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# Pentavalent vs Trivalent Phosphorus-Bridged Ligands. Synthesis and Structural Characterization of Unexpected Group 4 Metal Complexes Incorporating an Indenylide Unit, $[\sigma{:}\sigma\text{-}{}^{i}Pr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2$

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Treatment of $^{i}Pr_2NP(C_9H_7)(C_2B_{10}H_{11})$ with excess 30% hydrogen peroxide in toluene gave the corresponding pentavalent phosphorus-bridged indenyl−carboranyl compound $^{i}Pr_2NP(O)(C_9H_7)(C_2B_{10}H_{11})$ (**2**). The equimolar reaction of **2** with $M(NR_2)_4$ in toluene at room temperature afforded unexpected group 4 metal amides incorporating an indenylide unit, $[\sigma{:}\sigma\text{-}{}^{i}Pr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2(L)$ (R = Me, L = $HNMe_2$, M = Ti (**3**), Zr (**4**), Hf (**5**); R = Et, L = THF, M = Hf (**6**)). The formation of these new types of group 4 metal complexes was ascribed to the high oxophilicity of the $M^{4+}$ ions. These new complexes were fully characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray diffraction studies (except for **5**).

## Introduction

Bridging units have a great impact on the reaction chemistry of *ansa*-metallocenes.[1] Of the known bridging elements such as B, C, Si, Ge, N, and P,[2] the phosphorus atom is of particular interest, because of its electronic and steric properties. In principle, phosphorus-bridged ligands can exhibit a wide range of structural types, as the phosphorus atom has the two common oxidation states +3 and +5. The former is represented by the phosphine ligands −PR−,[3] whereas pentavalent phosphorus is found in phosphine oxides and diylides based on −R(O)P− and $-R_2P-$ units, respectively.[4−6] Such changes in the oxidation states would be expected to modulate the reactivity of the metal center. We recently reported the phosphine-bridged ligand $^{i}Pr_2NP(C_9H_7)(C_2B_{10}H_{11})$ and its applications in group 3 and 4 metal chemistry.[7] To compare the similarities and differences between the tri- and pentavalent phosphorus-bridged ligands in coordination chemistry, we extended our research to include pentavalent phosphorus-bridged systems.

Attempts to prepare $[^{i}Pr_2NP(X)(C_9H_6)(C_2B_{10}H_{10})]M(NMe_2)_2$ (X = O, S) by treatment of $[^{i}Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]M(NMe_2)_2$[7b] with excess $O_2$ or $S_8$ under various reaction conditions failed. Reactions of $[^{i}Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]M(NMe_2)_2$ with $BH_3{\cdot}SMe_2$ or $CH_3I$ generated a mixture of inseparable products. These results showed clearly that $[^{i}Pr_2NP(C_9H_6)(C_2B_{10}H_{10})]M(NMe_2)_2$ were not good starting materials for the preparation of the corresponding pentavalent phosphorus derivatives, due to the multiple reactive sites presented in the molecules. Alternative synthetic routes were desired. We then prepared the new pentavalent phosphorus-bridged ligand $^{i}Pr_2NP(O)(C_9H_7)(C_2B_{10}H_{11})$ by treatment of $^{i}Pr_2NP(C_9H_7)(C_2B_{10}H_{11})$[7a] with $H_2O_2$. Interaction of $M(NMe_2)_4$ with $^{i}Pr_2NP(O)(C_9H_7)(C_2B_{10}H_{11})$ gave the unexpected products $[\sigma{:}\sigma\text{-}{}^{i}Pr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2$ (M = Ti, Zr, Hf; R = Me, Et) with interesting structural features. These new results are reported in this article.

## Experimental Section

**General Procedures.** All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a

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glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $^iPr_2NPCl_2$,[8] $Li_2C_2B_{10}H_{10}$,[9] $^iPr_2NP(C_9H_7)(C_2B_{10}H_{11})$ (**1**),[7a] and $M(NR_2)_4$ (M = Ti, Zr, R = Me; M = Hf; R = Me, Et)[10] were prepared according to literature methods. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. $^{11}B$ and $^{31}P$ NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 and 161.91 MHz, respectively. All chemical shifts were reported in $\delta$ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3\cdot OEt_2$ (0.00 ppm) for boron chemical shifts, and to external 85% $H_3PO_4$ (0.00 ppm) for phosphorus chemical shifts. Elemental analyses were performed by MEDAC Ltd., Surrey, U.K.

**Preparation of $^iPr_2NP(O)(C_9H_7)(C_2B_{10}H_{11})$ (2).** An excess amount of hydrogen peroxide (30% aqueous solution, 5.0 mL, 44.0 mmol) was added to a toluene solution (5 mL) of $^iPr_2NP(C_9H_7)(C_2B_{10}H_{11})$ (**1**; 389 mg, 1.0 mmol) at room temperature, and the mixture was stirred for 2 days. The organic layer was separated and washed with a saturated solution of $Na_2S_2O_3$ (15 mL × 2), $NaHCO_3$ (15 mL × 2), and NaCl (20 mL × 2), respectively. Removal of the solvent afforded a white solid. Recrystallization from toluene at room temperature gave **2**, a mixture of allylic and vinylic isomers with a molar ratio of 3:1, as colorless crystals (291 mg, 72%). $^1H$ NMR (benzene-$d_6$): $\delta$ 8.62 (d, $J$ = 7.5 Hz, indenyl), 8.24 (d, $J$ = 7.2 Hz, indenyl), 7.23 (d, $J$ = 7.5 Hz, indenyl), 7.18 (m, indenyl), 7.11 (m, indenyl), 7.07 (d, $J$ = 7.2 Hz, indenyl), 6.67 (d, $J$ = 3.3 Hz, indenyl), 6.51 (d, $J$ = 5.4 Hz, indenyl), 6.22 (d, $J$ = 5.4 Hz, indenyl), 4.49 (br, cage C$H$), 4.31 (br, cage C$H$), 3.99 (d, $^2J_{PH}$ = 28.8 Hz, indenyl), 3.21 (m, NC$H$(CH$_3$)$_2$), 2.94 (d, $J$ = 3.3 Hz, indenyl), 2.77 (m, NC$H$(CH$_3$)$_2$), 1.15 (d, $J$ = 6.3 Hz, NCH(C$H_3$)$_2$), 0.96 (d, $J$ = 6.3 Hz, NCH(C$H_3$)$_2$), 0.86 (d, $J$ = 6.3 Hz, NCH(C$H_3$)$_2$), 0.44 (d, $J$ = 6.3 Hz, NCH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 146.9, 144.3 (d, $^1J_{PC}$ = 62.4 Hz), 142.5, 139.0, 134.2, 129.9, 127.2, 125.9, 124.2, 121.4, 54.7 (d, $^1J_{PC}$ = 65.5 Hz), 40.4 (indenyl), 75.6 (br), 74.9 (br), 63.6, 62.7 (cage $C$), 47.4 (br), 46.9 (br) (N$C$H(CH$_3$)$_2$), 23.8, 22.9, 22.6, 22.0 (NCH($C$H$_3$)$_2$). $^{11}B\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −0.4 (1B), −2.0 (1B), −7.6 (2B), −12.4 (6B). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 32.0, 19.7 with an intensity ratio of 1:3. IR (KBr, cm$^{-1}$): $\nu$ 3060 (w), 2982 (s), 2593 (s), 1397 (m), 1172 (vs), 1004 (s), 757 (m), 529 (m). HRMS: $m/z$ calcd for $C_{17}H_{32}NOP^{11}B_8{}^{10}B_2{}^+$, 405.3219; found, 405.3227.

**Preparation of $[\sigma:\sigma\text{-}^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2(HNMe_2)$ (3).** A toluene solution (10 mL) of **2** (405 mg, 1.0 mmol) was slowly added to a toluene solution (10 mL) of $Ti(NMe_2)_4$ (225 mg, 1.0 mmol) at −30 °C, and the reaction mixture was stirred at room temperature overnight. The resulting clear dark red solution was concentrated to about 5 mL. Complex **3** was isolated as red crystals after this solution stood at room temperature for 2 days (338 mg, 58%). $^1H$ NMR (benzene-$d_6$): $\delta$ 7.98 (d, $J$ = 7.2 Hz, 1H, indenyl), 7.80 (m, 1H, indenyl), 7.66 (d, $J$ = 7.2 Hz, 1H, indenyl), 7.19 (m, 2H, indenyl), 6.99 (m, 1H, indenyl), 3.67 (m, 2H, NC$H$(CH$_3$)$_2$), 2.79 (s, 12H, N(C$H_3$)$_2$), 2.00 (s, 6H, HN(C$H_3$)$_2$), 1.31 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$), 0.86 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 138.8, 137.0, 122.5, 121.9, 117.5, 117.2, 116.0, 107.8, 78.3 (d, $^1J_{PC}$ = 141.9 Hz) (indenyl), 96.4, 80.8 (d, $^1J_{PC}$ = 96.0 Hz) (cage $C$), 48.6 (br), 39.7 (br) (N$C$H(CH$_3$)$_2$), 44.7, 43.1, 39.1 (N($C$H$_3$)$_2$), 31.3, 25.8, 24.2, 22.4 (NCH($C$H$_3$)$_2$). $^{11}B\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −0.3 (1B), −2.0 (2B), −4.0 (2B), −8.3 (3B), −12.3 (2B). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 43.5. IR (KBr, cm$^{-1}$): $\nu$ 3025 (w), 2972 (m), 2922 (m), 2566 (vs), 1460 (s), 1411 (s), 1261 (s), 1183 (s), 1137 (m), 1075 (m), 1006 (vs), 933 (s), 738 (m), 652 (m), 608 (m). Anal. Calcd for $C_{22}H_{45.5}B_{10}N_{3.5}OPTi$ (**3** − $0.5HNMe_2$): C, 47.10; H, 8.16; N, 8.72. Found: C, 47.06; H, 8.33; N, 8.87.

**Preparation of $[\sigma:\sigma\text{-}^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2(HNMe_2)$ (4).** This compound was prepared as yellow crystals from the reaction of **2** (405 mg, 1.0 mmol) with $Zr(NMe_2)_4$ (267 mg, 1.0 mmol) in toluene using a procedure identical with that reported for **3**: yield 402 mg (64%). $^1H$ NMR (benzene-$d_6$): $\delta$ 7.95 (d, $J$ = 7.8 Hz, 1H, indenyl), 7.82 (m, 1H, indenyl), 7.55 (d, $J$ = 7.8 Hz, 1H, indenyl), 7.16 (m, 2H, indenyl), 6.98 (m, 1H, indenyl), 3.63 (m, 2H, NC$H$(CH$_3$)$_2$), 2.60 (s, 12H, N(C$H_3$)$_2$), 1.96 (s, 6H, HN(C$H_3$)$_2$), 1.37 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$), 0.99 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 138.3, 137.1, 123.0, 121.9, 117.4, 117.0, 115.8, 108.4, 78.5 (d, $^1J_{PC}$ = 167.5 Hz) (indenyl), 94.7, 81.4 (d, $^1J_{PC}$ = 85.4 Hz) (cage $C$), 48.5 (N($C$H$_3$)$_2$), 40.2 (br), 38.1 (br) (N$C$H(CH$_3$)$_2$), 31.8, 24.1, 22.3 (NCH($C$H$_3$)$_2$). $^{11}B\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −1.2 (1B), −0.3 (1B), −2.9 (1B), −6.3 (2B), −7.9 (2B), −10.8 (3B). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 43.3. IR (KBr, cm$^{-1}$): $\nu$ 3040 (w), 2968 (s), 2922 (m), 2876 (m), 2565 (vs), 1459 (s), 1412 (s), 1259 (s), 1181 (m), 1139 (m), 1006 (vs), 929 (s), 739 (s), 561 (s). Anal. Calcd for $C_{22.2}H_{45.5}B_{10}N_{3.5}OPZr$ (**4** − $0.5HNMe_2$): C, 43.65; H, 7.58; N, 8.10. Found: C, 43.57; H, 7.72; N, 8.29.

**Preparation of $[\sigma:\sigma\text{-}^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Hf(NMe_2)_2(HNMe_2)$ (5).** This compound was prepared as yellow crystals from the reaction of **2** (405 mg, 1.0 mmol) with $Hf(NMe_2)_4$ (354 mg, 1.0 mmol) in toluene using a procedure identical with that reported for **3**: yield 458 mg (64%). $^1H$ NMR (benzene-$d_6$): $\delta$ 7.93 (d, $J$ = 7.5 Hz, 1H, indenyl), 7.79 (m, 1H, indenyl), 7.52 (d, $J$ = 7.5 Hz, 1H, indenyl), 7.19 (m, 1H, indenyl), 7.11 (m, 1H, indenyl), 6.95 (m, 1H, indenyl), 3.56 (m, 2H, NC$H$(CH$_3$)$_2$), 2.85 (s, 12H, N(C$H_3$)$_2$), 2.10 (s, 6H, HN(C$H_3$)$_2$), 1.25 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$), 0.83 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 138.4, 137.1, 122.5, 121.9, 117.4, 115.7, 108.5, 105.5, 78.2 (d, $^1J_{PC}$ = 167.5 Hz) (indenyl), 91.0, 81.5 (d, $^1J_{PC}$ = 91.1 Hz) (cage $C$), 48.3 (N($C$H$_3$)$_2$), 39.9 (br), 38.3 (br) (N$C$H(CH$_3$)$_2$, 31.8, 24.0, 22.3 (NCH($C$H$_3$)$_2$). $^{11}B\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −0.9 (1B), −0.6 (1B), −3.2 (1B), −6.8 (2B), −8.1 (2B), −11.5 (3B). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 43.2. IR (KBr, cm$^{-1}$): $\nu$ 3055 (w), 2970 (m), 2879 (m), 2569 (vs), 1459 (s), 1415 (s), 1261 (vs), 1185 (m), 1135 (s), 1008 (vs), 936 (s), 734 (m), 561 (s). Anal. Calcd for $C_{23}H_{49}B_{10}HfN_4OP$ (**5**): C, 38.62; H, 6.91; N, 7.83. Found: C, 38.59; H, 6.84; N, 7.47.

**Preparation of $[\sigma:\sigma\text{-}^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Hf(NEt_2)_2(THF)\cdot(toluene)$ (6·toluene).** This compound was prepared as yellow crystals from the reaction of **2** (405 mg, 1.0 mmol) with $Hf(NEt_2)_4$ (467 mg, 1.0 mmol) in toluene using a procedure identical with that reported for **3**, followed by recrystallization from toluene/THF: yield 534 mg (60%). $^1H$ NMR (benzene-$d_6$): $\delta$ 7.94 (d, $J$ = 7.5 Hz, 1H, indenyl), 7.82 (m, 1H, indenyl), 7.49 (d, $J$ = 7.5 Hz, 1H, indenyl), 7.17 (m, 1H, indenyl), 7.04 (m, 1H, indenyl), 6.95 (m, 1H, indenyl), 3.88 (m, 2H, NC$H$(CH$_3$)$_2$), 3.30 (q, $J$ = 6.9 Hz, 4H, N(C$H_2$CH$_3$)$_2$), 3.65 (m, 4H, THF), 2.60 (q, $J$ = 6.9 Hz, 4H, N(C$H_2$CH$_3$)$_2$), 1.62 (m, 4H, THF), 1.28 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$), 1.02 (t, $J$ = 6.9 Hz, 6H, N(CH$_2$C$H_3$)$_2$), 0.88 (t, $J$ = 6.9 Hz, 6H, N(CH$_2$C$H_3$)$_2$), 0.80 (d, $J$ = 6.6 Hz, 6H, NCH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 138.6, 137.1, 125.6, 121.6, 117.8, 117.2, 116.2, 108.2, 77.8 (d, $^1J_{PC}$ = 171.1 Hz) (indenyl), 90.5, 81.8 (d, $^1J_{PC}$ = 91.0 Hz) (cage $C$), 67.7, 25.7 (THF), 48.5 (br), 38.7 (br) (N$C$H(CH$_3$)$_2$), 44.2, 42.0 (N($C$H$_2$CH$_3$)$_2$), 24.1, 22.3 (NCH($C$H$_3$)$_2$), 14.4, 13.5, 13.4, 12.8 (N(CH$_2$$C$H$_3$)$_2$). $^{11}B\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −0.5 (1B), −0.6 (1B), −3.1 (1B), −7.0 (2B), −7.9 (2B), −11.4 (3B). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 44.1. IR (KBr, cm$^{-1}$): $\nu$ 3025 (w), 2971 (vs), 2927 (m), 2554 (vs), 1453 (s), 1412 (s), 1370 (s),

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**Table 1. Crystal Data and Summary of Data Collection and Refinement Details for 2−4 and 6**

| | **2** | **3** | **4** | **6**·$C_6H_5CH_3$ |
|---|---|---|---|---|
| formula | $C_{17}H_{32}B_{10}NOP$ | $C_{23}H_{49}B_{10}N_4OPTi$ | $C_{23}H_{49}B_{10}N_4OPZr$ | $C_{36}H_{66}B_{10}HfN_3O_2P$ |
| cryst size, mm | 0.40 × 0.30 × 0.20 | 0.50 × 0.40 × 0.20 | 0.40 × 0.30 × 0.20 | 0.50 × 0.40 × 0.20 |
| fw | 405.5 | 584.6 | 628.0 | 890.5 |
| cryst syst | triclinic | orthorhombic | orthorhombic | monoclinic |
| space group | $P\bar{1}$ | *Pbca* | *Pbca* | $P2_1/c$ |
| *a*, Å | 10.609(1) | 15.554(1) | 15.740(1) | 11.275(2) |
| *b*, Å | 11.418(1) | 15.375(1) | 15.393(1) | 21.105(4) |
| *c*, Å | 20.027(2) | 28.002(1) | 27.970(1) | 18.833(4) |
| α, deg | 84.34(1) | 90 | 90 | 90 |
| *β*, deg | 85.43(1) | 90 | 90 | 92.21(3) |
| *γ*, deg | 77.00(1) | 90 | 90 | 90 |
| *V*, Å$^3$ | 2348.2(3) | 6696.5(5) | 6776.7(6) | 4474.4(16) |
| *Z* | 4 | 8 | 8 | 4 |
| $D_{calcd}$, Mg/m$^3$ | 1.147 | 1.160 | 1.231 | 1.322 |
| radiation (*λ*), Å | Mo Kα (0.710 73) | Mo Kα (0.710 73) | Mo Kα (0.710 73) | Mo Kα (0.710 73) |
| 2*θ* range, deg | 2.0−48.0 | 3.9−50.0 | 2.9−50.0 | 4.1−50.1 |
| *μ*, mm$^{-1}$ | 0.127 | 0.328 | 0.396 | 2.401 |
| *F*(000) | 856 | 2480 | 2624 | 1824 |
| no. of obsd rflns | 7340 | 5896 | 5969 | 7898 |
| no. of params refnd | 560 | 361 | 361 | 478 |
| goodness of fit | 0.955 | 1.062 | 1.096 | 0.942 |
| R1 | 0.093 | 0.055 | 0.091 | 0.050 |
| wR2 | 0.237 | 0.153 | 0.216 | 0.116 |

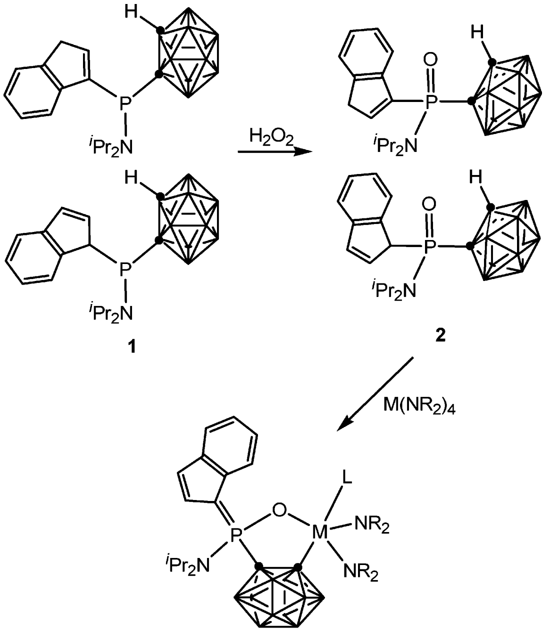
**Table 2. Selected Bond Distances (Å) and Angles (deg) for 2−4 and 6**

| | **2** | **3** (M = Ti) | **4** (M = Zr) | **6** (M = Hf) |
|---|---|---|---|---|
| P−O | 1.484(1) | 1.541(2) | 1.549(6) | 1.541(1) |
| P−N | 1.632(2) | 1.638(3) | 1.650(8) | 1.640(1) |
| P−C(cage) | 1.877(2) | 1.860(3) | 1.867(8) | 1.866(1) |
| P−C(ring) | 1.830(2) | 1.717(4) | 1.705(9) | 1.692(1) |
| M−C(cage) | | 2.243(3) | 2.386(9) | 2.346(1) |
| av M−N(amido) | | 1.860(3) | 1.998(8) | 1.991(1) |
| M−N(amine) | | 2.252(3) | 2.375(7) | |
| M−O | | 1.983(2) | 2.095(6) | 2.075(1) |
| O−P−C(cage) | 109.6(1) | 100.1(1) | 100.5(3) | 100.6(1) |
| O−M−C(cage) | | 80.2(1) | 77.0(3) | 77.8(1) |
| P−O−M | | 127.0(1) | 126.1(3) | 129.3(1) |
| ∑∠C(17) | 330.4 | 359.1 | 359.5 | 359.9 |
| ∑∠N(1) | 359.6 | 360.1 | 360.0 | 359.9 |
| ∑∠N(2) | | 360.0 | 360.0 | 359.8 |
| ∑∠N(3) | | 359.5 | 360.0 | 360.0 |
| ∑∠N(4) | | 337.2 | 337.4 | |

1263 (s), 1184 (vs), 1145 (s), 1003 (vs), 732 (s), 530 (m). Anal. Calcd for $C_{29}H_{58}B_{10}HfN_3O_2P$ (**6**): C, 43.63; H, 7.32; N, 5.26. Found: C, 43.83; H, 7.65; N, 4.92.

**X-ray Structure Determination**. All single crystals were immersed in Paratone-N oil and sealed under $N_2$ in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-IIC imaging plate using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An empirical absorption correction was applied using the SADABS program.[11] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on $F^2$ using the SHELXTL program package.[12] There were two crystallographically independent molecules in the unit cell of **2**, in which one P═O moiety was disordered over two sets of positions with 0.75:0.25 occupancies. The solid-state structure of **6** showed one toluene of solvation. Hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Selected bond distances and angles are compiled in Table 2. Further details are given in the Supporting Information.

**Scheme 1**



| | **3** | **4** | **5** | **6** |
|---|---|---|---|---|
| M | Ti | Zr | Hf | Hf |
| R | Me | Me | Me | Et |
| L | HNMe$_2$ | HNMe$_2$ | HNMe$_2$ | THF |

## Results and Discussion

**Ligand**. The compound $^i$Pr$_2$NP($C_9H_7$)($C_2B_{10}H_{11}$) (**1**) is stable in air and moisture, owing to the presence of very bulky substituents. It was, however, readily oxidized to its corresponding phosphine oxide $^i$Pr$_2$NP(O)($C_9H_7$)($C_2B_{10}H_{11}$) (**2**) by hydrogen peroxide in a mixed solvent of toluene and $H_2O$ at room temperature (Scheme 1). This reaction was clean, and **2** was isolated in 72% yield as colorless crystals. On the other hand, **1** was inert toward $S_8$ even under forced reaction conditions or in the presence of a catalytic amount of pyridine, indicating that the P in **1** was a very weak nucleophile.[5,13] Both $^{31}$P and $^{11}$B NMR data were very informative. The $^{11}$B NMR

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(11) Sheldrick, G. M. SADABS: Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 1996.

(12) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

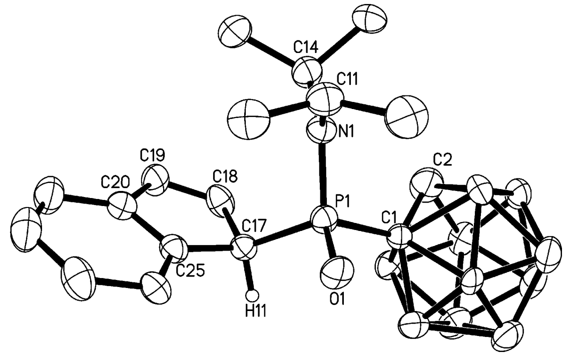

**Figure 1.** Molecular structure of ${}^{i}Pr_2NP(O)(C_9H_7)(C_2B_{10}H_{11})$ (**2**) showing one of the two crystallographically independent molecules in the unit cell.

spectrum of **2** exhibited a 1:1:2:6 splitting pattern, which was very different from that of 3:1:1:2:1:2 observed in its parent compound **1**.[7a] The ${}^{31}P$ chemical shifts of **2** (23.0 and 19.7 ppm) for the two isomers were considerably shifted upfield of those for its parent compound **1** (74.1 and 40.1 ppm), probably due to the enhanced $N(p\pi)\rightarrow P(d\pi)$ interactions.[13a] The molar ratio of allylic to vinylic isomers was estimated to be 3:1 by ${}^{31}P$ NMR. This phenomenon has been commonly observed in indene derivatives.[14] The solid-state IR spectrum displayed characteristic absorptions of P═O at 1397 $cm^{-1}$ and B−H at 2593 $cm^{-1}$.[13a,15]

An X-ray analysis revealed that **2** crystallized in favor of an allylic isomer in which the P atom is bonded to the $sp^3$ C of the indenyl group with a P(1)−C(17) distance of 1.830(2) Å. Figure 1 shows one of the two crystallographically independent molecules in the unit cell. Selected bond distances and angles are given in Table 2. The P−N distance of 1.632(2) Å is much shorter than the corresponding value of 1.673(2) Å observed in its parent compound **1**, suggesting a stronger $N(p\pi)\rightarrow P(d\pi)$ interaction. This result is consistent with the ${}^{31}P$ NMR data. The C(17)−C(18) distance of 1.432(5) Å and C(18)−C(19) distance of 1.369(5) Å are indicative of single and double bonds, respectively. The P═O distance of 1.484(1) Å and the P(1)−C(1) distance of 1.877(2) Å are comparable to the corresponding values of 1.484(5) and 1.811(7) Å found in $[NBu_4][7\text{-}P(O)Ph_2\text{-}8\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10}]$.[16]

**Amide Complexes.** Our previous work showed that interactions of the group 4 metal dialkylamides $M(NR_2)_4$ with the protic reagents $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ (A = C, Si) and ${}^{i}Pr_2NA'(C_9H_7)(C_2B_{10}H_{11})$ (A′ = B, P) in toluene resulted in the clean formation of $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2$[17] and $[\eta^5{:}\sigma\text{-}{}^{i}Pr_2NA'(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2$,[7b,18] respectively. We attempted to prepare the corresponding pentavalent phosphorus-bridged complexes for studies on ansa effects. Treatment of **2** with 1 equiv of $M(NR_2)_4$ in toluene at room temperature gave the unexpected products $[\sigma{:}\sigma\text{-}{}^{i}Pr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2(L)$ (R = Me, L = $HNMe_2$, M = Ti (**3**), Zr (**4**), Hf (**5**); R = Et, L = THF, M = Hf (**6**)) in good yields (Scheme 1). They represent new types of group 4 metal complexes. These reactions proceeded much more quickly than those of $M(NR_2)_4$ with ${}^{i}Pr_2NP(C_9H_7)(C_2B_{10}H_{11})$.[7b]

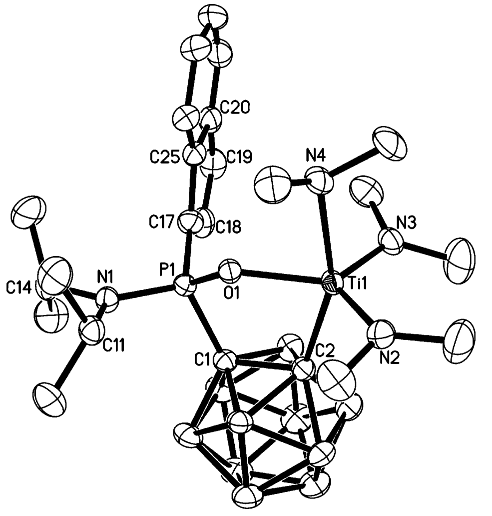

**Figure 2.** Molecular structure of $[\sigma{:}\sigma\text{-}{}^{i}Pr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2(HNMe_2)$ (**3**).

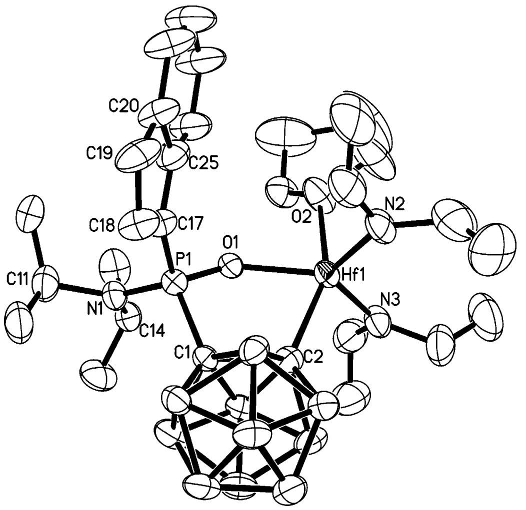

**Figure 3.** Molecular structure of $[\sigma{:}\sigma\text{-}{}^{i}Pr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})]Hf(NEt_2)_2(THF)$ (**6**).

Only one resonance at about 43.5 ppm was observed in the ${}^{31}P$ NMR spectra of **3**−**6**, which was shifted downfield of that for **2**. Their ${}^{11}B$ NMR spectra exhibited two types of splitting patterns, 1:2:2:3:2 for **3** and 1:1:1:2:2:3 for **4**−**6**. Unique P═C ${}^{13}C$ chemical shifts were observed at ca. 78 ppm in the ${}^{13}C$ NMR spectra of **3**−**6** with a large one-bond coupling to phosphorus (${}^{1}J_{PC}$ = 117−142 Hz).[19]

Single-crystal X-ray analyses revealed that **3** and **4** are isomorphous and isostructural. Figure 2 shows the representative structure of **3**. The molecular structure of **6** is shown in Figure 3. The coordination geometry around the central metal atom is basically the same except for the coordinated Lewis base: $Me_2NH$ in **3** and **4** and THF in **6**.

The sums of angles around the N(4) atom of 337.2° in **3** and 337.4° in **4** associated with the corresponding long M−N(4) distances of 2.252(3) Å in **3** and 2.375(7) Å in **4** indicate that the N(4) atom is from the coordinated amine molecule. The N(1), N(2), and N(3) atoms in **3**, **4**, and **6** are all planar,

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(13) (a) The ${}^{31}P$ chemical shifts are 22.3 ppm for [HC(3-methylindolyl)$_3$]P and −11.4 ppm for [HC(3-methylindolyl)$_3$]P═O; see: Barnard, T. S.; Mason, M. R. *Organometallics* **2001**, *20*, 206. (b) Balema, V. P.; Blaurock, S.; Hey-Hawkins, E. *Polyhedron* **1998**, *18*, 545.

(14) Malefetse, T. J.; Swiegers, G. F.; Coville, N. J.; Fernandes, M. A. *Organometallics* **2002**, *21*, 2898.

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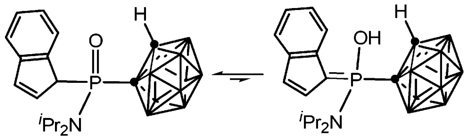
suggestive of the presence of N(p$\pi$)−M(d$\pi$) or N(p$\pi$)−P(d$\pi$) interactions. The M−N(2,3) and M−C(cage) distances (Table 2) are very close to the corresponding values[20a] observed in [$\eta^5$:$\sigma$-$Me_2A(C_9H_6)(C_2B_{10}H_{10})$]$M(NR_2)_2$ (A = C, Si),[17] [$\eta^5$:$\sigma$-$^iPr_2NA'(C_9H_6)(C_2B_{10}H_{10})$]$M(NR_2)_2$ (A′ = B, P),[7b,18] [$\eta^5$:$\sigma$-$Me_2Si(C_5Me_4)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$,[20b] [$\eta^5$:$\sigma$-$PhHC(C_5H_4)(SC_2B_{10}H_{10})$]$Ti(NMe_2)_2$,[20c] and [$\eta^1$:$\eta^5$-$(C_6H_5CH_2)_2N(CH_2CH_2)$-$C_2B_9H_{10}$]$Ti(NMe_2)_2$.[20d] The bond distances and angles around the P atom in these structures are almost identical. The P−O distances (1.541(2)−1.549(6) Å) are much longer than that of 1.484(1) Å in **2**, whereas the P−C(17) distances (1.692(1)−1.717(4) Å) are significantly shorter than that of 1.830(2) Å in **2**. These data, together with the planar geometry of C(17), confirm the formation of a P(1)═C(17) double bond. The measured values are almost the same as the reported P═C double-bond distance of 1.718(2) Å in $Ph_3P(C_5H_4)$.[21] Alternating single and double bonds within the $C_5$ ring are also observed in all three metal complexes. The Ti−O distance of 1.983(2) Å in **3** and the Zr−O distance of 2.095(6) Å in **4** are comparable to the corresponding values of 1.953(5) Å in $Cp_2Ti(P_2S_4O_2(OEt)_2)$[22a] and 2.004(4) Å in [(Me){Zr(Me)($\eta^5$-$C_5H_5)_2$(O)}P]-Mo[N(C($CD_3)_2$Me)-$C_6H_3Me_2$-3,5]$_3$.[22b]

It was reported that the compounds [Ph(E)P($\eta^5$-$C_5Me_4)_2$]$MX_2$ (E = O. S, Se; X = Cl, CO, Me, $Se_{1.5}$, $Te_{1.5}$) were stable, and no isomerization was observed.[5] The formation of **3**−**6** did not likely result from the isomerization of initially generated [$\eta^5$:$\sigma$-$^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})$]$M(NR_2)_2$. In view of the much faster rate for the reaction of $M(NR_2)_4$ with **2** than **1**, it is proposed that **3**−**6** were produced directly from the reaction of $M(NR_2)_4$ with the isomer **II**, as shown in Scheme 2. The high oxophilicity of the $M^{4+}$ ion provided the driving force for the reaction.

**Scheme 2**



I II

## Conclusion

The new pentavalent phosphorus-bridged compound $^iPr_2NP(O)(C_9H_7)(C_2B_{10}H_{11})$ (**2**) was conveniently prepared by treatment of $^iPr_2NP(C_9H_7)(C_2B_{10}H_{11})$ (**1**) with excess $H_2O_2$. Compound **1**, however, did not show any activity toward $S_8$, even under forced reaction conditions, due to its poor nucleophilicity. Reactions of **2** with $M(NR_2)_4$ did not give the expected complexes [$\eta^5$:$\sigma$-$^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})$]$M(NR_2)_2$ but, rather, a new type of group 4 metal amides containing an indenylide unit, [$\sigma$:$\sigma$-$^iPr_2NP(O)(C_9H_6)(C_2B_{10}H_{10})$]$M(NR_2)_2$(L) (L = $HNMe_2$, THF). The high oxophilicity of the group 4 metal ion is proposed to be the driving force for the reaction.

**Acknowledgment.** This work was supported by grants from the Research Grants Council of The Hong Kong Special Administration Region (Project No. 403103) and State Key Laboratory of Elemento-Organic Chemistry, Nankai University (Project No. 0314).

**Supporting Information Available:** Crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **2**−**4** and **6** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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