ORGANOMETALLICS

C-P or C-H Bond Cleavage of Phosphine Oxides Mediated by an Yttrium Hydride

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Supporting Information

ABSTRACT: Reactions of the yttrium anilido hydride $[LY(NH(DIPP))(\mu-H)]_2$ (1; L = $[MeC(N(DIPP))CHC-(Me)(NCH_2CH_2NMe_2)]^-$, DIPP = 2,6-ⁱPr₂C₆H₃)) with three phosphine oxides and two phosphine sulfides are reported. The reaction of 1 with Ph₃P=O gives C–P bond cleavage and an yttrium anilido phosphinoyl complex, while those with R₂MeP=O (R = Me, Ph) result in C–H bond



cleavage and two yttrium anilido alkyl complexes. 1 also reacted with $R_3P=S$ (R = Me, Ph), which demonstrated P-S bond cleavage via hydride-based reduction and gave an yttrium anilido sulfide.

B ond cleavage and formation is the focus of synthetic chemistry. There are numerous examples concerning C– $H_{,1}^{1}$ C–O,² C–N,³ and C–S⁴ bond cleavage mediated by transition-metal complexes. In comparison, the examples of transition-metal-mediated C–P bond cleavage are fewer, and most of these involve the C–P bond cleavage of PR₃ (R = aryl or alkyl group).⁵

The phosphine oxides $(R_3P=O)$ are an important class of organophosphorus compounds.⁶ Due to the stability of phosphine oxides, they are commonly used as neutral dative ligands in transition-metal complexes.⁷ There are a few examples of phosphine oxides acting as oxygen-transfer reagents with P–O bond cleavage.⁸ The C–P bond cleavage of phosphine oxides mediated by transition-metal complexes has been rarely observed, and most of the examples involve the oxidative addition of low-valent palladium to the C–P bond.⁹ Herein we present reactions of an yttrium anilido hydride with three phosphine oxides and two phosphine sulfides. Depending on the substrates, C–P, C–H, or P–S bond cleavage was observed.

RESULTS AND DISCUSSION

Reaction of 1 with Ph₃P=O. When the yttrium anilido hydride $[LY(NH(DIPP))(\mu-H)]_2$ (1; L = $[MeC(N(DIPP))-CHC(Me)(NCH_2CH_2NMe_2)]^-$, DIPP = 2,6-ⁱPr₂C₆H₃)¹⁰ was mixed with 2 equiv of triphenylphosphine oxide (Ph₃P=O) in C₆D₆ at room temperature, the reaction solution turned from pale yellow to brown immediately and to pale yellow again within 2 min. ¹H NMR spectroscopic monitoring of the reaction showed that 1 was mostly converted into the new complex 2 in 1 h with concomitant formation of a minor amount of other intractable contaminants. ³¹P{¹H} NMR spectroscopy revealed the disappearance of Ph₃P=O and the formation of a new phosphorus compound which displays a doublet at 91.7 ppm with a characteristic ²J_{Y-P} coupling constant of 5.2 Hz. A subsequent scaled-up reaction in toluene provided **2** as a white crystalline solid in 56% yield. Complex **2** was characterized by NMR spectroscopy (¹H, ¹³C, and ³¹P-{¹H}), elemental analysis, and single-crystal X-ray diffraction, confirming that **2** is an yttrium anilido phosphinoyl complex, as shown in Scheme 1. Thus, in the reaction of **1** with Ph₃P==O,



one $C^{Ph}-P$ bond of $Ph_3P=O$ is cleaved and a $[O-PPh_2]^$ anion is formed. To the best of our knowledge, **2** is the first rare-earth-metal diorganophosphinoyl complex. It is noteworthy that the reaction of the rare-earth-metal hydride $[Cp*_2Sm(\mu-H)]_2$ with $Ph_3P=O$ results in $o \cdot C^{Ph}-H$ bond cleavage and the cyclometalated product $[Cp*_2SmC_6H_4P(O)-Ph_2]$.¹¹ It is also noteworthy that Hill and co-workers recently reported that the reaction of $\{Ca[N(SiMe_3)_2]_2(OPPh_3)_2\}$ or $\{Ca[CH(SiMe_3)_2]_2(OPPh_3)_2\}$ with PhSiH₃ occurred to give $C^{Ph}-P$ bond cleavage, in which the calcium hydride was proposed as the reaction intermediate.¹² As a consequence of the formation of **2**, C_6H_6 was observed when we carried out the reaction of **1** with 2 equiv of $Ph_3P=O$ in d_8 -toluene (Figure S13, Supporting Information).

 Received:
 May 2, 2012

 Published:
 June 5, 2012

The molecular structure of 2 is shown in Figure 1. The most interesting structural feature of 2 is the monoanionic



Figure 1. Molecular structure of **2** with ellipsoids set at the 30% probability level. Isopropyl groups at the DIPP substituents and hydrogen atoms (except the anilide hydrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y–O = 2.121(3), Y–N1 = 2.328(3), Y–N2 = 2.339(3), Y–N3 = 2.489(3), Y–N4 = 2.210(3), P–O = 1.576(3), P–C34 = 1.836(4), P–C40 = 1.837(4), C1–C2 = 1.511(5), C2–C3 = 1.390(5), C3–C4 = 1.398(6), C4–C5 = 1.510(5), C2–N1 = 1.338(5), C4–N2 = 1.325(5); Y–O–P = 151.1(2), O–P–C34 = 104.5(2), O–P–C40 = 103.1(2), C34–P–C40 = 96.2(2), Y–N4–C22 = 152.5(3).

phosphinoyl ligand. The phosphinoyl ligand coordinates to the yttrium center with a Y–O bond of 2.121(3) Å, which falls in the range 2.02–2.15 Å observed for Y–O single bonds in yttrium alkyloxy/aryloxy complexes.¹³ The phosphorus atom of the phosphinoyl ligand is pyramidal (O–P–C34 = 104.5(2)°, O–P–C40 = 103.1(2)°, C34–P–C40 = 96.2(2)°; $\sum = 303°$) with a lone electron pair situated at the top of the pyramid. The distance from the phosphorus atom to the yttrium center, 3.58 Å, is long, indicating that there is no interaction between the lone electron pair of phosphorus and the empty d orbital of yttrium. The P–O bond (1.576(3) Å), which is significantly longer than the P=O double bond in Ph₃P=O (1.499(2) Å),¹⁴ is consistent with a single bond. The P–C^{ipso} bond lengths (1.836(4) and 1.837(4) Å) are close to those in Ph₃P= O (1.798–1.801 Å).¹⁴

Reactions of 1 with MeR₂P=O (R = Me, Ph). To investigate the influence of the substituents on the phosphorus atom in the reaction, the reactions of 1 with Me₃P=O and MePh₂P=O were studied. ¹H NMR spectroscopic monitoring of the reaction of 1 with 2 equiv of Me₃P=O or MePh₂P=O in C_6D_6 showed that 1 was almost completely converted into the new complex 3 or 4 in 15 or 45 min at room temperature, and the formation of hydrogen gas (H_2) was observed (4.47) ppm). In the ${}^{31}P{}^{1}H$ NMR spectra, the signal for Me₃P=O or MePh₂P=O disappeared, while a new signal at 53.1 ppm for the reaction with Me₃P=O or at 47.7 ppm for the reaction with Ph₂MeP=O was observed. Subsequent scaled-up reactions in toluene provided 3 and 4 as white crystalline solids in 70% and 58% yields, respectively. Complexes 3 and 4 were characterized by NMR spectroscopy (¹H, ¹³C, and ³¹P{¹H}), elemental analysis, and single-crystal X-ray diffraction, which revealed that 3 and 4 are the yttrium anilido alkyl complexes (Scheme 2). Therefore, in the reaction of 1 with Me₃P=O or MePh₂P=O, one C-H bond on the methyl

group of $MeR_2P = O(R = Me, Ph)$ is cleaved instead of the C-P bond.



The molecular structures of **3** and **4** are shown in Figure 2. In **3** and **4**, the monoanionic ligand $[R_2P(O)CH_2]^-$ coordinates to the yttrium center in a $\kappa^2(C,O)$ manner. The Y–O bonds in **3** and **4** (2.307(2) and 2.323(3) Å) are much longer than that in **2** (2.121(3) Å), because the O atom acts as a neutral donor in **3** and **4** but as an anionic donor in **2**. The Y–C bond lengths in **3** and **4** are 2.585(2) and 2.604(4) Å, respectively. The P–O bond (1.548(2) Å for **3**, 1.538(3) Å for **4**) is shorter than the P–O single bond in **2** (1.576(3) Å) and longer than the P=O double bond in Ph₃P=O (1.499(2) Å).¹⁴

Reactions of 1 with R₃P=S (R = Ph, Me). The reaction of 1 with triphenylphosphine sulfide (Ph₃P=S) was also studied. The reaction of 1 with 2 equiv of Ph₃P=S in C₆D₆ led to nearly complete conversion of 1 into the new complex 5 at room temperature in 15 min with concomitant formation of PPh₃ (-5.3 ppm in the ³¹P{¹H} NMR spectrum) and H₂ (4.47 ppm in the ¹H NMR spectrum) and unreacted Ph₃P=S. No further transformation was observed when the reaction time was extended to 12 h. A subsequent scaled-up reaction in toluene with a reactant molar ratio of 1:1 provided 5 as a pale yellow crystalline solid in 82% yield. Complex 5 was characterized by NMR spectroscopy (¹H and ¹³C), elemental analysis, and single-crystal X-ray diffraction, confirming that 5 is an yttrium anilido sulfide (Scheme 3).

The foregoing observation revealed that the reaction is a hydride-based reduction, as shown in Scheme 4,¹⁵ and the P–S bond of Ph₃P=S was cleaved in this case. The molecular structure of **5** is shown in Figure 3. In **5**, the two yttrium centers are bridged by a μ -S²⁻ ligand. Y1–S and Y2–S bond lengths are 2.548(1) and 2.545(1) Å, respectively, which are obviously shorter than those in the μ_3 -S²⁻ yttrium(III) complex [(Cp₂Y)₂(μ^3 -S)(thf)]₂ (2.63–2.70 Å).¹⁶ The Y1–S–Y2 angle is 165.72(5)°. The reaction of **1** with Me₃P=S proceeded in a same way as that with Ph₃P=S, and ¹H NMR spectroscopic monitoring of the reaction in C₆D₆ showed the formation of **5**, PMe₃, and H₂ (Figure S12, Supporting Information).

In summary, reactions of the yttrium anilido hydride 1 with three phosphine oxides (Ph₃P=O, Me₃P=O, and MePh₂P=O) and two phosphine sulfides (Ph₃P=S and Me₃P=S) show diverse reaction patterns. Depending on the substrate, C-P, C-H, or P-S bond cleavage was observed. It is noteworthy that the reaction of 1 with Ph₃P=O gives the first example of a rare-earth-metal diorganophosphinoyl complex via C-P bond cleavage.

EXPERIMENTAL SECTION

General Procedures. All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen-filled glovebox. Toluene, hexane, C_6D_6 , and d_8 -toluene were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. Ph₃P=O,



Figure 2. Molecular structures of 3 and 4 with ellipsoids set at the 30% probability level. Isopropyl groups of the DIPP substituents and hydrogen atoms (except the anilide hydrogen atoms) have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for 3: Y-O = 2.307(2), Y-C36 = 2.585(2), Y-N1 = 2.405(2), Y-N2 = 2.314(2), Y-N3 = 2.615(2), Y-N4 = 2.242(2), O-P = 1.548 (2), P-C34 = 1.795(3), P-C35 = 1.791(3), P-C36 = 1.721(2), C1-C2 = 1.520(3), C2-C3 = 1.421(3), C3-C4 = 1.409(4), C4-C5 = 1.523(4), C2-N1 = 1.324(3), C4-N2 = 1.322(3); Y-C36-P = 86.5(9), C36-P-O = 106.8(1), P-O-Y = 101.1(8), O-Y-C36 = 64.6(6), C34-P-C35 = 106.0(1). Selected bond lengths (Å) and angles (deg) for 4: Y-O = 2.323(3), Y-C34 = 2.604(4), Y-N1 = 2.370(4), Y-N2 = 2.363(4), Y-N3 = 2.496(4), Y-N4 = 2.265(4), P-O = 1.538(3), P-C34 = 1.721(4), P-C35 = 1.817(5), P-C41 = 1.809(4), C1-C2 = 1.507(6), C2-C3 = 1.401(7), C3-C4 = 1.405(7), C4-C5 = 1.509(7), C2-N1 = 1.347(6), C4-N2 = 1.316(6); Y-C34-P = 86.2(2), C34-P-O = 106.9(2), P-O-Y = 101.2(1), O-Y-C34 = 63.9(1), C35-P-C41 = 106.3(2).







Me₃P==O, MePh₂P==O, and Ph₃P==S were purchased from Alfa-Aesar and used without further purification. Me₃P==S was preapred from the reaction of PMe₃ with S. The yttrium anilido hydride 1 was synthesized as we previously reported.¹⁰ ¹H, ¹³C, and ³¹P{¹H} NMR spectra were recorded on a Varian Mercury 300 MHz or a Varian 400 MHz spectrometer. All chemical shifts are reported in δ units with reference to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts and to external H₃PO₄ (85%) for phosphorus chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

[LY(NH(2,6-ⁱ**Pr**₂-**C**₆**H**₃)**(OPPh**₂)] (2). Ph₃P=O (46.8 mg, 0.168 mmol) in 1 mL of toluene was added to 1 (100 mg, 0.084 mmol) in 3 mL of toluene at room temperature. The reaction solution turned from pale yellow to brown immediately and to pale yellow again within 5 min. After the reaction solution stood at room temperature for 2 h, the volatiles were removed under vacuum to give a yellow solid. The solid was extracted with hexane (2 × 2 mL), and the extract was cooled to -35 °C to afford **2** as a white crystalline solid (117 mg, 0.094 mmol, 56% yield). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 7.60 (m, 2H, ArH), 7.31 (m, 2H, ArH), 7.21–7.17 (m, 4H, ArH), 7.13–7.00 (m, 7H, ArH), 6.88 (t, ³J_{H-H} = 7.6 Hz, 1H, ArH), 4.92 (s, 1H, MeC(N)CH), 4.87 (br, 1H, Y–NHDIPP), 3.37 (sept, ³J_{H-H} = 6.8 Hz, 1H, ArCHMe₂), 3.04–2.86 (m, 4H, ArCHMe₂ and NCH₂), 2.75 (m, 1H, NCH₂), 2.27 (m, 1H, NCH₂), 2.13 (s, 3H, NMe₂), 2.03 (s, 3H, NMe₂), 1.96 (m, 1H, NCH₂), 1.68 (s, 3H, MeC), 1.57 (s, 3H)

Figure 3. Molecular structure of **5** with ellipsoids set at the 30% probability level. Isopropyl groups of the DIPP substituents, hydrogen atoms (except the anilide hydrogen atoms), and solvent molecules in the lattice have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-S = 2.548(1), Y2-S = 2.545(1), Y1-N1 = 2.356(3), Y1-N2 = 2.337(3), Y1-N3 = 2.515(3), Y1-N4 = 2.205(3), Y2-N5 = 2.346(3), Y2-N6 = 2.337(3), Y2-N7 = 2.507(3), Y2-N8 = 2.219(3), C1-C2 = 1.507(5), C2-C3 = 1.399(5), C3-C4 = 1.405(5), C4-C5 = 1.523(5), C2-N1 = 1.333(5), C4-N2 = 1.334(5), C33-C34 = 1.507(5), C34-C35 = 1.396(5), C35-C36 = 1.402(5), C36-C37 = 1.519(5), C34-N5 = 1.339(5), C36-N6 = 1.327(5); Y1-S-Y2 = 165.72(5), Y1-N4-C22 = 151.3(3), Y2-N8-C54 = 152.1(3).

MeC), 1.40 (d, ${}^{3}J_{H-H} = 7.2$ Hz, 6H, ArCHMe₂), 1.32 (d, ${}^{3}J_{H-H} = 6.4$ Hz, 6H, ArCHMe₂), 1.26 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂), 1.23 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂), 1.23 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂), 1.09 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂). 13 C NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 167.6, 166.7 (imine C), 151.7 (d, ${}^{3}J_{P-C} = 4.4$ Hz, C^{meta} of P–Ph), 150.8 (d, ${}^{1}J_{P-C} = 29.0$ Hz, C^{ipso} of P–Ph), 150.1 (d, ${}^{1}J_{P-C} = 28.8$ Hz, C^{ipso} of P–Ph), 150.0, 143.7, 143.3, 142.6, 133.1 (ArC), 129.8 (d, ${}^{2}J_{P-C} = 23.2$ Hz, C^{ortho} of P–Ph), 129.2 (d, ${}^{2}J_{P-C} = 23.8$ Hz, C^{ortho} of P–Ph), 127.5, 126.3 (ArC), 124.6 (d, ${}^{3}J_{P-C} = 3.0$ Hz, C^{meta} of P–Ph), 122.9, 115.4 (ArC), 99.0 (MeC(N)CH), 58.1, 47.6, 46.0, 43.6 (NCH₂ and NMe₂), 31.9, 30.4, 28.7, 28.5, 25.2, 24.9,

24.8, 24.3, 24.2, 24.1, 23.7, 23.6, 23.0 (ArⁱPr and MeC). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) 91.7 (d, ²J_{Y-P} = 5.2 Hz, Y-OPPh₂). Anal. Calcd for C₄₅H₆₂N₄OPY: C, 68.00; H, 7.86; N, 7.05. Found: C, 68.79; H, 7.94; N, 7.27.

 $[LY(NH(2,6^{-i}Pr_2-C_6H_3)(\kappa^2(C,O)-CH_2P(O)Me_2)]$ (3). Me₃P=O (15.5 mg, 0.168 mmol) in 1 mL of toluene was added to 1 (100 mg, 0.084 mmol) in 2 mL of toluene at -35 °C. Evolution of gas (H₂) was observed immediately. After the reaction solution stood at room temperature for 1 h, the volatiles were removed under vacuum to give a pale orange solid. The solid was washed with cold hexane (3×0.5) mL) and dried under vacuum to afford 3 as a white crystalline solid (80.6 mg, 0.117 mmol, 70% yield). Some ¹H, ¹³C, and ³¹P NMR signals of the complex are broad at 25 °C and become sharp at 60 °C. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) 7.16–7.13 (m, 5H, ArH), 6.81 (t, ${}^{3}J_{H-H} = 7.6$ Hz, 1H, ArH), 4.92 (s, 1H, MeC(N)CH), 4.18 (br, 1H, Y-NHDIPP), 3.90 (br, 1H, ArCHMe2 or NCH2), 3.50-2.95 (br, 5H, ArCHMe2 and NCH2), 2.13 (s, 3H, NMe2), 2.00 (br, 3H, NMe₂), 1.76 (s, 3H, MeC), 1.72 (br, 1H, ArCHMe₂ or NCH₂), 1.69 (s, 3H, MeC), 1.60-0.80 (m, 30H, ArCHMe2 and PMe2), 0.44 (br, 2H, YCH₂P(O)). ¹H NMR (400 MHz, C₆D₆, 60 °C): δ (ppm) 7.14–7.09 (m, 5H, ArH), 6.74 (t, ${}^{3}J_{H-H} = 7.2$ Hz, 1H, ArH), 4.92 (s, 1H, MeC(N)CH), 4.23 (br, 1H, Y-NHDIPP), 3.79 (br, 1H, ArCHMe, or NCH₂), 3.40–3.14 (br, 2H, ArCHMe₂ or NCH₂), 3.08–2.96 (br, 2H, ArCHMe₂ or NCH₂), 2.08 (br, 6H, NMe₂), 1.85 (m, 1H, ArCHMe₂ or NCH₂), 1.79 (s, 3H, MeC), 1.69 (s, 3H, MeC), 1.43 (d, ${}^{3}J_{H-H} = 6.4$ Hz, 3H, ArCHMe₂), 1.38–1.14 (br, 15H, ArCHMe₂), 1.09 (\hat{d} , ${}^{3}J_{H-H}$ = 6.8 Hz, 3H, ArCHMe₂), 1.04 (br, 3H, ArCHMe₂), 0.42 (s, 2H, YCH₂P(O)). ¹³C NMR (100 MHz, C₆D₆, 60 °C): δ (ppm) 165.2 (imine C), 152.8, 144.3, 133.6, 133.4, 125.8, 124.8, 123.7, 122.9, 114.4 (ArC), 96.6 (MeC(N)CH), 59.7, 47.4 (NCH₂ and NMe₂), 28.3 (d, ${}^{1}J_{P-C} = 23.6 \text{ Hz}, \text{ PMe}_{2}$, 25.1, 25.0, 24.9, 24.6, 24.4, 24.1, 24.0, 22.3, 20.6, 20.3, 18.7, 18.1 (MeC or ArⁱPr), 15.5 (dd, ${}^{1}J_{Y-C} = 60.8$ Hz, ${}^{1}J_{P-C}$ = 17.1 Hz, Y-CH₂P). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) 53.1 (s, Y-CH₂P(O)). ³¹ $P{^1H}$ NMR (162 MHz, C₆D₆, 60 °C): δ (ppm) 52.9 (d, ${}^{2}J_{Y-P} = 6.4$ Hz, Y–CH $_{2}P(O)$). Anal. Calcd for C36H60N4OPY: C, 63.14; H, 8.83; N, 8.18. Found: C, 62.66; H, 9.07; N. 8.02

[LY(NH(2,6-^{*i*}Pr₂-C₆H₃)($\kappa^{2}(C,O)$ -CH₂P(O)Ph₂)] (4). 4 was obtained by the procedure described for 3, but with 1 (100 mg, 0.084 mmol) and MePh₂P=O (36 mg, 0.168 mmol), as a white crystalline solid (79.2 mg, 0.098 mmol, 58% yield). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ (ppm) 7.93 (m, 2H, ArH), 7.74 (m, 2H, ArH), 7.08 (m, 11H, ArH), 6.77 (t, ${}^{3}J_{H-H} = 7.2$ Hz, 1H, ArH), 4.60 (s, 1H, MeC(N)CH), 4.29 (br s, 1H, Y–NHDIPP), 4.03 (sept, ${}^{3}J_{H-H} = 7.2$ Hz, 1H, ArCHMe₂), 3.28-3.10 (m, 3H, ArCHMe₂ and NCH₂), 2.89 (m, 1H, NCH2), 2.30 (s, 3H, NMe2), 2.10 (s, 3H, NMe2), 1.89 (m, 1H, NCH₂), 1.62 (s, 3H, MeC), 1.47 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 3H, ArCHMe₂), 1.20 (l 1.35 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 3H, ArCHMe₂), 1.32 (s, 3H, MeC), 1.30 (d, ³J_{H-H} = 6.9 Hz, 3H, ArCHMe₂), 1.16–1.06 (m, 17H, ArCHMe₂ and Y–CH₂P). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ (ppm) 164.4, 162.9 (imine C), 152.5 (d, ³J_{P-C} = 3.7 Hz, C^{meta} of P–Ph), 152.4, 147.7, 144.1, 141.9 (ArC), 139.4 (d, ${}^{1}J_{P-C}$ = 39.9 Hz, C^{ipso} of P-Ph), 138.1 (d, ${}^{1}J_{P-C} = 43.9$ Hz, C^{ipso} of P–Ph), 131.2 (d, ${}^{2}J_{P-C} = 10.5$ Hz, C^{ortho} of P–Ph), 130.8 (d, ${}^{3}J_{P-C} = 1.8$ Hz, C^{meta} of P–Ph), 130.7 (d, ${}^{2}J_{P-C} = 10.3$ Hz, C^{ortho} of P–Ph), 130.3 (d, ${}^{3}J_{P-C} = 1.6$ Hz, C^{meta} of P–Ph), 130.7 (d, ${}^{2}J_{P-C} = 10.3$ Hz, C^{ortho} of P–Ph), 130.3 (d, ${}^{3}J_{P-C} = 1.6$ Hz, C^{meta} of P–Ph), 125.8, 124.8, 123.4, 122.9, 114.4 (ArC), 96.5 (MeC(N)CH), 59.8, 47.0, 46.3, 43.6 (NCH₂ and NMe₂), 28.8, 27.9, 25.2, 25.1, 24.8, 24.7, 24.3, 22.1 (ArⁱPr and $\tilde{M}eC$), 11.8 (dd, ${}^{1}J_{Y-C}$ = 68.0 Hz, ${}^{1}J_{P-C}$ = 16.4 Hz; Y–CH₂P). ³¹P{¹H} NMR (121 MHz, C₆D₆, 25 °C): δ (ppm) 47.7 (d, ${}^{2}J_{Y-P} = 8.4$ Hz; Y–CH₂P(O)). Anal. Calcd for C₄₆H₆₄N₄OPY: C, 68.30; H, 7.97; N, 6.93. Found: C, 68.46; H, 8.04; N, 6.78.

[(LY(NHDIPP))₂(μ -S)] (5). Ph₃P=S (24.5 mg, 0.084 mmol) in 0.5 mL of toluene was added to 1 (100 mg, 0.084 mmol) in 2 mL of toluene at -35 °C. Evolution of gas (H₂) was observed immediately. After the reaction solution stood at room temperature for 30 min, the volatiles were removed under vacuum to give a pale yellow solid. The solid was recrystallized in a mixture of toluene and hexane to afford 5 as colorless crystals (82.0 mg, 0.0672 mmol, 82% yield). 5 exists as the two isomers **A** and **B** with an **A**:**B** ratio of of 1:0.2 at room temperature in C₆D₆ solution. Repeated recrystallization did not change the ratio of

two isomers. The A:B ratio changes from 1:0.2 to 1:0.3 when the complex's C₆D₆ solution temperature is increased from 25 to 80 °C and goes back to 1:0.2 when the solution temperature is decreased to 25 °C. The NMR spectral data of the major isomer A are presented here. ¹H NMR (400 MHz, $C_6 D_{62} 25 \text{ °C}$): δ (ppm) 7.19 (d, ³ $J_{H-H} = 7.6$ Hz, 2H, ArH), 7.01 (m, 3H, ArH), 6.85 (t, ${}^{3}J_{H-H} = 7.6$ Hz, 1H, ArH), 4.91 (s, 1H, MeC(N)CH), 4.85 (s, 1H, Y-NHDIPP), 3.64 (sept, ${}^{3}J_{H-H}$ = 6.8 Hz, 1H, ArCHMe₂), 3.17 (sept, ${}^{3}J_{H-H}$ = 6.4 Hz, 1H, ArCHMe₂), 3.07 (m, 1H, NCH₂), 2.98-2.88 (m, 4H, NCH₂ and ArCHMe2), 2.08 (s, 3H, NMe2), 1.77 (s, 3H, NMe2), 1.71 (s, 3H, MeC), 1.65 (m, 1H, NCH₂), 1.59 (s, 3H, MeC), 1.46 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 6H, ArCHMe₂), 1.44 (d, ${}^{3}J_{H-H}$ = 6.8 Hz, 6H, ArCHMe₂), 1.43 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂), 1.29 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂), 1.18 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂), 1.13 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂). 1.13 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, ArCHMe₂). 13 C NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 167.0, 166.4 (imine C), 152.2, 145.8, 144.0, 143.0, 132.9, 129.3, 128.5, 125.6, 125.3, 124.5, 124.0, 122.9, 114.8 (ArC), 99.0 (MeC(N)CH), 56.9, 50.2, 47.8, 43.1 (NCH₂ and NMe₂), 30.2, 28.1, 28.0, 25.7, 25.3, 24.8, 24.6, 24.3, 24.2, 23.1 (ArⁱPr and MeC). Anal. Calcd for C₆₆H₁₀₄N₈SY₂·C₇H₈: C, 66.85; H, 8.61; N, 8.54. Found: C, 66.50; H, 8.64; N, 8.57.

X-ray Crystallography. Suitable single crystals of 2–5 were mounted under a nitrogen atmosphere on a glass fiber, and data collection was performed at 133(2) K on a Bruker APEX2 diffractometer with graphite-monochromated Mo K α radiation ($\lambda =$ 0.71073 Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculations. All calculations were carried out using the SHELXL-97 program. The software used is given in ref 17. Crystallographic data and refinement details for 2–5 are given in Table S1 (Supporting Information).

ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for 2-5, a table giving crystallographic data and refinement parameters for 2-5, and figures giving NMR spectra of 2-5 and ¹H NMR spectra of the reaction of 1 with 1 equiv of Me₃P=S in C₆D₆ and the reaction of 1 with 2 equiv of Ph₃P=O in d_8 -toluene. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the State Key Basic Research & Development Program (Grant No. 2011CB808705), the National Natural Science Foundation of China (Grant Nos. 21072209, 21132002, and 21121062), and the Chinese Academy of Sciences.

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