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Amine olefin rhodium(I) complexes: pK_a and NH bond strength†

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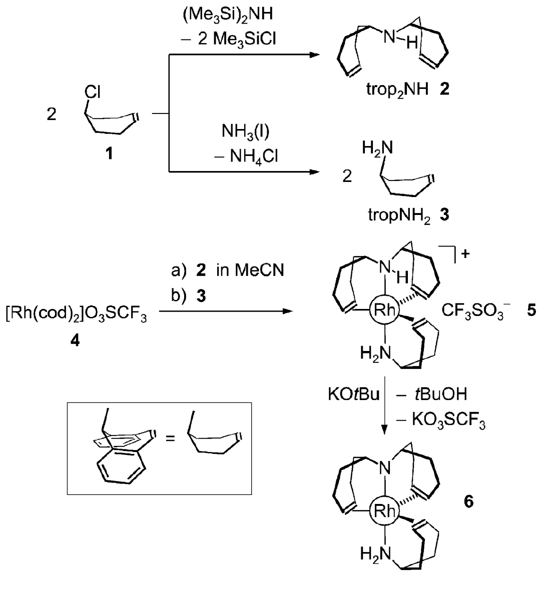
A combination of the rigid bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine (trop$_2$NH) and 5-amino-5*H*-dibenzo[*a*,*d*]cycloheptene (tropNH$_2$) ligand allowed the synthesis of the stable pentacoordinated 18 electron amine olefin rhodium(I) complex [Rh(trop$_2$NH)(tropNH$_2$)]O$_3$SCF$_3$ (5); this complex can be cleanly deprotonated [pK_a^{DMSO} = 20.6(1)] to the corresponding amide [Rh(trop$_2$N)(tropNH$_2$)] (6) which is reversibly oxidised at −0.466 V (*vs.* Fc/Fc$^+$). The coordinated NH bond strength in 5 is estimated to be 379 ± 10 kJ mol^{-1}.

Olefins have become recognized as steering ligands for transition metal catalysts[1–3] and rhodium(I)[4,5] and iridium(I)[6,7] olefin amine complexes have been successfully applied in catalytic transfer hydrogenations. Here we report on (i) the synthesis and structure of a rhodium(I) olefin amine complex[8] ligated by a primary and a secondary amine, (ii) the synthesis and structure of the corresponding neutral rhodium amide complex,[9] (iii) the determination of the pK_a value and (iv) the estimate of the N–H bond strength of a coordinated amine. Such data may be useful for the understanding of the mechanisms operative in catalytic reactions with rhodium or iridium complexes where an NH function plays a crucial role.[10]

Bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine[11] **2** (trop$_2$NH) and 5-amino-5*H*-dibenzo[*a*,*d*]cycloheptene[11] **3** (tropNH$_2$) were prepared as shown in Scheme 1.

Our synthesis uses hexamethyldisilazane and the chloride **1** as reagents in toluene as solvent and gives **2** in one step in almost quantitative yield.‡ Reaction of this tridendate ligand with [Rh(cod)$_2$]O$_3$SCF$_3$ (**4**) in MeCN leads to the complex [Rh(trop$_2$NH)(MeCN)$_2$]O$_3$SCF$_3$ which is reacted *in situ* with the amine **3** to yield the cationic rhodium(I) amine olefin complex **5** as yellow powder. Crystallisation from a mixture of MeCN–toluene–*n*-hexane gave nicely shaped single crystals. The deprotonation of the cationic complex **5** with an excess of KOtBu in THF as solvent gave cleanly the neutral amide complex **6**, which was isolated as orange-red crystals after layering the reaction mixture with *n*-hexane. The NMR data and the IR spectrum showing the symmetric and asymmetric *ν*(NH) stretches at 3266 and 3225 cm^{-1} revealed that the secondary amine trop$_2$NH is selectively deprotonated in this reaction.



Scheme 1 Syntheses of trop amine ligands **2** and **3** and the rhodium complexes **5** and **6**. The annelated benzo groups in the 5*H*-dibenzo[*a*,*d*]-cycloheptenyl (trop) moieties are omitted for clarity.

Both **5** and **6** were characterised by X-ray structure analyses§ and the results are shown in Figs. 1(a) and (b); selected bond lengths and angles are given in the figure caption. The structures do not

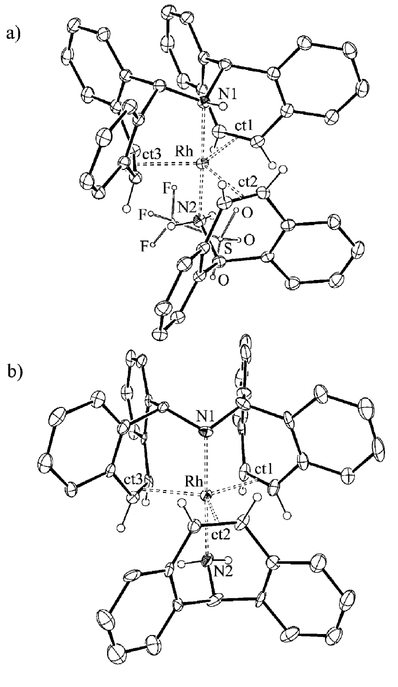


Fig. 1 Structures of **5** and **6**. The triflate counter-anion in **5** is shown in thin lines and binds to the cation *via* a H···F (2.865 Å) and H···O (2.099 Å) interaction. Only one of the two molecules of the asymmetric unit is shown for both complexes. Selected distances [Å] and angles [°] {values for the second molecule are given in parentheses}: (a) **5**: Rh–N1 2.089(3) {2.097(3)}, Rh–N2 2.077(3) {2.075(3)}, Rh–ct1 2.108(3) {2.135(3)}, Rh–ct2 2.168(3) {2.199(3)}, Rh–ct3 2.100(3) {2.073(3)}; N1–Rh–N2 179.3(1) {178.6(1)}, ct1–Rh–ct3 126.3(1) {124.7(1)}, ct1–Rh–ct2 117.4(1) {113.5(1)}, ct2–Rh–ct3 117.9(1) {120.2(1)}, C–N1–Rh 117.4(2) {116.5(2)}, 116.3(2) {116.5(2)}, C–N1–C 109.1(2) {109.7(2)}; (b) **6**: Rh–N1 2.056(7) {2.065(7)}, Rh–N2 2.131(7) {2.113(7)}, Rh–ct1 2.086(9) {2.050(9)}, Rh–ct2 2.173(9) {2.203(8)}, Rh–ct3 2.090(9) {2.072(8)}; N1–Rh–N2 176.8(3) {178.9(3)}, ct1–Rh–ct3 125.7(3) {127.9(3)}, ct1–Rh–ct2 118.5(3) {117.9(3)}, ct2–Rh–ct3 115.8(3) {114.0(3)}, C–N1–Rh 115.2(5) {116.6(5)}, 115.1(5) {115.0(5)}, C–N1–C 109.6(6) {108.7(6)}.

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† Electronic supplementary information (ESI) available: experimental details, NMR data, IR (Raman), UV–vis, mass spectra and elemental analyses of compounds **2**, **5** and **6**. Determination of bond dissociation energies. See http://www.rsc.org/suppdata/cc/b4/b409981h/

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differ much, especially the N1-environments which vary little. That is, the neutral complex **6** has a pyramidalised amide nitrogen centre [sum of C–N1–Rh and C–N1–C bond angles: 339.4° (**6**); 342.6° (**5**)].[12] In both compounds, the C=C double bond of the bidentate tropNH$_2$ ligand has a slightly longer distance to the metal centre than the two C=C units of the tridentate trop$_2$NH ligand. While both Rh–N bonds have almost the same length in the cationic complex **5**, the Rh–N1 bond in the neutral amide **6** is slightly shorter than the Rh–N2 bond, which may indicate some labilisation of the ligand *trans* to the amide function.

Note that both compounds have very rigid structures and do not contain any rotating groups. We have no indication for any dynamic phenomena (that is Berry or turnstile rotation) and both the ^{1}H and ^{13}C NMR spectra show sharp and distinct signals for each type of olefinic carbon or proton [trop$_2$NH in **5**(**6**): ^{13}C δ 79.1 (77.7), 74.3 (71.1); ^{1}H δ 5.49 (5.01), 3.66 (3.33); tropNH$_2$: ^{13}C δ 89.4 (91.6), ^{1}H δ 4.26 (3.56)]. These data show that the formally increased negative charge density at the amide nitrogen is not significantly depleted into the ligand framework.

The pK_a value of **5** was determined as follows:[13] in the equilibrium, **5** + ref$^-$ **6** + refH, the relative concentrations of all species were determined by ^{1}H NMR spectroscopy in DMSO-d$_6$ to give the equilibrium constant $K = c(\mathbf{6}) \times c(\mathrm{refH})/c(\mathbf{5}) \times c(\mathrm{ref}^-)$. The indolide/indole pair (pK_a^{DMSO} = 20.95) was used as reference ref$^-$/refH. The pK_a^{DMSO} of **5** is then given by pK_a^{DMSO}(**5**) = pK_a(ref) − log K. The mean value of several measurements gave a pK_a(**5**) = 20.6(1). Compared to the pK_a of free amines[14] this value is at least 10 orders of magnitude lower, compared to ammonium salts[14,15] and amines coordinated to metal centers[16] with higher formal oxidation states like Ru^{3+} roughly 10 orders of magnitude larger.[17]

The amide complex **6** is reversibly oxidised to the radical cation [Rh(trop$_2$N)(tropNH$_2$)]$^{\bullet +}$ (**7**) at $E^\circ = -0.466$ V referenced to the ferrocene/ferrocenium couple (DMSO/0.1 M *n*Bu$_4$NPF$_6$ electrolyte, Pt-electrode, scan rate 100 mV s^{-1}). This result allows an estimate of the NH bond dissociation energy, BDE, of the coordinated trop$_2$NH using the equation, BDE = 5.73 pK_a + 96.5 $E^\circ_{\mathrm{fc/fc+}} + C$ = **379 ± 10** kJ mol^{-1} (C = 306.4 kJ mol^{-1} for DMSO).[15] This NH-BDE lies in between the range given for tertiary alkyl ammonium salts as NMe$_3$H$^+$ (398 kJ mol^{-1}) and (DABCO)H$^+$ (378 kJ mol^{-1}) and the range of lower values estimated for arylammonium salts (NMe$_2$PhH$^+$ 356 kJ mol^{-1}) (all data for DMSO as solvent).[18] The NH bond strength in **5** is comparable to the methyl–C–H bond strength in toluene (PhCH$_2$–H: 368.2 kJ mol^{-1}).[19]

The high stability of and the easy access to complexes of type **5** and **6** should answer the question of how far the pK_a and the NH-BDE's in such compounds are influenced by the coordination sphere around the metal centre.

Notes and references

‡ *Experimental*: **2**: 3 g **1** (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-hexamethyldisilazane is added. The mixture is refluxed for 4 h. Subsequently, all volatile components are evaporated. After addition of 30 ml of *n*-hexane, the suspension was heated until a white powder was obtained which was filtered off. Yield: 95%. Analytical data are in agreement with ref. 11. **5**: 256 mg [Rh(cod)$_2$]O$_3$SCF$_3$ (**4**) (0.55 mmol) and 217 mg **2** are suspended in 25 ml MeCN 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$_2$Cl$_2$ and 115 mg tropNH$_2$ (**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 MeCN–toluene–*n*-hexane. **6**: in an NMR tube, to a solution of 5 mg **5** in 0.5 mL THF-d$_8$ was added 1 mg of KOtBu. The colour of the solution changed from yellow to orange. Crystals of the product were obtained upon addition of 2 ml *n*-hexane.

§ *Crystal structure data for* **5**: C$_{45}$H$_{36}$N$_2$F$_3$O$_3$SRh · 0.5 MeCN, M = 877.27, monoclinic, a = 21.419(1), b = 16.571(1), c = 22.822(1) Å, U = 7647.5(6) Å^3, T = 200 K, space group $P2_1/c$, Z = 8, μ(Mo–Kα) = 0.564 mm^{-1}, 62096 reflections measured, 15645 unique (R_{int} = 0.0527) which were used in all calculations. Final R indices: R_1 = 0.0492 and wR_2 (all data) = 0.1250; **6**: C$_{45}$H$_{35}$N$_2$Rh · 1 THF/0.5 *n*-hexane, M = 821.85, tetragonal, $a = b$ = 35.519(2), c = 12.879(2) Å, U = 16248(2) Å^3, T = 150 K, space group $I\bar{4}$, Z = 16, μ(Mo–Kα) = 0.462 mm^{-1}, 42552 reflections measured, 9939 unique (R_{int} = 0.0966) which were used in all calculations. Final R indices: R_1 = 0.0567 and wR_2 (all data) = 0.1226. CCDC 244149 and 244150. See http://www.rsc.org/suppdata/cc/b4/b409981h/ for crystallographic data in .cif or other electronic format.

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