Synthesis and Structure of Trimethyllead Niobocene Dihydride☆

Georgii I. Nikonov*[a], Evgeni V. Avtomonov[b], and Werner Massa[b]

Chemistry Department, Moscow State University[a],
Vorob'evy Gory, 119899, Moscow, Russia
E-mail: nikonov@org.chem.msu.su

Fachbereich Chemie, Philipps-Universität Marburg[b],
Hans-Meerwein-Strasse, D-35032 Marburg / Lahn, Germany

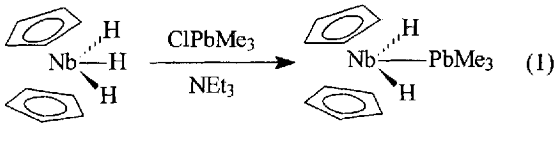
Received May 15, 1997

Keywords: Lead / Niobium / Hydrides / Group 5 / Group 14

The reaction of niobocene trihydride [Cp_2NbH_3] with $ClPbMe_3$ in the presence of amine affords the plumbido dihydride complex [$Cp_2NbH_2(PbMe_3)$] (**1**). Compound **1** represents the first example of a stable complex with neighbouring hydride and terminal plumbyl substituents. The structure of this compound has been established by NMR and IR spectroscopy and confirmed by an X-ray structure analysis.

Group 14-substituted transition metal complexes are the subject of general interest. Most of the work in this area has been focused on silyl- and tin-substituted complexes, whereas the plumbyl derivatives have received very little attention, and their study is mainly confined to carbonyl compounds.[1] Oxidative addition of silanes and stannanes HER_3 to a metal center is a well established procedure to make the hydrido complexes $H-M-ER_3$.[2] In contrast, the plumbanes $HPbR_3$ are not very stable[1a][3] and the analogous oxidative addition of plumbanes is unknown. Only two hydridoplumbyl derivatives, prepared by different methods, have been reported to date.[4][5] One of these compounds, [$Fe(CO)(dppe)H_2(PbMe_3)\{Si(OEt)_3\}$], has a combination of neighbouring hydride and terminal plumbyl substituents, and is very unstable.[5] The usual synthetic route to the lead substituted complexes involves the action of metallates $[L_nM]^-$ on lead halides.[1][5] We have been exploring an alternative approach to the synthesis of the main-group element substituted complexes, based on the reaction of halides $X-ER_n$ with the transition metal hydrides L_nM-H.[6] We report here an application of this methodology to the facile synthesis of the first stable plumbyl-substituted group 5 metallocene, [$Cp_2NbH_2PbMe_3$] (**1**), having a unique combination of a metallocene moiety, a terminal plumbyl group, and hydride ligands.

Bulychev et al. showed that Cl_3SnMe and Cl_2SnMe_2 react with the d^0 complex [Cp_2TaH_3] to give [$Cp_2TaH_2(Cl_nSnMe_{3-n})$] ($n$ = 1, 2), whereas $ClSnMe_3$ does not give this reaction.[7] The highest yields were observed when these reactions were carried out in the presence of an amine to consume the HCl released. Inspired by these findings, we allowed $ClPbMe_3$ to react with [Cp_2NbH_3] in THF in the presence of NEt_3 (Eq. 1).

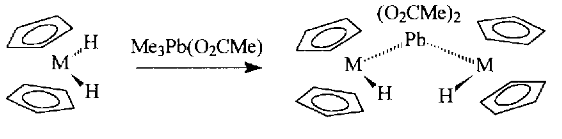


(1)

1

The reaction starts immediately after the reactants are mixed and is accompanied by the formation of a flocculent precipitate of $Et_3HN^+Cl^-$. However, overnight stirring is required to complete the reaction. [$Cp_2NbH_2(PbMe_3)$] (**1**) was obtained after filtration and removal of the solvent as a greenish air and light sensitive crystalline material. Surprisingly, complex **1** is thermally quite stable and decomposes only above 90 °C, although it could be expected that the presence of neighbouring plumbyl and hydride substituents would facilitate the reductive elimination of plumbane ($HPbMe_3$). Moreover, **1** is even more stable than [Cp_2NbH_3], which starts to decompose at about 50 °C. This observation parallels the thermal stability of the analogous tin compounds [$Cp_2MH_2(SnMe_3)$] (M = Nb,[8a] Ta[8b]). In contrast, the bismuthido-substituted niobocene complex [$Cp_2NbH_2(BiPh_2)$] was found to be both light and thermally sensitive.[6f] The remarkable thermal stability of **1** is also in sharp contrast to the extreme instability of [$Fe(CO)(dppe)H_2(PbMe_3)\{Si(OEt)_3\}$], which was prepared by the reaction of the anionic precursor complex [$Fe(CO)(dppe)H_2\{Si(OEt)_3\}]^-$ with $ClPbMe_3$ and studied only by spectroscopic methods. Decomposition occurs when **1** is stored in solutions or as a solid exposed to light, whereas complex **1** does not decompose significantly over several months at −30 °C in the dark. Thus **1** is the first example of a stable transition metal complex with neighbouring hydrido and terminal plumbyl substituents.

The ^1H-NMR spectrum of **1** displays the resonance due to the cyclopentadienyl protons at $\delta = 4.82$, a signal for the methyl groups at $\delta = 1.05$ [^2J(Pb-H) = 13.8 Hz] and the hydride signal at $\delta = -3.55$ [^2J(Pb-H) = 478.8 Hz]. The value of the coupling constant between ^{207}Pb and the methyl group protons in **1** is considerably lower than the value of 60–80 Hz observed for Me_4Pb and Me_3PbX (X = Cl, Br, I),[1b] which probably implies a decrease in the 's' electron character of the Pb–Me bonds and therefore an increase in the 's'-character of the Nb–Pb bond. This deduction is further supported by the X-ray structure data for **1** (vide infra). An analogous trend has been documented for trimethyltin-substituted niobocene and tantalocene hydrides.[8] The IR spectrum of **1** confirms the presence of the Nb–H bond (band at 1742 cm^{-1}). It is apparent that complex **1** is formed by an interaction between the Nb–H bond of $[Cp_2NbH_3]$ and the Pb–Cl bond of $ClPbMe_3$, although the mechanistic aspects of this interaction are not quite clear. It is interesting that the reaction of the anionic hydride complex $[CpVH(CO)_3]^-$with $ClPbPh_3$ gives the product of the formal plumbyl for hydride exchange, i.e. the anionic complex $[CpV(PbPh_3)(CO)_3]^-$, rather than the simple nucleophilic substitution product $[CpV(PbPh_3)H(CO)_3]$.[9] An analogous exchange process is probably operative in the synthesis of the plumbio-bridged complex $[(Cp_2MoH)_2\{\mu\text{-}Pb(O_2CMe)_2\}]$ (**2**), which is obtained by the reaction of $[Cp_2MoH_2]$ with $Me_3Pb(O_2CMe)$ (Eq. 2). It has been proposed that complex **2** was formed through an alkane elimination reaction to initially give the monomeric complex $[Cp_2MoH\{PbMe_2(O_2CMe)\}]$ (**3**).[4] Our results lead us to believe that the initial products of the latter reaction could be $[Cp_2MoH(PbMe_3)]$ and HO_2CMe. Further protonolysis of the Pb–C bond would result in the formation of the proposed complex **3** and eventually in **2**.



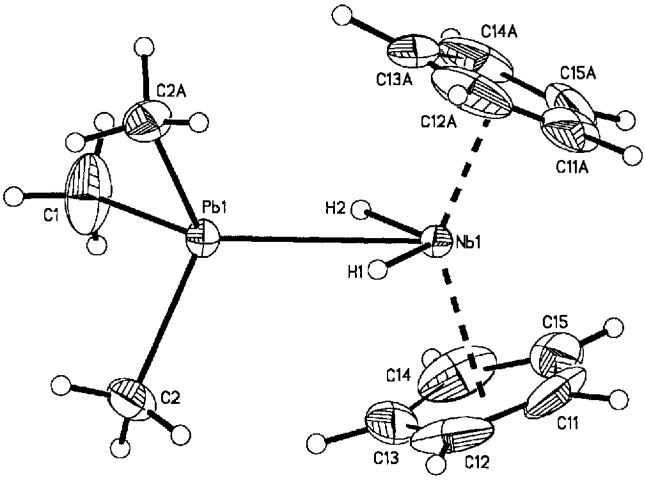
(2)

M = Mo, W

2

Very few complexes with terminal plumbyl groups have been structurally characterised.[1c,10] Since complex **1** contains the previously unknown combination of a terminal plumbyl substituent and hydrido ligands, an X-ray structure determination of **1** was undertaken. The molecular structure and selected bond lengths and angles of **1** are shown in Figure 1. Complex **1** has a typical trisubstituted d^0 niobocene geometry with a central position of the lead substituent. The cyclopentadienyl rings are in the eclipsed conformation due to the crystallographically imposed mirror plane symmetry. The Nb–Pb bond distance is 2.8991(4) Å, which is about 0.19 Å less than the calculated distance (3.09 Å) obtained by adding the niobocene radius of 1.55 Å[11] to the Pb covalent radius of 1.54 Å.[12] This bond shortening can be attributed to the higher Pb 's' orbital character in the Nb–Pb bond, which is a similar case to the high contribution of the Sn and Sb 's' orbitals in the M–E bonds (E = Sn, Sb).[6f,7,13] Both hydrido ligands were located in the bisecting plane of the niobocene moiety and could be refined isotropically to the distances of 1.62(5) Å. This Nb–H bond length is typical for the Nb–H distances found from the X-ray diffraction experiments [for Cp_2NbH_3 the average Nb–H bond length is 1.69 (4) Å].[14] The H1–Nb–H2 angle of 119(4)° is close, within the limits of experimental error, to that in Cp_2NbH_3 [126(3)°]. For the relevant complexes $[Cp_2NbH_2AsEt_2]$ and $[Cp_2NbH_2SbPh_2]$ these angles were 112.1°[6d] and 122.6°,[6f] respectively.

Figure 1. ORTEP plot of a molecule of **1** with atomic-numbering scheme. The thermal displacement ellipsoids are scaled to the 50% probability level[a]



[a] Selected bond lengths [Å] and angles [°]: Nb1–Pb1 2.8991(4), Nb1–H1 (Nb1–H2) 1.62(5), Nb1–Cent1 2.066(2), Cent1–Nb1–Cent1a 140.7(3), H1–Nb1–H2 119.1(41).

G. I. N. thanks *The Russian Fund for Basic Research* for support of this work. Support provided by the government of Hessen (Germany) within the framework of *HSP-II/III-Programme* for E. V. A. is also gratefully acknowledged.

Experimental Section

All manipulations were carried out using conventional Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl. – NMR: Bruker AC-300 spectrometer (300 MHz and 75.4 MHz, for ^1H and ^{13}C, respectively). For ^1H NMR, $[D_6]$benzene as solvent, TMS as internal standard. For ^{13}C NMR, $[D_6]$benzene as solvent. – FT-IR: Nicolet 501. – Elemental analysis was performed by the analytical division of the Fachbereich Chemie der Philipps-Universität Marburg. Cp_2NbH_3 was prepared by a modified procedure as reported earlier.[6a]

1. Preparation of $Cp_2NbH_2(PbMe_3)$ (**1**): 0.570 g (2.52 mmol) of $[Cp_2NbH_3]$ and 0.725 g (2.52 mmol) of Me_3PbCl were mixed in 100 ml of THF. 3 ml of NEt_3 was added to this mixture. The mixture was stirred overnight in the dark. The solution was filtered and all volatile components were removed under vacuum to give a light-green powder. Recrystallisation from diethyl ether yielded 0.952 g (1.99 mmol, 79%) of pure **1**.

IR (Nujol): $\tilde{\nu}$ = 1742 cm^{-1} (Nb–H). – ^1H NMR ($[D_6]$benzene): δ = 4.82 (s, 10 H, Cp), 1.05 [s + d, ^2J(Pb–H) = 13.8 Hz, 6 H, CH_3], –3.55 [s + d, ^2J(Pb–H) = 478.8 Hz, 2 H, Nb–H]. – ^{13}C NMR ($[D_6]$benzene): δ = 87.11 (s, Cp), –1.51 [s + d, ^1J(Pb–C) = 167.2 Hz, CH_3]. – $C_{13}H_{21}NbPb$ (477.4): calcd. C 32.71, H 4.43; found C 32.46, H 4.54.

2. X-ray Crystallographic Study of **1**: The crystals were grown by cooling an ethereal solution of **1** at –30°C. A greenish-yellow coloured specimen of **1** with dimensions of 0.19 × 0.14 × 0.13 mm was mounted onto a glass capillary and investigated using a Stoe IPDS area detector system (Mo-K_α, graphite monochromator) at −83°C. Crystal data: M = 477.4; orthorhombic, space group *Pnma*, a = 11.5537(7), b = 13.2956(7), c = 9.1757(5) Å, Z = 4, V = 1409.51(14) Å^3, $d_{\text{calcd.}}$ = 2.25 g cm^{-3}. Data collection: Φ-scan,Φ range from 0 to 240°, ΔΦ = 1.1°, exposure time = 2 min; Θ range from 2.70 to 27.93°, *hkl* range −15 to 15, −17 to 17, −12 to 12, 9419 measured reflections, 1757 unique [R(int) = 0.0347], analytical absorption correction based on face-indexing (μ = 12.712 mm^{-1}, $T_{\text{max.}}$ = 0.567, $T_{\text{min.}}$ = 0.299) with the SHELXTL-Plus programme package[15] and Stoe IPDS software. Lorentz factors and polarisation effects were taken into account. Structure solution was carried out by heavy-atom methods with the SHELXS-96 programme,[16] and refinement was performed by full-matrix least squares on F^2 on the basis of all reflections with SHELXL-96.[17] All non-hydrogen atoms were refined anisotropically; the positions of the hydrogen atoms were located from the difference Fourier-maps and were refined with common isotropic displacement factors except for the hydrogen atoms of the methyl groups and H(111) at the C(11) atom. The latter were included as idealised contributions and refined using a riding model. The positional parameters as well as the isotropic displacement factors of the hydrogen atoms at the niobium center were refined in a restrained model with d(Nb−H1) = d(Nb−H2).

The position of the lead atom was found to be split between two sites with occupations of 0.979 and 0.021 of the major and minor component, respectively. This disorder can be assigned either to the incorporation of another isomer that possesses the trimethyllead group in the lateral position of the niobocene bisecting plane and two hydride ligands in the central and in the lateral position, or to a positional disorientation of the molecules of **1**. However, there is no categorical evidence to support one explanation over the other, although one could assume that the first possibility is less realistic since the formation of lateral isomers of main-group element substituted group-5 complexes has only been observed in the case of silyl-substituted tantalocene hydrides where the reactions were carried out under forcing conditions.[2a] Furthermore, for heavier main-group derivatives, e.g. [$Cp_2NbH_2SnMe_3$], no evidence for a second isomer was found.[8a] In contrast, positional disorientation is a common phenomenon which is associated with the crystallisation conditions. Taking into account that the crystallisation of **1** proceeded at low temperature and the crystal growth was complete within a few hours, the probability of such defect formation is rather high. The positions of the carbon atoms of the minor site could not be located due to the very low contribution of this component. $R1$ = 0.0200 (only observed reflections), $wR2$ = 0.0441 (all data), 99 parameters, GOOF = 1.001. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406975, the names of the authors and the journal citation.

☆ Dedicated to Professor *Jörg Lorberth* on the occasion of his 60th birthday.

[1] [1a] P. G. Harrison in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), vol. 2, Pergamon, Oxford, **1995**, chapter 7. – [1b] P. G. Harrison in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel) vol. 2, Pergamon, Oxford, **1982**, chapter 12. – [1c] S. Seebald, G. Kickelblick, F. Möller, U. Schubert, *Chem. Ber.* **1996**, *129*, 1131.

[2] [2a] Q. Jiang, P. J. Carrol, D. H. Berry, *Organometallics* **1991**, *10*, 3648. – [2b] G. I. Nikonov, L. G. Kuzmina, D. A. Lemenovskii, V. V. Kotov, *J. Am. Chem. Soc.* **1995**, *117*, 10133. – [2c] E. A. V. Ebsworth, D. M. Leitch, *J. Chem. Soc., Dalton Trans.* **1973**, 1287. – [2d] M. S. Holt, W. L. Wilson, J. H. Nelson, *Chem. Rev.* **1989**, *89*, 11.

[3] R. Duffy, J. Feeney, A. K. Holliday, *J. Chem. Soc.* **1962**, 1144.

[4] M. M. Kubicki, R. Kergoat, J. -E. Guerchais, P. L'Harridon, *J. Chem. Soc., Dalton Trans.* **1984**, 1791.

[5] U. Schubert, S. Gilbert, M. Knorr, *J. Organomet. Chem.* **1994**, *454*, 79.

[6] [6a] G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, *Organometallics* **1994**, *13*, 3127. – [6b] G. I. Nikonov, L. G. Kuzmina, P. Mountford, D. A. Lemenovskii, *Organometallics.* **1995**, *14*, 3588. – [6c] G. I. Nikonov, L. G. Kuzmina, Yu. K. Grishin, D. A. Lemenovskii, N. B. Kazennova, *J. Organomet. Chem.*, in press. – [6d] G. I. Nikonov, K. Harms, J. Lorberth, D. A. Lemenovskii, *Inorg. Chem.* **1995**, *34*, 2461. – [6e] G. I. Nikonov, A. J. Blake, J. Lorberth, D. A. Lemenovskii, S. Wocadlo, *J. Organomet. Chem.*, in press. – [6f] G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, *Polyhedron* **1996**, *15*, 1565. – [6g] G. I. Nikonov, L. G. Kuzmina, J. A. K. Howard, *Organometallics 1997*, *16*, 3723.

[7] T. M. Arkhireeva, B. M. Bulychev, A. N. Protsky, G. L. Soloveichik, V. K. Bel'sky, *J. Organomet. Chem.* **1986**, *317*, 33.

[8] [8a] M. L. H. Green, A. K. Hughes, P. Mountford, *J. Chem. Soc., Dalton Trans.* **1991**, 1407. – [8b] D. H. Harris, S. A. Keppie, M. F. Lappert, *ibid.* **1973**, 1653.

[9] R. Talay, D. Render, *J. Organomet. Chem.* **1984**, *262*, 25.

[10] [10a] B. Crociani, M. Nicolini, D. A. Clemente, G. Bandoli, *J. Organomet. Chem.* **1973**, *49*, 249. – [10b] F. Calderazzo, G. Pampaloni, G. Pelizzi, F. Vitali, *Polyhedron* **1988**, *7*, 2039. – [10c] V. G. Albano, C. Castellari, M. Monari, V. De Felice, M. L. Ferrara, F. Ruffo, *Organometallics* **1995**, *14*, 4213.

[11] J. Arnold, T. D. Tilley, A. L. Reingold, S. J. Geib, *Organometallics* **1987**, *6*, 473.

[12] J. Emsley, *The Elements*; Clarendon Press, Oxford, **1991**.

[13] [13a] A. N. Protskii, B. M. Bulychev, G. L. Soloveichik, V. K. Bel'sky, *Inorg. Chim. Acta* **1986**, *115*, 121. – [13b] A. N. Protskii, B. M. Bulychev, G. L. Soloveichik, *ibid.* **1983**, *71*, 35.

[14] R. D. Wilson, T. F. Koetzle, D. W. Hart, A. Kvick, D. L. Tipton, R. Bau, *J. Am. Chem. Soc.* **1977**, *99*, 1775.

[15] G. M. Sheldrick, *SHELXTL-Plus.* Release 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, U.S.A. **1996**.

[16] G. M. Sheldrick, *SHELXS-96. Programme for Crystal Structure Solution*, University of Göttingen, Germany **1996**.

[17] G. M. Sheldrick, *SHELXL-96. Programme for Crystal Structure Refinement*, University of Göttingen, Germany **1996**.

[97118]