Synthesis and Molecular Structure of $(NBu_4)_2\{Pb[Pt(C_6F_5)_4]_2\}$, the First Lead(II) Compound Linearly Bonded to Two Metal Atoms

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Received March 20, 1992

The first example of a compound containing a naked digonal Pb atom linked to two transition metal atoms, $Pb[Mn(\eta\text{-}Cp)(CO)_2]_2$, has been recently described by Herrmann et al.,[1] and the structural data have been interpreted in terms of multiple bonds between the central Pb(IV) atom and the two Mn atoms.

Here, we report the synthesis and structural characterization of the first compound containing a central Pb(II) atom linearly coordinated to two Pt(II) atoms through single covalent bonds, the lone pair of the Pb(II) atom being stereochemically inactive. Some interesting pyramidal tricoordinated Pb(II) complexes containing Mo–Pb bonds and, as expected, a stereochemically active lone pair of electrons have been described recently.[2]

The 2:1 reaction between $(NBu_4)_2[Pt(C_6F_5)_4]$ and $Pb(NO_3)_2$ in methanol (eq 1)[3] takes place without precipitation of metallic

$$2(NBu_4)_2[Pt(C_6F_5)_4] + Pb(NO_3)_2 \xrightarrow{MeOH} 2(NBu_4)(NO_3) + \underset{\mathbf{1}}{(NBu_4)_2\{Pb[Pt(C_6F_5)_4]_2\}} \quad (1)$$

lead and renders (after addition of water) a yellow-green crystalline solid (82% yield), **1**, whose structure has been established by a single-crystal X-ray study.[4] A drawing of the trinuclear anion in **1** is presented in Figure 1. The lead atom lies on the shared apex of two square pyramids and is linearly bonded to the two Pt centers in the $Pt(C_6F_5)_4$ groups whose basal planes, each defined by the set of four C_{ipso} atoms, are essentially parallel (3.8°) and almost eclipsed, with a mean C_{ipso}–Pt···Pt–C_{ipso} torsion angle of 8.1°. The shift of the Pt atoms from each basal plane is 0.14 Å toward the lead atom; the Pt–Pb–Pt angle is 178.6 (1)°. Both Pb–Pt bonds are almost perpendicular to the basal planes (deviation <2°) and the Pb–Pt distances are 2.769 (2) and 2.793 (2) Å, suggesting the presence of single Pb–Pt bonds.[5]

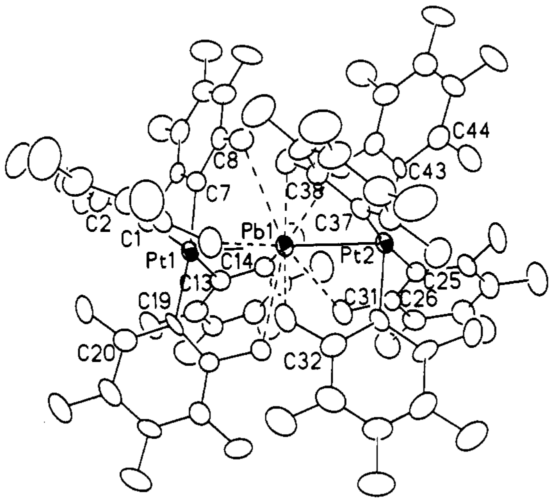

Figure 1. Molecular structure of the anion $\{Pb[Pt(C_6F_5)_4]_2\}^{2-}$. Selected bond lengths (Å) and bond angle (deg): Pb1–Pt1, 2.769 (2); Pb1–Pt2, 2.793 (2); Pt1–C1, 2.071 (14); Pt1–C7, 2.098 (17); Pt1–C13, 2.049 (15); Pt1–C19, 2.070 (17); Pt2–C25, 2.067 (14); Pt2–C31, 2.065 (17); Pt2–C37, 2.097 (15); Pt2–C43, 2.065 (15); Pb1···F6, 2.798 (2); Pb1···F8, 2.995 (3); Pb1···F14, 2.826 (2); Pb1···F24, 2.795 (2); Pb1···F26, 2.761 (2); Pb1···F32, 2.820 (2); Pb1···F38, 2.918 (2); Pb1···F48, 2.845 (2); Pt1–Pb1–Pt2, 178.6 (1).

Another important feature in the structure of **1** is the existence of eight Pb···*o*-F short contacts (from 2.761 (2) to 2.995 (3) Å; average 2.845 Å), with one of the *o*-F atoms of each C_6F_5 group. The eight *o*-F atoms involved form an axially compressed square antiprism (Figure 2), which requires a twist of each C_6F_5 group by an average angle of about 27.2° out of the respective C–Pt···Pt–C plane. Alternatively, the normals to the C_6F_5 groups make an average angle of 62.8° with the Pt–Pb vector. The anion has very nearly D_4 symmetry; the crystal is, however, racemic.

Heteronuclear Pt–Ag[6] and Pt–Sn[7] complexes containing C_6F_5 or C_6Cl_5 groups bonded to platinum show similar Ag···*o*-X or Sn···*o*-F contacts which appear to be determinant for both the stability and the structure of the complexes. The parameter ρ (defined as experimental distance/sum of covalent radii)[8,9]

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(1) Herrmann, W. A.; Kneuper, H. J.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *241*, 1062.

(2) Hitchcock, P. B.; Lappert, M. F.; Michalczyk, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2635.

(3) To a methanolic solution (15 mL) of 0.2000 g (0.1483 mmol) of $(NBu_4)_2[Pt(C_6F_5)_4]$[12] was added 0.0246 g (0.0741 mmol) of $Pb(NO_3)_2$, and the mixture was stirred at room temperature for 15 min, during which the color of the solution changed from colorless to greenish-yellow. Addition of deionized water (50 mL) produced the precipitation of a greenish-yellow solid, **1**, which was washed with two portions (20 mL) of water and air-dried. The solid was redissolved in methanol, evaporated to dryness again, and, finally, washed with *n*-hexane (5 × 10 mL): 82% yield; correct C, H, and N analysis; mp 60 °C dec; molar conductivity $\Lambda_M = 217$ S m^2 mol^{-1}. IR (Nujol), ν (cm^{-1}): C_6F_5 groups 1639 (w), 1608 (w), 1502 (vs), 1052 (vs), 952 (vs); X-sensitive 795 (m), 774 (vs); NBu_4^+ 880 (br). ^{19}F NMR (188 MHz, reference $CFCl_3$, –60 °C, saturated $CDCl_3$ solution), δ: F_o –115.8 (m), –117.6 (d) ($^3J_{F_o-F_m} = 28$ Hz, $^3J_{Pt-F_o} = 299$ Hz); F_m –164.0 (br), –164.9 (m); F_p –163.2 (t) (integration: ortho:meta:para = 2:2:1).

(4) Crystals of **1** suitable for X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a saturated solution of **1** in chloroform at room temperature. Out of the mother liquors, they very quickly undergo loss of solvent, to prevent which the crystal was removed from the test tube already covered with grease. Data collection was performed at 233 K, the crystal showing no signs of decomposition. X-ray structure analysis: $C_{80}H_{72}F_{40}N_2PbPt_2\cdot0.8CHCl_3$; greenish-yellow, laminar crystals; space group $P\bar{1}$, $a = 15.088$ (13) Å, $b = 16.697$ (13) Å, $c = 21.645$ (14) Å, $\alpha = 105.64$ (6)°, $\beta = 97.08$ (6)°, $\gamma = 113.48$ (6)°, V = 4649 (6) Å^3, Z = 2; size 0.78 × 0.015 × 0.48 mm^3; $\lambda = 0.710\,73$ Å; μ(Mo Kα) = 51.40 cm^{-1}; absorption correction (nine Ψ scans, with transmission factors 0.269–0.681); four-circle diffractometer, Siemens/Stoe AED2; $3° \le 2\theta \le 47°$; ω–θ scan method; total number of reflections 12 653; 7353 unique reflections with $F_o^2 \ge 3\sigma(F_o^2)$; heavy-atom method; refinement on F to $R = 0.0459$, $R_w = 0.0634$, GOF = 1.20 [13]; all atoms treated as anisotropic except C_7 and solvent atoms; weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0020F_o^2$; 1146 variables. A full report of the structure determination will be published later. Scattering factors were taken from ref 14.

(5) The Pt–Pb distance for *cis*-$[Pt(PPh_3)_2(Ph)(PbPh_3)]$ is 2.698 Å: Crociani, B.; Nicolini, M.; Clementi, D. A.; Bandoli, G. *J. Organomet. Chem.* **1973**, *49*, 249.

(6) Usón, R.; Forniés, J.; Tomás, M. *J. Organomet. Chem.* **1988**, *358*, 525 and references therein.

(7) Usón, R.; Forniés, J.; Tomás, M.; Usón, I. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1449.

(8) There is scarce information in the literature regarding a covalent radius for Pb(II). For this case, we subtracted the radius of Pt(II) from the average Pt–Pb distance. The Pt(II) radius (1.33 Å) was derived by subtracting the covalent radius of carbon[9] from the mean Pt–C bond distance. We do not imply transferability of the Pb(II) radius thus obtained (1.45 Å) to other compounds.

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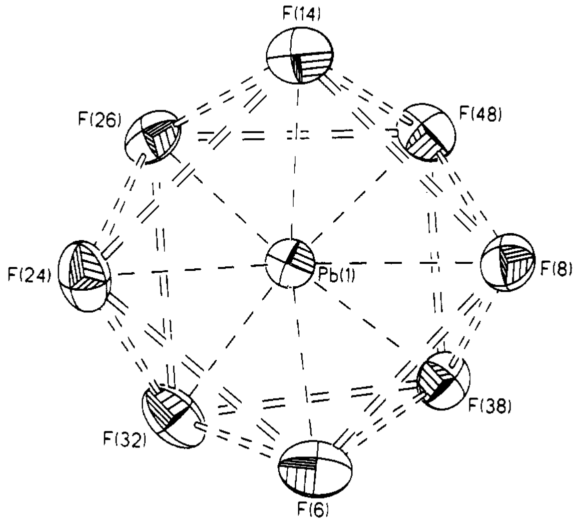

Figure 2. Polyhedron formed by the eight *o*-F atoms which make short nonbonded contacts with the central lead atom on the anion $\{Pb[Pt(C_6F_5)_4]_2\}^{2-}$. The Pb···F distances are given in caption for Figure 1.

averages 1.36 for complex **1** and lies at the low end of the range obtained for Pt–Ag complexes (ρ = 1.31–1.47), pointing to a relatively strong interaction. As with the Pt–Ag compounds,[6] we believe that the strong *o*-F···Pb contacts are implicated in the stability of compound **1** and that they may even be responsible for the formation of this unusual, linear Pb(II) complex. Recently, a mononuclear lead(II) complex, $\{Pb[2,4,6\text{-}(CF_3)_3C_6H_2]_2\}$ has been reported in which four Pb···F contacts (average distance 2.845 Å) between one F atom of each *o*-CF_3 group and the central Pb(II) are present and possibly acting in a similar way, i.e. donating electron density to the Pb(II) acceptor.[10]

The interactions between the Pb center and the endo ortho fluorine atoms observed in the solid state are maintained even in $CDCl_3$ solution at –60 °C. In the ^{19}F NMR spectrum, two sets of signals are observed[3] in the ortho fluorine region: for the endo ortho fluorine nuclei a symmetric unresolved multiplet, which is the result of superimposing signals ($^3J_{F_o-F_m}$, J_{Pb-F_o}, $a_{^{207}Pb} = 22.4\%$; $^2J_{Pt-F}$, $^3J_{Pt-F}$ $a_{^{195}Pt} = 33.8\%$), and for the exo ortho fluorine a doublet ($^3J_{F_o-F_m}$) with platinum satellites (J_{Pt-F}). The meta nuclei give rise to two sets of peaks: a multiplet and a broad peak. For the para nuclei, a pseudotriplet is observed. At room temperature (20 °C), the system is dynamic and a broad hump is observed in the ortho fluorine region. Fast exchange is almost attained at 50 °C: a somewhat broad doublet along with platinum satellites is observed for the ortho fluorine nuclei.

Moreover, acetone solutions of complex **1** are conducting (Λ_M = 217 S m^2 mol^{-1}, as expected for a 1:2 electrolyte), showing that the donor solvent is unable to cleave the Pt–Pb bond, in contrast to the behavior of some Pt–Ag complexes.[11] Neither a color change nor any other sign of decomposition can be observed in this solvent.

Acknowledgment. We are grateful to the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT) for financial support (Project PB88-0076) and for a Formación de Personal Investigador grant to I.U.

Supplementary Material Available: A brief textual description of the crystal structure determination, a table of atomic coordinates and equivalent isotropic displacement parameters, and ^{19}F NMR spectra of compound **1** (6 pages). Ordering information is given on any current masthead page.

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