Journal of Organometallic Chemistry, 441 (1992) 109–116
Elsevier Sequoia S.A., Lausanne
JOM 22942

On the problem of stabilization of α-metallocenylcarbocations. Synthesis, ^1H and ^{13}C NMR spectra of metallocenyldiphenylmethyl hexafluorophosphates and X-ray investigation of $(C_5H_5OsC_5H_4CPh_2)^+PF_6^-$

U. Turpeinen

Department of Inorganic Chemistry of Helsinki University, Vuorikatu 20, SF-00100, Helsinki (Finland)

A.Z. Kreindlin, P.V. Petrovskii and M.I. Rybinskaya

A N. Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilov Str. 28, 117813 Moscow (Russian Federation)

(Received April 17, 1992)

Abstract

Previously unknown $(RcCPh_2)^+PF_6^-$ (Rc = $C_5H_5RuC_5H_4$) and $(OcCPh_2)^+$ PF_6^- (Oc = $C_5H_5OsC_5H_4$) have been prepared and their ^1H and ^{13}C NMR spectra investigated For comparison, NMR spectra of known $(FcCPh_2)^+$ PF_6^- (Fc = $C_5H_5FeC_5H_4$) were also studied. It has been shown that the shielding of the ^{13}C nuclear of exocyclic carbon atoms (α-C) increases in going from Fe to Ru. A single crystal X-ray diffraction study of $(OcCPh_2)^+$ PF_6^- has been carried out. Comparison of these data with those for the Fe-containing analogue has shown that the M–C_α distance of the Os-containing cation (Os–C_α) (2.39 Å) is smaller than for $(FcCPh_2)^+$ BF_4^- (2.715(6) Å). The inclination angle of the CPh_2 group to the Os-atom ($\alpha = 38.4°$ is significantly larger than that in $(FcCPh_2)^+$ BF_4^- (20.7°). Comparison of X-ray data for $(OcCPh_2)^+$ PF_6^- with those for the primary cation $(Oc^9CH_2)^+$ ($Oc^9 = C_5Me_5OsC_5Me_4$) shows that the presence of two bulky phenyl substituents did not change dramatically the geometry of ion $(Oc^9CPh_2)^+$. The NMR spectra and X-ray diffraction studies have shown that stabilization of the α-carbocationic centre for diphenylsubstituted cations increases in the order Fe < Ru < Os.

Introduction

The phenomenon of α-carbocation centre stabilization by metallocenyl fragments has received considerable attention during the past 30 years (reviews [1,2]). Earlier we had investigated this problem on the basis of permethylated metallo-

---

Correspondence to: Dr. U. Turpeinen or Dr M.I. Rybinskaya.

cenylcarbocations of the iron subgroup metals [3–6]. We had shown that stabilization of the carbocationic centre in primary and secondary cations increases going down the sub-group. The donor–acceptor interaction of metal lone electron pairs with the primary α-carbocationic centre in the case of Ru- and Os-containing ions is so strong that the usual M–CH_2 σ-bond arises (see X-ray data [4,5]). These cations practically are not carbocations but onium compounds with the onium transition metal atom. Therefore these cations should be called metallocenonium compounds. Stable cations of this type were synthesized for the first time [4,5]. Unfortunately Fe-containing primary carbocations were not investigated by X-ray diffraction because even the permethylated cation changes on attempts to grow the crystals [6]. The stable secondary and tertiary carbocations, differrocenylmethyl- [7] and ferrocenyldiphenylcarbocations [8], were investigated previously by X-ray diffraction. Berens [8] had found that the carbocation centre in $(FcCPh_2)^+BF_4^-$ is inclined to the metal atom from the Cp-ring plane by an angle of 20.7° and the $Fe{-}\overset{+}{C}Ph_2$ distance 2.715(6) Å is longer than the Fe–C σ-bond (2.10 Å [9]). It was not possible to use these data for comparison with the data for Ru- and Os-containing primary cations with Ru–CH_2 and Os–CH_2 bonds, since the presence of two bulky phenyl substituents, which delocalize the positive charge in the Fe-containing cations, could give rise to considerable changes. In this study we have synthesized previously unknown $(C_5H_5MC_5H_4CPh_2)^+PF_6^-$ (M = Ru, Os) ions and investigated their ^1H and ^{13}C NMR spectra. To clarify the influence of the two phenyl groups on the geometry and stabilization of the carbocations, for comparison of spectral characteristics, the Fe containing analogue $(C_5H_5FeC_5H_4\text{-}CPh_2)^+PF_6^-$ has been obtained. The salt $(C_5H_5OsC_5H_4CPh_2)^+PF_6^-$ was investigated by means of X-ray diffraction.

Results and discussion

Synthesis of cations was carried out by the following scheme:

$$(C_5H_5)_2M + PhCOCl \xrightarrow{AlCl_3} C_5H_5MC_5H_4COPh \ (M = Fe, Ru, Os) \quad (1)$$

$$C_5H_5MC_5H_4COPh + PhLi \longrightarrow C_5H_5MC_5H_4C(OH)Ph_2 \quad (2)$$

$$C_5H_5MC_5H_4C(OH)Ph_2 + HPF_6 \longrightarrow (C_5H_5MC_5H_4CPh_2)^+PF_6^- \quad (3)$$

Benzoylmetallocenes ($C_5H_5MC_5H_4COPh$) were obtained by Friedel–Crafts acylation of the metallocenes. Metallocenyldiphenylcarbinols ($C_5H_5MC_5H_4C(OH)Ph_2$) were synthesized by reaction of $C_5H_5MC_5H_4COPh$ with PhLi. Metallocenyldiphenylhexafluorophosphates $(C_5H_5MC_5H_4CPh_2)^+\cdot PF_6^-$ were prepared by reaction of $C_5H_5MC_5H_4C(OH)Ph_2$ with aqueous HPF_6 (M = Fe, Ru, Os). It should be noted that $C_5H_5MC_5H_4COPh$ (Fe, Ru, Os), $C_5H_5FeC_5H_4C(OH)Ph_2$ [10–12] and $Fc\overset{+}{C}Ph_2BF_4^-$ [8] were known previously. The Ru-and Os-containing tertiary carbinols and cations have been synthesized for the first time. All cationic compounds were air stable for some months. Their colour depends on the metal (M = Fe, dark blue; Ru, orange; Os, yellow). We have investigated the ^1H and ^{13}C NMR spectra of all the carbinols and cations synthesized. It should be noted that shielding of the ^{13}C nuclear for the exocyclic carbon atom (C^+) of $(C_5H_5MC_5H_4CPh_2)^+$-cations increases in the order Fe < Ru < Os (The value of

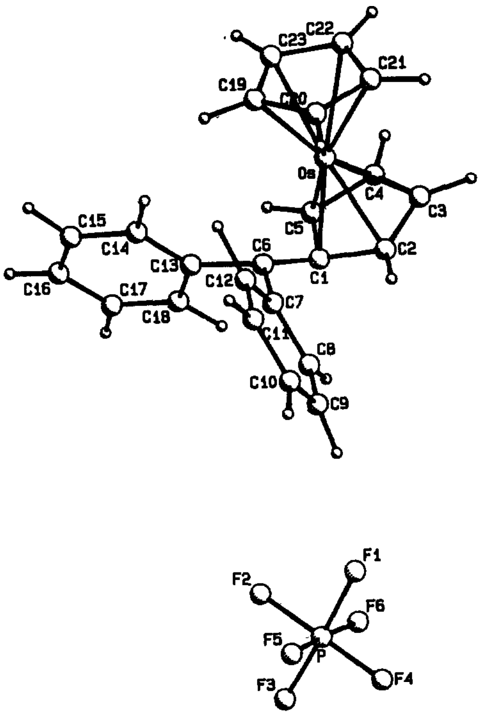

Fig. 1 PLUTO drawings with atomic numbering.

the chemical shift decreases in the order 171.6 ppm > 139.6 ppm > 95.6 ppm, respectively). This phenomenon was previously observed by us for other synthesized metallocenyl cations [3], and it is in accordance with the interaction of lone electron pairs of metal atoms with carbocationic centres in the order Fe < Ru < Os. The NMR data correspond to those of X-ray diffraction.

The X-ray diffraction study of $(FcCPh_2)^+$ ($Fc = C_5H_5FeC_5H_4$) has been published [8]. We carried out a single-crystal X-ray diffraction study of $(OcCPh_2)^+PF_6^-$ ($Oc = C_5H_5OsC_5H_4$).

The structure of the salt is shown in Fig. 1; the stereoscopic view of the crystal structure of this salt is shown in Fig. 2. Bond lengths and angles are listed in Tables 2 and 3. These data show that the distortion of the metallocene structure of the tertiary $(OcCPh_2)^+$ ion is somewhat greater than that for the primary $(Oc^9CH_2)^+$-ion ($Oc^9 = C_5Me_5OsC_5Me_4$) [4]. Thus the dihedral angle (β) formed by the Cp-ring planes in the $(OcCPh_2)^+$-ion is 14.1° (see Fig. 3), while for the $(Oc^9CH_2)^+$-ion, $\beta = 6.9°$. The shift of the metal atom projection onto the C(1)–C(5) ring plane to the centre of the ring (d) is equal to 0.46 Å and 0.20 Å, respectively. Comparison of the length of the Os-C_{Cp} bonds for ions $(Oc^9CH_2)^+$ and $(OcCPh_2)^+$ shows that these bonds differ little one from another ($\pm$0.02–0.05 Å) (see Table 2) in spite of the presence of Me-groups in the Cp-rings in the former and of two Ph-groups at the exocyclic carbon atom in the latter. The differences in the length of the Os–C (α)-bond and the inclination angles (inclinating deviation of the CH_2 and of the CPh_2 groups from the Cp ring plane to the metal atom) are more noticeable (see Fig. 3). Thus, the length of the Os–C bond in $(OcCPh_2)^+$ is equal

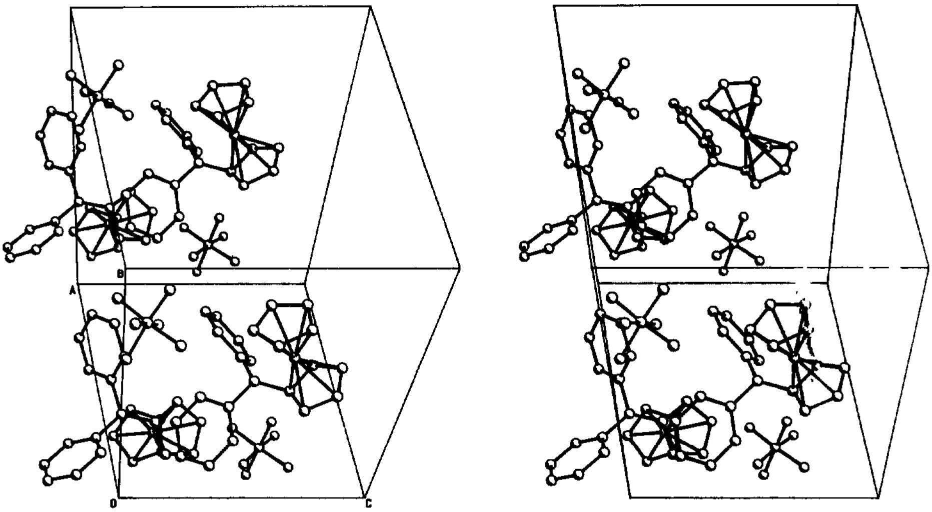

Fig. 2. Stereoscopic view of crystal structure.

to 2.387(9) Å (see Table 2) and in $(Oc^9CH_2)^+$ to 2.224 Å [4]. (The length of the normal Oc–C σ-bond is 2.22 Å [13].) The displacement of the "C^+" atom from the plane of the C(1)–C(5) ring (*h*) (see Fig. 3) is 0.91 Å and 0.961 Å in $(Oc^9CH_2)^+$ [4]. However, these differences did not change dramatically the geometry of the $(OcCPh_2)^+$-ion in comparison to that of the $(Oc^9CH_2)^+$-ion. The lengthening of the Os–C_α-bond by 0.14 Å in the $(OcCPh_2)^+$-ion show that it is more stretched.

The results allow us to make some suppositions about the geometry of primary Fe-containing cations for which X-ray diffraction studies were not performed. The Fe–C distances in the ions $(Fc_2CH)^+$ [7] and $(FcCPh_2)^+$ [8] studied significantly exceed the usual Fe–C σ-bond length (lit. data $\sim$ 2.1 Å [9]). Therefore it should be supposed that the length of this bond in the unsubstituted ion does not change significantly in comparison to the substituted ions. All these data show that the stabilization of the α-carbocationic centre for diphenylsubstituted compound as for unsubstituted cations increases in the order Fe < Ru < Os.

Experimental

NMR spectra were recorded with a Bruker WP-200 SY spectrometer (^1H 200.13 Hz and ^{13}C 50.31 MHz) with TMS as internal standard. Benzoylosmocen (OcCOPh), benzoylruthenocene (RcCOPh) [10], benzoylferrocene (FcCOPh), and ferrocenyldiphenylcarbinol (FcC(OH)Ph) [11,12] were prepared by the literature procedures.

Synthesis of $OcC(OH)Ph_2$

To a solution of OcCOPh (0.3 g, 0.7 mmol) in dry ether (100 ml) was added dropwise 2 ml of a 1.2 *M* ether solution of PhLi in an argon atmosphere. After 30 min the solution was poured into an aqueous solution of NH_4Cl, and extracted with ether. The organic layer was dried over Na_2SO_4 and evaporated. Recrystal-

Table 1

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2). $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

	x	y	z	U_{eq}
Os	2347(1)	686(1)	1815(1)	0.046
C(1)	1926(7)	1754(3)	1749(5)	0.058
C(2)	2905(7)	1633(3)	2840(5)	0.064
C(3)	2383(7)	1200(3)	3716(5)	0.070
C(4)	1082(7)	1054(3)	3167(5)	0.076
C(5)	799(7)	1396(3)	1952(5)	0.061
C(6)	2304(9)	1700(4)	483(8)	0.048
C(7)	3583(5)	1973(3)	305(6)	0.052
C(8)	4007(5)	2606(3)	890(6)	0.063
C(9)	5178(5)	2891(3)	705(6)	0.089
C(10)	5925(5)	2543(3)	−66(6)	0.100
C(11)	5501(5)	1910(3)	−652(6)	0.079
C(12)	4329(5)	1625(3)	−466(6)	0.062
C(13)	1257(5)	1731(3)	−704(4)	0.044
C(14)	1318(5)	1334(3)	−1804(4)	0.054
C(15)	360(5)	1401(3)	−2896(4)	0.058
C(16)	−658(5)	1866(3)	−2889(4)	0.065
C(17)	−719(5)	2263(3)	−1788(4)	0.069
C(18)	239(5)	2196(3)	−696(4)	0.057
C(19)	2776(12)	−23(4)	285(6)	0.090
C(20)	3911(12)	72(4)	1219(6)	0.086
C(21)	3670(12)	−185(4)	2421(6)	0.075
C(22)	2385(12)	−439(4)	2230(6)	0.087
C(23)	1833(12)	−339(4)	910(6)	0.106
P	2608(3)	5513(1)	1380(3)	0.076
F(1)	3223(9)	4805(4)	1934(12)	0.161
F(2)	1543(10)	−106(6)	5444(11)	0.173
F(3)	1898(10)	−1180(5)	5786(10)	0.155
F(4)	3521(15)	−921(6)	7337(13)	0.218
F(5)	3572(11)	−545(6)	5480(10)	0.170
F(6)	1703(12)	−489(8)	7396(10)	0.201

lization from a hexanebenzene mixture gave 0.21 g (56%) OcC(OH)Ph, m.p. 134–135°C. PMR spectrum ($CDCl_3$): δ 2.79 (s, 1H, OH), 4.57 (t, 2H, 1.6 Hz); 4.70 (t, 2H, 1.6 Hz); 4.74 (s, 5H); 7.2–7.4 (m, 10H, Ph). ^{13}C NMR spectrum (CH_2Cl_2):

Table 2

Bond lengths (Å) [a]

Os–C(1)	2.088(7)	Os–C(20)	2.205(12)
Os–C(2)	2.136(6)	Os–C(21)	2.195(10)
Os–C(3)	2 222(6)	Os–C(22)	2.194(9)
Os–C(4)	2.229(7)	Os–C(23)	2.205(9)
Os–C(5)	2.147(7)	C(6)–C(1)	1.459(12)
Os–C(6)	2.387(9)	C(6)–C(7)	1.489(12)
Os–C(19)	2.212(9)	C(6)–C(13)	1.514(10)
P–F(1)	1.569(10)	P–F(4)	1.485(14)
P–F(2)	1.564(11)	P–F(5)	1.508(13)
P–F(3)	1.554(11)	P–F(6)	1.554(14)

[a] Cyclopentadienyl and phenyl rings are rigid groups and bond lengths are 1.420 and 1.395 Å, respectively.

δ 68.69 (C(2, 5)); 65.07 (C(1')); 66.41 (C(3, 4)); 75.66 (C(1)); 99.26 (C–CH), 126.81 (C_m); 127.54 ($C_o + C_p$); 146.22 (C_i).

Synthesis of $OcCPh_2 + PF_6^-$

To a solution of $OcC(OH)Ph_2$ (0.2 g, 0.4 mmol) in ether at 20°C was added dropwise to 0.5 ml of a 70% aqueous solution of HPF_6. The crystals formed were washed with ether, dissolved in methylene chloride and precipitated with ether. The yield of $(OcCPh_2)^+PF_6^-$ was 0.18 g 73%). PMR spectrum (CD_2Cl_2): δ 5.32 (t, 2H, 2.0 Hz, H(2, 5); 5.47 (s, 5H, H(1')); 6.34 (t, 2H, 2.0 Hz, H(3, 4)). ^{13}C NMR spectrum (CH_2Cl_2): δ 75.8 (C(2, 5)); 81.4 (C(1')); 84.0 (C(3, 4)); 95.7 (C^+); 106.5 (C(1)); 128.6 (C_m); 129.4 (C_p); 130.1 (C_o); 141.1 (C_i). Single crystals for the X-ray diffraction study were obtained by slow partial evaporation of the solvent Et_2O/CH_2Cl_2.

Synthesis of $RcC(OH)Ph_2$

This was carried out similarly to the synthesis of the Os-analogue, starting from RcCOPh (0.35 g, 1.05 mmol), 2 ml of a 1.2 *M* ether solution of PhLi. Recrystallization from hexane/benzene gave 0.26 g (60%) of $RcC(OH)Ph_2$. Anal. Found C 66.03; H 4.78. $C_{23}H_{20}ORu$ calc.: C 66.81; H 4.86%. PMR spectrum ($CDCl_3$): δ 2.97 (s, 1H, OH); 4.40 (t, 2H, 1.7 Hz); 4.56 (t, 2H, 1.6 Hz); 4.58 (s, 5H); 7.20–7.30 (M, 10H, Ph) ^{13}C NMR spectrum (CH_2Cl_2): δ 70.94 (C(2, 5)); 71.26 (C(1')); 72.23 (C(3, 4)); 76.01 (C(1)); 105.29 (C–OH); 126.85 (C_m), 127.35 (C_o), 127.57 (C_p), 146.74 (C_i).

Synthesis of $RcCPh_2{}^+PF_6^-$

This was carried out similarly to the synthesis of the Os-analogue starting from $RcC(OH)Ph_2$ (0.2 g, 0.48 mmol) and 0.5 ml of a 70% aqueous solution of HPF_6. $RcCPh_2^+PF_6^-$ was obtained after precipitation by Et_2O from CH_2Cl_2. The yield of $(RcCPh_2)^+PF_6^-$ was 0.2 g (75%). PMR spectrum (CD_2Cl_2): δ 5.15 (t, 2H, 2.1 Hz, H (2, 5); 5.32 (s, 5H, H(1')); 6.23 (t, 2H, 2.1 Hz, H(3, 4)); 7.19–7.56 (m, 10H, Ph). ^{13}C NMR spectrum (CH_2Cl_2): δ 83.1 (C(2, 5)), 86.3 (C(1')); 92.6 (C(3, 4)); 103.2 (C(1)); 129.5 (C_m); 131.4 (C_p); 131.7 (C_o); 139.6 (C^+); 140.5 (C_i).

PMR spectrum of $FcC(OH)Ph_2$ ($CDCl_3$): δ 3.43 (s, 1H, OH); 4.04 (t, 2H, 1.7 Hz); 4.16 (s, 5H); 4.26 (t, 2H, 1.8 Hz); 7.05–7.36 (m, 10H, Ph). ^{13}C NMR spectrum (CH_2Cl_2): δ 68.64 (C(2, 5)); 68.77 (C(3, 4)); 127.56 ($C_{o,p}$); 147.40 (C_i).

PMR spectrum of FcCPh $^+PF_6^-$ (CD_2Cl_2): δ 4.88 (s, 5H, H(1')); 6.63 (m, 2H, H(2, 5)); 7.47 (m, 10H, Ph); 7.82 (m, 2H, C(3, 4)). ^{13}C NMR spectrum (CH_2Cl_2): δ 79.6 (C(2, 5)); 83.0 (C(1')); 94.9 (C(3, 4)); 101.8 (C(1) 130.2 (C_m); 132.4 (C_o); 132.6 (C_p); 139.8 (C_i), 171.6 (C^+).

Structure determination

X-Ray measurements were made on a crystal $0.10 \times 0.10 \times 0.25$ mm^3. Crystal data for $[Os(C_5H_5)(C_{18}H_{14})]PF_6$: $M = 630.57$, monoclinic space group $P2_1/c$ with $a = 10.550(5)$, $b = 19.121(7)$, $c = 10.514(3)$ Å, $\beta = 100.18(3)°$, $V = 2088(1)$ Å^3, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 65.6$ cm^{-1}, $F(000) = 1208$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $d_{calc} = 2.006$ g cm^{-3}. Data collection: Nicolet P3 diffractometer with ω-scan mode. Data collection range $4.0° < 2\theta < 50.0°$, $-12 \le h \le 12$, $0 \le k \le 22$, $0 \le l \le 12$. 3585 reflections measured, of which 2493 used in the refinement ($I > 2\sigma(I)$). The data were

Table 3

Bond angles (°) [a]

C(1)-Os-C(2)	39.3(2)	C(4)-Os-C(19)	151.7(4)
C(1)-Os-C(3)	64.3(2)	C(4)-Os-C(20)	155.8(3)
C(1)-Os-C(4)	64.2(2)	C(4)-Os-C(21)	118.4(3)
C(1)-Os-C(5)	39.2(3)	C(4)-Os-C(22)	100.0(3)
C(1)-Os-C(6)	37.3(3)	C(4)-Os-C(23)	115.2(4)
C(1)-Os-C(19)	130.2(3)	C(5)-Os-C(6)	65.8(3)
C(1)-Os-C(20)	132.6(3)	C(5)-Os-C(19)	133.8(3)
C(1)-Os-C(21)	150.8(3)	C(5)-Os-C(20)	166.4(3)
C(1)-Os-C(22)	164.1(4)	C(5)-Os-C(21)	155.9(3)
C(1)-Os-S(23)	145.2(3)	C(5)-Os-C(22)	126.4(4)
C(2)-Os-C(3)	38.0(3)	C(5)-Os-C(23)	117.3(4)
C(2)-Os-C(4)	63.5(3)	C(6)-Os-C(19)	93.3(3)
C(2)-Os-C(5)	64.9(3)	C(6)-Os-C(20)	101.8(3)
C(2)-Os-C(6)	65.3(3)	C(6)-Os-C(21)	137.1(4)
C(2)-Os-C(19)	144.4(4)	C(6)-Os-C(22)	155.6(3)
C(2)-Os-C(20)	116.2(3)	C(6)-Os-C(23)	119.4(3)
C(2)-Os-C(21)	113.1(3)	C(19)-Os-C(20)	37.5(4)
C(2)-Os-C(22)	137.5(3)	C(19)-Os-C(21)	62.9(3)
C(2)-Os-C(23)	175.2(3)	C(19)-Os-C(22)	62.9(3)
C(3)-Os-C(4)	37.2(3)	C(19)-Os-C(23)	37.5(4)
C(3)-Os-C(5)	63.4(2)	C(20)-Os-C(21)	37.7(3)
C(3)-Os-C(6)	99.4(3)	C(20)-Os-C(22)	63.0(4)
C(3)-Os-C(19)	162.3(3)	C(21)-Os-C(23)	63.0(4)
C(3)-Os-C(20)	126.6(3)	C(22)-Os-C(23)	37.7(3)
C(3)-Os-C(21)	99.5(3)	Os-C(1)-C(2)	72.2(4)
C(3)-Os-C(22)	105.0(3)	Os-C(1)-C(5)	72.7(4)
C(3)-Os-C(23)	138.2(3)	Os-C(1)-C(6)	82.5(5)
C(4)-Os-C(5)	37.8(2)	C(2)-C(1)-C(6)	116.6(7)
C(4)-Os-C(6)	99.6(3)	C(5)-C(1)-C(6)	118.3(6)
Os-C(2)-C(1)	68.6(4)	F(1)-P-F(2)	90.5(6)
Os-C(2)-C(3)	74.3(4)	F(1)-P-F(3)	175.3(6)
Os-C(3)-C(2)	67.7(4)	F(1)-P-F(4)	91.5(7)
Os-C(3)-C(4)	71.6(4)	F(1)-P-F(5)	89.3(7)
Os-C(4)-C(3)	71.1(4)	F(1)-P-F(6)	89.1(7)
Os-C(4)-C(5)	68.0(4)	F(2)-P-F(3)	85.1(6)
Os-C(5)-C(1)	68.2(4)	F(2)-P-F(4)	174.5(8)
Os-C(5)-C(4)	74.2(4)	F(2)-P-F(5)	96.6(7)
Os-C(6)-C(1)	60.2(4)	F(2)-P-F(6)	87.6(7)
Os-C(6)-C(7)	115.8(5)	F(3)-P-F(4)	92.9(7)
Os-C(6)-C(13)	116.8(5)	F(3)-P-F(5)	92.6(7)
C-(1)-C(6)-C(7)	119.3(7)	F(3)-P-F(6)	89.4(7)
C(1)-C(6)-C(13)	118.2(8)	F(4)-P-F(5)	88.6(8)
C(7)-C(6)-O(13)	115.3(7)	F(4)-P-F(6)	87.3(8)
C(6)-C(7)-C(8)	118.4(6)	F(5)-P-F(6)	175.5(6)
C(6)-C(7)-C(12)	121.6(6)		
C(6)-C(13)-C(14)	121.9(6)		
C(6)-C(13)-C(18)	118.0(6)		
Os-C(19)-C(20)	71.0(5)		
Os-C(19)-C(23)	71.0(5)		
Os-C(20)-C(19)	71.5(7)		
Os-C(20)-C(21)	70.8(7)		
Os-C(21)-C(20)	71.6(6)		
Os-C(21)-C(22)	71.1(6)		
Os-C(22)-C(21)	71.1(5)		
Os-C(22)-C(23)	71.6(5)		
Os-C(23)-C(19)	71.5(5)		
Os-C(23)-C(22)	70.8(5)		

---

[a] Cyclopentadienyl and phenyl rings are rigid groups and bond angles are 108° and 120°, respectively.

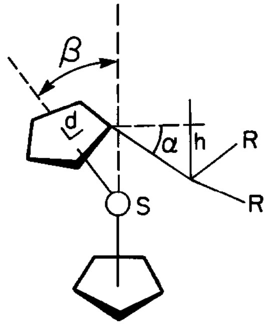

Fig. 3. Cations $(C_5R'_5OsC_5R'_4\overset{+}{C}R_2)$ (R = Ph, R' = H; R = H, R' = Me).

corrected for Lorentz and polarization effects and absorption from empirical ϕ-scan data.

Structure refinement: the structure was solved by direct methods using the SHELXS-86 program [1] and refined with anisotropic temperature factors for non-hydrogen atoms using the SHELX-76 program [2]. Phenyl and cyclopentadienyl rings were refined as rigid groups. Hydrogen atoms were introduced in the calculated positions and refined with fixed geometry with respect to their carrier atoms. Final values for R and R_w with $w = 1/\sigma^2(F_o)$ are, respectively, 0.040 and 0.038 for 251 variables. Residual electron density was within ±0.7 e Å^{-3} and largest Δ/σ 0.11. Scattering factors and anomalous dispersion corrections were taken from ref. 3. Calculations were performed on a VAX 8650 computer. Final coordinates and U_{eq} values are listed in Table 1.

References

1 W.E. Watts, J. Organomet. Chem. Libr., 7 (1979) 399.
2 A.A. Koridze, Usp. Khim., 55 (1986) 277; Russ. Chem. Rev., 55 (1986) 133.
3 M.I Rybinskaya, A.Z. Kreindlin and S.S. Fadeeva, J. Organomet. Chem., 358 (1988) 363.
4 M.I Rybinskaya, A.Z. Kreindlin, Yu.T. Struchkov and A.I. Yanovsky, J. Organomet. Chem., 359 (1989) 233.
5 A.I. Yanovsky, Yu.T. Struchkov, A.Z. Kreindlin and M.I. Rybinskaya, J. Organomet. Chem., 369 (1989) 125.
6 E I. Fedin, A.L. Blumenfeld, P.V. Petrovskii, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, J. Organomet. Chem., 292 (1985) 257.
7 M. Cais, S. Danis, F.M. Herbstein and M. Kapon, J Am. Chem. Soc., 100 (1978) 5554; S. Lupan, M. Kapon, M. Cais and F.M. Herbstein, Angew. Chem., Int. Ed. Engl., 11 (1972) 1025.
8 U Berens, J. Organomet. Chem., 182 (1979) 89
9 G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Ney York, 1982, p. 344.
10 M.D. Rausch, E.O. Fischer and H. Gubert, J. Am. Chem. Soc., 82 (1960) 76.
11 M.D. Rausch, M. Vogel and M. Rosenberg, J. Organomet. Chem., 22 (1957) 903.
12 R.A. Benkeser, W.P. Fitzgerald and M.S. Melzer, J. Organomet. Chem., 26 (1961) 2569.
13 K.M. Motyl, J.R. Norton, C.K. Schaner and O.P. Anderson, J. Am. Chem. Soc., 104 (1982) 7325.
14 G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Göttingen, Germany, 1986.
16 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.
17 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974