Synthesis and Characterization of Polyalkylated $Pb(C_5Me_4R)_2$ Plumbocenes, Including the X-ray Crystal Structure of $Pb(C_5Me_4H)_2$

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Received February 1, 1999

Summary: The reaction of 2 equiv of LiC_5Me_4R (R = H, ^iPr, ^nBu) with $PbCl_2$ affords the $Pb(C_5Me_4R)_2$ metallocenes in good yields. $Pb(C_5Me_4{}^iPr)_2$ and $Pb(C_5Me_4{}^nBu)_2$ were isolated as red oils, while $Pb(C_5Me_4H)_2$ was isolated as an orange solid whose X-ray crystal structure reveals a bent-metallocene structure which has a 139.7° (ring centroid)−Pb−(ring centroid) angle.

Introduction

Although cyclopentadienyl complexes of the transition metals are numerous, there are relatively few examples of cyclopentadienyl complexes of divalent lead. To our knowledge, only six have been reported to date: $Pb(C_5H_5)_2$,[1] $Pb(C_5Me_5)_2$,[2] $Pb[C_5(CH_2Ph)_5]_2$,[3] $Pb[C_5Me_4(SiMe_2{}^tBu)]_2$,[4] $Pb(C_5Me_4Et)_2$,[5] and $Pb[C_9H_5(SiMe_3)_2\text{-}1,3]_2$.[6] During the course of our studies on sterically crowded tris(peralkylcyclopentadienyl)lanthanide complexes,[5,7] some new peralkylcyclopentadienyl lead complexes were needed for syntheses of the type shown in eq 1 (R = H, alkyl). Accordingly, we synthesized $Pb(C_5Me_4{}^iPr)_2$, $Pb(C_5Me_4{}^nBu)_2$, and $Pb(C_5Me_4H)_2$, and their synthesis and characterization are reported here.

$$2(C_5R_5)_2Sm + Pb(C_5R_5)_2 \rightarrow 2(C_5R_5)_3Sm + Pb \quad (1)$$

Results and Discussion

$PbCl_2$ reacts with 2 equiv of LiC_5Me_4R (R = H, ^iPr, ^tBu) to form the corresponding metallocenes in 60−70% yield according to eq 2. $Pb(C_5Me_4{}^nBu)_2$ and $Pb(C_5Me_4{}^iPr)_2$ were isolated as red oils and characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The NMR spectra of these complexes are similar to the spectra of previously known $Pb(C_5Me_4R)_2$ (R = Me, Et) complexes (Table 1).

$$2LiC_5Me_4R + PbCl_2 \rightarrow Pb(C_5Me_4R)_2 + 2LiCl \quad (2)$$

Table 1. Room-Temperature ^1H and ^{13}C NMR Spectra of Plumbocenes in C_6D_6

complex	shift, δ	ref
$Pb(C_5Me_4{}^iPr)_2$	^1H: 1.30 (d, 6H), 2.20 (s, 6H), 2.21 (s, 6H), 3.00 (m, 1H)	this work
$Pb(C_5Me_4{}^nBu)_2$	^1H: 0.94 (t, 3H), 1.40 (m, 2H), 2.21 (s, 6H), 2.22 (s, 6H), 2.23 (m, 2H), 2.59 (t, 2H) ^{13}C: 10.3, 14.6, 23.5, 25.4, 38.3, 117.5	this work
$Pb(C_5Me_4H)_2$	^1H: 2.14 (s, 6H), 2.27 (s, 6H), 5.51 (s, 1H). ^{13}C:10.3, 12.0, 106.5, 118.2, 121.1	this work
$Pb(C_5Me_5)_2$	^1H: 2.18 (s, 15H) ^{13}C: 10.1, 117.8	this work, 2
$Pb(C_5Me_4Et)_2$	^1H: 1.05 (t, 3H), 2.17 (s, 6H), 2.19 (s, 6H), 2.56 (q, 2H) ^{13}C: 10.4, 18.9, 20.0, 117.4, 117.7, 126.9	5

The tetramethylcyclopentadienyl derivative $Pb(C_5Me_4H)_2$ was isolated as an orange powder and was characterized not only by analytical and spectroscopic methods but also by X-ray crystallography. Its structure is shown in Figure 1; bond distance and angle data are given in Table 2, and comparison of these parameters with those of other plumbocenes is presented in Table 3.

$Pb(C_5Me_4H)_2$ crystallizes as a bent metallocene with a 139.7° (ring centroid)−Pb−(ring centroid) angle. The bend angle in $Pb(C_5Me_4H)_2$ is not as close to the 151° angle in $Pb(C_5Me_5)_2$[2] as might be expected. The methyl groups are staggered with C(methyl)−C(ring)−C(methyl) torsional angles of 23−30°. The hydrogen-substituted ring carbon of one ring, C(1), is located at the widest part of the wedge formed by the two cyclopentadienyl rings. The other C−H ring carbon, C(10), is at the closed part of the wedge; i.e., they are in opposite locations in the metallocene.

The Pb−C bond lengths in $Pb(C_5Me_4H)_2$ span a large range, 2.66(2)−2.88(2) Å, and the Pb−(ring centroid) distances for the two rings are suprisingly different, 2.54 Å for C(1−5) and 2.42 Å for C(10−14). The Pb−C average distances for each of the two rings, 2.82(7) and 2.71(4) Å, also have different numerical values, although they are indistinguishable within the large error limits. As shown in Table 3, it is typical of plumbocenes to display a large range of Pb−C bond lengths. This is quite reasonable in the several polymeric/oligomeric forms of $Pb(C_5H_5)_2$, since one ring is bridging and has longer bond distances than the terminal cyclopentadienyl ring. The closest intermolecular Pb−C contact in $Pb(C_5Me_4H)_2$ is 3.23 Å and involves, interestingly, the C(1) to C(5) ring, which has the longer intramolecular Pb−C distances. Although the 3.23 Å distance is too long to be associated with a strong interaction and a poly-

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10.1021/om990064m CCC: $18.00
Publication on Web 06/07/1999

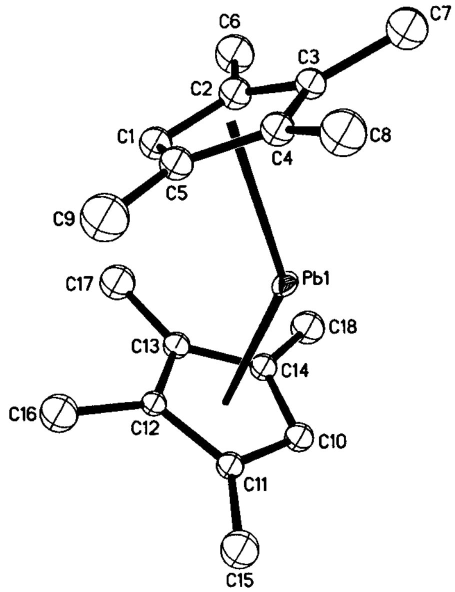

Figure 1. Thermal ellipsoid plot of $Pb(C_5Me_4H)_2$ drawn at the 50% probability level. Calculated hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) for $(C_5Me_4H)_2Pb$

Pb−C(1)	2.69(2)	Pb−C(10)	2.73(2)
Pb−C(2)	2.77(2)	Pb−C(11)	2.77(2)
Pb−C(3)	2.89(2)	Pb−C(12)	2.68(2)
Pb−C(4)	2.88(2)	Pb−C(13)	2.66(2)
Pb−C(5)	2.82(2)	Pb−C(14)	2.70(2)

Table 3. (Ring Centroid)−Pb−(Ring Centroid) Angles and Range of Pb−C Bonds in Structurally Characterized Plumbocenes

formula	Cnt−M−Cnt angle (deg)	Pb−C bond length (Å)	ref
$Pb(C_5Me_4H)_2$	139.7	2.66(2)−2.88(2)	this work
$Pb(C_5Me_5)_2$	151	2.69(1)−2.90(1)	2
$Pb[C_5(CH_2Ph)_5]_2$	153.4	2.680(9)−2.871(9)	3
$Pb[C_5Me_4(SiMe_2{}^tBu)]_2$	180	2.707(5)−2.773(5)	4
$Pb[1,3\text{-}(SiMe_3)_2C_9H_5]_2$	173.3, 172.9	2.653(11)−2.910(12)	6
$Pb(C_5H_5)_2{}^a$		2.64(1)−3.11(7)	1

[a] $Pb(C_5H_5)_2$ crystallizes in several polymeric/oligomeric forms depending on the conditions.

meric structure, the orientation of the open part of the wedge to the next closest C_5Me_4H ring, the smaller than expected (ring centroid)−Pb−(ring centroid) angle, and the disparate Pb−C bond lengths are all in the direction of a polymeric structure.

Experimental Section

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried over sodium/benzophenone ketyl and distilled prior to use. The lithium cyclopentadienides were prepared by reacting the corresponding cyclopentadiene with a 10% molar excess of ^nBuLi in hexane. C_5Me_4H was purchased from Strem Chemicals. $C_5Me_4{}^iPrH$ and $C_5Me_4{}^nBuH$ were prepared from tetramethylcyclopentenone and ^iPrMgCl and ^nBuLi respectively, as described elsewhere.[7]

Synthesis of $Pb(C_5R_5)_2$ (R = H, ^{i}Pr, ^{n}Bu). The following procedure for $Pb(C_5Me_4{}^iPr)_2$ is representative. In a nitrogen-filled glovebox in a flask protected from light by aluminum foil, $LiC_5Me_4{}^iPr$ (0.772 g, 4.54 mmol) and $PbCl_2$ (0.631 g, 2.27 mmol) were added to THF (10 mL) to form a slurry. The THF solution gradually turned yellow, then orange, and finally deep red. This color change was accompanied by the formation of a white precipitate. The mixture was stirred for 24 h. The red solution was filtered to remove LiCl, and the tacky red solid was redissolved in hexane and centrifuged to remove traces of LiCl. This procedure was repeated until no more LiCl was observed to precipitate from the red hexane solution. Final removal of hexane afforded $Pb(C_5Me_4{}^iPr)_2$ as a red oil (0.816 g, 70% yield). Anal. Calcd for $C_{24}H_{38}Pb$: C, 54.01; H, 7.13; Pb, 38.86. Found: C, 53.74; H, 7.01; Pb, 38.95. $Pb(C_5Me_4{}^nBu)_2$ (0.885 g, 70% yield) was prepared similarly from $LiC_5Me_4{}^nBu$ (0.832 g, 4.52 mmol) and $PbCl_2$ (0.625 g, 2.25 mmol). $Pb(C_5Me_4H)_2$ (0.431 g, 62% yield) was prepared similarly from LiC_5Me_4H (0.401 g, 3.13 mmol) and $PbCl_2$ (0.437 g, 1.57 mmol). Anal. Calcd for $C_{18}H_{26}Pb$: C, 48.09; H, 5.83. Found: C, 47.87; H, 5.71.

Crystals of $Pb(C_5Me_4H)_2$ suitable for X-ray crystallographic analysis were prepared by cooling a hexanes solution at −40 °C.

X-ray Data Collection and Solution and Refinement for $Pb(C_5Me_4H)_2$. An orange crystal of approximate dimensions 0.09 × 0.27 × 0.37 mm was mounted on a glass fiber and transferred to the Siemens P4 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard procedures.[8] Intensity data were collected at 158 K using the $2\theta/\omega$ scan technique with Mo Kα radiation. The raw data were processed with a local version of CARESS[9] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 2152 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$. The two possible monoclinic space groups are $P2_1$ or $P2_1/m$. It was later determined that the noncentrosymmetric space group $P2_1$ was correct.

All calculations were carried out using the SHELXL program.[10] Analytical scattering factors for neutral atoms were used throughout the analysis.[11] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. Anisotropic refinement of the carbon atoms resulted in several becoming nonpositive-definite. Final refinement was carried out using isotropic thermal parameters for all carbon atoms. At convergence, wR2 = 0.1244 and GOF = 1.176 for 83 variables refined against all 2022 unique data (As a comparison for refinement on F, R1 = 0.0447 for those 1841 data with $F > 4.0\sigma(F)$.) The highest eight residual peaks range from 2.8 to 4.6 e Å^{-3} and are within 1.0 Å of Pb(1). The absolute structure was assigned by refinement of the Flack parameter.[12]

Acknowledgment. We thank the National Science Foundation for support of this research and the U.S. Department of Education Graduate Assistance for National Needs program for a fellowship (to K.J.F.).

Note Added in Proof: A paper on plumbocene anions has recently appeared: Beswick, M. A.; Gronitzka, H.; Kärcher, J.; Mosquera, M. E. G.; Palmer, J. S.; Raithby, P. R.; Russell, C. A.; Stalke, D.; Steiner, A.; Wright, D. S. *Organometallics* **1999**, *18*, 1148.

Supporting Information Available: Tables of X-ray crystallographic data, bond lengths, and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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