Synthesis of the First M(η^2-H_2) Complexes Containing S-Donor Ligands

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The discovery of dihydrogen complexes has been an important contribution to homogeneous catalysis. Applications of M(η^2-H_2) complexes in this field include hydrogenation of alkynes,[1] alkenes,[2] arenes,[3] ketones, and α,β-unsaturated ketones,[4] hydrosilylation of alkynes,[5] hydrogen-transfer reactions of 2-propanol to unsaturated substrates such as alkynes, ketones, and α,β-unsaturated ketones,[6] hydrogen production from alcoholic substrates,[7] and dimerization of alkynes.[8] Thus, from a mechanistic point of view, it has been proved that this type of compound can play a fundamental role in homolytical[9] and heterolytical hydrogen activation.[10] Furthermore, the η^2-H_2 ligand may behave as a good leaving group and acts to stabilize unsaturated complexes in solution, without affecting the coordination of substrates to the metal center of the catalysts.[11]

Since the first report by Kubas *et al.* on the coordination of molecular hydrogen to a transition metal,[12] numerous η^2-H_2 complexes have been reported.[13] However, investigations of the roles that this type of compound can play in homogeneous catalysis has been limited to the aforementioned cases. This has in part been due to the reported compounds, and the ancillary ligands contained by them, being very similar. This problem is a result of the scarce number of useful synthetic routes described for the preparation of η^2-H_2 complexes. Here, we report a new path which leads to the formation of a new type of dihydrogen compound.

Two years ago, the synthesis, reactivity, and catalytic activity of the complex $OsH_2Cl_2(PiPr_3)_2$ (**1**) was reported by Werner and our group.[14] We have now observed that this complex reacts with K[$EtOCS_2$] and K[CH_3COS] in methanol to give the dihydrogen complexes **2–5** (Scheme I). The most characteristic spectroscopic data in the ^1H NMR spectra of **2–5** are the dihydrogen ligand signals which are observed at room temperature as triplets, at about −7 ppm for the xanthate derivatives **2** and **3** and at about −10 ppm for the thiocarboxylate complexes **4** and **5**. These triplets have P–H coupling constants between 9 and 11.8 Hz. At temperatures lower than room temperature, a broadening of these signals is observed. The T_1(min) values found at 200 MHz are between 19 and 33 ms. In agreement with the nonclassical structure, the hydrogen–hydrogen distances calculated from T_1(min) values, assuming rapid internal motion of the dihydrogen ligand, are about 1.0 Å (Table I).[13d,16]

Interestingly, it was found that in the ^1H NMR spectrum of **5** the signals of the methyl groups of the thioacetate ligands were temperature dependent. At room temperature, the methyl groups appear as broad signals at 2.66 ($\omega_{1/2}$ = 20.59 Hz) and 1.90 ($\omega_{1/2}$ = 20.59 Hz) ppm, while at −55 °C they are observed as singlets at 2.83 and 2.00 ppm, respectively. This suggests that **5** only possesses a rigid structure in solution, at low temperature. As the temperature does not influence the chemical shift of the dihydrogen ligand, we believe that the fluxional process involves the carbonyl groups of both thioacetate ligands but does involve the sulfur atoms.

Furthermore, it was observed that in agreement with the proposed structures in Scheme I, the IR spectra of **2** and **4** contain characteristic absorptions for one bidentate xanthate (**2**) or thioacetate (**4**) ligand coordinated as bidentate, while the IR spectra of **3** and **5** contain bands due to two anionic coordinated ligands, one monodentate and the other bidentate.[15]

In addition, it is interesting to note that the substitution of the chloride anions in **1** by [$EtOCS_2$]$^-$ and [MeCOS]$^-$ produces a dihydride–dihydrogen transformation, most probably as a result of the rearrangement of the coordination polyhedron, which changes from a square antiprism with two vacant coordination sites in **1**[17] to an octahedron in **2–5**.

The M(η^2-H_2) compounds previously reported have been prepared by coordination of molecular hydrogen to an unsaturated metallic fragment or by protonation of saturated hydride complexes.[13] We have recently observed that the oxidative addition of HX molecules to osmium(II) hydrides also leads to η^2-H_2 complexes by subsequent intramolecular reduction. Thus, the silyl dihydrogen derivative $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$[5] and the alkynyl–hydride–dihydrogen compounds $OsH(C_2R)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (R = Ph, $SiMe_3$)[6a] were prepared by reaction of $OsHCl(CO)(PiPr_3)_2$ and $OsH_2(CO)(PiPr_3)_2$ with $HSiEt_3$ and HC≡CR (R = Ph, $SiMe_3$), respectively. We now report a new method for the preparation of Os(η^2-H_2) complexes starting from **1**. The conclusion is that this compound is a very useful starting material to prepare Os(η^2-H_2) derivatives; the metathetical reactions of dihydride **1** with K[$EtOCS_2$] and K[CH_3COS] lead to dihydrogen complexes **2–5**, which are the first η^2-H_2 compounds to contain S-donor ligands.

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(15) (a) **2**: IR (Nujol) ν(CS) 970 cm^{-1}. **3**: IR (Nujol) ν(CS) 1045, 1035, and 1010 cm^{-1}. **4**: IR (Nujol) ν(CO) 1460, ν(CS) 1190 cm^{-1}. **5**: IR (Nujol) ν(CO) 1625 and 1450, ν(CS) 1185 and 1110 cm^{-1}. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; Part III-22, pp 342–349.
(16) At the temperature of minimum T_1, $\tau = 0.62/(2\pi\nu)$ and the equation for dipolar relaxation simplifies to $r_{HH} = 4.611(T_1(\text{min})/\nu)^{1/6}$ for rapid rotation (ν(MHz), T_1(s)). See: Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876.
(17) The unusual structure of **1** has been determined by X-ray investigations. See ref 14.

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Scheme I

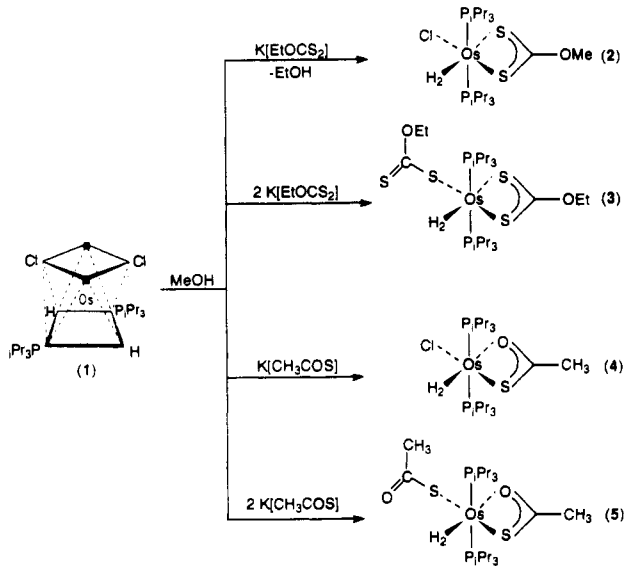

Table I. Minimum T_1 Value and Distance r_{HH} of the Dihydrogen Ligand

complex	ν (MHz)	T (K)	T_1 (min) (ms)	r_{HH} (Å)
2	200	223	30	1.06
3	200	233	19	0.98
4	200	223	33	1.08
5	200	233	25	1.03

Experimental Section

Under an atmosphere of argon a suspension of compound **1** (150 mg, 0.26 mmol) in 10 mL of methanol was treated with potassium *O*-ethyl dithiocarbonate (41.2 mg, 0.26 mmol) or potassium thioacetate (29.3 mg, 0.26 mmol). After being stirred for 80 min, the solution was concentrated to dryness; then 10 mL of dichloromethane was added, and the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL; addition of methanol caused the precipitation of a yellow solid (**2**) at room temperature or a brown solid (**4**) after storing at −78 °C for 3 h. The solvent was decanted, and the solid was twice washed with methanol and then dried in vacuo. Yield, analysis, and spectroscopic data at room temperature are as follows. **2**: Yield 110 mg (65%). Anal. Calcd for $C_{20}ClH_{47}OS_2OsP_2$: C, 36.65; H, 7.24. Found: C, 37.02; H, 7.64. ^{1}H NMR (200 MHz, C_6D_6): δ 3.58 (s, 3 H, OCH_3), 2.68 (m, 6 H, $PCHCH_3$), 1.32 (dvt, N = 12.3, J(HH) = 6.8 Hz, 18 H, $PCHCH_3$), 1.27 (dvt, N = 12.2, J(HH) = 6.9 Hz, 18 H, $PCHCH_3$), −7.59 (t, J(PH) = 11.8 Hz, 2H, Os(η^2-H_2)). ^{31}P{^{1}H} NMR (80.98 MHz, C_6D_6): δ 2.90. T_1 of Os(η^2-H_2) (200 MHz, toluene-d_8) = 113 (293 K), 53 (253 K), 34 (233 K), 30 (223 K), 35 (213 K), 94 (193 K). **4**: Yield 100 mg (62%). Anal. Calcd for $C_{20}ClH_{47}OSOsP_2$: C, 38.54; H, 7.62. Found: C, 38.91; H, 8.41. ^{1}H NMR (200 MHz, C_6D_6): δ 2.58 (m, 6 H, $PCHCH_3$), 1.85 (s, 3 H, CH_3), 1.22 (dvt, N = 12.9, J(HH) = 6.6 Hz, 18 H, $PCHCH_3$), 1.18 (dvt, N = 13.8, J(HH) = 6.9 Hz, 18 H, $PCHCH_3$), −10.25 (t, J(PH) = 11.1 Hz, 2H, Os(η^2-H_2)). ^{31}P{^{1}H} NMR (80.98 MHz, C_6D_6): δ 8.94. T_1 of Os(η^2-H_2) (200 MHz, toluene-d_8) = 160 (293 K), 59 (253 K), 37 (233 K), 33 (223 K), 36 (213 K), 100 (193 K).

Complexes **3** and **5** were prepared analogously as described for **2** and **4** starting from **1** (150 mg, 0.26 mmol) and potassium *O*-ethyl dithiocarbonate (123.6 mg, 0.78 mmol) or potassium thioacetate (88.1 mg, 0.78 mmol). After stirring for 15 or 45 min, respectively, the reaction mixture was worked up as described for **2** and **4**, respectively. Orange solids were formed. Yield, analysis, and spectroscopic data at room temperature are as follows. **3**: Yield 130 mg (67%). Anal. Calcd for $C_{24}H_{54}O_2S_4OsP_2$: C, 38.18; H, 7.22. Found: C, 38.43; H, 7.65. ^{1}H NMR (200 MHz, C_6D_6): δ 4.8 (q, J(HH) = 7 Hz, 2H, CH_2CH_3), 4.2 (q, J(HH) = 7 Hz, 2H, CH_2CH_3), 2.58 (m, 6 H, $PCHCH_3$), 1.30 (dvt, N = 12.3, J(HH) = 6.4 Hz, 18 H, $PCHCH_3$), 1.24 (dvt, N = 12.8, J(HH) = 6.2 Hz, 18 H, $PCHCH_3$), 1.1 (t, J(HH) = 7 Hz, 3H, CH_2CH_3),[18] −7.25 (t, J(PH) = 9 Hz, 2H, Os(η^2-H_2)). ^{31}P{^{1}H} NMR (80.98 MHz, C_6D_6): δ −0.95. T_1 of Os(η^2-H_2) (200 MHz, toluene-d_8) = 48 (293 K), 22 (253 K), 19 (233 K), 33 (213 K). **5**: Yield 110 mg (67%). Anal. Calcd for $C_{22}H_{50}O_2S_4OsP_2$: C, 39.85; H, 7.62. Found: C, 39.98; H, 8.23. ^{1}H NMR (200 MHz, C_6D_6): δ 2.66 (broad, 3H, CH_3), 2.55 (broad, 6 H, $PCHCH_3$), 1.90 (broad, 3H, CH_3), 1.30 (broad, 36 H, $PCHCH_3$), −10.31 (t, J(PH) = 10.3 Hz, 2H, Os(η^2-H_2)). ^{31}P{^{1}H} NMR (80.98 MHz, C_6D_6): δ 5.05. T_1 of Os(η^2-H_2) (200 MHz, toluene-d_8) = 83 (293 K), 35 (253 K), 25 (233 K), 28 (213 K).

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(18) The other CH_2CH_3 signal is masked by the P–CH–CH_3 resonances.