A Dihydrogen Complex, $[Os(\eta^2\text{-}H_2)(CO)(quS)(PPh_3)_2]^+$, in Equilibrium with its Coordinated Thiol Tautomer (quS = quinoline-8-thiolate)

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The mixture of two isomers of the new complex $Os(H)(CO)(quS)(PPh_3)_2$ **3** reacts with $HBF_4{\cdot}Et_2O$ at −80 °C to form the complexes $[Os(\eta^2\text{-}H_2)(CO)(quS)(PPh_3)_2]^+$ with dihydrogen *trans* to sulfur **4a** or nitrogen **4b** along with tautomeric thiol complexes $[Os(H)(CO)(quSH)(PPh_3)_2]^+$ **4c,d**; the tautomeric equilibria shift with temperature.

Little is known about the factors which favour the intramolecular proton transfer within a transition metal complex from coordinated dihydrogen to a co-ligand which acts as the base, eqn. (1).

$$M(\eta^2\text{-}H_2)(L)_n \rightleftarrows M(H)(HL)(L)_{n-1} \quad (1)$$

Several catalytic processes might have this step in their reaction cycle including methanol synthesis on Cu–ZnO catalysts, hydroformylation reactions[1,2] and dihydrogen oxidation in hydrogenase enzymes[3–5] or dihydrogen evolution from nitrogenase.[6] Several reactions of hydride complexes might follow the path of eqn. 1 where the coordinated base (L) is a nitrogen,[7] carbon[8] or sulfur donor,[9] particularly when the metal ion is iridium(III). Wander *et al.* recently described the synthesis of the complex $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$, which exclusively gives the coordinated thiol tautomer $[(PhSH)Fe(H)(CO)_2(P(OPh)_3)_2]^+$ upon protonation and does not show an equilibrium with the dihydrogen tautomer.[10] Their result is consistent with our use of the ligand additivity model, which for the corresponding hypothetical dinitrogen complex $[(PhS)Fe(N_2)(CO)_2(P(OPh)_3)_2]^+$ predicts a redox potential $E_{1/2}(Fe^{3+}/Fe^{2+})$ of 3.2 V—*ca.* 1.2 V above the 2 V threshold for the formation of a stable dihydrogen complex.[11] We report here the first instance where both tautomers of eqn. (1) can be observed simultaneously.

We recently reported the properties of the highly acidic but stable dihydrogen complexes $[Os(\eta^2\text{-}H_2)(CO)(pyS)(PPh_3)_2][BF_4]$ with dihydrogen trans to nitrogen, **2a**, or sulfur, **2b** which were synthesized by reacting isomers of $OsH(CO)(pyS)(PPh_3)_2$, **1a, b** with $HBF_4{\cdot}Et_2O$.[12] We have now made the complexes $Os(H)(CO)(quS)(PPh_3)_2$ **3a, b**,† where an isomeric mixture of the two possible configurations, hydride *trans* to sulfur (major) **3a** and *cis* to sulfur (minor) **3b**, is obtained in a ratio of *ca.* 3 : 1. The assignment of stereochemistry is based on an NOE difference experiment performed on the completely isostructural homologous ruthenium complexes $Ru(H)(CO)(quS)(PPh_3)_2$ **5a, b**.‡

Protonation of the isomeric mixture of **3a, b** with excess $HBF_4{\cdot}Et_2O$ at 193 K in CD_2Cl_2 under argon or dihydrogen atmosphere results in the formation of the isomeric dihydrogen complexes **4a** (H_2 *trans* to S), **4b** (H_2 *cis* to S) and their tautomeric coordinated thiol forms **4c** (H *trans* to SH), **4d** (H *cis* to SH).§ Fig. 1 shows the hydride region of the 400 MHz ^1H NMR spectrum at this temperature with the spectral assignments. The ratio ([**4a**] + [**4c**]) : ([**4b**] + [**4d**]) is 3 : 1, the same as that for [**3a**] : [**3b**]. This and other NMR experiments show that **4a** and **4c** are the kinetic products from the protonation of **3a** at hydride and sulfur, respectively while **4b** and **4d** are products derived from **3b**. The coordinated thiol protons appear as doublets of doublets or, at temperatures above 253 K, as triplets in the organic region of the spectrum due to rapid inversion of the thiol proton rendering the two phosphorus nuclei magnetically equivalent. The formation of the coordinated thiol complexes, which was not observed with the analogous pyridine-2-thiolate complexes, reflects a slight shift in relative basicity of the hydride and sulfur sites.

A variable temperature 400 MHz T_1 study of the H_2 ligand *cis* to the sulfur in isomer **4b** gives a minimum value of 14.3 ± 0.2 ms at 233 K. Accounting for the relaxation contribution from the two PPh_3 ligands,[13] the T_1(min.) value corresponds to an H–H distance of 0.83 Å (fast spinning) or 1.06 Å (slow spinning).[13–15] The T_1 value of the H_2 ligand of **4a** was determined only at 273 K when this dihydrogen tautomer reaches its highest relative concentration. The value was 17.8 ± 0.6 ms which is very close to 17.5 ± 0.6 ms obtained for **4b** at this temperature. These short T_1 values show that there is a short H–H distance in each isomer.

The ratio of integrals of proton resonances of **4b** to **4d** (Fig. 2) were measured as a function of temperature. After protonation of **3** in CD_2Cl_2 at 193 K, this ratio was measured at 193 K and, after 10 min at 213 K. There was no significant change in the ratio **4b : 4d**. The next step in temperature to 233 K gave a large increase in this ratio. Therefore the formation of isomer **4d** (protonation at sulfur) is favoured kinetically at 193 K but not thermodynamically. The sample was then taken through a warming and cooling cycle in 5 degree steps and spectra were recorded at each temperature after allowing a 10 min waiting

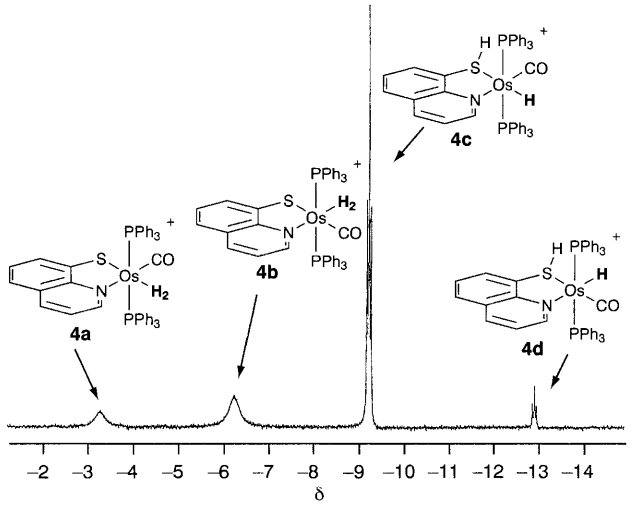


Fig. 1 ^1H NMR spectrum at 400 MHz of the hydride region of complexes **4a–d** at 193 K in CD_2Cl_2

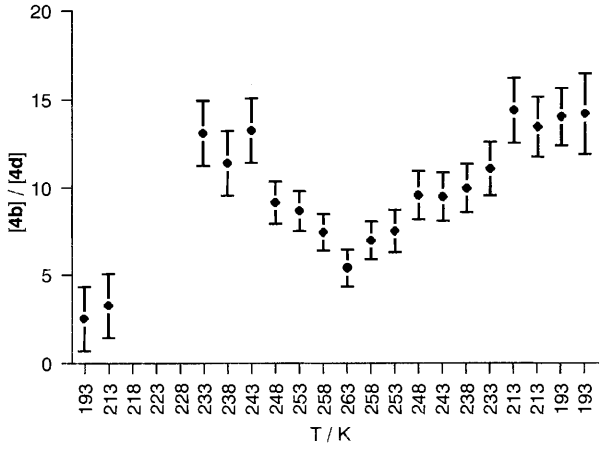
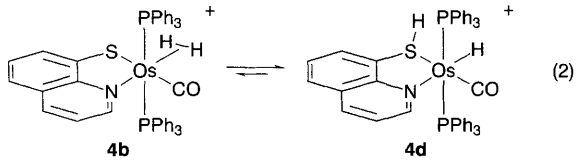


Fig. 2 Plot of [**4b**]/[**4d**] as a function of temperature. The data were collected starting from the left with a period of approx. 10 min between points.

period to allow equilibration of the system; the equilibria may not be fully established at temperatures below 233 K. There is a clear trend in the ratio **4b : 4d** as a function of temperature (Fig. 2) which serves to indicate a reversible shift of the equilibrium, favouring the coordinated thiol form with increasing temperature (eqn. 2).



(2)

A second warming and cooling cycle with 10 degree steps verified this trend although the scatter in the values of **4b : 4d** was greater because there was not enough time for equilibration at the lower temperatures.

The ratio **4a : 4c** for the *trans* isomer displays a similar albeit less expressed temperature dependence. Whether the proton exchange between the two protonation sites is an intra or intermolecular process, possibly *via* excess free HBF_4, is presently under investigation. No decomposition of either tautomer occurred during the entire variable temperature sequence as judged by ^{31}P and ^{1}H NMR. Slow degradation of the sample occurs above 273 K.

It is interesting that the analogous pyridine-2-thiolate complexes **1** and **2** have a different, inverted ratio (**2a : 2b** *ca.* 5 : 1) of isomers[12] relative to those of **3** and **4**. Also thiol analogues **2c** and **2d** corresponding to **4c** and **4d** were not observed in the pyridine-2-thiolate case. Substitution of the chelating pyridine-2-thiolate in **1** with quinoline-8-thiolate in **3** and **5**, *i.e.* enlarging the size of the ring containing the metal by one carbon atom, has two effects: it increases the bite angle of the chelate and it changes the formal charge distribution in the ligand. For pyridine-2-thiolate donor atoms the charge can formally be localized on either the N or S while for quinoline-8-thiolate the charge can only reside on the sulfur. These effects must be the basis for the changes observed in the reactivity of complexes **2** and **3**. Further experiments designed to learn more about the nature of the observed equilibrium and acidity studies involving the set of complexes $[M(\eta^2\text{-}H_2)(CO)(L)(PPh_3)_2]^+$ and $[M(H)(CO)(LH)(PPh_3)_2]^+$, M = Ru, Os, L = pyS, quS, are currently under way.

This research was supported by grants to R. H. M by the NSERC (Canada) and by a generous loan of osmium tetroxide by Johnson Matthey Co. We thank Nick Plavac for NMR spectra.

Received, 24th November 1994; Com. 4/07180H

Footnotes

† The isomeric mixture **3a**, **b** (major : minor *ca.* 3 : 1) was isolated as a deep purple solid in 60% yield by reaction of $OsH_2CO(PPh_3)_2$ with a 1.5 fold excess of quinoline-8-thiol in refluxing toluene under argon atmosphere and recrystallization from CH_2Cl_2–Et_2O. ^{31}P NMR (300 MHz, toluene, relative to 85% H_3PO_4 by use of an $P(OMe_3)_3$–C_6D_6 insert at δ 140.4) δ: 19.93 (s, **3a**), 17.83 (s, **3b**); ^{1}H NMR (400 MHz, $CDCl_3$) δ: −9.54 (t, J_{HP} 17.3 Hz; OsH of **3a**), −12.71 (t, J_{HP} 18.2 Hz; OsH of **3b**), 8.42 (d, J_{HH} 4.2 Hz, H *ortho* to N of **3a**); 8.59 (d, J_{HH} 4.9 Hz, H *ortho* to N of **3b**). IR (CH_2Cl_2), ν(CO)/cm^{-1} **3a** 1923; **3b** 1903. FAB-MS: Calc. for $C_{46}H_{37}NOOsP_2S$: 905. Observed 905 M^+.

‡ The synthesis and properties of this compound and the details of the NOE experiment will be discussed in a future paper.

§ NMR data at 193 K: ^{31}P (300 MHz, CH_2Cl_2, 85% H_3PO_4) δ: **4a** 0.93 (s), **4b** 8.23 (s), **4c** 29.12 (d, J_{PP} 233.7 Hz), 21.54 (d, J_{PP} 233.8 Hz); the peaks for **4d** are not resolved and appear as shoulders on the peaks of **4c**. Above 253 K **4c** broadens due to an increased rate of inversion at the sulfur. ^{1}H (400 MHz, CD_2Cl_2), δ: −3.30 (br s, $Os(H_2)$ of **4a**), −6.3 (br s, $Os(H_2)$ of **4b**), −9.34 (t, J_{HP} 17.6 Hz, OsH of **4c**), −13.04 (t, J_{HP} 15.9 Hz, OsH of **4d**), 5.17 (dd, J_{HP} 13.2, 6.8 Hz, Os(quSH) of **4c**); 4.95 (dd, J_{HP} 21.4, 14.2 Hz, Os(quSH) of **4d**). Above 253 K quSH resonances become triplets: 5.16 (t, J_{HP} 12.2 Hz, **4c**), 4.83 (t, J_{HP} 16.0 Hz, **4d**). The spectral assignments were confirmed by a heteronuclear ^{1}H–^{31}P decoupling experiment to be presented in a future paper.

References

1 L. Versluis and T. Ziegler, *Organometallics*, 1990, **9**, 2985.
2 P. Pino, A. Major, F. Spindler, R. Tannenbaum, G. Bor and I. T. Horvath, *J. Organomet. Chem.*, 1991, **417**, 65.
3 R. H. Crabtree, *Inorg. Chim. Acta*, 1986, **125**, L7.
4 R. T. Hembre and S. McQueen, *J. Am. Chem. Soc.*, 1994, **116**, 2141.
5 L. L. Efros, H. H. Thorp, G. W. Brudvig and R. H. Crabtree, *Inorg. Chem.*, 1992, **31**, 1722.
6 D. J. Lowe, K. Fisher and R. N. F. Thorneley, *Biochem. J.*, 1990, **272**, 621.
7 R. Koelliker and D. Milstein, *J. Am. Chem. Soc.*, 1991, **113**, 8524.
8 A. C. Albeniz, G. Schulte and R. H. Crabtree, *Organometallics*, 1992, **11**, 242.
9 P. G. Jessop and R. H. Morris, *Inorg. Chem.*, 1993, **32**, 2236.
10 S. A. Wander, J. H. Reibenspies, J. S. Kim and M. Y. Darensbourg, *Inorg. Chem.*, 1994, **33**, 1421.
11 R. H. Morris, *Inorg. Chem.*, 1992, **31**, 1471.
12 M. Schlaf, A. J. Lough and R. H. Morris, *Organometallics*, 1993, **12**, 3808.
13 P. J. Desrosiers, L. Cai, Z. Lin, R. Richards and J. Halpern, *J. Am. Chem. Soc.*, 1991, **113**, 4173.
14 M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer and A. Sella, *J. Am. Chem. Soc.*, 1988, **110**, 7031.
15 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126.