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Coupling of Coordinated 2-Iminophosphorano-1-phosphaallyl Leading to Bridged Iminophosphoranato Complexes of Zirconium and Hafnium

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Reaction of MCl_4 (M = Zr, Hf) with 2 equiv of 2-iminophosphorano-1-phosphaallyl lithium [Li{P(Ph)C(=CHPh)P(Me)$_2$=NSiMe$_3$}(THF)$_{1.5}$] (**1**) affords ligand coupling complexes **3** and **4**, respectively, while similar treatment of $ZrCl_4$ with [Li{P(Ph)C(=C(SiMe$_2$Bu^t)Ph)P(Me)$_2$=NSiMe$_3$}(THF)$_2$] (**2**) yields ligand transfer complex **5**.

P,N-Chelating ligands continue to attract considerable attention in coordination and organometallic chemistry because of their ability to act as hemilabile ligands.[1] This class of ligands possesses a combination of hard and soft donor atoms and can stabilize metal ions in a variety of oxidation states and geometries.[2] A number of early and late metal complexes of such ligands have been obtained, and some of them showed versatile reactivity or catalytic activity.[3−5] Recently, we prepared a new class of anionic P,N-ligands containing an iminophosphorano group, [P(Ph)C{=C(R)Ph}P(Me)$_2$=NSiMe$_3$]$^-$ (R = H, SiMe$_2$Bu^t).[6] Attempts have been made to investigate their complexation with group 4 metal ions. Group 4 metal complexes have been extensively explored because of their potential application in organic synthesis and as catalysts for α-olefin polymerization.[7] Some group 4 metal-assisted coupling reactions have also attracted increasing attention.[8] However, these complexes mainly feature hard donor atoms such as N,N-chelating ligands.[7b−d,9] The complexes with hard/soft combining ligands may display different coordination modes, reactivity, or catalytic activity.[2b,c] Herein, we report the reaction of MCl_4 (M = Zr, Hf) with the anioic P,N-ligands and the structural characterization of the produced ligand coupling and ligand transfer complexes.

The reactions of iminophosphorano-1-phosphaallyl lithium with MCl_4 (M = Zr, Hf) are shown in Scheme 1. Treatment of MCl_4 (M = Zr, Hf) with 2 equiv of **1** in Et_2O results in the formation of yellow-brown solution, from which com-

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(6) Wang, Z.-X.; Li, Y.-X. *Organometallics*, in press. NMR spectral data, **1**. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.23 (s, 9H, SiMe$_3$), 1.44 (d, J = 11.68 Hz, 6H, PMe), 1.23−1.26 (m, 6H, THF), 3.44−3.47 (m, 6H, THF), 6.74−6.80 (m, 1H, =CH), 6.92−7.02 (m, 4H, Ph), 7.13−7.17 (m, 2H, Ph), 7.32−7.36 (t, J = 7.32 Hz, 2H, Ph), 7.93 (d, J = 7.96 Hz, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 4.91, 19.81 (d, J = 59.58 Hz), 25.88, 68.83, 121.32, 126.61, 127.72 (d, J = 7.04 Hz), 129.15, 130.25 (d, J = 18.91 Hz), 131.00 (d, J = 2.31 Hz), 131.51, 134.70 (d, J = 17.20 Hz), 137.25 (d, J = 23.23 Hz), 139.63 (d, J = 24.75 Hz). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ −46.60, 25.76. **2**. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.06 (s, 9H, SiMe$_3$), 0.14−0.50 (b, 3H, SiMe), 0.82−1.14 (b, 3H, SiMe), 1.29 (s, 9H, Bu^t), 1.42−1.46 (m, 8H, THF), 3.61−3.64 (m, 8H, THF), 6.83 (t, J = 7.21 Hz, 1H, Ph), 7.03−7.07 (m, 1H, Ph), 7.11−7.18 (m, 6H, Ph), 7.38 (t, J = 6.87 Hz, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 0.85, 4.86, 20.29, 26.05, 30.76, 68.97, 158.26 (dd, J = 63.38, 58.95 Hz), 166.27 (dd, J = 30.58, 8.35 Hz), 19.75, 126.39, 127.99 (d, J = 4.23 Hz), 129.18 (d, J = 8.81 Hz), 129.43, 148.26 (t, J = 11.67 Hz), 159.03, 159.62. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ −27.72, 17.74.

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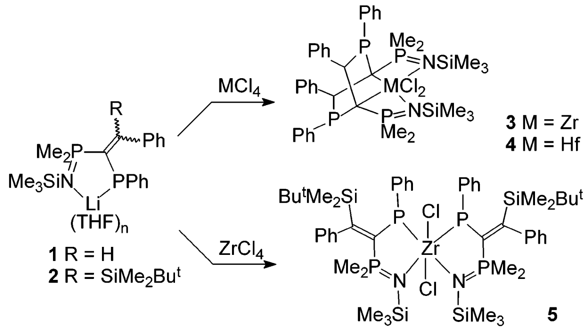
Scheme 1



plexes **3** and **4** can be isolated in 33.8% and 51.1% yields, respectively, by crystallization from Et_2O (for **3**) or CH_2Cl_2 (for **4**). In each case, no other crystalline species can be obtained. Reaction between $ZrCl_4$ and 2 equiv of **2** in Et_2O produces a deep red solution with precipitates. From the reaction mixture, complex **5** was obtained as the only crystalline product in 31.1% yield by crystallization from a mixed solvent of CH_2Cl_2 and Et_2O. It is proposed that the reaction between MCl_4 (M = Zr, Hf) and **1** proceeds through $[PhPC({=}CHPh)P(Me)_2{=}NSiMe_3]_2MCl_2$ intermediate similar to **5**, followed by an intramolecular cross conjugate addition between the two ligands. That no ligand coupling takes place in the reaction of **2** with $ZrCl_4$ is ascribed to steric hindrance of the $SiMe_2Bu^t$ group attached on the carbon−carbon double bond of the ligand.

Both **3** and **4** are pale yellow crystals, while **5** is a deep red crystalline solid. Complex **3** is stable in the solid state but decomposes slowly in the Et_2O solution in the course of crystallization, and the decomposed species cannot be redissolved in organic solvents such as Et_2O and THF. Both **4** and **5** are stable either in the solid state or in the solution. Each of complexes **3**−**5** is very soluble in CH_2Cl_2 and soluble in Et_2O and gives satisfactory microanalytical data (except **3**), as well as ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra.[10−12] Single-crystal X-ray diffraction data established molecular structures of the complexes.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **3** and **4** give a set of $SiMe_3$ and metal-bound carbon signals, showing that the iminophosphoranato moieties equally chelate to the metal center. The phosphorus-bound methyl groups exhibit two sets of signals, consistent with their respective chemical environment. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **5** also reveal that two 2-imino-phosphorano-1-phosphaallyl ligands symmetrically chelate to the zirconium center in solution.

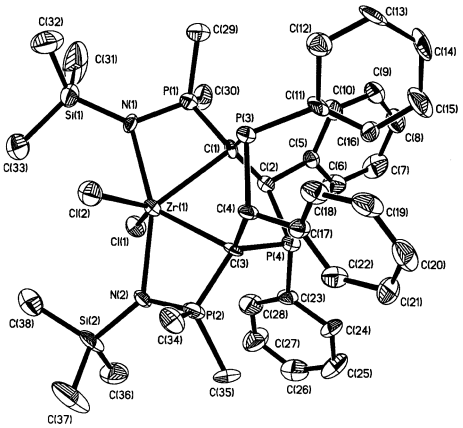


Figure 1. Molecular structure of **3** shown with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Zr(1)−C(1) 2.425(8), Zr(1)−C(3) 2.427(9), Zr(1)−N(1) 2.249(7), Zr(1)−N(2) 2.256(7), Zr(1)−Cl(1) 2.461(3), Zr(1)−Cl(2) 2.428(3), Cl(1)−Zr(1)−Cl(2) 133.01(10), C(1)−Zr(1)−N(1) 68.3(3), C(3)−Zr(1)−N(2) 67.7(3), N(1)−Zr(1)−N(2) 158.1(3), C(1)−Zr(1)−C(3) 68.0(3).

Complex **3** crystallizes with two molecules in the asymmetric unit (Figure 1, only one molecule shown).[13] The bridged ligand chelates to the zirconium atom through carbon and nitrogen atoms. The zirconium atom is six-coordinate, having a strongly distorted octahedral geometry with trans-apical chloride ligands. The bond angle of Cl(1)−Zr(1)−Cl(2) is 133.01(10)°. The C(1)−Zr(1)−C(3) bond angle [68.0(3)°] is much narrower than that of N(1)−Zr(1)−N(2) [158.1(3)°] because of the rigidity of the bridged ligand. In the bridged ring consisting of Zr(1), C(1), C(2), P(4), C(3), C(4), and P(3) atoms, the phenyl group attached to P(4) adopts exo-orientation, and the others are endo (Chart 1a).

The structure of complex **4** is shown in Figure 2.[14] In the

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(10) Spectral data for **3**. ^1H NMR (400.1 MHz, C_6D_6): δ 0.42 (s, 18H, $SiMe_3$), 0.63 (d, $J = 12.24$ Hz, 6H, PMe), 1.35 (d, $J = 11.74$ Hz, 6H, PMe), 5.27−5.35 (m, 2H, CH), 6.43−6.68 (m, 2H, Ph), 6.86−6.90 (m, 2H, Ph), 6.95−7.04 (m, 6H, Ph), 7.26−7.51 (m, 4H, Ph), 7.50 (d, $J = 7.14$ Hz, 4H, Ph), 7.89 (b, 2H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 3.78, 16.97 (d, $J = 58.25$ Hz), 21.40 (d, $J = 48.09$ Hz), 44.96 (m), 47.13−47.63 (m), 50.05 (m), 126.19 (d, $J = 12.17$ Hz), 127.09, 128.92, 129.67, 131.41, 137.15 (dd, $J = 7.85$, 11.97 Hz), 138.62−139.45 (m), 142.05−142.13 (m), 143.70 (t, $J = 8.55$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 28.18, 37.34.

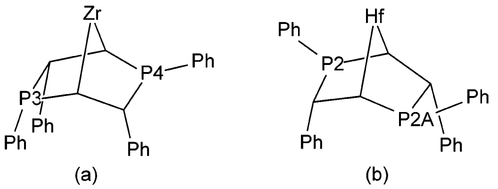
(11) Spectral data for **4**. ^1H NMR (400.1 MHz, C_6D_6): δ 0.39 (s, 18H, $SiMe_3$), 0.58 (d, $J = 11.94$ Hz, 6H, PMe), 1.36 (d, $J = 11.72$ Hz, 6H, PMe), 4.30 (s, 2H, CH_2Cl_2), 5.28−5.35 (m, 2H, CH), 6.41−6.83 (m, 2H, Ph), 6.96−7.05 (m, 8H, Ph), 7.18−7.29 (b, 4H, Ph), 7.47 (d, $J =$ 7.05 Hz, 4H, Ph), 7.85−7.88 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 3.15, 16.17 (d, $J = 58.05$ Hz), 24.03 (d, $J = 55.23$ Hz), 44.48−44.65 (m), 46.04−46.57 (m), 50.18 (dm, $J = 62.56$ Hz), 53.11, 126.02, 127.00, 128.04, 128.16, 128.35, 128.85, 129.70, 131.35, 137.30−137.51 (m), 138.90 (b), 138.54 (dd, $J = 13.88$, 26.36 Hz), 142.62, 142.94 (d, $J = 18.81$ Hz), 144.47 (t, $J = 9.26$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 26.15, 33.65.

(12) Spectral data for **5**. ^1H NMR (400.1 MHz, $CDCl_3$): δ −0.06 (s, 6H, $SiMe_2$), 0.08 (s, 18H, $SiMe_3$), 0.30 (s, 6H, $SiMe_2$), 1.07 (s, 18H, Bu^t), 1.20 (d, $J = 10.67$ Hz, 6H, PMe), 1.22 (t, $J = 6.96$ Hz, 6H, Et_2O), 1.92 (d, $J = 10.88$ Hz, 6H, PMe), 3.49 (q, $J = 6.96$ Hz, 4H, Et_2O), 5.31(s, 1.2H, CH_2Cl_2), 6.92 (t, $J = 7.26$ Hz, 2H, Ph), 7.11−7.17 (m, 6H, Ph), 7.22−7.38 (m, 8H, Ph), 7.69−7.71 (b, 4H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ −0.64, −0.34, 5.58, 15.37, 19.63, 21.10 (d, $J = 55.33$ Hz), 23.66 (d, $J = 45.67$ Hz), 29.28, 53.50, 65.93, 122.56, 126.11, 126.49, 127.56, 127.98 (d, $J = 14.99$ Hz), 129.04, 131.06 (t, $J = 8.15$ Hz), 144.60 (t, $J = 7.55$ Hz), 151.25 (t, $J = 22.13$ Hz), 155.23−156.08 (m). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ 32.23, 43.77.

(13) Although **3** decomposes slowly in solution, crystalline **3** is stable, and no effect was observed during X-ray diffraction data collection. Crystal data for **3**: $C_{38}H_{52}Cl_2N_2P_4Si_2Zr$, $M = 879.00$, monoclinic, space group $P2(1)/c$, $a = 13.072(3)$ Å, $b = 16.424(4)$ Å, $c = 40.458(10)$ Å, $\beta = 92.040(4)°$, $V = 8681(4)$ Å^3, $T = 298(2)$ K, $Z = 8$, μ(Mo Kα) = 0.608 mm^{-1}, 37410 reflections measured, 12190 unique ($R_{int} = 0.1638$), R1 = 0.0667, wR2 = 0.1146 [$I > 2\sigma(I)$]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number: 184921.

(14) Crystal data for $4{\cdot}CH_2Cl_2$: $C_{39}H_{54}Cl_4HfN_2P_4Si_2$, $M = 1051.19$, monoclinic, space group $C2/c$, $a = 15.457(2)$ Å, $b = 18.370(3)$ Å, $c = 16.999(3)$ Å, $\beta = 104.379(2)°$, $V = 4675.4(12)$ Å^3, $T = 298(2)$ K, $Z = 4$, μ(Mo Kα) = 2.677 mm^{-1}, 11909 reflections measured, 4004 unique ($R_{int} = 0.0316$), R1 = 0.0258, wR2 = 0.0467 [$I > 2\sigma(I)$]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number: 184922.

Chart 1. Orientations of Phenyl Groups in Complexes **3** (a) and **4** (b)[a]



[a] Only bridging ring moieties shown for clarity.

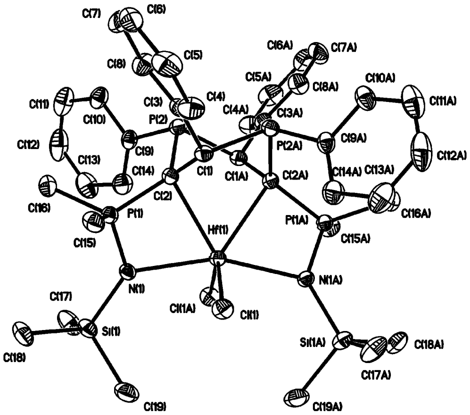


Figure 2. Molecular structure of complex **4** shown with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Hf(1)−N(1) 2.245(3), Hf(1)−C(2) 2.366(3), Hf(1)−Cl(1) 2.4203(9), P(1)−N(1) 1.607(3), P(1)−C(2) 1.756(3), P(2)−C(2) 1.871(3), Cl(1)−Hf(1)−Cl(1A) 126.97(5), N(1)−Hf(1)−N(1A) 158.64(13), C(2)−Hf(1)−C(2A) 68.70(15), C(2)−Hf(1)−N(1) 68.15(10).

asymmetric unit of **4**, a solvent CH_2Cl_2 molecule is also present which does not show any interaction with the organohafnium complex. Complex **4** has a similar skeletal structure to that of **3**. However, compared with complex **3**, the bond angle Cl(1)−Hf(1)−Cl(1A) [126.97(5)°] is narrower. In the bridged ring consisting of Hf(1), C(2), P(2), C(1A), C(2A), P(2A), and C(1) atoms, both phenyl groups attached to P(2) and P(2A) atoms adopt exo-orientation, being different from those of complex **3** (Chart 1b). One of the reasons may be, if both phenyl groups on the phosphorus atoms in complex **3** adopted exo-orientation, the repulsion between the chlorine atoms and the exo-phenyl groups would be stronger than that in complex **4** because of the wider Cl−Zr−Cl angle.

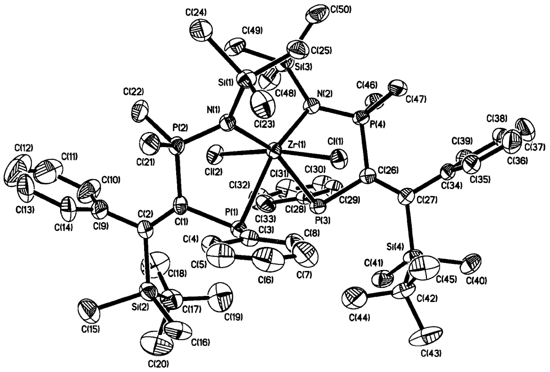


Figure 3. Molecular structure of complex **5** shown with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Zr(1)−P(1) 2.7698(15), Zr(1)−P(3) 2.7596(15), Zr(1)−N(1) 2.210(4), Zr(1)−N(2) 2.215(4), Zr(1)−Cl(1) 2.4237(15), Zr(1)−Cl(2) 2.4405(16), Cl(1)−Zr(1)−Cl(2) 170.96(6), P(1)−Zr(1)−N(1) 78.66(12), P(3)−Zr(1)−N(2) 78.22(11), N(1)−Zr(1)−N(2) 119.67(16), P(1)−Zr(1)−P(3) 83.45(4).

The structure of crystalline complex **5** (Figure 3)[15] reveals a quasioctahedral coordination environment about the metal. The equatorial plane is defined by Zr(1)N(1)N(2)P(1)P(3) ($\sum$Zr = 359.99°) with Cl(1) and Cl(2) in trans-apical positions. The bond angle Cl(1)−Zr(1)−Cl(2) is 170.96(6)°. The P(1) and P(3) atoms are adjacent, showing cis-arrangement of the equatorial coordination atoms. The C═C bonds are on opposite sides of the equatorial plane. However, in the solution, **5** may exist as an equilibrium mixture of isomers with the C═C bonds on the same and opposite sides of the equatorial plane because only the isomer with the C═C bonds on the same sides of the plane could form a complex analogous to **3** according to the assumption that complexes analogous to **5** are precursors to **3**. The bond angles N(1)−Zr(1)−N(2) and P(1)−Zr(1)−P(3) are 119.67(6)° and 83.45(4)°, respectively. The average Zr−N distance of 2.213 Å is shorter than those in complex **3** (av 2.253 Å), but both are within the range usually found for molecules containing a Zr−N bond such as $[Zr\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}_2Cl_2]$,[7c] $[Zr(NMe_2)_3\{4\text{-}Bu^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}]$,[16] and $[Zr\{(NC_6H_4Me\text{-}4)_2P(Ph)_2\}_2Cl_2]$.[7d]

In summary, a new P−C coupling reaction at a zirconium or hafnium center has been discovered in the reaction of 2-iminophosphorano-1-phosphaallyl lithium with MCl_4 (M = Zr, Hf). The reaction is dependent on the steric hindrance of substituted groups attached on the carbon−carbon double bond of the ligand. The existence of bulky substituents on the carbon−carbon double bond prevents the coupling reaction, producing a ligand transfer complex.

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Supporting Information Available: Synthetic procedure of **3**−**5**. X-ray crystallographic files for **3**, **4**·CH_2Cl_2, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) X-ray quality single crystals of **5** were obtained by slow recrystallization of the adduct **5**·Et_2O·0.6CH_2Cl_2 from its Et_2O solution. Crystal data for **5**: $C_{50}H_{80}Cl_2N_2P_4Si_4Zr$, M = 1107.52, monoclinic, space group $P2(1)/c$, a = 11.6893(17) Å, b = 21.514(3) Å, c = 26.308(4) Å, β = 92.633(2)°, V = 6609.1(17) Å^3, T = 298(2) K, Z = 4, μ(Mo Kα) = 0.446 mm^{-1}, 27827 reflections measured, 9086 unique (R_{int} = 0.0712), R1 = 0.0512, wR2 = 0.1110 [$I > 2\sigma(I)$]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number: 184923.

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