A) Experimental Details, NMR data, IR (RAMAN), UV/vis, mass spectra, and elemental analyses of compounds 2, 5, and 6:

\[
\text{trop}_2\text{NH (2)}
\]

MF: C\textsubscript{30}H\textsubscript{30}N

MW: 397.51 g/mol

3 g tropCl (13.2 mmol) are dissolved in 60 ml toluene and 1 ml (1.41 g; 8.7 mmol; 30% excess) of 1,1,1,3,3,3-hexamethyl-disilazane is added. The mixture is refluxed for 4 h. Subsequently, all volatile components are evaporated. For the following procedures, working under argon is no longer necessary. 30 ml of n-hexane are added and the suspension heated until a white powder was obtained.

Yield: 95%

Analytical data was in agreement with the values reported in the literature\[5\]

\[
[Rh(trop_2NH)(tropNH_3)]O_2SCF_3 (5)
\]

MF: C\textsubscript{46}H\textsubscript{38}F\textsubscript{3}N\textsubscript{2}O\textsubscript{3}RhS

MW: 856.76 g/mol

MP: > 250°C

For the preparation of 5, 256 mg [Rh(cod)\textsubscript{2}]O\textsubscript{2}SCF\textsubscript{3} (4) (0.55 mmol) and 217 mg trop\textsubscript{2}NH 2 are suspended in 25 ml CH\textsubscript{3}CN and heated for 20 min. to 50 °C whereby a yellow solution is obtained. All volatile products are evaporated under vacuum, the residue dissolved in 25 mL CH\textsubscript{3}Cl\textsubscript{2} and 115 mg tropNH\textsubscript{3} (3) are added. After refluxing the solution for 10 min., 50 ml n-hexane were added to precipitate the yellow product complex in almost quantitative yield. Crystals were grown from CH\textsubscript{3}CN/toluene/n-hexane.

\[1^1\text{H NMR (400.1 MHz, CD}_2\text{CN):} 2.16 (s, 2 H, NH\textsubscript{2}), 3.45 (s, 1 H, NH), 3.66 (d, \textit{J\textsubscript{NNH} = 9.6 Hz}, 2 H, H\textsubscript{2} CN), 4.26 (d, \textit{J\textsubscript{NH} = 0.8 Hz}, 2 H, H\textsubscript{1} CN), 4.67 (s, 2 H, H\textsubscript{3} CN), 4.92 (s, 1 H, H\textsubscript{4} CN), 5.49 (dd, \textit{J\textsubscript{NNH} = 9.6, J\textsubscript{NH} = 1.3 Hz}, 2 H, H\textsubscript{5} CN), 6.86 (m, 8 H, H\textsubscript{6}/H\textsubscript{7}/H\textsubscript{8}/H\textsubscript{9}), 6.97 (m, 2 H\textsubscript{1} CN), 7.07 (d, J = 7.4 Hz, 2 H\textsubscript{1} CN), 7.28 (m, 4 H, H\textsubscript{6}/H\textsubscript{7}/H\textsubscript{8}), 7.31 (m, 2 H, H\textsubscript{9}), 7.42 (m, 6 H, H\textsubscript{10}/H\textsubscript{11}/H\textsubscript{12})\]

\[13^1\text{C NMR (100.6 MHz, CD}_2\text{CN):} \delta = 60.9 (s, 1 C, C\textsubscript{5}), 70.8 (s, 2 C, C\textsubscript{10}), 74.3 (d, \textit{J\textsubscript{C-CN} = 5.5 Hz}, 2 C, C\textsubscript{8}), 127.3 (s, 2 C, C\textsubscript{2}), 128.0 (s, 2 C, C\textsubscript{8}), 128.1 (s, 2 C, C\textsubscript{8}), 128.2 (s, 2 C, C\textsubscript{9}), 128.6 (s, 2 C, C\textsubscript{9}), 128.7 (s, 2 C, C\textsubscript{16}), 129.1 (s, 2 C, C\textsubscript{16}), 129.5 (s, 2 C, C\textsubscript{1}), 129.8 (s, 2 C, C\textsubscript{10}), 130.2 (s, 2 C, C\textsubscript{10}), 130.2 (s, 2 C, C\textsubscript{10}), 131.0 (s, 2 C, C\textsubscript{15}), 131.4 (s, 2 C, C\textsubscript{16}), 134.5 (s, 2 C, C\textsubscript{16}), 135.4 (s, 2 C, C\textsubscript{16}), 136.8 (s, 2 C, C\textsubscript{16}), 137.0 (s, 2 C, C\textsubscript{16}), 137.6 (s, 2 C, C\textsubscript{16})\]

\[19^\text{F NMR (282.4 MHz, CD}_2\text{CN):} \delta = -79.8 (s)\]

\[103^\text{Rh NMR (12.7 MHz, CD}_2\text{CN):} \delta = 1599 (s)\]

ATR IR – neat in cm\textsuperscript{-1}: 3157 (br with shoulder; NH/CH\textsubscript{2} stretch); 3050 – 2860 (CH stretch); 1601 (s); 1489 (s); 1428 (w); 1252 (s); 1225 (s); 1142 (s); 1029 (s); 941 (w); 875 (w); 741 (s); 635 (s); 594 (s)

Raman in cm\textsuperscript{-1}: 3048 (s); 1600 (vs); 1578 (w); 1488 (s); 1477 (s); 1427 (s); 1313 (s); 1224 (w); 1199 (s); 1044 (s); 884 (w); 573 (s); 402 (s); 392 (s); 332 (s); 325 (s); 238 (s); 178 (s), 146 (s)

UV/vis in CH\textsubscript{3}CN - \lambda \text{ in nm (c in l mol}^{-1}\text{ cm}^{-1}): 207 (shoulder), 254 (38300), 289 (38900), 360 (shoulder)

ESI MS of M\textsuperscript{+}OTf in CH\textsubscript{3}CN; m/z (fragment, intensity in %): 500 (M\textsuperscript{+} tropNH\textsubscript{3}, 5); 541 (M\textsuperscript{+} tropNH\textsubscript{3} + CH\textsubscript{3}CN, 8); 707 (M\textsuperscript{+}, 100)

Elemental analysis: found in % (calc. in %): C 64.36 (64.49); H 4.43 (4.24); N 3.27 (3.27); S 3.54 (3.74); F 6.52 (6.65)
The amide complex 6 was prepared in small quantities. To a solution of 5 mg of 5 in 0.5 ml THF[$d_8$] in an NMR tube, 1 mg of KO[t-Bu] was added and the colour of the solution changed immediately from yellow to orange. Crystals of the product were obtained upon slow diffusion of 2 ml $n$-hexane into the reaction mixture.

In situ deprotonation of 5 in DMSO[$d_6$] gave the $pK_a$ value of the secondary amine function ($pK_a = 20.6$) using indole as reference acid.

$^1$H NMR (400.1 MHz, DMSO-$d_6$) $\delta = 2.42$ (s will be exchanged with time, 2H, N$_2$H), 3.33 (d, $^3J_{HH} = 9.5$ Hz, 2H, H$^{4a}$), 3.56 (s, 2H, H$^{5a}$), 3.70 (s, 2H, H$^{5}$), 4.74 (s, 1H, H$^{17}$), 5.01 (d, $^3J_{HH} = 9.5$ Hz, 2H, H$^{11}$), 6.48 – 7.32 (H$_{ar}$)

$^1$H NMR (700.1 MHz, THF-$d_8$) $\delta = 3.27$ (d, $^3J_{HH} = 9.6$ Hz, 2H, H$^{13}$), 3.75 (s, 4H, H$^{5}/H^{12}$), 4.81 (s, 1H, H$^{15}$), 4.89 (d, $^3J_{HH} = 9.6$ Hz, 2H, H$^{11}$), 5.61 (m, 2H, H$^2$), 6.52 (d, $^3J_{HH} = 7.4$ Hz, 2H, H$^3$), 6.64 (m, 2H, H$^3$), 6.75 (d, $^3J_{HH} = 7.4$ Hz, 2H, H$^3$), 6.78 (d, $^3J_{HH} = 7.4$ Hz, 2H, H$^{13}$), 7.01 (m, 4H, H$^{4}/H^{4a}$), 7.07 (m, 2H, H$^{4}$), 7.17 (m, 2H, H$^{15}$), 7.21 (m, 2H, H$^{16}$), 7.24 (m, 2H, H$^{16a}$), the resonance of the NH$_2$ protons was not detected, probably due to rapid exchange of these protons with the OH protons of the tert.-butanol formed in the reaction.

$^{13}$C NMR (176.1 MHz, THF-$d_8$) $\delta = 62.8$ (s, 1C, C$^{17}$), 71.1 (d, $^1J_{RhC} = 9.2$ Hz, 2C, C$^{13}$), 77.7 (d, $^1J_{RhC} = 7.2$ Hz, 2C, C$^{15}$), 78.8 (s, 2C, C$^4$), 91.6 (d, $^1J_{RhC} = 5.4$ Hz, 2C, C$^{15}$), 124.4 (s, 2C, C$^3$), 125.0 (s, 2C, C$^3$), 126.2 (s, 4C, C$^1/C^2$), 126.5 (s, 2C, C$^{13}$), 126.6 (s, 2C, C$^4$), 126.8 (s, 2C, C$^{14}$), 127.7 (s, 2C, C$^{16}$), 128.4 (s, 4C, C$^1/C^2$), 129.0 (s, 2C, C$^3$), 131.2 (s, 2C, C$^{13}$), 134.8 (s, 2C, C$^{13a}$), 137.2 (s, 2C, C$^{16}$), 137.3 (s, 2C, C$^{15a}$), 137.8 (s, 2C, C$^{16a}$), 145.1 (s, 2C, C$^{14}$), 145.5 (s, 2C, C$^{14}$)

$^{103}$Rh NMR (22.2 MHz, THF-$d_8$): $\delta = 1053$ (s)

ATR IR – neat in cm$^{-1}$: 3266 (s, NH$_2$ stretch); 3225 (s, NH$_2$ stretch); 3010 (m, CH stretch); 2831 (m, CH stretch); 1597 (m); 1575 (m); 1476 (s); 1230 (vs); 1135 (vs); 981 (s); 732 (s)
B) Determination of bond dissociation energies (BDE’s) using electrode potentials and thermodynamic cycles\textsuperscript{S1-S3}.

Bond dissociation energies (BDE’s) can be obtained by combining the equilibrium acidity constants, p\(K_a\), of weak acids [BH]\(^+\) with the oxidation potentials of their conjugate bases, B, both measured in the same solvent (dmso or acetonitrile are commonly used). This method is based on the thermodynamic cycle shown in Scheme S1 for a compound [BH]\(^+\):

\begin{equation} \text{Scheme S1. Thermodynamic cycle used to estimate the B-H bond dissociation energy of [BH]}^{+} \text{in solution} \end{equation}

\[
\begin{align*}
\text{BH}^{+} & \quad \text{E}_{\text{ox}}(\text{B}) \\
\text{B} + \text{H}^{+} & \quad -e^{-} \rightarrow \text{B}^{+} + \text{H}^{+} \\
pK_{a} & \quad \text{BDE} \\
\text{B} - \text{H}^{+} & \quad \text{E}_{\text{red}}(\text{H}^{+}) \\
\end{align*}
\]

The bond dissociation Gibbs energy \(\Delta G^\circ_{\text{BDE}}\) [kJ mol\(^{-1}\)] is given by:

\[
\Delta G^\circ_{\text{BDE}} = 2.303 \, RT \, pK_{a} - \text{E}_{\text{red}}^{\circ}(\text{H}^{+}) + \text{E}_{\text{ox}}^{\circ}(\text{B})
\]

\(\Delta G^\circ_{\text{BDE}}\) is related to gas phase bond dissociation energies BDE’s which were quantitatively determined by various methods and are generally considered to be quite accurate:

\[
\Delta G^\circ_{\text{BDE}} \approx \text{BDE} + \Delta G_{\text{solv}}(\text{H}^{+}) - S_{\text{red}}^{\circ}(\text{H}^{+})
\]

This equation is based on the assumption that the difference in the solvation energies and entropies of [BH]\(^+\) and [BH]\(^{+}\) is negligible. The magnitude of \(\Delta G_{\text{solv}}(\text{H}^{+})\) has been estimated in various solvents and \(S_{\text{red}}^{\circ}(\text{H}^{+})\) is equal to 114.6 \(\text{J K}^{-1} \, \text{mol}^{-1}\). \(\text{E}_{\text{red}}^{\circ}(\text{H}^{+})\) has also been determined for various solvents.

Bordwell derived the following equation \((I)\) which allows a quite accurate estimation of BDE’s from measurements in solution and that allows comparisons to be made between compounds belonging to different compound families and with gas-phase values.

\[
(I) \quad \text{BDE} = 5.73 \, pK_{a} + 96.5 \, \text{E}_{\text{fc/fc}^{+}}^{\circ} + C
\]

Here the term 5.7 \(pK_{a}\) is the equilibrium acidity constant of the weak acid expressed in kJ mol\(^{-1}\). The term 96.5 \(\text{E}_{\text{fc/fc}^{+}}^{\circ}\) is the oxidation potential of the conjugate base of the weak acid expressed in kJ mol\(^{-1}\) and referenced against the ferrocene/ferrocenium couple, \(\text{Fc/Fc}^{+}\). The constant C is empirically derived for a given solvent by comparing the solution BDE’s with accurate gas phase data and contains the above mentioned values for \(\Delta G_{\text{ox}}(\text{H}^{+}), \Delta G_{\text{solv}}^{\circ}(\text{H}^{+})\) and \(\text{E}_{\text{ox}}^{\circ}(\text{B})\). Values of \(C = 306.4 \, \text{kJ mol}^{-1}\) and 248.7 kJ mol\(^{-1}\) are given for dmso or acetonitrile, respectively\textsuperscript{S3a}. For a number of compound families (hydrocarbons, RH, amines, RNH\(_2\) and R\(_2\)NH, and alcohols, ROH) the BDE’s were thus determined and solution and gas phase BDE’s coincide mostly within \(\pm 4\) kJ mol\(^{-1}\).

References:

S3 For N-H BDE’s in amines see: a) W.-Z. Liu, F.G. Bordwell, J. Org. Chem., 1996, 61, 4778 and references therein; b) F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish, X. Zhang, J. Am. Chem. Soc. 1991, 113, 9790. Bordwell gives the equation BDE = 1.37 \(pK_{a}\) + 23.1 \(\text{E}_{\text{fc/fc}^{+}}^{\circ}\) + C expressing the data in kcal mol\(^{-1}\) with C = 73.3 kcal mol\(^{-1}\) or 59.5 kcal mol\(^{-1}\) for dmso or acetonitrile, respectively.