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Phosphinidene Complexes of Scandium: Powerful PAr Group-Transfer Vehicles to Organic and Inorganic Substrates

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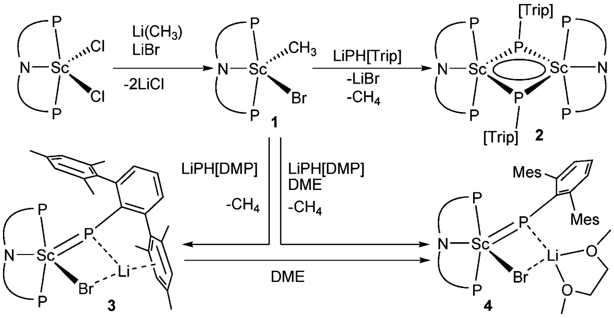
Due to the mismatch in orbital energies or the soft−hard contrast among the metal ion and phosphorus,[1] terminal phosphinidene complexes of the early transition metals represent an attractive moiety for the purposes of group transfer[2,3] and catalytic transformations such as carboamination, hydrophosphination of alkynes, and the dehydrocoupling of phosphines.[4] Recently, our group has utilized the (PNP)Sc(III) scaffold, (PNP = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$), to support unusual moieties like oxo, methylidene, and imide, all of which could be trapped with a Lewis acid like Al(CH$_3$)$_3$.[5] In the absence of the Lewis acid, a moiety like a scandium imide could engage in intermolecular C−H activation reactions of benzene or pyridine.[5a] Intrigued by this finding and the recent work establishing dinuclear Lu(III) phosphinidene complexes as promising reagents for "PAryl" group transfer,[6] we wanted to expand this methodology to create reactive scandium phosphinidene complexes. Our choice of Sc is strategic, given that this metal ion should represent the most favorable lanthanide to engage in metal−ligand multiple bonding due to its d-orbital energies, electronegativity, and ion size, when compared to the heavier group 3 congeners. Herein, we present the first examples of phosphinidene complexes of scandium, in both neutral and ionic forms, and demonstrate the reactive phosphinidene ligand to be readily delivered to both organic and inorganic fragments.

Our approach to implanting a phosphinidene ligand onto scandium(III) involved a similar route to that reported for the transient imido (PNP)Sc═NAr fragment (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[5a] Accordingly, complex (PNP)Sc(CH$_3$)Br (**1**),[7] prepared readily from (PNP)ScCl$_2$ and 1 equiv of Li(CH$_3$)·LiBr, was reacted with 1 equiv of LiPH[Trip] (Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) in toluene to yield the dinuclear scandium phosphinidene complex [(PNP)Sc(μ_2-P[Trip])]$_2$ (**2**) in 57% yield (Scheme 1).[7] The most diagnostic spectroscopic feature of complex **2** is the presence of a phosphinidene resonance at 227.4 ppm (^{31}P NMR, 25 °C), which is highly deshielded from the broadened PNP-pincer phosphine resonance (7.0 ppm). Dinuclear aggregation to **2** from putative (PNP)Sc═P[Trip] was unambiguously ascertained by single crystal X-ray diffraction studies (Figure 1).[7] Interestingly, the solid state structure of **2** deviates from the Lu(III) analogue[6] in that the Sc$_2$P$_2$ core is highly symmetrical. For example, a center of inversion relates the equivalent but short Sc−P distances in the planar Sc$_2$P$_2$ core (Sc(1)−P(3′) = 2.5527(10) Å and Sc(1)−P(3) = 2.5446(8) Å, deviation in planarity of the core is 2.1°, and the sum of the angles around the core is 359.92°), when compared to the Sc−PNP phosphine distances (~2.83 Å). In addition, the aryl ring on the phosphorus is not coplanar with the core, deviating by a dihedral angle of −33°. These structural features presumably allow the lone pair of each phosphorus atom to become delocalized throughout the four-membered ring. Formation of the phosphinidene dimer, **2**, inferred that a more hindered secondary phosphide may prevent such an aggregation.

Scheme 1. Synthesis of Dinuclear and Mononuclear Phosphinidene Complexes of Scandium



Treating LiP(H)[DMP] (DMP = 2,6-Mes$_2$C$_6$H$_3$) with precursor **1** elicited an immediate color change from yellow to orange, and the ^{31}P and ^{1}H NMR spectral data suggested formation of an asymmetric complex of scandium (~70% isolated yield). Only upon cooling to 0 °C could three broad and inequivalent ^{31}P NMR resonances be observed at 13.2, 9.8, and 8.0 ppm. Because of its temperature dependence, the phosphorus resonance at 9.8 ppm has been tentatively assigned to the phosphinidene. The mesityl groups on the DMP moiety are inequivalent when assayed by ^{1}H NMR spectroscopy, and no fluxional behavior is observed when the solution is heated to 80 °C. A single crystal X-ray structure revealed the connectivity to be that of a mononuclear, phosphinidene ate complex, [(PNP)Sc(μ_2-P[DMP])(μ_2-Br)Li] (**3**) wherein a LiBr residue (Sc−Br, 2.6931(16) Å; P−Li, 2.481(11) Å) has added across the shortest known Sc−P bond (2.338(2) Å) and linear ligand (Sc−P−C, 162.4(2)°).[7] Consequently, the unsaturated Li ion, having bridging phosphinidene and bromide ligands, interacts in an η^6-fashion with one mesityl aryl moiety (Figure 1). We expect the latter interaction to be weak (36−50 kcal/mol), based on published calculations,[8] and due to the long C$_{\mathrm{arene}}$−Li interactions (2.411−2.539 Å) in comparison to the solid state structures of other lithium terphenyls (2.31−2.28 Å).[9] Although the arene−Li interaction could be negligible, our vt ^{7}Li NMR does not suggest dissociation of the Li$^+$ ion. In fact, the ^{7}Li NMR spectrum of **3** displays a doublet resulting from strong coupling to the phosphinidene phosphorus (−0.20 ppm, $^1J_{\mathrm{Li-P}}$ = 34 Hz, 25 °C), which is in the low range but comparable to other values observed for LiPHR or LiPR$_2$ salts (36−56 Hz).[10] The $^1J_{\mathrm{Li-P}}$ value is relatively insensitive to vt while a ^{1}H NMR experiment at temperatures 80−100 °C reflects fluxional mesityl rings as well as the aryl groups on the PNP ligand.[7]

Analysis of the bonding and structure in **3** by high level DFT calculations reproduced the key geometrical features expectedly well and implied a strong interaction between the phosphinidene lone

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10.1021/ja100214e

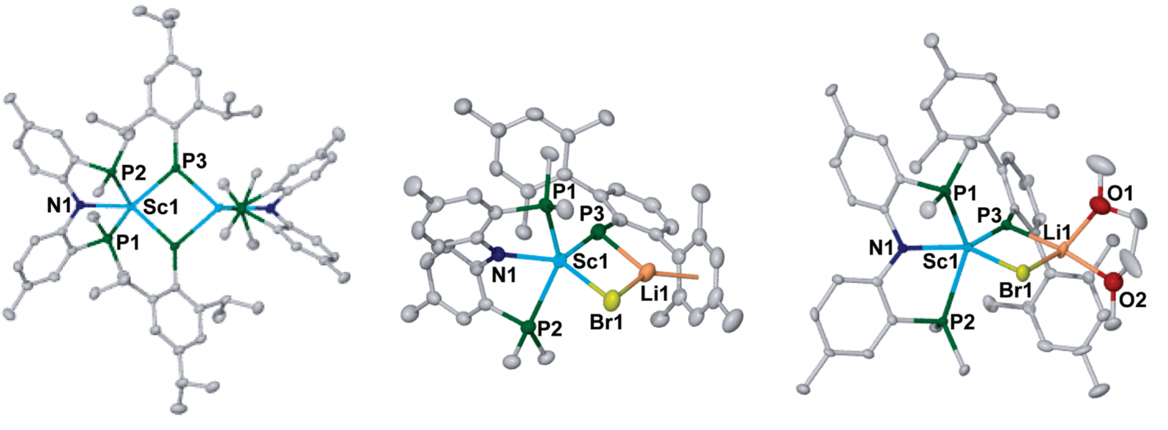
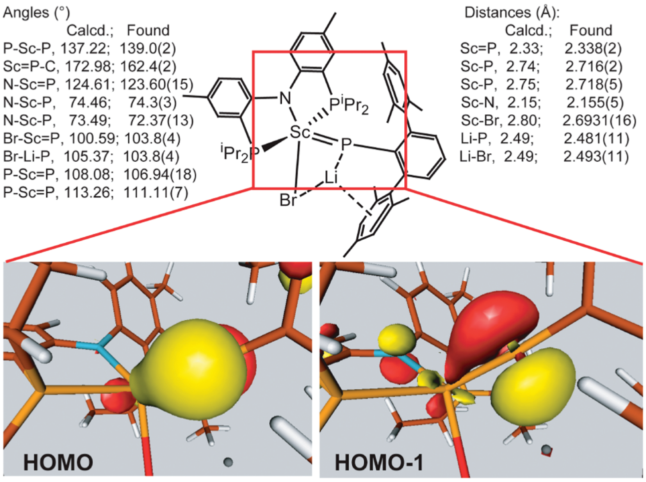


Figure 1. Perspective views of the molecular structures of complexes **2**, **3**, and **4**. Metrical parameters for each structure are reported in the SI.



Angles (°)

	Calcd.;	Found
P-Sc-P,	137.22;	139.0(2)
Sc=P-C,	172.98;	162.4(2)
N-Sc=P,	124.61;	123.60(15)
N-Sc-P,	74.46;	74.3(3)
N-Sc-P,	73.49;	72.37(13)
Br-Sc=P,	100.59;	103.8(4)
Br-Li-P,	105.37;	103.8(4)
P-Sc=P,	108.08;	106.94(18)
P-Sc=P,	113.26;	111.11(7)

Distances (Å):

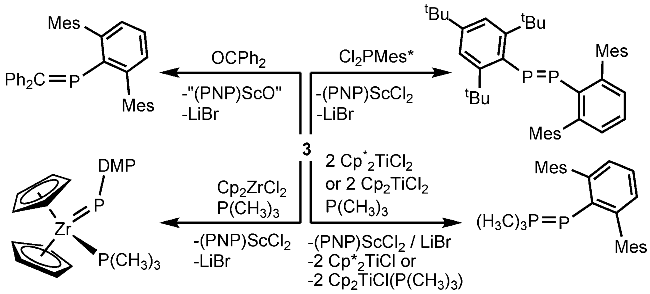
	Calcd.;	Found
Sc=P,	2.33;	2.338(2)
Sc-P,	2.74;	2.716(2)
Sc-P,	2.75;	2.718(5)
Sc-N,	2.15;	2.155(5)
Sc-Br,	2.80;	2.6931(16)
Li-P,	2.49;	2.481(11)
Li-Br,	2.49;	2.493(11)

Figure 2. Expanded region of the most important orbitals (HOMO at −4.255 eV, and HOMO-1 at −4.453 eV) of the computed model of **3**.

pair and the empty d-orbital on Sc (HOMO, Figure 2). However, the energetically similar HOMO-1 orbital suggests a highly polarized bond dominated by the phosphinidene phosphorus p-orbital with nonoptimal orbital overlap with the electropositive Sc d-orbital, but oriented more toward the Li$^+$ counterion (Figure 2).[7] Presumably due to the in-phase combination between the atoms P−Sc−N, HOMO-1 is slightly lower in energy than the π-based orbital observed in the HOMO. HOMO-1 also clearly illustrates the dissimilarities in electronegativities between the phosphinidene P and the PNP amide nitrogen given their respective orbital contributions. The computed Mayer bond (1.41) and natural bond order (NBO, 1.62) implies a multiple bond between Sc and the phosphinidene P atom, since these values are over three times larger than the average Mayer bond order between Sc and PNP phosphines (∼0.38) and is also significantly larger than the Sc−P Mayer bond (1.00) value computed for the phosphinidene dimer **2**.[7] Interestingly, omitting the Li$^+$ from our calculations inflicted no significant perturbation to the overall core distances, Mayer Sc−P bond orders, NBO's, and overall molecular orbital scheme between Sc and P, although some distortions in the angles, Sc−P−C$_{ipso}$ and (PNP)Sc, were observed due to no Li−arene interactions (see Supporting Information (SI) for details).[7] As a result, the large contribution of P character to HOMO-1 suggests substantial charge localization at this site. The ligand is therefore implied to be highly nucleophilic in character, independent of whether the Li$^+$ ion is present.

Lithium−arene decomplexation in **3** can be easily accomplished by treatment with 1,2-dimethoxyethane (DME), to form the ate

Scheme 2. Reactivity of **3** with Organic and Inorganic Reactants



analogue, [(PNP)Sc(μ_2-P[DMP])(μ_2-Br)Li(DME)] (**4**), in 21% isolated yield. Complex **4** can also be independently prepared (in ∼47% yield) by Li encapsulation of LiP(H)[DMP] with DME prior to addition to **1** (Scheme 1).[7] Apart from the DME component, most salient, multinuclear NMR spectroscopic features are similar to **3** (^{1}H, ^{13}C, ^{7}Li), but the ^{31}P NMR spectrum collected at 25 °C evinced a slightly more downfield phosphinidene resonance at 56.1 ppm from the two inequivalent PNP resonances (13.3 and 8.2 ppm). To conclusively establish the role of DME in **4** and whether Li$^+$ coordination to P and/or Br was still persistent, both a single crystal structure and vt ^{7}Li NMR spectra were collected.[7] Although the Sc−P (2.3732(18) Å), Sc−P−C (155.2(2)°), and Sc−Br (2.6032(13) Å) metrical parameters in **4** are similar to those of **3**, coordination of DME to Li results in a slight elongation of the countercation from the Br (2.563(11) Å) and the phosphinidene P atoms (2.499(12) Å). Coordination of DME to Li completely fractures all Li(arene) interactions, which in turn promotes tilting of the Mes groups away from the Li(DME) component. The Sc−Br distances in **3** and **4** are unremarkable with respect to neutral Sc(III) complexes having Br ligands,[11] while the Li−Br distance in **4** falls within range for the reported tetrameric complex, [LiBr(OEt)]$_4$ (2.54−2.62 Å).[12] Despite DME complexation to Li$^+$ in **4**, vt ^{7}Li NMR data do not suggest substantial abstraction of the alkali metal from the phosphinidene site ($^1J_{\text{Li-P}}$ = 41 Hz, 25 °C), and addition of excess DME and thermolysis of the complex (100 °C) do not appear to induce formation of a discrete salt or elimination of Li(DME)Br. DFT calculations also suggest a highly polarized phosphinidene, having multiple bond character between Sc and P (Mayer bond order, 1.46; NBO, 1.58).[7]

Unlike compound **2**, which reacts sluggishly with ketones, complex **3** shows clean phospha-Wittig chemistry toward ketones and phosphorus dichlorides (Scheme 2). Accordingly, the reaction of **3** with benzophenone immediately yielded the phosphaalkene, Ph$_2$C=P[DMP] (^{31}P NMR: 234.8 ppm),[7,13] in very high yield when the mixture is assayed by ^{31}P NMR spectroscopy. Putative "(PNP)ScO" could not be isolated from the complicated metal-based mixture. As opposed to complexes of the type $Cp_2Zr{=}P[Ar](P(CH_3)_3)$ (Ar = Mes*[3b] or DMP[14]), the reaction of highly ionic **3** with Mes^*PCl_2 cleanly yielded the asymmetric diphosphene, [Mes*]P═P[DMP] (^{31}P NMR: 526.2, 455.5 ppm),[15] and (PNP)$ScCl_2$ in yields greater than 70%, as established by ^{31}P NMR spectroscopy (Scheme 2).[7] Since **3** fails to react with phosphines, transfer and trapping experiments could be pursued with this Lewis base. Hence, intermetal phosphinidene group transfer can be conducted with **3**, since treatment with 1 equiv of Cp_2ZrCl_2 and excess $P(CH_3)_3$ rapidly promoted formation of (PNP)$ScCl_2$ and the known complex, $Cp_2Zr{=}P[DMP](P(CH_3)_3)$ (^{31}P NMR: 771.0 and −6.7 ppm, $^2J_{P-P}$ = 23 Hz),[14] an analogous effective phosphinidene reagent to the Mes* derivative reported by Stephan[3b] (Scheme 2). Unfortunately, decomposition products are observed in the reaction mixture thus preventing separation of the Zr phosphinidene. In contrast, the reaction with 2 equiv of $Cp^*_2TiCl_2$ and excess $P(CH_3)_3$ resulted in quantitative formation of (PNP)$ScCl_2$, the phospha-Wittig reagent, $[DMP]P{=}P(CH_3)_3$ (^{31}P NMR: −2.8 and −114.7 ppm, $^1J_{P-P}$ = 582 Hz, 46%),[16] as well as [DMP]P═P[DMP] (9%, ^{31}P NMR: 493.2 ppm), (PNP)H (20%, ^{31}P NMR: −12.7), $H_2P[DMP]$ (7%, ^{31}P NMR: −146.5), phosphaindole (5%, ^{31}P NMR: −27.4 ppm), and traces of another product (∼1%, dm, ^{31}P NMR: −91.6 ppm, J_{H-P} = 205 Hz), which has been tentatively assigned as the phosphinidene insertion into the C−H bond of one of the mesityl methyl groups to make a dihydrophosphanthridine.[17] Although we have been unable to characterize the titanium product produced from this reaction, we propose the generation of phosphanylidene-σ^4-phosphorane to occur via reductive coupling between a titanium phosphinidene (possibly a dimer) and $P(CH_3)_3$.[18,19] Our speculation is corroborated by the reaction of **3** with Cp_2TiCl_2 to rapidly form (PNP)$ScCl_2$ as well as a metastable complex we propose to be a titanium phosphinidene (^{31}P NMR: 1065.3 ppm),[4,18] which transforms to $[DMP]P{=}P(CH_3)_3$ and a new paramagnetic titanium species.[19] As observed with $Cp^*_2TiCl_2$, complete consumption of **3** can only be achieved when 2 equiv of Cp_2TiCl_2 are used. The reaction mixture also reveals formation of the diphosphene [DMP]P═P[DMP] (36%), (PNP)H (5%), $H_2P[DMP]$ (5%), dihydrophosphanthridine (∼1%), and another unidentified product (9%).[17] To our knowledge, the transfer of a PAr unit directly to a phosphine is a rare phenomenon[20,21] therefore rendering complex **3** a powerful delivery vehicle, presumably due to the polarized nature of the Sc−P bond as well as the nonredox behavior of the Sc(III) ion.

Other intermetal PAr transfer studies as well as current efforts to remove the Li^+ are underway in our laboratories. Complexes such as **3** can deliver the PAr unit to common metal−halide precursors, therefore rendering them even more powerful than prototypical phospha-Wittig reagents such as $ArP{=}P(CH_3)_3$,[16,22] or even early transition metal phosphinidene complexes such as $Cp_2Zr{=}P[Ar](P(CH_3)_3)$.[2,3b,14]

Acknowledgment. Financial support of this research was provided by the National Science Foundation (CHE-0848248). J.S. acknowledges postdoctoral financial support from NSERC. We also thank Prof. John D. Protasiewicz for insightful discussions.

Supporting Information Available: Experimental procedures, X-ray crystallographic information and spectral data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA100214E