Cationic hexamethylbenzene-diene cobalt complexes

D. A. Loginov, A. A. Pronin, Z. A. Starikova, P. V. Petrovskii, and A. R. Kudinov★

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085. E-mail: arkudinov@ineos.ac.ru

Cationic complexes $[(\text{diene})\text{Co}(\eta\text{-C}_6\text{Me}_6)]^+$ (diene is buta-1,3-diene (**2a**), 5-isopropyl-2-methylcyclohexa-1,3-diene (**2b**), cycloocta-1,3-diene (**2c**), and cyclohexa-1,5-diene (**2d**)) were synthesized by the reaction of $[\text{Co}(\eta\text{-C}_6\text{Me}_6)_2]^+$ (**1**) with dienes in a CH_2Cl_2—Me_2CO mixture. In the absence of dienes, cation **1** undergoes hydrogenation to form $[(1,2,3,4,5,6\text{-HMCD-}1,3)\text{-Co}(\eta\text{-C}_6\text{Me}_6)]^+$ (HMCD is hexamethylcyclohexadiene, **2e**). Structures $[\textbf{2c—e}]\text{PF}_6$ were determined by X-ray diffraction analysis. According to the DFT calculations, the Co—C_6H_6 bond in the complexes with conjugated dienes is stronger than that in the complexes with nonconjugated dienes.

Key words: arene complexes, diene complexes, cobalt, sandwich compounds.

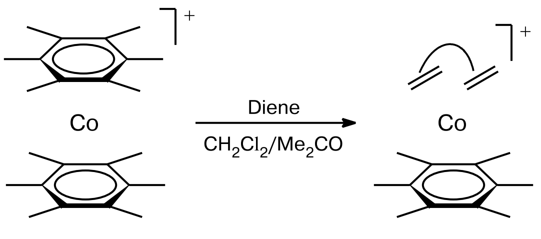
Among arene complexes, the dicationic derivatives $[(\eta\text{-C}_5\text{R}_5)\text{Co}(\eta\text{-arene})]^{2+}$ are studied in most detail.[1—6] We have earlier synthesized the monocationic complexes containing the cyclobutadiene and borol ligands, $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\eta\text{-C}_6\text{H}_6)]^+$ (see Ref. 7) and $[(\eta\text{-C}_4\text{H}_4\text{BR})\text{Co}(\eta\text{-C}_6\text{H}_6)]^+$.[8] They were used in organometallic synthesis as synthones of the $(\eta\text{-C}_4\text{Me}_4)\text{Co}$ и $(\eta\text{-C}_4\text{H}_4\text{BR})\text{Co}$ fragments due to the lability of the Co—C_6H_6 bond.[9—16]

At the same time, the complexes with simple diene ligands remain poorly studied. The general method for the synthesis of the $[(\text{diene})\text{Co}(\eta\text{-arene})]^+$ complexes (diene is cyclopentadiene, cyclohexa-1,3-diene, and cycloocta-1,5-diene) was developed.[17] The method is based on the protonation of $(\eta^1,\eta^2\text{-COK})\text{Co}(\eta\text{-arene})$ (COK is cyclooctenyl) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in the presence of dienes. The cyclooctadiene complex $[(\eta^2,\eta^2\text{-COD})\text{Co}(\eta\text{-}1,2,4,5\text{-C}_6\text{H}_2\text{Me}_4)]\text{BF}_4$ (COD is cyclooctadiene) has recently been characterized structurally[18]. The $[(\text{diene})\text{Co}(\eta\text{-C}_6\text{Me}_6)]^+$ cations were prepared by the reaction of the labile 20-electron complex $[\text{Co}(\eta\text{-C}_6\text{Me}_6)_2]^+$ (**1**) with dienes in propylene carbonate.[19,20] Cyclohexa-1,3-diene, cyclohepta-1,3-diene, norbornadiene, and cycloocta-1,5-diene were used as dienes. The results of more detailed study of this reaction and the structures of the synthesized complexes are described in this work.

Results and Discussion

The substitution of one hexamethylbenzene ligand in cation **1** for diene gave the complexes with buta-1,3-diene (**2a**) and 5-isopropyl-2-methylcyclohexa-1,3-diene (**2b**) and the earlier known derivatives with cyclohexa-1,3-diene (**2c**) and cycloocta-1,5-diene (**2d**) (Scheme 1) in high (80—90%) yields.* Dichloromethane with an additive of a small amount of acetone (~1%) was used as a solvent, which significantly simplifies the isolation procedure compared to earlier described propylene carbonate used for this purpose.

Scheme 1



1 **2a—d**

Diene is buta-1,3-diene (**a**), 5-isopropyl-2-methylcyclohexa-1,3-diene (**b**), cyclohexa-1,3-diene (**c**), and cycloocta-1,5-diene (**d**)

However, in the case of the reaction of cation **1** with pentamethylcyclopentadiene, quinone, 1,1,4,4-tetramethylbutadiene, and cycloheptatriene, the complexe with 1,2,3,4,5,6-hexamethylcyclohexa-1,3-diene (**2e**) was isolated in 30% yield instead of the expected diene derivatives. The same complex is formed in the absence of diene ligands, after the 24-h storage of a solution of compound **1** in a CH_2Cl_2—Me_2CO mixture (Scheme 2). According to the X-ray diffraction data (see further), the hydrogen atoms in the diene ligand are in the *exo*-position. The related

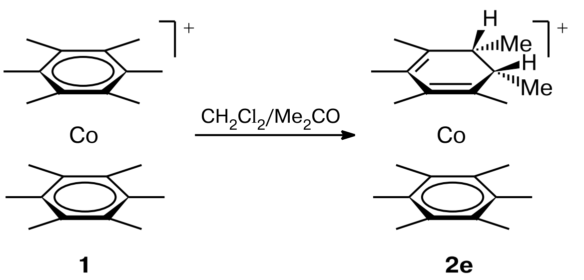
---

* All obtained cationic complexes were isolated as salts with the PF_6^- anion (anions are omitted in the schemes).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 44—49, January, 2012.

rhodium complex has been obtained earlier[21] by the reduction of $[\mathrm{Rh}(\eta\text{-}\mathrm{C_6Me_6})_2]^+$ with Zn/HCl. It is likely that the hydrogenation is heterogeneous on the zinc surface without participation of the rhodium atom. In our case, a similar process can involve active cobalt-containing particles* formed during the reaction upon the decomposition of the initial complex **1**. Probably, the driving force of these reactions is the formation of the stable 18-electron complex from the 20-electron complex.

Scheme 2



Diene complexes [**2a**—**e**]$\mathrm{PF_6}$ are yellow solids stable in air. Their structures were confirmed by the ^{1}H NMR spectroscopy data, and the structures of complexes [**2c**—**e**]$\mathrm{PF_6}$ were also confirmed by X-ray diffraction analysis (the structures of cations **2c**—**e** are shown in Figs 1—3, and selected bond lengths are given in Tables 1—3). The folding angle of the cyclohexadiene ligand in structure **2c** (32.4°) is somewhat smaller than that in the $[(\mathrm{CHD})\mathrm{Co(CO)_2}]_2$ complex (CHD is cyclohexa-1,3-diene, 36.8°).[22] The folding angle is significantly increased in methylated analog **2e** (40.5°) due to steric hindrances caused by the presence of the methyl groups in the *endo*-positions. Note that the distance from the cobalt atom to the plane of the hexamethylbenzene ligand (Co...$\mathrm{C_6}$) in structure **2e** (1.641 Å) is much longer than that in structure **2c** (1.571 Å), which is also due, most likely, to steric hindrance in structure **2e**. For the same reason, the distance from the cobalt atom to the plane passing through the coordinated atoms of the cyclohexadiene ligand in **2e** (1.602 Å) is noticeably longer than that in **2c** (1.568 Å).

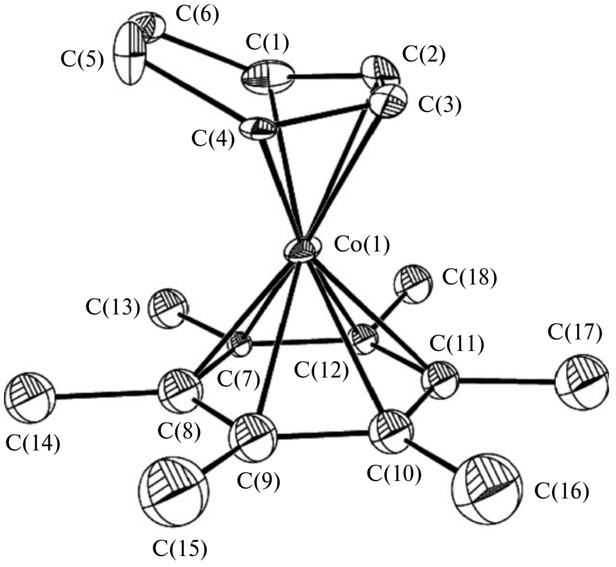


Fig. 1. Structure of cation **2c** (thermal ellipsoids of 30% probability). Hydrogen atoms are omitted.

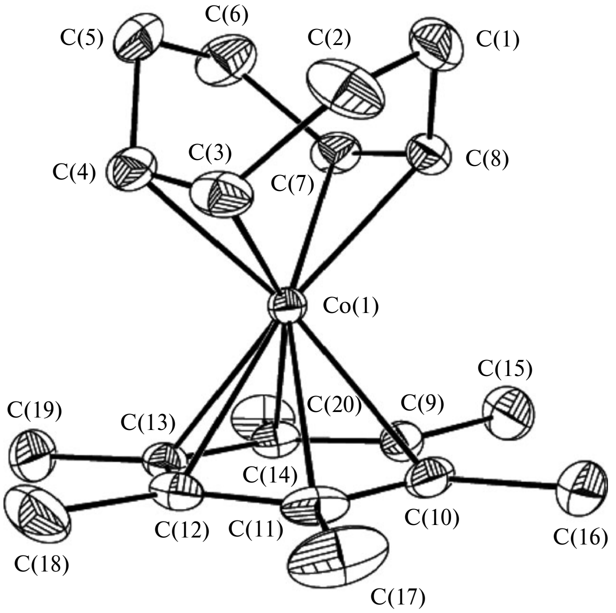


Fig. 2. Structure of cation **2d** (thermal ellipsoids of 50% probability). Hydrogen atoms are omitted.

The Co...$\mathrm{C_6}$ distance in cyclooctadiene complex **2d** (1.636 Å) is substantially longer than that in cyclohexa-

Table 1. Selected bond lengths (*d*) and angles (φ) in cation **2c**

Parameter	Value	Parameter	Value
Bond length	*d*/Å	Bond length	*d*/Å
Co(1)—C(1)	2.130(7)	C(2)—C(3)	1.457(10)
Co(1)—C(2)	2.032(7)	C(3)—C(4)	1.389(11)
Co(1)—C(3)	1.980(4)	C(4)—C(5)	1.536(10)
Co(1)—C(4)	2.005(7)	C(5)—C(6)	1.496(12)
Co(1)—C(7)	2.113(3)	C(1)—C(6)	1.516(11)
Co(1)—C(8)	2.040(4)		
Co(1)—C(9)	2.027(5)	Angle	φ/deg
Co(1)—C(10)	2.089(4)	C(1)—C(2)—C(3)	117.6(6)
Co(1)—C(11)	2.160(4)	C(2)—C(3)—C(4)	114.6(4)
Co(1)—C(12)	2.172(4)	C(1)—C(6)—C(5)	110.6(5)
C(1)—C(2)	1.342(11)	C(4)—C(5)—C(6)	114.1(6)

---

* A black precipitate (presumably, cobalt metal) is formed in the reaction.

Table 2. Selected bond lengths (d) and angles (φ) in cation **2d**

Parameter	Value	Parameter	Value
Bond length	d/Å	Bond length	d/Å
Co(1)—C(3)	2.049(3)	C(3)—C(4)	1.405(4)
Co(1)—C(4)	2.072(3)	C(4)—C(5)	1.516(4)
Co(1)—C(7)	2.050(3)	C(5)—C(6)	1.520(4)
Co(1)—C(8)	2.048(3)	C(6)—C(7)	1.513(4)
Co(1)—C(9)	2.129(3)	C(7)—C(8)	1.400(4)
Co(1)—C(10)	2.174(3)	C(1)—C(8)	1.510(4)
Co(1)—C(11)	2.182(3)	Angle	φ/deg
Co(1)—C(12)	2.134(3)		
Co(1)—C(13)	2.179(2)	C(1)—C(2)—C(3)	115.5(4)
Co(1)—C(14)	2.194(3)	C(6)—C(1)—C(2)	115.4(3)
C(1)—C(2)	1.520(4)	C(3)—C(4)—C(5)	111.9(3)
C(2)—C(3)	1.514(4)	C(4)—C(5)—C(6)	111.2(3)

Table 3. Selected bond lengths (d) and angles (ω) in cation **2e**

Parameter	Value	Parameter	Value
Bond length	d/Å	Bond length	d/Å
Co(1)—C(1)	2.008(4)	C(2)—C(3)	1.414(5)
Co(1)—C(2)	2.021(4)	C(3)—C(4)	1.543(5)
Co(1)—C(3)	2.076(4)	C(4)—C(5)	1.504(5)
Co(1)—C(6)	2.116(4)	C(5)—C(6)	1.539(5)
Co(1)—C(13)	2.178(4)	C(1)—C(6)	1.431(6)
Co(1)—C(14)	2.173(4)	Angle	φ/deg
Co(1)—C(15)	2.165(4)		
Co(1)—C(16)	2.128(4)	C(1)—C(2)—C(3)	115.5(4)
Co(1)—C(17)	2.152(4)	C(6)—C(1)—C(2)	115.4(3)
Co(1)—C(18)	2.186(4)	C(3)—C(4)—C(5)	111.9(3)
C(1)—C(2)	1.417(6)	C(4)—C(5)—C(6)	111.2(3)

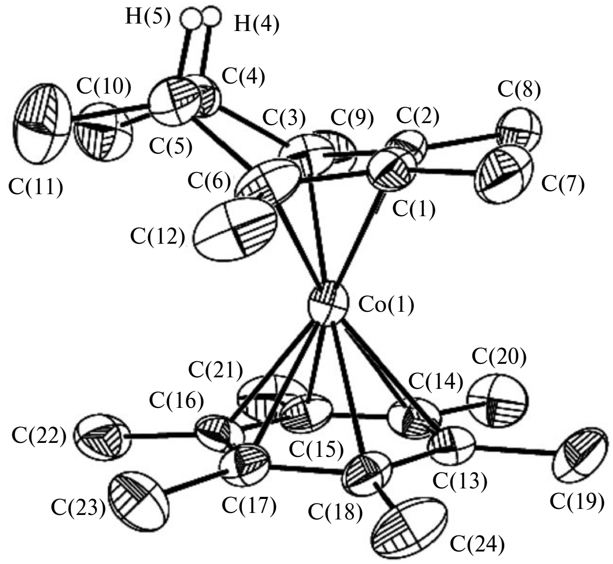


Fig. 3. Structure of cation **2e** (thermal ellipsoids of 50% probability). Hydrogen atoms, except for H(4) and H(5), are omitted.

diene analog **2c** (1.571 Å). This indicates a weaker bonding of C_6Me_6 with the $[(\text{COD})\text{Co}]^+$ fragment (COD is cycloocta-1,5-diene) compared to $[(\text{CHD})\text{Co}]^+$, which agrees with the DFT calculation results (vide intra). It should be emphasized that in 20-electron cation **1** this distance is still longer (1.765 Å).[21]

The strength of the $\text{Co—C}_6\text{H}_6$ bond in the $[(\text{diene})\text{Co}(\eta\text{-C}_6\text{H}_6)]^+$ complexes was estimated using DFT calculations (BP86/TZ2P) on the basis of energy decomposition analysis.[23—28] Using this method, we have earlier studied the $\text{M—C}_6\text{H}_6$ interaction in the arene complexes of iron,[29] cobalt,[30] and rhodium.[31] As can be seen from Table 4, the energy of the $\text{Co—C}_6\text{H}_6$ (ΔE_{int}) bond decreases with an increase in the number of carbon atoms in the diene ligand. A slight increase in the electrostatic attraction energy (ΔE_{elstat}) is compensated by a decrease in the stabilizing orbital interactions (ΔE_{orb}). The main reason for the $\text{Co—C}_6\text{H}_6$ bond weakening is an increase in the Pauli repulsion energy (ΔE_{Pauli}). The $\text{Co—C}_6\text{H}_6$ bond energy correlates with the distance from the cobalt atom to the benzene ligand plane: the stronger the bond, the

Table 4. Energy decomposition analysis for the $[(\text{diene})\text{Co}(\eta\text{-C}_6\text{H}_6)]^+$ complexes (using the $[(\text{diene})\text{Co}]^+$ and C_6H_6 fragments) at the BP86/TZ2P level

Diene	$-\Delta E_{\text{int}}$	ΔE_{Pauli}	$-\Delta E_{\text{elstat}}$*	$-\Delta E_{\text{orb}}$*	ΔE_{prep}	D_{e}	$\text{Co...C}_6\text{H}_6$
	kcal mol^{-1}						Å
Buta-1,3-diene	81.89	171.39	110.35 (43.6)	142.94 (56.4)	5.11	76.78	1.571
Cyclopentadien	80.84	165.83	107.94 (43.8)	138.73 (56.2)	3.98	76.86	1.572
Cyclohexa-1,3-diene	78.90	172.10	111.58 (44.5)	139.42 (55.5)	4.06	74.84	1.570
Cyclohepta-1,3-diene	75.29	178.11	114.96 (45.4)	138.43 (54.6)	5.46	69.83	1.580
Norbornadiene	71.91	176.97	114.68 (46.1)	134.20 (53.9)	5.30	66.61	1.591
Cyclohexa-1,4-diene	71.84	176.91	114.40 (46.0)	134.35 (54.0)	4.89	66.95	1.593
Cycloocta-1,5-diene	67.02	185.25	117.73 (46.7)	134.54 (53.3)	8.58	58.44	1.610
Cyclobutadiene	90.76	151.23	100.78 (41.6)	141.20 (58.4)	2.61	88.15	1.552

* The contribution in percents to the total bonding interaction is given in parentheses.

shorter the Co...C_6H_6 distance. The dissociation energy (D_e) also decreases with an increase in the diene size, because the preparation energy (ΔE_{prep}) is approximately the same in almost all cases (except the complex with cycloocta-1,5-diene). An analysis of the $\Delta E_{elstat}/\Delta E_{orb}$ ratio shows that the Co—C_6H_6 bond has a predominantly covalent character (52—56%).

The butadiene (D_e = 76.78 kcal mol^{-1}) and cyclopentadiene (D_e = 76.86 kcal mol^{-1}) complexes are the most stable in this series, and the cyclooctadiene complex (D_e = 58.44 kcal mol^{-1}) is the least stable. The difference in dissociation energies is 18 kcal mol^{-1}, which is fairly high for complexes of the same type. It should be mentioned that the benzene complexes with conjugated dienes (buta-1,3-diene, cyclopentadiene, cyclohexa-1,3-diene, and cycloheptatriene) are stronger than those with nonconjugated dienes (norbornadiene, cyclohexa-1,4-diene, and cycloocta-1,5-diene). However, even in the most stable complex with cyclopentadiene the Co—C_6H_6 bond is weaker (by 9 kcal mol^{-1}) than in the cyclobutadiene analog $[(\eta\text{-}C_4H_4)Co(\eta\text{-}C_6H_6)]^+$.

Thus, in this work we synthesized the (arene)diene complexes $[(\text{diene})Co(\eta\text{-}C_6Me_6)]^+$ and determined their structures. The DFT calculations showed that the bond energy of the cobalt atom with the arene ligand decreased with an increase in the size of the diene ligand due to an increase in the Pauli repulsion energy.

Experimental

All reactions were carried out under argon using absolute solvents. The products were isolated in air. Complex [**1**]PF_6 was synthesized using a known procedure.[32] ^{1}H NMR spectra were recorded on a Bruker Avance-400 instrument (400.13 MHz).

[(η^4-Buta-1,3-diene)(η-hexamethylbenzene)cobalt]hexafluorophosphate, [(η^4-C_4H_6-1,3)Co(η-C_6Me_6)]PF_6 ([2a]PF_6). Me_2CO (0.03 mL) was added to a solution of complex [**1**]PF_6 (50 mg, 0.095 mmol) in CH_2Cl_2 (3 mL). Then butadiene was bubbled through the obtained solution for 20 min. The reaction mixture was stirred for 1 h at ~20 °C. The orange precipitate that formed was filtered off, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Complex [**2a**]PF_6 was obtained as an orange powder. The yield was 30 mg (75%). Found (%): C, 43.75; H, 5.56. $C_{16}H_{24}CoF_6P \cdot 0.25CH_2Cl_2$. Calculated (%): C, 44.20; H, 5.54. ^{1}H NMR (acetone-d_6), δ: 6.41 (m, 2 H, C_4H_6); 5.24 (m, 4 H, C_4H_6); 2.20 (s, 18 H, C_6Me_6).

[(Diene)(η-hexamethylbenzene)cobalt]hexafluorophosphates, [(C_nH_{2n-4})Co(η-C_6Me_6)]PF_6 ([2b—d]PF_6). Diene (0.1 mL) and Me_2CO (0.03 mL) were added to a solution of complex [**1**]PF_6 (50 mg, 0.095 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 1 h at ~20 °C. The solvent was evaporated, and the residue was extracted with CH_2Cl_2. The obtained solution was filtered through a small layer of Al_2O_3, and Et_2O was added to the filtrate. The yellow filtrate that formed was filtered off and dried.

Complex [**2b**]PF_6 (diene is 5-isopropyl-2-methylcyclohexa-1,3-diene) was obtained in a yield of 40 mg (85%). Found (%): C, 52.48; H, 6.73. $C_{22}H_{34}CoF_6P$. Calculated (%): C, 52.60; H, 6.77. ^{1}H NMR (acetone-d_6), δ: 5.34 (m, 3 H, CH); 2.42 (s, 18 H, C_6Me_6); 2.24 (m, 1 H, CH_{tert}); 2.17 (m, 2 H, CH_2); 2.09 (s, 3 H, Me); 1.92 (m, 1 H, Pr^i); 1.04 (m, 6 H, Pr^i).

Complex [**2c**]PF_6 (diene is cyclohexa-1,3-diene) was obtained in a yield of 38 mg (90%). ^{1}H NMR (acetone-d_6), δ: 5.45 (m, 2 H, C_6H_8); 3.40 (m, 2 H, C_6H_8); 2.47 (s, 18 H, C_6Me_6); 1.59 (m, 2 H, C_6H_8); 0.67 (m, 2 H, C_6H_8) (*cf.* Ref. 20).

Complex [**2d**]PF_6 (diene is cycloocta-1,5-diene) was obtained in a yield of 38 mg (85%). ^{1}H NMR (acetone-d_6), δ: 3.41 (s, 4 H, C_8H_{12}); 2.60 (m, 4 H, C_8H_{12}); 2.18 (s, 18 H, C_6Me_6); 1.85 (m, 4 H, C_8H_{12}) (*cf.* Ref. 19).

[(η^4-1,2,3,4,5,6-Hexamethylcyclohexa-1,3-diene)(η-hexamethylbenzene)cobalt]hexafluorophosphate, [(η^4-1,2,3,4,5,6-$C_6H_2Me_6$-1,3)Co(η-C_6Me_6)]PF_6 ([2e]PF_6). Me_2CO (0.03 mL) was added to a solution of complex [**1**]PF_6 (50 mg, 0.095 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 24 h at ~20 °C. The solvent was evaporated, and the product was extracted with CH_2Cl_2. The obtained solution was filtered through a small layer of Al_2O_3, and Et_2O was added to the filtrate. The orange precipitate that formed was filtered off and dried. The yield was 15 mg (30%). Found (%): C, 47.90; H, 6.43. $C_{24}H_{38}CoF_6P \cdot 1.25CH_2Cl_2$. Calculated (%): C, 47.63; H, 6.37. ^{1}H NMR (acetone-d_6), δ: 2.36 (s, 18 H, C_6Me_6); 2.31 (m, 2 H, CH); 1.98 (s, 6 H, Me); 1.03 (d, 6 H, Me); 0.97 (s, 6 H, Me).

X-ray diffraction study of complexes [2c]PF_6—[2e]PF_6. The crystals of [**2c**]PF_6—[**2e**]PF_6 were grown by slow diffusion from solutions in a CH_2Cl_2—petroleum ether ([**2d**]PF_6) or Et_2O ([**2c**]PF_6 and [**2e**]PF_6) bilayer system. The crystallographic parameters and characteristics of experiments, decoding, and structure refinements are listed in Table 5. The structures were solved by a direct method, and all non-hydrogen atoms were localized in difference electron density syntheses and refined for F^2_{hkl} in the anisotropic approximation; all hydrogen atoms were placed in geometrically calculated positions and refined in the riding model with $U(H) = nU(C)$, where $U(C)$ is the equivalent temperature factor of the C atom to which the H atom is bound, n = 1.2 for the CH and CH_2 groups, n = 1.5 for the Me groups. The carbon atoms of the hexamethylbenzene ligand in complex [**2c**]PF_6 were refined in the isotropic approximation. All calculations were performed using the SHELXTL PLUS 5 program package.[33] The atomic coordinates, temperature factors, and full data on the geometric parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 808369, 808370, and 808371 for [**2c**]PF_6, [**2d**]PF_6, and [**2e**]PF_6, respectively).

DFT calculations. Geometric parameters were optimized without symmetry restraints using the PRIRODA 6 program (see Ref. 34) using the PBE functional,[35] scalar relativistic Hamiltonian,[36] atomic basis sets of Gaussian functions,[37] and density-fitting technique.[38] The L2 full-electron three-exponential basis set with two polarization functions was used.[39]

The energy decomposition analysis was performed using the ADF (2006.01) program[40,41] by the Morokuma—Ziegler method,[42,43] according to which the energy ΔE_{int} can be decomposed into three components

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}.$$

The energy ΔE_{elstat} was calculated at the fixed electron density distribution with the geometric parameters of the complex.

Table 5. Crystallographic data and refinement parameters for complexes [**2c**]PF_6—[**2e**]PF_6

Parameter	[**2c**]PF_6	[**2d**]PF_6	[**2e**]PF_6
Empirical formula	$C_{18}H_{26}CoF_6P$	$C_{20}H_{30}CoF_6P$	$C_{24}H_{38}CoF_6P$
M	446.29	474.34	530.44
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	14.381(2)	8.5430(5)	8.0561(8)
b/Å	8.697(1)	14.3066(9)	13.304(1)
c/Å	14.871(2)	16.331(1)	21.675(2)
$V/Å^3$	1860.0(4)	1996.0(2)	2323.1(4)
Z	4	4	4
$d_{calc}/g\ cm^{-3}$	1.594	1.578	1.517
Crystal sizes/mm	0.45×0.35×0.20	0.55×0.35×0.27	0.50×0.30×0.20
Color, crystal habitus	Red, plate-like	Red, prismatic	Red, needle-like
Diffractometer	«Bruker APEX II»	«Bruker SMART»	«Bruker SMART»
Radiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
μ/mm^{-1}	1.065	0.998	0.866
Absorption correction	SADABS	SADABS	SADABS
Temperature/K	100(2)	120(2)	120(2)
Scan mode	ω	φ, ω	φ, ω
$2\theta_{max}$/deg	52.00	58.00	56.00
Total number of reflections	13052	21880	23929
Number of independent reflections (R_{int})	3601 (0.0285)	5299 (0.0287)	5552 (0.0676)
R_1 (for *F* for reflections with $I > 2\sigma(I)$)	0.0658 (3391 reflections)	0.0390 (4864 reflections)	0.0482 (3608 reflections)
wR_2 (for F^2 for all reflections)	0.1392	0.1020	0.0899
Number of refined parameters	164	253	302
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (\alpha P)^2 + \beta P$, where $P = 1/3(F_0^2 + 2F_c^2)$		
α	0.0235	0.0610	0.0263
β	13.9458	1.7500	—
Goodness-of-fit	0.997	1.011	1.018
F(000)	920	984	1112
Residual electron density/e $Å^{-3}$, ρ_{max}/ρ_{min}	1.142/–0.633	0.886/–0.508	1.200/–0.583

The energy D_e was calculated by the formula

$$D_e = -(\Delta E_{int} + \Delta E_{prep}),$$

where ΔE_{prep} is the energy necessary for the transition of isolated fragments from equilibrium geometry and the ground electron state to the geometry and electron state of the optimized structure of the complex. The calculations were performed using the BP86 functional[44,45] and full-electron three-exponential TZ2P basis set with two polarization functions (integration accuracy 6.0). The scalar relativistic effects were taken into account by the zero-order regular approximation (ZORA).[46] The ChemCraft program was used for molecular modeling and visualization.[47]

References

1. E. O. Fischer, R. D. Fischer, *Z. Naturforsch.*, *Teil B*, 1961, **16**, 475.
2. M. L. H. Green, R. B. A. Pardy, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 355.
3. G. Fairhurst, C. White, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 1531.
4. U. Koelle, B. Fuss, M. V. Rajasekharan, B. L. Ramakrishna, J. H. Ammeter, M. C. Böhm, *J. Am. Chem. Soc.*, 1984, **106**, 4152.
5. V. S. Kaganovich, A. R. Kudinov, M. I. Rybinskaya, *J. Organomet. Chem.*, 1987, **323**, 111.
6. K. D. Plitzko, V. Boekelheide, *Organometallics*, 1988, **7**, 1573.
7. A. R. Kudinov, E. V. Mutseneck, D. A. Loginov, *Coord. Chem. Rev.*, 2004, **248**, 571.
8. D. A. Loginov, A. A. Pronin, Z. A. Starikova, P. V. Petrovskii, A. R. Kudinov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 1620 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 1650].
9. A. R. Kudinov, A. A. Fil´chikov, P. V. Petrovskii, M. I. Rybinskaya, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 1364 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1999, **48**, 1352].
10. A. R. Kudinov, D. A. Loginov, S. N. Ashikhmin, A. A. Fil´chikov, L. S. Shul´pina, P. V. Petrovskii, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 1647 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 1637].
11. M. V. Butovskii, U. Englert, A. A. Fil´chikov, G. E. Herberich, U. Koelle, A. R. Kudinov, *Eur. J. Inorg. Chem.*, 2002, 2656.
12. D. A. Loginov, D. V. Muratov, D. S. Perekalin, Z. A. Starikova, E. A. Petrovskaya, E. I. Gutsul, A. R. Kudinov, *Inorg. Chim. Acta.*, 2008, **361**, 1715.

13. D. S. Perekalin, M. V. Babak, V. V. Novikov, P. V. Petrovskii, K. A. Lyssenko, M. Corsini, P. Zanello, A. R. Kudinov, *Organometallics*, 2008, **27**, 3654.
14. P. O′Donohue, S. A. Brusey, C. M. Seward, Y. Ortin, B. C. Molloy, H. Müller-Bunz, A. R. Manning, M. J. McGlinchey, *J. Organomet. Chem.*, 2009, **694**, 2536.
15. D. A. Loginov, A. A. Pronin, Z. A. Starikova, P. V. Petrovskii, A. R. Kudinov, *Mendeleev Commun.*, 2010, **20**, 271.
16. D. A. Loginov, A. A. Pronin, Z. A. Starikova, A. V. Vologzhanina, P. V. Petrovskii, A. R. Kudinov, *Eur. J. Inorg. Chem.*, 2011, 5422.
17. H. Bonnemann, R. Goddard, J. Grub, R. Mynott, E. Raabe, S. Wendel, *Organometallics*, 1989, **8**, 1941.
18. D. A. Loginov, A. A. Pronin, Z. A. Starikova, P. V. Petrovskii, A. R. Kudinov, *Koord. Khim.*, 2010, **36**, 805 [*Russ. J. Coord. Chem.* (*Engl. Transl.*), 2010, **36**, 795].
19. J. Edwin, W. E. Geiger, *Organometallics*, 1984, **3**, 1910.
20. J. M. Mevs, W. E. Geiger, *Organometallics*, 1996, **15**, 2350.
21. M. R. Thompson, C. S. Day, V. W. Day, R. I. Mink, E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 2979.
22. F. S. Stephens, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 1752.
23. G. Frenking, N. Frohlich, *Chem. Rev.*, 2000, **100**, 717.
24. G. Frenking, K. Wichmann, N. Frohlich, C. Loschen, M. Lein, J. Frunzke, V. M. Rayon, *Coord. Chem. Rev.*, 2003, **238—239**, 55.
25. T. Ziegler, J. Autschbach, *Chem. Rev.*, 2005, **105**, 2695.
26. M. Lein, J. Frunzke, A. Timoshkin, G. Frenking, *Chem. Eur. J.*, 2001, **7**, 4155.
27. J. Frunzke, M. Lein, G. Frenking, *Organometallics*, 2002, **21**, 3351.
28. V. Rayón, G. Frenking, *Organometallics*, 2003, **22**, 3304.
29. A. R. Kudinov, P. Zanello, R. H. Herber, D. A. Loginov, M. M. Vinogradov, A. V. Vologzhanina, Z. A. Starikova, M. Corsini, G. Giorgi, I. Nowik, *Organometallics*, 2010, **29**, 2260.
30. D. A. Loginov, A. A. Pronin, L. S. Shul′pina, E. V. Mutsenek, Z. A. Starikova, P. V. Petrovskii, A. R. Kudinov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 535 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 546].
31. D. A. Loginov, M. M. Vinogradov, Z. A. Starikova, E. A. Petrovskaya, P. Zanello, F. Laschi, F. Rossi, A. Cinquantini, A. R. Kudinov, *J. Organomet. Chem.*, 2007, **692**, 5777.
32. D. O′Hare, A. Rai-Chaudhuri, V. Murphy, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3071.
33. *SHELXTL v. 5.10*, *Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.
34. D. N. Laikov, Yu. A. Ustynyuk, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 804 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 820].
35. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
36. K. G. Dyall, *J. Chem. Phys.*, 1994, **100**, 2118.
37. D. N. Laikov, *Chem. Phys. Lett.*, 2005, **416**, 116.
38. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
39. E. Ya. Misochko, A. V. Akimov, V. A. Belov, D. A. Tyurin, D. N. Laikov, *J. Chem. Phys.*, 2007, **127**, 84301.
40. *ADF 2006.01*, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands: http://www.scm.com.
41. F. M. Bickelhaupt, E. J. Baerends, *Rev. Comput. Chem.*, 2000, **15**, 1.
42. K. Morokuma, *Chem. Phys.*, 1971, **55**, 1236.
43. T. Ziegler, A. Rauk, *Theor. Chim. Acta*, 1977, **46**, 1.
44. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
45. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
46. E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597.
47. G. A. Zhurko, ChemCraft 1.6, http://www.chemcraft-prog.com, 2008.

Received January 19, 2011;
in revised form September 22, 2011