Carbon−Hydrogen Bond Activation of Aromatic Imines by $(Cp^*{}_2SmH)_2$

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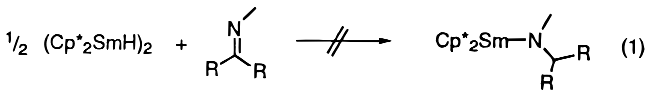
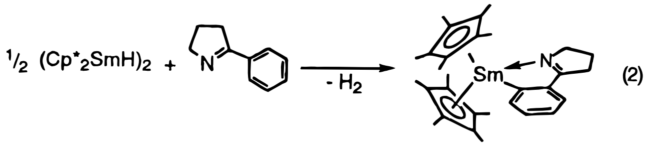
Summary: Treatment of $(Cp^*{}_2SmH)_2$ with 2-phenyl-1-pyrroline forms product **1**, *via ortho-metalation. Complex* **1** *was characterized spectroscopically and by single-crystal X-ray diffraction. The C−H bond activation reaction also occurs for acyclic aromatic ketimines and aldimines.*

Organolanthanide complexes of the type $Cp^*{}_2LnR$ ($Cp^* = \eta^5$-C_5Me_5, Ln = lanthanide, R = alkyl, H)[1] are highly active catalysts for the hydrogenation,[2] hydrosilylation,[3] and polymerization of terminal olefins,[4] oligomerization of alkynes,[5] and cyclization of 1,5- and 1,6-dienes[6] and aminoolefins.[7] In contrast, study of the reactivity of lanthanide compounds toward imines has been limited, involving only $Ln(OTf)_3$[8] or SmI_2.[9] For the past few years our group had investigated the use of group 4 transition metal compounds,[10] especially metallocene complexes of Ti(III),[11] in the reduction of unsaturated substrates. In particular, we have examined the hydrogenation of imines and have recently reported the first early transition metal catalyst for the asymmetric reduction of imines.[12] As an extension of this research, we have initiated an investigation of the reactivity of imine substrates with lanthanide complexes, given the similarity of the chemistry exhibited by Ti(III) and group 3 (Sc, Y, Ln) transition metal complexes.[13] Herein, we report that $(Cp^*{}_2SmH)_2$ reacts with aromatic imines *via* ortho-metalation, rather than the anticipated 1,2-insertion of the imine into the Sm−H bond to form an amide complex (eq 1).



When the progress of the reaction between $(Cp^*{}_2SmH)_2$ and 2-phenyl-1-pyrroline was followed by ^1H NMR spectroscopy, we observed facile (benzene-d_6, 10 min, room temperature) conversion to the ortho-metalated complex **1** (eq 2). In the ^1H NMR spectrum, the



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presence of H_2 (δ 4.46) and the absence of a tertiary pyrrolidine proton indicated that the C═N bond had not been reduced. Furthermore, the ^1H NMR spectrum of **1** displayed a single Cp* resonance at δ 1.35 (30 H) and showed four resonances at δ −1.24, 6.39, 8.01, and 8.80, each integrating to one proton; these were assigned to the aromatic protons. In addition, the pyrroline ring resonances are observed at δ −7.02, −0.61, and 3.33.[14] A subsequent preparative-scale reaction yielded yellow crystals of **1** suitable for X-ray analysis which confirmed the proposed molecular structure of **1** (Figure 1; *vide infra*).[15]

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[14] All spectroscopic and analytical data for the compounds reported here had been provided as Supporting Information.

[15] Crystal data for **1**: $C_{30}H_{40}NSm$, triclinic, $P\bar{1}$, $V = 2624.2(12)$ Å^3, Mo Kα ($\lambda = 0.710\,69$ Å), $d_{calc} = 1.422$ Mg/m^3, $a = 11.441(4)$ Å, $b = 15.032(3)$ Å, $c = 15.432(3)$ Å, $T = 193$ K, $Z = 4$, $R(F) = 9.75\%$, $R(wF) = 24.93\%$. Details of the structure determination are provided as Supporting Information.

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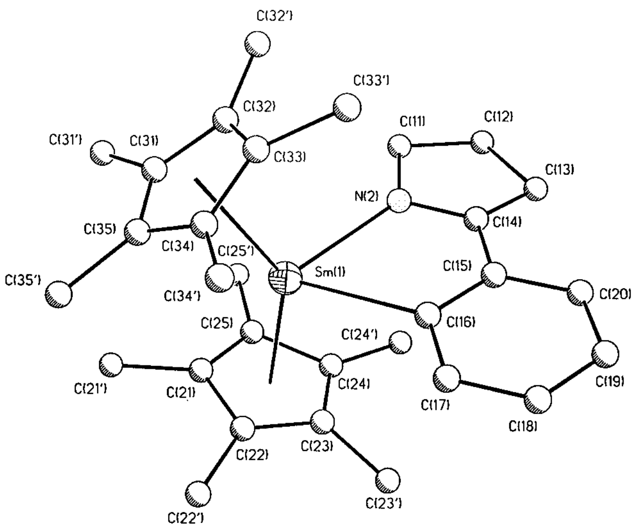
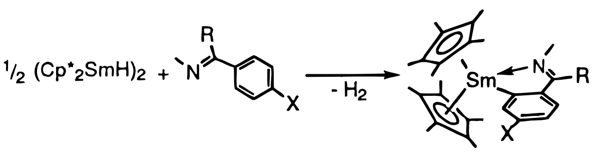


Figure 1. Diagram of the molecular structure of $Cp^{*}{}_2Sm[o\text{-}C_6H_4C{=}NCH_2CH_2CH_2]$ (**1**) showing a thermal ellipsoid (50% probability level) for Sm(1).

The ortho-metalation pathway is not limited to cyclic imines (eq 3). This reaction also occurs with acyclic



(3)

2, R = Me; X = H
3, R = Me; X = Cl
4, R = Me; X = Br
5, R = H; X = H

imines (**2**), halogen-containing ketimine substrates (**3**, **4**), and aldimines (**5**).[14] These reactions proceed rapidly (*ca.* 10 min, room temperature) and in quantitative yield as estimated by ^1H NMR spectroscopy. However, the high solubility in nonpolar solvents of compounds **1**−**4** leads to lower isolated yields ranging from 35% (for **2**) to 70% (for **1**). These complexes are extremely air- and moisture-sensitive but can be stored (solid state) under inert atmosphere for several weeks. In contrast, the thermal decomposition of compound **5** prevented its purification, and attempts to isolate it resulted in a yellow powder of ca. 80% purity.

Characteristic in the ^1H NMR spectra of all these compounds is the upfield chemical shift of the NCH_2− (for **1**) or NMe (for **2**−**5**) resonance which is paramagnetically shifted (δ −7.0 to −10.5; *cf.* around δ 3.0−4.0 for the parent imine), suggesting the presence of a Sm−N dative interaction in solution. The chemical shift of this resonance is similar to the −N*Me* shift observed in $Cp^{*}{}_2SmNMe_2$ (δ −7.35).[16] This interaction is also present in the solid state, as shown by the IR (Nujol) spectrum of **1** which displays a C=N stretch (1579 cm^{-1}) at a slightly lower frequency than ν_{CN} (1615 cm^{-1})[12b] for 2-phenyl-1-pyrroline. In addition, this dative bond is in evidence in the X-ray structure of **1** (*vide infra*).

Complex **1** crystallizes in space group $P\bar{1}$, by cooling a saturated pentane solution (−40 °C), with two crystallographically independent molecules of **1** contained in the asymmetric unit.[15] The refinement was plagued by severe disorder, and four molecular structures of **1** resulted, one of which is shown in Figure 1. The local environment around the samarium atom is as expected for trivalent $Cp^{*}{}_2Sm(X)(L)$ compounds,[17] with a Sm−C(phenyl) bond distance (2.51(3)−2.57(2) Å) which is remarkably similar to that found in $Cp^{*}{}_2SmPh(THF)$ of 2.511(8) Å.[18] The Sm−N bond length (2.40(4)−2.54(3) Å) appears reasonable in comparison to related structures which contain Ln−N dative bonds: $Cp_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$, 2.43(2) and 2.54(2) Å;[19] $Cp^{*}Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$, 2.568(5) and 2.506(6) Å;[20] $Lu(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3$, 2.468(6), 2.478(5), and 2.588(5) Å.[21] The N=C bond distance within the imine moiety (1.31(6)−1.32(5) Å) is somewhat longer than those reported for other ketimine complexes, such as $[(\eta^6\text{-}C_6Me_6)Ru(Ph)N{=}C(H)C_6H_4(PMe)][BF_4]$ (1.294(4) Å),[22] $[Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}N\text{-}2',4',6'\text{-}Me_3C_6H_2)\text{-}3,5\text{-}Me_2C_6H_2\}Br]_2$ (1.298(8) Å),[23] or MnCl(salen) derivatives (1.27 Å).[24] The C−N bond distance (1.47(6)−1.53(6) Å) of the pyrroline ring is within normal range (1.47 Å) for a C−N single bond.[25]

Lanthanide complexes are well-known to exhibit a rich C−H bond activation chemistry toward saturated and unsaturated hydrocarbons.[20,26] Recently it has been shown that they can also activate C−H bonds of heteroatom-containing unsaturated substrates.[20] For example, $Cp^{*}{}_2LnR$ (Ln = Y, La, Ce, Lu; R = $CH(SiMe_3)_2$, H) complexes metalate nitriles (CH_3CN)[27] and pyridine.[5a,26,28] This study presents the first example of ortho-metalation of arylimines by a lanthanide complex. Although, insertion into the C=N bond might be expected, the ortho-metalation reaction is actually favored due to dihydrogen formation.[16] In contrast to this Sm system, which gives only ortho-metalation of the phenyl ring, in the reaction of $(Cp^{*}{}_2YH)_2$ with PhR (R = OMe, SMe, CH_2NMe_2, PMe_2, $P(Me){=}CH_2$) a competition between ortho-metalation and intramolecular C−H bond activation of the Cp* ligand occurs.[29] Comparable reactivity is also seen in the chemistry of electropositive main group elements, such as beryllium. For example, the reactivity of beryllium alkyls with imines is highly dependent on steric effects, yielding reduction, addition, complex formation, and ortho-metalation products.[30]

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Notable is the reaction of Et_2Be with PhCH═NMe which gives the C═N insertion product, $[EtBeN(Me)CHEtPh]_2$, while with PhCH═N^{t}Bu only ortho-metalation is observed. Finally, it is interesting to compare the Sm reaction chemistry described above with that observed for the hydrogenation of 2-phenyl-1-pyrroline catalyzed by (*R*,*R*)-(ETBHI)TiH (EBTHI = ethylenebis(tetrahydroindenyl), which we have previously reported.[12a] Mechanistic studies of this reaction suggest that two independent processes occur, the reduction of the imine *and* ortho-metalation. Therefore, in the Sm system only the C−H bond activation route is observed, while titanium catalyzes both 1,2-insertion of the imine and C−H bond activation. We are currently examining this difference and the extension of this chemistry to the synthesis of ortho-substituted aromatic compounds.

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Supporting Information Available: Text describing complete experimental procedures as well as analytical and spectroscopic data for complexes **1**−**5** and text describing details of the structure determination of **1** along with tables of crystal data, positional and thermal parameters, and bond lengths and angles and additional ORTEP drawings for the four molecules of **1** resulting from the refinement of the two disordered $Cp^*_2Sm[o\text{-}C_6H_4C{=}NCH_2CH_2CH_2]$ molecules (22 pages). Ordering information is given on any current masthead page.

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