

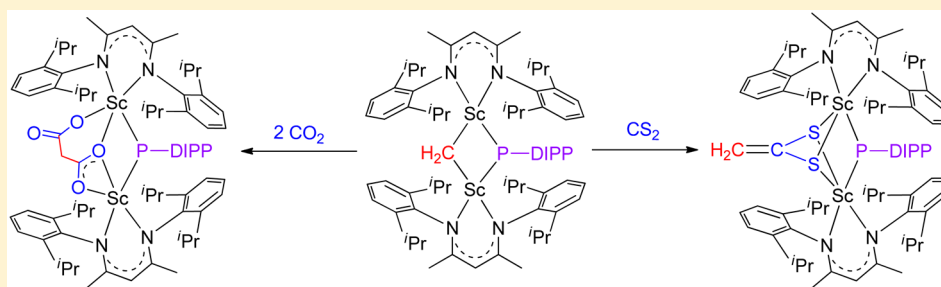
A Scandium Complex Bearing Both Methylidene and Phosphinidene Ligands: Synthesis, Structure, and Reactivity

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S Supporting Information



ABSTRACT: The scandium complex bearing both methylidene and phosphinidene ligands, $[(\text{LSc})_2(\mu_2\text{-CH}_2)(\mu_2\text{-PDIPP})]$ ($\text{L} = [\text{MeC}(\text{NDIPP})\text{CHC}(\text{NDIPP})\text{Me}]^-$, $\text{DIPP} = 2,6\text{-(}i\text{Pr)}_2\text{C}_6\text{H}_3$) (**2**), has been synthesized, and its reactivity has been investigated. Reaction of scandium methyl phosphide $[\text{LSc}(\text{Me})\{\text{P}(\text{H})\text{DIPP}\}]$ with 1 equiv of scandium dimethyl complex $[\text{LScMe}_2]$ in toluene at 60 °C provided complex **2** in good yield, and the structure of complex **2** was determined by single-crystal X-ray diffraction. Complex **2** easily undergoes nucleophilic addition reactions with CO_2 , CS_2 , benzonitrile, and *tert*-butyl isocyanide. In the above reactions, the unsaturated substrates insert into the $\text{Sc}\text{--}\text{C}(\text{methylidene})$ bond to give some interesting dianionic ligands while the $\text{Sc}\text{--}\text{P}(\text{phosphinidene})$ bond remains untouched. The bonding situation of complex **2** was analyzed using DFT methods, indicating a more covalent bond between the scandium ion and the phosphinidene ligand than between the scandium ion and the methylidene ligand.

INTRODUCTION

Alkylidene (or carbene) and phosphinidene complexes of transition metals have attracted intense interest and been extensively studied in the past decades.^{1,2} The research on such complexes has revealed rich reactivity and applications in group-transfer and catalytic reactions. One exception is those complexes with rare-earth metal (Sc, Y, and lanthanide metal) ions. Rare-earth metal ions are among the hardest Lewis acids, whereas alkylidene and phosphinidene ligands are soft Lewis bases; thus, the rare-earth metal–alkylidene (or phosphinidene) coordination is mismatched based on the Pearson's HSAB principle.³ Up to now, the rare-earth metal alkylidene and phosphinidene complexes remain limited.^{4–6} The reactivity study showed that most of the rare-earth metal alkylidene and phosphinidene complexes can react as the alkylidene or phosphinidene transfer agents with ketones to give alkenes or phosphalkenes.⁴ It was also found that some of the rare-earth metal alkylidene and phosphinidene complexes undergo nucleophilic addition reactions with unsaturated substrates, such as CO, isocyanate, carbodiimide, and isocyanide.^{5k,l,6f,g}

We have developed a type of β -diketiminato based tridentate ligands, which can stabilize a series of rare-earth metal dialkyl complexes,⁷ and a scandium terminal imido complex.⁸ Recently, we obtained a scandium bridged phosphinidene complex

$[\{\text{MeC}(\text{NDIPP})\text{CHC}(\text{Me})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})_2\}\text{Sc}\{\mu\text{-PC}_6\text{H}_3\text{-(2,6-Me}_2\text{)}\}_2]$ ($\text{DIPP} = 2,6\text{-(}i\text{Pr)}_2\text{C}_6\text{H}_3$), in which the pendant arm of the tridentate ligand is not coordinated to the scandium ion due to the phosphinidene ligand having a strong tendency to bridge two or more rare-earth metal centers.^{6f} Thus, we carried out a study to synthesize a scandium phosphinidene complex supported by the bulky β -diketiminato ligand, $[\text{MeC}(\text{NDIPP})\text{CHC}(\text{NDIPP})\text{Me}]^-$ ($\text{DIPP} = 2,6\text{-(}i\text{Pr)}_2\text{C}_6\text{H}_3$).⁹ During this study, we obtained an unprecedented scandium complex which bears both phosphinidene and methylidene ligands. This scandium methylidene phosphinidene complex reacts with a variety of unsaturated small molecules, and favoring reaction with the methylidene ligand over the phosphinidene ligand.

RESULTS AND DISCUSSION

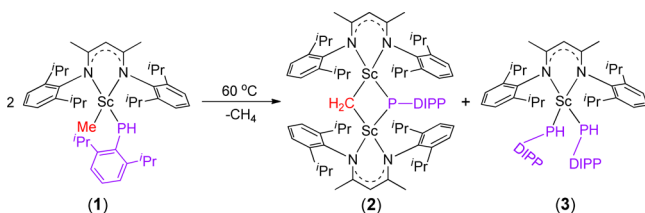
A salt elimination reaction of scandium methyl chloride $[\text{LSc}(\text{Me})\text{Cl}]$ ($\text{L} = [\text{MeC}(\text{NDIPP})\text{CHC}(\text{NDIPP})\text{Me}]^-$, $\text{DIPP} = 2,6\text{-(}i\text{Pr)}_2\text{C}_6\text{H}_3$)¹⁰ with 1 equiv of $\text{K}[\text{P}(\text{H})\text{DIPP}]$ in toluene at room temperature yielded a scandium methyl phosphide $[\text{LSc}(\text{Me})\{\text{P}(\text{H})\text{DIPP}\}]$ (**1**) in 85% yield. Complex **1** was

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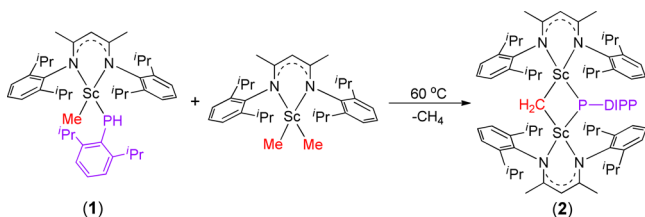
characterized by NMR spectroscopy, and elemental analysis. This complex slowly undergoes a methane elimination in toluene at 60 °C to provide a scandium complex 2 which contains both methylidene and phosphinidene ligands (Scheme 1). Besides the formation of this scandium methylidene

Scheme 1. Thermal Decomposition of Scandium Methyl Phosphide (1)



phosphinidene complex, a scandium diphosphide 3 is also formed. ¹H NMR spectral monitoring of thermal decomposition of complex 1 in C₆D₆ showed that complexes 2 and 3 were formed in about a 1:1 ratio. A reaction of scandium methyl phosphide with 1 equiv of scandium dimethyl complex at 60 °C was subsequently carried out (Scheme 2). Monitoring

Scheme 2. Modified Procedure for the Synthesis of Scandium Methylidene Phosphinidene (2)



the reaction by ¹H NMR spectroscopy in C₆D₆ showed that the complex 2 was generated in nearly quantitative yield. A scaled-up reaction in toluene provided complex 2 in 77% isolated yield. Complexes 2 and 3 were both structurally characterized by single-crystal X-ray diffraction. The molecular structure of 2 is shown in Figure 1, while that of 3 is given in the Supporting Information (Figure S1). Complex 2 exists as a bimetallic complex; each scandium ion adopts a distorted tetrahedral geometry, being coordinated by a β-diketiminato ligand, a μ₂-methylidene ligand, and a μ₂-phosphinidene ligand. Two scandium ions, the carbon atom of the μ₂-methylidene ligand, and the phosphorus atom of the μ₂-phosphinidene ligand are coplanar. The μ₂-methylidene ligand coordinates to two scandium centers with two unequal Sc–C bond lengths of 2.193(3) and 2.232(3) Å, respectively. These Sc–C bonds are significantly shorter than those in the reported scandium complexes containing μ₃-methylidene ligands, such as [(PNP)Sc(μ₃-CH₂)(μ₃-CH₃)₂{Al(CH₃)₂}₂][−] (PNP = [N{2-P(Pr)₂-4-methylphenyl}]₂)[−] (2.317(2) Å)^{5e} and [{(NCN)Sc(μ₂-CH₃)₃(μ₃-CH₃)(μ₃-CH₂)] (NCN = [PhC{NC₆H₄(Pr-2,6)}₂][−]) (2.367 Å on the average).^{5h} It is noteworthy that the small-sized methylidene ligand usually coordinates to three rare-earth metal ions or one rare-earth metal ion and two other metal ions;⁵ the complex 2 represents the first example of a rare-earth metal μ₂-methylidene complex. The μ₂-phosphinidene ligand coordinates to two scandium centers with two nearly equivalent Sc–P bonds; the bond lengths (2.495(1) and 2.508(1) Å) are slightly shorter than those observed for the

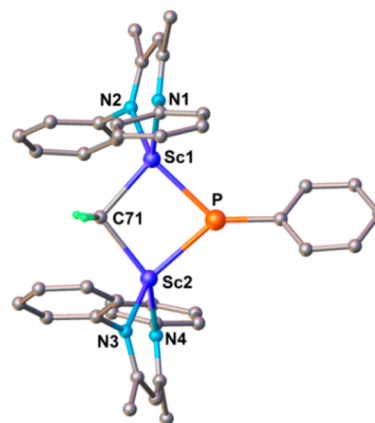


Figure 1. Molecular structure of complex 2 (ball-and-stick representation). DIPP isopropyl groups, hydrogen atoms (except the methylidene hydrogen atoms), and solvents in the lattice were omitted for clarity. Selected bond distances [Å] and angles [deg]: Sc1–N1 2.180(2), Sc1–N2 2.144(2), Sc2–N3 2.147(2), Sc2–N4 2.178(2), Sc1–P 2.495(1), Sc2–P 2.508(1), Sc1–C71 2.193(3), Sc2–C71 2.232(3), Sc1–C71–Sc2 99.76(14), Sc1–P–Sc2 85.10(3).

scandium bridged phosphinidene complexes [{MeC(NDIPP)CHC(Me)NCH₂CH₂N(Pr)₂}Sc{μ-PC₆H₃-(2,6-Me₂)}]₂ (2.523 Å on the average)^{6f} and [(PNP)Sc(μ-P[trip])]₂ (PNP = [N{2-P(Pr)₂-4-methylphenyl}]₂[−], Trip = 2,3,6-(Pr)₃C₆H₂) (2.548 Å on the average).^{6c} The μ₂-methylidene ligand appears as a doublet at δ = 5.62 ppm with a ³J_{P-H} coupling constant of 2.0 Hz in the ¹H NMR spectrum of 2. Finally, the ³¹P NMR spectrum of 2 displays a singlet at δ = 84.1 ppm for the μ₂-phosphinidene ligand, which is dramatically upfield from those observed for [{MeC(NDIPP)CHC(Me)NCH₂CH₂N(Pr)₂}Sc{μ-PC₆H₃-(2,6-Me₂)}]₂ (183.8 ppm) and [(PNP)Sc(μ-P[trip])]₂ (227.4 ppm).

Reaction of complex 2 with CO₂ was monitored by ¹H NMR spectroscopy in C₆D₆. About 50% of 2 was converted into a new complex 4 as the main product when 1 equiv of CO₂ was added. When the amount of CO₂ was increased up to 2 equiv, most of 2 was converted into 4. The reaction was scaled up in toluene, and 3 equiv of CO₂ was used to ensure a complete conversion of 2. Complex 4 was isolated as a dark purple crystalline solid in 50% yield. The ¹H NMR spectrum of the crude product revealed that the complex 4 was formed in high yield; the low isolated yield is due to some loss in the crystallization of the crude product in toluene. Complex 4 was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, confirming that 4 is a scandium phosphinidene dicarboxylate, as shown in Scheme 3. The formation of 4 implies that two CO₂ molecules were activated and inserted into the Sc–CH₂–Sc functional unit during the reaction. In complex 4 (Figure 2), the formed [CH₂(CO₂)₂]^{2−} dianion coordinates to two scandium centers through three oxygen atoms, displaying an asymmetric coordination fashion. The Sc1–O1 bond length (2.008(4) Å) is much shorter than other Sc–O bond lengths (2.174(4), 2.190(4), and 2.219(4) Å, respectively).

Complex 2 reacts with CS₂ at room temperature to provide a new product; the X-ray crystallography analysis (Figure 3) showed this product is a scandium phosphinidene ethene-1,1-dithiolate 5 (81% isolated yield). We proposed that the formation of 5 proceeds through an initial nucleophilic addition and a subsequent isomerization as shown in Scheme 4. To the

Scheme 3. Reactions of Scandium Methylidene Phosphinidene (**2**) with CO_2 , CS_2 , PhCN , and $t\text{BuNC}$

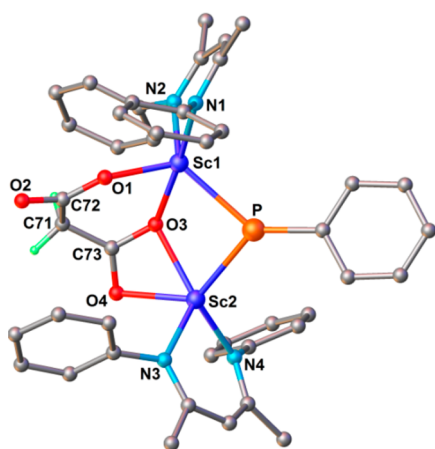
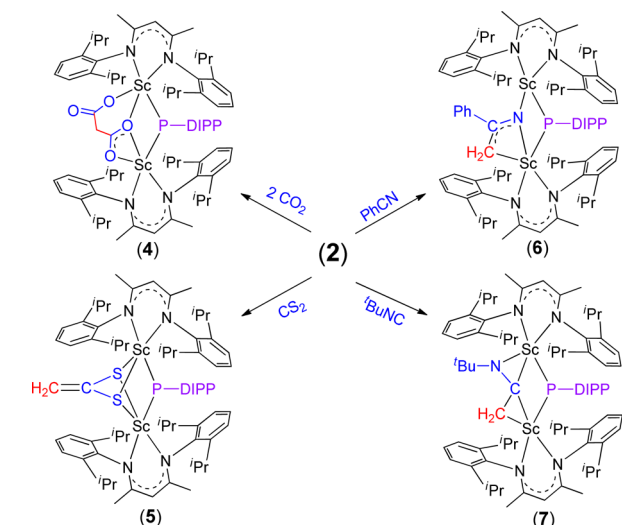


Figure 2. Molecular structure of complex **4** (ball-and-stick representation). DIPP isopropyl groups, hydrogen atoms (except the methylidene hydrogen atoms), and solvents in the lattice were omitted for clarity. Selected bond distances [Å] and angles [deg]: Sc1–N2 2.143(4), Sc1–N1 2.172(4), Sc2–N3 2.158(5), Sc2–N4 2.120(4), Sc1–P 2.588(2), Sc2–P 2.542(2), Sc1–O1 2.008(4), Sc1–O3 2.174(4), Sc2–O3 2.190(4), Sc2–O4 2.219(4), Sc2–C73 2.561(6), C72–O1 1.280(7), C72–O2 1.229(7), C73–O3 1.301(7), C73–O4 1.259(7), C71–C72 1.554(9), C71–C73 1.451(8), Sc1–P–Sc2 93.46(5), Sc1–O3–Sc2 117.68(17), C72–C71–C73 112.3(5).

best of our knowledge, no ethene-1,1-dithiolate derivative of rare-earth metal has been reported before. ^1H NMR spectral monitoring showed that the formed monoaddition product **5** does not react with an excess CS_2 at room temperature or 50°C . In complex **5**, the $[\text{CH}_2\text{CS}_2]^{2-}$ dianion coordinates to two scandium centers in a $\mu\text{-}\kappa^2\text{:}\kappa^2$ coordination mode through two sulfur atoms with the Sc–S bond lengths ranging from 2.565(1) to 2.749(1) Å. The C71–C72 bond length (1.303(5) Å) is consistent with that of a double bond, whereas the C72–S1 and C72–S2 bond lengths (1.772(4) and 1.769(4) Å) reveal single-bond characters.

Complex **2** also undergoes nucleophilic addition reactions with benzonitrile and *tert*-butyl isocyanide at room temperature to provide the monoaddition products **6** and **7** in 79% and 65% isolated yields (Scheme 3). Both complexes were characterized

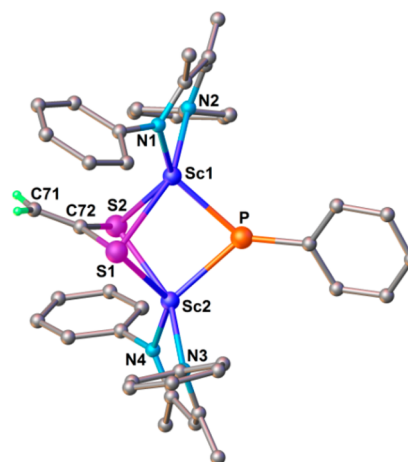
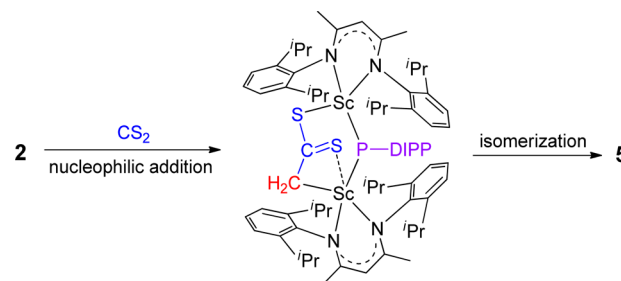


Figure 3. Molecular structure of complex **5** (ball-and-stick representation). DIPP isopropyl groups and hydrogen atoms (except the methylidene hydrogen atoms) were omitted for clarity. Selected bond distances [Å] and angles [deg]: Sc1–N1 2.157(3), Sc1–N2 2.206(3), Sc2–N3 2.168(3), Sc2–N4 2.170(3), Sc1–P 2.499(1), Sc2–P 2.510(1), Sc1–S1 2.744(1), Sc1–S2 2.565(1), Sc2–S1 2.577(1), Sc2–S2 2.663(1), S1–C72 1.772(4), S2–C72 1.769(4), C71–C72 1.303(5), Sc1–P–Sc2 83.16(3), Sc2–S1–Sc1 77.26(3), Sc1–S2–Sc2 78.94(3), S2–C72–S1 111.1(2), C71–C72–S2 125.4(4), C71–C72–S1 123.5(3).

Scheme 4. Proposed Pathway for the Formation of **5**



by NMR spectroscopy, elemental analysis, and X-ray crystallography. In **6**, the $[\text{CH}_2\text{C}(\text{Ph})\text{N}]^{2-}$ dianion displays a delocalized electronic structure with the C71–C72 bond length of 1.379(3) Å and the C72–N5 bond length of 1.348(3) Å (Figure 4). This dianion coordinates to one scandium center in an η^3 fashion through two carbon atoms and one nitrogen atom with the Sc2–C71 bond of 2.429(3) Å, the Sc2–C72 bond length of 2.493(2) Å, and the Sc2–N5 bond length of 2.160(2) Å. It coordinates to the other scandium center in an η^1 fashion through the nitrogen atom with the Sc1–N5 bond length of 1.981(2) Å. In **7**, the $[\text{CH}_2\text{CN}^t\text{Bu}]^{2-}$ dianion coordinates to two scandium centers in a $\mu\text{-}\eta^2\text{-N,C}\ \eta^2\text{-C,C}$ coordination mode (Figure 5). The Sc1–N5, Sc1–C72, Sc2–C71, and Sc2–C72 bond lengths are 2.105(4), 2.352(6), 2.243(5), and 2.272(5) Å, respectively. Similar to **5**, the monoaddition products **6** and **7** do not react with an excess benzonitrile or *tert*-butyl isocyanide at room temperature or 50°C .

In order to get more insights into the bonding of complex **2**, calculations were carried out at the DFT (B3PW91) level. The main geometrical features of complex **2** are nicely reproduced by the calculations, indicating the validity of the method to analyze the density and especially the bonding situation. Among all geometrical parameters, the Sc–N (2.18, 2.18, 2.21, 2.21 Å), the Sc–P (2.53, 2.54 Å), and the Sc–C (2.15, 2.15 Å)

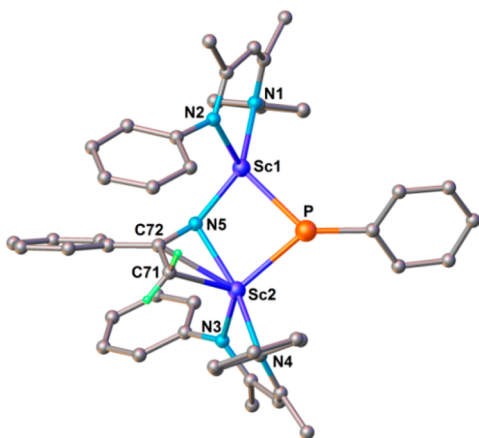


Figure 4. Molecular structure of complex **6** (ball-and-stick representation). DIPP isopropyl groups, hydrogen atoms (except the methylidene hydrogen atoms), and solvents in the lattice were omitted for clarity. Selected bond distances [Å] and angles [deg]: Sc1–N1 2.2022(19), Sc1–N2 2.169(2), Sc2–N3 2.148(2), Sc2–N4 2.253(2), Sc1–P 2.4971(8), Sc2–P 2.5073(7), Sc1–N5 1.981(2), Sc2–N5 2.160(2), Sc2–C71 2.429(3), Sc2–C72 2.493(2), C72–N5 1.348(3), C71–C72 1.379(3), Sc1–P–Sc2 84.54(2), Sc1–N5–Sc2 108.68(9).

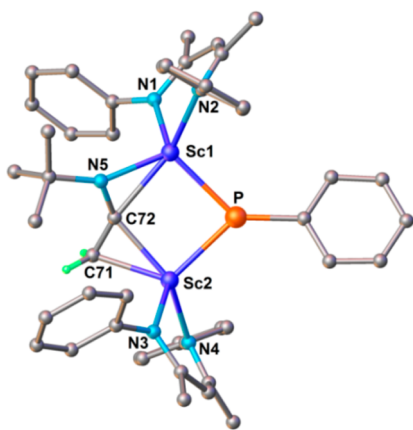


Figure 5. Molecular structure of complex **7** (ball-and-stick representation). DIPP isopropyl groups and hydrogen atoms (except the methylidene hydrogen atoms) were omitted for clarity. Selected bond distances [Å] and angles [deg]: Sc1–N1 2.152(3), Sc1–N2 2.227(3), Sc2–N3 2.162(3), Sc2–N4 2.195(3), Sc1–P 2.5285(14), Sc2–P 2.4922(13), Sc1–N5 2.105(4), Sc2–C71 2.243(5), Sc1–C72 2.352(6), Sc2–C72 2.272(5), C72–N5 1.343(7), C71–C72 1.280(7), Sc2–P–Sc1 88.48(4), Sc2–C72–Sc1 98.5(2), C71–C72–N5 134.4(5).

bond distances agree with the experimental ones with a maximum deviation of 0.08 Å. The Wiberg bond indexes were computed in order to get a better insight into the nature of the interaction between the formal phosphinidene and methylidene ligands and the two scandium centers. Two single bonds were found between the phosphinidene ligand and the two scandium metals (WBI of 0.79). Similarly, two single bonds were also found between the methylidene and the two scandium centers (WBI of 0.59). The greater WBI for the phosphinidene ligand is in line with the greater radial extension of the *p* orbital at the phosphorus, allowing a better overlap with the *d* orbital of the scandium. This is in line with slightly more covalent bonds between the two scandium centers and the phosphinidene

ligand than between the two scandium centers and the methylidene.

CONCLUSIONS

Thermal decomposition of scandium methyl phosphide, [LSc(Me){P(H)DIPP}] (L = [MeC(NDIPP)CHC(NDIPP)–Me][–], DIPP = 2,6-(*i*-Pr)₂C₆H₃) (**1**), produced an unexpected four-coordinate scandium methylidene phosphinidene complex, [(LSc)₂(μ₂-CH₂)(μ₂-PDIPP)] (**2**). Complex **2** was finally synthesized from the reaction of scandium methyl phosphide [LSc(Me){P(H)DIPP}] with 1 equiv of scandium dimethyl complex [LScMe₂] in good yield. In **2**, the methylidene ligand adopts a μ₂-coordination fashion due to the steric congestion around the scandium center. Complex **2** is able to activate unsaturated small molecules, and the unsaturated substrates selectively insert into the Sc–C(methylidene) bond of **2**. Considering the high reactivity observed for our previously synthesized four-coordinate scandium phosphinidene complex [{MeC(NDIPP)CHC(Me)NCH₂CH₂N(*i*-Pr)₂}Sc{μ-PC₆H₃-(2,6-Me₂)}]₂, in which CS₂, benzonitrile, and *tert*-butyl isocyanide readily insert into the Sc–P(phosphinidene) bond,^{6f} the high selectivity in the reactions of **2** with unsaturated substrates is highly interesting. DFT studies of **2** revealed that the Sc–P(phosphinidene) bond appears to be more covalent than the Sc–C(methylidene) bond. Thus, the latter might be more reactive.

EXPERIMENTAL SECTION

General. All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen-filled glovebox. Toluene, THF, hexane, and C₆D₆ were dried over Na/K alloy, transferred under vacuum, and stored in the glovebox. [LSc(Me)Cl] was synthesized following the literature.¹⁰ K[P(H)C₆H₃-(2,6-*i*-Pr₂)] was prepared by deprotonation of (2,6-*i*-Pr₂)-C₆H₃PH₂ with KH. Benzonitrile were dried over activated 4 Å molecular sieves and degassed by three freeze–pump–thaw cycles before use. CS₂ and *tert*-butyl isocyanide were dried over activated 4 Å molecular sieves, transferred under vacuum, and stored in the glovebox. The highly pure CO₂ (>99.99%) was further dried by passing through the activated 4 Å molecular sieves. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian 400 MHz, an Agilent 400 MHz, or an Agilent 600 MHz spectrometer. Chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external H₃PO₄ (85%) for phosphorus chemical shifts.

Synthesis of Complex 1. [LSc(Me)Cl] (513 mg, 1.0 mmol) and K[P(H)C₆H₃-(2,6-*i*-Pr₂)] (232 mg, 1.0 mmol) were mixed in 6 mL of toluene. After stirring at room temperature for 2 h, the precipitate was separated by centrifugation. The volatiles of the solution were removed under vacuum to give a red solid. The solid was washed with hexane (1 mL × 3) and dried under vacuum to give **1** as a yellow solid (570 mg, 85% yield). ¹H NMR (400 MHz, C₆D₆, 25 °C): 7.22–7.14 (m, overlapped with C₆D₆, Ar-H), 7.06 (m, 3H, Ar-H), 5.01 (s, 1H, MeC(N)CH), 3.43 (sept, ³J_{H-H} = 6.8 Hz, 2H, CH(CH₃)₂), 3.20 (m, 2H, CH(CH₃)₂), 3.16 (d, ¹J_{P-H} = 181 Hz, 1H, PH), 3.09 (sept, ³J_{H-H} = 6.8 Hz, 2H, CH(CH₃)₂), 1.57 (s, 6H, C(CH₃)₃), 1.45 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.31 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.18 (m, 18H, CH(CH₃)₂), 1.04 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 0.15 (s, 3H, Sc-CH₃). ¹³C NMR (100 MHz, C₆D₆, 25 °C): 168.2 (imine C), 148.0 (d, J_{C-P} = 7.2 Hz), 143.6, 143.0, 140.5, 139.8 (d, J_{C-P} = 36.8 Hz), 127.7, 124.8, 124.7, 123.9, 122.1 (Ar-C), 96.8 (MeC(N)CH), 36.4 (br, ScMe), 34.0, 33.9, 29.6, 28.8, 26.4, 24.7, 24.5, 24.3, 24.0, 23.7 (Ar-*i*-Pr and CMe). ³¹P NMR (162 MHz, C₆D₆, 25 °C): –90.9. Anal. Calcd for C₄₂H₆₂N₂PSc: C, 75.19; H, 9.31; N, 4.18. Found: C, 74.86; H, 9.19; N, 4.08.

Thermal Decomposition of Complex 1. 1 (201 mg, 0.3 mmol) was dissolved in 4 mL of toluene. After stirring at 60 °C for 36 h, the volatiles of the solution were removed under vacuum to give a dark red solid. The solid was washed with hexane (1 mL \times 4), and the residue was dried under vacuum to give a brownish-red solid which contains complex 2 and a small amount of complex 3. The volatiles of the hexane solution were removed under vacuum to give a dark red solid which contains complex 3 and a small amount of complex 2. Single crystals of complexes 2 and 3 suitable for single-crystal X-ray diffraction were obtained by recrystallization of these two solids in hexane. Complex 3: ^1H NMR (600 MHz, C_6D_6 , 25 °C): 7.20–7.14 (m, overlapped with C_6D_6 , Ar-H), 7.10–7.02 (m, 6H, Ar-H), 5.07 (s, 1H, MeC(N)CH), 3.42 (d, $^1J_{\text{P-H}} = 201$ Hz, 2H, PH), 3.21 (br, 4H, $\text{CH}(\text{CH}_3)_2$), 2.93 (br, 4H, $\text{CH}(\text{CH}_3)_2$), 1.58 (s, 6H, C(CH_3)), 1.30 (br, 12H, $\text{CH}(\text{CH}_3)_2$), 1.18 (m, 24H, $\text{CH}(\text{CH}_3)_2$), 1.02 (m, 12H, $\text{CH}(\text{CH}_3)_2$). Some ^1H signals of complex 3 are broad at 25 °C, and become sharp at 70 °C. ^1H NMR (600 MHz, C_6D_6 , 70 °C): 7.20 (m, 6H, Ar-H), 7.02 (m, 6H, Ar-H), 5.18 (s, 1H, MeC(N)CH), 3.44 (d, $^1J_{\text{P-H}} = 200$ Hz, 2H, PH), 3.23 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 3.03 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 1.67 (s, 6H, C(CH_3)), 1.35 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.16 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.05 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{31}P NMR (243 MHz, C_6D_6 , 25 °C): –56.9 (br), –61.9 (br). Complex 3 has two ^{31}P signals at 25 °C because the rotation of the P–C(Ar) bond is hindered. The coalescence of two ^{31}P signals was observed at 70 °C. ^{31}P NMR (243 MHz, C_6D_6 , 70 °C): –57.1 (br).

Synthesis of Complex 2. [$\text{LS}(\text{ScMe}_2)$] (197 mg, 0.4 mmol) and 1 (268 mg, 0.4 mmol) were mixed in 3 mL of toluene. After stirring at 60 °C for 24 h, the volatiles of the solution were removed under vacuum to give a brown solid. The solid was washed with hexane (2 mL \times 2) and dried under vacuum to give 2 as a brownish-red solid (332 mg); the hexane solution stood at room temperature for 5 days to provide a second crop of 2 (30 mg). 362 mg of 2 was obtained in total (77% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): 7.32 (m, 4H, Ar-H), 7.22 (m, 4H, Ar-H), 7.17–7.14 (m, overlapped with C_6D_6 , Ar-H), 7.12 (m, 3H, Ar-H), 5.62 (d, $^3J_{\text{P-H}} = 2.0$ Hz, 2H, ScCH₂), 4.64 (s, 2H, MeC(N)CH), 3.76 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.28 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 2.92 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.41 (s, 12H, C(CH_3)), 1.26 (m, 28H, $\text{CH}(\text{CH}_3)_2$ and hexane-CH₂), 1.02 (m, 24H, $\text{CH}(\text{CH}_3)_2$), 0.94 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.89 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 3H, hexane-CH₃). ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): 168.2 (imine C), 150.0 (d, $J_{\text{C-P}} = 16.7$ Hz), 148.2, 144.7, 143.0, 142.6, 126.7, 125.1, 124.0, 123.8, 121.5 (d, $J_{\text{C-P}} = 4.6$ Hz) (Ar-C), 98.2 (MeC(N)CH), 34.3, 34.2, 29.4, 28.3, 26.2, 25.1, 24.7, 24.2, 23.7, 23.4 (Ar'Pr, CMe); 32.0, 23.1, 14.4 (hexane-C); 30.2 (ScCH₂). ^{31}P NMR (162 MHz, C_6D_6 , 25 °C): 84.1. Anal. Calcd for $\text{C}_{71}\text{H}_{101}\text{N}_4\text{PSc}_2 \cdot 0.5\text{hexane}$: C, 75.67; H, 9.27; N, 4.77. Found: C, 75.69; H, 9.12; N, 4.67.

Synthesis of Complex 4. CO_2 (12.5 mL, 0.51 mmol) was slowly injected into a 10 mL bottle containing 2 (200 mg, 0.17 mmol) and 3 mL of toluene. After standing at room temperature for 3 h, the solution was concentrated to approximately 1 mL and cooled to –35 °C to give a dark purple crystalline solid. The solid was dried under vacuum to give 4 as a purple solid (103 mg, 50% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): 7.26–7.20 (m, 7H, Ar-H), 7.12 (m, 2H, Ar-H), 7.04 (br, 2H, Ar-H), 6.96 (m, 4H, Ar-H), 5.15 (s, 2H, MeC(N)CH), 3.76 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 2.96 (br, 3H, $\text{CH}(\text{CH}_3)_2$), 2.15 (br, 2H, CH₂), 1.60 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.58 (s, 12H, C(CH_3)), 1.32 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 1.10 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.97 (m, 18H, $\text{CH}(\text{CH}_3)_2$), 0.79 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.65 (br, 6H, $\text{CH}(\text{CH}_3)_2$). Some signals of the isopropyl methines are too broad to be assigned and integrated. The ^{13}C NMR spectrum of 4 was not obtained due to the low solubility of the complex. ^{31}P NMR (162 MHz, C_6D_6 , 25 °C): 165.0. Anal. Calcd for $\text{C}_{73}\text{H}_{101}\text{N}_4\text{O}_4\text{PSc}_2$: C, 71.90; H, 8.35; N, 4.59. Found: C, 72.03; H, 8.20; N, 4.06.

Synthesis of Complex 5. 2 (141 mg, 0.12 mmol) and CS_2 (18 mg, 0.24 mmol) were mixed in 4 mL of toluene. After standing at room temperature for 5 h, the solution was concentrated to approximate 0.5 mL and then cooled to –35 °C to give a brown

solid. The solid was dried under vacuum to give 5 as a brownish-red solid (129 mg, 83% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): 7.22–7.01 (m, overlapped with C_6D_6 , Ar-H), 5.32 (s, 2H, MeC(N)CH or C=CH₂), 5.09 (s, 2H, MeC(N)CH or C=CH₂), 3.23 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.13 (br, 4H, $\text{CH}(\text{CH}_3)_2$), 2.83 (br, 4H, $\text{CH}(\text{CH}_3)_2$), 2.11 (s, 3H, toluene-CH₃), 1.60 (s, 12H, C(CH_3)), 1.43 (br, 12H, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.91 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.79 (br, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): 168.2 (br, imine C), 150.3 (d, $J_{\text{C-P}} = 12.2$ Hz), 148.1 (d, $J_{\text{C-P}} = 3.1$ Hz), 144.1, 142.1 (br), 126.3 (br), 125.6, 125.2 (br), 124.9 (br), 123.5 (br), 122.4 (d, $J_{\text{C-P}} = 5.3$ Hz), 122.3 (d, $J_{\text{C-P}} = 4.5$ Hz) (Ar-C, C=CH₂), 99.5 (MeC(N)CH); 37.4, 37.3, 29.9 (br), 28.1, 26.7 (br), 25.7, 25.5, 25.3, 23.5 (br) (Ar'Pr and CMe), 137.9, 129.3, 128.6, 125.7, 21.4 (toluene-C). ^{31}P NMR (162 MHz, C_6D_6 , 25 °C): 219.2. Anal. Calcd for $\text{C}_{72}\text{H}_{101}\text{N}_4\text{PS}_2\text{Sc}_2 \cdot \text{toluene}$: C, 73.00; H, 8.45; N, 4.31. Found: C, 72.65; H, 8.39; N, 4.38.

Synthesis of Complex 6. 2 (141 mg, 0.12 mmol) and PhCN (13 mg, 0.12 mmol) were mixed in 4 mL of toluene. After standing at room temperature for 3 h, the volatiles of the solution were removed under vacuum to give a red solid. Approximate 1 mL of hexane was added in, and then cooled to –35 °C to give a red solid. The solid was dried under vacuum to give 6 as a red solid (126 mg, 79% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): 7.29–7.10 (m, overlapped with C_6D_6 , Ar-H), 7.10–6.94 (m, 8H, Ar-H), 6.85 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, Ar-H), 6.79 (m, 1H, Ar-H), 6.69 (m, 2H, Ar-H), 6.49 (m, 1H, Ar-H), 5.11 (s, 1H, MeC(N)CH), 5.02 (s, 1H, MeC(N)CH), 4.33 (s, 1H, ScCH₂), 3.90 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.57 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.35 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.12 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.88 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.61 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.41 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.24 (s, 1H, ScCH₂), 2.11 (s, 3H, toluene-CH₃), 1.71 (s, 3H, C(CH_3)), 1.63 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.55 (m, 9H, $\text{CH}(\text{CH}_3)_2$ and C(CH_3)), 1.51 (s, 3H, C(CH_3)), 1.44 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.40 (m, 6H, $\text{CH}(\text{CH}_3)_2$), 1.36 (s, 3H, C(CH_3)), 1.25 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.14 (m, 6H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.87 (m, 9H, $\text{CH}(\text{CH}_3)_2$), 0.82 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.79 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.35 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.10 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$). The ^{13}C NMR spectrum of 6 was not obtained due to the low solubility of the complex. ^{31}P NMR (162 MHz, C_6D_6 , 25 °C): 143.1. Anal. Calcd for $\text{C}_{78}\text{H}_{106}\text{N}_5\text{PSc}_2 \cdot \text{toluene}$: C, 76.95; H, 8.66; N, 5.28. Found: C, 76.65; H, 8.69; N, 5.43.

Synthesis of Complex 7. 2 (141 mg, 0.12 mmol) and $^i\text{BuNC}$ (11 mg, 0.13 mmol) were mixed in 4 mL of toluene. After standing at room temperature for 1 h, the volatiles of the solution were removed under vacuum to give a dark-brown solid. Approximate 1 mL of hexane was added in, and then cooled to –35 °C to give a brown solid. The solid was dried under vacuum to give 7 as a brownish-red solid (96 mg, 65% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): 7.28 (m, 3H, Ar-H), 7.20–7.10 (m, overlapped with C_6D_6 , Ar-H), 6.99 (m, 3H, Ar-H), 6.93 (m, 2H, Ar-H), 6.82 (m, 1H, Ar-H), 5.37 (s, 1H, MeC(N)CH), 5.27 (s, 1H, MeC(N)CH), 3.92 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.76 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.53 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.45 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.30 (m, 3H, $\text{CH}(\text{CH}_3)_2$), 3.13 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.05 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.96 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 1.84 (s, 3H, C(CH_3)), 1.69 (s, 3H, C(CH_3)), 1.68 (s, 3H, C(CH_3)), 1.65 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.58 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.55 (s, 3H, C(CH_3)), 1.41 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.35 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.23 (m, 11H, $\text{CH}(\text{CH}_3)_2$ and hexane-CH₂), 1.15 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.10 (m, 10H, $\text{CH}(\text{CH}_3)_2$ and ScCH₂), 1.04 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 1.01 (s, 1H, ScCH₂), 0.99 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.92 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.89 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 6H, hexane-CH₃), 0.66 (s, 9H, C(CH_3)), 0.54 (m, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): 228.4 (d, $J_{\text{C-P}} = 13.4$ Hz, ScC(CH₂)(N)Sc), 170.0, 169.5, 168.3, 166.8 (imine C); 150.3 (d,

J_{C-P} = 26.4 Hz), 149.2, 148.1 (d, J_{C-P} = 3.7 Hz), 147.1, 146.6, 145.7, 145.1, 144.9, 144.4, 144.2, 144.1, 143.0, 142.5, 141.7, 141.3, 127.3, 126.3, 126.2, 126.0, 125.9, 125.7, 125.1, 124.8, 124.5, 124.3, 124.1, 124.0, 123.3, 122.9 (d, J_{C-P} = 4.0 Hz), 122.4 (d, J_{C-P} = 3.9 Hz) (Ar-C); 101.1, 99.9 (MeC(N)CH), 85.5 (d, J_{C-P} = 6.7 Hz, $ScCH_2$), 59.4 ($C(CH_3)_3$); 38.6, 38.5, 35.9, 35.8, 29.8, 28.7 (d, J_{C-P} = 2.6 Hz), 28.6, 28.5, 27.9 (d, J_{C-P} = 1.9 Hz), 27.8, 27.7, 27.6, 27.5, 27.4, 27.0, 26.8, 26.4, 26.2, 26.1, 25.9, 25.8, 25.59, 25.53, 25.51, 25.48, 25.41, 25.38, 25.35, 25.30, 24.8, 24.4, 24.2, 23.5 (Ar^iPr , CMe); 28.9 ($C(CH_3)_3$); 32.0, 23.1, 14.4 (hexane-C). ^{31}P NMR (162 MHz, C_6D_6 , 25 °C): 136.1. Anal. Calcd for $C_{76}H_{110}N_5PSc_2 \cdot hexane$: C, 75.71; H, 9.61; N, 5.38. Found: C, 76.47; H, 9.97; N, 5.23.

X-ray Crystallography. Single crystals of **2** and **3** suitable for single-crystal X-ray diffraction were grown from the hexane solutions, those of **4**, **6**, and **7** were from the toluene solutions, and those of **5** were from the benzene solution. The single crystals of **2–7** were mounted under a nitrogen atmosphere on a glass fiber, and data collection was performed on a Bruker APEX2 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 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 nonhydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. Calculations were carried out using the SHELXL-97, SHELXL-2014, or Olex2 program. The software used is listed in ref 11. Crystallographic data and refinement for **2–7** are listed in Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

■ Supporting Information

CIF files giving X-ray crystallographic data for complexes **2–7**, a table giving crystallographic data and refinement parameters for complexes **2–7**, a figure showing the molecular structure of complex **3**, figures giving NMR spectra of complexes **1–7**, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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