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Alkyl scandium complexes coordinated by dianionic O,N,N- and O,N,O-ligands derived from Schiff bases

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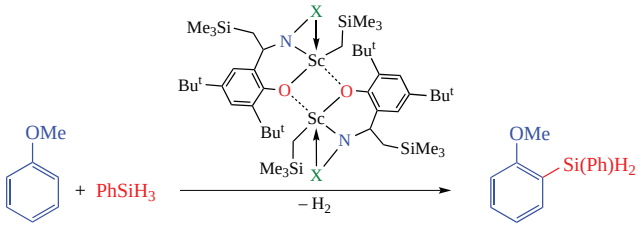
The reactions of imino phenols 3,5-Bu^t_2-2-HOC_6H_2CH=NX (X = 8-C_9H_6N, 2-MeO-5-MeC_6H_3 and 2-$PhOC_6H_4$) with $Sc(CH_2SiMe_3)_3(THF)_2$ in toluene proceed with silane elimination and reductive alkylation of the C=N group affording dimeric base-free monoalkyl scandium complexes. X-ray analysis of the two complexes revealed their dimeric structures due to μ-bridging amidophenolato dianions. The complexes catalyze hydrophosphination of styrene, phenylacetylene and tolane with Ph_2PH as well as dehydrogenative coupling of anisole with hydrosilanes.

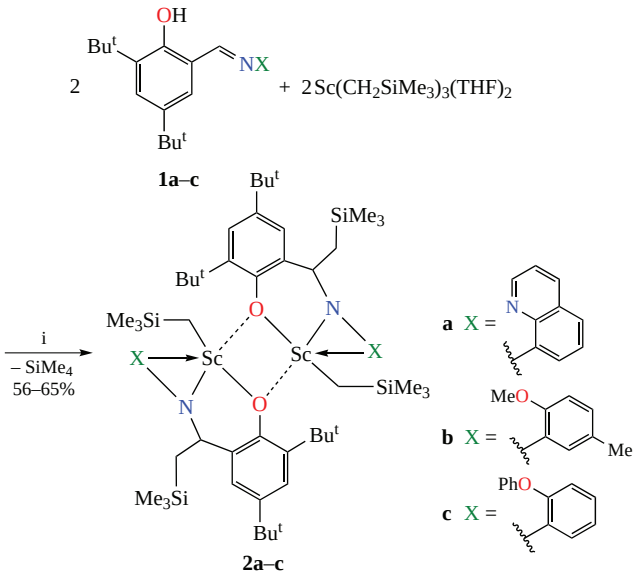


Keywords: scandium, alkyl complexes, catalysis, hydrophosphination, dehydrocoupling, organosilicon compounds, organophosphorus compounds.

Organoscandium compounds supported by polydentate ligands have proven to be efficient catalysts for a variety of organic reactions.[1–4] In particular, scandium derivatives were successfully applied for catalysis of hydrofunctionalization of olefins and acetylenes,[3,5–7] isoprene[3,8–10] and lactide polymerization,[11–13] as well as C–H bond activation[14–18] reactions. The dependence of stability of organorare-earth complexes on coordination and steric saturation of the metal center resulted from the large size of these ions emphasizes the importance of ancillary ligand design as a means of modification and control of the reactivity. 'Tailoring' of new ligand systems suitable for coordination to rare-earth metals and allowing for the synthesis of isolable alkyl species, investigation of structure–reactivity relationships are currently one of the main trends in the organorare-earth chemistry.[1–4] Schiff bases are among the types of ligands which found broad applications.[19–26] Due to accessibility and facile tuning of the steric and electronic properties, imino phenols are successfully used in the synthesis of organic derivatives of rare-earth elements of various radii.[27–36]

Herein we report on the synthesis of alkyl scandium complexes supported by Schiff base ligands with various substituents and their application in catalytic C–P and C–Si bonds formation. The reactions of equimolar amounts of $Sc(CH_2SiMe_3)_3(THF)_2$ and tridentate imino phenols 3,5-Bu^t_2-2-HOC_6H_2CH=NX **1a–c** in toluene afford mono(alkyl) scandium complexes **2a–c** coordinated by dianionic tridentate O,N,N- and O,N,O-ligands and featuring dimeric structures due to μ-bridging phenoxide ligands (Scheme 1). The compounds were isolated as red (**2a**), yellow (**2b**) microcrystals or yellow powder (**2c**) in 56–65% yields. The complexes are soluble in THF and toluene and sparingly soluble in hexane.

The formation of complexes **2a–c** results from two reactions. The first one is protonolysis of one Sc–C bond by the phenolic hydroxy group resulting in the liberation of $SiMe_4$ and the formation of Sc–O bond. The second reaction is the addition of Sc–C bond to the C=N fragment which leads to the migration of one CH_2SiMe_3 group to the imino carbon atom and the formation of Sc–N and C–C bonds. Similar pathway was previously described for the reactions of $Ln(CH_2SiMe_2R)_3(THF)_2$ (Ln = Sc, Y, Dy, Yb, Lu; R = Me, Ph) with aldimino pyrroles,[37] alkylimino indole[38] and imino phenols.[28,31]



Scheme 1 *Reagents and conditions*: i, toluene, 0 °C, 1.5 h.

According to monitoring by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, complexes **2a**–**c** turned out to be rather stable. No evidences of their decomposition in dry benzene-d_6 solution in inert atmosphere at ambient temperature was detected during three weeks.

Transparent single crystalline samples of **2a**,**b** suitable for X-ray diffraction study were obtained by crystallization from toluene–hexane mixture or hexane, respectively (Figure 1).[†] For **2c**, no samples of quality appropriate for single-crystal structure determination were obtained, its composition was unequivocally determined by NMR spectroscopy and elemental analysis. Molecules of **2a** and **2b** crystallize in orthorhombic $P2_12_12_1$ (**2a**) and triclinic $P\bar{1}$ (**2b**) space groups with the unique complex molecules in the asymmetric units. Complexes crystallize as solvates **2a**·2C_7H_8 and **2b**·C_6H_{14}. The X-ray diffraction study revealed that both complexes adopt dimeric structures due to two phenoxide oxygens μ^2-bridging two metal centers. The coordination environment of the scandium ion in **2a** is composed of amido and quinoline nitrogens of the same dianionic amido phenolate ligand, two μ^2-bridging phenoxide oxygens and alkyl carbon atom of CH_2SiMe_3 moiety. In **2b**, the oxygen atom of 2-MeO-5-MeC_6H_3 fragment is involved in coordination with the Sc^{3+} instead of quinoline nitrogen in **2a**. Thus, the formal coordination number of scandium ions in **2a**,**b** is five. In both complexes, the coordination polyhedron of Sc^{3+} adopts a geometry of distorted trigonal bipyramid. In **2a**, O(1) and N(1) atoms occupy the apical positions, and N(2), O(2) and C(29) form the equatorial plane (τ_5 = 0.62). In **2b**, O(1) and O(2) lie in the apical positions, but τ_5 = 0.44 shows that geometry of the coordination polyhedron is intermediate between trigonal bipyramidal and square pyramidal. The Sc_2O_2-cores in **2a**,**b** are nearly planar, the dihedral angles between OScO planes are 169.2(2) and 164.0(2)°, respectively. The Sc–C bonds in **2a** [2.223(6), 2.230(6) Å] and **2b** [2.201(4), 2.219(3) Å] have close lengths. In **2a**, the Sc–$O_{phenoxide}$ [2.084(4)–2.156(4) Å] and Sc–N_{amido} [2.070(5), 2.081(5) Å] bond lengths are somewhat longer than those in **2b** [Sc–$O_{phenoxide}$: 2.064(2)–2.101(2); Sc–N_{amido}: 2.030(3), 2.045(3) Å]. The Sc–N_{quin} distances in **2a** are 2.292(5) and 2.309(5) Å. For **2b**, the Sc–O_{OMe} distances are 2.181(2) and 2.182(2) Å. The lengths of former 'imino' C–N bonds in **2a** [1.462(7), 1.468(7) Å] and **2b** [1.457(4), 1.471(4) Å] are indicative of their single character (1.47 Å).[39] For more details on the molecular structures, see Online Supplementary Materials.

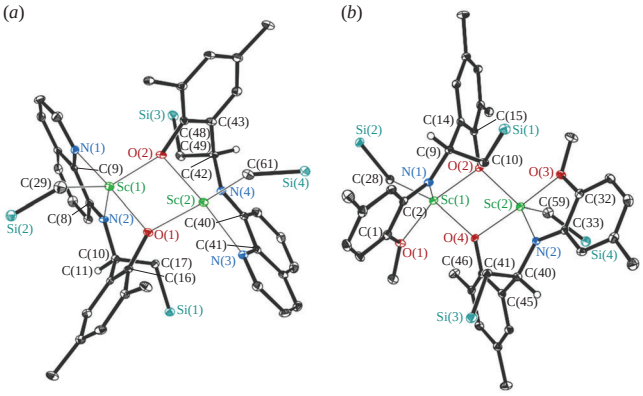


Figure 1 Molecular structures of (*a*) compound **2a** and (*b*) compound **2b**. Thermal ellipsoids are drawn with 30% probability level. Me groups of Bu^t- and $SiMe_3$-substituents, and hydrogen atoms (except quaternary CH groups) are omitted for clarity.

[†] *Crystal data for* **2a**. $C_{64}H_{98}N_4O_2Sc_2Si_4 \cdot 2(C_7H_8)$, M = 1342.01, space group $P2_12_12_1$, T = 100 K, a = 13.3474(6), b = 21.4833(9) and c = 26.6196(10) Å, V = 7633.1(5) Å^3, Z = 4, d_{calc} = 1.168 g cm^{-3}, F_{000} = 2896. Red-colored single crystal with dimension 0.33 × 0.26 × 0.14 mm was selected and intensities of 101751 reflections were measured using Rigaku OD Xcalibur diffractometer (Mo$K\alpha$-radiation, ω-scans technique, λ = 0.71073 Å). After merging of equivalents and absorption correction, 13474 independent reflections (R_{int} = 0.1105) were used for the structure solution and refinement. Final R factors: R_1 = 0.0570 [10601 reflections with $I > 2\sigma(I)$], wR_2 = 0.1383 (all reflections), $S(F^2)$ = 1.039, Flack parameter is 0.00(5), largest diff. peak and hole are 0.67 and –0.48 e Å^{-3}, respectively.

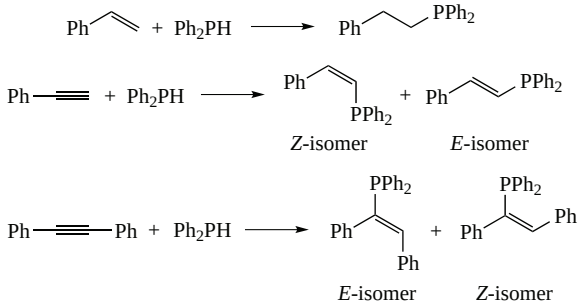
Crystal data for **2b**. $C_{62}H_{104}N_2O_4Sc_2Si_4 \cdot C_6H_{14}$, M = 1229.92, space group $P\bar{1}$, T = 100 K, a = 14.6937(11), b = 15.5893(12) and c = 16.7925(13) Å, α = 104.966(2)°, β = 96.494(2)°, γ = 97.000(2)°, V = 3646.2(5) Å^3, Z = 2, d_{calc} = 1.120 g cm^{-3}, F_{000} = 1340. Yellow single crystal with dimension 0.20 × 0.19 × 0.04 mm was selected and intensities of 28218 reflections were measured using Bruker D8 Quest diffractometer (Mo$K\alpha$-radiation, ω-scans technique, λ = 0.71073 Å). After merging of equivalents and absorption correction, 12621 independent reflections (R_{int} = 0.0664) were used for the structure solution and refinement. Final R factors: R_1 = 0.0644 [8453 reflections with $I > 2\sigma(I)$], wR_2 = 0.1262 (all reflections), $S(F^2)$ = 1.027, largest diff. peak and hole are 0.54 and –0.43 e Å^{-3}, respectively.

The intensity data were integrated using APEX3[49] and CrysAlis^{Pro}[50] software packages. The structures were solved *via* intrinsic phasing algorithm and refined by full-matrix least squares against F^2 using SHELX.[51,52] SADABS[53] and scaling algorithms implemented in CrysAlis^{Pro} were used to perform absorption corrections. All non-hydrogen atoms in **2a** and **2b** were found from Fourier syntheses of electron density and refined anisotropically. All hydrogen atoms were placed in calculated positions and refined isotropically in the 'riding' model with $U(H)_{iso}$ = 1.2 U_{eq} of their parent atoms [$U(H)_{iso}$ = 1.5 U_{eq} for methyl groups]. For more details, see Online Supplementary Materials.

CCDC 2071595 (**2a**) and 2071596 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

All complexes reveal high catalytic activity in hydrophosphination of styrene with Ph_2PH (Scheme 2, Table 1): after 48 h, quantitative yields of exclusively anti-Markovnikov addition products were obtained. Complexes **2a**–**c** proved to be good catalysts for addition of Ph_2PH to both internal and terminal acetylenes at 60 °C. In case of phenylacetylene, the conversions were 31–63% and *Z*-isomers were preferentially formed (78–87%). Complex **2c** demonstrated the highest activity while **2b** was the most stereoselective. Hydrophosphination of internal triple bond with Ph_2PH expectedly turned out to be noticeably slower: when 1,2-diphenylacetylene was used as a substrate, conversion was 10–24% after 48 h; however, *Z*-selectivity was very high (95–96%, see Scheme 2, Table 1).

Valuable organosilicon compounds[40–45] can be accessed by dehydrogenative coupling of organosilanes with arenes.[45–47] Hou and co-workers reported on C–H-silylation of anisoles catalyzed by Sc^{3+} alkyl complexes supported by cyclopentadienyl-amido ligands.[48] The reactions required harsh conditions (120 °C) and a 3–10 fold molar excess of anisole to achieve 17–89% conversions. In this work, complexes **2a**–**c** were



Scheme 2 *Reagents and conditions*: 1 : 1 substrates molar ratio, catalyst **2a**–**c** (2 mol%), neat, 60 °C, 48 h.

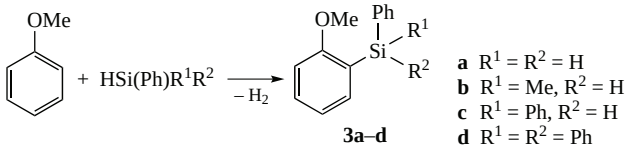
Table 1 Hydrophosphination of styrene and acetylenes with Ph_2PH.[a]

Entry	Catalyst	Substrate	Conversion[b] (%)	Isomer composition[c]	
				Z	*E*
1	**2a**	$PhCH{=}CH_2$	>99	n.a.	n.a.
2	**2b**	$PhCH{=}CH_2$	>99	n.a.	n.a.
3	**2c**	$PhCH{=}CH_2$	>99	n.a.	n.a.
4	**2a**	PhC≡CH	40	78	22
5	**2b**	PhC≡CH	31	87	13
6	**2c**	PhC≡CH	63	80	20
7	**2a**	PhC≡CPh	10	96	4
8	**2b**	PhC≡CPh	24	95	5
9	**2c**	PhC≡CPh	12	95	5

[a]Conditions: neat, 1 : 1 Ph_2PH/substrate molar ratio, 60 °C, 48 h (not optimized), 2 mol% of catalyst. [b]From ^1H NMR. [c]From $^{31}P\{^1H\}$ NMR.

evaluated as catalysts for silylation of anisole with various hydrosilanes ($PhSiH_3$, $PhMeSiH_2$, Ph_2SiH, Ph_3SiH). Catalytic tests were carried out at 80 °C in benzene-d_6 solution at an equimolar ratio of substrates in the presence of 5 mol% of catalyst. The silylation of anisole occurred exclusively in *ortho*-position under rather mild conditions (80 *vs*. 120 °C, Scheme 3). Compounds **2a**–**c** demonstrate close catalytic activities and provide 19–31% conversions. The highest conversions (28–31%) were reached when primary silane $PhSiH_3$ was used (Table 2, entries 1, 5, 9). With secondary silanes $PhMeSiH_2$ and Ph_2SiH_2, the conversion was somewhat lower 19–25% (entries 2–3, 6–7, 10–11). In the case of the most sterically demanding Ph_3SiH, no reaction took place (entries 4, 8, 12). It is noteworthy that no dehydrogenative coupling of silanes occurs in the presence of **2a**–**c**.

In an attempt to synthesize scandium hydride species coordinated by amido phenolate ligand, complex **2b** featuring the least steric crowd around the scandium center was treated with an equimolar amount of $PhSiH_3$. However, this compound proved to be totally inert towards $PhSiH_3$ even at heating at 80 °C for 36 h. Previously, for the related Sc alkyl complexes coordinated by cyclopentadienyl-amido ligand Hou demonstrated



Scheme 3 *Reagents and conditions*: 1 : 1 substrates molar ratio, catalyst **2a**–**c** (5 mol%), C_6D_6, 80 °C, 36 h.

Table 2 Dehydrogenative coupling of anisole with hydrosilanes.[a]

Entry	Precatalyst	Product	Conversion[b] (%)
1	**2a**	**3a**	28
2	**2a**	**3b**	21
3	**2a**	**3c**	19
4	**2a**	**3d**	–
5	**2b**	**3a**	31
6	**2b**	**3b**	20
7	**2b**	**3c**	20
8	**2b**	**3d**	–
9	**2c**	**3a**	29
10	**2c**	**3b**	25
11	**2c**	**3c**	23
12	**2c**	**3d**	–

[a]Conditions: precatalyst (0.025 mmol), anisole (0.55 mmol), hydrosilane (0.5 mmol), C_6D_6 (0.4 ml), 80 °C, 36 h. [b]From ^1H and $^{29}Si\{^1H\}$ NMR (C_6D_6).

that two possible pathways to the formation of two different catalytically active particles could be realized in the reaction mixtures LScAlkyl–anisole–hydrosilane.[48] Thus, the reaction of scandium alkyl complex with $PhSiH_3$ can lead to hydrido species, while activation of sp^2-CH bond of anisole in *ortho*-position to MeO group can afford the benzylic derivative. In principle, both species can perform catalytic cycle of dehydrogenative coupling of anisole with hydrosilanes. Unlike Sc alkyl complexes coordinated by cyclopentadienyl-amido ligand, compound **2b** does not react with $PhSiH_3$ at 80 °C suggesting that the C–H-metalation of anisole by alkyl species is responsible for the formation of the catalytically active species.

In summary, a series of three mono(alkyl) scandium complexes supported by amido phenolate ligands was synthesized *via* alkane elimination protocol between $Sc(CH_2SiMe_3)_3(THF)_2$ and imino phenols **1a**–**c**. The protonolysis of Sc–C bond with the phenolic hydroxyl is accompanied by intramolecular alkylation of the C=N bond of a Schiff base. Complexes **2a**–**c** constitute suitable precatalysts for intermolecular hydrophosphination of styrene, phenyl- and diphenylacetylene with Ph_2PH enabling regiospecific formation of the anti-Markovnikov addition products. Hydrophosphination of 1,2-diphenylacetylene with Ph_2PH leads to highly stereoselective (~95%) formation of *Z*-isomer. Alkyl scandium species **2a**–**c** catalyze the *ortho*-dehydrocoupling of anisole with hydrosilanes. At present, an intensive work to optimize the conditions of catalytic silylation of aromatic C–H bonds and to evaluate the scope of this reaction is underway in our laboratories.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.013.

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