2874 *Organometallics* **2000,** *19,* 2874−2881

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

Terphenyl Ligand Stabilized Lead(II) Derivatives of Simple Organic Groups: Characterization of $Pb(R)C_6H_3$-2,6-$Trip_2$ (R = Me, t-Bu, or Ph; Trip = C_6H_2-2,4,6-i-Pr_3), $\{Pb(\mu\text{-}Br)C_6H_3\text{-}2,6\text{-}Trip_2\}_2$, py·$Pb(Br)C_6H_3$-2,6-$Trip_2$ (py = Pyridine), and the Bridged Plumbylyne Complex $[\{W(CO)_4\}_2(\mu\text{-}Br)(\mu\text{-}PbC_6H_3\text{-}2,6\text{-}Trip_2)]$

Lihung Pu, Brendan Twamley, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

Received February 18, 2000

The reaction between 1 equiv of the sterically encumbered lithium terphenyl $Et_2O\cdot LiC_6H_3$-2,6-$Trip_2$ and $PbBr_2$ in diethyl ether afforded the organolead(II) halide compound $\{Pb(\mu\text{-}Br)C_6H_3\text{-}2,6\text{-}Trip_2\}_2$ (**1**) as orange crystals. Treatment of **1** with a stoichiometric amount of pyridine (py) gave the complex py·$Pb(Br)C_6H_3$-2,6-$Trip_2$ (**2**) as yellow needles. The addition of 1 equiv of methylmagnesium bromide, *tert*-butyllithium, or phenyllithium to **1** resulted in the diorganolead(II) compounds $Pb(R)C_6H_3$-2,6-$Trip_2$ (R = Me, **3**; t-Bu, **4**; or Ph, **5**) in good yield. The compounds **3** and **5** are the first stable, monomeric lead(II) derivatives involving the simplest alkyl and aryl groups Me and Ph. Reaction of **1** with $W(CO)_5THF$ did not yield the expected plumbylene complex $(CO)_5W\{Pb(Br)C_6H_3\text{-}2,6\text{-}Trip_2\}$. Instead, the bridged plumbylyne species $[\{W(CO)_4\}_2(\mu\text{-}Br)(\mu\text{-}Pb\text{-}C_6H_3\text{-}2,6\text{-}Trip_2)]$ (**6**) was obtained in low yield. All compounds were characterized by X-ray crystallography, ^{1}H and ^{13}C NMR, IR, and UV−vis spectroscopy. ^{207}Pb NMR spectra of **3**−**5** were also obtained. The results demonstrate the effectiveness of the terphenyl ligand in creating a protected cavity at a site in which normally unstable moieties are stabilized against decomposition reactions.

Introduction

Organolead chemistry is primarily concerned with compounds of lead in the oxidation state IV. In contrast, the chemistry of Pb(II) tends to be dominated by compounds with inorganic ligands, and bivalent organolead compounds are relatively rare and their chemistry is poorly explored.[1,2] The first well-characterized organolead(II) species was the bent sandwich complex $Pb(\eta^5\text{-}C_5H_5)_2$,[3] and this has been supplemented by a number of related derivatives that have a variety of substituents at the cyclopentadienyl ring.[4] For many years, however, $Pb\{CH(SiMe_3)_2\}_2$ was the only stable σ-bonded organolead(II) compound.[5] More recent work has resulted in the isolation of several further examples of PbR_2 species (R = σ-bonded alkyl or aryl group), which may exist either as monomers or weakly associated metal−metal bonded dimers in the solid.[6,7] The latter, since they are formally analogous to alkenes, have attracted considerable attention owing to the current interest in the nature of the Pb−Pb bonding interaction.[7] Closely related to these are the heteroleptic, σ-bonded organolead(II) derivatives in which one of the organic substituents is replaced by either a halide[8−10] or a transition metal fragment.[11] The halide compounds, in particular, are potentially useful since they can be easily derivatized by substitution of the halide, which allows access to an expanded range of organolead(II) species. For example, the recently described metalloplumbylenes[11] $(\eta^5\text{-}C_5H_5)(CO)_3MPbC_6H_3$-2,6-$Trip_2$ (M = Cr, Mo, or W; Trip = C_6H_2-2,4,6-i-Pr_3), which feature

---

[1] Harrison, P. G. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1984; Vol. 2, Chapter 12. Harrison, P. G. *Comprehensive Organometallic Chemistry II*; Elsevier: Amsterdam, 1995; Vol. 2, Chapter 7.

[2] Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 1061.

[3] Fischer, E. O.; Grubert, H. *Z. Anorg. Allg. Chem.* **1956**, *286*, 237.

[4] Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969.

[5] (a) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (c) A much higher yield (95%) synthesis of $Pb\{(CH(SiMe_3)_2\}_2$ has also been reported in: Burton, N. C.; Cardin, C. J.; Cardin, D. J.; Twamley, B.; Zubavichus, Y. *Organometallics* **1995**, *14*, 5708. (d) The structure of $Pb\{CH(SiMe_3)_2\}_2$ shows that it is weakly dimerized in the solid with Pb−Pb = 4.129 Å; data cited in: Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. *Organometallics* **1998**, *17*, 4425.

[6] Kano, N.; Tokitoh, N.; Okazaki, R. *J. Synth. Org. Chem. Jpn.* **1998**, *56*, 919.

[7] Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 187.

[8] Heteroleptic organolead halide derivatives with cyclopentadienyl ligands have been known for over 20 years, see in: Holliday, A. K.; Makin, P. H.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 435; Jutzi, P.; Dickbreder, R.; Nöth, H. *Chem. Ber.* **1989**, *122*, 865.

[9] Eaborn, C.; Izod, K.; Hitchcock, P. B.; Sözerli, S. E.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1995**, 1829.

[10] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1997**, *16*, 5653.

[11] Pu, L.; Power, P. P.; Boltes, I.; Herbst-Irmer, R. *Organometallics* **2000**, *19*, 352.

10.1021/om0001624 CCC: $19.00 © 2000 American Chemical Society
Publication on Web 06/23/2000

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

a bent, two-coordinate lead geometry and a stereochemically active lead lone pair, were synthesized by the treatment of $Na[M(\eta^5\text{-}C_5H_5)(CO)_3]$[12] (M = Cr, Mo or W) with $Pb(Br)C_6H_3\text{-}2,6\text{-}Trip_2$. The latter compound, which was generated in situ from $PbBr_2$ and $Et_2O\cdot LiC_6H_3\text{-}2,6\text{-}Trip_2$, is a potentially useful transfer agent for the "PbR" moiety. It was decided therefore to characterize this aryl lead halide both spectroscopically and structurally and to investigate some of its reaction chemistry. In particular it was hoped that the presence of the extremely large $-C_6H_3\text{-}2,6\text{-}Trip_2$ substitutent[13] would allow, for the first time, the isolation of Pb(II) species with bonds to the simplest alkyl (i.e., CH_3) and aryl (i.e., C_6H_5) groups. The results of these investigations are now described.

Experimental Section

General Procedures. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed twice before use. The lithium aryls $Et_2O\cdot LiC_6H_3\text{-}2,6\text{-}Trip_2$[14] and LiPh[15] were prepared according to literature procedures. The compounds $PbBr_2$, $W(CO)_6$, t-BuLi (1.5 M in *n*-pentane), and CH_3MgBr (3.0 M in Et_2O) were purchased commercially and used as received. Pyridine (py) was dried by distillation from CaH_2. ^1H and ^{13}C NMR data were recorded on a Bruker 300 MHz or Varian 400 MHz instrument and referenced to the deuterated solvent. Infrared data were recorded on a Perkin-Elmer PE-1430 instrument. UV−vis data were recorded on a Hitachi-1200 instrument.

$\{Pb(Br)C_6H_3\text{-}2,6\text{-}Trip_2\}_2$ (1). $Et_2O\cdot LiC_6H_3\text{-}2,6\text{-}Trip_2$[14] (2.40 g, 4.26 mmol) in diethyl ether (25 mL) was added to a suspension of $PbBr_2$ (1.56 g, 4.26 mmol) in diethyl ether (10 mL) at ca. 0 °C with constant stirring. The reaction mixture, which became an orange color, was stirred at ca. 0 °C for 20 min and for a further 24 h at room temperature. The solvent was removed under reduced pressure, and the orange residue was extracted with hexane (30 mL). After filtering through Celite, the orange filtrate was reduced to incipient crystallization and stored in a ca. −20 °C freezer for 24 h to afford **1** as orange crystals: yield 2.09 g, 64%; mp 217−219 °C; ^1H NMR (C_6D_6) δ 1.07 (d, 12H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.6 Hz; 1.29 (d, 12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.9 Hz; 1.34 (d, 12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.9 Hz; 2.84 (sept, 2H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.9 Hz; 3.11 (sept, 4H, *o*-CH(CH_3)$_2$); 7.15 (s, 4H, *m*-Trip); 7.29 (tr, 1H, *p*-C_6H_3), $^3J_{HH}$ = 7.5 Hz; 7.97 (d, 2H, *m*-C_6H_3), $^3J_{HH}$ = 7.5 Hz; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 23.69 (*o*-CH(CH_3)$_2$); 26.43 (*p*-CH(CH_3)$_2$); 30.74 (*o*-CH(CH_3)$_2$); 34.87 (*p*-CH(CH_3)$_2$); 121.23 (*m*-Trip); 125.72 (*p*-C_6H_3); 137.07 (*i*-Trip); 137.33 (*m*-C_6H_3); 147.62 (*o*-Trip); 148.54 (*p*-Trip); 148.78 (*o*-C_6H_3); 169.10 (*i*-C_6H_3); 287.88 (*i*-C_6H_3). Anal. Calcd for $C_{72}H_{98}Br_2Pb_2$: C, 56.24; H, 6.42. Found: C, 56.68; H, 6.59. UV−vis (hexane): λ_{max} 416.5 nm, ϵ = 1580 L M^{-1} cm^{-1}.

$py\cdot Pb(Br)C_6H_3\text{-}2,6\text{-}Trip_2$ (2). Pyridine (0.14 mL, 1.75 mmol) was added to **1** (1.04 g, 0.68 mmol) in hexane (35 mL) at ca. 0 °C with constant stirring. The reaction mixture became a yellow color and was stirred at ca. 0 °C for 20 min and for a further 2 h at room temperature. The yellow solution was separated from the small amount of white precipitate by decanting. The volume of the yellow solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer for 2 days to give **2** as yellow crystals: yield 0.91 g, 79.8%; mp 110−112 °C dec; ^1H NMR (C_6D_6) δ 1.12 (12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 1.21 (d, 12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 7.2 Hz; 1.42 (d, 12H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 2.76 (sept, 2H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 3.36 (sept, 4H, *o*-CH(CH_3)$_2$), J_{HH} = 6.8 Hz; 6.38 (t of t, 2H, *m*-C_5H_5N), $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.6 Hz; 6.73 (t of t, 1H, *p*-C_5H_5N), $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz; 7.11 (s, 4H, *m*-Trip); 7.29 (tr, 1H, *p*-C_6H_3), J_{HH} = 7.6 Hz; 7.78 (d of d, 2H, *m*-C_6H_3), $^3J_{HH}$ = 7.4 Hz; $^4J_{HH}$ = 1.6 Hz; 7.98 (br, 2H, *o*-C_5H_5N); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 23.56 (*o*-CH(CH_3)$_2$); 24.29 (*o*-CH(CH_3)$_2$); 26.39 (*p*-CH(CH_3)$_2$); 30.75 (*o*-CH(CH_3)$_2$); 34.53 (*p*-CH(CH_3)$_2$); 120.97 (*m*-Trip); 124.25 (*m*-C_5H_5N); 125.30 (*p*-C_6H_3); 136.42 (*p*-C_5H_5N, *i*-Trip); 137.42 (*m*-C_6H_3); 147.32 (*o*-Trip); 147.90 (*p*-Trip); 148.63 (*o*-C_6H_3); 149.49 (*o*-C_5H_5N). Anal. Calcd for $C_{41}H_{53}BrNPb$: C, 58.18; H, 6.31. Found: C, 57.97; H, 6.34. UV−vis (hexane): λ_{max} 417 nm, ϵ = 1760 L M^{-1} cm^{-1}.

$Pb(Me)C_6H_3\text{-}2,6\text{-}Trip_2$ (3). A diethyl ether solution of CH_3MgBr (0.77 mL, 2.31 mmol) was added to a solution of **1** (1.77 g, 1.15 mmol) in diethyl ether (25 mL) at ca. 0 °C with constant stirring. The reaction mixture, which had assumed a red color, was stirred until the ice bath had thawed to room temperature. The solvent was removed under reduced pressure, and the purple residue was extracted with hexane (50 mL). After filtering through Celite, the red solution was reduced to incipient crystallization and stored in a ca. 4 °C refrigerator to give **3** as red crystals: yield 1.22 g, 75.3%; mp 202−203 °C; ^1H NMR (C_6D_6) δ 0.08 (s, 3H, CH_3), $^2J_{Pb-H}$ = 40 Hz; 1.14 (12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 1.18 (d, 12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 1.39 (d, 12H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 7.2 Hz; 2.77 (sept, 2H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 3.35 (sept, 4H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 7.18 (s, 4H, *m*-Trip); 7.41 (tr, 1H, *p*-C_6H_3), $^3J_{HH}$ = 7.6 Hz; 7.76 (d, 2H, *m*-C_6H_3), $^3J_{HH}$ = 7.2 Hz; $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.438 (Pb−CH_3; J_{Pb-C} = 248 Hz; δ 23.67 (*o*-CH(CH_3)$_2$); 24.21 (*o*-CH(CH_3)$_2$); 26.58 (*p*-CH(CH_3)$_2$); 30.86 (*o*-CH(CH_3)$_2$); 34.69 (*p*-CH(CH_3)$_2$); 114.70 (Pb−CH_3); 121.26 (*m*-Trip); 124.75 (*p*-C_6H_3); 135.26 (*i*-Trip); 136.42 (*m*-C_6H_3); 145.60 (*o*-Trip); 147.20 (*p*-Trip); 148.65 (*o*-C_6H_3); 256.85 (*i*-C_6H_3); $^{207}Pb\{^1H\}$ NMR (C_6D_6) δ 7420. Anal. Calcd for $C_{37}H_{52}Pb$: C, 63.13; H, 7.44. Found: C, 63.69; H, 7.61. UV−vis (hexane): λ_{max} (nm); ϵ (L M^{-1} cm^{-1}), 466 (710), 332 (610).

$Pb(t\text{-}Bu)C_6H_3\text{-}2,6\text{-}Trip_2$ (4). A pentane solution of *tert*-butyllithium (1.17 mL of a 1.5 M solution) was added to a rapidly stirred solution of **1** (1.35 g, 0.88 mmol) in diethyl ether (30 mL) with cooling to ca. −78 °C. The reaction mixture, which had assumed a violet color, was stirred for 1 h and then allowed to warm to room temperature. The solvents were removed under reduced pressure, and the violet residue was extracted with hexane (30 mL). The violet solution was separated from the white precipitate (LiBr) by decanting. The volume of the solution was reduced to incipient crystallization and stored in a ca. 4 °C refrigerator to give the product **4** as violet crystals: yield 1.07 g, 81.7%; mp 129−130 °C; ^1H NMR (C_6D_6) δ 1.13 (12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.6 Hz; 1.20 (d, 12H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.9 Hz; 1.44 (d, 12H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.3 Hz; 2.78 (sept, 2H, *p*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.9 Hz; 3.35 (sept, 4H, *o*-CH(CH_3)$_2$), $^3J_{HH}$ = 6.9 Hz; 3.75 (s, 9H, C(CH_3)$_3$); 7.19 (s, 4H, *m*-Trip); 7.47 (tr, 1H, *p*-C_6H_3), $^3J_{HH}$ = 7.6 Hz; 7.86 (d, 2H, *m*-C_6H_3,), $^3J_{HH}$ = 7.5 Hz; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 23.48 (C(CH_3)$_3$), 24.20 (*o*-CH(CH_3)$_2$); 24.62 (*o*-CH(CH_3)$_2$); 27.29 (*p*-CH(CH_3)$_2$); 31.16 (*o*-CH(CH_3)$_2$); 34.78 (*p*-CH(CH_3)$_2$); 121.49 (*m*-Trip); 124.41 (*m*-C_6H_3); 128.16 (*p*-C_6H_3), 137.26 (*i*-Trip); 145.65 (*p*-Trip); 147.29 (*o*-Trip); 148.74 (*o*-C_6H_3); 171.49 (*i*-C_6H_3); 171.49 (*C*(CH_3)$_3$); 262.33 (*i*-C_6H_3); $^{207}Pb\{^1H\}$ NMR (C_6D_6) δ 7853. Anal. Calcd for $C_{40}H_{58}Pb$: C, 64.40; H, 7.84. Found: C, 65.11; H, 8.01. UV−vis (hexane): λ_{max} 470 nm, ϵ = 720 L M^{-1} cm^{-1}.

$Pb(Ph)C_6H_3\text{-}2,6\text{-}Trip_2$ (5). The solution of phenyllithium (0.139 g, 0.88 mmol) in diethyl ether (20 mL) was added to a rapidly stirred solution of **1** (0.68 g, 0.44 mmol) in diethyl ether (10 mL) with cooling to ca. −78 °C. The reaction mixture became a red color and was stirred for 1 h and then allowed

---

[12] Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1989**, *26*, 341.

[13] Twamley, B. T.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1.

[14] Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

[15] Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

Table 1. Crystallographic Data for Compounds 1−6

	1	**2**·0.5C_6H_{12}	**3**	**4**	**5**	**6**
formula	$C_{72}H_{98}Pb_2Br_2$	$C_{44}H_{55.5}PbBrN$	$C_{37}H_{52}Pb$	$C_{40}H_{58}Pb$	$C_{42}H_{54}Pb$	$C_{44}H_{49}PbW_2O_8Br$
fw	1537.70	855.49	703.98	746.05	766.04	1360.63
color, habit	orange, block	yellow, needle	dichroic red/pink, block	purple, block	red, block	orange plate
cryst syst	monoclinic	monoclinic	orthorhombic	monclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	*Pbcm*	$C2/c$	$P2_1/c$	*Pnma*
a, Å	18.330(2)	17.4582(12)	10.9737(8)	32.3169(17)	12.6017(8)	15.2672(7)
b, Å	14.184(2)	14.4136(10)	12.0562(8)	9.5877(5)	18.2376(11)	18.6878(9)
c, Å	26.215(3)	17.3971(12)	25.3639(17)	24.7261(13)	16.5121(10)	15.4719(7)
β, deg	91.760(10)	97.3830(10)		106.8590(10)	105.5330(10)	
V, Å^3	6812.5(14)	4341.4(5)	3355.7(4)	7332.0(7)	3656.3(4)	4414.3(4)
Z	4	4	4	8	4	4
d_{calc}, Mg/m^3	1.499	1.355	1.393	1.352	1.392	2.047
θ range, deg	1.11−2.500	1.84−31.51	1.86−25.00	2.22−27.50	2.02−31.53	1.71−31.49
μ, mm^{-1}	6.174	4.833	5.049	4.626	4.640	9.958
obs data $I > 2\sigma(I)$	6340	10 017	2031	2933	7520	5604
R1	0.0685	0.0475	0.0424	0.0606	0.0352	0.0290
wR2	0.1092	0.1149	0.0955	0.1201	0.0573	0.0586

to come to room temperature. Diethyl ether was removed under reduced pressure, and the red residue was extracted with benzene (20 mL). After filtering through Celite, the red solution was reduced to incipient crystallization and stored in a ca. 4 °C refrigerator to give **5** as red crystals: yield 0.47 g, 70%; mp 197 °C (dec); ^{207}Pb{^{1}H} NMR (C_6D_6) δ 6657; ^{1}H NMR (C_6D_6) δ 1.09 (12H, o-CH(CH_3)$_2$), $^3J_{HH}$ = 7.2 Hz; 1.10 (d, 12H, o-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 1.14 (d, 12H, p-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 2.68 (sept, 2H, p-CH(CH$_3$)$_2$), $^3J_{HH}$ = 6.8 Hz; 3.35 (sept, 4H, o-CH(CH$_3$)$_2$), $^3J_{HH}$ = 6.8 Hz; 7.10 (s, 4H, m-Trip); 7.40 (tr, 1H, p-C_6H_3), $^3J_{HH}$ = 7.2 Hz; 7.67 (t, 2H, m-Ph), $^3J_{HH}$ = 7.6 Hz; 7.82 (d, 2H, m-C_6H_3), $^3J_{HH}$ = 8.0 Hz; 8.65 (d of d, 2H, o-Ph), $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.2 Hz; ^{13}C{^{1}H} NMR (C_6D_6) δ 23.27 (o-CH(CH$_3$)$_2$); 24.14 (o-CH(CH$_3$)$_2$); 26.89 (p-CH(CH$_3$)$_2$); 31.15 (o-CH(CH$_3$)$_2$); 34.66 (p-CH(CH$_3$)$_2$); 121.40 (m-Trip); 124.84 (p-C_6H_3); 127.42 (p-Ph); 132.78 (m-Ph); 134.54 (i-Trip); 137.66 (m-C_6H_3); 139.71 (o-Ph); 146.11 (o-Trip); 147.63 (p-Trip); 148.95 (o-C_6H_3); 259.85 (i-Ph); 275.25 (i-C_6H_3). Anal. Calcd for $C_{41}H_{54}Pb$: C, 65.85; H, 7.1. Found: C, 66.01; H, 7.21. UV−vis (hexane): λ_{max} 460 nm, ϵ = 350 L M^{-1} cm^{-1}.

[{W(CO)$_4$}$_2$(μ-Br)(μ-PbC$_6$H$_3$-2,6-Trip$_2$)] (6). A solution of W(CO)$_6$ (0.53 g, 1.15 mmol) in THF (45 mL), irradiated by UV light for 8 h, was added to the solution **1** (0.87 g, 0.57 mmol) in hexane (15 mL) at room temperature. The reaction mixture became a brown color and was stirred for a further 16 h. The solvent was then removed under reduced pressure, and the brown residue was extracted with hexane (20 mL). After filtering through Celite, the brown solution was concentrated under reduced pressure to incipient crystallization and stored in a ca. −20 °C freezer to give **6** as orange crystals: yield 0.11 g, 7.2%; mp 183−185 °C; ^{1}H NMR (C_6D_6) δ 1.01 (12H, o-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 1.06 (d, 12H, o-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 1.55 (d, 12H, p-CH(CH_3)$_2$), $^3J_{HH}$ = 6.8 Hz; 2.56 (sept, 2H, p-CH(CH$_3$)$_2$), $^3J_{HH}$ = 6.8 Hz; 3.39 (sept, 4H, o-CH(CH$_3$)$_2$), $^3J_{HH}$ = 6.8 Hz; 7.14 (s, 4H, m-Trip), 7.35 (tr, 1H, p-C_6H_3), $^3J_{HH}$ = 7.6 Hz; 8.02 (d, 2H, m-C_6H_3), $^3J_{HH}$ = 7.6 Hz; ^{13}C{^{1}H} NMR (C_6D_6) δ 23.39 (o-CH(CH$_3$)$_2$); 24.42 (o-CH(CH$_3$)$_2$); 27.00 (p-CH(CH$_3$)$_2$); 31.13 (o-CH(CH$_3$)$_2$); 34.43 (p-CH(CH$_3$)$_2$); 122.62 (m-Trip); 128.11 (p-C_6H_3); 132.39 (i-Trip); 138.97 (m-C_6H_3); 143.42 (o-Trip); 147.64 (p-Trip); 151.00 (o-C_6H_3); 190.43 (CO); 191.09 (CO); 193.10 (CO); 201.47 (CO); IR (Nujol mull, cm^{-1}) ν 2050(m), 2018(s), 1978(s), 1965(sh), 1958(s), 1907(s), 1899(s), 1600(vw), 1572(s), 1360(sh), 1260(m), 1100(m), 880(w), 800(m), 720(m), 560(s), 475(vw), 425(vw), 355(m). Anal. Calcd for $C_{44}H_{49}BrO_8PbW_2$: C, 38.84; H, 3.63. Found: C, 38.10; H, 3.53. UV−vis (hexane): λ_{max} 344 nm, ϵ = 6050 L M^{-1} cm^{-1}.

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[16] Compound **1** was mounted on a glass fiber using epoxy resin. Data for **1** were collected at 293 K, **2**−**5** at 90 K, and **6** at 93 K using a Bruker SMART 1000 system (Mo Kα (λ = 0.70173 Å) radiation and a CCD area detector). The Bruker SHELXTL 5.1 program package[17] was used for the structure solutions and refinement. An absorption correction was applied using the program SADABS.[18] The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. An isopropyl group in **5** was subject to a disorder which could be modeled successfully using partial occupancies for the disordered atoms as described in the Supporting Information. Hydrogen atoms associated with the disordered atom sites were determined geometrically and fixed in position. The structure of **2** contains a six-atom fragment, which was modeled as a methylcyclopentane molecule with 50% occupancy. This six-carbon species, of formula C_6H_{12}, is a 10% contaminant in the hexanes solvent. Anomalous electron densities were observed in the neighborhood of the heavy atom sites in **1**−**6**. These were attributed to uncorrected absorption effects. Some details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information. Selected bond distances and angles for **1**−**6** are listed in Table 2.

Discussion

The Halide Derivatives {Pb(Br)C$_6$H$_3$-2,6-Trip$_2$}$_2$ (1) and py·Pb(Br)C$_6$H$_3$-2,6-Trip$_2$ (2). The aryllead halide compound **1** was synthesized in a straightforward manner, and in over 60% yield, by treatment of an diethyl ether suspension of lead(II) bromide with a diethyl ether solution of Et$_2$O·LiC$_6$H$_3$-2,6-Trip$_2$.[14] It was isolated as orange crystals, which were stable up to their melting point of 217−219 °C. Lead(II) bromide was used in preference to the other lead(II) halides since it was found that the product **1** could be more readily dissolved in and crystallized from hexane solvent. Both the ^{1}H and ^{13}C NMR (including the ipso-carbon signal of the C_6H_3 moiety) spectra of **1** are readily obtainable in C_6D_6, but no ^{207}Pb NMR resonance could be observed. It is possible that the difficulty in detecting this signal is associated with the large anisotropies expected for the three diagonal components of the chemical shift tensor. This is particularly true for **1**, and to a lesser extent **2**,

---

[16] Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1.

[17] *SHELXTL* version 5.1; Bruker AXS, Madison, WI, 1998.

[18] *SADABS*, an empirical absorption correction program part of the SAINTPlus NT version 5.0 package; BRUKER AXS: Madison, WI, 1998.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 1−6

1		2		3	
Pb(1)−C(1)	2.329(11)	Pb(1)−C(1)	2.322(4)	Pb(1)−C(1)	2.272(9)
Pb(2)−C(37)	2.306(13)	Pb(1)−Br(1)	2.7063(6)	Pb(1)−C(20)	2.274(15)
Pb(1)−Br(1)	2.7892(16)	Pb(1)−N(1)	2.502(4)	C(1)−Pb(1)−C(20)	101.4(4)
Pb(1)−Br(2)	3.0157(17)	C(1)−Pb(1)−Br(1)	92.39(11)	C(2)−C(1)−Pb(1)	121.9(4)
Pb(2)−Br(1)	2.9902(17)	C(1)−Pb(1)−N(1)	103.81(13)	C(2)−C(1)−(2A)	117.4(8)
Pb(2)−Br(2)	2.7841(16)	N(1)−Pb1)−Br(1)	90.45(9)		
Br(1)−Pb(1)−Br(2)	85.07(4)	C(2)−C(1)−Pb(1)	130.9(3)		
Br(1)−Pb(2)−Br(2)	85.64(4)	C(6)−C(1)−Pb(1)	111.3(3)		
Pb(1)−Br(1)−Pb(2)	94.83(4)	C(2)−C(1)−C(6)	118.5(4)		
Pb(1)−Br(2)−Pb(2)	94.37(4)				
C(1)−Pb(1)−Br(1)	95.4(3)				
C(37)−Pb(2)−Br(2)	98.0(3)				
C(2)−C(1)−Pb(1)	133.2(9)				
C(6)−C(1)−Pb(1)	108.6(8)				
C(2)−C(1)−C(6)	118.0(11)				
C(38)−C(37)−Pb(2)	109.8(9)				
C(42)−C(37)−Pb(2)	133.0(10)				
C(38)−C(37)−C(42)	117.1(2)				
4		**5**		**6**	
Pb(1)−C(1)	2.289(11)	Pb(1)−C(1)	2.321(3)	W(1)−Pb(1)	2.7517(3)
Pb(1)−C(37)	2.329(14)	Pb(1)−C(37)	2.264(3)	W(2)−Pb(1)	2.7423(3)
C(1)−Pb(1)−C(37)	100.5(5)	C(1)−Pb(1)−C(37)	95.64(11)	W(1)−Br(1)	2.6341(6)
C(2)−C(1)−Pb(1)	118.9(7)	C(2)−C(1)−Pb(1)	111.7(2)	W(2)−Br(1)	2.6534(6)
C(6)−C(1)−Pb(1)	122.8(8)	C(6)−C(1)−Pb(1)	128.2(2)	Pb(1)−C(1)	2.183(5)
C(2)−C(1)−C(6)	117.1(10)	C(2)−C(1)−C(6)	119.6(3)	Br(1)−W(1)−Pb(1)	108.379(15)
		C(38)−C(37)−Pb(1)	123.9(2)	Br(1)−W(2)−Pb(1)	108.094(15)
		C(42)−C(37)−Pb(1)	118.2(3)	W(1)−Br(1)−W(2)	73.350(16)
		C(42)−C(37)−C(38)	117.4(3)	W(2)−Pb(1)−W(2)	70.177(8)

where in addition to the very low local symmetry at lead, the aryl and bromine substituents are quite different electronically. Since large chemical shift anisotropies result in short T_1 and T_2 relaxation times,[19] very broad and difficult to detect isotropic signals are often the result. In addition, the presence of the very large terphenyl substituent could slow the molecular tumbling rates required to average the three anisotropic shift components. The presence of the quadrupolar nuclei ^{79}Br or^{81}Br bound to the lead atom could also be a factor in broadening of the ^{207}Pb NMR signal.[20] The difficulty in obtaining ^{207}Pb NMR signals for **1** and **2** is consistent with the observations of Eaborn, Smith, and co-workers on the organolead chlorides $[Pb(\mu\text{-}Cl)\{C(SiMe_2Ph)_3\}]_2$,[9,10] $[Pb(\mu\text{-}Cl)\{C(SiMe_3)_3\}]_3$,[10] and $\{Pb(\mu\text{-}Cl)C(SiMe_3)_2(SiMe_2OMe)\}_2$;[10] a solution signal was obtained only in the case of the latter species.

The X-ray crystal structure of **1** (Figure 1) shows that the molecule is dimerized through bridging of the metal centers by the bromides. The dimeric structure of **1** thus differs from the mononuclear structures[21] observed for $Ge(Cl)C_6H_3$-2,6-Trip$_2$ and $Sn(I)C_6H_3$-2,6-Trip$_2$. This is probably a result of the reduction in steric congestion owing to the larger size of the lead. The $Pb_2Br_2C(1)C(37)$ array almost possesses a center of symmetry, and the Pb_2Br_2 parallelogram core is essentially perfectly planar with internal angles near 85.5° at the lead atoms and 94.5° at the bromides. There are two pairs of Pb−Br distances, one averaging 2.79 Å and the other near 3.00 Å. The Pb−C distances 2.329(11) and 2.306(13) Å differ by only two standard deviations. It is difficult to compare the Pb−Br distances in **1** with those found in other crystal structures where the coordination number of the Pb(II) center is much higher (generally six or greater). For instance, an X-ray study of $[NH_4][Pb_2Br_5]$[22] features two bromides 2.89(5) Å distant from the lead, two bromides at 3.16(2) Å, and four at 3.35(5) Å. On the other hand, an electron diffraction study of $PbBr_2$ vapor,[23] where the lead is two-coordinate, afforded a much shorter Pb−Br length of 2.60(3) Å. The latter value is somewhat less than the sum of the metallic radius of lead, 1.54 Å,[24] and the covalent radius of bromine, 1.14 Å.[25] However, the ionic character of the Pb−Br bond leads to the expectation of some shortening in the bond. Although bonding to lead often shows effects that are not normally observed in its lighter congeners,[2] it is possible to say that in **1** the shorter

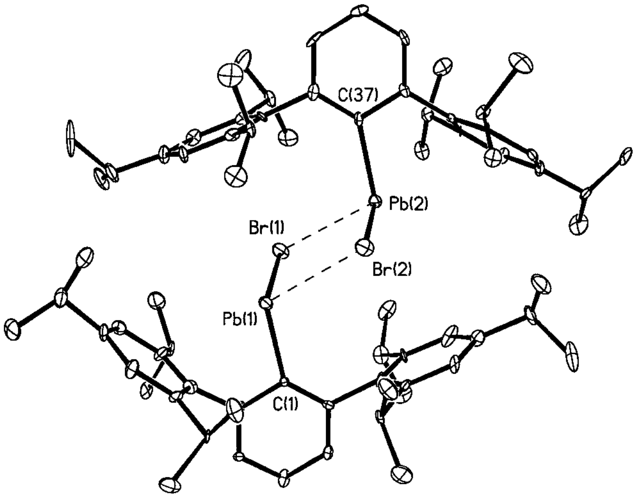

Figure 1. Thermal ellipsoidal (30%) plot of **1**. H atoms are not shown for clarity. Selected bond distances and angles are given in Table 2.

---

[19] Poole, C. P.; Farach, H. A. *Relaxation in Magnetic Resonance*; Academic Press: New York, 1971; p 75.

[20] Sebald, A.; Harris, R. K. *Organometallics* **1990**, *9*, 2096.

[21] Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1998**, *17*, 5602.

[22] Powell, H. M.; Tasker, H. S. *J. Chem. Soc.* **1937**, 119.

[23] Lister, M. W.; Sutton, L. E. *Trans Faraday Soc.* **1941**, *37*, 406.

[24] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 257.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

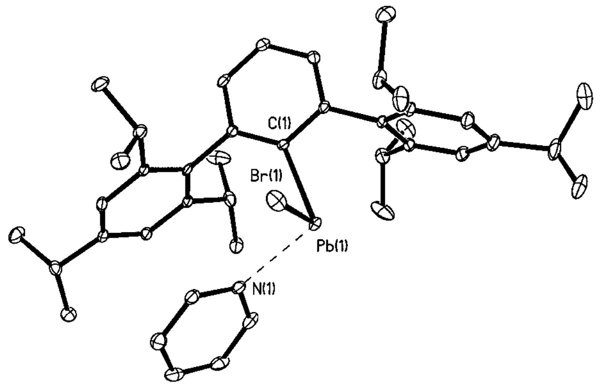

Figure 2. Thermal ellipsoidal (30%) plot of **2**. H atoms are not shown for clarity. Selected bond distances and angles are given in Table 2.

Pb−Br distances (2.79 Å) seem to be in keeping with the three-coordination at the metal, whereas the longer Pb−Br distances near 3.00 Å are more consistent with a higher coordination number. We also note that Pb−Br distances of 2.623(1) and 2.656(7) Å were observed in the sterically crowded Pb(IV) molecules $PbBr_2(Tbt)_2$ (Tbt = C_6H_2-2,4,6-$\{CH(SiMe_3)_2\}_3$)[26] and $Pb(Br)(CMe_2C_6H_3$-2,5-t-$Bu_2)_3$,[27] which are close to the 2.60(3) Å observed for the vapor phase structure of $PbBr_2$. The longer Pb−Br distances in the dimer **1** may suggest that dissociation might occur in solution, although there is no direct evidence for this. The observation of a 0.21 Å difference in the bridging lead−halogen distances in **1** is consistent with the structures of the dimers $[Pb(\mu\text{-}Cl)\{C(SiMe_2Ph)_3\}]_2$[9,10] (Pb−Cl = 2.729(3) and 2.962(3) Å) and $[Pb(\mu\text{-}Cl)\{C(SiMe_3)_2SiMe_2OMe\}]_2$[10] (Pb−Cl = 2.680(5) and 2.868(5) Å), where the Pb−Cl distances differ by ca. 0.24 and 0.19 Å, respectively. It is also notable that, on the basis of the ca. 0.15 Å difference[25] in the radius of chlorine and bromine, the Pb−Br distances in **1** are ca. 0.04−0.1 Å shorter than expected. The average Pb−C bond length in **1**, ca. 2.32 Å, is also shorter than the 2.435(10) and 2.37(2) Å values in $[Pb(\mu\text{-}Cl)\{C(SiMe_2Ph)_3\}]_2$[9,10] or $\{Pb(\mu\text{-}Cl)C(SiMe_3)_2\text{-}SiMe_2OMe\}_2$.[10] Taken together, the above data suggest that $-C(SiMe_2Ph)_3$ and $-C(SiMe_3)_2SiMe_2OMe$ ligands are more sterically crowding than the $-C_6H_3$-2,6-$Trip_2$ ligand. However, there are very large differences (ca. 24°) in the external (Pb−C−C) angles at the C(1) and C(37) ipso-carbons in **1**, which suggest the presence of some steric congestion in this molecule, although this is not supported by other distortions such as a deviation of the Pb(1)−C(1) bond from the plane of the central aryl ring (angle = 2.3°).

The addition of pyridine to a hexane solution of **1** results in cleavage of the bridged structure and the formation of a 1:1 monomeric complex **2**. The ^1H and ^{13}C NMR spectra of **2** were readily obtainable, but, as in the case of **1**, a ^{207}Pb NMR signal was not observed. In the X-ray crystal structure (Figure 2), the lead is pyramidally coordinated ($\sum°Pb = 286.65°$) by the C(1) of the aryl, the pyridine nitrogen, and a bromine. The pyridine nitrogen lone pair is obviously coordinated through the "empty" 6p-orbital on lead. However, the N−C(para) vector deviates 10° from the line of the Pb(1)−N(1) bond toward the less crowded side of the molecule. The large size of the aryl ligand is also reflected in the over 13° difference in the N(1)−Pb−Br(1) = 90.45(9)° and N(1)−Pb−C(1) = 103.81(3)° angles. Similar to **1**, there is also a very large difference, ca. 19°, in the external angles at the C(1) (i.e., ipso) carbon atom, but there is very little deviation of the Pb(1)−C(1) bond from the plane of the central ring (angle = 2.3°). The Pb(1)−C(1) bond length is essentially identical to that in **1**, while the Pb(1)−Br(1) bond (2.7063(6) Å) is ca. 0.08 Å shorter than the short pair of bridging Pb−Br distances in the dimer **1**. This contraction is consistent with the terminal nature of the Pb−Br moiety. The Pb−N bond distance 2.502(4) Å may be compared to the 2.59(4) or 2.60(2) Å seen in the $PbBr_2$ complexes[28] $\{(4\text{-}MeH_4C_5N)_2\cdot PbBr_2\}_n$ and $\{(3\text{-}MeH_4C_5N)_2\cdot PbBr_2\}_n$ that feature infinite chains in which the six-coordinate lead atoms are bridged by bromides. In addition there are complexes[29] such as $\{(1,10\text{-phenanthroline})\cdot PbBr_2\}_n$ (also with six-coordinate Pb^{2+}) that have Pb−N distances as short as 2.521(7) Å. At the other end of the Pb−N distance scale are the recently reported[30] complexes $TMEDA\cdot Pb(\eta^5\text{-}C_5H_5)_2$ and 4,4′-$Me_2bipyridyl\cdot Pb(\eta^5\text{-}C_5H_5)_2$, which have Pb−N distances of 2.879(3) and 2.702(5) Å, which are dissociated in solution. The longer Pb−N bonds in these complexes reflect the higher formal eightfold coordination of lead, if the η^5-C_5H_5 ligand is considered to occupy three coordination sites.

The Diorganolead(II) Compounds $Pb(R)C_6H_3$-2,6-$Trip_2$ (R = Me, 3; t-Bu, 4; Ph, 5). The diorgano compounds **3**−**5** were synthesized by the reaction of **2** with 1 equiv of CH_3MgBr, Li(t-Bu), or LiPh. The reactions proceed smoothly and in moderate yield to afford the products as thermally robust red or purple dichroic crystals. The stability of these derivatives is attributable to the almost unique steric properties of the $-C_6H_3$-2,6-$Trip_2$ substituent, which creates a relatively sheltered (by the ortho-Trip substituents) cavity in which the Pb−C bond to the smaller organo substituent is less prone to further reaction. The high steric protection of the $-C_6H_3$-2,6-$Trip_2$ ligand is supported by the fact that attempts to substitute a second $-C_6H_3$-2,6-$Trip_2$ group at the lead have so far failed.[31] Nonetheless, it is possible to synthesize the compound $Pb\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$,[32] which features somewhat less bulky terphenyl groups. Attempts[10] to synthesize $Pb(Ph)\{C(SiMe_2Ph)_3\}$, via the reaction of $[Pb(Cl)\{C(SiMe_2Ph)_3\}]_2$ with LiPh, did not afford the desired product but a mixture of species that contained the lead−lead bonded compound $Ph_3PbPbPh_3$.

---

[25] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford, 1984; p 286.

[26] Kano, N.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 2748.

[27] Okazaki, R.; Shibata, K.; Tokitoh, N. *Tetrahedron Lett.* **1991**, *32*, 6601.

[28] Engelhardt, L. M.; Patrick, J. M.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 2107.

[29] Bowmaker, G. A.; Harrowfield, J. M.; Miyamae, H.; Shand, T. M.; Skelton, B. M.; Doudi, A. A.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 1089.

[30] Beswick, M. A.; Cromhout, N. L.; Harmer, C. N.; Raithby, P. R.; Russell, C. A.; Smith, J. S. B.; Steiner, A.; Wright, D. S. *Chem. Commun.* **1996**, 1977.

[31] Pu, L.; Power, P. P. Unpublished work.

[32] Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

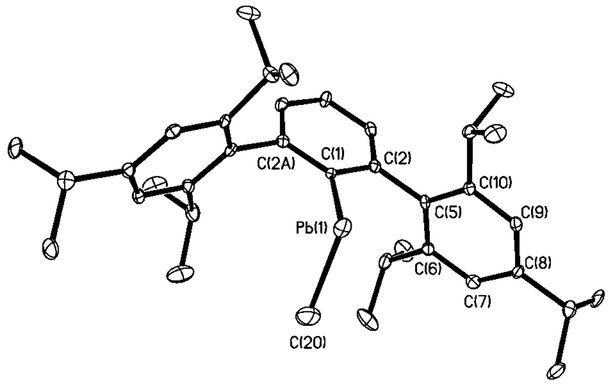

Figure 3. Thermal ellipsoidal (30%) plot of **3**. H atoms are not shown for clarity. Selected bond distances and angles are given in Table 2.

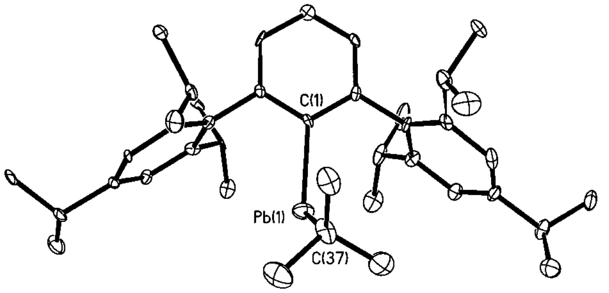

Figure 4. Thermal ellipsoidal (30%) plot of **4**. H atoms are not shown for clarity. Selected bond distances and angles are given in Table 2.

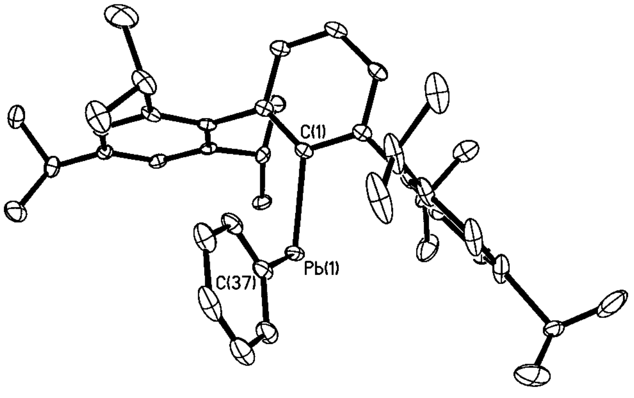

Figure 5. Thermal ellipsoidal (30%) plot of **5**. H atoms are not shown for clarity. Selected bond distances and angles are given in Table 2.

The structures of **3**−**5** are illustrated in Figures 3−5. The lead centers have two-coordinate, V-shaped geometries in the three molecules. It can be seen from Table 2 that the Pb−C distances fall within the narrow range of 2.264(3)−2.329(14) Å. These distances are similar to those reported (2.278(9)−2.294(4) Å) for the metalloplumbylenes (η^5-C_5H_5)(CO)$_3$MPbC_6H_3-2,6-Trip$_2$ (M = Cr, Mo, or W).[11] The C−Pb−C angles in the two alkyl derivatives **3** and **4** are within 0.5° of 101°, whereas the angle in the diaryl compound **5** is ca. 5° narrower, 95.64(11)°. As in **1** and **2**, the deviation of the Pb−C(1) bonds from the plane of the C(1) aryl ring are relatively small: 10° for **3**, 8.4° for **4**, and 4° for **5**. However, in contrast to what is observed in **1** and **2**, the Pb−C(ipso)−C(ortho) angles in **3** are identical (owing to the existence of a plane of symmetry) and those of **4** differ by only 5.7°. The same angles in **5** differ by 16.5°, and the torsion angle between the lead coordination plane and the plane of the phenyl ring is 21.4°. The Pb−C(phenyl) bond is also shorter (by ca. 0.06 Å) than the Pb−C_6H_3-2,6-Trip$_2$ bond. These features suggest the existence of an interaction between the p-orbital on lead and the π-electrons of the phenyl group.

The main structural and spectroscopic (^{207}Pb NMR) features of **3**−**5** may also be compared with those of the known monomeric diorganolead(II) species.[5d,32−35] These data are presented in Table 3. For the previously published complexes the range of Pb−C distances is 2.327(13)−2.476(14) Å. Thus, five of the six Pb−C distances in the derivatives **3**−**5** fall below this range, and the remaining distance 2.329(14) Å is essentially identical to the shortest of the previously published values. The C−Pb−C angles in **3**−**5** (none wider than 101.4(4)°) are also in the lower third of the known range of C−Pb−C angles (Table 3). These data illustrate the differences in the steric characteristics of the terphenyl ligand, whose effectiveness is associated with the creation of a protected space surrounding the central atom, whereas for most bulky alkyl or aryl groups, protection is achieved by the occupation of the space in immediate proximity to the central atom. In the latter case, the steric crowding near the protected center is often sufficient to produce lengthening of the bonds and a widening of the angles. This may be the most likely explanation for the longer Pb−C bond distances seen in the previously published compounds. Such differences however should not obscure the fact that the Pb(II)−C bond lengths in all the compounds are generally longer than those observed in lead(IV) organo compounds (cf. 2.19(3) Å in PbPh$_4$,[36] 2.238(9) Å in PbMe$_4$[37]). Nonetheless, “long” Pb(IV)−C bonds can also be observed in very crowded molecules such as PbBr$_2$(Tbt)$_2$, which has very distorted tetrahedral coordination and Pb−C = 2.274(6) Å.[26]

The ^{207}Pb NMR spectroscopic data for **3**−**5** display a strong downfield shift, which is consistent with the low coordination number.[38] The values of **3**−**5** are well within the range (4878−10 050 ppm) previously observed for two-coordinate species. The ^{1}H NMR spectra of **3** and **4** also display features of interest. For instance the lead methyl resonance in **3** is (not unexpectedly) near 0 ppm, whereas the t-Bu resonance in **4** appears well downfield at 3.75 ppm. Possibly, the proximity of the t-Bu hydrogens to the aromatic rings of the terphenyl ligands could produce this anomalous shift. The coupling between the ^{207}Pb nucleus and the Pb−CH$_3$ hydrogens is 40 Hz. This is significantly less than the 60 Hz observed in PbMe$_4$.[39] In contrast the J(^{207}Pb−^{13}C) coupling is 248 Hz, which is almost identical to the

---

(33) Brooker, S.; Buijink, J.-K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25.

(34) Eaborn, C.; Ganicz, T.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1997**, *16*, 5621.

(35) Kano, N.; Shibata, K.; Tokitoh, N.; Okazaki, R. *Organometallics* **1999**, *18*, 2999.

(36) Busetti, V.; Mammi, M.; Signor, A.; Del Pra, A. *Inorg. Chem. Acta* **1967**, *1*, 424.

(37) Oyamada, T.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2638.

(38) Wrackmeyer, B.; Horchler, K. *Ann. Reports on NMR Spectroscopy* **1990**, *22*, 249.

(39) Fritz, H. P.; Scharzhous, K. *J. Organomet. Chem.* **1964**, *1*, 297.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624

Table 3. Important Spectroscopic and Structural Parameters for Monomeric Diorganolead(II) Compounds Including 3−5

compound	Pb−C (Å)	C−Pb−C (deg)	^{207}Pb NMR (δ)	UV−vis (nm)
$Pb\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$[33]	2.361(4), 2.371(4)	94.5(1)	4878	
$Pb\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$[32]	2.334(12)	114.5(6)	8844[a]	526
$Pb\overline{C(SiMe)_2SiMe_2CH_2CH_2SiMe_2C}(SiMe_3)_2$[34]	2.397(6), 2.411(5)	117.1(2)	10050	610
$Pb(C_6H\text{-}2,3,5\text{-}Me_3\text{-}6\text{-}t\text{-}Bu)_2$[5d]	2.357(4), 2.376(4)	103.04(13)	6927	490
$PbMes^*(CH_2CMe_2C_6H_2\text{-}2,5\text{-}t\text{-}Bu)_2$[5d,b]	2.344(9), 2.476(14)	94.8	5067	406
$Pb(Tbt)_2$[35,b]	2.327(13)	116.3(7)	9751	610
Pb(Tbt)Trip[35,b]			8888	550
$Pb(Tbt)\{C_6H_2\text{-}2,4,6\text{-}(CH_2SiMe_3)_3\}$[35]			8873	560
$Pb(Tbt)\{CH(SiMe_3)_2\}$[35]			8884	531
$Pb\{CH(SiMe_3)_2\}_2$[c]			9112	
$Pb(Me)C_6H_3\text{-}2,6\text{-}Trip_2$ (**3**)	2.272(9), 2.274(15)	101.41(4)	7420	466
$Pb(t\text{-}Bu)C_6H_3\text{-}2,6\text{-}Trip_2$ (**4**)	2.289(11), 2.329(14)	100.5(5)	7853	570
$Pb(Ph)C_6H_3\text{-}2,6\text{-}Trip_2$ (**5**)	2.321(3), 2.264(3)	95.64(11)	6657	460

[a] Newly recorded value; the value previously given in ref 32 was in error. [b] $Mes^* = C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3$; $Tbt = C_6H_2\text{-}2,4,6\text{-}\{CH(SiMe_3)_2\}_3$. [c] Data cited in ref 38, p 293.

250 Hz found for $PbMe_4$.[40] The ^{13}C NMR spectra of **1** and **3**−**5** are also notable in that the chemical shift of the carbon atoms attached directly to lead appear at extremely low field (generally >250 ppm). The UV−vis spectra of **3**−**5** are characterized by absorbances that appear below 500 nm. These absorbances are usually thought to arise from an n−p electronic transitions.[37] Since the energy difference between these two levels is expected to decrease with increasing the interligand angle at lead, a longer absorption wavelength would be expected for the wider angle. It can be seen that, although longer wavelengths are often found to correspond to the wider angle, the correlation is not a strong one and the wavelength of the absorption is obviously influenced by other factors as well.

The Bridged Plumbylyne Complex $[\{W(CO)_4\}_2(\mu\text{-}Br)(\mu\text{-}PbC_6H_3\text{-}2,6\text{-}Trip_2\}]$ (6). This unusual complex was synthesized in low (ca. 7%) yield by the reaction between $W(CO)_5THF$ and **1**. It was hoped that this reaction would result in the formation of the plumbylene complex $(OC)_5W\{Pb(Br)C_6H_3\text{-}2,6\text{-}Trip_2\}$. However **6** was the only crystalline product isolated from the reaction mixture. The other components of this mixture included $W(CO)_6$, the arene $1,3\text{-}Trip_2C_6H_4$, lead metal, and $PbBr_2$. Possibly, **6** results from the oxidative addition of **1** to $W(CO)_5THF$ or $W(CO)_6$ to yield $(OC)_4(Br)WPb\{C_6H_3\text{-}2,6\text{-}Trip_2\}$, which may react further with $W(CO)_6$ or $W(CO)_5THF$ to give **6** with CO or THF elimination. An X-ray crystal structure determination of the orange crystals of **6** showed that the molecules (Figure 6) were characterized by a plane of symmetry that includes the W_2PbBr core in addition to four of the carbonyls and the ipso and para carbons of the central aryl ring of the terphenyl group. Formally, the structure may be described as consisting of two edge-bridged octahedra in which the lead and bromine atoms define the common edge, with the other apexes of the octahedra being occupied by eight carbonyl ligands.

The structure resembles that found for $\{W(CO)_4(\mu\text{-}I)\}_2$,[41] in which two iodine atoms form the common edge of the two octahedra. It was found to have a W−W single bond of 3.155 Å, which is very close to the 3.158(2) Å observed in **6**. In the bonding model of the iodide derivative, each bridging ligand supplies three electrons to the metals such that each tungsten-centered unit has seventeen electrons. An 18-electron configuration is then attained by forming a W−W single bond. The $PbC_6H_3\text{-}2,6\text{-}Trip_2$ moiety, since it employs three electrons for bonding to the metals, may therefore be properly regarded as a plumbylyne moiety. This is in accord with the geometry at lead, which is planar as crystallographically required. The trigonal geometry at lead is very distorted, however, with an acute W(1)−Pb(1)−W(2) angle (70.177(8)°) and two wide W−Pb−C angles that differ by ca. 10°. The two Pb−W bonds are very similar at 2.7517(3) and 2.7423(3) Å, and these are a good deal shorter than the ca. 3.0 Å recently observed for the structure of $(\eta^5\text{-}C_5H_5)(CO)_3WPbC_6H_3\text{-}2,6\text{-}Trip_2$.[11] Since tungsten and molybdenum are of almost equal size, a structural comparison may also be made with the metalloplumbylene $THF\cdot Pb\{Mo(\eta^5\text{-}C_5Me_5)(CO)_3\}_2$,[42] which also has three-coordinate lead and Pb−Mo distances of 2.989(2) and 3.019(2) Å. The Pb−C(1) distance in **6**, 2.183(5) Å, is also short, and a comparison with the structures of **1**−**5** shows that it is ca. 0.1−0.14 Å shorter than the corresponding Pb−C bonds in those compounds. The Pb−C shortening can be attributed to

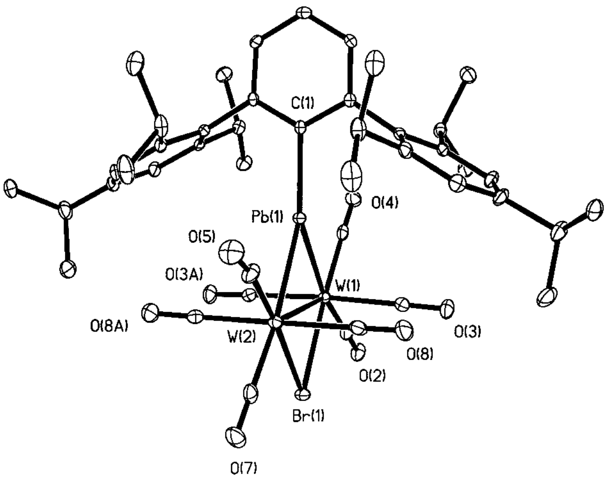

Figure 6. Thermal ellipsoidal (30%) plot of **6**. H atoms are not shown for clarity. Selected bond distances and angles are given in Table 2.

---

(40) McFarlane, W. *Mol. Phys.* **1967**, *13*, 587.

(41) Schmid, G.; Böse, R. *Chem. Ber.* **1976**, *109*, 2148.

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

the geometrical changes at lead, which have resulted in a planar geometry and a change in the σ-orbital composition in the bonding to carbon. These also imply that there is an "empty" p-orbital at the lead, which could interact with the tungsten d-orbitals in a back-bonding fashion. However, the CO stretching frequencies of **6** are similar to those[43] found in $\{W(CO)_4(\mu\text{-}I)\}_2$, which suggests limited back-bonding by the plumbylyne ligand.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0001624

---

[43] Schmid, G.; Boese, R.; Welz, E. *Chem. Ber.* **1975**, *108*, 260.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on June 23, 2000 on http://pubs.acs.org | doi: 10.1021/om0001624