than the others. This is also a confirmation of Siebert's results on the analogous iron complex and an indication that the iron group metals sometimes prefer this type of coordination to C_8H_8, in which both metals coordinate to a η^5-dienyl portion of COT sharing two carbons. This type of double coordination of two carbons to trans complexed metals is also exhibited by $(C_8H_8Ti)_2C_8H_8$,[32] again a different type of "slipped" triple-decker sandwich. The reduction of this complex to a dianion has been studied and a genuine triple-decker structure proposed for this species, although sufficient evidence does not exist so far to validate this claim.[33]

It is at this point impossible to say why a triple-decker sandwich molecule with a planar bridging C_8H_8 ring should not exist although, of the large number of multidecked species characterized so far, only two types have an all-carbon central ring, namely, $[(C_5H_5Ni)_2C_5H_5]^+$[34] and $(C_5H_5V)_2C_6H_6$ and derivatives.[35] It should be noted, however, that even in monomeric complexes η^8-coordination is only found in the early transition metals, as well as the lanthanides and actinides.[26b] A common feature of these elements are large ionic and atomic radii, possibly more suitable for simultaneous interactions with all carbons of C_8H_8. The bonding in these complexes also appears to be more ionic than in the late-transition-metal series.

A comparison of aromatic species derived from C_4H_4 to C_8H_8 shows a dramatic increase in ring size, and, therefore, it is unlikely that the relatively small metals discussed in this paper are equally capable of η^8-coordination as they are for η^4 or η^5 bonding to smaller rings. The metals have to move much closer to the center of the larger rings to achieve the same M–C distance, and this prevents optimum overlap between metal and ring orbitals. Coordination to two metals simultaneously joined by a metal–metal bond, therefore, appears to be the more favorable type of coordination.

It is a general phenomenon that cisoid dimetallic complexes of conjugated cyclic polyolefins have activation barriers for internal reorientation which are much smaller than in the related transoid complexes. This is again apparent from the molecules described in this paper, where either the trans complexes are nonfluxional or the slow-exchange limit in the ^{13}C NMR is reached on moderate cooling, while all cis complexes with eight coordinated carbons show fluxional behavior down to −100 °C, the lowest temperature we have reached for solubility reasons. In that respect, they resemble the monomeric complexes like $COTFe(CO)_3$, the prime example for a "ring-whizzer" molecule.[26b]

Conclusions

Results presented in this paper for dimetallic complexes with bridging cyclooctatraene ligands reveal an astonishing variety of coordination modes for this polyolefinic (or aromatic) ligand, depending on the electronic or steric requirements of the organometallic groups involved. This flexibility is also mirrored in the redox properties of some complexes which adapt to reversible two-electron changes by structural rearrangements, which ensure that each metal center retains a noble gas configuration. The bridging ligand acts here as an "electron reservoir" that supplies or withdraws electrons as required. This type of behavior is very rarely found in mononuclear complexes.[36]

In addition, most complexes show a high degree of fluxional movements of different types in solution, as evidenced by variable-temperature ^{13}C NMR experiments. ^{103}Rh NMR has been routinely employed and provides a convenient additional probe to determine structural features and metal–metal interactions.

The general reaction principle described here allows the preparation of a wide selection of dimetallic complexes with metal–metal bonds, either homo- or heterodimetallic. The extension to still further transition metals is currently under investigation, as well as experiments concerning the electrochemical properties of all complexes and their suitability for the preparation of heterometallic catalysts.

Experimental Section

Materials and Instrumentation. All manipulations were carried out in oxygen-free, rigorously dried solvents under nitrogen. The ^{13}C NMR spectra were measured on a Varian XL-100 spectrometer at 25.2 MHz. ^{103}Rh NMR spectra were obtained on a Bruker AM-400 spectrometer (12.6 MHz) and a spectrometer especially developed for investigations of weak NMR signals operating at 2.8 MHz and utilizing steady-state pulse techniques.[13] IR spectra were recorded on a Beckman IR 12 and mass spectra on a Varian MAT 711. Microanalytical data for C, H, F, Rh, and Ru were provided by Analytische Laboratorien, D-5250 Engelskirchen, West Germany.

X-ray Crystallography Procedures. The intensities were collected on a Nicolet-R3 diffractometer in the ω scan mode using Mo Kα radiation (graphite monochromator), and the usual corrections were applied, including an empirical absorption correction for **1**, **2**, and **11**. For those reflections whose intensities I were below $0.5\sigma(I)$, I was set to $0.25\sigma(I)$. The heavy atoms were determined by direct methods, and molecules were developed by subsequent difference Fourier syntheses and least-squares refinements.[37] In **2** and **11**, all H atoms were located in difference density maps, while in **1** they could be found only in part. In **8**, due to the poor quality of the crystal, no attempt was made to locate them. In **2**, they were refined freely with individual isotropic temperature factors. In **11**, their local coordinates were also freely refined but only two temperature factors were varied, one for those belonging to the cyclooctatetraene moieties and one for the cyclopentadienyl rings. In **1**, they were allowed to "ride" on the atoms to which they were bonded with isotropic temperature factors being 1.2 times as large as the equivalent isotropic temperature factor of their pivot atoms. In **8**, they were not considered at all. In all four structures, the other atoms were refined with anisotropic temperature factors. In the last blocked cascade refinements with ca. 100 variables per block, all unique reflections were used to bring the variables to convergence, **8** being an exception where only the 1197 reflections with $I > 2\sigma(I)$ were included.

Preparation of the Complexes. Published procedures were used for CpCo(COT),[38] CpRh(COT),[39] $[C_5Me_5RhCl_2]_2$,[20]

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$[C_5Me_5IrCl_2]_2$,[20] $[CpRu(CH_3CN)_3]PF_6$,[21] $[ClRh(C_8H_8)RhCl]_n$,[27] $Mg(Ind)_2$,[40] and $[(C_2H_4)_2RhCl]_2$.[41] $[(CO)_2RhCl]_2$, $(COT)Fe(CO)_3$, TlCp, $AgBF_4$, and pentamethylcyclopentadiene were purchased from STREM Chemicals. C_5Me_5CoCOT was kindly supplied from Dr. U. Koelle, University of Aachen.

$[CpCo(COT)RhC_5Me_5](BF_4)_2$ (3), $[CpRh(COT)RhC_5Me_5](BF_4)_2$ (4), and $[CpRh(COT)IrC_5Me_5](BF_4)_2$ (5). $[C_5Me_5RhCl_2]_2$ (0.5 mmol, 309 mg) or $[C_5Me_5IrCl_2]_2$ (398 mg) in 5 mL of acetone was treated with 2 mmol of $AgBF_4$ (390 mg). The precipitate of AgCl was filtered off and washed. To the stirred yellow filtrate was added 1.2 mmol of CpCo(COT) (275 mg) or CpRh(COT) (326 mg) with immediate darkening of the solution. Addition of 100 mL of ether precipitated light to dark brown microcrystalline powders which were separated by filtration, washed with ether, and dried under vacuum; yield 80–90%.

Anal. Calcd for $C_{23}H_{28}B_2CoF_8Rh$ (3): C, 43.16; H, 4.41; F, 23.75; M_r, 639.90. Found: C, 42.92; H, 4.22; F, 23.53.

Anal. Calcd for $C_{23}H_{28}B_2F_8Rh_2$ (4): C, 40.39; H, 4.12; F, 22.22; M_r, 683.87. Found: C, 40.76; H, 3.91; F, 22.05.

Anal. Calcd for $C_{23}H_{28}B_2F_8IrRh$ (5): C, 35.72; H, 3.65; F, 19.66; Rh, 13.31; M_r, 773.19. Found: C, 35.61; H, 3.58; F, 19.55; Rh, 13.50.

$[CpCo(COT)RuCp]PF_6$ (6) and $[CpRh(COT)RuCp]PF_6$ (7). These complexes were prepared likewise from an acetone suspension of 1 mmol of $[CpRu(CH_3CN)_3]PF_6$ (434 mg) and treatment with 1.2 mmol of CpCo(COT) (275 mg) or CpRh(COT) (326 mg). After the solution was stirred for 30 min, addition of 100 mL of ether precipitated dark brown powders, which were separated by filtration, washed with ether, and dried under vacuum, and recrystallized from nitromethane/ether: yield 75–85%.

Anal. Calcd for $C_{18}CoF_6PRu$ (6): C, 40.08; H, 3.36; F, 21.13; M_r, 539.29. Found: C, 39.67; H, 3.48; F, 21.42.

Anal. Calcd for $C_{18}H_{18}F_6PRhRu$ (7): C, 37.06; H, 3.11; F, 19.54; M_r, 583.26. Found: C, 37.32; H, 3.05; F, 19.66.

***cis*-$(CpRh)_2COT$ (8).** A suspension of 1.93 mmol of $[(C_2H_4)_2RhCl]_2$ (751 mg) in 60 mL of pentane was treated with 3.86 mmol of CpRh(COT) (1050 mg) and stirred at room temperature until the evolution of ethylene had ceased completely. The precipitate was filtered and washed with pentane. The solid was suspended in CH_2Cl_2, cooled to −80 °C, and reacted with 8.5 mmol of TlCp (2300 mg); the mixture was stirred for 2 h at −80 °C and allowed to warm to room temperature within 12 h. The solution was filtered and the residue of TlCl washed with hexane until colorless. The solution was evaporated, redissolved in hexane, and filtered again. Hexane was evaporated under reduced pressure and the solid residue dissolved in CH_2Cl_2 and filtered. Evaporation of the solution gave dark red crystals of 8: 1.32 g (78%); mass spectrum (70 eV), *m/z* (relative intensity) 440 (M^+, 12.5), 336 (4.1), 233 (100), 168 (22.5), 103 (7.1). Anal. Calcd for $C_{18}H_{18}Rh_2$: C, 50.10; H, 4.20; M_r, 440.12. Found: C, 50.82; H, 4.53.

$[CpRh(COT)RhCp](BF_4)_2$ (9). 8 (1 mmol) was dissolved in 20 mL of acetone, cooled to −30 °C, and treated with a solution of 2 mmol of $AgBF_4$ (390 mg) in 10 mL of acetone. The solution was filtered after 15 min, reduced to 10 mL, and treated with 100 mL of ether, which precipitated a dark red powder. This was separated by filtration, washed with ether, and dried; yield 550 mg (90%). Anal. Calcd for $C_{18}H_{18}B_2F_8Rh_2$: C, 35.22; H, 2.95; F, 24.76; M_r, 613.74. Found: C, 35.46; H, 2.90; F, 24.52.

$CpRh(COT)RhC_5Me_5$ (10). 4 (0.58 mmol, 400 mg) was suspended in 30 mL of THF, treated with Na amalgam (1.3 mmol of Na (30 mg)), and stirred for 18 h. The red solution was filtered and evaporated and the residue taken up in hexane. This solution was chromatographed over Al_2O_3 (activity grade 3, neutral, 30-cm column). The first of three red fractions was collected, reduced in volume, and slowly cooled to −80 °C. Red crystals of 10 separated; 140 mg (47%). Anal. Calcd for $C_{23}H_{28}Rh_2$: C, 54.13; H, 5.53; M_r, 510.25. Found: C, 53.86; H, 5.44.

***trans*-$(CpRh)_2COT$ (11).** The method is the same as for 8, but addition of TlCp was at room temperature. Stirring for 5 h precipitated yellow 11. After removal of the solvent and extraction of the residue with chloroform and filtration over Al_2O_3, the product can be crystallized from chloroform at −30 °C: 1.25 g (76%); mass spectrum (70 eV), *m/z* (relative intensity) 440 (M^+, 9.1), 336 (15.6), 233 (100), 168 (23.2), 103 (8.6). Anal. Calcd for $C_{18}H_{18}Rh_2$: C, 50.10; H, 4.20; M_r, 440.12. Found: C, 50.12; H, 4.31.

CpRh(COT)Rh(Ind) (12). To a suspension of 0.5 mmol (200 mg) of $[CpRh(COT)RhCl]_2$, prepared as for 8 or 11, in hexane, was added 0.5 mmol of $Mg(Ind)_2$ (120 mg) at −50 °C and allowed to warm to room temperature within 4 h. Evaporation of the solvent and extraction of the residue with chloroform yielded 164 mg (67%) of yellow 12. Anal. Calcd for $C_{22}H_{20}Rh_2$: C, 53.90; H, 4.11; M_r, 490.18. Found: C, 53.84; H, 4.20.

CpRh(COT)Rh(acac) (13). The reaction was as above, but with 0.5 g of K_2CO_3 and 2 mL of acetylacetone. The mixture was stirred until the evolution of CO_2 ceased. Evaporation of the solvent and extraction with acetone gave 380 mg (81%) of yellow 13: mass spectrum (70 eV), *m/z* (relative intensity) 474 (M^+, 7). Anal. Calcd for $C_{18}H_{20}O_2Rh_2$: C, 45.58; H, 4.22; M_r, 474.14. Found: C, 46.04; H, 4.47.

$[CpRh(COT)Rh(Hmbz)]BF_4$ (14). $[(C_2H_4)_2RhCl]_2$ (1 mmol, 389 mg) was suspended in hexane and treated with 1 mL of COT. $[(COT)RhCl]_2$ was formed with evolution of ethylene. The solid was filtered and washed, taken up in acetone, and treated with 2 mmol of $AgBF_4$ (390 mg). After filtration of AgCl, the acetone solution of $[(COT)Rh]BF_4$ was reacted with 3 mmol of hexamethylbenzene (486 mg). Precipitation with ether yielded 690 mg (75%) of $[(Hmbz)Rh(COT)]BF_4$. One millimole of this complex (460 mg) was added to a suspension of $[(C_2H_4)_2RhCl]_2$ (0.5 mmol, 195 mg) in acetone and the mixture stirred with evolution of ethylene. After 2 h this reaction mixture was treated with 1 mmol of TlCp (270 mg) and stirred for 2 h. Solvent was removed and the residue extracted with chloroform. After filtration over a little Al_2O_3 and evaporation of the solvent 550 mg of 14 (88%) were obtained. Anal. Calcd for $C_{25}H_{31}BF_4Rh_2$: C, 48.06; H, 5.00; M_r, 624.22. Found: C, 48.73; H, 5.22.

$((Ind)Rh)_2COT$ (15). A suspension of 300 mg of $[ClRh(COT)RhCl]_n$ in 15 mL of hexane was reacted with 1.9 mmol of $Mg(Ind)_2$ (500 mg) and the mixture stirred for 4 h. Solvent was evaporated and the residue extracted with chloroform; after filtration over Al_2O_3 and evaporation of the solvent 280 mg of 15 was obtained (80%) as yellow crystals. Anal. Calcd for $C_{26}H_{22}Rh_2$: C, 57.80; H, 4.10; M_r, 540.3. Found: C, 57.92; H, 4.30.

CpCo(COT)RhCp (16). This was prepared as 11, substituting CpCoCOT for CpRhCOT: yield 53%. Anal. Calcd for $C_{18}H_{18}CoRh$: C, 54.55; H, 4.55; M_r, 396.17. Found: C, 54.83; H, 4.91.

$[((Hmbz)Rh)_2(COT)](BF_4)_2$ (17). $[ClRh(COT)RhCl]_n$ (500 mg) in acetone was treated with 2.6 mmol of $AgBF_4$ (500 mg) and stirred for 1 h. After filtration of AgCl the solution was added to a solution of 500 mg of Hmbz in 15 mL of acetone and stirred for 2 h. Addition of 200 mL of ether precipitated a yellow salt, which was filtered and washed. Recrystallization from nitromethane/ether gave 510 mg (66%). Anal. Calcd for $C_{32}H_{44}B_2F_8Rh_2$: C, 47.55; H, 5.49; M_r, 808.23. Found: C, 47.92; H, 6.01.

$[C_5Me_5Co(COT)RhC_5Me_5](BF_4)_2$ (18) was prepared as 3 or 4 with C_5Me_5CoCOT; yield 85%. Anal. Calcd for $C_{28}H_{38}B_2CoF_8Rh$: C, 47.34; H, 5.39; M_r, 710.33. Found: C, 47.74; H, 5.78.

$C_5Me_5Co(COT)Rh(CO)_2]BF_4$ (19). $[(CO)_2RhCl]_2$ (0.37 mmol, 145 mg) was dissolved in 5 mL of acetone and treated with 0.74 mmol of $AgBF_4$ (145 mg). After filtration 0.37 mmol of $C_5Me_5Co(COT)$ (110 mg) was added and stirring continued. Precipitation with ether yielded a black powder of 19: 180 mg (89%); IR ($CHCl_3$) 2064, 2019 cm^{-1} (C≡O). Anal. Calcd for $C_{20}H_{23}BCoF_4O_2Rh$: C, 44.15; H, 4.26; M_r, 544.02. Found: C, 44.36; H, 4.15.

$(CpRu)_2COT$ (20). K (3.4 mmol, 133 mg) in THF was treated with 1.7 mmol of C_8H_8 (180 mg) at −30 °C and stirred until all potassium had dissolved. This solution was added to a suspension of 3.4 mmol of $[CpRu(CH_3CN)_3]PF_6$ (1500 mg) in THF at −78 °C. Within 4 h the solution was warmed to room temperature and evaporated under reduced pressure. The residue was extracted with toluene and filtered. After addition of hexane, the solution was slowly cooled to −80 °C. Orange crystals separated from which the supernatant liquid was decanted. After the mixture was dried under reduced pressure, 320 mg (43%) of 20

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were obtained. Anal. Calcd for $C_{18}H_{18}Ru_2$: C, 49.53; H, 4.15; Ru, 46.31; M_r, 436.46. Found: C, 49.38; H, 4.04; Ru, 46.20.

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Registry No. **1**, 80951-04-8; **2**, 80967-94-8; **3**, 104715-97-1; **4**, 104715-99-3; **5**, 104716-01-0; **6**, 104716-03-2; **7**, 104716-05-4; **8**, 104716-06-5; **9**, 104738-02-5; **10** (isomer A), 104716-07-6; **10** (isomer B), 104716-08-7; **11**, 104716-09-8; **12**, 104760-97-6; **13**, 104716-10-1; **14**, 104716-12-3; **15**, 104760-98-7; **16**, 104716-13-4; **17**, 104716-15-6; **18**, 104716-17-8; **19**, 104738-04-7; **20**, 104738-05-8; $[C_5Me_2RHCl_2]_2$, 12354-85-7; $[C_5Me_2IrCl_2]_2$, 12354-84-6; CpCo(COT), 12110-49-5; CpRh(COT), 55480-71-2; $[CpRu(CH_3CN)_3]PF_6$, 80049-61-2; $[(C_2H_4)_2RhCl]_2$, 12081-16-2; $[CpRh(COT)RnCl]_2$, 104716-18-9; $Mg(Ind)_2$, 53042-25-4; Hmbz, 87-85-4; $[ClRh(COT)RhCl]_n$, 98092-07-0; C_5Me_5CoCOT, 78063-03-3; $[(CO)_2RhCl]_2$, 14523-22-9.

Supplementary Material Available: Tables of bond angles, anisotropic temperature factors, and hydrogen coordinates (19 pages); listings of structure factor amplitudes (99 pages). Ordering information is given on any current masthead page.

Metal–Formaldehyde Chemistry: Metal-Promoted Elementary Transformations of Formaldehyde

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Paraformaldehyde reacts with vanadocene, cp_2V (I; cp = η^5-C_5H_5), in a toluene solution to form $[cp_2V(\eta^2\text{-}CH_2O)]$ (II). The bonding mode of formaldehyde was determined by an X-ray analysis [V–C = 2.092 (8) Å, V–O = 1.955 (5) Å, and C–O = 1.353 (10) Å]. The formation of II occurred with simultaneous generation of a significant amount of HCOOMe, as a consequence of the fact that II can react further with paraformaldehyde to form HCOOMe. Disproportionation of CH_2O to HCOOMe was observed when the CH_2O ligand was removed from II by using carbon monoxide. Oxymethylene ligands containing a vanadium–carbon σ bond have been formed by reacting complex II with Lewis acids and alkylating agents. Lewis acids, like BF_3 or $TiCl_4$, or alkylating agents, such as Et_3OBF_4 or $MeSO_3F$, gave very unstable oxymethylene compounds which underwent homolytic fission of one V–C σ bond. Stable oxymethylene compounds were isolated when the alkylation of II was carried out by using acyl halides MeCOCl and PhCOCl. Compounds isolated in crystalline forms were $[cp_2V(Cl)(OC(O)Me)]$ (VI; ν(CO) = 1710 cm^{-1}) and $[cp_2V(Cl)(OC(O)OPh)]$ (VII; ν(CO) = 1690 cm^{-1}). The ionization of the V–Cl bond in VI and VII allowed the second oxygen to bind vanadium forming metallacycles $[cp_2V(CH_2\text{–}O\text{–}C(O)\text{–}Me)](BPh_4)$ (VIII) and $[cp_2V(CH_2\text{–}O\text{–}C(O)\text{–}Ph)](BPh_4)$ (IX). The CO stretching band is significantly lowered, to 1605 cm^{-1} in VIII and to 1600 cm^{-1} in IX. An important lengthening of the V–C and C–O bond distances accompanying the acylation of formaldehyde [V–C = 2.159 (4) Å and C–O = 1.474 (5) Å in complex VIII; V–C = 2.170 (7) Å, and C–O = 1.481 (8) Å in complex IX] was observed. Complexes VIII and IX did not react or only slightly reacted with CO, inducing homolytic cleavage of the V–C bond and forming $[cp_2V(CO)_2]^+$. Nickel(0)–phosphine complexes $[Ni(PR_3)_4]$ (R = *n*-Bu, XV; R = Ph, XVI) and $[Ni(PPh_3)_2(C_2H_4)]$ (XVII) promoted decomposition of formaldehyde to CO and H_2, and they formed $[Ni(PR_3)_3(CO)]$ (XVIII and XIX) and $[Ni(PPh_3)_2(CO)_2]$ (XX), respectively. Reaction of these complexes was stoichiometric, but for XVII the reaction was slightly catalytic when carried out in vacuo. A titanium(III) complex, $[cpTi(Cl)_2(THF)_{1.5}]$ (XXI), was able to promote the deoxygenation of formaldehyde to ethylene, while titanium is converted into different oxo complexes, namely, $[cpTi(Cl)_2]_2(\mu\text{-}O)$ (XXII) and $[cpTi(Cl)(\mu\text{-}O)]_4$ (XXIII). Suggestions are given on the organometallic precursors leading to the deoxygenation of formaldehyde. Crystallographic details for complex II: space group $C2/c$ (monoclinic); a = 13.634 (3) Å, b = 6.812 (1) Å, c = 20.528 (4) Å, β = 103.24 (2); V = 1855.9 (6) Å^3; Z = 8; D_{calcd} = 1.51 g cm^{-3}. The final R factor was 0.050 (R_w = 0.051) for 820 observed reflections. Crystallographic details for complex VIII: space group $P\bar{1}$ (triclinic); a = 14.542 (4) Å, b = 11.108 (4) Å, c = 10.019 (3) Å, α = 103.51 (3)°, β = 90.59 (3)°, γ = 110.39 (3)°; V = 1467.5 (9) Å^3; Z = 2; D_{calcd} = 1.30 g cm^{-3}. The final R factor was 0.057 (R_w = 0.064) for 2949 observed reflections. Crystallographic details for complex IX: space group Cc (monoclinic); a = 11.233 (1) Å, b = 16.748 (1) Å, c = 17.475 (1) Å, β = 95.57 (1)°; V = 3272.1 (4) Å^3; Z = 4; D_{calcd} = 1.29 g cm^{-3}. The final R factor was 0.037 (R_w = 0.039) for 1789 observed reflections.

Introduction

The $[M(CH_2O)]$ functionality has an unquestionable role in carbon monoxide hydrogenation promoted either by homogeneous or heterogeneous catalysts.[1] Full understanding of the chemistry of such a functionality requires, of course, syntheses of the $[M(CH_2O)]$ and $[M_2(\mu\text{-}CH_2O)]$ units and exploration of their chemistry. A number of significant issues related to this problem are listed below.

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