Low-Coordinate Species

Synthesis and Characterization of a Quasi-One-Coordinate Lead Cation**

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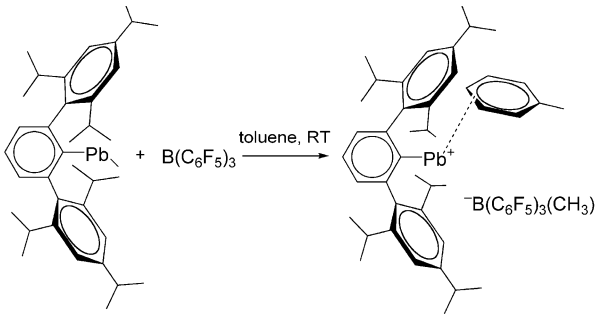
There has been intense, recent interest in the synthesis and properties of heavier Group-14-element (Si–Pb) analogues of carbocations.[1–26] However, they have proven difficult to isolate in the absence of stabilization by further coordination of the Group 14 element. Many have been intramolecularly stabilized by solvation of the cationic center by either unsaturated moieties,[25,26] or by N-, O-, S-, or P-centered Lewis base donors.[8,10,13,14,18,19,21,24] Others have been intermolecularly stabilized through coordination with various solvent molecules.[5–7,9,12,20] Nonetheless, a number of groups have shown that essentially free, uncomplexed silicon, germanium, and tin species can be isolated and structurally characterized.[11,15,18,20,21,23] For the heaviest Group 14 elements, tin and lead, work had been focused primarily on derivatized cyclopentadienyl half-sandwich complexes, where the metal cation is η^5 bonded to five carbon atoms of the cyclopentadienyl ring.[1–3,17] Parallel, recent work has shown that bulky terphenyl ligands can stablize a range of low-coordinate neutral and anionic species with unusual or previously unknown bonding.[27] We were therefore anxious to test the effectiveness of these useful monodentate ligands in stabilizing cationic Group 14 species with unusually low coordination numbers. We chose to focus initially on the synthesis of a one-coordinate lead cation because $[Ar^*Pb]^+$, ($Ar^* = 2,6\text{-}Trip_2\text{-}C_6H_3$; $Trip = C_6H_2\text{-}2,4,6\text{-}i Pr_3$), is isoelectronic to the neutral Ar*Tl compound which has a one coordinate thallium center.[28] We now show that weakly solvated, quasi-one-coordinate lead cations can be prepared by the reaction of Ar*PbMe with $B(C_6F_5)_3$ to give the salt $[Ar^*Pb{\cdot}\eta^2\text{-}PhMe][MeB(C_6F_5)_3]$ (**1**) as shown in Equation (1). Furthermore we



(1)

show that the weakly complexed toluene in **1** can be readily displaced by pyridine to afford the salt $[Ar^*Pb(py)_2][MeB(C_6F_5)_3]$ (**2**).

The reaction of Ar*PbMe with 1 equiv of $B(C_6F_5)_3$[29] in toluene yielded an orange oil. Upon recrystallization from hexane, the salt **1** was obtained as red-orange needles. Single-crystal X-ray crystallography[30] showed that **1** (Figure 1) consisted of an $[Ar^*Pb]^+$ ion as well as a $[MeB(C_6F_5)_3]^-$ counterion. There are no close interactions (≤ 3.964 Å) between the lead and the anion. The metal is bound to the

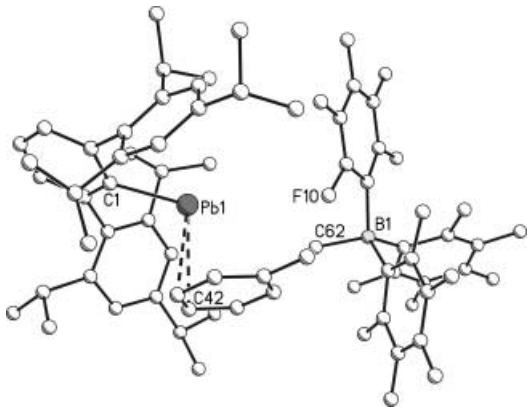


Figure 1. Molecular structure of **1**; hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [°]: Pb1-C1 2.250(7), Pb1-C37 2.832(10), Pb1-C42 2.907(9), Pb-(centroid) 2.827, Pb1-F10A 3.963; C1-Pb1-C37 99.3(2), C1-Pb1-(centroid) 127.0(2), Pb1-C37-C42 79.4(2), Pb1-C37-C38 86.1(2).

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Ar* ligand through the C1-ipso carbon atom and interacts with the solvent toluene through the C37 and C42 carbon atoms. The Pb–C1 bond length is 2.250(7) Å, and this is marginally shorter than the corresponding bond length (2.272(9) Å) in the precursor Ar*PbMe.[31] The Pb–toluene centroid distance is 2.827 Å and the C1-Pb1-centroid angle is 127.0°. However, the Pb–C interactions involving the toluene-ring carbon atoms span a wide range from 2.832–3.438 Å, and the closest involve atoms C37 (2.832(10) Å) and C42 (2.907(9) Å), which suggests that the Pb–toluene interaction is best described as being of η^2 type. The closest contact between the cationic lead center and $[B(CH_3)(C_6F_5)_3]^-$ is 3.963(6) Å for Pb1···F10A. This separation is substantially longer than the Pb^{II}–F bond lengths found in complexes such as $[PbF(AsF_6)]$ or $[Pb(HF)(AsF_6)_2]$, which have Pb–F bond lengths in the ranges 2.272(8) to 3.071(9) and 2.48(4) to 3.06(3) Å, respectively.[32] The ^{207}Pb NMR spectrum of **1** in C_6D_6 displayed a broad signal, far downfield at 8974 ppm.[32] The ^{19}F NMR spectrum displayed three distinct signals characteristic of $[MeB(C_6F_5)_3]^-$ due to the *ortho*, *meta*, and *para* F atoms of the C_6F_5 groups. These signals appear at similar shifts to those observed in transition-metal[33] and main-group-metal[9] salts that have $[MeB(C_6F_5)_3]^-$ as a counterion. DFT calculations[34] on the model species $[PhPb{\cdot}C_6H_6]^+$ or $[PhPb{\cdot}PhMe]^+$ afforded an energy of interaction versus aryl ring distance plot (Figure 2), which had a

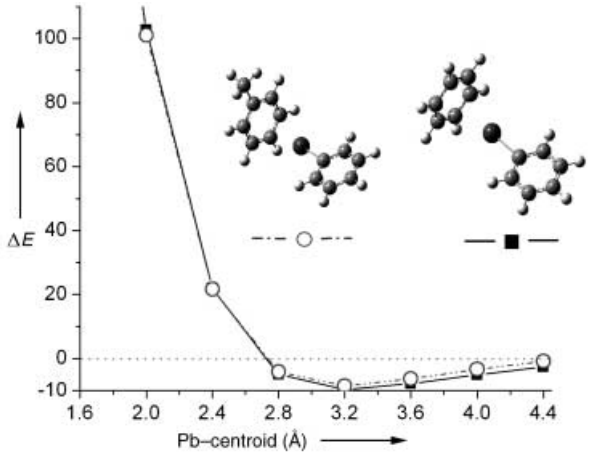
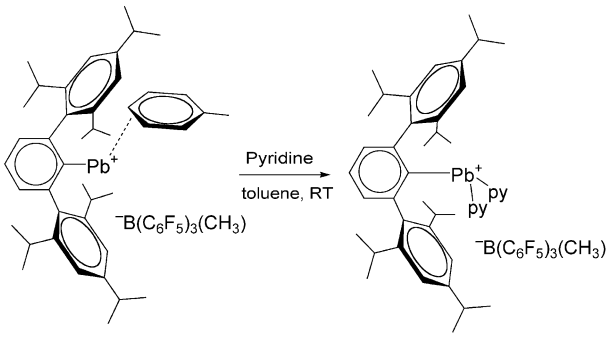


Figure 2. Calculated interaction energies between $[PhPb]^+$ and benzene or toluene. Interaction energies (ΔE) are given in kcal mol^{-1}.

minimum near 3.2 Å (compared with ≈2.85 Å in the crystal structure). The calculated maximum interaction energy (8–9 kcal mol^{-1}) suggests significant dissociation in solution. However, the actual energy may be significantly lower due to the greater bulk of the ligand in **1** and the fact that, at the experimental distance near 2.85 Å, the interaction energy is calculated to be ≈5 kcal mol^{-1}.

The reaction of **1** in toluene at 25 °C with 2 equiv of pyridine [Eq. (2)] results in an immediate color change from orange to pale yellow. X-ray quality crystals of **2** were isolated after recrystallization from hexane.[30] The structure of **2** (Figure 3) consists of well-separated cations and anions. The lead center in the cation is bound to Ar* and two pyridine



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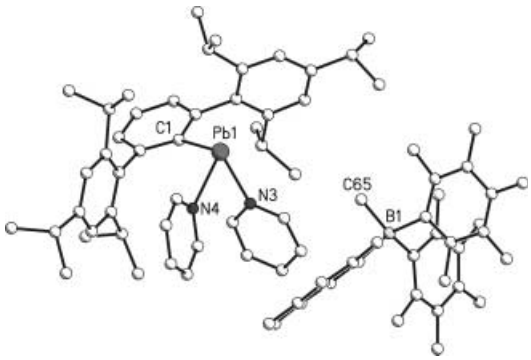

Figure 3. Molecular structure of **2**; hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [°]: C1-Pb1 2.313(5), Pb1-N3 2.409(5), Pb1-N4 2.512(5); C1-Pb1-N3 90.39(2), C1-Pb1-N4 106.67(2), N3-Pb1-N4 80.10(2).

groups to produce a pyramidal metal coordination. Clearly, pyridine has readily displaced the coordinated toluene to afford the salt $[Ar*Pb(py)_2][MeB(C_6F_5)_3]$ (**2**). The Pb–C bond length is lengthened to 2.313(5) Å and the two Pb–N separations are 2.409(5) and 2.512(5) Å. The pyramidal coordination geometry at the Pb center is indicated by the angles C1-Pb1-N3, C1-Pb1-N4, and N3-Pb1-N4 (90.39(2), 106.67(2), and 80.10(2)°, respectively; sum of angles = 277.16°). The ^{207}Pb NMR spectrum of **2** in C_6D_6 displayed a signal at 4764 ppm—about 4000 ppm upfield of **1**.

The long Pb–C(toluene) bond lengths and low-field ^{207}Pb NMR chemical shift observed for **1** support the view that it is primarily a one-coordinate $[Ar*Pb]^+$ ion that is loosely coordinated to a solvent toluene molecule. The Pb–C(η^2-PhMe) distances may be compared with the Pb–C separations found in the salts $[(\eta^5\text{-}C_5Me_5)Pb]^+X^-$ ($X = BF_4^-$ or $CF_3SO_3^-$),[1] which range from 2.512 to 2.598 Å. The Pb–centroid length for $[(\eta^5\text{-}C_5Me_5)Pb]^+$ was found to be near 2.27 Å.[17] Thus, the Pb–centroid separation in **1** is over 0.5 Å longer than those in the above salts.[17,35] It is also notable that within the toluene ring in **1**, the C–C bonds average 1.38 Å, and the crucial C37–C42 (1.370(2) Å) bond is not elongated relative to free toluene.[36] The downfield ^{207}Pb NMR chemical shift of 8974 ppm may be compared to the −4961 and −5041 ppm observed for $[(\eta^5\text{-}C_5Me_5)Pb]CF_3SO_3$ and $[(\eta^5\text{-}C_5Me_5)Pb]BF_4$, respectively.[1] The chemical shift for compound **1** is thus more than 13500 ppm downfield of these $[(\eta^5\text{-}C_5Me_5)Pb]^+$ salts. This very large difference is consistent with

a lower effective coordination number in **1** and weak coordination of PhMe to lead. It is notable that the ^{207}Pb NMR chemical shift of the two-coordinate precursor Ar*PbMe (7420 ppm)[31] also lies upfield of that of **1**, which further supports the weak η^2-solvation of Pb by toluene.

The $[Ar*Pb]^+$ fragment is isoelectronic to [Ar*Tl], the structure of which has been already described.[28] In [Ar*Tl], the thallium center is monocoordinate and the Tl–C(ipso) bond length is 2.34(1) Å,[28] which is ≈0.09 Å longer than the Pb–C bond in **1**. The shorter value for Pb–C1 is probably due to the cationic character of $[Ar*Pb]^+$; however, since Pb and Tl have similar covalent radii,[37] the lack of any increase in the Pb–C(ipso) distance upon interaction with toluene is consistent with weak solvation. In $[Ar*Pb(py)_2]^+$, the large size of the aryl substituent is reflected in the over 15° difference in bond angles of N3-Pb1-C(ipso) (90.39(2)°) and N4-Pb1-C(ipso) (106.67(2)°) and the very narrow N3-Pb1-N4 angle (80.10(2)°). The Pb–C(ipso) bond distance increases to 2.313(5) Å (compared with 2.251(7) Å in **1**), which is consistent with the higher lead coordination number. The Pb–N bond lengths (2.409(5) and 2.512(5) Å) are similar to those seen in [Pb(Br)Ar*]·py (2.502(4) Å),[31] and are much shorter than those found in the $PbBr_2$ complexes $[\{(4\text{-}MeH_4C_5N)_2{\cdot}PbBr_2\}_n]$[38] and $[\{(3\text{-}MeH_4C_5N)_2{\cdot}PbBr_2\}_n]$ (both 2.60(2) Å),[38] and in the plumbocene–pyridine complexes $[Pb(\eta^5\text{-}C_5H_5)_2]$·TMEDA and $[Pb(\eta^5\text{-}C_5H_5)_2]$·4,4′-$Me_2$bpy (Pb–N 2.702–2.879 Å; bpy = bipyridyl),[39] which have higher effective coordination numbers at their Pb centers. The ^{207}Pb NMR chemical shift of **2** is at ≈4000 ppm higher field compared to **1**, which is consistent with an increase in coordination number from one to three.

In summary, the plumbyl cation **1**, which contains a quasi-one-coordinate lead center, was obtained through methanide-ion capture using $B(C_5F_6)_3$. The structural and spectroscopic data show that it is stabilized by a weak interaction with a toluene molecule that can be readily displaced by pyridine.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions.

1: The compound Ar*PbMe[31] (0.704 g, 1.0 mmol) was dissolved in toluene (20 mL) and added dropwise to a solution of $B(C_6F_5)_3$ (0.518 g, 1.0 mmol) in toluene (20 mL) at ≈0 °C with constant stirring. The reaction mixture, which was initially red, became orange after about 4 h. The reaction was allowed to warm to room temperature and stirred overnight. The toluene was removed under reduced pressure and the orange oil was extracted with hexane (50 mL). After filtering through celite, the volume of the orange solution was reduced to initiate crystallization and stored in a freezer at −20 °C for 2 days to give product **1** as orange crystals (0.682 g, 52 %); m.p. 228–236 °C; ^{1}H NMR (C_6D_6, 300 K): δ = 0.632 (s, 3H, B-CH_3), 1.019 (d, 12H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.6 Hz), 1.059 (d, 12H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.211 (d, 12H, *p*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 2.104 (s, 3H, C_6H_5-CH_3), 2.753 (sept, *p*-CH(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 2.913 (sept, *o*-CH(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 6.997 (t, 1H, *p*-C_6H_5-CH$_3$, $^3J_{HH}$ = 7.5 Hz), δ 7.017 (d, 2H, *o*-C_6H_5-CH$_3$, $^3J_{HH}$ = 7.4 Hz), 7.107 (t, 2H, *m*-C_6H_5-CH$_3$, $^3J_{HH}$ = 7.5 Hz), 7.263 (s, 4H, *m*-Trip), 7.911 (d, 2H, *m*-C_6H_3, $^3J_{HH}$ = 7.2 Hz), 8.508 ppm (t, 1H, *p*-C_6H_3, $^3J_{HH}$ = 7.6 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ = 14.29 ($[H_3CB(C_6F_5)_3]^+$, CH_3), 21.36 (CH_3-C_6H_5), 23.69 (*o*-CH(CH_3)$_2$), 23.85 (*o*-CH(CH_3)$_2$), 24.92 (*p*-CH(CH_3)$_2$), 30.53 (*o*-CH(CH$_3$)$_2$), 34.65 (*p*-CH(CH$_3$)$_2$), 122.72 (*m*-Trip), 125.53 (*p*-C_6H_5-CH$_3$), 125.63 (*p*-C_6H_3), 128.48 (*m*-C_6H_5-CH$_3$), 129.14 ($[H_3CB(C_6F_5)_3]^+$, ipso-C), 129.42 (*o*-C_6H_5-CH$_3$), 133.89 (ipso-Trip), 138.29 ($[H_3CB(C_6F_5)_3]^+$, *m*-C, *p*-C), 142.24 (*m*-C_6H_3), 145.18 (*o*-Trip), 148.33 ($[H_3CB(C_6F_5)_3]^+$, *o*-C), 149.54 (*p*-C_6H_3), 152.34 (*o*-C_6H_3), 356.57 ppm (ipso-C_6H_3); ^{207}Pb{^{1}H} NMR (C_6D_6, 300 K): δ = 8974 ppm; ^{11}B{^{1}H} NMR (C_6D_6, 300 K): δ = −11.62 ppm; ^{19}F{^{1}H} NMR (C_6D_6, 300 K): δ = −104.45 (t, 6F, $^3J_{FF}$ = 24.4 Hz), −102.13 (s br, 3F), −69.27 ppm (d, 6F, $^3J_{FF}$ = 20.8 Hz).

2: **1** (1.40 g, 1.07 mmol), was dissolved in toluene (25 mL). Pyridine (0.2 mL, 2.48 mmol) was added to the orange solution while stirring. The reaction mixture, which immediately became pale yellow on the addition of pyridine, was then stirred overnight. The volatile solvent was then removed and the residue was extracted with hexanes (50 mL). The solution was filtered through celite and concentrated to induce crystallization (15 mL) and stored in a freezer at −20 °C for 2 days to afford **2** as colorless crystals (0.615 g, 40 %); m.p. 210–215 °C; ^{1}H NMR (C_6D_6, 300 K): δ = 0.529 (s, 3H, B-CH_3), 0.856 (d, 12H, *p*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz); 1.030 (d, 12H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.4 Hz), 1.169 (d, 12H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 2.696 (sept, *p*-CH(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 2.887 (sept, *o*-CH(CH$_3$)$_2$, $^3J_{HH}$ = 7.28 Hz), 6.584 (t, 4H, *m*-C_5H_5N, $^3J_{HH}$ = 6.4 Hz), 6.969 (s, 4H, *m*-Trip), 7.228 (t, 1H, *p*-C_5H_5N, $^3J_{HH}$ = 7.6 Hz), 7.249 (t, 2H, *p*-C_5H_5N, $^3J_{HH}$ = 7.6 Hz), 7.452 (*m*-C_6H_3, $^3J_{HH}$ = 7.2 Hz), 7.818 ppm (d, 4H, *o*-C_5H_5N, $^3J_{HH}$ = 6.6 Hz), ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ = 14.319 (CH_3-B), 24.198 (*o*-CH(CH_3)$_2$), 24.424 (*o*-CH(CH_3)$_2$), 26.381 (*p*-CH(CH_3)$_2$), 30.819 (*o*-CH(CH$_3$)$_2$), 34.862 (*p*-CH(CH$_3$)$_2$), 121.118 (*m*-Trip), 124.887 (*m*-C_5H_5N), 125.693 (*p*-C_6H_3), 131.958 ($[H_3CB(C_6F_5)_3]^-$, ipso-C), 135.448 (*o*-C_5H_5N), 136.770 (ipso-Trip), 137.35 ($[H_3CB(C_6F_5)_3]^-$, *p*-C), 137.56 ($[H_3CB(C_6F_5)_3]^-$, *m*-C), 141.235 (*m*-C_6H_3), 145.605 (*o*-Trip), 146.823 (*p*-Trip), 147.475 ($[H_3CB(C_6F_5)_3]^-$, *o*-C), 147.839 (*o*-C_6H_3), 149.253 ppm (*p*-C_5H_5N); ipso-C_6H_3 not observed; ^{207}Pb{^{1}H} NMR (C_6D_6, 300 K): δ = 4764 ppm; ^{11}B{^{1}H} NMR (C_6D_6, 300 K): δ = −13.62 ppm; ^{19}F{^{1}H} NMR (C_6D_6, 300 K): δ = −105.65 (t, 6F, $^3J_{FF}$ = 24.4 Hz), −103.34 (s br, 3F), −70.21 ppm (d, 6F, $^3J_{FF}$ = 20.8 Hz).

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[30] Crystal data for **1**: orange needles ($0.43\times0.28\times0.22$ mm) from hexanes, $C_{62}H_{60}BF_{15}Pb$, $M_r=1308.1$, monoclinic, space group $P2_1$, $a=12.7298(11)$, $b=17.0590(14)$, $c=13.7485(11)$ Å, $\beta=110.064(2)°$, $V=2804.2(4)$ Å^3, $Z=2$, $\rho_{calcd}=1.549$ g cm^{-1}, $F(000)=1308$, $\mu(Mo_{K\alpha})=3.097$ mm^{-1}, $T=90(2)$ K, 10990 unique reflections [$R_{int}=0.0734$], $R_1=0.0537$, and $wR_2=0.1154$ for [$I>2\sigma(I)$] **2**: colorless plates ($0.10\times0.07\times0.04$ mm) from hexanes, $M_r=1374.17$, triclinic, space group $P\bar{1}$, $a=12.6990(11)$, $b=16.6977(14)$, $c=17.7177(14$ Å, $\alpha=72.346(2)$, $\beta=71.0481(2)$, $\gamma=69.827(2)°$, $V=3256.7(5)$ Å^3, $Z=2$, $\rho_{calcd}=1.401$ g cm^{-1}, $F(000)=1376$, $\mu(Mo_{K\alpha})=2.672$ mm^{-1}, $T=91(2)$ K, 11702 unique reflections [$R_{int}=0.0653$], $R_1=0.0508$ and $wR_2=0.1149$ for [$I>2\sigma(I)$]. CCDC-224533 (**1**) and CCDC-224534 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[32] a) The ^{207}Pb NMR spectrum of **1** in C_6D_6 was externally referenced to $Pb(NO_3)_2$ and displayed a broad signal at 6013 ppm. The ^{207}Pb chemical shift was converted to the Me_4Pb scale by adding 2961 ppm to afford a chemical shift at 8974 ppm; b) B. Wrackmeyer, K. Horchler, *Annu. Rep. NMR Spectrosc.* **1989**, *27*, 249.

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[34] The calculations were performed using DFT theory with a hybrid B3LYP functional, including Becke's three-parameter non-local exchange potential and the non-local Lee–Yang–Parr correlation functional. To reduce computational costs without neglecting the relativistic effects, the effects of the core electrons on the Pb valence shell were represented by the quasi-relativistic Effective-Core Potential (ECP). For this purpose, the Wood-Boring Stuttgart/Dresden pseudopotential ECP (ECP78MWB) with a valence basis (78[Xe + 4f + 5d] (4 s,4p,1d)→[2s,2p,1d]—78 electrons in the core and [4s,4p,1d] contracted-valence) was used for the Pb atom.[a] H and C atoms were described with a 6–31 g* basis set. The starting geometry for the optimization of the lead complex was extracted from its crystal structure. The DFT calculations were carried out using the GAUSSIAN 03 package[b] and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program.[c] The DFT optimized structure of the model complexes remains close to that obtained from the X-ray study. In the optimized structure the orientation of the toluene molecule is found to be slightly different with longer distances (range 2.984–3.741 Å) than those in **1**. The optimized Pb–C(terphenyl) distance is almost identical with the crystal structure data (2.273 and 2.251 Å, respectively). To investigate the binding affinity of the R–Pb$^+$ fragment to the toluene molecule, we calculated the interaction energy for the optimized structure using the following scheme [Eq. (3)]: The calculated interaction

$$[\text{R-Pb}]+[\text{toluene}]\xrightarrow{\Delta E}[\text{R-Pb-toluene}]^+ \qquad (3)$$

energy (-9.86 kcal mol^{-1}) is relatively high compared to what we expected for an interaction of this kind. We then performed an additional set of calculations on the hypothetical phenyl–lead complexes with benzene and toluene (Figure 2). A possible explanation for these rather high energy values might be related to the poor quality of the description of the relativistic effects in this particular system in terms of the ECP approximation. Further DFT calculations using basis sets optimized for the use in the zeroth-order regular approximated (ZORA) relativistic equation, such as implemented in the Amsterdam Density Function (ADF) program, are currently in progress. a) W. Kuechle, K. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1991**, *74*, 1245. b) Gaussian 03 (Revision B.04), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**. c) MOLEKEL 4.3, P. Flükiger, H. P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), **2000–2002**.

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