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Notes

Stereochemical Activity of the Metal-Centered Lone Electron Pair in Group 14 Metallocenes. Crystal Structure of the Linear Sandwich Complex $[C_5(iPr)_3H_2]_2Pb$

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Introduction

Both stannocene (Cp_2Sn) and plumbocene (Cp_2Pb) possess structures with nonparallel rings in the solid state,[1−3] in solution,[4,5] and in the gas phase.[6] The operation of a stereochemically active lone pair of metal valence electrons in the complexes has traditionally been cited as the source of the bent ring structures,[7] a conclusion reinforced by early MO calculations.[8] Not surprisingly, therefore, the report[9] of the structure of the linear stannocene $(C_5Ph_5)_2Sn$ received close scrutiny, as it was the first structurally authenticated group 14 metallocene to possess parallel rings.[10] Subsequently, other linear metallocenes of the group 14 elements were discovered, including one conformer of $Cp^*{}_2Si$,[11] two more stannocenes ($[C_5Me_4(SiMe_2Bu^t)]_2Sn$[12] and $[C_5(Pr^i)_5]_2Sn$),[13] and the plumbocene $[C_5Me_4(SiMe_2Bu^t)]_2Pb$.[14] Although its structure has not been determined by single-crystal X-ray diffraction, the X-ray powder pattern of $(C_5Ph_5)_2Ge$ is similar to that of $(C_5Ph_5)_2Sn$, and it is likely that the germanium compound is also linear.[15]

The accumulation of structural data on the linear metallocenes, combined with more sophisticated theoretical work,[16] has served to refine the stereochemical role for the lone pair of electrons in group 14 metallocenes.[17] We now report the synthesis and crystal structure of a second linear plumbocene, which in concert with other related compounds allows us to evaluate the importance of intramolecular steric crowding as a contributor to the structure of linear group 14 metallocenes.

Experimental Section

Materials. Anhydrous PbI_2 was a commercial sample and was used as received. KCp^{3i} ($[Cp^{3i}]^- = 1,2,4\text{-}(C_3H_7)_3C_5H_2$) was prepared as previously described.[18] Its isomeric purity was ensured by reaction of the originally prepared $(C_3H_7)_3C_5H_3$ hydrocarbon with KH, followed by hydrolysis and a subsequent secondary reaction with KH; ^1H NMR analysis was used to check the composition. Solvents for the reaction were distilled under nitrogen from sodium or potassium benzophenone ketyl.[19]

Physical Measurements. Proton and carbon (^{13}C) NMR spectra were obtained on a Bruker NR-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual resonances of C_6D_6 (δ 7.15 and 128.0) or THF-d_8 (δ 3.58 and 67.4). Assignments of the signals in the ^{13}C NMR spectrum were made with the help of DEPT pulse experiments. Infrared data were obtained on a Perkin-Elmer 1600 Series FT-IR spectrometer as a neat sample between sealed KBr plates.

Synthesis of $(Cp^{3i})_2Pb$. KCp^{3i} (0.67 g, 2.93 mmol) and PbI_2 (0.67 g, 1.46 mmol) were added to 45 mL of THF, and the orange suspension was stirred for 12 h. The THF was removed under vacuum, leaving a reddish-orange residue, which was extracted with 50 mL of hexanes. The extract was then filtered through a glass frit, and removal of the hexanes from the resulting red filtrate gave 0.58 g (68% yield) of $(Cp^{3i})_2Pb$ as an orange-red oil. ^1H NMR (C_6D_6), δ: 5.64 (s, ^2J(Pb−H) = 34.4 Hz, 4 H, ring C*H*); 3.06 (septet, J = 6.8 Hz, 2 H, C*H*Me_2); 2.88 (septet, J = 6.8 Hz, 4 H, C*H*Me_2); 1.20−1.24 (two overlapping doublets, 24 H, C*H*$_3$); 1.18 (d, J = 6.8 Hz, 12 H, C*H*$_3$). ^{13}C NMR (C_6D_6), δ: 134.5 (ring *C*$CHMe_2$); 134.2 (ring *C*$CHMe_2$); 102.6 (^1J(Pb−C) = 61.3 Hz, ring *C*H); 27.9 (*C*H_3); 27.6 (*C*HMe_2); 26.5 (*C*H_3); 26.2 (*C*H_3); 25.7 (*C*HMe_2). Principal IR bands (neat) cm^{-1}: 2960 (s), 2870 (sh), 1462 (m), 1452 (m, sh), 1408 (w), 1381 (m), 1361 (m), 1325 (w), 1278 (w), 1262 (w), 1176 (w), 1150 (w), 1084 (m), 1021 (s), 980 (w), 864 (w), 800 (m), 668 (m), 502 (w), 465(w). Although initially isolated as an oil, samples of $(Cp^{3i})_2Pb$ left standing (7−10 days) at ambient temperature partially solidified to form deep red, needle-shaped crystals (mp 34−35 °C).

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(1) Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 925−927.

(2) Overby, J. S.; Hanusa, T. P.; Young, V. G., Jr. *Inorg. Chem.* **1998**, *37*, 163−165.

(3) Beswick, M. A.; Lopez-Casideo, C.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Steiner, A.; Wright, D. S. *Chem. Commun.* **1997**, 109−110.

(4) Fischer, E. O.; Grubert, H. *Z. Anorg. Allg. Chem.* **1956**, *286*, 237−242.

(5) Fischer, E. O.; Grubert, H. *Z. Naturforsch., B* **1956**, *11*, 423−424.

(6) Almenningen, A.; Haaland, A.; Motzfeldt, T. *J. Organomet. Chem.* **1967**, *7*, 97−104.

(7) Dave, L. D.; Evans, D. F.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3684−3688.

(8) Jutzi, P.; Kohl, F.; Hofmann, P.; Krueger, C.; Tsay, Y. H. *Chem. Ber.* **1980**, *113*, 757−769.

(9) Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259−4261.

(10) Williamson, R. L.; Hall, M. B. *Organometallics* **1986**, *5*, 2142−2143.

(11) Jutzi, P.; Holtmann, U.; Kanne, D.; Krueger, C.; Blom, R.; Gleiter, R.; Hyla, K. I. *Chem. Ber.* **1989**, *122*, 1629−1639.

(12) Constantine, S. P.; Hitchcock, P. B.; Lawless, G. A.; DeLima, G. M. *J. Chem. Soc., Chem. Commun.* **1996**, 1101−1102.

(13) Sitzmann, H.; Boese, R.; Stellberg, P. *Z. Anorg. Allg. Chem.* **1996**, *622*, 751−755.

(14) Constantine, S. P.; Hitchcock, P. B.; Lawless, G. A. *Organometallics* **1996**, *15*, 3905−3906.

(15) Heeg, M. J.; Herber, R. H.; Janiak, C.; Zuckerman, J. J.; Schumann, H.; Manders, W. F. *J. Organomet. Chem.* **1988**, *346*, 321−332.

(16) Recent ab initio calculations place the energy difference between the bent (preferred) and linear forms of Cp_2Sn and Cp_2Pb at 17 and 2.8 kJ/mol, respectively (Armstrong, D. R.; Duer, M. J.; Davidson, M. G.; Moncrieff, D.; Russell, C. A.; Stourton, C.; Steiner, A.; Stalke, D.; Wright, D. S. *Organometallics* **1997**, *16*, 3340−3351). Preliminary density functional calculations on stannocene and plumbocene suggest that the bent and linear forms are nearly isoenergetic (Hanusa, T. P., Smith, J. D. Unpublished results).

(17) Burkey, D. J.; Hanusa, T. P. *Comments Inorg. Chem.* **1995**, *17*, 41−77.

(18) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843−4851.

(19) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988.

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Table 1. Crystallographic Data for $(Cp^{3i})_2Pb$

formula: $C_{28}H_{46}Pb$	$Z = 1$
fw = 589.87	space group: $P\bar{1}$ (No. 2)
$a = 9.318(1)$ Å	$T = -171$ °C
$b = 9.677(1)$ Å	$\lambda = 0.710\ 69$ Å
$c = 8.475(1)$ Å	$\rho_{calcd} = 1.475$ g cm^{-3}
$\alpha = 95.011(8)$°	$\mu = 64.13$ cm^{-1}
$\beta = 116.249(6)$°	R^a ($I > 2.33\sigma(I)$) = 0.0224
$\gamma = 75.709(8)$°	$R_w{}^b$ ($I > 2.33\sigma(I)$) = 0.0206
$V = 664.0(4)$ Å^3	GOF = 0.911

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w(F_o{}^2)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) for $(Cp^{3i})_2Pb$

Pb(1)−C(2)	2.744(4)	C(2)−C(7)	1.513(7)
Pb(1)−C(3)	2.748(5)	C(4)−C(10)	1.513(6)
Pb(1)−C(4)	2.767(4)	C(6)−C(13)	1.512(6)
Pb(1)−C(5)	2.743(3)	C(7)−C(8)	1.518(9)
Pb(1)−C(6)	2.738(4)	C(7)−C(9)	1.528(9)
Pb(1)-ring centroid	2.470	C(10)−C(11)	1.517(8)
C(2)−C(3)	1.420(6)	C(10)−C(12)	1.518(9)
C(2)−C(6)	1.414(6)	C(13)−C(14)	1.535(8)
C(3)−C(4)	1.416(7)	C(13)−C(15)	1.512(8)
C(4)−C(5)	1.403(7)		
C(5)−C(6)	1.418(7)		

$CH_3-CH-CH_3$ (av)	110.2(9)°
planarity of rings	within 0.004 Å
ring centroid−Pb(1)−ring centroid	180°
av displacement of methine carbon from ring plane	0.079 Å

X-ray Crystallography. Crystals of $(Cp^{3i})_2Pb$ were isolated directly from the solidification of the initially formed oil. Data were collected on a suitable orange crystal, measuring 0.10 × 0.10 × 0.12 mm, in a low-temperature study performed at Indiana University. Relevant crystallographic data for the present study are given in Table 1.

A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima having symmetry consistent with the triclinic space group $P\bar{1}$. Subsequent solution and refinement of the structure confirmed the choice; no additional symmetry was detected with the ADDSYM algorithm of PLATON. Data were collected using a continuous $\theta-2\theta$ scan with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent data averaged. The structure was readily solved by direct methods (MULTAN-78) and standard Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier synthesis and were refined isotropically in the final least-squares cycles. A final difference Fourier map revealed a large peak (2.03 e Å^{-3}) at the site of the Pb atom; the map was otherwise featureless, with the largest peak being 0.25 e Å^{-3}. Selected bond distances listed in Table 2.

Results and Discussion

Synthesis and Chemical Properties. $(Cp^{3i})_2Pb$ was prepared from the metathetical reaction of KCp^{3i} and PbI_2 in THF; it was separated from the KI byproduct with hexanes extraction. Spectroscopic data (^{1}H and ^{13}C NMR) for the metallocene confirm the proposed formulation.

$(Cp^{3i})_2Pb$ melts near room temperature (34−35 °C) and begins to decompose within minutes in air, although complete decomposition requires several hours (cf. $(Cp^{3i})_2Sn$: mp −18 °C and decomposition within minutes in air).[20] $(Cp^{3i})_2Pb$ is thermochromic; the metallocene gradually changes from bright yellow at −196 °C to dark red at its melting point. Analogous thermochromic behavior has been reported for Cp_2Pb,[4] $(C_5Ph_4H)_2Pb$, $[C_5(Bu^tPh)Ph_4]_2Pb$, and $(C_5Ph_5)_2Pb$.[15,21]

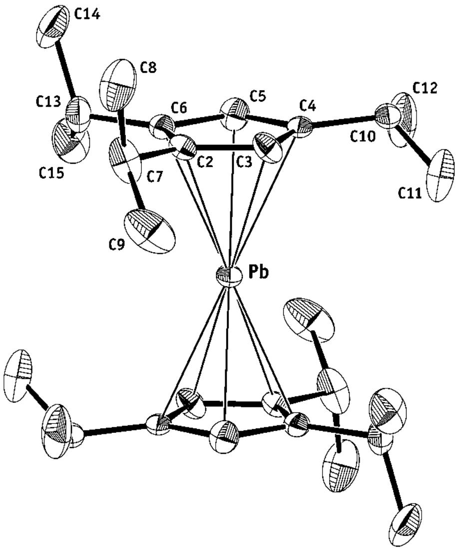

Figure 1. ORTEP plot of the non-hydrogen atoms of $(Cp^{3i})_2Pb$. Thermal ellipsoids are shown at the 30% level.

Structure of $(Cp^{3i})_2Pb$. A low-temperature X-ray structure analysis of $(Cp^{3i})_2Pb$ found that the molecule lies on a crystallographic inversion center with the $[C_5(^iPr)_3H_2]^-$ rings rigorously parallel (Figure 1). The complex is isomorphous with the analogous transition metal metallocenes $(Cp^{3i})_2M$ (M = V−Co;[22−25] Ru[26]). It is only the second crystallographically characterized plumbocene that has parallel cyclopentadienyl rings, but it is the sixth linear group 14 metallocene. The cyclopentadienyl ligands of $(Cp^{3i})_2Pb$ exhibit nearly symmetric pentahapto coordination to the lead atom, as indicated by the narrow range of Pb−C distances (2.738(4)−2.767(4) Å); similarly narrow ranges are found for $(C_5Ph_5)_2Sn$,[9] the linear conformer of $Cp^*{}_2Si$,[11] and $[C_5Me_4(SiMe_2Bu^t)]_2Pb$.[14] The average Pb−C distance in $(Cp^{3i})_2Pb$ (2.748(8) Å) is somewhat shorter than the corresponding distances in other structurally characterized bent plumbocenes (e.g., 2.79(2) Å in $Cp^*{}_2Pb$[1] and $[C_5(CH_2Ph)_5]_2Pb$[27]) but is indistinguishable from that in the linear plumbocene $[C_5Me_4(SiMe_2Bu^t)]_2Pb$ (2.743(11) Å).[14]

The isopropyl groups in $(Cp^{3i})_2Pb$ display orientations of 73.6, 66.9, and 16.6° relative to the ring plane. The methyl groups on the last (C(11), C(12)) are actually bent *toward* the metal, with displacements of 0.72 and 0.38 Å below the ring plane for C(11) and C(12), respectively.

Origin of the Parallel Ring Geometry. Steadily accumulating experimental and theoretical evidence has made it apparent that the link between a metal-centered lone pair of electrons and bent group 14 metallocenes is more subtle than originally supposed.[17] To a substantial degree, especially with the heavier elements, the valence electrons are held in nondirectional, metal-based *n*s orbitals, a fact that precludes stereochemical activity. This conclusion is directly supported by photoelectron spec-

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(20) Burkey, D. J.; Hanusa, T. P. *Organometallics* **1995**, *14*, 11−13.

(21) Schumann, H.; Janiak, C.; Zuckerman, J. J. *Chem. Ber.* **1988**, *121*, 207−218.

(22) Overby, J. S.; Jayaratne, K. C.; Schoell, N. J.; Hanusa, T. P. *Organometallics* **1999**, *18*, 1663−1668.

(23) Overby, J. S.; Schoell, N. J.; Hanusa, T. P. *J. Organomet. Chem.* **1998**, *560*, 15−19.

(24) Hays, M. L.; Burkey, D. J.; Overby, J. S.; Hanusa, T. P.; Yee, G. T.; Sellers, S. P.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 5521−5527.

(25) Burkey, D. J.; Hays, M. L.; Duderstadt, R. E.; Hanusa, T. P. *Organometallics* **1997**, *16*, 1465−1475.

(26) Overby, J. S.; Farrar, J. M.; Hanusa, T. P. *Acta Crystallogr., Sect. C* **1997**, *C53*, 1605−1606.

(27) Schumann, H.; Janiak, C.; Hahn, E.; Kolax, C.; Loebel, J.; Rausch, M. D.; Zuckerman, J. J.; Heeg, M. J. *Chem. Ber.* **1986**, *119*, 2656−2667.

troscopic studies of germanocenes, stannocenes, and plumbocenes,[28−30] which indicate that the metal valence electrons are tightly bound relative to the ring electrons. In addition, ^{119}Sn Mössbauer spectra have confirmed that the valence electrons in stannocenes are largely confined to the 5s orbital.[31]

Indirect support for the lack of direct correlation between the metal valence electrons and structures of group 14 metallocenes is provided by the *bent* geometries of most group 2 metallocenes of calcium, strontium, and barium,[18,32,33] whose metal centers possess no valence electrons. Bosnich[34] and Allinger[35] have suggested that attractive van der Waals forces between the cyclopentadienyl ligands contribute to the bent structures of group 2, group 14, and lanthanide metallocenes. In any case, the accumulated evidence supports the characterization of these molecules as conformationally "floppy" systems, with low barriers to rearrangement and bending.

The structural characterization of $(Cp^{3i})_2Pb$ provides an opportunity to analyze the factors that could contribute to its linear geometry. It is clear that the structures of $(Cp^{3i})_2Pb$ and $[C_5Me_4(SiMe_2Bu^t)]_2Pb$ cannot be attributed to strong inter-ring steric repulsions between the two Cp′ ligands, as was claimed for $(C_5Ph_5)_2Sn$.[9] The closest intramolecular Me···Me′ contacts in $(Cp^{3i})_2Pb$ and $[C_5Me_4(SiMe_2Bu^t)]_2Pb$ are 4.17 and 4.30 Å, respectively, well outside the sum of the van der Waals radii for two methyl groups (4.0 Å)[36] (cf. inter-C_5 ring C(phenyl)···C(phenyl)′ contacts in $(C_5Ph_5)_2Sn$ as close as 3.61 Å). The average displacement of the methine carbon atoms of the isopropyl groups in $(Cp^{3i})_2Pb$ from the C_5 ring plane is only 0.079 Å (0.072 Å for the methyl carbons/silicon atom of $[C_5Me_4(SiMe_2Bu^t)]_2Pb$), further underscoring the lack of significant interaction between the rings. This can be appreciated in space-filling drawings of the two plumbocenes (Figure 2), in which the relatively open coordination spheres of the metal centers are apparent. Further evidence for the lack of a sterically imposed geometry in the case of $(Cp^{3i})_2Pb$ is provided by the bent geometry found for decaisopropylplumbocene, $[(C_5(Pr^i)_5]_2Pb$, with an angle between the ring normals of 170°.[37] Obviously, if a plumbocene can bend with five isopropyl groups on its cyclopentadienyl rings, there is enough room around the metal center for a bent geometry in the less heavily substituted $(Cp^{3i})_2Pb$. In addition, it should be noted that $(Cp^{3i})_2Ca$ is bent (centroid−Ca−centroid = 169.7°), even though the Ca−C distance is substantially shorter (2.62(2) Å) than the analogous distance in $(Cp^{3i})_2Pb$.[32] It appears that, given the combination of metal−ligand distance and the trisubstitution of the cyclopentadienyl rings, intramolecular steric crowding cannot be realistically maintained as the source of the linear geometry of $(Cp^{3i})_2Pb$.

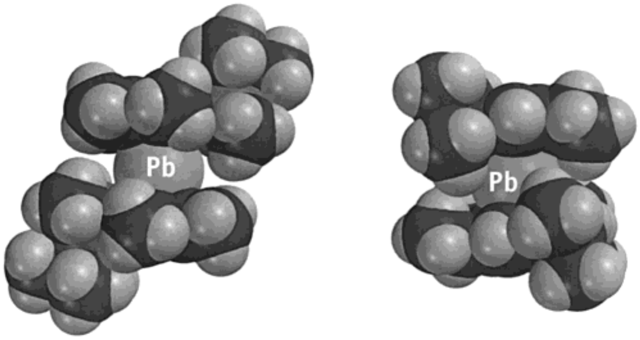

Figure 2. Space-filling drawings of $(Cp^{3i})_2Pb$ (left) and $[C_5Me_4(SiMe_2Bu^t)]_2Pb$ (right).[19] The closest Me···Me′ contacts in each are 4.17 and 4.30 Å, respectively.

There are no especially close intermolecular contacts in either $(Cp^{3i})_2Pb$ or $[C_5Me_4(SiMe_2Bu^t)]_2Pb$; the minimum Me···Me′ distances are 3.74 and 3.75 Å, respectively, which are longer than the 3.3−3.5 Å contacts typically found in bent $(C_5Me_5)_2M$ complexes.[33] Nevertheless, it is possible that crystal packing helps enforce the linear geometries observed in the plumbocenes. With the exception of $(Cp^{3i})_2Ca$,[32] all structurally authenticated metallocenes containing $[Cp^{3i}]^-$ or $[C_5Me_4(SiMe_2Bu^t)]^-$ rings adopt fully staggered configurations, with the metals located on crystallographic inversion centers. A staggered, parallel packing arrangement may be especially favorable for these two cyclopentadienyl ligands.

In summary, we have found a second linear plumbocene whose metal-centered lone pair of electrons is stereochemically inactive. Its geometry is almost certainly not a consequence of intramolecular steric forces. Of the ∼20 group 14 metallocenes that have been crystallographically characterized, roughly a quarter are now known to possess linear geometries; such structures should not continue to be regarded as anomalous.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for $(Cp^{3i})_2Pb$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064−4069.

(29) Bruno, G.; Ciliberto, E.; Fragala, I. L.; Jutzi, P. *J. Organomet. Chem.* **1985**, *289*, 263−270.

(30) Cradock, S.; Duncan, W. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 194−202.

(31) Dory, T. S.; Zuckerman, J. J. *J. Organomet. Chem.* **1984**, *264*, 295−303.

(32) Burkey, D. J.; Hanusa, T. P.; Huffman, J. C. *Adv. Mater. Opt. Electron.* **1994**, *4*, 1−8.

(33) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128−1134.

(34) Bosnich, B. *Chem. Soc. Rev.* **1994**, *23*, 387−395.

(35) Timofeeva, T. V.; Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1995**, *117*, 7452−7459.

(36) Pauling, L. *The Nature of the Chemical Bond*, 3rd. ed.; Cornell University Press: Ithaca, NY, 1960.

(37) Sitzmann, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 553−556.