

Pt(0) and Pd(0) based metallocryptands: metallophilic hosts for Pb(II) ion†

Vincent J. Catalano,^{*a} Byron L. Bennett^a and Bruce C. Noll^b^a Department of Chemistry, University of Nevada, Reno, NV 89557, USA. E-mail: vjc@unr.edu^b Department of Chemistry, University of Colorado, Boulder, CO 80309, USA

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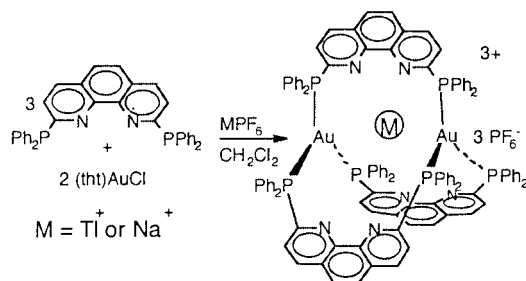
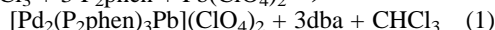
Metallocryptands based on trigonally coordinated Pt(0) or Pd(0) with P₂phen [2,9-bis(diphenylphosphino)-1,10-phenanthroline] bind Pb(II) ion through very strong, closed-shell metallophilic interactions; their syntheses, characterization and X-ray crystallography are presented.

The bonding interaction between closed-shell, heavy metal ions is gaining increasing attention.¹ In the absence of unpaired electrons to form covalent bonds or opposite charges to form strong ionic bonds, the close approach of closed-shelled species might be expected to exhibit no net attraction or be repulsive; however, there are numerous examples of heavy metal ions like Au(I), Tl(I) or Pb(II) associating with other metals or aggregating with short separations.² The origin of this metallophilic attraction is not completely understood, but relativistic effects appear to be important.³

Recently (Scheme 1), we reported the application of a unique Au(I)-based inorganic host complex to probe the resulting aurophilic interactions between the capping metal and the encapsulated guest ion.⁴ In this work we observed a very strong and short (*ca.* 2.9 Å) Au(I)–Tl(I) interaction. The highly luminescent Tl(I) containing species is substitution inert and stable in solution while the Na⁺ containing species readily dissociates the sodium ion indicating that the Au–Tl interaction is strong enough to maintain this assembly. We were unable to explore any Au(I)–Pb(II) interactions using this system probably because of the higher charge on the purported complex leads to dissociation and ultimately decomposition.

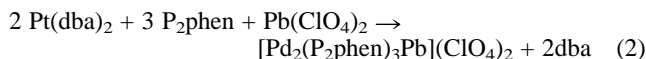
We now have extended this system to include zero-valent d¹⁰ metals and report the synthesis and characterization of the Pd(0)- and Pt(0)-based metallocryptates with exceptionally short Pd(0)–Pb(II) and Pt(0)–Pb(II) interactions. To our knowledge this is the first report of an unsupported Pd(0) or Pt(0)–Pb(II) bond. Further, these metallocryptands represent a new type of host complex that employ attractive metallophilic interactions for metal ion binding rather than Lewis acid–base interactions.

The deep green–brown, air-stable [Pd₂(P₂phen)₃Pb](ClO₄)₂ **1** or [Pt₂(P₂phen)₃Pb](ClO₄)₂ **2** [P₂phen = 2,9-bis(diphenylphosphino)-1,10-phenanthroline], are easily synthesized in good yield in acetonitrile according to eqns. (1) and (2).[‡] Although the



Scheme 1

† Electronic supplementary information (ESI) available: preparation, spectral data and MALDI-TOF spectrum for compound **2**. See <http://www.rsc.org/suppdata/cc/b0/b003758n/>



solutions of **1** or **2** are stable, the Pb(II) can be replaced by addition of an excess of Tl(I) ion. The ³¹P{¹H} NMR spectra contain a single resonance at +29.8 ppm for **1** and +48.1 ppm (¹J_{Pt–P} 4085 Hz) for **2**. Interestingly coupling to ²⁰⁷Pb (22% spin 1/2) is not observed. A similar phenomena is observed in the Tl⁺ containing species reported elsewhere.⁵ The ¹⁹⁵Pt NMR spectrum of **2** shows the anticipated quartet at 2916 ppm without resolvable ¹J_{Pt–Pb} coupling. For comparison, Balch *et al.*⁶ reported a ¹J_{Pt–Pb} coupling of 214 Hz for the Pt(II) containing species, [(MeCO₂)Pb(P₂-crown)Pt(CN)₂]⁺ (P₂-crown = 1,10-bis[(diphenylphosphino)methyl]-1,10-diaza-4,7,13,16-tetraoxaocadecane). Direct observation of a ²⁰⁷Pb resonance was unsuccessful likely due to the low receptivity and natural abundance of ²⁰⁷Pb coupled with the moderate solubility of **2**.

The X-ray crystal structure[§] of **1** (Fig. 1) confirms the formulation. The Pb atom resides in the center of the D₃ symmetric cavity formed by the P₂phen ligands coordinated to the two trigonal Pd(0) centers. The Pd(1)–Pb(1) and Pd(2)–Pb(1) separations are nearly identical at 2.7095(6) and 2.6902(6) Å respectively, and a Pb center is nearly linearly bonded with the Pd(1)–Pb(1)–Pd(2) angle of 178.75(1)° indicating the lone pair is stereochemically inactive. The Pb–N separations range from 3.095(1) to 3.215(1) Å (av. Pb–N 3.142(1) Å) and are considered non-bonding. Each Pb atom is slightly displaced out of the respective trigonal plane towards the central Pb atom by *ca.* 0.2 Å.

As shown in Fig. 1, the molecule crystallizes in a non-centrosymmetric space group with an overall helical geometry. However, the bulk material is racemic because both enantio-

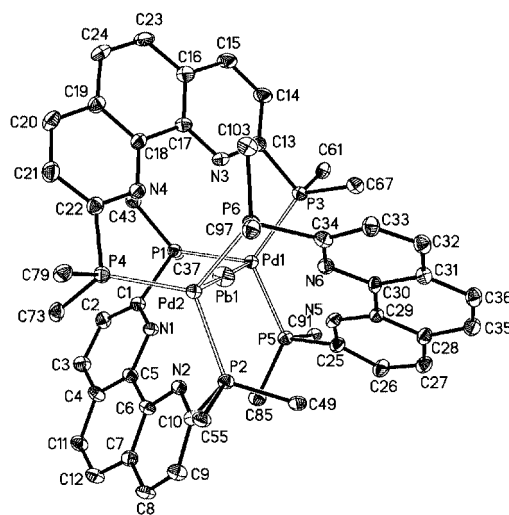


Fig. 1 Thermal ellipsoid plot for the cation of **1**. Hydrogen atoms and phenyl rings are removed for clarity. Selected distances (Å) and angles (°): Pd1–Pb(1) 2.7095(6), Pd2–Pb1 2.6902(6), Pb1–N1 3.090(2), Pb1–N2 3.095(2), Pb1–N3 3.090(2), Pb1–N4 3.215(2), Pb1–N5 3.156(2), Pb1–N6 3.166(2); Pd1–Pb1–Pd2 178.75(1), P1–Pd1–P3 119.41(5), P1–Pd1–P5 117.27(4), P3–Pd1–P5 121.30(5), P2–Pd2–P4 120.15(4), P2–Pd2–P6 116.42(4), P4–Pd2–P6 120.21(5).

mers are present in the crystal. The helicity is reflected in the large P(1)–Pd(1)–Pd(2)–P(2), P(3)–Pd(1)–Pd(2)–P(4) and P(5)–Pd(1)–Pd(2)–P(6) torsion angles of 116.9, 123.1 and 115.9°, respectively. This twisting of the trigonal planes compresses the metallocryptate to accommodate the requisite Pd(1)⋯Pd(2) separation of 5.399(1) Å.

Crystals of **2** were obtained but did not produce satisfactory refinement. However, reliable Pt–Pb separations of 2.7469(6) and 2.7325(6) Å were measured, and the cation is nearly identical to **1** in every other respect.

Pd– or Pt–Pb bonding is rare, and a search of the Cambridge Crystallographic Data Centre produced only a few examples of structurally characterized Pd– or Pt–Pb bonds,^{5,7} and none of these contained a formally zero-valent transition metal. Most of these are formed either through strong ligand interaction or through insertion reactions producing covalently bonded M–Pb complexes;⁸ however, a few cases exist for unsupported Pb(II)–M bonds.⁹ For example, Usón *et al.* reported the structure of Pb[Pt(C₆F₅)₄]₂²⁻ that contains short Pb(II)–Pt(II) separations of 2.769(2) and 2.793(2) Å along with short Pb⋯F contacts believed to stabilize the complex. In contrast, neither **1** or **2** have any stabilizing Pb⋯ligand interactions.

The MALDI-TOF mass spectra of **1** and **2** (not shown here) confirm the presence of Pb in each complex. Molecular ion peaks corresponding to [M₂Pb(P₂phen)₃]⁺ (M = Pt or Pd) with and without the perchlorate counter ion are easily identified. Interestingly, the intensity of the peak corresponding to the empty metallocryptand is very small, indicating that the Pb ion is strongly held in the gas phase.

The attractive metal–metal interactions observed here can be rationalized by employing a qualitative MO diagram (Fig. 2) similar to that proposed by Balch *et al.*¹⁰ by combining the filled d_{z²} and empty p_z orbitals on the transition metals with the filled Pb 6s and empty Pb 6p_z orbitals. Mixing between levels stabilizes the filled orbitals relative to their unfilled counterparts leading to an attractive interaction between these metals. Further, Fackler and coworkers¹¹ have employed a similar model with additional relativistic contributions from the 6s orbital to describe attractive Au–Tl interactions.

The electronic absorption spectra of **1** and **2** in acetonitrile contain absorptions attributable to ligand π–π* transitions between 230 and 310 nm. Both complexes exhibit a low energy band at 481 for **1** and 470 for **2** tentatively assigned to the M_{ds*} → M_{po*} transition depicted in the MO scheme. For comparison, both Pd(PPh₃)₃ and Pt(PPh₃)₃ exhibit weak absorptions in the same region,¹² but unlike these trigonal complexes, neither **1** or **2** are luminescent in solution, nor do these complexes exhibit reversible cyclic voltammetry.

The compounds reported here are examples of a rapidly expanding class of easily synthesized inorganic host complexes that employ strong, closed-shell attractive interactions for metal

ion binding. By eliminating ligand–ion interactions these metallocryptands provide a simple probe the metal–metal bonding both in solution and in the solid state. Substitution of Pb(II) for other heavy metal ions should provide a numerous combination of heavy metal interactions for further study. We are currently probing these systems.

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Notes and references

† *Preparations:* [Pd₂Pb(P₂phen)₃](ClO₄)₂ **1**: a 100 mL Schlenk flask was charged with 0.100 g (0.182 mmol) of 2,9-bis(diphenylphosphino)-1,10-phenanthroline dissolved in 10 mL of CH₂Cl₂. To this solution was added 1.39 g (0.304 mmol) of Pb(ClO₄)₂ (dissolved in 5 mL of 1:1 DCM–MeOH) with stirring. After 10 min the vessel was capped and the contents subjected to two freeze–pump–thaw cycles and moved to a glovebox. A suspension of 0.063 g of Pd₂(dba)₃·CHCl₃ (0.0061 mmol) in MeCN (10 mL) was added dropwise affording a dark solution. After stirring an additional 30 min and volatiles were removed and the residue dissolved in a minimum amount of MeCN. Flash chromatography (alumina) eluting with MeCN and precipitation with Et₂O afforded a brown solid. Yield: 100 mg (73%). C₁₀₈H₇₈N₈Cl₂O₈P₆PbPd₂·2DCE. Calc. C, 54.63; H, 3.52; N, 3.41. Found: C, 55.21; H, 3.43; N, 3.52%. ¹H NMR (300 MHz, CD₃CN, 25 °C) δ 8.246 (d, *J* 8.0 Hz), 7.879 (s), 7.470 (d, *J* 8.0 Hz), 7.292 (m), 7.023 (m), 6.858 (m), 6.439 (m), 6.163 (m); ³¹P{¹H} (121 MHz, CH₂Cl₂–CDCl₃, 25 °C): δ 29.8 (s br).

[Pt₂Pb(P₂phen)₃](ClO₄)₂ **2** (see ESI†).

§ *Crystal data:* for C₁₁₂H₇₈Cl₂O₈P₆PbPd₂ **1**·2DCE, *M* = 2454.31, orthorhombic, *a* = 26.665(7), *b* = 14.449(3), *c* = 25.967(5) Å, *V* = 10 005(4) Å³, *T* = 140 K, space group Pna2₁, *Z* = 4, μ(Mo–K) = 2.353 mm^{–1}, 87 599 reflections measured, 28 762 unique (*R*_{int} = 0.0452) were used in all calculations. The final *R*₁(all data) was 0.057 and *wR*₂ (all data) was 0.0815. Single crystals of [Pd₂(P₂phen)₃Pb](ClO₄)₂·2DCE were grown by slow diffusion of benzene into a DCE solution of the complex.

CCDC 182/1694. See <http://www.rsc.org/suppdata/cc/b0/b003758n/> for crystallographic data in .cif format.

For nitrate salt of **2**: [Pt₂Pb(P₂phen)₃]₂(NO₃)₄·Pb(NO₃)₂·4DCE·MeOH, *M* = 5493, triclinic, *a* = 18.2425(3), *b* = 25.6650(4), *c* = 29.2485(6) Å, α = 64.932(1), β = 79.399(1), γ = 78.724(1)°, *V* = 12054(4) Å³, *T* = 140 K, space group P $\bar{1}$, *Z* = 2, 81 238 reflections measured, 30591 unique (*R*_{int} = 0.0533) were used in all calculations. The final *R*₁(all data) was 0.1074 and *wR*₂ (all data) was 0.1433. The anions were severely disordered and could not be reliably located.

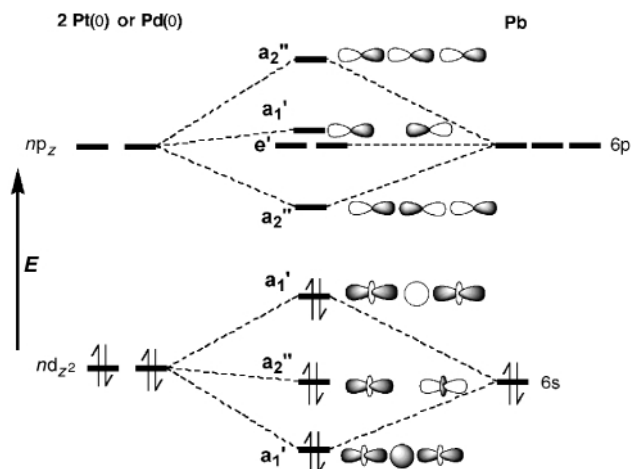


Fig. 2 Simplified molecular orbital diagram depicting the interaction between two trigonally coordinated d¹⁰ metal ions with the filled s and empty p_z orbital on a Pb²⁺ ion in the D_{3h} point group.

- P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451.
- O. Crespo, E. J. Fernandez, P. G. Jones, A. Laguna, J. M. Lopez-de-Luzuriaga, A. Mendia, M. Monge and E. Olmos, *Chem. Commun.*, 1998, 2233; S. Wang, G. Garzón, C. King, J.-C. Wang and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 4623; S. Wang, J. P. Fackler, Jr., C. King and J. C. Wang, *J. Am. Chem. Soc.*, 1988, **110**, 3308; M. Malariak, K. Berg, J. Claser, M. Sandström and I. Tróth, *Inorg. Chem.*, 1998, **37**, 2910.
- N. Kaltsoyanis, *J. Chem. Soc., Dalton Trans.*, 1997, 1; E. J. Fernandez, J. M. Lopez-de-Luzuriaga, M. Monge, M. A. Rodriguez, O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *Inorg. Chem.*, 1998, **37**, 6002; K. Balasubramanian, *Relativistic Effects in Chemistry, Part A*, Wiley-Interscience, New York, 1997.
- V. J. Catalano, B. B. Bennett, H. M. Kar and B. C. Noll, *J. Am. Chem. Soc.*, 1999, **121**, 10 235.
- V. J. Catalano, B. B. Bennett, R. L. Yson and B. C. Noll, *J. Am. Chem. Soc.*, 2000, (submitted).
- A. L. Balch, E. Y. Fung, J. K. Nagle, M. M. Olmstead and S. P. Rowley, *Inorg. Chem.*, 1993, **32**, 3295.
- V. G. Albano, C. Castellari, M. Monari, V. De Felice, M. L. Ferrara and F. Ruffo, *Organometallics*, 1995, **14**, 4213; J. M. Casas, J. Fornies, A. Martin, V. M. Orera, A. G. Orpen and A. J. Rueda, *Inorg. Chem.*, 1995, **34**, 6514.
- B. Crociani, M. Nicolini, D. A. Clemente and G. Bandoli, *J. Organomet. Chem.*, 1973, **49**, 249; G. Carturan, G. Deganello, T. Boschi and U. Belluco, *J. Chem. Soc. A*, 1969, 1142.
- R. Usón, J. Fornies, L. R. Ralvello, M. A. Usón and I. Usón, *Inorg. Chem.*, 1992, **31**, 3697.
- A. L. Balch, V. J. Catalano, M. A. Chatfield, J. K. Nagle, M. M. Olmstead and P. E. Reedy, Jr., *J. Am. Chem. Soc.*, 1991, **113**, 1252.
- S. Wang, G. Garzón, C. King, J.-C. Wang and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 4623.
- P. D. Harvey and H. B. Gray, *J. Am. Chem. Soc.*, 1988, **110**, 2145.