Loosely bonded adducts of plumbocene; structures and solution dynamics of $[(\eta\text{-}C_5H_5)_2Pb\cdot tmeda]$ and $[(\eta\text{-}C_5H_5)_2Pb\cdot 4,4'\text{-}Me_2bipy]$ (tmeda = $Me_2NCH_2CH_2NMe_2$, 4,4'-Me_2bipy = 4,4'-dimethylbipyridine)

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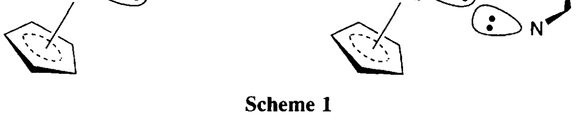
The first Lewis-base adducts of a neutral p-block group metallocene, $[(\eta\text{-}C_5H_5)_2Pb\cdot tmeda]$ 1 and $[\eta\text{-}C_5H_5)_2Pb\cdot 4,4'\text{-}Me_2bipy]$ 2, result from the addition of tmeda and 4,4'-Me_2bipy to $[Pb(\eta\text{-}C_5H_5)_2]$ (1 : 1 equiv.); X-ray and solution studies reveal that the Lewis bases are only loosely associated to the Pb^{II} centres in these complexes.

Owing to minimal d-orbital involvement and to the more varied (ionic and covalent) nature of their metal–ligand interactions, main-group metallocenes are more structurally diverse and have less restricted electronic requirements[1,2] than transition-metal metallocenes. The simplest Group 14 metallocenes, $[E(\eta\text{-}C_5H_5)]$ (E = Sn, Pb), have 14 e bent sandwich structures in the gas phase.[2h] The stability of the bent (rather than the linear) conformation has been explained by the admixing of the metal p_x atomic orbital with the initially antibonding lone-pair orbital, giving the required seven bonding molecular orbitals.[3] Despite the presence of stoichiometrically active metal lone pairs, we have recently observed that nucleophilic addition of $C_5H_5^-$ to $[E(\eta\text{-}C_5H_5)]$ produces complexes containing $[E(\eta\text{-}C_5H_5)_3]^-$ anions, in which the Sn and Pb centres accept, rather than donate, electron density.[4] We report here that simple Lewis-base adducts of $[Pb(\eta\text{-}C_5H_5)_2]$ are readily prepared by dissolving plumbocene in toluene solutions containing bidentate N donors (Scheme 1).† The solid-state structures and solution dynamics of $[(\eta\text{-}C_5H_5)_2Pb\cdot tmeda]$ **1** and $[(\eta\text{-}C_5H_5)_2Pb\cdot 4,4'\text{-}Me_2bipy]$ **2** show that the weak Lewis acidity of plumbocene is subtly controlled by steric factors. These complexes are the first structurally characterised Lewis-base adducts of a neutral metallocene of any p-block metal.

Low-temperature X-ray crystallographic studies were undertaken on both complexes.‡ Complexes **1** (Fig. 1) and **2** (Fig. 2) are both monomeric Lewis-base adducts in the solid state, in which the bidentate tmeda and 4,4'-Me_2bipy ligands chelate their Pb^{II} centres. In both complexes the C_5H_5 ligands adopt similar approximately η^3-bonding modes. The Pb–C distances are on average longer than those observed for $[Pb(\eta\text{-}C_5H_5)_2]$ {Pb–C 2.801(5)–2.911(4) in **1**, 2.759(6)–2.926(7) Å in **2**; *cf.* 2.78 Å in the solid state and 2.76 Å[2i] in the gas phase for $[Pb(\eta\text{-}C_5H_5)_2]$[2h]}. In contrast to the staggered orientation of the C_5H_5 rings found in the gas-phase structure of monomeric $[Pb(\eta\text{-}C_5H_5)_2]$,[2h] the C_5H_5 ligands of **1** and **2** are eclipsed. This conformation of the C_5H_5 ligands results in the molecules of both complexes having overall C_2 symmetry.



Scheme 1

The coordination of the Pb^{II} centres of **1** and **2** by the tmeda and 4,4'-Me_2bipy ligands reflects the inherent steric congestion in the $[Pb(\eta\text{-}C_5H_5)_2]$ unit. The approach of the tmeda ligand in **1**, perpendicular to the $Cp_{centroid}$–Pb–$Cp_{centroid}$ axis, is hindered by the steric confrontation between the N-attached Me groups of the donor and the C_5H_5 rings. This situation results in extremely long Pb–N bond lengths [2.879(3) Å; *cf.* sum of the covalent radii of Pb and N 2.28 Å]. In contrast, the essentially planar geometry of 4,4'-Me_2bipy and the likely smaller coordination radius of the pyridyl-N centres (compared to that

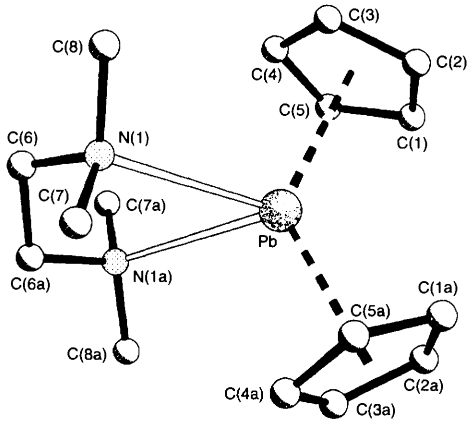


Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Key bond lengths (Å) and angles (°): Pb–N(1) 2.879(3), Pb–C(1) 2.911(4), Pb–C(2) 2.890(4), Pb–C(3) 2.818(4), Pb–C(4) 2.801(5), Pb–C(5) 2.846(4), N(1)···N(1a) 3.046(4), $Cp_{centroid}$–Pb(1) 2.59; $Cp_{centroid}$–Pb–$Cp_{centroid}$ 128.8, N(1)–Pb–N(1a) 63.9.

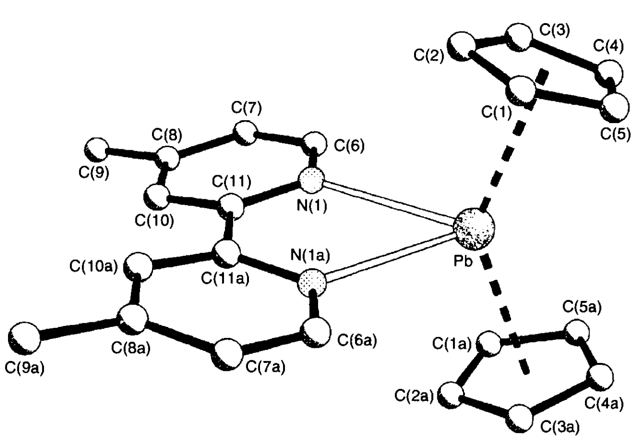


Fig. 2 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Key bond lengths (Å) and angles (°): Pb–N(1) 2.702(5), Pb–C(1) 2.819(6), Pb–C(2) 2.759(6), Pb–C(3) 2.826(7), Pb–C(4) 2.926(7), Pb–C(5) 2.907(7), N(1)···N(1a) 2.683(6), $Cp_{centroid}$–Pb 2.59; $Cp_{centroid}$–Pb–$Cp_{centroid}$ 139.7, N(1)–Pb(1)–N(1a) 59.6.

in aliphatic N donors) lead to closer approach of the ligand and to significantly shorter Pb–N bond lengths in **2** [2.702(5) Å]. As a consequence of the reduced steric demands of the bidentate ligand of **2**, the $[Pb(\eta\text{-}C_5H_5)_2]$ unit is less deformed than that in **1** [$Cp_{centroid}$–Pb–$Cp_{centroid}$ 128.8° in **1** and 139.7° in **2**; *cf.* 138° for $[Pb(\eta\text{-}C_5H_5)_2]$ in the gas phase[2h]].

Cryoscopic molecular mass measurements[§] of **1** in benzene are consistent with a dynamic equilibrium involving the dissociation of the complex into $[Pb(\eta\text{-}C_5H_5)_2]$ and tmeda. A variable-temperature ^1H NMR study (*ca.* 0.02 mol dm^{-3}) confirms the nature of this equilibrium process. The singlet C_5H_5 resonance at δ 5.79 observed at 298 K splits into two singlets at 233 K. On the basis of the relative ratios of these resonances (*ca.* 1 : 2) and their chemical shifts, the resonance at δ 6.02 can be assigned to $[Pb(\eta\text{-}C_5H_5)_2]$ and that at δ 6.03 to *intact* molecules of **1**.

Surprisingly, despite the relative shortness of the Pb–N bond lengths in the solid-state structure of **2**, molecular-mass measurements show that the complex is completely dissociated in benzene over a range of concentrations.[§] There are also no significant changes in the ^1H NMR spectrum of **2** (*ca.* 0.01 mol dm^{-3}) down to 183 K and the pattern of the aromatic resonances shows that the 4,4′-Me_2bipy ligand is uncoordinated. These apparently anomolous observations may simply reflect the presence of greater interaction between the 4,4′-Me_2bipy ligand and the aromatic solvents employed, which could encourage dissociation of **2**.

We gratefully acknowledge the EPSRC (M. A. B., C. N. H., P. R. R., D. S. W.), the European Union (Fellowship for A. S.), Sidney Sussex College Cambridge (Fellowship for C. A. R. and the ORS and The Commonwealth Trust (N. L. C.) for financial support.

Footnotes

† *Syntheses.* **1**: to a freshly prepared sample of $[Pb(\eta\text{-}C_5H_5)_2]$ (1.10 g, 3.0 mmol) dissolved in toluene (20 ml) was added tmeda (0.45 ml, 3.0 mmol), the yellow solution was heated to reflux and filtered while hot (porosity 3, Celite). The filtrate was reduced under vacuum (*ca.* 10 ml), resulting in the formation of a pale yellow precipitate which redissolved on warming. Storage at room temp. (12 h), gave pale yellow crystalline blocks of **1** (0.84 g, 62%); decomp. 125–130 °C; IR (Nujol), ν/cm^{-1} 3068w ν(C–H) C_5H_5; ^1H NMR (400.14 MHz, $[^2H_8]$toluene, 0.02 mol dm^{-3}); 298 K, δ 5.79 (s, 10 H, C_5H_5), 2.26 (s, 4 H, CH_2, tmeda), 2.08 (s, 12 H, Me_2N); 233 K, δ 6.03 (s, C_5H_5, intact **1**), 6.02 {s, C_5H_5, $[Pb(\eta\text{-}C_5H_5)_2]$} (10 H, ratio *ca.* 1 : 2), 1.70 (s, 16 H, CH_2, Me_2N, tmeda). Cooling to 183 K only resulted in broadening of the C_5H_5 and tmeda resonances. Calc. for $[C_{16}H_{26}N_2Pb]_n$: C, 42.4; H, 5.8; N, 6.2. Found; C, 42.3; H, 5.7; N, 6.1%.

2: the complex was prepared in an identical manner to **1**, addition of 4,4′-$MeMe_2$bipy (0.55 g, 3 mmol) to $[Pb(\eta\text{-}C_5H_5)]$ (1.10 g, 3.0 mmol) dissolved in toluene (20 ml), giving a yellow solution which was filtered while hot (porosity 3, Celite). Reduction of the filtrate (*ca.* 10 ml) gave a pale yellow precipitate which was recrystallised at room temp. (12 h), giving orange crystalline blocks of **2** (0.72 g, 46%); mp 135 °C; IR (Nujol), ν/cm^{-1} 3068w ν(C–H) C_5H_5; ^1H NMR (+25 °C, 400.14 MHz, $[^2H]$toluene, 0.01 mol dm^{-3}); 298 K, δ 8.55 [d, J_{HH} 0.6 Hz, 2 H, C(3)–H], 8.46 [d, J_{H-H} 5.0 Hz, 2 H, C(5)–H], 6.62 [d, J_{H-H} 5.0 Hz, 2 H, C(6)–H], 5.77 (s, 10 H, C_5H_5), 1.96 [s, 6 H, C(4)–Me]. Cooling to 183 K gave no significant changes in the spectrum. Calc. for $[C_{22}H_{22}N_2Pb]_n$: C, 50.6; H, 4.2; N, 5.4: Found; C, 50.5; H, 4.3; N, 5.4%.

‡ *Crystal data*: **1**; $C_{16}H_{26}N_2Pb$, M = 453.58, monoclinic, space group $C2/c$, a = 14.242(2), b = 9.296(2), c = 13.512(2) Å, β = 111.04(2)°, U = 1669.6(5) $Å^3$, Z = 4, D_c = 1.804 Mg m^{-3}. λ = 0.71073 Å, T = 153(2) K, μ(Mo-Kα) = 10.095 mm^{-1}. Data were collected on a Stoe–Siemens AED diffractometer using an oil-coated rapidly cooled crystal of dimensions 0.3 × 0.2 × 0.2 mm in an oil drop[5] by the θ–ω method (4.38 < θ < 27.42°). Of a total of 2803 collected reflections, 1863 were independent (R_{int} = 0.040). The data were corrected for absorption by a semiempirical method based on ψ-scans. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 to final values of $R1[F > 4\sigma(F)]$ = 0.022 and wR2 (all data) = 0.058.[6] Largest peak and hole in the final difference map; 1,263, −1.044 e A^{-3}.

2; $C_{22}H_{22}N_2Pb$, M = 521.61, orthorhombic, space group $Pbcn$, a = 13.492(3), b = 9.866(2), c = 14.250(2) Å, U = 1896.8(7) $Å^3$, Z = 4, D_c = 1.826 Mg m^{-3}. λ = 0.71073 Å, T = 153(2) K, μ(Mo-Kα) = 8.900 mm^{-1}. Data were collected on a Stoe–Siemens AED diffractometer using an oil-coated rapidly cooled crystal of dimensions 0.2 × 0.2 × 0.2 mm in an oil drop[5] by the θ–ω method (4.13 < θ < 27.46°). Of a total of 2885 collected reflections, 1231 were independent (R_{int} = 0.045). The data were corrected for absorption by a semiempirical method based on ψ-scans. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 to final values of $R1\ [F > 4\sigma(F)]$ = 0.023 and $wR2$ (all data) = 0.060 [$R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2/3)$].[6] Largest peak and hole in the final difference map; 0.662, −0.921 e A^{-3}. Symmetry transformations used to generate equivalent atoms for **1** and **2**, $-x, y, -z + \frac{1}{2}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/174.

§ Cryoscopic measurements were carried out using a specially designed apparatus which allows the freezing points of solutions to be determined under dry anaerobic conditions.[7] Predried (molecular sieve, 13X), degassed (Ar) cryoscopic grade benzene (Fisons) was used in all measurements. For $[(\eta\text{-}C_5H_5)_2Pb\cdot tmeda]_n$ **1**; M_r = 227 ± 5, n = 0.50 ± 0.01 (0.009 mol dm^{-3}), M_r = 251 ± 2, n = 0.55 ± 0.01 (0.031 mol dm^{-3}). These data give an equilibrium constant for dissociation of *ca.* 0.05 mol dm^{-3}.[7] For $[(\eta\text{-}C_5H_5)_2Pb\cdot 4,4'\text{-}Me_2bipy]_n$ **2**, M_r = 251 ± 5, n = 0.48 ± 0.01 (0.013 mol dm^{-3}), M_r = 253 ± 3, n = 0.49 ± 0.01 (0.021 mol dm^{-3}).

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Received, 28th May 1996; Com. 6/03694E