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A Novel Unreactive Hydrido–Iminoyl Complex of Rh(III) with an Unusual ^{13}C Imine Resonance

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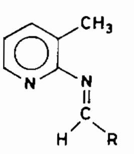
In the course of our studies on the interaction of aldehyde and imine C–H bonds with transition metals [1] we have prepared [2] a series of Rh(III) complexes of type **2**, which are easily obtained from the ligands **1** as shown in eqn. (1).

$$[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2 + \mathbf{1} + 4PPh_3 \xrightarrow[THF]{} \mathbf{2} + 4\ cyclooctene \qquad (1)$$



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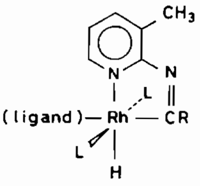

L = PPh₃

R = substituted aryl

3

Ligands: a = C=N(cyclohexyl), b = CO, c = CN$^-$, d = P(OCH$_3$)$_3$, e = I. **3a**, **3d** are Cl salts, **3b** is a PF$_6$ salt.

The complexes **2** (ligand = Cl) are readily converted to a new series of complexes, **3**, in which the Cl ligand has been substituted. The complexes **3a**–**3c** are novel in that they represent rare examples of stable hydride complexes, with two *cis* carbon type ligands, which neither reductively eliminate nor insert the carbon ligand(s) into the metal–hydride bond. Although the failure of hydride to attack CO or CN$^-$ is not unexpected, there is precedence [3] for isonitrile insertion into a Rh(III)–H bond.

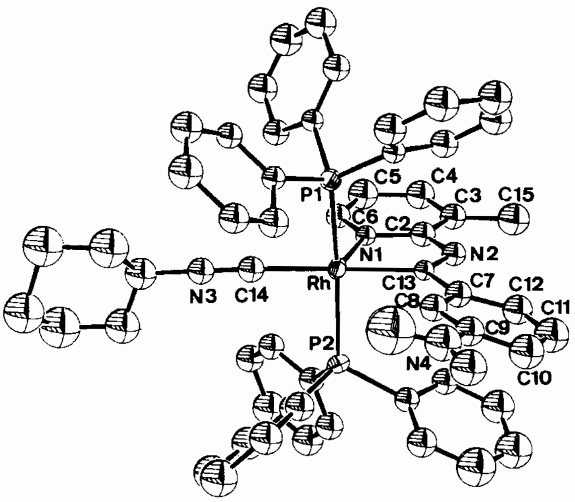

Fig. 1. ORTEP plot of complex **3a** showing the cyclometallated imine.

The molecular structures of **3a** and **3e** both with R = 3-nitrophenyl have been determined and we show preliminary data for **3a** in Fig. 1. To our knowledge this is the first crystallographically determined structure of a rhodium–hydride complex with two *cis* (non carbonyl) carbon ligands. The geometry about rhodium is distorted octahedral, with *trans* phosphine ligands and the isonitrile *trans* to the imine carbon.

For **3a** in solution, the ^{1}H NMR spectroscopy indicates the hydride, $\delta = -11.78$ with coupling both to ^{103}Rh, 14.9 Hz, and two ^{31}P spins, 10.0 Hz. The ^{31}P{^{1}H} spectrum shows the expected [4] doublet at $\delta = 33.7$ with $^1J(^{103}Rh, ^{31}P) = 103$ Hz. We have measured the ^{103}Rh spectrum of the complex with R = 4-nitrophenyl using the INEPT methodology [5] and find the metal resonance at $\delta = 198.7$ (relative to 3.16 MHz). Perhaps the most interesting spectroscopic observation is the very low field position for the ^{13}C resonance of the imine carbon at $\delta = 227.5$, $^1J(^{103}Rh, ^{13}C) = 27$ Hz* (once again for the 4-nitrophenyl analog). This represents a change of *ca.* 69 ppm relative to the non-metallated ligand, $\delta = 159.1$. This low field position would be consistent with some carbene-like character at the imine carbon; however, as the carbon–nitrogen bond separation of this moiety, *ca.* 1.29(3)

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*A complex of type **3d**, but with R = 2-hydroxylphenyl shows $\delta = 252.0$, $^1J(^{103}Rh, ^{13}C) = 25$ Hz.

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Å*, is consistent with an imine function, this low-field position may require a more subtle explanation.

Returning to the reactivity question, we feel that the relative robustness of this type of complex (the Rh–C bond is even inert to excess CF_3SO_3H at ambient temperature) stems from (i) the 18 electron configuration, *i.e.*, they are coordinatively saturated, (ii) the presence of the chelate ring and (iii) the relatively slow kinetics of d^6 octahedral systems.

A more detailed report, including extensive ^{103}Rh data, is in preparation.

Acknowledgements

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*From a preliminary X-ray structure determination, compound **3a** is monoclinic, space group $P2_1/c$, $a = 17.804(1)$, $b = 15.035(3)$, $c = 19.996(9)$, $\beta = 100.98(2)$, $V = 5255$ Å^3, $Z = 4$. Data were collected on a Nonius CAD-4 diffractometer up to $2\theta \leqslant 44.0°$ using a $\theta/2\theta$ scan technique and variable scan speed. A total of 4473 observed reflections ($F_o \geqslant 2.5\sigma(F_o)$) was used for the solution of the structure by Patterson method, and for the refinement (using the block diagonal least squares with anisotropic temperature factors for the rhodium and phosphorus atoms). The present R factor is 0.104.