Novel Sandwich Cations of Platinum with Tetramethylcyclobutadiene and Cyclopentadienyl or Hexamethylbenzene Ligands†

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Highly reactive cations $[Pt(\eta^4\text{-}C_4Me_4)(solv)_x]^{2+}$ (solv = acetone or nitromethane) can be obtained from $[\{Pt(\eta^4\text{-}C_4Me_4)Cl_2\}_2]$ by chloride abstraction with $AgCF_3SO_3$. The solvento complex $[Pt(\eta^4\text{-}C_4Me_4)(Me_2CO)_x][CF_3SO_3]_2$ reacts with cyclopentadienes and with hexamethylbenzene to form the sandwich compounds $[Pt(\eta^4\text{-}C_4Me_4)(dienyl)]CF_3SO_3$ (dienyl = $\eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5H_4Me$ or $\eta^5\text{-}C_5H_5$) and $[Pt(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2\cdot Me_2CO$. The new compounds are characterised by ^1H, ^{13}C and ^{195}Pt NMR spectroscopy and cyclic voltammetry. The structure of the hexamethylbenzene complex, determined by X-ray crystallography, reveals an average Pt–C distance of 2.138 Å for the C_4Me_4 ligand and 2.351 Å for the C_6Me_6 ligand indicating a pronounced structural *trans* effect.

Half-sandwich complexes with three labile ligands, for example $[Ru(\eta^6\text{-}C_6Me_6)(Me_2CO)_3]^{2+}$ [1] and $[Rh(\eta^5\text{-}C_5Me_5)(Me_2CO)_3]^{2+}$,[2] are versatile building blocks in organometallic synthesis. These so-called soft-centre hard-shell[3] complexes are undeveloped so far for nickel-group metals. We wished to use the solvento species $[Pt(\eta^4\text{-}C_4Me_4)(solv)_x]^{2+}$ **1** (solv = acetone or nitromethane) in a comparative study on the reactivity of organometallic cations. In this paper we describe the formation of the new species **1** and their transformation into several new sandwich cations.

Experimental

Measurements.—The ^1H and $^{195}Pt\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker WP-80 PFT and the $^{13}C\text{-}\{^1H\}$ NMR spectra on a Bruker WH-270 PFT spectrometer at 306 K. Chemical shifts (relative to internal $SiMe_4$ for ^1H and ^{13}C and to 21.4 MHz for $^{195}Pt^4$) are positive to high frequency of the reference. Cyclic voltammetry was performed with a PAR model 173 potentiostat and a model 175 programmer. Cyclic voltammograms were recorded in a three-electrode cell containing a platinum inlay electrode as the working electrode, a platinum auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode, in acetonitrile (for **3a**–**3c**) or nitromethane (for **4**) solution ($\approx 10^{-3}$ mol dm^{-3}) with NBu_4PF_6 ($\approx 10^{-1}$ mol dm^{-3}) as supporting electrolyte; scan rate = 200 mV s^{-1} for **3a**–**3c** and 100 mV s^{-1} for **4**. Potentials are calibrated relative to internal ferrocene [$E^{0/+} = 0.400$ V *vs.* SCE,[5a] *cf.* 0.400 V *vs.* normal hydrogen electrode (NHE)[5b]]. Microanalyses were obtained from Labor Pascher, An der Pulvermühle 3, D-5480 Remagen 8.

Preparations.—Experiments were carried out under dinitrogen using conventional Schlenk techniques. Solvents were dried, deoxygenated and distilled under dinitrogen. Acetone was dried by the method of Burfield and Smithers.[6]

$[\{Pt(\eta^4\text{-}C_4Me_4)Cl_2\}_2]$. The dimer was prepared by a slightly modified literature procedure.[7] Hydrochloric acid–dichloromethane was added to the reaction mixture and the product was extracted with the help of a liquid–liquid extraction apparatus after Ludwig. $^{195}Pt\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ −2143.

$[Pt(\eta^4\text{-}C_4Me_4)(Me_2CO)_x][CF_3SO_3]_2$ ($x \approx 1.7$) **2**. Silver trifluoromethanesulfonate (silver triflate) (275 mg, 1.07 mmol) was added to a yellow suspension of $[\{Pt(\eta^4\text{-}C_4Me_4)Cl_2\}_2]$ (200 mg, 0.27 mmol) in acetone (10 cm^3). After stirring for 10 min the white precipitate of AgCl was removed by filtration through a frit (G3) covered with sea-sand (1 cm). The colourless solution of $[Pt(\eta^4\text{-}C_4Me_4)(Me_2CO)_x][CF_3SO_3]_2$ so obtained can be stored at −30 °C but slowly turns brown at room temperature due to decomposition. Removing the solvent *in vacuo* affords a white solid which can be redissolved in nitromethane. NMR: ^1H (CD_3NO_2), δ 1.71 [s, 12 H, C_4Me_4, *J*(PtH) 24] and 2.14 (s, 10 H, Me_2CO); ^{13}C (CD_3NO_2), δ 212.6 (CO), 119.0 [q, CF_3, *J*(CF) 319 Hz], 105.4 (br, C_4Me_4), 31.1 (*Me*$_2$CO) and 8.8 (C_4*Me*$_4$); $^{195}Pt\text{-}\{^1H\}$ [$(CD_3)_2CO$], δ +1256.

$[Pt(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_5Me_5)]CF_3SO_3\cdot Me_2CO$ **3a**·Me_2CO. Pentamethylcyclopentadiene (0.15 cm^3, 1.0 mmol) was added to a solution of compound **2** (0.54 mmol) in acetone (10 cm^3). After stirring at room temperature for 10 min $KOBu^t$ [0.54 mmol, 1 mol dm^{-3} solution in tetrahydrofuran (thf)] was added and the volatiles were removed *in vacuo*. Extraction of the residue with chloroform (3 × 10 cm^3) and filtration afforded a yellow solution which, after concentrating *in vacuo* and addition of hexane (10 cm^3), afforded a pale brown solid. Recrystallisation from acetone–diethyl ether at −30 °C gave **3a**·Me_2CO (260 mg, 82%) as white crystals (Found: C, 40.6; H, 5.15. Calc. for $C_{22}H_{33}F_3O_4PtS$: C, 40.9; H, 5.15%). NMR: ^1H ($CDCl_3$), δ 1.94 [12 H, C_4Me_4, *J*(PtH) 23], 2.04 [15 H, C_5Me_5, *J*(PtH) 21] and 2.16 (6 H, Me_2CO); ^{13}C [$(CD_3)_2CO$], δ 104.2 [*C*$_5$Me$_5$, *J*(PtH) 64], 91.9 [*C*$_4$Me$_4$, *J*(PtH) 153 Hz], 8.7 (C_5*Me*$_5$) and 6.8 (C_4*Me*$_4$); $^{195}Pt\text{-}\{^1H\}$ [$(CD_3)_2CO$], δ −2430. $E_p^c = -2.10$ V.

$[Pt(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_5H_4Me)]CF_3SO_3$ **3b**. As above the reaction mixture of methylcyclopentadiene (0.15 cm^3, 1.60 mmol) and complex **2** (0.54 mmol) in acetone (10 cm^3) was neutralised with $KOBu^t$ in thf. Extraction with chloroform (3 × 10 cm^3) gave a dark brown solution. Repeated precipitation with hexane and redissolution in acetone gave **3b** (140 mg, 50%) as a pale brown solid. NMR [$(CD_3)_2CO$]: ^1H, δ 2.25 [3 H, C_5H_4*Me*, *J*(PtH) 24], 2.30 [12 H, C_4Me_4, *J*(PtH) 20] and 6.16 [br, 4 H, C_5*H*$_4$Me, *J*(PtH) 27]; ^{13}C, δ 109.8 (C^1, C_5H_4Me), 96.8 [*C*$_4$Me$_4$, *J*(PtH) 162], 93.8 and 91.8 [C^2, C^5 and C^3, C^4, C_5H_4Me, *J*(PtC) 44 and 63], 11.8 (C_5H_4*Me*) and 8.3 [C_4*Me*$_4$, *J*(PtH) 17 Hz]; $^{195}Pt\text{-}\{^1H\}$, δ −2523. $E_p^c = -1.73$ V.

$[Pt(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_5H_5)]CF_3SO_3$ **3c**. Preparation from cyclopentadiene (0.15 cm^3, 1.80 mmol), complex **2** (0.54 mmol)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

in acetone (10 cm^3) and KOBu^t in thf afforded **3c** (167 mg, 60%) as a pale brown solid. NMR [$(CD_3)_2CO$]: ^1H, δ 2.37 [12 H, C_4Me_4, J(PtH) 17] and 6.30 [5 H, C_5H_5, J(PtH) 27]; ^{13}C, δ 98.0 [C_4Me_4, J(PtH) 166], 93.0 [C_5H_5, J(PtC) 57] and 8.7 [C_4Me_4, J(PtH) 16 Hz]; $^{195}Pt-\{^1H\}$, δ −2548. $E_p{}^c = -1.63$ V.

[Pt(η^4-C_4Me_4)(η^6-C_6Me_6)][CF_3SO_3]$_2$·Me_2CO **4**. A solution of complex **2** (1.08 mmol) in acetone (30 cm^3) was added to a suspension of C_6Me_6 (200 mg, 1.23 mmol) in acetone (10 cm^3). The colourless solution so obtained was kept at −30 °C for 12 h. White crystals of **4** formed which were collected, washed with Et_2O and dried. A small further crop was precipitated from the mother liquor by adding hexane giving a near quantitative yield of **4** (842 mg, 95%) (Found: C, 36.2; H, 4.50. Calc. for $C_{25}H_{36}F_6O_7PtS_2$: C, 36.5; H, 4.40%). NMR: ^1H [$(CD_3)_2CO$], δ 2.34 [12 H, C_4Me_4, J(PtH) 23] and 2.70 [18 H, C_6Me_6, J(PtH) 17 Hz]; ^{13}C [$(CD_3)_2CO$, −20 °C], δ 125.3 (C_6Me_6), 111.4 (C_4Me_4), 16.6 (C_6Me_6) and 7.5 (C_4Me_4); $^{195}Pt-\{^1H\}$ (CD_3NO_2), δ −1650. $E_p{}^c = -0.77$ and $E_p{}^a = 1.67$ V.

X-Ray Crystallography.—Geometry and intensity data for complex **4** were obtained on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation at 243 K.

Crystal data. $C_{22}H_{30}F_6O_6PtS_2$·C_3H_6O, $M = 821.77$, monoclinic, space group $P2_1/n$, $a = 8.708(5)$, $b = 28.84(1)$, $c = 12.365(3)$ Å, $\beta = 90.87(5)°$, $U = 3105(4)$ Å^3, $Z = 4$, $D_c = 1.76$ g cm^{-3}, μ(Mo-Kα) = 47.7 cm^{-1}, $F(000) = 1624$.

Data collection and processing. From a crystal of approximate dimensions 0.1 × 0.1 × 0.6 mm, 7913 reflections were recorded in the $+h$, $+k$, $\pm l$ quadrant of the reflection sphere with ω scans in the range $3 < \theta < 28°$. An empirical absorption correction[8] (transmission factors, minimum 0.91, maximum 1.00) was applied.

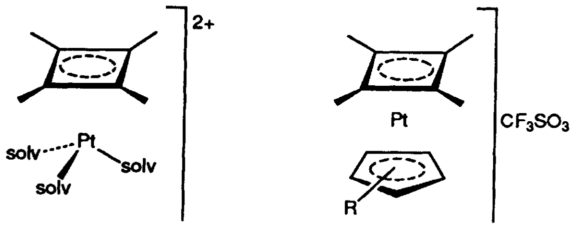
Structure solution and refinement. The structure was solved by Patterson and subsequent Fourier difference syntheses (SDP program system)[9] using 4983 unique reflections with $I > 3\sigma(I)$. In the final full-matrix least-squares refinement, non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included isotropically as riding atoms [C–H 0.98 Å, B_{iso} 1.3 × B_{eq}(C)] in structure-factor calculations; a correction for secondary extinction[10] was applied to F_{calc}. Refinement converged at $R = 0.033$, $R' = 0.041$ [$w^{-1} = \sigma^2(F_o)$] for 371 variables. A final Fourier difference map showed a local residual maximum of 1.26 e Å^{-3} close (0.9 Å) to the metal atom.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Characterisation of the New Complexes.—The complex [{Pt(η^4-C_4Me_4)Cl_2}$_2$][7] forms a stable dilute solution in acetone or nitromethane (solv). Chloride abstraction with Ag^+ or Tl^+ gives a white precipitate of AgCl or TlCl respectively and a colourless solution containing [Pt(η^4-C_4Me_4)(solv)$_x$]$^{2+}$ cations **1**. The stability of these cations is rather limited and depends on the solvent and counter ion used. Solutions in nitromethane with trifluoromethanesulfonate as anion are stable at room temperature while solutions in acetone or with tetraphenylborate as anion slowly turn brown due to decomposition. Addition of acetonitrile causes rapid decomposition. In the case of the reaction with silver trifluoromethanesulfonate in acetone the salt [Pt(η^4-C_4Me_4)(Me_2CO)$_x$][CF_3SO_3]$_2$ **2** could be isolated as a white solid. This solid contains approximately 1.7 molecules of acetone per platinum as judged from its ^1H NMR spectrum. It seems likely that during the evaporation of the solvent the solvent ligands are in part replaced with trifluoromethanesulfonate anions. In solution the true value of x is not known although a value of 3 seems likely.

In the ^1H NMR experiments with [$^2H_6$]acetone as solvent it was found that the cations **1** react with cyclopentadienes to form new sandwich cations [Pt(η^4-C_4Me_4)(dienyl)]$^+$ (dienyl = η^5-C_5Me_5, η^5-C_5H_4Me or η^5-C_5H_5). Analogous cations [M(η^4-C_4R_4)(η^5-C_5H_5)]$^+$ of nickel (M = Ni, R = Me[11] or Ph[12]) and palladium (M = Pd, R = Ph[12]) are known. On a preparative scale the reaction of **2** with pentamethylcyclopentadiene in acetone was straightforward and afforded white crystals of an acetone solvate [Pt(η^4-C_4Me_4)(η^5-C_5Me_5)]CF_3SO_3·Me_2CO **3a**·Me_2CO. The reactions with methylcyclopentadiene and cyclopentadiene itself were more difficult because of rather fast decomposition and it was necessary to remove the acid formed in the reaction. Addition of one equivalent of KOBu^t and repeated precipitation from acetone–hexane yielded the trifluoromethanesulfonates **3b** or **3c** as pale brown solids. Complex **3c** can also be made from complex **2** and trimethylsilylcyclopentadiene. Although **3b** and **3c** could be crystallised from chloroform at low temperature satisfactory elemental analyses could not be obtained. An exploratory cyclic voltammetric study of the complexes **3a**–**3c** showed that these compounds are electronically inflexible. Only an irreversible reduction could be detected within the electrochemical windows of acetonitrile and of dichloromethane and no electrochemically-active product was found. The substituent effect of the methyl groups amounts to 94 mV per methyl group. This effect is large compared to the 52 mV per methyl group observed for ferrocene derivatives[13] and to the 56 mV per methyl group found for [Ni(η^4-C_4Me_4)(η^5-C_5H_5)]$^+$,[12] thus indicating strong Pt–C_5H_5 bonding.[14]



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	R
3a	Me_5
3b	H_4Me
3c	H_5

In NMR tube experiments in acetone or nitromethane the cations **1** are seen to react with hexamethylbenzene to form the novel sandwich cation [Pt(η^4-C_4Me_4)(η^6-C_6Me_6)]$^{2+}$. This is an analogue of the nickel complex [Ni(η^4-C_4Ph_4)(η^6-C_6Me_6)][$AlCl_4$]$_2$[15] and, to the best of our knowledge, the labile solution species [Pt(η^3-C_3H_4Me-2)(η^6-C_6Me_6)]$^+$[16] is the only previous example of a platinum arene complex. The preparation works best in acetone where the solvate [Pt(η^4-C_4Me_4)(η^6-C_6Me_6)][CF_3SO_3]$_2$·Me_2CO **4** readily crystallises from the reaction mixture as thin white leafy crystals. The arene ligand seems to be quite labile and is readily displaced by Cl^- from LiCl or by acidified water (*cf*. ref. 17). More basic reagents such as F^- or acetonitrile induce decomposition. The NMR spectral data of complex **4** also indicate only weak interaction between the hexamethylbenzene ligand and the platinum centre. Complexation of the arene ligand is accompanied by comparatively small changes in the ^{13}C NMR chemical shifts (from δ 132.0 and 16.8 in the free arene to δ 125.3 and 16.6 in complex **4**); likewise the direct coupling [$^1J(^{195}Pt-^{13}C) = 25$ Hz] is rather small. Cyclic voltammetric studies revealed an irreversible oxidation ($E_p{}^a = 1.67$ V) and an irreversible reduction ($E_p{}^c = -0.77$ V) but no product could be detected. Note that analogous ruthenium and rhodium complexes exhibit reduction products with η^4-co-ordination of hexamethylbenzene.[18]

Crystal Structure Determination for Complex **4**.—Low temperature diffraction data (−30 °C) afforded a satisfactory structure solution. The cation shows a sandwich structure (Fig.

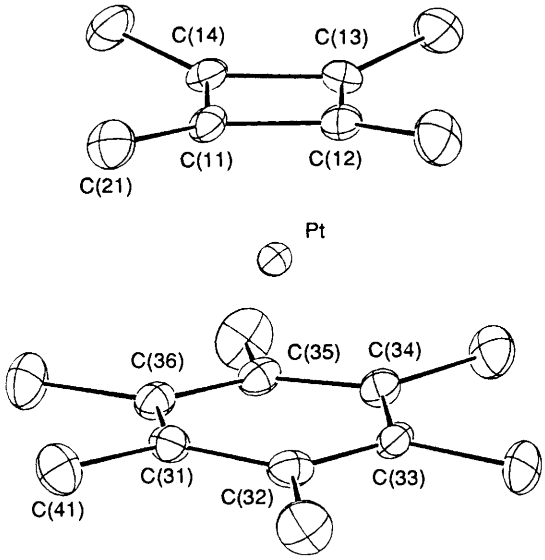

Fig. 1 View of the cation in $[Pt(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2\cdot Me_2CO$ **4**

1 and Tables 1 and 2). While the cyclobutadiene ring is planar (maximal perpendicular displacement 0.010 Å), the arene ring shows irregular deviations from planarity [maximal perpendicular displacements −0.050 Å for C(34) and +0.040 Å for C(35) with C(31) and C(34) bent towards the metal]. An earlier room-temperature measurement had produced more pronounced distortions of the arene ligand while the anion and the acetone molecule could not be refined satisfactorily. From this situation we conclude that we should not attach too much significance to the smaller deviations from planarity found at the lower temperature. The two best planes through the C_4- and C_6-ring skeletons are coplanar (interplanar angle 0.4°).

For the cyclobutadiene ligand the average Pt–C distance, 2.138 Å [2.126(5)–2.155(5) Å], is slightly shorter than that in the complex $[Pt(\eta^4\text{-}C_4Me_2\text{-}1,2\text{-}Ph_2\text{-}3,4)(PPh_3)Cl_2]$,[19] 2.165 Å [2.116(9)–2.214(8) Å]. Structure determinations for $[Pt_2(\mu\text{-}Cl)_3(\eta^4\text{-}C_4Pr_4)_2][Pt(CO)Cl_3]$[20] and $[PtMe(\eta^4\text{-}C_4Me_4)(PMe_2Ph)_2]SbF_6$[21] have also been reported but the data obtained are not sufficiently accurate and reliable for a meaningful comparison.

For the arene the average Pt–C bond length is 2.351 Å [ranging from 2.319(5) to 2.380(6) Å]. Thus the arene ligand is much less tightly bonded than the cyclobutadiene ring, and the data demonstrate a pronounced structural *trans* effect with a strong cyclobutadiene–platinum interaction and a much weaker arene–platinum bond. This observation can readily be understood on the basis of qualitative molecular-orbital considerations. In ferrocene-type complexes the main contribution to the bonding is the interaction between the e_1 ligand orbitals [*i.e.*, e for a $Pt(C_4R_4)$ fragment and e_1 for a $Pt(C_6R_6)$ fragment] and the $e_1{}^*$ metal orbitals.[22] The e orbital set of a cyclobutadiene ring is closer in energy to the $e_1{}^*$ metal orbitals (of $5d_{xy}$ and $5d_{xz}$ origin) than the e_1 set of an arene. As a consequence of this, cyclobutadiene–platinum bonding is stronger and the arene–platinum interaction is weakened.

Table 1 Fractional atomic coordinates for $[Pt(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2\cdot Me_2CO$ **4**

Atom	*x*	*y*	*z*
Pt	0.238 97(2)	0.147 70(1)	0.107 96(2)
S(1)	0.230 8(3)	0.214 02(7)	0.565 3(2)
S(2)	0.730 9(3)	0.027 49(8)	0.253 5(2)
F(11)	0.345(1)	0.156 1(3)	0.704 9(5)
F(12)	0.339(1)	0.130 6(2)	0.551 8(6)
F(13)	0.143(1)	0.136 8(3)	0.637(1)
F(21)	0.913 6(9)	0.023 8(4)	0.415 8(6)
F(22)	0.727(1)	−0.024 0(3)	0.426 2(5)
F(23)	0.910(1)	−0.038 1(3)	0.320 5(9)
O(11)	0.161(1)	0.207 8(3)	0.466 2(5)
O(12)	0.144(1)	0.235 6(3)	0.643 1(6)
O(13)	0.377(1)	0.230 0(4)	0.557(1)
O(21)	0.854 0(8)	0.042 6(2)	0.189 3(5)
O(22)	0.637(1)	−0.008 6(3)	0.202 4(6)
O(23)	0.648(1)	0.061 3(3)	0.305 5(8)
O(31)	0.724 4(9)	0.125 4(3)	0.742 3(6)
C(1)	0.261(1)	0.156 6(3)	0.615 6(8)
C(2)	0.821(2)	−0.006 4(4)	0.355(1)
C(3)	0.717(1)	0.104 1(4)	0.659 9(7)
C(4)	0.756(2)	0.127 2(5)	0.554(1)
C(5)	0.674(2)	0.055 8(5)	0.649(1)
C(11)	0.218 9(7)	0.198 4(2)	0.231 7(5)
C(12)	0.105 0(7)	0.162 5(2)	0.247 0(5)
C(13)	0.224 6(8)	0.129 4(2)	0.274 7(5)
C(14)	0.340 0(7)	0.166 0(2)	0.262 3(5)
C(21)	0.213 6(9)	0.249 6(2)	0.212 8(6)
C(22)	−0.065 1(8)	0.161 7(3)	0.252 0(7)
C(23)	0.227(1)	0.081 3(2)	0.316 0(6)
C(24)	0.506 0(8)	0.170 7(3)	0.285 2(6)
C(31)	0.276 1(7)	0.179 3(2)	−0.062 2(5)
C(32)	0.126 5(7)	0.158 4(2)	−0.066 9(5)
C(33)	0.107 2(7)	0.111 4(2)	−0.038 5(5)
C(34)	0.237 0(7)	0.083 8(2)	−0.005 9(5)
C(35)	0.387 8(7)	0.103 1(2)	−0.013 3(5)
C(36)	0.406 6(7)	0.151 0(2)	−0.038 0(5)
C(41)	0.294 4(9)	0.230 0(2)	−0.088 3(6)
C(42)	−0.008 3(8)	0.187 3(3)	−0.104 0(7)
C(43)	−0.049 5(8)	0.089 5(3)	−0.044 1(7)
C(44)	0.213 7(9)	0.034 8(2)	0.029 8(6)
C(45)	0.525 3(8)	0.072 5(3)	0.005 4(7)
C(46)	0.567 9(8)	0.170 8(3)	−0.039 6(7)

Table 2 Selected bond lengths (Å) for $[Pt(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2\cdot Me_2CO$ **4**

Pt–C(11)	2.126(5)	Pt–C(32)	2.380(6)
Pt–C(12)	2.136(5)	Pt–C(33)	2.373(5)
Pt–C(13)	2.134(5)	Pt–C(34)	2.319(5)
Pt–C(14)	2.155(5)	Pt–C(35)	2.375(5)
Pt–C(31)	2.320(5)	Pt–C(36)	2.340(5)
C(11)–C(12)	1.448(7)	C(11)–C(21)	1.496(8)
C(12)–C(13)	1.450(9)	C(12)–C(22)	1.483(8)
C(13)–C(14)	1.468(8)	C(13)–C(23)	1.478(8)
C(14)–C(11)	1.454(8)	C(14)–C(24)	1.475(8)
C(31)–C(32)	1.435(8)	C(31)–C(41)	1.507(8)
C(32)–C(33)	1.410(8)	C(32)–C(42)	1.506(8)
C(33)–C(34)	1.436(8)	C(33)–C(43)	1.504(7)
C(34)–C(35)	1.431(7)	C(34)–C(44)	1.493(8)
C(35)–C(36)	1.423(8)	C(35)–C(45)	1.502(8)
C(36)–C(31)	1.427(8)	C(36)–C(46)	1.518(8)

Platinum-195 *NMR Spectra*.—Although a large body of ^{195}Pt NMR data is available,[23] no studies of sandwich-type complexes have been published. We report here data for $[\{Pt(\eta^4\text{-}C_4Me_4)Cl_2\}_2]$ and the compounds **2**, **3a**–**3c** and **4**. The chemical shifts observed for the sandwich cations show extremely low values and are, as far as the cations **3a**–**3c** are concerned, outside the hitherto documented range.[23] However, comparing chemical-shift patterns for magnesium[24] and for transition-metal nuclei,[24,25] the very low values are not surprising. Within the cyclopentadienyl compounds **3a**–**3c** $\delta(^{195}Pt)$ decreases linearly with increasing number of methyl groups. This trend corresponds to an increasing HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) gap and is expected from the paramagnetic term of the Ramsey equation.

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