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Synthesis and Structure of [Pb(2-Py)$_3$Li·THF], Containing a Low-Valent Group 14 Tris(pyridyl) Ligand (2-Py = 2-Pyridyl)

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*Summary: The reaction of [2-PyLi] with [Cp$_2$Pb] produces [Pb(2-Py)$_3$Li·THF] (**1**), containing the first example of a low oxidation state group 14 tris(pyridyl) ligand. The solid-state structure of **1** is that of a cage resulting from the symmetrical complexation of the Li$^+$ cation by all the pyridyl-N centers of the [Pb(2-Py)$_3$]$^-$ anion.*

Neutral tris(pyridyl) ligands containing main group 14 [XC(2-Py)$_3$; X= OH, H][1] and 15 [E(2-Py)$_3$; E = N, P, As][2] bridgehead atoms have an extensive coordination chemistry with transition metals. These species exhibit acceptor behavior and thus have been observed to stabilize low oxidation state transition metal ions.[3] This property appears to be an intrinsic feature of the pyridyl groups themselves, and the coordination characteristics are largely unaffected by interchanging the main group bridgehead atom for another in the same group, implying that there is little charge transfer from or to the coordinated metal ion to the bridgehead.[1,2] However, for the heavier (more metallic) main group elements, where the “lone pair” ($n - 2$) oxidation state is more accessible (n = number of valence electrons), we reasoned that greater electrochemical participation of the bridgehead atom may be possible. The latter appears to be confirmed by synthetic and electrochemical studies of [*n*-BuSn(2-Py)$_3$], which (in contrast to [HC(2-Py)$_3$][1h]) gives a stable Cu(I) complex on reaction with [CuCl$_2$].[4]

Scheme 1

$$[\mathrm{Cp_2Pb}] \;+\; 3[\text{2-PyLi}] \xrightarrow{\mathrm{THF}} [\mathrm{Pb(2\text{-}Py)_3Li.THF}] \;+\; 3[\mathrm{CpLi}]$$

1

We report here that the reaction of [2-PyLi] with [Cp$_2$Pb] (3:1 equiv) at −78 °C in THF gives [Pb(2-Py)$_3$Li·THF] (**1**), containing the first example of a low oxidation state group 14 tris(pyridyl) ligand (Scheme 1).[5]

A low-temperature X-ray crystallographic study of **1** shows it to be composed of ion-contacted monomers [Pb(2-Py)$_3$Li·THF], formed by the association of the tris(pyridyl) lead(II) plumbate anion [Pb(2-Py)$_3$]$^-$ with a THF-solvated Li$^+$ cation (Figure 1).[6] The coordination of the plumbate anion to Li by all three of the pyridyl-*N* centers is highly symmetrical and results in little distortion of the pyridyl groups, with the Li centers only being *ca.* 6° out of the planes of the pyridine rings. This can be compared to the situation in [*n*-BuSn(2-Py)$_3$LiBr], where distortion of the tris(pyridyl) Sn(IV) ligand occurs in order to accommodate the Li$^+$ cation.[4] Despite the very acute C−Pb−C angles present in **1** {C(Py)−Pb−C(Py) average 91.8°; cf. C(Py)−Sn−C(Py) *ca.* 102° in [*n*-BuSn(2-Py)$_3$LiBr][4]}, the presence of a larger bridgehead atom results in a greater ligand bite than for the [*n*-BuSn(2-Py)$_3$] ligand. Thus, the Li$^+$ cation is accommodated without significant re-orientation of the pyridine rings and with nearly tetrahedral N−Li−N coordination angles (average 106.7° in **1**; cf. average 101.0° in [*n*-BuSn(2-Py)$_3$LiBr][4]). The Pb···Li distance in **1**

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[5] *Synthesis of **1**:* *n*-BuLi (8.0 mL, 1.5 mol L^{-1}, 12 mmol) was added dropwise to a solution of 2-bromopyridine (1.90 g, 12 mmol) in THF (30 mL) at −78 °C. After being stirred (1 hr) at −78 °C, a solution of [Cp$_2$Pb] (1.35 g, 4 mmol) in THF (10 mL) was slowly added. The light yellow solution produced was filtered (Celite) and the filtrate reduced to *ca.* 8mL under vacuum, whereupon a yellow solid precipitated. The solid was warmed back into solution and storage (20 °C, 24 h) gave yellow cubic crystals of **1**: yield 1.17 g (56%); decomp 150−160 °C; IR (Nujol) 3050 (w) (C−H aryl str), 1565 (m), 1547 (m) (C$\overline{\cdot\cdot}$N str), other bands at 1259 (m), 1146 (m), 1040 (s), 888 (s), 798 (m), 756 (s), 730 (s); ^{1}H NMR (250Mz, DMSO-d_6, +25 °C) 8.36 [d, 3H, C(6)−H], 8.13 [d, 3H, C(3)−H], 7.10 (d d, 3H) and 6.65 (m, 3H) [C(4)−H and C(5)−H], 3.64 (m, 4H, −CH$_2$−, THF), 1.42 (m, 4H, −CH$_2$−, THF); ^{13}C NMR (250Mz, DMSO-d_6, +25 °C) 150.6 [C(6), 2-Py], 136.7, 133.3, and 119.6 [C(3,4,5), 2-Py], 68.2 [C(2,5), THF], 25.8 [C(3,4), THF]. Anal. Found: C, 43.8; H, 3.8; N, 7.7. Calcd: C, 44.2; H, 3.1; N, 8.1.

[6] *Crystal data for **1**:* C$_{19}$H$_{20}$LiN$_3$PbO, M = 520.51, monoclinic, space group $P2_1/c$, a = 8.684(3) Å, b = 22.731(8) Å, c = 10.075(4) Å, β = 108.92(3)°, V = 1881(1) Å^3, Z = 4, ρ_{calc} = 1.538 Mg m^{-3}, λ = 0.710 73 Å, T = 153(2) K, μ(Mo Kα) = 8.978 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal[10] of dimensions 0.3 × 0.3 × 0.3 mm by the θ/ω method (4.17° $\leq \theta \leq$ 22.51°). Of a total of 2969 collected reflections, 2439 were independent. The data were corrected for absorption using ψ-scans (max, min transmission, 0.524, 0.105). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ ($F > 4\sigma(F)$) = 0.037 and w$R2$ = 0.101 (all data) [$R1 = \sum|F_o - F_c|/\sum F_o$ and w$R2 = (\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2)^{0.5}$, $w = 1/[\sigma^2(F_o{}^2) + (xP)^2 + yP]$, $P = F_o{}^2 + (2F_c{}^2/3)$].[11] Largest peak and hole in the final difference map: 1.053 and −1.150 e Å^{-3}.

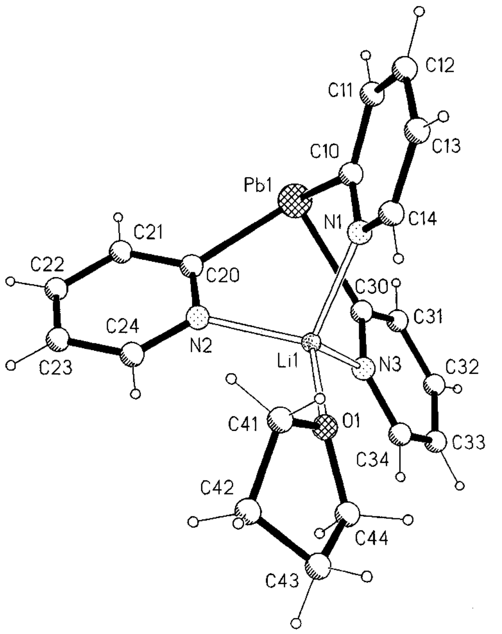

Figure 1. Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Key bond lengths (Å) and angles (deg): Pb(1)−C(10) 2.35(1), Pb(1)−C(20) 2.34(1), Pb(1)−C(30) 2.34(1), average (Py) C$\overline{\cdot\cdot}$C 1.38, average (Py) C$\overline{\cdot\cdot}$N 1.34, average Li−N 2.04, Pb(1)···Li(1) 3.42(2), C(10)−Pb(1)−C(20) 91.9(4), C(10)−Pb(1)−C(30) 92.2(4), C(20)−Pb(1)−C(10) 91.3(3), average N−Li−N 106.6, average N−Li(1)−O(1) 112.1, average Pb(1)−C(Py)−N(Py) 121.6, average C(Py)−N(Py)−Li(1) 114.2, Pb(1)···Li(1)−O(1) 175.1.

[3.42(2) Å] is far longer than the Pb−Li bond in [Ph_3PbLi·PMDETA] [2.85(1) Å],[7] and it is unlikely, particularly bearing in mind the typical pseudotetrahedral geometry of the Li center, that there is any significant bonding involved.

The pattern of C$\overline{\cdot\cdot}$N and C$\overline{\cdot\cdot}$C bond lengths in **1** can be compared to that occurring in the related anions $[E(2\text{-}Py)_2]^-$ (E = P, As,[8a] CH[8b,c]). In the latter the short bridgehead E−C bond lengths and alternating pyridyl C$\overline{\cdot\cdot}$N and C$\overline{\cdot\cdot}$C bond lengths suggest that there is significant dispersion of the formal negative charge on the bridgehead centers throughout the aromatic system. In contrast, the uniform distances within the pyridyl groups of **1** illustrate that there is little charge transfer from the Pb to the pyridyl rings. Clearly, this is a consequence of the inaccessibility of the (essentially 6s^7) lone pair on Pb which is of far lower energy than those present in the lighter elements.

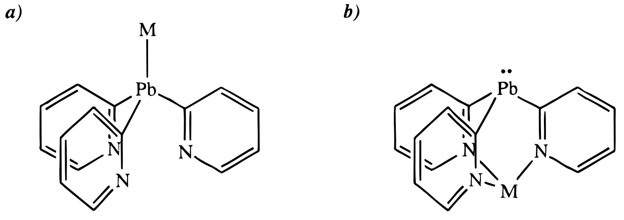

Figure 2. Potential modes of coordination of $[Pb(2\text{-}Py)_3]^-$ to metals (M).

Complex **1** is a rare example of a structurally characterized s block metal tris(organo) plumbate. To our knowledge, only $2[(\eta^3\text{-}Cp)_3Pb]^-[Mg(THF)_6]^{2+}$, $[(\eta^5\text{-}Cp)_2Pb(\mu\text{-}Cp)Na$·PMDETA],[9] and [$Ph_3PbLi$·PMDETA][7] have so far been structurally elucidated. The title compound is the only example containing a functionalized tris(organo)plumbate and the first example of a +2 oxidation state tris(pyridyl) Group 14 ligand to be reported. The investigation of the coordination chemistry of this new class of ligand ($[E(2-Py)_3]^-$) is an interesting prospect, particularly in view of the dual functionality of the ligand and the potential of this system for alternative modes of metal complexation (Figure 2).

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Supporting Information Available: Tables X-ray data, positional and thermal parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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