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Preliminary communication

FORMATION OF AN η^1-YLIDIC ENAMINE COMPLEX OF RHODIUM(III) DURING USE OF TRIETHYLAMINE FOR A BASE-PROMOTED REACTION

SUJATHA N. GAMAGE, ROBERT H. MORRIS *, STEVEN J. RETTIG and BRIAN R. JAMES*
Department of Chemistry, University of British Columbia Vancouver, British Columbia, V6T 1Y6 (Canada)

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Summary

Reaction of triethylamine with *mer*-$RhCl_3(dmso)_3$ leads to dehydrogenation of an alkyl group of the amine, and formation of isomers of the ylid complex $RhCl_3(dmso)_2(\eta^1\text{-}CH_2CH{=}NEt_2)$, with accompanying production of equivalent amounts of rhodium(I) species.

Tertiary amines have been widely used as cocatalysts for a range of reactions catalyzed by platinum metal complexes, dominantly of palladium(II) [1] and rhodium(III or I) [2]. In catalyzed hydrogenation reactions, amine bases particularly have been used to stabilize the proton released in net heterolytic splitting of H_2 to generate monohydrides (e.g. $Rh^{III}X + H_2 \rightleftharpoons Rh^{III}H + X^- + H^+$) [3]; on using *mer*-$RhCl_3(dmso)_3$ (**1**) [4] as precursor in such studies, we have discovered that **1** reacts readily in solution under an inert atmosphere with NEt_3 according to the basic stoichiometry of reaction 1 to give an η^1-ylidic enamine (**2**)

$$2RhCl_3(dmso)_3 + NEt_3 \rightarrow$$

$$RhCl_3(dm\underline{s}o)_2(CH_2CH{=}NEt_2) + 2H^+ + 2Cl^- + Rh^ICl + 4dmso \qquad (1)$$

(dm$\underline{s}$o = S-bonded dmso)

In the reaction, dehydrogenation of an alkyl group of the amine furnishes 2 reducing equivalents ($Rh^{III} \rightarrow Rh^I$), while the resulting enamine fragment coordinates at rhodium(III) to give **2**. Synthetically, the reaction is more conveniently carried out with sufficient excess base to convert liberated HCl to base hydrochloride. A suspension of $RhCl_3(dmso)_3$ (1.0 g, 2.25 mmol) in 25 ml acetone was stirred

* Present address, Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 1A1 (Canada).

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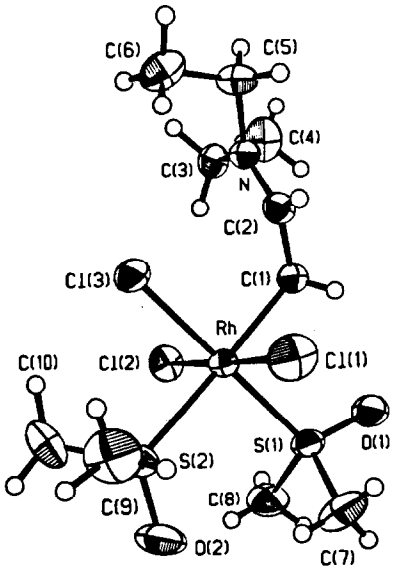


Fig. 1. A view of the molecule **2b**. Relevant dimensions (Å or °) are: bond lengths: Rh–C(1) 2.125(2), C(1)–C(2), 1.439(3), C(2)–N 1.291(3), N–C(3) 1.475(3), N–C(5) 1.481(3), Rh–Cl(1) 2.3342(6), Rh–C(2) 2.3480(5), Rh–Cl(3) 2.3578(5), Rh–S(1) 2.2800(5), Rh–S(2) 2.3906(5), S(1)–O(1) 1.472(2), S(2)–O(2) 1.476(2); angles: Rh–C(1)–C(2) 110.4(1), C(1)–C(2)–N 126.7(2).

with NEt_3 (0.60 ml, 4.5 mmol) under Ar for 12 h; this gave a red solution and white, precipitated $NEt_3 \cdot HCl$, which was filtered off. Concentration of the filtrate to ~ 5 ml by warming under vacuum, and then cooling, yielded **2** as a yellow product. This was isolated as the analytically pure *mer-trans* isomer (**2a**) in ~ 50% yield based on eq. 1. (Analysis: Found C, 25.9; H, 5.3; N, 3.0. $C_{10}H_{25}NO_2S_2Cl_3Rh$ calcd.: C, 25.85; H, 5.42; N, 3.02%)

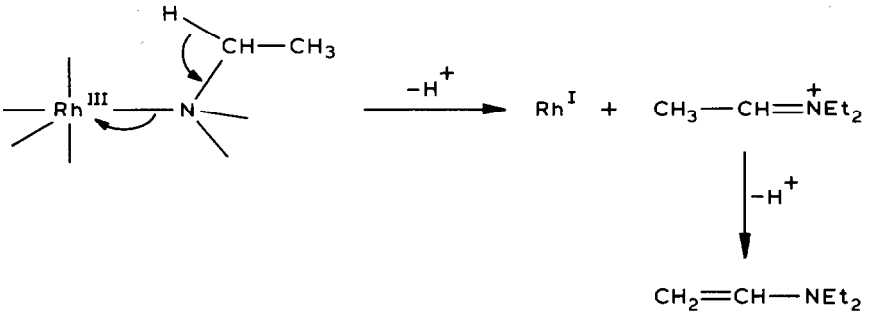
Complex **2a** has been characterized by spectroscopy: IR: ν(C=N) 1645 cm^{-1}, ν(SO) 1110 cm^{-1}; ^1H NMR (δ, ppm) $\delta(CDCl_3)$ 8.26 (1H, t, CH_2CH=N, J 8.5 Hz), 3.77 (2H, q, NCH_2CH_3, J 6.5 Hz), 3.63 (2H, dd, $RhCH_2CH$, J(HH) 8.5 Hz, J(Rh–H) 2.5 Hz), 3.59 (2H, q, NCH_2CH_3, J 6.5 Hz), 3.52 (12H, s, dmso), 1.48 (3H, t, CH_2CH_3, J 6.5 Hz), 1.37 (3H, t, CH_2CH_3) J 6.5 Hz); ^{13}C {^1H} NMR: $\delta(CDCl_3)$ 187.5 (C=N), 53.3 (N–C), 45.8 (N–C), 42.8 (dmso), 23.2 (C–CH_3), 19.2 (C–CH_3), 12.6 (d, Rh–CH_2, J 10 Hz). Complex **2a** slowly isomerizes in $CDCl_3$ to the *mer-cis* isomer **2b**, which was obtained in a crystalline form suitable for X-ray analysis by slow diffusion of ether into the $CDCl_3$ solution. The NMR data for **2b** are comparable to those for **2a** except that there are now two types of dmso ligands seen at δ 3.47 and 3.26 (^1H) and δ 42.6 and 42.4 (^{13}C). The structure of **2b** is shown in Fig. 1, which also includes important bond lengths and angles.

Crystal data: $C_{10}H_{25}Cl_3NO_2Rh_2$, M = 464.7, triclinic, a 9.780(1), b 11.716(1), c 8.199(1) Å, α 95.291(8), β 99.251(8), γ 94.858(8)°, U 918.5(2) $Å^3$, Z = 2, D_c 1.680 g cm^{-3}; $F(000)$ = 472, μ(Mo-K_α) 15.7 cm^{-1}, space group $P\bar{1}$ from structure analysis. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures (non-hydrogen atoms anisotropic, hydrogen atoms isotropic) to R = 0.026 and R_w = 0.035 for 4513 absorption-corrected reflec-

tions with $I \geqslant 3\sigma(I)$ and $\theta \leqslant 30°$ collected at 22°C on an Enraf–Nonius CAD4-F diffractometer *.

The bond lengths and angles at the $\rangle C{=}N\langle$ moiety are consistent with the double bond character shown, and there is an interaction of the C(2) carbon of this moiety with the Rh atom. The X-ray and NMR data are in line with those reported for a related dimeric Pd^{II}-η^1-ylidic enamine complex formed similarly from ethyldiisopropylamine [1]. We have been unable to isolate any pure rhodium(I) species from reaction 1, but the extreme sensitivity of an in situ final reaction solution toward O_2 indicates the presence of the low valent species.

The enamine ligand could be formed via the mechanism suggested for the palladium(II) system [1]: complexation at the metal by the amine N atom, insertion of *N*-complexed metal into an α-C–H bond, and β-hydride elimination (in the rhodium system, as $Rh^{III}H$, this leading to Rh^I via loss of a proton). However, replacement of the relatively labile single O-bonded dmso of **1** [4] by the amine, followed by deprotonation and a concerted electron transfer to the rhodium(III), seems more plausible for this coordinatively saturated metal system, reaction 2. Such redox reactions have been invoked for dehydrogenation of amines using, for example, mercuric acetate [5] or tris (2,2′-dipyridine)ruthenium(II) [6]. Both deprotonation steps shown would be assisted by free amine present.



(2)

Complexes **2a** and **2b** are readily hydrolyzed according to the stoichiometry of equation 3.

$$\mathbf{2} + H_2O + HCl \rightarrow [NEt_2H_2][RhCl_4(dmso)_2] + CH_3CHO \qquad (3)$$
$$(\mathbf{3})$$

Complex **3**, which has been characterized by X-ray analysis [8], exists in two distinct forms. The data for the *trans*-anion correspond well with the literature data [7]; in one crystal type, the cation is H-bonded to a chloride ligand from each of two adjacent anions, while in the other form the H-bonding interactions are via the oxygen atoms of dmso of adjacent anions.

The base "proton sponge", 1,8-bis(dimethylamino)naphthalene, has been used successfully to promote reactivity of H_2 toward ruthenium(III) tertiary phosphine complexes, again via a heterolytic mechanism involving release of proton(s) [9].

* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. A complete set of bond distances and angles is also available.

However, solutions of the rhodium(III) precursor **1** under an inert atmosphere are found to react readily with proton sponge. The formation of some rhodium(I) species and proton sponge · HCl indicates again a redox reaction similar to that shown in equation 1. Dehydrogenation of a methyl group of the base seems likely but we have as yet been unable to characterize an isolated rhodium product (cf. **2**) because of contamination by the base hydrochloride.

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