Highly Active, Chemo- and Regioselective YbII and SmII Catalysts for the Hydrophosphination of Styrene with Phenylphosphine

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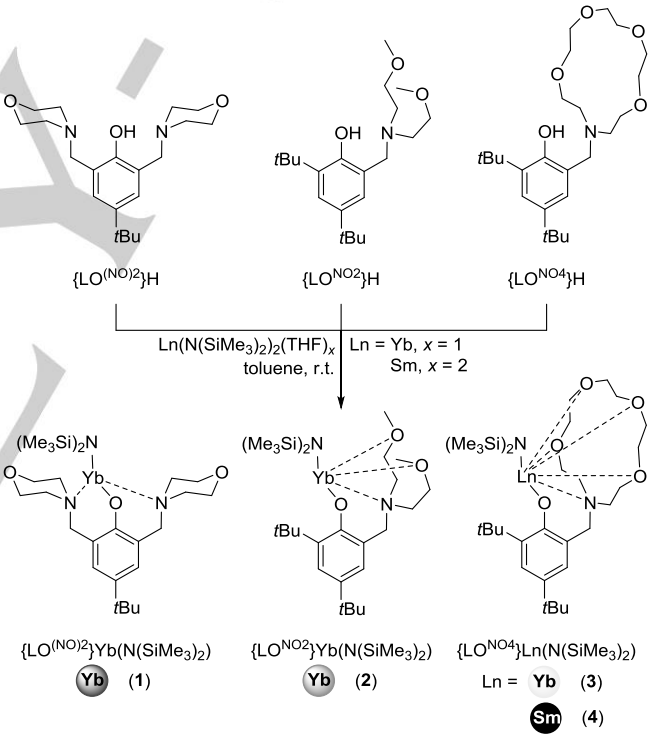
Highly active, chemo- and regioselective Yb(II) and Sm(II) catalysts for the hydrophosphination of styrene with $PhPH_2$

Ivan V. Basalov,[a,b] Vincent Dorcet,[c] Georgy K. Fukin,[a,b] Jean-François Carpentier,*[c] Yann Sarazin,*[c] and Alexander A. Trifonov*[a,b]

Abstract: Stable heteroleptic amido Yb(II) and Sm(II) complexes bearing aminoether-phenolate ligands and devoid of coordinated solvent have been structurally characterized. They afford highly active, chemoselective and, in the case of monoadditions, 100% *anti*-Markovnikov regiospecific catalysts (down to 0.04 mol-% loading) for the hydrophosphination of styrene with $PhPH_2$ under mild conditions.

The ability of complexes of trivalent rare-earth metals to catalyze the polymerization,[1] hydrogenation,[2] hydrosilylation,[3] hydroamination,[4] hydrophosphination,[5] hydroalkoxylation,[6] hydrothiolation,[6] and hydroboration[7] of C=C-containing substrates is abundantly documented. By comparison, little is known of the behavior of divalent lanthanide (Ln) complexes in the catalysis of these transformations. This is somewhat surprising, since the larger ionic radii and the redox-active nature of Ln(II) ions makes them attractive for catalytic purposes (effective ionic radii for C.N. = 6: Yb^{2+}, 1.02 Å; Sm^{2+}, 1.22 Å;[8] standard oxidation potentials: Yb^{3+}/Yb^{2+}, −1.05 V; Sm^{3+}/Sm^{2+}, −1.55 V), and perhaps it owes much to the synthetic difficulties inherently associated to these elements. The formation of P–C bonds by addition of P–H across C=C double bonds during intermolecular hydrophosphination reactions yields phosphines, but it is no easy task. Some success has been achieved with late-transition metals[9,10] and, more recently, with hard oxophilic elements;[5e,11] however the need for more active and selective catalysts persists. Heteroleptic amido Ln(II) complexes bearing *N*-based ancillary ligands – *e.g.* imino-anilide, amidinates – competently catalyze the hydrophosphination of secondary phosphines with dienes and styrene derivatives,[11e-g] but accounts of reactions using primary phosphines as reagents to give valuable secondary organophosphines remain scarce.[5,11a,11g-h] We here report on stable heteroleptic Yb(II) and Sm(II) amido complexes supported by chelating aminoether-phenolate ligands. Their very high catalytic activity, productivity and selectivity in the benchmark intermolecular hydrophosphination of styrene with $PhPH_2$ is presented.

The three aminoether-phenols[12] $\{LO^{(NO)2}\}H$, $\{LO^{NO2}\}H$ and $\{LO^{NO4}\}H$ reacted at r.t. in toluene with stoichiometric amounts of $Yb(N(SiMe_3)_2(THF)$ to give the corresponding Yb(II) heteroleptic, THF-free amido complexes $\{LO^{(NO)2}\}Yb(N(SiMe_3)_2)$ (**1**, dark red), $\{LO^{NO2}\}Yb(N(SiMe_3)_2)$ (**2**, orange) and $\{LO^{NO4}\}Yb(N(SiMe_3)_2)$ (**3**, bright yellow) in 80–90% isolated yields (Scheme 1). The Sm(II) complex $\{LO^{NO4}\}Sm(N(SiMe_3)_2)$ (**4**, black) was obtained in 40% yield using a similar procedure. The formulation for **1**–**4** was established on the basis of XRD and, where possible, NMR data; their purity was attested by elemental analyses. Repeated attempts at reacting $\{LO^{NO2}\}H$ with $Sm(N(SiMe_3)_2(THF)_2$ only returned crystals of the dark green, homoleptic $\{LO^{NO2}\}_2Sm$ and of the colorless, *trivalent* $\{LO^{NO2}\}Sm(N(SiMe_3)_2)_2$ complexes; both were characterized by XRD crystallography (See SI).



Scheme 1. Syntheses of heteroleptic Yb(II) and Sm(II) aminoether-phenolate amido complexes **1**–**4**, with bonding patterns for **2**–**4** as established by XRD (that for **1** remain hypothetical; see Text).

The molecular structure of **2** in the solid state features a mononuclear complex with a 5-coordinate metal center as a result of *O*,*N*,*O*,*O*-κ^4-chelation of the aminoether-phenolate ligand (Figure 1). The metal rests in a distorted environment, between *sq* and *tbp* geometries (τ = 0.58). The $Yb–O_{phenolate}$ bond length in **2** (2.245(12) Å) is at the top end of those found in related monometallic Yb(II)-phenolate complexes (2.177–2.244 Å) listed in the CCDC database, but we were unable to find other occurrences of solvent-free, 5-coordinate Yb(II)-amide phenolate complex. The $Yb–N_{amide}$ bond length (2.326(16) Å) is

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expectedly shorter than the distance to the side-arm N_{amine} atom (2.572(12) Å); it is also smaller than in the aminotroponiminate complex {ATI$^{(iPr)2}$}Yb(N(SiMe$_3$)$_2$)(THF)$_2$ (2.380(12) Å).[13] The Yb–N_{amide} bond distance in the mononuclear **3** (2.466(2) Å) featuring a 7-coordinate metal center (Supporting information) is much longer. This presumably reflects the greater electron-releasing capability of the aminoether-phenolate ligand in **3**, resulting in a weaker (and more reactive, *vide infra*) Yb–N_{amide} bond.

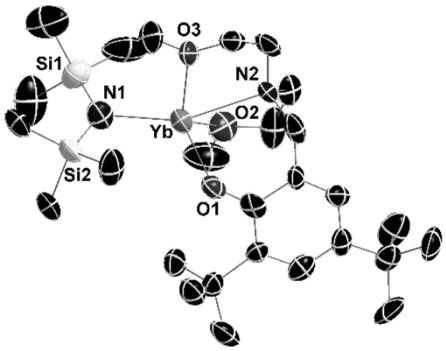


Figure 1. ORTEP plot of the molecular structure of {LO^{NO2}}Yb(N(SiMe$_3$)$_2$) (**2**). Ellipsoids at the 50% level of probability. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Yb–O1 = 2.245(12), Yb–O2 = 2.430(13), Yb–O3 = 2.384(11), Yb–N1 = 2.326(16), Yb–N2 = 2.572(12); O1–Yb–N1 = 119.9(5), O1–Yb–O3 = 114.2(4), N1–Yb–O3 = 95.3(5), O1–Yb–O2 = 94.8(4), N1–Yb–O2 = 112.4(5), O3–Yb–O2 = 122.3(4), O1–Yb–N2 = 81.9(4), N1–Yb–N2 = 157.4(5), O3–Yb–N2 = 68.4(4), O2–Yb–N2 = 67.9(4).

The molecular structure of the mononuclear Sm(II) complex **4** (Figure 2) features all heteroatoms in the tether bound to the metal, which is therefore 7-coordinated. The {LO^{NO4}}$^-$ ligand also coordinated in similar κ^6-fashion in the strontium complex {LO^{NO4}}Sr(N(SiMe$_2$H)$_2$),[12] with a metal ion presenting size (Sr^{2+}: 1.18 Å for C.N = 6)[8] and oxophilicity comparable to those of Sm^{2+}. We were unable to find another example of structurally characterized Sm(II)–N(SiMe$_3$)$_2$ phenolate complex in the CCDC database. One notes a deformation of the amido fragment in **4**, with the SiMe$_3$ moiety corresponding to Si1 being much closer to the metal center (Sm–Si1 = 3.437(3) Å; Sm–N32–Si1 = 106.0(3)°) than the other (Sm–Si2 = 3.884(4) Å; Sm–N32–Si2 = 130.8(4)°). Accordingly, the distance Sm···C35 (3.209(10) Å) is much smaller than the Sm···C36 one (4.107(11) Å). These observations point at Sm···MeSi agostic interactions. They are reminiscent of the agostic distortions in the hydrotris(indazolyl)borate complex {F$_{12}$-Tp^{4Bo,3Ph}}Sr(N(SiMe$_3$)$_2$),[14] but one cannot be assertive in the case of **4** owing to the absence of NMR data to support this claim.

The structure of **1** could not be determined. However, on the basis of similarities[15] between Ca^{2+} (Ca^{2+}: 1.00 Å for C.N = 6)[8] and Yb^{2+} and in view of the structures of [{μ-*O*-LO$^{(NO)2}$}Ca(N(SiMe$_2$R)$_2$)]$_2$ (R = Me,[16] H[12]), one can perhaps anticipate for **1** a dinuclear species with 5-coordinate metal centers bridged by $O_{phenolate}$ atoms.

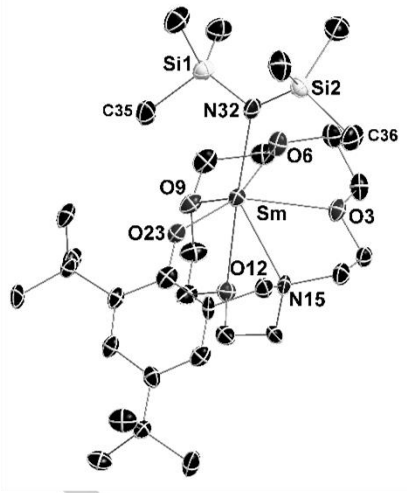
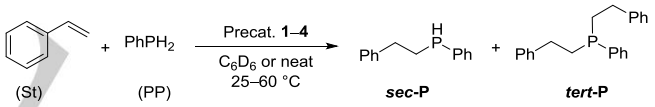


Figure 2. ORTEP plot of the molecular structure of {LO^{NO4}}Sm(N(SiMe$_3$)$_2$) (**4**). Ellipsoids at the 50% level of probability. H atoms omitted for clarity. Representative bond lengths (Å) and angles (°): Sm–O3 = 2.660(5), Sm–O6 = 2.765(6), Sm–O9 = 2.895(6), Sm–O12 = 2.773(6), Sm–N15 = 2.787(7), Sm–O23 = 2.376(6), Sm–N32 = 2.560(7); N32–Sm–O12 = 175.0(2), Sm–Si1–N32 = 106.0(3), Sm–Si2–N32 = 130.8(4).

The performances of **1**–**4** as precatalysts for the chemo- and regioselective intermolecular hydrophosphination of alkenes to produce secondary organophosphines was assessed in a benchmark reaction,[11g-h] the addition of phenylphosphine (PP) to styrene (St, Scheme 2).



Scheme 2. Hydrophosphination of styrene with $PhPH_2$ catalyzed by **1**–**4**.

Reproducibility between experiments was overall excellent. Preliminary experiments indicated that, under the chosen experimental conditions (T = 25–60 °C, t = 0.5–24 h, in C_6D_6 or neat substrates, [St]/[PP]/[Precat] = 50:50:1), the metal-amides Yb(N(SiMe$_3$)$_2$)$_2$(THF) and Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ were entirely inactive. With the Yb(II) precatalysts **1**–**3**, oxidation of the metal was never detected (*e.g.* significant change of coloration and/or loss of NMR resolution) during the catalyzed reactions, even after several days. With the Sm(II)-based **4**, gradual disappearance of the intense brown coloration was observed after the first 20–24 h.

Several key features emerge upon examination of the selected data displayed in Table 1: (*i*) high catalytic activities and productivities, with **3** converting 500-2,000 equiv of substrates in 15-72 h, under very mild reaction conditions; (*ii*) with all active precatalysts, excellent chemoselectivity towards the formation of the desired secondary phosphine *sec*-P, with a selectivity typically around 95% or more; (*iii*) entire regioselectivity during the formation of *sec*-P, with exclusive formation of the *anti*-Markovnikov product, as established by

NMR spectroscopy; (*iv*) an increase of catalytic activity according to **1** << **2** << **4** < **3**, that is, for the family of Yb(II) complexes, the activity increased very significantly with the electron-donating ability and the denticity of the ancillary aminoether-phenolate ligand.

Table 1. Data for the hydrophosphination of styrene with $PhPH_2$ using **1**–**4**.[a]

Run	Precat	$[St]_0$ / $[PP]_0$ / $[Precat]_0$	T [°C]	t [h]	Conv[b] [%]	*sec*-P / *tert*-P [c] [%]
1[d]	**1**	50:50:1	60	24	4	n.d.
2	**2**	50:50:1	60	24	52	99:1
3[d]	**2**	50:50:1	60	24	100	95:5
4	**3**	50:50:1	60	0.5	100	94:6
5	**3**	50:50:1	25	1	74	97:3
6	**4**	50:50:1	60	0.5	80	97:3
7	**4**	50:50:1	60	24	98	94:6
8	**4**	50:50:1	25	1	63	97:3
9[e]	**3**	100:100:1	60	3	91	95:5
10[f]	**3**	500:500:1	60	15	100	93:7
11[g]	**3**	2,500:2,500:1	60	72	86	80:20
12	**3**	100:50:1	60	24	100	0:100

[a] Reaction in C_6D_6 with $[precat]_0$ = 11.5 mM unless otherwise specified. The formation of *sec*-P was 100% *anti*-Markovnikov regiospecific, as established by NMR spectroscopy. [b] Conversion of styrene, determined by NMR spectroscopy. [c] Product chemoselectivity determined by ^{31}P NMR spectroscopy. [d] Reaction in neat substrates with $[precat]_0$ = 11.5 mM. [e] $[precat]_0$ = 9.35 mM. [f] $[precat]_0$ = 6.99 mM. [g] $[precat]_0$ = 1.62 mM.

More specifically, if precatalyst **1** proved disappointing, converting only 4% of the substrates after 24 h in the absence of solvent (Table 1, entry 1), in the same time interval, **2** achieved complete (in neat substrates, entry 3) or 52% (in C_6D_6, entry 2) conversions with excellent selectivity. The best precatalysts were **3** and **4** supported by the very chelating ligand $\{LO^{NO4}\}^-$. They easily converted 50–100 equiv of substrates within 1 h at 60 °C (for **4**) or even 25 °C (for **3**) with excellent selectivity towards the formation of *sec*-P (entries 4–8). Because the initial catalytic results were somewhat better with **3** compared to **4**, and owing to its greater stability, ease of access and diamagnetism, subsequent experiments focused on the use of the Yb(II) precatalyst. Remarkably, **3** readily achieved complete conversion of 100–500 equiv of substrates within 3–15 h (TOF ≈ 30–33 h^{-1}) at 60 °C in diluted solution while maintained excellent selectivity (entries 9–10). It also converted 86% of 2,500 equiv in 72 h at 60 °C (TON = 2,150, TOF = 30 h^{-1}, entry 11), although in this case longer (unoptimized) exposure time led to a decrease of the final chemoselectivity (*sec*-P/*tert*-P = 80:20); this possibly reflects catalyst degradation over long time periods. The productivities and activities observed with **3** under mild conditions still outclass those achieved with recently reported precatalysts, *e.g.* our Yb(II)-carbazole amide (30% conv. of 50 equiv of neat substrates at 60 °C in 10 h, TOF = 1.5 h^{-1}),[11g] and Waterman's exquisitely versatile zirconium-triamidoamine (89% conversion of 20 equiv in 12 h at 25 °C, TOF = 1.5 h^{-1}).[11h,17] With $[St]_0/[PP]_0$ = 2:1, the formation of the tertiary organophosphine $PhP(CH_2CH_2Ph)_2$ catalyzed by **3** is both quantitative and chemoselective (entry 12).

The calcium analogues of **1**–**4** were less efficient for this catalysis. For instance, $\{LO^{NO2}\}Ca(N(SiMe_3)_2)(THF)$ (**5**) only converted 40% of neat substrates ($[St]_0/[PP]_0/[Ca]_0$ = 50:50:1, $[Ca]_0$ = 11.5 mM) in 24 h at 60 °C (TOF = 0.8 h^{-1}; *sec*-P/*tert*-P= 99:1), *i.e.* it was less active than **2**, and 1 to 2 orders of magnitude less active than **3**. Even if the influence of the coordinated THF molecule in **5** towards catalysis was not elucidated, the differences can certainly be linked to the identity of these oxophilic metals. The superiority of Yb(II) precatalysts over congeneric calcium ones has been observed before, for instance in polymerization catalysis.[15b,18]

The identity of the ancillary aminoether-phenolate ligand considerably impacts the efficiency of the Yb(II) precatalysts **1**–**3**. Catalytic activity very clearly increased with the electron-donating and chelating ability of the ligand (Table 1, entries 1, 2 and 4). We believe this may translate the intrinsic stability of the complexes, both against the presence of residual impurities during catalysis and against oxidation of the metal center. In this respect, the synthesis of **4** was (relatively) straightforward, but all attempts to obtain $\{LO^{NO2}\}Sm(N(SiMe_3)_2)$ returned the oxidized complex $\{LO^{NO2}\}Sm(N(SiMe_3)_2)_2$ along with $\{LO^{NO2}\}_2Sm$ (*vide supra*).

In conclusion, the preparation of rare Yb(II) and Sm(II) heteroleptic amido complexes supported by aminoether-phenolate ligands of varying denticity was rewarding, as it yielded potent precatalysts for the hydrophosphination of styrene with $PhPH_2$. The catalytic activity observed with **3** in this benchmark reaction is unique, and the resulting secondary phosphine is produced with excellent chemoselectivity and 100% *anti*-Markovnikov regiospecificity. It is for now surmised that the reaction classically proceeds *via* (*i*) insertion of the C=C double bond in the Ln(II)–P bond of a catalytically active metal-phosphide complex, followed by (*ii*) protonolysis of the newly formed metal-alkyl species with $PhPH_2$, thus releasing the secondary phosphine and regenerating the phosphido active species. These preliminary results offer scope for the production of much-coveted secondary organophosphines using a panel of activated alkenes. This line of investigations is now being carried out in our laboratories, together with pertinent mechanistic investigations and efforts to optimize the ligand platforms.

Experimental Section

All experimental details are given in the Supporting information.

Acknowledgements

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Keywords: divalent lanthanides • aminoether-phenolate • hydrophosphination • phenylphosphine • styrene

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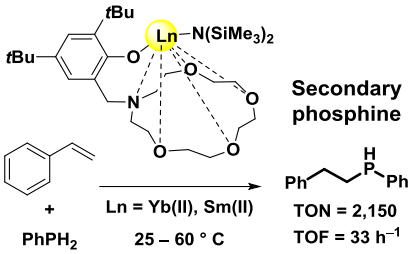
COMMUNICATION

Structurally characterized, stable heteroleptic amido Yb(II) and Sm(II) complexes bearing aminoether-phenolate ligands constitute highly active (TON = 2,150; TOF up to 33 h^{-1}, down to 0.04 mol-% loading), chemoselective (up to 99%) and anti-Markovnikov regioselective catalysts for the hydrophosphination of styrene with $PhPH_2$ under mild conditions.



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