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Nucleophilic Scandium Carbene Complexes

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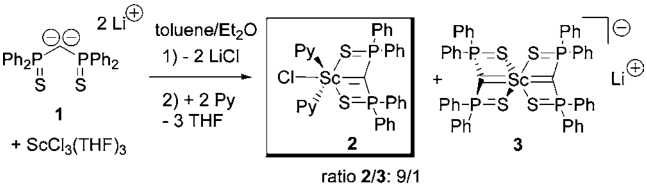
Abstract: Using a geminal dianion as precursor, a nucleophilic scandium carbene complex (**2**) has been synthesized by salt metathesis on $ScCl_3(THF)_3$ in 52% isolated yield. The X-ray structure as well as an NBO analysis points to a double interaction between the carbon and the scandium atoms. Quantification of the electron density donation from the carbon to the metal center, from both σ and π symmetry orbitals, predicts a "nucleophilic carbene" behavior. Addition of benzophenone on complex **2** results in the formation of the expected alkene derivative and the trapping of a rare, μ^3-oxo-Sc species via a "scandia-Wittig" reaction.

Early transition metal carbene/alkylidene complexes[1,2] possess nucleophilic behavior.[1b,3] The generation of the alkylidene fragment, a key issue in the syntheses of the complexes, relies on the deprotonation of an alkyl ligand.[1b,c] To form monometallic species, the $\sigma+\pi$ interaction between the carbene fragment and the metal must be favorable, requiring (a) orbitals of appropriate energy, (b) adequate steric congestion to prevent the formation of multinuclear complexes,[1b,d] and (c) a planar geometry at C. If point (a) is satisfactory for early transition metals of groups 5 and 4, then the energy mismatch between orbitals of rare earth (RE) metals (group 3 and Ln) and carbon is undoubtedly responsible for the paucity of RE metal carbene complexes.[4] In 2008, the groups of Anwander[5] and Mindiola[6] reported on the successful syntheses of analogues of Tebbe's reagent[2] with RE metal fragments, both relying on the deprotonation of a $RE(CH_3)_2$ fragment by $Al(CH_3)_3$. As for Tebbe's reagent, the CH_2 moiety is involved in two σ interactions rather than a double $\sigma+\pi$ interaction with the RE, highlighting the importance of point (b). In 2000, Cavell et al. used the in situ deprotonation of a bisiminophosphorane ligand ($Me_3SiN{=}P(Ph)_2$-$CH_2P(Ph)_2{=}NSiMe_3$) to form the first Sm(III) carbene complex.[7] Since 2008, Liddle et al. and some of us have obtained related RE(III) complexes.[8] In 2005, we used the geminal dianion $dppmS_2Li_2$ (**1**) to synthesize both Sm and Tm(III) mono- and biscarbene complexes.[9a,b] The latter complexes showed a pronounced nucleophilic behavior, reminiscent of Schrock-type carbene complexes. In contrast with these results, in 2009, Liddle et al. showed a lack of nucleophilic behavior for the carbene center in the case of Y.[8a]

Here we present the first example of a monometallic scandium carbene complex featuring a Sc−C interaction with multiple bond character, as shown by experimental data as well as DFT analysis. Its nucleophilic behavior toward benzophenone in a "scandia-Wittig" reaction is evidenced by the trapping of a rare Sc=O fragment.

When a toluene solution of the dianion $DPPMS_2Li_2$ (**1**,[9c] 1 equiv) was added to a suspension of the scandium trichloride salt $ScCl_3(THF)_3$ in toluene, formation of two novel complexes was observed by ^{31}P NMR, in an approximately 9:1 ratio. Filtration of the residual salts (LiCl and slight excess of $ScCl_3(THF)_3$) followed by addition of 2 equiv of pyridine allowed the easy separation of the two complexes. Indeed, white crystals of the major carbenic scandium complex **2** readily deposited from the solution (isolated in 52% yield, Scheme 1). The minor product of this reaction was characterized as the homoleptic anionic complex **3**.

Scheme 1. Synthesis of Complexes **2** and **3**



Complex **2** is, as expected, highly reactive. It is characterized in ^{31}P NMR by a singlet at 10.5 ppm in toluene, 11 ppm upfield from the signal of the starting dianion **1**. As previously noted for other complexes, the signal of the quaternary P−C−P carbon atom was not observed in the ^{13}C NMR spectrum. The monometallic nature of the first scandium carbene complex was confirmed by an X-ray structure analysis (Figure 1).

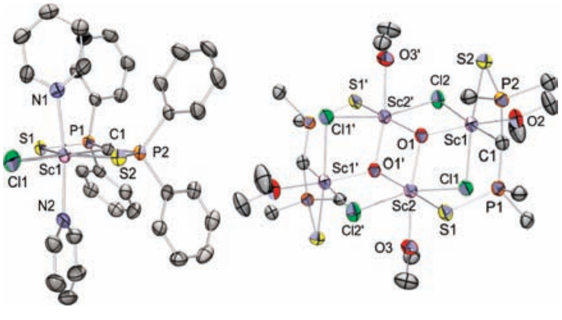


Figure 1. ORTEP plots of complexes **2** (left) and **4** (right) with thermal ellipsoids drawn at the 50% probability level (carbon atoms of Ph and THF omitted for clarity in complex **4**).

The scandium atom is at the center of a distorted octahedron. The geometry of the chelating tridentate ligand S∼C∼S is planar. The 2.2072(1) Å long Sc−C bond is much shorter than the $Sc-CH_2$ (2.3167(17) Å) bridging moiety reported by Mindiola[6] yet in the range for single $Sc-CH_3$ bonds. Most importantly, the geometry at C1 is planar ($\Sigma_{angles} = 359.7°$), and the Sc atom lies exactly in the P−C−P plane, which is most favorable for a π overlap of the Sc and C orbitals. The P1−C1−P2 bond angle of 159.3(2)° is similar to the one found in the Sm carbene complex (156.4(4)°)

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and wider than the ones in the Tm carbene complex (151.1(2)°) and the Zr carbene complex[9d] (145.7(1)°). On the other hand, the P−C and P−S bond distances found in the dianion **1**, the Zr complex, the Sc complex **2**, and the Sm or Tm carbene complexes[9a,b] are identical within experimental error.

Aiming at describing more precisely the nature of the metal−carbon bond, we performed a theoretical study using Density Functional Theory. The optimized structure is in excellent agreement with the crystallographic structure, especially with a scandium−carbon bond of 2.21 Å in the calculated structure vs 2.207(3) Å in the solid-state structure.

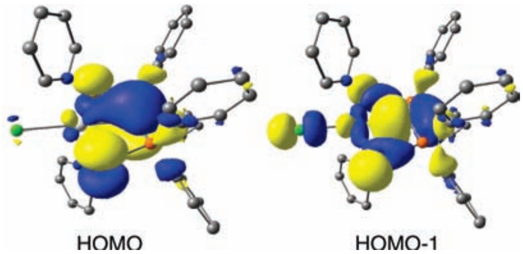


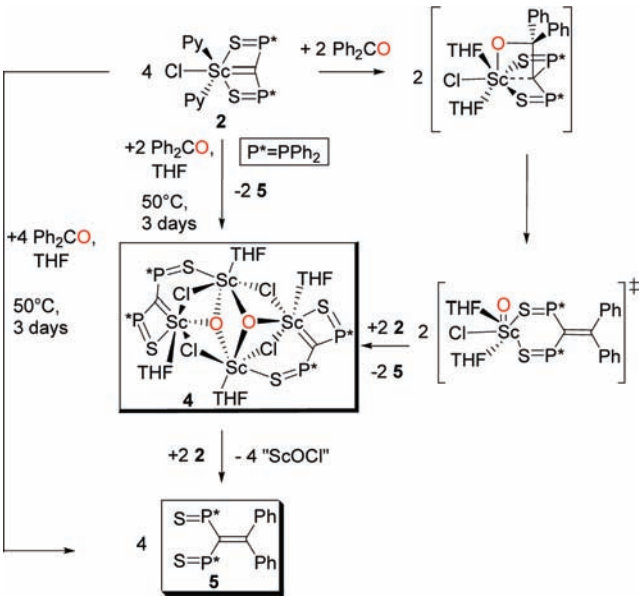
Figure 2. Contour plots of HOMO and HOMO−1 for the complex $(DPPMS_2)ScCl(Py)_2$ (**2**).

The scandium−carbon interaction is described by the two highest molecular orbitals, which are both mainly developed on the carbon center, as expected from the difference between the vacant Sc d orbitals and the SCS frontier orbitals (Figure 2). The HOMO−1 describes the σ interaction between C and Sc atoms, whereas the HOMO describes the π interaction, central to the present work. This latter orbital results from the bonding interaction between a vacant scandium-centered d orbital and the highest occupied fragment orbital (HOFO) of the ligand (of π symmetry).[9d] Most importantly, the involvement of the Sc atom in these two orbitals appears significant and excludes a purely electrostatic interaction between a charged dianion and a metal cation, which is further supported by the magnitude of the Wiberg bond index of 0.60 (cf. 0.80 in the Zr complex);[9d] the index for the dianion **1** is 0.0.[9c]

An NBO[10] analysis reveals that the σ donation to the Sc center (d orbitals) is almost twice as strong (total of 98.4 kcal/mol) as the stabilization by negative hyperconjugation into the two σ^* P−C and the two σ^* P−S orbitals (total of all stabilizing interactions for the σ lone pair, 56.4 kcal/mol; see Supporting Information). On the other hand, the π interaction between C and Sc (d orbitals) is quantified to 39.2 kcal/mol, whereas the stabilization by hyperconjugation into each of the four σ^* P−C orbitals amounts to 13.9 kcal/mol (total of all hyperconjugative stabilizing interactions for the π lone pair, 55.4 kcal/mol).[11] Overall, although the total stabilization by the substituents PPh_2S is larger, the major stabilizing interaction is the π donation toward the Sc center, thus validating the Sc═C drawing and the "scandium carbene" description.

Reactivity of complex **2** toward electrophiles has been evaluated. In sharp contrast with the recently reported lack of reactivity of a related yttrium carbene complex (with bisiminophosphorane ligand),[8a] 1 equiv of **2** in THF reacts with 1 equiv of benzophenone to afford the corresponding metathesis product **5** in 82% yield. In a first stage, a singlet at 46.6 ppm was observed, which we postulate to be the benzophenone adduct, by analogy with our isolated, related Ln adduct.[9a] A second intermediate, **4**, characterized by two small singlets at 18 and 31 ppm, was observed in apparent constant, low concentration during the major part of the reaction. This points to two different chemical environments for the phosphorus atoms in this species, as well as a low solubility in the reaction medium. The synthesis of complex **4** was optimized by the reaction of 0.5 equiv of benzophenone in THF (Scheme 2). Under these conditions, crystals deposited from the crude mixture in 40% yield.[12] Note that complex **4** further reacted with another 0.5 equiv of benzophenone to yield compound **5**.

Scheme 2. Reaction of Complexes **2** and **4** with Benzophenone



The crystal structure of **4** (Figure 1) is centrosymmetric and reveals two different hexacoordinated scandium centers. The first one is similar to the initial complex **2**, bearing the SCS ligand coordinated by the central carbon and one S atom and having replaced one sulfur atom by a bridging chloride ligand. The second one corresponds to the ScOCl fragment; it completes its coordination sphere by sharing a chloride ligand from the first scandium unit and the remaining sulfur from SCS ligand. This induces the differentiation of the two phosphorus atoms, in accord with the solution NMR spectrum. The dimeric structure of **4** obviously results from the stabilization of the highly nucleophilic oxo moiety by three scandium atoms. The Sc−O bond distances of 2.003(2)−2.020(2) Å are as short as the one reported by Mindiola et al.[6] yet slightly longer than in Sc−OR complexes (∼1.9 Å). Apart from the dissymmetry of the ligand $DPPMS_2$ in **4**, an elongation of all Sc−Cl bonds is observed (from 2.462(1) Å in **2** to 2.578 Å (av) in **4**), especially the one in the *trans* position from the SCS carbon (2.6214(1) Å). Remarkably, despite the coordination of one of the sulfurs to the ScO moiety, the metrical parameters within the carbenic moiety are unchanged, which is fully consistent with the analogous reactivity of **4** and **2** toward electrophiles.

We have presented here the first scandium carbene complex that demonstrates a clear double $\sigma+\pi$ donation toward the metal center. This interaction has been evaluated by the means of DFT calculations. The unprecedented "scandia-Wittig" reactivity of this type of carbene fragment allowed the trapping of a rare oxo-Sc moiety. The elucidation of the mechanism by DFT is currently under investigation and will be reported in due course.

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Supporting Information Available: Experimental details, including characterizations and X-ray structure data (CIF) for complexes **2** and

4; computational details, including optimized geometry and NBO analysis for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Note that a NBO analysis has been carried out recently on a Nb complex featuring an α-agostic interaction. The calculated stabilization energy for the donation of the σ CH bond into an empty d orbital at a Nb center amounts to 18 kcal/mol:Pantazis, D. A.; McGrady, J. E.; Besora, M.; Maseras, F.; Etienne, M. *Organometallics* **2008**, *27*, 1128.

(12) This reaction, when carried out in benzene, leads to the analogous complex **4′** bearing coordinated pyridine in place of THF, proving that the O atom in complex **4** comes from the benzophenone.

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