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Tetranuclear Homo- or Heterobimetallic Asymmetric Palladium(II)–Platinum(II) Complexes with Single Halide Bridges. Molecular Structure of $[Pt(C_6F_5)_2(\mu\text{-}Br)Pd(\eta^4\text{-}1,5\text{-}C_8H_{12})(\mu\text{-}Br)Pt(C_6F_5)_2(\mu\text{-}Br)Pd(\eta^4\text{-}1,5\text{-}C_8H_{12})(\mu\text{-}Br)]$

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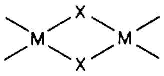
Treatment of *cis*-$[M(C_6X_5)_2(THF)_2]$ (M = Pd, Pt; X = F, Cl; THF = tetrahydrofuran) with $M'X'_2(COD)$ (M′ = Pd, Pt; X′ = Cl, Br, I; COD = 1,5-cyclooctadiene) results in the formation of homo- and heteronuclear palladium or platinum complexes of general formula $[(C_6X_5)_2M(\mu\text{-}X')_2M'(COD)]_n$ which are binuclear (n = 1) in $CHCl_3$ solutions. The molecular structure of $[Pt(C_6F_5)_2(\mu\text{-}Br)Pd(COD)(\mu\text{-}Br)Pt(C_6F_5)_2(\mu\text{-}Br)Pd(COD)(\mu\text{-}Br)]$ has been established by single-crystal X-ray crystallography, showing that the complex is tetranuclear in the solid state. The molecule resides on a center of symmetry and can be regarded as an eight-membered ring skeleton being made up of two "$Pt(C_6F_5)_2$" and two "$Pd(\eta^4\text{-}1,5\text{-}C_8H_{12})$" groups in an alternate way connected by single bromide bridges. Crystal data: monoclinic, a = 26.742 (6) Å, b = 9.3916 (18) Å, c = 18.133 (5) Å; β = 108.424 (22)°; space group $C2/c$; Z = 4. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.0369 for 3059 observed reflections.

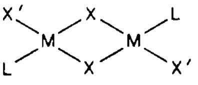
Introduction

Homobinuclear Pd(II) or Pt(II) complexes with halide bridges most frequently contain the moiety (X = halogen).

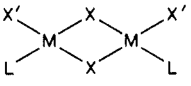


When two of the four terminal ligands are neutral (L = CO, olefin, group VB ligands) and the other two are anionic (X′ = halide, alkyl, aryl), neutral complexes of the type $[M_2(\mu\text{-}X)_2L_2X'_2]$ result. If the four terminal ligands are anionic (X′ = halide, aryl), anionic complexes $[M_2(\mu\text{-}X)_2X'_4]^{2-}$ are obtained.[1-4]

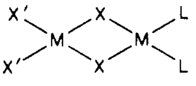
For binuclear complexes of the type $[M_2(\mu\text{-}X)_2X'_2L_2]$ three isomers, A, B, and C, are theoretically expected, but



A
trans



B
cis



C
gem or asymm

most of the hitherto reported complexes adopt structure A and complexes with structure B have been described only occasionally.[5,6] No complex with geometry C has previously been reported, despite intensive research on binuclear palladium and platinum derivatives during the last ca. 50 years.

Moreover, the only heterobimetallic halide-bridged Pd–Pt complexes isolated and unambiguously characterized so far are of type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ (structure A),[7] although other complexes containing bidentate[8-18] or polydentate[19] bridging ligands have been described.

To the best of our knowledge, the only homo- or heterobinuclear Pd(II)–Pt(II) complexes with both metal atoms linked by a single halide bridge are of the type $[(N\text{-}C\text{-}N)M'(\mu\text{-}X)M(N\text{-}C\text{-}N)]^+$ (where (N–C–N) = *o,o′*-$(Me_2NCH_2)_2C_6H_3$; M, M′ = Pd or Pt; X = halide).[20,21]

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Table I. Analytical Results (Calculated Values in Parentheses) and Other Characteristic Data

	C	H	X		mp, °C
$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(COD)]_n$ (1)	26.7 (26.6)	1.3 (1.35)	7.6 (7.8)	842 (903)	189 dec
$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pt(COD)]_n$ (2)	24.2 (24.2)	1.4 (1.2)	15.9 (16.1)	999 (992)	169 dec
$[(C_6F_5)_2Pt(\mu\text{-}I)_2Pt(COD)]_n$ (3)	22.1 (22.1)	1.15 (1.10)		1025 (1086)	170 dec
$[(C_6Cl_5)_2Pt(\mu\text{-}I)_2Pt(COD)]_n$ (4)	18.90 (19.20)	0.95 (0.95)		*a*	215 dec
$[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(COD)]_n$ (5)	33.15 (33.10)	1.85 (1.65)	9.20 (9.75)	*a*	130 dec
$[(C_6F_5)_2Pd(\mu\text{-}Br)_2Pd(COD)]_n$ (6)	29.80 (29.50)	1.75 (1.50)	19.10 (19.60)	776 (815)	142 dec
$[(C_6Cl_5)_2Pd(\mu\text{-}Cl)_2Pd(COD)]_n$ (7)	26.85 (26.95)	1.35 (1.35)	47.75 (47.75)	*a*	160 dec
$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(COD)]_n$ (8)	29.55 (29.50)	1.95 (1.50)	8.55 (8.70)	762 (815)	170 dec
$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_n$ (9)	26.90 (26.60)	1.50 (1.30)	17.90 (17.70)	877 (903)	150 dec
$[(C_6Cl_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_n$ (10)	22.25 (22.50)	1.15 (1.10)		*a*	165 dec
$[(C_6F_5)_2Pd(\mu\text{-}Br)_2Pt(COD)]_n$ (11)	26.40 (26.60)	1.45 (1.20)	17.55 (17.70)	918 (904)	107 dec
$[(C_6Cl_5)_2Pd(\mu\text{-}Br)_2Pt(COD)]_n$ (12)	22.65 (22.50)	1.10 (1.10)		*a*	191 dec

[a] Not soluble enough in $CHCl_3$ for molecular weight determination.

Table II. Some Relevant IR Absorptions (in cm^{-1})

				C_6X_5			
	COD			X-sensitive	ν(M–C)	others	ν(M–X)
$[PdCl_2(COD)]$	1524, 1512, 1423	684	560, 454	...	...	...	336–327, 298
$[PdBr_2(COD)]$	1524, 1514, 1420	697	553, 450	...	...	...	...
$[PtCl_2(COD)]$	1496, ..., 1430	695	580, 474, 455	...	...	...	337, 316
$[PtBr_2(COD)]$	1500, ..., 1425	693	574, 469, 448	...	...	...	215
$[PtI_2(COD)]$	1500, ..., 1422	690	566, 459, 443	...	...	...	...
$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(COD)]_n$ (1)	..., 1430 (sh)	695	575, 469	817, 806	...	1505, 961	350, 340, 312
$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pt(COD)]_n$ (2)	..., 1430 (sh)	695	572, 466, 450	814, 803	...	1503, 960	215
$[(C_6F_5)_2Pt(\mu\text{-}I)_2Pt(COD)]_n$ (3)	..., 1428	690	566, 459	807, 798	...	1502, 963–927	...
$[(C_6Cl_5)_2Pt(\mu\text{-}I)_2Pt(COD)]_n$ (4)	1504, ..., 1430	694	560, 458	847, 851	630, 620	1328, 1310, 1290, 1213, 676	...
$[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(COD)]_n$ (5)	1518, ..., 1427	682	550, 447	800, 791	...	1500, 960	327, 312, 285, 270
$[(C_6F_5)_2Pd(\mu\text{-}Br)_2Pd(COD)]_n$ (6)	1515, ..., 1425	680	545, 440	796, 783	...	1500, 957	...
$[(C_6Cl_5)_2Pd(\mu\text{-}Cl)_2Pd(COD)]_n$ (7)	1520, 1502, 1424	...	555, 452	840, 834	624, 615	1327, 1317, 1290, 1220, 675	330, 282, 255
$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(COD)]_n$ (8)	1520, ..., 1430	679	556, 452	814, 803	...	1500, 960	335, 325, 305, 300
$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_2$ (9)	1524, ..., 1425	671	544, 436	812, 802	...	1500, 958	...
$[(C_6Cl_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_n$ (10)	1520, 1503, 1423	...	549, 444	849, 841	832, 622	1331, 1320, 1292, 1214, 678	...
$[(C_6F_5)_2Pd(\mu\text{-}Br)_2Pt(COD)]_n$ (11)	..., ..., 1430 (sh)	685	564, 464	803, 796	...	1503, 960	...
$[(C_6Cl_5)_2Pd(\mu\text{-}Br)_2Pt(COD)]_n$ (12)	1500, ..., 1432	...	567, 464	842, 838	623, 613	1324, 1317, 1288, 1220, 674	...

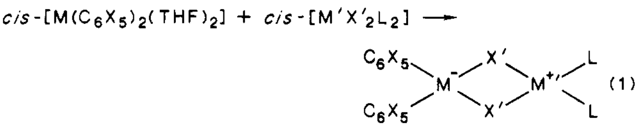
Here, we report the synthesis of homo- or heteronuclear Pd(II)–Pt(II) complexes of the type $[(C_6X_5)_2M^-(\mu\text{-}X')_2M^{+\prime}(COD)]_n$ which are binuclear ($n = 1$) in chloroform solution and, according to their NMR spectra, seem to be the first asymmetric (structure C) binuclear Pd–Pt complexes.

In the solid state, however, they rearrange to give a tetranuclear eight-membered ring with alternating Pd and Pt atoms singly bridged by halide ions, $[M(C_6X_5)_2(\mu\text{-}X')M'(COD)(\mu\text{-}X')M(C_6X_5)_2(\mu\text{-}X')M'(COD)(\mu\text{-}X')]$, as has been established by an X-ray crystallographic study on $[(C_6F_5)_2Pt(\mu\text{-}Br)Pd(COD)]_2$. Preliminary results on these complexes have been reported earlier,[22] and very recently other authors[23] have claimed the synthesis of mixed binuclear asymmetric complexes with double halide bridges but without structural support.

Results and Discussion

We have recently reported the synthesis of *cis*-$[M(C_6X_5)_2(THF)_2]$ (M = Pd, Pt; X = F, Cl; THF = tetrahydrofuran) and have shown that they are excellent precursors for the preparation of *cis*-dicarbonyl[24,25] or *cis*-bis(acetylene)[26] complexes of palladium and platinum because of the facile displacement of the neutral THF ligands from the original complexes.

Reaction of *cis*-$[M(C_6X_5)_2(THF)_2]$ with complexes of the type *cis*-$M'X'_2L_2$ (M′ = Pd, Pt; X′ = halide; L = neutral ligand) is a promising approach for the synthesis of binuclear asymmetric homo- or heterometallic complexes, as represented in eq 1.



(1)

To ensure that the complexes $M'X'_2L_2$ have the required cis configuration, we have used palladium(II) or platinum(II) complexes containing a chelating ligand (L_2 = COD = 1,5-cyclooctadiene). The room-temperature (1:1) reaction of *cis*-$[M(C_6X_5)_2(THF)_2]$ and *cis*-$[M'X'_2(COD)]$ causes in most cases a visible color change. The pentachlorophenyl derivatives (X = Cl) precipitate out during the reaction, while the isolation of the pentafluorophenyl complexes (X = F) requires evaporation of the solvent (CH_2Cl_2). Appropriate choice of the reagents allows the synthesis of homo- or heteronuclear complexes (eq 2).

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$$n\,cis\text{-}M(C_6X_5)_2(THF)_2 + nM'X'_2(COD) \rightarrow \underset{1-12}{[(C_6X_5)_2M(\mu\text{-}X')_2M'(COD)]_n} + 2nTHF \quad (2)$$

M = M′ = Pt; X = F, X′ = Cl (**1**), Br (**2**), I (**3**);
X = Cl, X′ = I (**4**)

M = M′ = Pd; X = F, X′ = Cl (**5**), Br (**6**);
X = Cl, X′ = Cl (**7**)

M = Pt, M′ = Pd; X = F, X′ = Cl (**8**), Br (**9**);
X = Cl, X′ = Br (**10**)

M = Pd, M′ = Pt; X = F, X′ = Br (**11**);
X =Cl, X′ = Br (**12**)

Table I collects analytical and other data for complexes **1**–**12**. Table II lists some relevant IR absorptions: along with bands due to the neutral ligand (COD)[27,28] all the complexes show two bands assignable to the X-sensitive mode of the C_6X_5 groups[3,4,29] which also retain their cis positions. This is further supported by the observation of two absorptions due to ν(M-C) in the pentachlorophenyl derivatives.[30] A maximum of four absorptions in the ν(metal–halide) region are also found (Table II).

The ^{19}F NMR spectra of bis(pentafluorophenyl)platinum complexes **1**, **2**, **3**, **8**, and **9** (the palladium complexes show decomposition during the time required to record the spectra) show three signals corresponding to F_o, F_m, and F_p, the first with platinum satellites (see Table III). Both C_6F_5 groups are equivalent and freely rotating around the Pt–C bonds.

All the data so far discussed are compatible with a value of 1 for n (eq 2), i.e. with a binuclear asymmetric structure for the reported complexes. Moreover, molecular weight determinations (isopiestic, in $CHCl_3$ solution) are in agreement with this view (Table I) for all the complexes which are soluble enough to permit the measurement **1**, **2**, **3**, **6**, **8**, and **9**.

All the complexes are soluble in acetone, and these solutions are nonconducting, and colorless or only pale yellow, in contrast with the deeply coloured solids. If acetone solutions of complexes **2** or **3** are vacuum evaporated to dryness, yellow solids are obtained. Their IR spectra show a strong absorption at ~1650 cm^{-1}, which indicates the presence of coordinated acetone. By heating the yellow solids at 60 °C under vacuum the original complexes **2** or **3** are recovered. Seemingly, an excess of acetone causes decomposition of the complexes (eq 3).

$$1/n[(C_6X_5)_2M(\mu\text{-}X')_2M'(COD)]_n \underset{-OCMe_2}{\overset{+OCMe_2}{\rightleftharpoons}} cis\text{-}[M(C_6X_5)_2(OCMe_2)_x] + [M'X'_2(COD)] \quad (3)$$

Upon vacuum concentration of an acetone solution of complex **3** yellow crystals of $PtI_2(COD)$ separate, in support of the proposed decomposition scheme (eq 3).

Generally, solutions of the complexes in nondonor solvents (CH_2Cl_2, $CHCl_3$) show changes in color, some of which are quite dramatic (see Table IV) which may be indicative of some structural change. To ascertain this possibility the structure of $[(C_6F_5)_2Pt^-(\mu\text{-}Br)_2Pd^+(COD)]$ (**9**) has been solved by single-crystal X-ray crystallography. General crystallographic information is presented in Table V. Positional parameters and bond distances and angles are given in Table VI and VII, respectively. The molecular structure (Figure 1) shows a tetranuclear complex $[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_2$ with an eight-membered ring as central core formed by two palladium, two platinum, and four bromine atoms. The ring has distorted chair structure about a center of symmetry (Figure 2), and platinum atoms are linked to palladium through single bridging bromine atoms. The Pd⋯Pt, Pt⋯Pt, or Pd⋯Pd distances are longer than 3.6 Å, thus precluding any kind of M–M interaction. The environment around the platinum atom is almost square-planar; the angles between cis ligand–metal bonds are in the range 87.2–95.0°. The Pt–C1 and Pt–C7 distances are 1.975 (9) and 1.967 (9) Å

Table III. ^{19}F NMR Spectra[a]

	F_o	F_p	F_m	$^3J_{Pt-F_o}$
$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(COD)]_n$ (**1**)	-120.1	-160.9	-164.1	494
$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pt(COD)]_n$ (**2**)	-121.1	-162.5	-165.5	390
$[(C_6F_5)_2Pt(\mu\text{-}I)_2Pt(COD)]_n$ (**3**)	-120.0	-162.9	-165.5	485
$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(COD)]_n$ (**8**)	-121.7	-162.7	-165.6	507
$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_n$ (**9**)	-120.9	-162.8	-165.6	504

[a] δ referenced to $CFCl_3$; J in Hz; solvent $CDCl_3$.

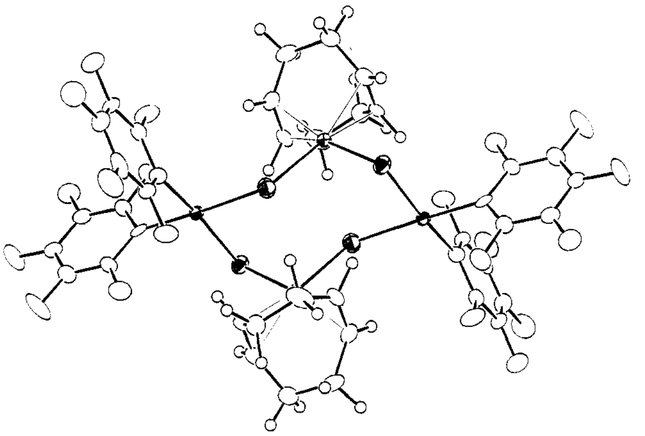

Figure 1. The molecular geometry of $[Pt(C_6F_5)_2(\mu\text{-}Br)Pd(\eta^4\text{-}1,5\text{-}C_8H_{12})(\mu\text{-}Br)Pt(C_6F_5)_2(\mu\text{-}Br)Pd(\eta^4\text{-}1,5\text{-}C_8H_{12})(\mu\text{-}Br)]$ complex (**9**).

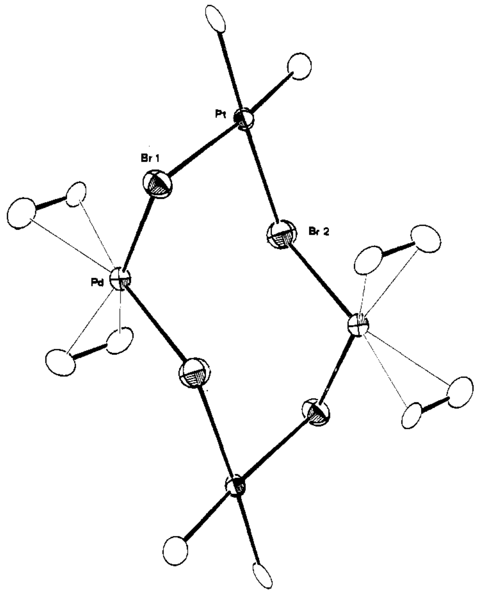

Figure 2. Central core of complex **9**.

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Table IV. Experimental Conditions in the Synthesis of Complexes 1-12 by Eq 2[a] and Other Data

complex	*cis*-[M(C_6X_5)$_2$(THF)$_2$], g (mmol)	[M′X′$_2$(COD)], g (mmol)	yield, %	color		
				solid	CH_2Cl_2 soln	acetone soln
1	0.17 (0.25)	0.093 (0.25)	96	yellow	yellow	colorless
2	0.17 (0.25)	0.137 (0.24)	61	yellow	yellow	colorless
3	0.17 (0.25)	0.071 (0.25)	81	yellow	orange	yellow
4	0.14 (0.17)	0.094 (0.17)	96	orange	orange[b]	yellow
5	0.14 (0.28)	0.070 (0.25)	87	yellow	orange	yellow
6	0.12 (0.21)	0.079 (0.21)	83	orange	red	yellow
7	0.16 (0.22)	0.063 (0.22)	77	red	red	yellow
8	0.17 (0.25)	0.071 (0.25)	81	salmon	green	yellow
9	0.17 (0.25)	0.090 (0.24)	83	garnet	green	yellow
10	0.14 (0.17)	0.063 (0.17)	83	garnet	green[b]	yellow
11	0.12 (0.21)	0.097 (0.21)	84	brown	yellow	colorless
12	0.14 (0.19)	0.087 (0.19)	60	yellow	orange	colorless

[a] The reactions have been carried out in 20 mL of CH_2Cl_2; room temperature. For complexes **7** and **11** at 0 °C. [b] Scarcely soluble.

Table V. Crystal Data for 9

formula	$C_{40}H_{24}Pd_2Pt_2Br_4F_{20}$
mol wt	1807.02
source of crystals	solvent diffusion (CH_2Cl_2; *n*-hexane), −30 °C
cryst size, mm	0.4 × 0.25 × 0.25
cryst system	monoclinic
space group	*C*2/*c*
a, Å	26.742 (6)
b, Å	9.3916 (18)
c, Å	18.133 (5)
β, deg	108.424 (22)
V, Å^3	4320.68
diffractometer	Enraf-Nonius CAD 4
T, K	185 ± 1
radiatn	Mo K*α*
λ, Å	0.71069
μ(Mo K*α*), cm^{-1}	106.87; empirical absorption correction was applied[40]
θ range, deg	1–25; $+h,+k,\pm l$
mode	ω–2θ scans
data measd	3788
data reductn procedure	CADABS;[41] no detectable crystal movement or decay over ~63 X-ray hours
data used ($F \geq 6\sigma(F)$)	3059
soln	direct methods (SHELX76), ΔF syntheses
refinement	full-matrix least squares
model	all atoms except hydrogen have been refined with anisotropic thermal parameters; the hydrogen atoms of the 1,5-cyclooctadiene rings has been placed in calculated positions; group *U*'s for hydrogen atoms (0.053 (11) Å^2)
weighting scheme	$w^{-1} = [\sigma^2(F) + 0.0016F^2]$
R	0.037
R_w	0.041
variables	308
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	1.13

Table VI. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters of Refined Atoms in Complex 9

	x	*y*	*z*	*B*, Å^2
Pt	3418 (1)	8537 (1)	6582 (1)	1.24 (2)
Pd	2021 (1)	7719 (1)	5782 (1)	1.36 (4)
Br1	2807 (1)	6541 (1)	6663 (1)	2.07 (5)
Br2	2951 (1)	9085 (1)	5184 (1)	2.34 (5)
F1	4590 (2)	8751 (6)	6541 (4)	2.87 (35)
F2	5213 (2)	11006 (7)	6557 (4)	3.30 (37)
F3	4847 (3)	13635 (7)	6584 (4)	4.19 (45)
F4	3837 (3)	14051 (6)	6611 (4)	3.55 (39)
F5	3217 (2)	11840 (6)	6584 (3)	2.50 (32)
F6	4344 (2)	6430 (6)	7440 (3)	2.68 (33)
F7	4941 (2)	6266 (6)	8943 (4)	2.81 (34)
F8	4751 (3)	8009 (9)	10003 (3)	4.22 (40)
F9	3956 (3)	9900 (9)	9580 (4)	5.15 (47)
F10	3345 (2)	10108 (6)	8090 (3)	2.67 (32)
C1	3880 (4)	10179 (10)	6582 (5)	1.65 (46)
C2	4397 (4)	10063 (10)	6563 (5)	1.86 (47)
C3	4710 (4)	11197 (11)	6569 (6)	2.14 (52)
C4	4531 (4)	12546 (11)	6587 (6)	2.60 (58)
C5	4025 (5)	12738 (10)	6599 (6)	2.70 (59)
C6	3719 (4)	11570 (10)	6592 (5)	1.96 (50)
C7	3817 (3)	8284 (9)	7689 (5)	1.30 (43)
C8	4225 (4)	7328 (9)	7953 (5)	1.60 (46)
C9	4540 (4)	7206 (10)	8725 (6)	2.11 (51)
C10	4445 (4)	8106 (12)	9267 (6)	2.25 (53)
C11	4043 (4)	9038 (11)	9037 (6)	2.40 (56)
C12	3737 (4)	9113 (10)	8275 (5)	1.73 (48)
C13	2095 (4)	9583 (11)	6558 (5)	1.91 (49)
C14	1818 (4)	8537 (11)	6789 (6)	2.41 (56)
C15	1219 (4)	8466 (13)	6570 (6)	2.94 (63)
C16	923 (4)	8877 (15)	5717 (7)	3.67 (69)
C17	1197 (4)	8375 (11)	5166 (6)	2.33 (54)
C18	1531 (4)	9232 (11)	4939 (5)	2.15 (51)
C19	1714 (5)	10711 (11)	5232 (7)	3.21 (69)
C20	1862 (4)	10875 (11)	6091 (6)	2.56 (57)

similar to those observed in other complexes containing the "*cis*-Pt(C_6F_5)$_2$" moiety.[26,31,32] Palladium atoms are in an almost square-planar environment defined by the two bromines and by the midpoints of the olefinic carbon–carbon bonds. The angle Br(1)–Pd–Br(2) is 86.61 (4)°, and the olefin midpoint–Pd–olefin midpoint angle is 86.4 (4)°. The C=C distances are C(13)–C(14) = 1.372 (14) Å and C(17)–C(18) = 1.360 (15) Å. The Pd–C(13), Pd–C(14), Pd–C(17), and Pd–C(18) distances are 2.215 (9), 2.202 (10), 2.222 (10), and 2.193 (9) Å, respectively, and the palladium–olefin midpoint distances are 2.099 and 2.100 Å. Thus the "Pd(COD)" fragment in **9** has similar distances and angles to those observed in $PdCl_2$(1,5-COD).[33]

Dimensions involving the bridging bromide ligands are of interest: Pt–Br(1) and Pd–Br(1) are 2.524 (1) and 2.463 (1) Å, respectively, whereas Pt–Br(2) and Pd′–Br(2) are 2.500 (1) and 2.455 (2) Å, respectively. These M–Br distances are similar to those observed in other palladium[34] and platinum[35] complexes with bridging bromide. However, although the covalent radii of (square-planar) Pd(II) and Pt(II) are nominally the same (1.31 Å),[36] the Pt–Br

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Table VII. Bond Distances (Å) and Bond Angles (deg) for Complex 9

Bond Distances

Br1–Pt	2.524 (1)	C6–F5	1.361 (12)	C12–C7	1.387 (13)
Br2–Pt	2.500 (1)	C8–F6	1.366 (10)	C9–C8	1.391 (13)
C1–Pt	1.974 (9)	C9–F7	1.348 (11)	C10–C9	1.380 (14)
C7–Pt	1.967 (9)	C10–F8	1.331 (11)	C11–C10	1.346 (15)
Br1–Pd	2.463 (1)	C11–F9	1.350 (12)	C12–C11	1.366 (14)
Br2′–Pd[a]	2.455 (1)	C12–F10	1.366 (10)	C14–C13	1.373 (14)
C13–Pd	2.215 (9)	C2–C1	1.399 (13)	C20–C13	1.497 (14)
C14–Pd	2.201 (10)	C6–C1	1.377 (13)	C15–C14	1.523 (15)
C17–Pd	2.221 (10)	C3–C2	1.354 (13)	C16–C15	1.547 (15)
C18–Pd	2.193 (9)	C4–C3	1.358 (14)	C17–C16	1.488 (16)
C2–F1	1.341 (11)	C5–C4	1.373 (16)	C18–C17	1.359 (15)
C3–F2	1.364 (12)	C6–C5	1.366 (14)	C19–C18	1.512 (14)
C4–F3	1.327 (11)	C8–C7	1.377 (13)	C20–C19	1.490 (15)
C5–F4	1.334 (12)				

Bond Angles

Br2–Pt–Br1	95.0 (1)	C1–C6–F5	119.2 (8)	C15–C14–Pd	106.4 (7)
C1–Pt–Br1	175.4 (3)	C5–C6–F5	115.9 (9)	C15–C14–C13	125.1 (10)
C1–Pt–Br2	87.2 (3)	C5–C6–C1	124.9 (9)	C15–C14–H14	117.4 (6)
C7–Pt–Br1	90.1 (2)	C8–C7–Pt	123.2 (7)	H15–C15–C14	108.2 (6)
C7–Pt–Br2	174.6 (3)	C12–C7–Pt	123.3 (7)	H15′–C15–C14	108.2 (6)
C7–Pt–C1	87.6 (4)	C12–C7–C8	113.3 (8)	C16–C15–C14	114.4 (9)
Br1–Pd–Br2′	86.6 (1)	C7–C8–F6	119.7 (8)	C16–C15–H15	108.2 (7)
C13–Pd–Br1	93.3 (2)	C9–C8–F6	115.8 (8)	C16–C15–H15′	108.2 (7)
C14–Pd–Br1	90.2 (3)	C9–C8–C7	124.5 (8)	H16–C16–C15	108.7 (7)
C14–Pd–C13	36.2 (4)	C8–C9–F7	121.5 (9)	H16′–C16–C15	108.6 (6)
C17–Pd–Br1	163.4 (3)	C10–C9–F7	120.1 (9)	C17–C16–C15	112.8 (9)
C17–Pd–C13	88.5 (4)	C10–C9–C8	118.4 (9)	C17–C16–H16	108.6 (7)
C17–Pd–C14	81.6 (4)	C9–C10–F8	118.6 (9)	C17–C16–H16′	108.6 (6)
C18–Pd–Br1	160.5 (3)	C11–C10–F8	122.3 (9)	C16–C17–Pd	111.8 (7)
C18–Pd–C13	81.0 (4)	C11–C10–C9	119.1 (9)	H17–C17–Pd	87.4 (3)
C18–Pd–C14	95.8 (4)	C10–C11–F9	117.9 (9)	H17–C17–C16	119.2 (7)
C18–Pd–C17	35.9 (4)	C12–C11–F9	121.4 (9)	C18–C17–Pd	70.9 (6)
Pd–Br1–Pt	93.7 (1)	C12–C11–C10	120.7 (9)	C18–C17–C16	121.7 (10)
Pt–Br2–Pd′	117.6 (1)	C7–C12–F10	119.2 (8)	C18–C17–H17	119.2 (6)
C2–C1–Pt	124.2 (7)	C11–C12–F10	116.8 (8)	C17–C18–Pd	73.2 (6)
C6–C1–Pt	122.9 (7)	C11–C12–C7	123.9 (9)	H18–C18–Pd	89.6 (3)
C6–C1–C2	112.9 (8)	H13–C13–Pd	88.5 (2)	H18–C18–C17	116.3 (6)
C1–C2–F1	117.8 (8)	C14–C13–Pd	71.4 (6)	C19–C18–Pd	107.1 (7)
C3–C2–F1	118.6 (8)	C14–C13–H13	117.1 (6)	C19–C18–C17	127.5 (9)
C3–C2–C1	123.6 (9)	C20–C13–Pd	110.1 (6)	C19–C18–H18	116.3 (6)
C2–C3–F2	120.5 (9)	C20–C13–H13	117.1 (6)	H19–C19–C18	108.2 (6)
C4–C3–F2	118.7 (9)	C20–C13–C14	125.8 (9)	H19′–C19-C18	108.3 (6)
C4–C3–C2	120.8 (9)	C13–C14–Pd	72.4 (6)	C20–C19–C18	114.3 (9)
C3–C4–F3	119.3 (10)	H14–C14–Pd	91.2 (3)	C20–C19–H19	108.3 (6)
C5–C4–F3	122.0 (10)	H14–C14–C13	117.5 (6)	C20–C19–H19′	108.3 (6)
C5–C4–C3	118.7 (9)			C19–C20–C13	115.7 (9)
C4–C5–F4	120.0 (10)			H20–C20–C13	107.9 (5)
C6–C5–F4	121.0 (11)			H20–C20–C19	107.9 (6)
C6–C5–C4	119.0 (10)			H20′–C20–C13	107.9 (5)
				H20′–C20–C19	107.9 (6)

[a] By symmetry.

bonds are both longer than Pd–Br, reflecting the different trans influences of the C_6F_5 and olefin ligands.

The two bromide bridges in **9** are themselves quite different in that the Pt–Br–Pd angle at Br(1) is 93.64 (4)° while that at Br(2) is much wider, 117.62 (4)°. Moreover, the Br(1)–Pt and Br(1)–Pd bonds are both longer, by 0.024 and 0.008 Å, respectively, than the corresponding bonds from Br(2).

The tetranuclear single-bridged structure of complex **9** in the solid state contrasts with the usual binuclear double-bridged structures of halide bridged palladium or platinum complexes (eq 1) and is the more remarkable in that the species is clearly only binuclear in $CHCl_3$ solution. The bi- to tetranuclear rearrangement, which involves the formal breaking of at least one metal–bromide bond, appears to be fully reversible on redissolution. Furthermore, this feature would appear to be quite general for complexes **1**–**12**; in fact complex **2** was examined crystallographically and shown to be isomorphous with complex **9** and must therefore be tetranuclear, showing that the rearrangement does not necessarily involve a change in color.

Experimental Section

The C, H analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates were used). Molecular weights were determined in $CHCl_3$ solution with a Knauer digital osmometer. Molar conductivities were determined in 5×10^{-4} M acetone solutions. Decomposition points of the complexes were determined with a Büchi (mod. Dr. Tottoli) apparatus; chlorine and bromine analyses were made as described by White,[37] a few milligrams of sucrose being added to facilitate combustion.[38] ^{19}F NMR spectra were recorded at room temperature on a Varian XL 200 instrument.

cis-$[Pt(C_6X_5)_2(OC_4H_8)_2]$ (X = F, Cl) was prepared as described elsewhere[25] and $[M'X'_2(COD)]$ (M′ = Pd, Pt; X′ = Cl, Br, I) were prepared according to ref 39.

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(a) *cis*-[Pd(C_6X_5)$_2$(OC_4H_8)$_2$] (X = F, Cl). X = F. $AgClO_4$ (0.256 g, 1.24 mmol) was added to a freshly distilled tetrahydrofuran solution (20 mL) of 0.944 g (0.62 mmol) of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$[3] under nitrogen, and the mixture was stirred at room temperature for 20 min. The resulting suspension was evaporated to dryness, and the residue was extracted from the insoluble residue ($AgCl + NBu_4ClO_4$) with 50 mL of diethyl ether. The solution was evaporated to ca. 5 mL, and, by addition of 20 mL of *n*-hexane, a white solid was obtained (0.37 g, 90% yield).

X = Cl was obtained similarly: 0.45 g (0.257 mmol) of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$[4] and 0.106 g (0.51 mmol) of $AgClO_4$ [0.3 g (80%) yield].

(b) $[(C_6X_5)_2M(\mu\text{-}X')_2M'(COD)]_n$ (1–12) (See Tables I–IV). Complexes 1–12 were obtained by reacting *cis*-$[M(C_6X_5)_2(THF)_2]$ with $[M'X'_2(COD)]$ (molar ratio 1:1) in CH_2Cl_2. A typical preparation is given below.

$[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)]_n$ (2). To a dichloromethane solution (20 mL) of *cis*-$[Pt(C_6F_5)_2(THF)_2]$ (0.17 g, 0.25 mmol) was added 0.111 g (0.25 mmol) of $[PdBr_2(COD)]$, and the solution was stirred for 10 min at room temperature. After evaporation to dryness the resulting residue was washed with *n*-hexane and stirred for 10 min with 10 mL of benzene. The yellow solid so obtained contains benzene of crystallization. This can be removed by heating (80 °C for 5 h), affording 0.15 g (61%) of pure complex **2**. Crystals suitable for X-ray diffraction were obtained by solvent diffusion (CH_2Cl_2/*n*-hexane) at −30 °C.

Table IV collects pertinent information on the preparation of the other complexes.

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Registry No. **1** (*n* = 1), 113778-23-7; **1** (*n* = 2), 113778-12-4; **2** (*n* = 1), 113778-24-8; **2** (*n* = 2), 113778-13-5; **3** (*n* = 1), 113778-33-9; **3** (*n* = 2), 113778-14-6; **4** (*n* = 1), 113778-25-9; **4** (*n* = 2), 113778-15-7; **5** (*n* = 1), 113778-26-0; **5** (*n* = 2), 113778-16-8; **6** (*n* = 1), 113778-27-1; **6** (*n* = 2), 113778-17-9; **7** (*n* = 1), 113778-28-2; **7** (*n* = 2), 113778-18-0; **8** (*n* = 1), 113778-29-3; **8** (*n* = 2), 113778-19-1; **9** (*n* = 1), 113778-30-6; **9** (*n* = 2), 113778-20-4; **10** (*n* = 1), 113778-31-7; **10** (*n* = 2), 113778-21-5; **11** (*n* = 1), 113778-32-8; **11** (*n* = 2), 113778-22-6; **12** (*n* = 1), 113792-86-2; **12** (*n* = 2), 113792-85-1; *cis*-$[Pd(C_6F_5)_2(OC_4H_8)_2]$, 97877-50-4; *cis*-$[Pd(C_6Cl_5)_2(OC_4H_8)_2]$, 97877-51-5; $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$, 74436-10-5; $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$, 86392-02-1; $[PdCl_2(COD)]$, 12107-56-1; $[PdBr_2(COD)]$, 12145-47-0; $[PtCl_2(COD)]$, 12080-32-9; $[PtBr_2(COD)]$, 12145-48-1; $[PtI_2(COD)]$, 12266-72-7; *cis*-$[Pt(C_6F_5)_2(OC_4H_8)_2]$, 97877-52-6; *cis*-$[Pt(C_6Cl_5)_2(OC_4H_8)_2]$, 97877-53-7.

Supplementary Material Available: Tables of H-atom coordinates and anisotropic thermal parameters (2 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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X-ray Structural Studies of Tricarbonyl(cyclohexadienyl)manganese, Dicarbonylnitrosyl(cyclohexadienyl)manganese, and Dicarbonylnitrosyl(cyclohexadiene)manganese Complexes

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X-ray structures are reported for three complexes relevant to the chemistry of arene functionalization as mediated by the $Mn(CO)_3$ and $Mn(CO)_2NO$ fragments. $(C_6H_6Ph)Mn(CO)_3$ (**4**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.159$ (3) Å, $b = 9.711$ (3) Å, $c = 12.990$ (3) Å, $\beta = 94.73$ (2)°, $Z = 4$, $R = 0.029$, and $R_w = 0.030$. The phenyl group is positioned exo to the metal, and the dihedal angle between the planar dienyl carbons (C5–C6–C7–C8–C9) and the nonbonded plane (C5–C4–C9) is 36.5°. $[(C_6H_6Me)Mn(CO)_2NO]PF_6$ (**5**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.241$ (2) Å, $b = 9.292$ (2) Å, $c = 11.088$ (2) Å, $\beta = 104.87$ (1)°, $Z = 4$, $R = 0.032$, and $R_w = 0.041$. The methyl group is exo, and the dihedral angle between the bonded plane (C3–C4–C5–C6–C7) and the nonbonded plane (C3–C2–C7) of the cyclohexadienyl ring is 39.6°. $[(C_6H_6Ph\ PBu_3)Mn(CO)_2NO]PF_6$ (**6**) crystallizes in the monoclinc space group $P2_1/c$ with $a = 9.911$ (2) Å, $b = 14.624$ (3) Å, $c = 21.771$ (4) Å, $\beta = 100.41$ (2)°, $Z = 4$, $R = 0.049$, and $R_w = 0.047$. The PBu_3 group is exo, and the dihedral angle between the diene plane (C5–C6–C7–C8) and the nonbonded plane (C5–C4–C3–C8) is 40.8°. The NO ligand in **5** and **6** is positioned under the unsaturated part of the coordinated ring.

Introduction

It recently has been demonstrated that manganese-mediated functionalization of arenes is a promising synthetic procedure.[1] Thus, the addition of phosphorus, hydride, and carbon donor nucleophiles to (arene)$Mn(CO)_3^+$ occurs with high regio- and stereoselectivity as shown in Scheme I. The functionalized arene can be

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[†] Contribution no. 4526.

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