Communication

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A Highly Reactive Scandium Phosphinoalkylidene Complex: C–H and H–H Bonds Activation

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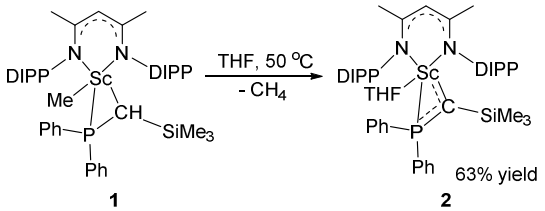
Supporting Information Placeholder

ABSTRACT: The first scandium phosphinoalkylidene complex was synthesized and structurally characterized. The complex has the shortest Sc–C bond lengths reported to date (2.089(3) Å). DFT calculations reveal the presence of a three center π interaction in the complex. This scandium phosphinoalkylidene complex undergoes intermolecular C–H bond activation of pyridine, 4-dimethylamino pyridine and 1,3-dimethylpyrazole at room temperature. Furthermore, the complex rapidly activates H_2 under mild conditions. DFT calculations also demonstrate that the C–H activation of 1,3-dimethylpyrazole is selective for thermodynamic reasons and the relatively slow reaction is due to the need of fully breaking the chelating effect of the phosphino group to undergo the reaction whereas this is not the case for H_2.

Mononuclear transition metal alkylidene (or carbene) complexes have attracted intense attention, and a great number of mononuclear transition metal alkylidene complexes have been synthesized in past decades.[1] One exception is those with rare-earth metal ions. Due to HOMO/LUMO orbital energies mismatch between the d^0 rare-earth metal ions and the alkylidene groups, the formation of mononuclear complexes is unfavorable.[2] The carbene groups have a strong tendency to bind more than one rare-earth metal ion or one rare-earth metal ion and two other metal ions.[3,4] For the purpose of stabilization of such mononuclear rare-earth metal complexes, methandiide dianions with P(V) substituents, such as $[C(PPh_2NSiMe_3)_2]^{2-}$ $[C(PPh_2S)_2]^{2-}$ and $[C(SiMe_3)PPh_2S]^{2-}$, were employed.[5] However, the reactivity of such rare-earth metal complexes is quite sluggish. The observed low activity is certainly due to the using of strong electronic withdrawing P(V) substituents, pincer-type structure and/or four-member chelating. With this in mind, we carried out a study on the synthesis of scandium phosphinoalkylidene complex. Compared to the P(V) substituted analogues, this ligand is less explored in the early-translation metal complexes,[6] and no rare-earth metal complexes of that type have been reported. Herein, we report the synthesis and bonding analysis (DFT) of the first scandium phosphinoalkylidene complex. This complex is highly reactive and is able to activate pyridine, 4-dimethylamino pyridine, 1,3-dimethylpyrazole and H_2 under mild conditions.

Scheme 1. Synthesis of Scandium Phosphinoalkylidene Complex 2.



1 **2**

Scandium methyl chloride [LSc(Me)Cl] (L = [MeC(NDIPP)CHC(NDIPP)Me]$^-$) was prepared as reported by Piers and coworkers.[7] Lithium salt Li[$CH(SiMe_3)PPh_2$](THF) was synthesized by using the method reported by Peterson,[8] and the complex was isolated and characterized by NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and elemental analysis. A salt metathesis of scandium methyl chloride [LSc(Me)Cl] with Li[$CH(SiMe_3)PPh_2$](THF) in toluene at room temperature provided a scandium methyl phosphinoalkyl complex [LSc{$CH(SiMe_3)PPh_2$}Me] (**1**) in 66% yield. The ^{1}H NMR spectrum of **1** in C_6D_6 clearly shows two featured signals at δ = 0.64 and -0.82 ppm for Sc–CH_3 and Sc–C*H*($SiMe_3$)PPh_2, respectively. The solid state structure of **1** was also obtained (the supporting information, Figure S1), in which the scandium center adopts a distorted square pyramidal geometry with two nitrogen atoms of L and carbon and phosphorus atoms of [$CH(SiMe_3)PPh_2$]$^-$ forming the basal plane and one methyl ligand occupying the apical position. Complex **1** is stable in benzene, toluene and THF at room temperature, but eliminates methane in THF at 50 °C to give a mononuclear scandium phosphinoalkylidene complex [LSc{$C(SiMe_3)PPh_2$}THF] (**2**) as shown in Scheme 1. Complex **2** was isolated in 63% yield, and characterized by NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and elemental analysis. In the ^{13}C{^{1}H} NMR, the alkylidene carbon (Sc–*C*($SiMe_3$)PPh_2) signal appears at δ = 151.7 (*d*, $^1J_{P\text{-}C}$ = 103 Hz), which is significantly downshifted in comparison with that of the alkyl carbon (Sc–*C*H($SiMe_3$)PPh_2) in **1** (46.8 ppm), in agreement with a sp^2 carbon. Interestingly, this carbon signal is also downshifted in comparison with that of the alkylidene carbon (Sc–*C*($SiMe_3$)PPh_2S) in [{MeC(NDIPP)CHC(Me)($NCH_2CH_2N(^iPr)_2$)}Sc{$C(SiMe_3)PPh_2S$}] (117.0 ppm).[5k] Complex **2** was further characterized by single crystal X-ray diffraction; its molecular structure is shown in Figure 1. Complex **2** has similar coordination geometry as that of complex **1** but with the anionic methyl group replaced by a neutral THF. The Sc–C bond length in

2 (2.089(3) Å) is 0.20 Å shorter than that in **1** (2.292(4) Å), indicating a bond-order increasing. To the best of our knowledge, the Sc–C bond length in **2** is the shortest Sc–C bond length to date.[9] On the other hand, the Sc–P and C–P bond lengths in **2** (2.597(1) and 1.743(3) Å) are slightly shorter than those in **1** (2.638(1) and 1.790(4) Å).

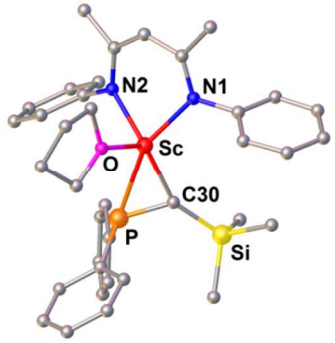


Figure 1. Molecular structure of complex **2** (ball and stick representation). DIPP isopropyl groups and hydrogen atoms were omitted for clarity.

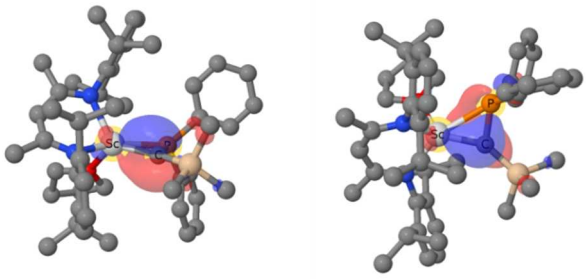
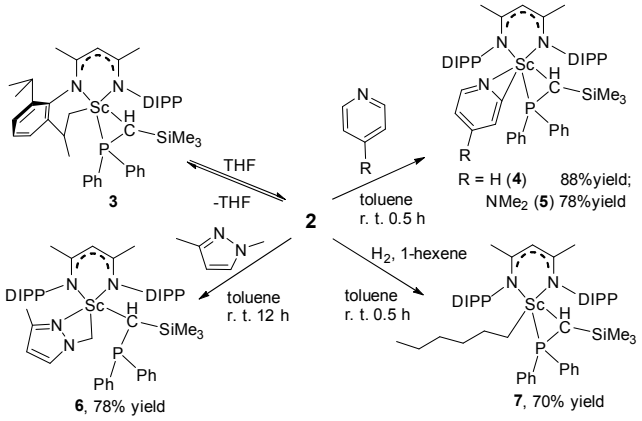


Figure 2. HOMO (3 centres π-type orbital) of complex **2**.

In order to get more insights into the nature of the bonding in complex **2** and especially on the Sc–C one, DFT calculations were carried out. For comparison purposes, a similar analysis was done on complex **1.** In complex **2**, the HOMO is clearly a 3 center(3c) π-type orbital mainly involving the Sc–C and P–C bonds(Figure 2), whereas the HOMO-1 and HOMO-2 are the Sc–C and P–C σ bonds, respectively (see the supporting information). The associated Lewis structure is therefore of allylic-type with π electron delocalization between the Sc, C and P centers, different from that in $(C_5Me_5)Ta(PMe_3)(^2\eta\text{-}CHPMe_2)$ where the electron is localized.[6g] Natural Bonding Orbital (NBO) analysis was then performed. In **2**, the two σ bonds were found in the bonding interaction and a 3c bond was also found between Sc, C and P atoms, in line with the Lewis structures drawn from the MOs. In the same way, the associated Wiberg Bond Indexes (WBI) are 0.75 for the Sc–C bond, 0.34 for the Sc-P and 1.21 for the P–C bond, indicating delocalized electron densities. For the latter, the comparison with the bonding in complex **1** is informative. Indeed, the WBI are strongly reduced with respect to complex **2** (0.39 for the Sc–C bond 0.36 for Sc-P and 0.99 for the P–C bond), in line with the lack of π interaction in the alkyl complex **1.** Therefore, DFT results indicate the alkylidene character of complex **2** with a π density delocalized in between the Sc, C and P centers.

Scheme 2. Reactivity of Scandium Phosphinoalkylidene Complex 2.



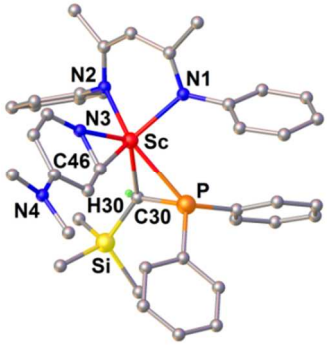


Figure 3. Molecular structure of complex **5** (ball and stick representation). DIPP isopropyl groups and hydrogen atoms (except the H30 atom) were omitted for clarity.

In contrast to the remarkable stability of titanium phosphinoalkylidene complex [(PNP)Ti(CHPPh$_2$)Ph] (PNP = [N{2-P(^{i}Pr)$_2$-4-methylphenyl}$_2$]$^-$) and scandium alkylidene complexes with P(V) substituent [L′Sc{C(SiR$_3$)PPh$_2$S}] (L′ = [MeC(NDIPP)CHC(Me)(NCH$_2$CH$_2$NMe$_2$)]$^-$, [MeC(NDIPP)CHC(Me)(NCH$_2$CH$_2$N(^{i}Pr)$_2$)]$^-$; R′ = Me, Ph),[5k, 6k] complex **2** rapidly undergoes an intramolecular C−H bond activation to give complex **3** accompanied by release of THF in C_6D_6 at room temperature (Scheme 2). The ^{1}H NMR spectral monitoring also revealed an equilibrium between the complexes **2** and **3** (see Figure S29 of the supporting information), and the equilibrium constant of the reaction at room temperature is 1.64 according to the equation K_e = ([**3**][THF])/([**2**]). Complex **3** was prepared in 69% isolated yield by a scaled-up reaction in toluene, and THF was removed under vacuum during the reaction for promoting the conversion of **2** into **3**. The molecular structure of **3** was determined by single crystal X-ray diffraction (the supporting information, Figure S2). While in the presence of pyridine, complex **2** rapidly converts into a scandium pyridyl phosphinoalkyl complex [LSc{CH(SiMe$_3$)PPh$_2$}(C$_5$H$_4$N)] (**4**). The mechanism by which complex **4** is formed can occur by two plausible pathways: 1) Path A, a 1,2-addtion of pyridine C−H bond to the Sc–C(alkylidene) bond of **2**; 2) Path B, an intramolecular C−H bond activation first to generate complex **3**, followed by a σ-bond metathesis of **3** with pyridine. The isotopic labeling experiment by using **2** with pyridine-d_5 was carried out, which cleanly produced the isotopomer [LSc{CD(SiMe$_3$)PPh$_2$}(C$_5$D$_4$N)], and no deuterium incorporation was observed into the aryl group of L. Therefore, the scandium pyridyl phosphinoalkyl complex **4** is formed via Path A. Complex **2** also readily reacts with 4-dimethylamino pyridine (DMAP) at room temperature to afford a C−H bond activation product **5**.

Solid state structures of **4** and **5** were also obtained; the molecular structure of **5** is shown in Figure 3, while that of **4** given in the supporting information (Figure S3). In **4** and **5**, the pyridyl and 4-dimethylamino pyridyl ligands are both η^2 bound with Sc–N bond lengths of 2.154(2) and 2.150(3) Å and Sc–C bond lengths of 2.227(2) and 2.219(4) Å, respectively.

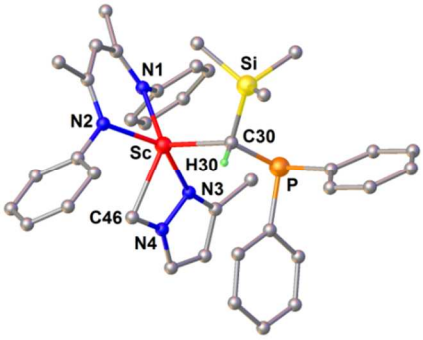


Figure 4. Molecular structure of complex **5** (ball and stick representation). DIPP isopropyl groups and hydrogen atoms (except the H30 atom) were omitted for clarity.

In the reaction of **2** with 1,3-dimethylpyrazole, a selective C−H bond activation occurs at the methyl group on nitrogen atom to give complex **6** as shown in Scheme 2, and no other product was observed. 1,3-dimethylpyrazolyl ligand coordinates to the scandium center in a K^2-C,N fashion with Sc–N and Sc–C bond lengths of 2.276(3) and 2.287(2) Å, respectively (Figure 4). It's worthy to note that the phosphorus atom of the phosphinoalkyl ligand is not coordinated to the scandium ion. Furthermore, complex **2** rapidly reacts with H_2 under one atmosphere of H_2 in benzene or toluene at room temperature. The product quickly decomposes, but it can be trapped by a reaction with 1-hexene.[10] The reaction gave a scandium hexyl complex **7** in high yield, and the complex was characterized by X-ray crystallography (see Figure S4 of the supporting information). The formation of **7** implied that complex **2** activates H_2 to produce a scandium hydride, which subsequently undergoes an addition reaction with 1-hexene. The isotopic labeling experiment of **2**, D_2 and 1-hexene gave the isotopomer [LSc{CD($SiMe_3$)PPh_2}(CH2CH(D)C_4H_9)], and no deuterium incorporation was observed into the aryl group of L. It was also found that addition of THF to **7** causes hexane elimination to regenerate the phosphinoalkylidene complex **2** at 50 °C. Furthermore, our initial study showed complex **2** can catalyze the hydrogenation of 1-hexene.

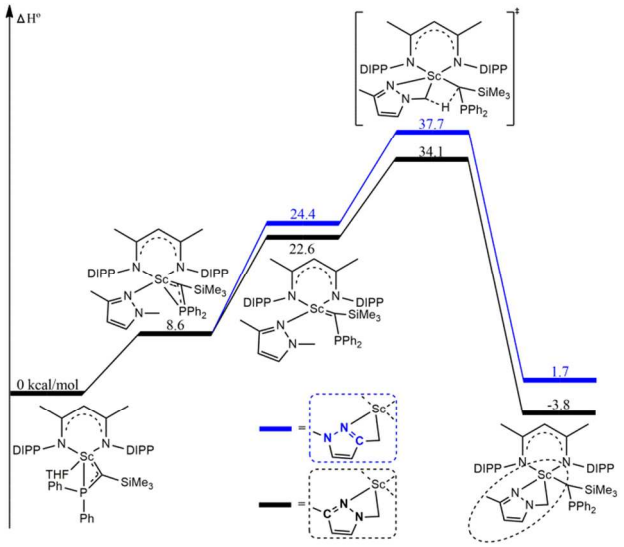


Figure 5. DFT computed enthalpy reaction profile for the reaction of **2** with 1,3-dimethylpyrazole at room temperature

DFT calculations were then carried out on the selective C−H activation of 1,3-dimethylpyrazole (Figure 5). The reaction with 1,3-dimethylpyrazole begins by the coordination of the pyrazole that induces the loss of the chelating effects of the phosphino group in **2**. This is overall disfavored by more than 20 kcal/mol. Then, the C−H bond activation transition state (TS) can be reached and the barrier is around 34 kcal/mol for the lowest in line with a 12h reaction. The selectivity of the C−H bond activation is both kinetic (lower barrier by 3.6 kcal/mol) and finally by the formation of the product that is more stable when the methyl on the nitrogen atom is activated. For comparison purposes, the H_2 activation was also computed (Figure 6). The coordination of H_2 does not imply the full disruption of the chelating effect of the phosphino group in **2**. The barrier is 15 kcal/mol, significantly lower than the C−H activation of the 1,3-dimethylpyrazole, in line with a much faster reaction.

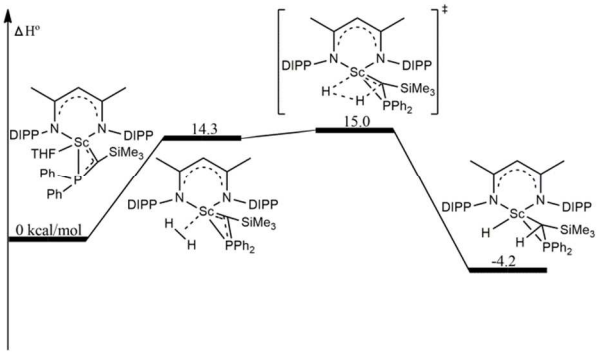


Figure 6. DFT computed enthalpy reaction profile for the reaction of **2** with H_2 at room temperature.

In summary, scandium methyl phosphinoalkyl complex [LSc{CH($SiMe_3$)PPh_2}Me] (**1**) eliminates methane in THF to produce scandium phosphinoalkylidene complex [LSc{C($SiMe_3$)PPh_2}THF] (**2**). X-ray diffraction analysis reveals the very short Sc−C bond length in **2**, and DFT analysis indicates electronic delocalization between the Sc, C and P centers. Complex **2** exhibits a much higher reactivity than the one reported to date for scandium alkylidene complexes containing P(V) substituent.[5k] DFT investigations of the reaction mechanisms explained

the rate and the selectivity of the C−H activation of 1,3-dimethylpyrazole because of the loss of P-chelation to allow the activation and the stability of the formed product. In the same way, the easiness of the H_2 activation appears to be due to the possibility to maintain chelation by the phosphino group unlike the C−H activation of 1,3-dimethylpyrazole. This is in line with the electronic delocalization found in the phosphinoalkylidene ligand by DFT analysis. This complex **2** is therefore a unique platform, and we are currently exploring its ability to perform catalytic reactions and enlarging the family of rare-earth metal phosphinoalkylidene complexes.

ASSOCIATED CONTENT

Supporting Information

Experimental and computational details and a zip file containing CIFs for **1**−**7**. 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 interests.

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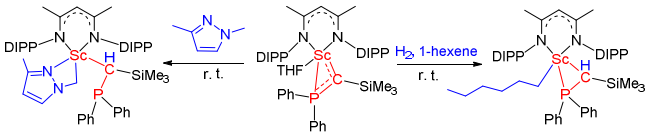
(9) The previous shortest Sc–C bond length is 2.1134(18) Å observed in [{MeC(NDIPP)CHC(Me)(NCH$_2$CH$_2$N(^{i}Pr)$_2$)}Sc{C(SiMe$_3$)PPh$_2$S)], see the reference 5k.

(10) The complexes 2 and 3 both do not react with 1-hexene.


DIPP
N
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H2, 1-hexene