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A new synthetic entry to phosphinophosphinidene complexes. Synthesis and structural characterisation of the first side-on bonded and the first terminally bonded phosphinophosphinidene zirconium complexes [μ-(1,2:2-η-^{t}Bu$_2$P=P){Zr(Cl)Cp$_2$}$_2$] and [{Zr(PPhMe$_2$)Cp$_2$}(η^1-P–P^{t}Bu$_2$)]†

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Received (in Cambridge, UK) 25th June 2004, Accepted 12th August 2004

First published as an Advance Article on the web 16th September 2004

The reactions of lithiated diphosphanes with transition metal chlorides constitute a new general entry to phosphinophosphinidene complexes: the reaction of Cp$_2$ZrCl$_2$ (Cp = C$_5$H$_5$) with ^{t}Bu$_2$P–P(SiMe$_3$)Li (molar ratio ~1 : 1) yields [μ-(1,2:2-η-^{t}Bu$_2$P=P){Zr(Cl)Cp$_2$}$_2$]; the reaction of Cp$_2$ZrCl$_2$ with ^{t}Bu$_2$P–P(SiMe$_3$)Li (molar ratio ~1 : 2) and an excess of PPhMe$_2$ in DME yields the first terminally bonded phosphinophosphinidene complex, [{Zr(PPhMe$_2$)Cp$_2$}(η^1-P–P^{t}Bu$_2$)].

The chemistry of the phosphinophosphinidene ligand ^{t}Bu$_2$P–P was established by the group of Prof. Gerhard Fritz, mainly starting from phosphinophosphinidene-σ^4-phosphoranes ^{t}Bu$_2$P–P=P(X)^{t}Bu$_2$ (X = Me, Br) as a source of the ^{t}Bu$_2$P–P moiety.[1,2] The η^2-coordination was found to be essential to stabilise the ^{t}Bu$_2$P–P ligand, and up to 2004 only d^{10} ML$_2$ Pt(0) metal centres were found to be able to stabilise this ligand as a two electron donor without additional η^1-coordination of a second metal centre at the phosphinidene P atom.[3] Very recently Cummins has shown another synthetic access to phosphinophosphinidene complexes with the synthesis of the first such complex of Nb(III).[4] Our current investigations on the reactivity of lithium and trimethylsilyl derivatives of di- and triphosphanes towards transition metal halides presented us with the up to now most general and simplest entry into this unique class of compounds. Using lithiated diphosphanes R$_2$P–P(SiMe$_3$)Li rather than R$_2$P–P=PR′$_3$ as precursors of the R$_2$P–P group offers substantial advantages:

i. The synthesis of R$_2$P–P(SiMe$_3$)Li is simpler[5] than the relatively tedious one of R$_2$P–P=PR′$_3$.[6]

ii. The range of well-characterized and easily accessible phosphinophosphinidene-σ^4-phosphoranes R$_2$P–P=PR′$_3$ is limited and some compounds of this type (R = Et$_2$N, SiMe$_3$) are not obtainable in the known way.[7]

iii. The reaction of R$_2$P–P(SiMe$_3$)Li with [L$_2$PtCl$_2$] (L = tertiary phosphine) yields complexes [L$_2$Pt{η^2-(R$_2$P=P)}] with new side-on bonded phosphinophosphinidene ligands R$_2$P=P (R = Ph, Et$_2$N, ^{i}Pr$_2$N, ^{i}Pr), which were not available in the known way, together with the previously known [L$_2$Pt{η^2-(^{t}Bu$_2$P=P)}].[8]

Now we extend our investigations to the reactivity of lithiated di- and triphosphanes towards titanocene and zirconocene dichlorides. Whereas the Ti(III) centre shows only a very low tendency to coordinate the ^{t}Bu$_2$P–P ligand,[9] the chemistry of this ligand bonded to Zr(III) and Zr(II) centres is very rich. Herein we report some of our latest results on the reaction of [Cp$_2$ZrCl$_2$] (Cp = C$_5$H$_5$) with ^{t}Bu$_2$P–P(SiMe$_3$)Li.

The reaction of the lithiated diphosphane ^{t}Bu$_2$P–P(SiMe$_3$)Li with [Cp$_2$ZrCl$_2$] in a molar ratio of about 1 : 1 in THF or DME yields [μ-(1,2:2-η-^{t}Bu$_2$P=P){Zr(Cl)Cp$_2$}$_2$] (**1**) in 32% yield (eqn. 1) together with ^{t}Bu$_2$P–P(SiMe$_3$)$_2$ and other compounds which we were not able to isolate, but which could be characterised by ^{31}P NMR spectroscopy. **1** is only for a limited time stable in THF solution. ^{31}P{^{1}H} NMR data of **1**: P2 −1.2 ppm (d), P1 93.9 ppm (d), ^1J(P–P) −520.6 Hz.

$$\begin{aligned}2\,[\mathrm{Cp_2ZrCl_2}] + 2\ {}^t\mathrm{Bu_2P{-}P(SiMe_3)Li} &\rightarrow {}^t\mathrm{Bu_2P{-}P(SiMe_3)_2}\\ &+ 2\,\mathrm{LiCl} + [\mu\text{-}(1,2{:}2\text{-}\eta\text{-}{}^t\mathrm{Bu_2P{=}P})\{\mathrm{Zr(Cl)Cp_2}\}_2]\ (\mathbf{1})\end{aligned} \tag{1}$$

The structure of **1** (Fig. 1)‡ reveals a pseudo five-fold coordination sphere of the ligands around Zr1. Zr2 adopts a pseudo tetrahedral coordination sphere with two η^5-Cp rings, a Cl and the P1 atom. The ^{t}Bu$_2$P–P ligand exhibits a side-on coordination to Zr1 with a short P–P distance of 211.28(6) pm, just in the range of side-on bonded phosphinophosphinidene complexes.[2,4] This is shorter than the P–P bond in [(η^2-MesP=PMes)ZrCp°$_2$], Cp° = C$_5$H$_4$Et (218.8 pm) with an η^2-bonded diphosphene ligand[10] but is almost the same as in the similar complex [μ-(1,2:2-η-^{t}Bu$_2$P=P){Mo(CO)$_2$Cp^t}$_2$] (Cp^t = C$_5$H$_4$^{t}Bu) – 211.4 pm.[11]

The Zr1–P2 bond length of 283.9(4) pm is very large whereas the Zr1–P1 distance of 267.9 pm is similar to the Zr–P distance (265.0 pm) in [(η^2-MesP=PMes)ZrCp°$_2$].[10] The bond length P1–Zr2 of 255.97(5) pm is in the same range as in [Cp$_2$(Cl)ZrP(SiMe$_3$)$_2$] (254.7 pm),[12] thus it provides the evidence of a moderate degree of Zr2–P1 π bonding in **1**. The geometry around P1 is not planar. The

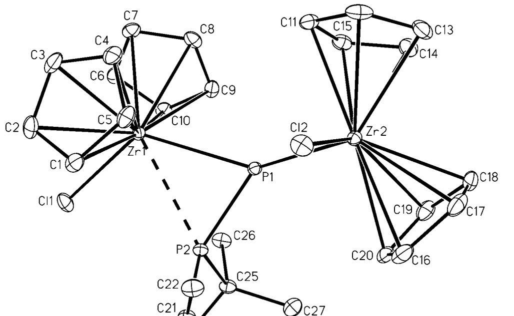

Fig. 1 Solid-state structure of **1** showing the atom labelling scheme, hydrogen atoms are omitted for simplicity. Selected bond distances (pm) and angles (°): Zr1–P1 267.98(5), Zr1–P2 283.9(4), Zr2–P1 255.97(5), P1–P2 211.28(6), P2–C21 191.0(2), P2–C25 191.04(18), P2–P1–Zr2 135.71(2), P2–P1–Zr1 71.549(18), Zr2–P1–Zr1 142.487(18), C21–P2–C25 109.06(8), Cl1–Zr1–P1 124.696(16), Cl2–Zr2–P1 99.338(16). Thermal ellipsoids at 35% probability.

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† Electronic supplementary information (ESI) available: experimental, NMR, crystallographic. See http://www.rsc.org/suppdata/cc/b4/b409673h/

DOI: 10.1039/b409673h

P2–P1–Zr2 angle of 135.71(2)° and the torsion angle Zr2–P1–P2–Zr1 of 148.8(2)° both suggest that $^tBu_2P$–P adopts the distorted geometry of 1,1-di-*tert*-butyldiphosphene, with a visible steric effect of an inert electron pair on P1 in this complex (Fig. 2, **1** and Fig. 3, **A**). The fragment $(^tBu)_2P{=}P{-}ZrCp_2Cl$ in **1** can be seen as related to the phosphanyl phosphenium ion[13] with a double P–P bond and an inert electron pair. The large value of ^1J(P–P) = −520.6 Hz additionally indicates the multiple bond character of P1–P2 in **1**.

Surprisingly, the unusual zirconium complex **1** is more stable than the hypothetical symmetric one $[(\mu_2\text{-}^tBu_2P{-}P)\{Cp_2ZrCl\}_2]$ (Fig. 2, **1a**) which is similar to the known $[(\mu^2\text{-}PMes)\{Cp_2ZrCl\}_2]$ (Fig. 2, **3**) (Mes = 2,4,6-$Me_3C_6H_2$).[14]

The special geometry of **1** (Fig. 2) only can be realised due to the conjugation between P2 with a free electron pair and the phosphinidene atom P1 (Fig. 3, **A**). This is not possible for **3**. The geometry of **1** cannot be explained in terms of an additional coordination of P2 to Zr1 in **1a** because this would not lead to the observed significant shortening of the P1–P2 bond, which is in the range of a side-on bonded short double bond.

The possible terminal coordination of H_2P–P to various metal centers was discussed,[15] however no compound with R_2P–P bonded only *via* the phosphinidene P atom to a metal center became known. Terminally bonded nucleophilic phosphinidene R–P complexes are rare and their stability is achieved by steric protection due to a bulky group R (R is not able to conjugate with the electron deficient P atom).[16] Recently, complexes of the electrophilic aminophosphinidene $^iPr_2N$–P were synthesized and in some cases the X-ray structures determined.[17,18]

Now we report our successful synthesis of the first metal complex containing a terminally bonded R_2P–P ligand. The reaction of $^tBu_2P{-}P(SiMe_3)Li{\cdot}2THF$ with a solution of Cp_2ZrCl_2 and $PPhMe_2$ (molar ratio 1 : 2 : 10) in DME and crystallization from pentane yields $[\{Zr(PPhMe_2)Cp_2\}(\eta\text{-}P{-}P^tBu_2)]$ (**2**), the zirconium complex with a terminally bonded $^tBu_2P$–P ligand in 44% yield together with $^tBu_2P{-}P(SiMe_3)_2$ and other products which were identified by ^{31}P NMR spectroscopy.

$$[Cp_2ZrCl_2] + 2\ ^tBu_2P{-}P(SiMe_3)Li + PPhMe_2 \rightarrow\ ^tBu_2P{-}P(SiMe_3)_2 + [\{Zr(PPhMe_2)Cp_2\}(\eta^1\text{-}P{-}P^tBu_2)]\ (\mathbf{2}) + 2\ LiCl \qquad (2)$$

Although solutions of **2** in DME are indefinitely stable in the presence of an excess of $PPhMe_2$ at ambient temperature, an attempt to dissolve **2** in THF-d_8 resulted in a partial decomposition of this compound. The $^{31}P\{^1H\}$ NMR spectrum clearly reflects the geometry of **2** in solution. The low field resonance of P1 is typical for terminal "bent" phosphinidene complexes.[19,20] The small coupling ^1J(P1–P2) of −283.7 Hz in **2** indicates a single bond character of the P–P bond within the $^tBu_2P$–P ligand.

The X-ray structure determination§ of **2** (one of the two independent molecules in the asymmetric unit is shown in Fig. 4) fully confirms the NMR results. The distance of 248.8(3) pm suggests a double bond character for Zr1–P1 and lies in the typical region of Zr–P distances of terminal phosphinidene zirconium complexes.[18,19] The relatively long P1–P2 distance of 220.0(4) pm and the Zr1–P1–P2 angle of 115.52(16)° confirm the NMR observations.

Apparently, in $[\{Zr(PPhMe_2)Cp_2\}(\eta^1\text{-}P{-}P^tBu_2)]$ the P^tBu_2 group does not conjugate with the electron deficient phosphinidene atom P1. This is in strong contrast to the side-on bonded phosphinophosphinidene ligand, *e.g.* in $[(R_3P)_2Pt\{\eta^2\text{-}(R_2P{=}P)\}]^2$ or in **1**, where the $^tBu_2P{=}P$ ligand adopts a 1,1-di-*tert*-butyldiphosphene geometry. Thus our ligand in **2** may be regarded as similar to structure **B** (Fig. 3). DFT calculations to elucidate the bondings in these systems and the stabilisation effect of the relatively small $^tBu_2P$ group are currently in progress.

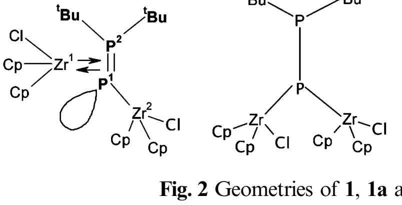

Fig. 2 Geometries of **1**, **1a** and **3**.

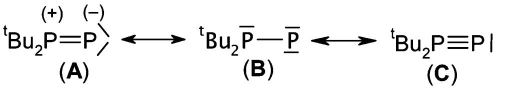

Fig. 3 Possible Lewis structures of the $^tBu_2P$–P group.

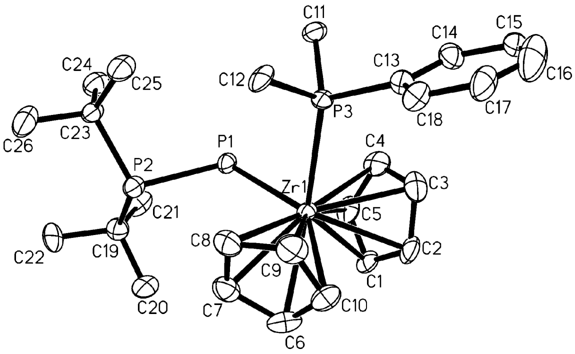

Fig. 4 Solid-state structure of **2**, showing the atom labelling scheme. Only one of two independent molecules in the asymmetric unit is shown. Hydrogen atoms are omitted for simplicity. Selected bond lengths (pm) and angles (°): Zr1–P1 248.8(3), Zr1–P3 273.4(3), P1–P2 220.0(4), P2–C19 194.9(13), P2–C23 190.9(12), P2–P1–Zr1 115.53(16), C19–P2–C23 108.3(5), P1–Zr1–P3 88.49(10), P1–P2–C23 104.1(4), P1–P2–C19 100.5(4). Thermal ellipsoids drawn at 25% probability. The data on the second molecule are given in the supplementary material.

J.P. and A.R. thank the Polish State Committee of Scientific Research (project No. 4 T09A 028 22 – phosphinophosphinidene R_2P–P, a novel π electron ligand) for financial support. We thank Prof. Dr H. Schnöckel (Institut für Anorganische Chemie der Universität Karlsruhe) for generous support and for providing the Stoe IPDS diffractometer time.

Notes and references

‡ CCDC 225538. See http://www.rsc.org/suppdata/cc/b4/b409673h/ for crystallographic data in .cif or other electronic format.

§ CCDC 232586. See http://www.rsc.org/suppdata/cc/b4/b409673h/ for crystallographic data in .cif or other electronic format.

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