Formation of Novel Phosphide Dichloride Zr Complex from Trichloride Zr Complex with a Secondary Phosphine-pendant Cyclopentadienyl Ligand: Structure of [{η^5-$C_5H_4(CH_2)_2$PMes-κP}$ZrCl_2$(N-methylimidazole)$_2$] (Mes = 2,4,6-Trimethylphenyl)

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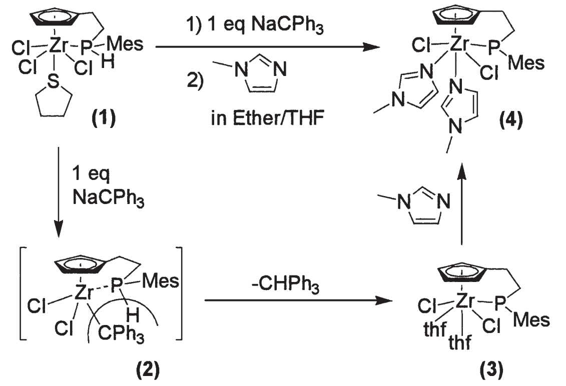
The reaction of [{η^5-$C_5H_4(CH_2)_2P(H)$Mes-κP}$ZrCl_3$(tht)] (**1**; Mes = 2,4,6-trimethylphenyl; tht = tetrahydrothiophene) with 1 equiv of $NaCPh_3$, followed by treatment with N-methylimidazole gave a novel phosphide-pendant dichloride complex [{η^5-$C_5H_4(CH_2)_2$PMes-κP}$ZrCl_2$(N-methylimidazole)$_2$] (**4**) with liberation of $HCPh_3$. The product (**4**) is the first dichloride terminal phosphide Zr complex characterized by X-ray crystallographic analysis.

Intensive studies have been continued on dihalide and dialkyl complexes of early transition metals which serve as Kaminsky-type precatalysts in olefin polymerization.[1a–c] Since it was reported that titanium complexes with an amide-pendant cyclopentadienyl ligand, [(η^5-$C_5Me_4SiMe_2N^tBu$-κN)TiL_2] (L = Cl, alkyl group) called constrained-geometry catalysts (CGC), are effective in olefin copolymerization,[1a] analogous phosphide-pendant cyclopentadienyl complexes have currently attracted much attention with respect to comparison with the above amide complexes.[2a–d] However, it is often difficult to prepare early transition-metal phosphide complexes antagonistic to the HSAB principle.[3a–c] For example, the conventional salt-elimination reaction of $ZrCl_4$ with the lithium phosphide ligand $Li_2C_5Me_4SiMe_2PR$ (R = Cy, 2,4,6-trimethylphenyl (Mes)) did not give any products of the [(η^5-$C_5Me_4SiMe_2PR$-κP)$ZrCl_2$] type.[2b,4] For group 4 transition-metal complexes of this type, only the diamide complexes [(η^5-$C_5Me_4ER_2PCy$-κP)M(NR'$_2$)$_2$] (M = Ti, ER_2 = CMe_2, $SiMe_2$, R' = Me; M = Zr, ER_2 = CH_2, CMe_2, $SiMe_2$, R' = Et) have been recently prepared via the salt-elimination reaction by Erker et al.[2a–c]

We recently prepared the Zr and Hf complexes with an ethylene-linked secondary phosphine-cyclopentadienyl ligand [{η^5-$C_5H_4(CH_2)_2P(H)$Mes-κP}MCl_3(tht)] (M = Zr (**1**), Hf; tht = tetrahydrothiophene),[5] which are expected to be useful starting complexes to terminal phosphide complexes[6a–b] and phosphide-bridged multinuclear complexes as well.[6c] In this paper, we report the synthesis of the dichloride Zr complex with a phosphide-pendant cyclopentadienyl ligand through tritylation of **1** followed by liberation of a trityl-H coupling product, and describe the molecular structure of its N-methylimidazole derivative (**4**).

The reaction of **1** with 1 equiv of $NaCPh_3$ in ether/THF was examined (Scheme 1). The ^{31}P NMR spectrum without proton irradiation showed a singlet at 236.2 ppm only, at the expense of a broad doublet at -86.7 ppm ($J_{PH} = 213$ Hz) attributed to the THF-solvated starting complex (**1**) with the secondary phosphine moiety freed from the Zr center.[5] The spectral change indicates that the product has a Zr–P covalent bond but not a P–H bond, suggesting quantitative formation of a phosphide complex. Taking account of the negative results obtained previously in the salt-elimination reaction with an alkali-metal phosphide[2b,4] and our recent findings in the reaction of **1** with $LiCH_2SiMe_3$,[7] we propose that the present reaction proceeds as shown in Scheme 1; the reaction firstly affords not a sodium phosphide but a secondary phosphine monotrityl complex (**2**) as an undetectable intermediate, which liberates immediately the trityl-H coupling product ($CHPh_3$) to give a phosphide dichloride complex (**3**), which is probably solvated with THF's. The concomitantly formed $CHPh_3$ was detected by the ^1H NMR spectrum. Though the phosphide complex (**3**) could not be isolated because of its high solubility similar to that of $CHPh_3$, it is expected to serve as a good precursor of a series of phosphide-pendant complexes. In order to convert it into an isolable derivative, N-methylimidazole was added to a solution containing **3** to result in narrow isolation of a highly air- and moisture-sensitive bis(N-methylimidazole)complex (**4**, 40%).[8] The product was identified by the ^1H, ^{13}C, and ^{31}P NMR spectra and the single-crystal X-ray diffraction analysis.[9]



Scheme 1.

The red single crystals of **4** were obtained from its THF/hexane solution. An asymmetric unit consists of two independent molecules. A THF molecule involved is disordered. One of the enantiomers is shown in Figure 1. The Zr atom possesses a distorted octahedral coordination. The two chloride groups coordinate to the Zr center in trans positions. The Zr–P bond distance (2.600 Å) and the low-field ^{31}P NMR resonance (162.8 ppm, s) point to an appreciable double bond character in the Zr–P bond.[3a] The sum of bond angles around the phosphorus atom (341.7°) indicates the phosphorus atom bearing some sp^2 character.[3a] The phosphide-pendant complex (**4**) is one of a few examples of group 4 transition-metal complexes with a heterochelate ligand containing a phosphide group.[2a–c,10a–b]

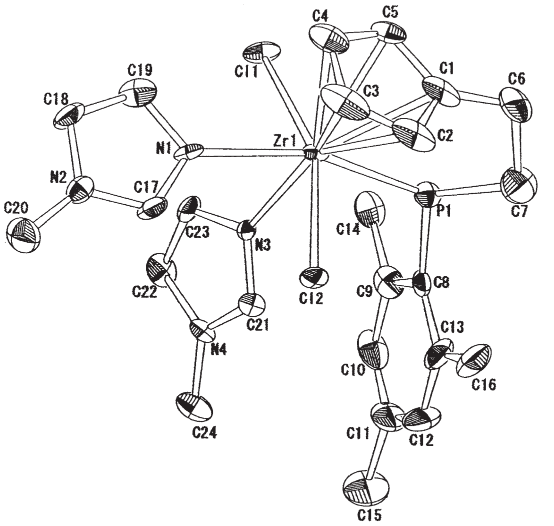


Figure 1. ORTEP drawing of **4**. Ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Zr1–P1, 2.600(2); Zr1–Cl1, 2.537(2); Zr1–Cl2, 2.563(2); Zr1–N1, 2.429(5); Zr1–N3, 2.366(5); Zr1–P1–C7, 110.3(3); Zr1–P1–C8, 119.4(2); C7–P1–C8, 111.9(3).

In this way, the novel phosphide-pendant dichloride Zr complex (**3**) is successfully generated via tritylation of the trichloride Zr complex with a secondary phosphine-pendant cyclopentadienyl ligand, followed by elimination of $CHPh_3$. There have appeared only a few reports on such a unique synthetic method utilizing the reaction of an alkyl complex with a P–H functionalized phosphine to prepare a phosphide complex.[11a–c] In contrast, most phosphide complexes of group 4 transition metals have been prepared by the conventional salt-elimination reactions,[2a–c,3a–c] which did not work at all in our study. The present mild synthetic method may have a potential to introduce a phosphide ligand into many kinds of metal complexes. The phosphide complex obtained here and some related complexes are now under investigation with respect to their reactivities involving catalytic activities in olefin polymerization. Details of characterization of **4** and related complexes will be reported elsewhere.

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7 The reaction of **1** with 3 equiv of $LiCH_2SiMe_3$ gave quantitatively a trialkyl complex $[\{\eta^5\text{-}C_5H_4(CH_2)_2P(H)Mes\}Zr(CH_2SiMe_3)_3]$ with the P–H bond intact, showing that the carbanion attacks preferentially not the P–H moiety but the Zr center.

8 (**4**): A solution of $NaCPh_3$, generated in situ (0.36 mmol) in 20 ml of ether, was slowly added to a solution of **1** (0.19 g, 0.36 mmol) in 25 ml of THF at room temperature. The reaction mixture was stirred for 30 min and then the solvents were removed in vacuo. The residue was dissolved in 20 ml of toluene and the solution was filtered. To the filtrate was slowly added a solution of *N*-methylimidazole (0.039 g, 0.47 mmol) in 10 ml of THF (addition of 2 equivalent or more of *N*-methylimidazole gave rise to decomposition of the product). After stirring for 10 min, the solution was reduced in volume in vacuo, and then the residue was washed with ether, followed by drying in vacuo to yield a red powder of **4** (40% based on **1**, 0.082 g). ^1H NMR (300 MHz, C_6D_6): δ 8.33 (s, 1H, imidazole), 8.23 (s, 1H, imidazole), 8.10 (s, 1H, imidazole), 8.00 (s, 1H, imidazole), 6.74 (s, 2H, *m*-H in Mes or Cp), 6.67 (s, 2H, *m*-H in Mes or Cp), 6.17 (s, 2H, Cp), 5.84 (s, 1H, imidazole), 5.69 (s, 1H, imidazole), 3.41 (m, 2H, PCH_2 or $CpCH_2$), 3.21–3.08 (m, 2H, PCH_2 or $CpCH_2$), 2.70 (s, 6H, *o*-Me in Mes), 2.15 (s, 6H, MeN), 2.08 (s, 3H, *p*-Me in Mes). ^{13}C NMR (75.5 MHz, C_6D_6): δ 144.0 (s, imidazole), 143.3 (s, imidazole), 143.2 (s, imidazole), 141.3 (s, imidazole), 139.9 (d, $J_{PC} = 3.7$ Hz, aromatic-C in Mes), 138.1 (s, 1-C in Cp), 136.0 (d, $J_{PC} = 1.9$ Hz, aromatic-C in Mes), 131.5 (br-s, aromatic-C in Mes), 129.9 (s, aromatic-C in Mes), 119.0 (s, imidazole or 2,5- or 3,4-C in Cp), 117.4 (s, imidazole or 2,5- or 3,4-C in Cp), 116.0 (s, imidazole or 2,5- or 3,4-C in Cp), 112.1 (s, imidazole or 2,5- or 3,4-C in Cp), 37.5 (s, $CpCH_2$), 32.5 (s, MeN), 32.4 (s, MeN), 27.7 (d, $J_{PC} = 19.8$ Hz, PCH_2), 24.0 (d, $J_{PC} = 9.9$ Hz, *o*-Me in Mes), 20.9 (s, *p*-Me in Mes). ^{31}P NMR (121.5 MHz, C_6D_6): δ 162.8 (s).

9 Crystallographic data for $\mathbf{4}\cdot(\mathrm{thf})_{0.5}$: formula $C_{26}H_{35}Cl_2N_4O_{0.5}PZr$; fw = 604.69; triclinic; $P\bar{1}$ (No. 2); $a = 8.0490(2)$ Å, $b = 16.4160(3)$ Å, $c = 21.9390(6)$ Å, $\alpha = 81.054(1)°$, $\beta = 88.255(1)°$, $\gamma = 89.857(1)°$, $V = 2862.3(1)$ Å^3; $Z = 4$; $D_{calcd} = 1.403$ g/cm^3. Out of a total of 12393 reflections measured, 7776 reflections with $2.00\sigma(I) < I$ and $2\theta < 50.00°$, were used in the refinement, and the structure was solved by direct methods and expanded using Fourier techniques: R (R_w) = 0.071 (0.115). The measurement was made on a Mac Science DIP2030 imaging plate area diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) at 200 K.

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