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Synthesis and Structure of the Novel "Paddle-Wheel" Complex $[\{(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp})\text{K}\}\cdot 2\text{THF}]$

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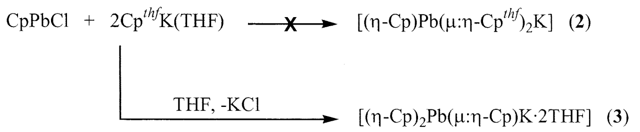
Summary: The reaction between CpPbCl and $\text{Cp}^{thf}\text{K(THF)}$ *(1:2 equiv,* Cp^{thf} *= 2-tetrahydrofurfurylcyclopentadienyl) in THF solvent unexpectedly results in formation of the homoleptic paddle-wheel complex* $[\{(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp})\text{K}\}\cdot 2\text{THF}]$ ***(3)****. The outcome of the reaction is likely to be due to a solvent-promoted ligand redistribution process.*

Previously, work in our group has focused on synthetic, structural, and theoretical studies of a range of group 14 tris-cyclopentadienyl complex anions of the type $[\text{Cp}_{2n+1}\text{E}_n]^-$ ($n = 1$, E = Sn; $n = 1, 2, 4$, E = Pb). It was found that the extent of aggregation in these "paddle-wheel" anions depends largely on the stoichiometry of the reagents employed and *inter*molecular solvation of the s block metal counter cation by added Lewis bases, such as crown ethers and cryptands.[1] The effects of *intra*molecular solvation of the counter cation were recently examined through structural characterization of $[\{(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp}^{thf})\text{Na}\}\cdot 0.5\text{THF}]$ (**1**) (Cp^{thf} = 2-tetrahydrofurfurylcyclopentadienyl), formed from the 1:1 nucleophilic addition reaction between Cp_2Pb and $\text{Cp}^{thf}\text{Na(THF)}$ in toluene solvent.[2] The unusual, undulating, polymeric honeycomb layer structure of **1** results from coordination of the pendant ether functionality to the Na^+ cations.

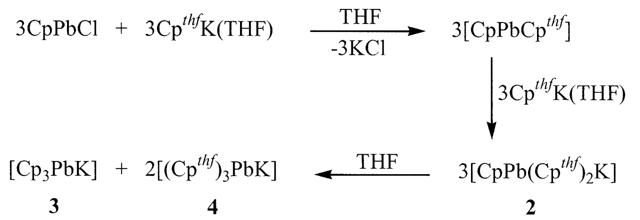
As a part of our continuing investigations into the effects of increasing the number of Cp^{thf} ligands on the crystal and molecular structures adopted by group 14 paddle-wheel anion systems, we have treated CpPbCl with $\text{Cp}^{thf}\text{K(THF)}$ (1:2 equiv) in THF solvent with the aim of preparing the complex $[(\eta^5\text{-Cp})\text{Pb}(\mu{:}\eta^5\text{-Cp}^{thf})_2\text{K}]$ (**2**). However, the unexpected product of the reaction is in fact the homoleptic complex $[\{(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp})\text{K}\}\cdot 2\text{THF}]$ (**3**) (Scheme 1).

Scheme 1



The most plausible explanation for the unexpected outcome of this reaction is presented in Scheme 2. The driving force for the first step is the formation of KCl, then a second equivalent of $\text{Cp}^{thf}\text{K(THF)}$ may add to the transient $[\text{CpPbCp}^{thf}]$ to generate **2** as an intermediate. However, subsequent ligand redistribution results in the formation of the two homoleptic paddle-wheel complexes Cp_3PbK (**3**) and $(\text{Cp}^{thf})_3\text{PbK}$ (**4**). Of the two paddle-wheel complexes formed in this process only **3** crystallizes, presumably due to its lower solubility. Attempts to synthesize **3** from the stoichiometric reaction between Cp_2Pb and CpK produced only an insoluble powder.

Scheme 2. Mechanism of Formation of $[\{(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp})\text{K}\}\cdot 2\text{THF}]$ (3)



The lability of cyclopentadienyl ligands in ionic or polar main group systems is a documented phenomenon, such as the dissociative process detected for $[\text{Cp}_2\text{SnCpNa(PMDETA)}]$ in arene solvents.[3] It has also been shown that addition of an equimolar amount of $[(\text{Me}_3\text{Si})_2\text{CH}]\text{Li}$ to $\text{Cp*}_2\text{Sn}$ in THF solvent results in ligand redistribution.[4] The solution-phase NMR spectrum (various solvents) of the diastereomeric, donor-stabilized aminoferrocenylplumbylene bis[2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]lead reveals a temperature dependence of the diastereomeric ratio, which has also been accounted for on the basis of an intermolecular ligand exchange process.[5] Ligand exchange rates in group 14 Cp complexes generally increase in the order Ge < Sn < Pb in tandem with increasing polarity of the M−C bonding.[6] However, a fact seemingly at odds with the mechanism of formation of **3** is the outcome of the reaction between Cp_2Pb and $\text{Cp}^{thf}\text{Na(THF)}$, resulting in the formation of **1**. The origins of this discrepancy can be traced to the solvents in which the reactions were carried out. The 1:1 reaction between Cp_2Pb and $\text{Cp}^{thf}\text{Na(THF)}$ was performed in toluene solvent, which, due to its weakly interacting nature, does not promote ligand

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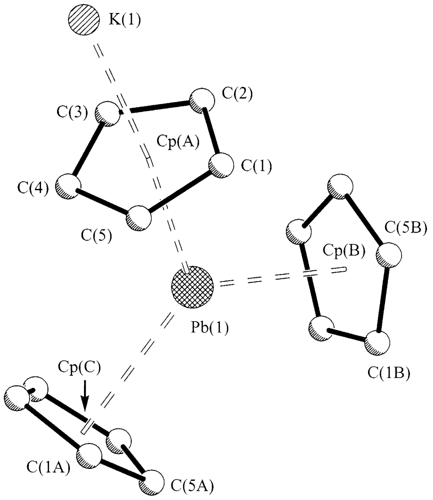

Figure 1. Asymmetric unit of **3**. Hydrogen atoms and uncoordinated (disordered) THF molecules are omitted for clarity. Selected bond distances/Å and angles/deg: range Pb−C 2.833(9)−2.976(9), average 2.91, all Pb(1)−Cp_c 2.64, range K−C 3.139(17)−3.159(17), average 3.15, all K(1)−Cp_c 2.91, all Cp_c−Pb−Cp_c 120.0(9), K(1)−Cp_c−Pb(1) 175.6(9).

redistribution, leading to formation of **1** as the only product.[2] The 1:2 reaction of CpPbCl with Cp^{thf}K(THF) in THF solvent may have initially led to the formation of the desired product, but the strongly interacting nature of the medium would promote ligand dissociation, ultimately resulting in a ligand redistribution into the homoleptic complexes **3** and **4**.

The asymmetric unit of **3** (Figure 1) is composed of perfectly trigonal planar $[(\eta^5\text{-Cp})_3\text{Pb}]^-$ paddle-wheel anions with respect to the mean plane of the Cp centroids [Cp_c−Pb(1)−Cp_c angles all 120.0°]. The Pb(1)−C distances [2.833(9)−2.976(9) Å] in this anion are consistent with η^5-bonding of the ligands. The $(\eta^5\text{-Cp})$K bridging interaction to K(1) is almost linear [K(1)−Cp_c−Pb(1) angle 175.6(9)°] with a narrow range of K(1)−C distances [3.139(17)−3.159(17) Å, average 3.15 Å].

The $[(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp})\text{K}]$ asymmetric units of **3** aggregate to form cyclic, hexagonal trimers, which themselves aggregate to form an infinite, honeycomb layer structure (Figure 2). In contrast to the layer structure of $[\{(\eta^5\text{-Cp})_2\text{Pb}(\mu{:}\eta^5\text{-Cp}^{thf})\text{Na}\}\cdot 0.5\text{THF}]$ (**1**), however, the layers of **3** are planar with respect to the metal centres and the centroids of the Cp ligands. This difference can be traced to the greater radius of the K^+ cation and the absence of intramolecular solvation in **3**. The layers in the crystal of **3** are offset such that the K^+ cations eclipse each other but the Pb(II) centers are only eclipsed in every other layer. The structure of **3** is very similar to that observed for $[\{(\eta^2\text{-Cp})_2\text{Mn}(\mu{:}\eta^2{:}\eta^5)\text{-CpK(THF)}\}\cdot 0.5\text{THF}]$, containing $[(\eta^2\text{-Cp})_3\text{Mn}]^-$ anions.[7] The average Pb−C distance of 2.91 Å in **3** is similar to the average Pb−C bridging distance in the zigzag polymeric structure of $[\text{Cp}_2\text{Pb}]_\infty$,[8] whereas the average K−C distance of 3.15 Å is ca. 0.10 Å longer than in $[\text{CpK}]_\infty$.[9] Another interesting feature of **3** is the large interlayer separation of 8.90 Å, measured as the perpendicular distance between adjacent mean planes generated by the K and Pb centers. The space between the layers is only partially occupied by uncoordinated, extensively disordered THF molecules. The presence of large spatial voids is reflected in an unusually low calculated density of 1.031 g cm^{-3} for a cyclopentadienyllead(II) complex (cf. the calculated density of **1**, 2.206 g cm^{-3}). An alternative description of the honeycomb sheets of **3** is to consider them as comprising $[(\eta^5\text{-Cp})_3\text{K}]^{2-}$ anions bridged by Pb^{2+} cations. Although the existence of $[(\eta\text{-Cp})_3\text{M}]^{2-}$ dianions (M = alkali metal) has been postulated previously by others,[10] the structure of **3** is only the second structurally authenticated tris(η-cyclopentadienyl)alkali metal unit, the first having been observed in the structure of $[\{(\eta^2\text{-Cp})_2\text{Mn}(\mu{:}\eta^2{:}\eta^5)\text{-CpK(THF)}\}\cdot 0.5\text{THF}]$.[7]

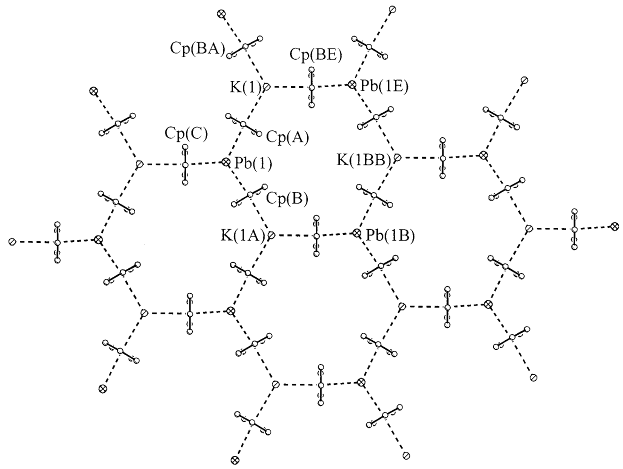

Figure 2. Ball and stick representation of a segment of the infinite honeycomb layer structure of **3** viewed along the crystallographic *b* axis (hydrogen atoms and disordered THF molecules are omitted for clarity). All Cp_c−K−Cp_c 119.9(7)°.

Experimental Section

Materials and Methods. THF was predried over sodium wire and distilled off Na/benzophenone. CpPbCl[11] and Cp^{thf}H[12] were prepared according to literature procedures. NMR spectra were recorded on a Bruker DPX400 NMR spectrometer at 400MHz in D_6-DMSO solvent. IR spectra were recorded on a Perkin-Elmer FT-IR Paragon 1000 spectrometer as Nujol mulls on KBr plates. Elemental analyses were performed on an Exeter Analytical CE-440 elemental analyser, and melting points were recorded on a Perkin-Elmer melting point apparatus. X-ray crystallographic data were collected on a Nonius KappaCCD diffractometer. Structure data were solved by direct methods and refined by full-matrix least squares on F^2.[13]

Synthesis of $\mathbf{Cp^{thf}K(THF)}$. Cp^{thf}H (1.05 g, 7.00 mmol) was added dropwise to a stirred suspension of small potassium chunks (0.27 g, 7.00 mmol) in THF (20 mL) at 0 °C over a period of 1 min. The pale yellow mixture was warmed to room

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temperature, stirred (2 h), and filtered (Celite, porosity 3) and the solvent removed in vacuo to leave Cp^{thf}K(THF) as an off-white powder (0.73 g, 40%). Cp^{thf}K(THF) decomposes to a brown solid on exposure to air. ^{1}H NMR (δ/ppm): 5.29 (4H, s, C_5H_4), 3.69 (1H, m, Cp^{thf} CHO), 3.61 (2H, m, Cp^{thf} CH_2O and THF CH_2OCH_2), 2.65 (2H, m, Cp^{thf}CH_2), 2.32 (1H, m, Cp^{thf} $OCHCHHCH_2$), 1.75 (2H, m, Cp^{thf} $CH_2CH_2CH_2$), 1.60 (THF $CH_2CH_2CH_2$-O), 1.40 (1H, m, Cp^{thf} $OCHCHHCH_2$). IR (ν/cm^{-1}): 3057 (medium, sharp, Cp C−H stretch), 1076 and 1047 (strong, sharp, C−O stretch). Melting point: 207 °C, to a pale yellow oil. Anal. Calcd for $C_{14}H_{21}O_2K$: C, 64.6; H, 8.1. Found: C, 64.3; H, 8.1.

Synthesis of [{(η^5-Cp)$_2$Pb(μ:η^5-Cp)K}·2THF] (3). A solution of Cp^{thf}K(THF) (0.26 g, 1.00 mmol) in THF (15 mL) was added dropwise over a period of 1 min to a suspension of CpPbCl (0.15 g, 0.50 mmol) in THF (5 mL) at 0 °C. The mixture was warmed to room temperature and stirred (2 h), filtered (Celite, porosity 3), and reduced in volume until a precipitate formed; this was redissolved and the yellow solution stored at 5 °C (24 h), affording yellow crystals of [{(η^5-Cp)$_2$Pb(μ:η^5-Cp)K}·2THF] (**3**) (0.09 g, 31%). ^{1}H NMR (δ/ppm): 5.33 (15H, s, Cp), 3.57 (4H, m, THF CH_2OCH_2), 1.7−1.4 (4H, THF CH_2CH_2-CH_2O). IR (ν/cm^{-1}): 3075.5 (weak, sharp, Cp C−H stretch); 1093.6 (strong, sharp, THF C−O stretch). Melting point: ca. 200 °C, decomposes to a black solid. Anal. Calcd for $C_{23}H_{31}O_2KPb$: C, 47.2; H, 5.3. Found: C, 47.6; H, 5.1. Crystal data for **3**: $C_{23}H_{31}KO_2Pb$, fw = 585.77, $T = 180(2)$ K, hexagonal $P6_3$, $a = b = 9.603(2)$ Å, $c = 17.805(10)$ Å, $\alpha = \gamma = 90.0°$, $\beta = 120.0°$, $V = 1421.9$ Å^3, $Z = 2$, $\rho_{calc} = 1.368$ g cm^{-3}, crystal dimensions = 0.14 × 0.07 × 0.05 mm, θ range = 2.45−25.00°, 4431 reflections were collected, of which 1486 were independent (R_{int} = 0.0723), final R indices [$I > 2\sigma(I)$], R1 = 0.0594, wR2 = 0.1637, R indices (all data) R1 = 0.0648, wR2 = 0.1671, largest peak and hole in final difference map 2.070 and −0.948 e Å^{-3}. The lattice-bound THF molecules in **3** are extensively disordered.

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