

# Preparation, characterisation and reactivity of a series of classical and non-classical rhenium hydride complexes ‡

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Hydride complexes [ReH(CO)<sub>4</sub>L] **1**, [ReH(CO)<sub>3</sub>L<sub>2</sub>] **2**, [ReH(CO)<sub>2</sub>L<sub>3</sub>] **3** and [ReH(CO)L<sub>4</sub>] **4** [L = P(OEt)<sub>3</sub> **a**, PPh(OEt)<sub>2</sub> **b**, PPh<sub>2</sub>(OEt) **c** or PPh<sub>2</sub>(OMe) **d**] were prepared by treating [ReH(CO)<sub>5</sub>] with the appropriate phosphite under UV irradiation or reflux. The complexes were characterised by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy and by crystal structure determinations of **1d** and **2d**. Protonation of the monocarbonyls [ReH(CO)L<sub>4</sub>] **4** in CD<sub>2</sub>Cl<sub>2</sub> with HBF<sub>4</sub>·Et<sub>2</sub>O resulted in an equilibrium mixture of the classical dihydride complexes [ReH<sub>2</sub>(CO)L<sub>4</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> and their non-classical tautomers [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)L<sub>4</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>. The dihydride [ReH<sub>2</sub>(CO){PPh(OEt)<sub>2</sub>}<sub>4</sub>]BPh<sub>4</sub> was also isolated as a solid by protonation of [ReH(CO){PPh(OEt)<sub>2</sub>}<sub>4</sub>] in ethanol. Thermally unstable [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>4</sub>L]<sup>+</sup>, [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>3</sub>L<sub>2</sub>]<sup>+</sup> and [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup> **7** cations were also prepared by protonation of the corresponding monohydrides **1**, **2** and **3** and fully characterised in solution. The unsaturated complexes [Re(CO)<sub>2</sub>L<sub>3</sub>]BPh<sub>4</sub> and [Re(CO)L<sub>4</sub>]BPh<sub>4</sub> **11** and the triflate [Re(η<sup>1</sup>-OSO<sub>2</sub>CF<sub>3</sub>)(CO)<sub>3</sub>L<sub>2</sub>] were obtained from the η<sup>2</sup>-H<sub>2</sub> derivatives by evolution of H<sub>2</sub>. The new complexes [Re(C≡CPh)(CO)<sub>3</sub>L<sub>2</sub>], [Re(C≡CPh)(CO)L<sub>4</sub>] **13**, [Re(4-MeC<sub>6</sub>H<sub>4</sub>CN)(CO)<sub>2</sub>L<sub>3</sub>]BPh<sub>4</sub>, [Re(4-MeC<sub>6</sub>H<sub>4</sub>NC)(CO)<sub>2</sub>L<sub>3</sub>]BPh<sub>4</sub> and [Re(4-MeC<sub>6</sub>H<sub>4</sub>NC)(CO)L<sub>4</sub>]BPh<sub>4</sub> were prepared by treating the triflate compounds or the unsaturated compounds [Re(CO)<sub>2</sub>L<sub>3</sub>]BPh<sub>4</sub> and [Re(CO)L<sub>4</sub>]BPh<sub>4</sub> with Li<sup>+</sup>C≡CPh<sup>-</sup> or with the appropriate ligand.

Since the initial discovery of the first transition metal dihydrogen complexes<sup>1</sup> the chemistry of 'classical' and 'non-classical' metal hydrides has been systematically developed, with the support of several ancillary ligands such as tertiary phosphine, carbon monoxide and cyclopentadienyl ligands.<sup>2</sup> As a result, a number of dihydrogen complexes have been synthesized and several studies on the stability and the reactivity of these complexes have been reported.<sup>2,3</sup> These studies have addressed not only the structure, bonding and chemical properties of this important class of compounds, but also the catalytic and stoichiometric activation of H<sub>2</sub> by transition metals, and now it seems certain that changes in the nature of the ancillary ligands may greatly change the properties of the η<sup>2</sup>-H<sub>2</sub> compounds.

We have previously reported<sup>4</sup> the synthesis and some properties of molecular dihydrogen complexes of several metals containing phosphites as the supporting ligands, and recently have addressed our attention to rhenium complexes,<sup>5</sup> describing the synthesis and the protonation reaction of new polyhydrides of the type ReH<sub>3</sub>L<sub>4</sub>, ReH<sub>5</sub>L<sub>3</sub> and Re<sub>2</sub>H<sub>8</sub>L<sub>4</sub>. Now we have extended these studies to rhenium monohydrides and in this paper report the synthesis and protonation reactions of a series of new hydrides of Re<sup>I</sup> containing phosphites as ancillary ligands. The crystal structures of two hydrides and the characterisation of the new η<sup>2</sup>-H<sub>2</sub> complexes are also reported.

## Experimental

All synthetic work was carried out under an appropriate atmosphere (H<sub>2</sub>, Ar) using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under an inert atmosphere at -25 °C. All solvents were dried over

appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. Triethyl phosphite was an Aldrich product, purified by distillation under nitrogen; the phosphines PPh(OEt)<sub>2</sub>, PPh<sub>2</sub>(OEt) and PPh<sub>2</sub>(OMe) were prepared by the method of Rabinowitz and Pellon.<sup>6</sup> The complex [Re<sub>2</sub>(CO)<sub>10</sub>] was from Pressure Chemical Co. (Pittsburgh) and used as received, HBF<sub>4</sub>·Et<sub>2</sub>O (54% solution), triflic acid, CF<sub>3</sub>CO<sub>2</sub>H, CF<sub>3</sub>CO<sub>2</sub>D and phenylacetylene were Aldrich products, used without further purification. Lithium phenylacetylide Li<sup>+</sup>[PhC≡C]<sup>-</sup> was prepared by treating a slight excess of phenylacetylene (40 mmol, 4.4 cm<sup>3</sup>) with lithium (35 mmol, 0.24 g) in tetrahydrofuran (thf) (10 cm<sup>3</sup>). *p*-Tolyl isocyanide was obtained by the phosgene method of Ugi *et al.*<sup>7</sup> Other reagents were from commercial sources in the highest available purity and used as received. The photolysis was carried out under an argon atmosphere with a standard 400 W medium-pressure mercury arc lamp using a Pyrex Schlenk flask. Infrared spectra were recorded on a Digilab Bio-Rad FTS-40 or a Bruker Vector 22 FT spectrophotometer, NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) on a Bruker AC200 or AMX400 spectrometer at temperatures varying between +30 and -90 °C, unless otherwise noted. Proton and <sup>13</sup>C spectra are referred to internal tetramethylsilane, while <sup>31</sup>P-<sup>1</sup>H chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>, with downfield shifts considered positive. Proton T<sub>1</sub> values were measured in CD<sub>2</sub>Cl<sub>2</sub> at 200 and at 400 MHz by the inversion-recovery method between +30 and -90 °C with a standard 180°-τ-90° pulse sequence. The conductivity of 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the complexes in MeNO<sub>2</sub> at 25 °C was measured with a Radiometer CDM 83 instrument.

## Preparation of the complexes

The hydride [ReH(CO)<sub>5</sub>] was prepared as previously reported.<sup>8</sup>

*cis*-[ReH(CO)<sub>4</sub>L] **1** [L = PPh<sub>2</sub>(OEt) **c** or PPh<sub>2</sub>(OMe) **d**]. To a solution of [ReH(CO)<sub>5</sub>] (2.5 mmol, 0.82 g) in thf (20 cm<sup>3</sup>) an equimolar amount of the appropriate phosphite was added

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‡ Non-SI unit employed: cal = 4.184 J.

and the reaction mixture refluxed for about 10 h. The solvent was removed under reduced pressure giving an oil which was triturated with ethanol or methanol (5 cm<sup>3</sup>) until a white solid separated. The product was filtered off and crystallised from dichloromethane (2 cm<sup>3</sup>) and ethanol or methanol (4 cm<sup>3</sup>); yield  $\geq 60\%$  (Found: C, 41.1; H, 3.1. C<sub>18</sub>H<sub>16</sub>O<sub>5</sub>PRe **1c** requires C, 40.8; H, 3.05. Found: C, 39.5; H, 2.8. C<sub>17</sub>H<sub>14</sub>O<sub>5</sub>PRe **1d** requires C, 39.6; H, 2.9%).

**mer,trans-[ReH(CO)<sub>3</sub>L<sub>2</sub>] 2 [L = PPh<sub>2</sub>(OEt) c or PPh<sub>2</sub>(OMe) d].** An excess of the appropriate phosphine (12 mmol) was added to a solution of [ReH(CO)<sub>3</sub>] (5 mmol, 1.64 g) in thf (30 cm<sup>3</sup>) and the reaction mixture refluxed for 5 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol or methanol (15 cm<sup>3</sup>). A white solid slowly separated which was filtered off and crystallised from CH<sub>2</sub>Cl<sub>2</sub> (4 cm<sup>3</sup>) and ethanol or methanol (10 cm<sup>3</sup>); yield  $\geq 90\%$  for **2c**,  $\geq 45\%$  for **2d** (Found: C, 51.0; H, 4.2. C<sub>31</sub>H<sub>31</sub>O<sub>5</sub>P<sub>2</sub>Re **2c** requires C, 50.9; H, 4.3. Found: C, 49.0; H, 4.1. C<sub>29</sub>H<sub>27</sub>O<sub>5</sub>P<sub>2</sub>Re **2d** requires C, 49.5; H, 3.9%).

**mer,trans- and fac,cis-[ReH(CO)<sub>3</sub>{PPh(OEt)<sub>2</sub>}] 2b and 2b-fac.** A slight excess of diethoxyphenylphosphine (12 mmol, 2.4 cm<sup>3</sup>) was added to a solution of [ReH(CO)<sub>3</sub>] (5 mmol, 1.64 g) in toluene (30 cm<sup>3</sup>) and the reaction mixture irradiated at room temperature for 40 min (in a Pyrex Schlenk flask using a standard 400 W medium-pressure mercury arc lamp). The solvent was then evaporated under reduced pressure to give an oil which was chromatographed on a silica gel column (length 70 cm, diameter 4 cm) using a mixture of light petroleum (b.p. 40–60 °C), benzene and diethyl ether (10:1:1) as eluent. The first fraction eluted (500 cm<sup>3</sup>) was evaporated to dryness leaving an oil which was treated with ethanol (5 cm<sup>3</sup>). By cooling the resulting solution to –25 °C white crystals of the *mer,trans* complex **2b** were obtained; yield  $\geq 60\%$ . From the second fraction eluted (500 cm<sup>3</sup>), after evaporation of the solvent and treatment with ethanol, the *fac,cis* isomer **2b-fac** was obtained; yield  $\geq 10\%$  (Found for the *mer,trans* isomer: C, 41.1; H, 4.8. Found for the *fac,cis* isomer: C, 41.5; H, 4.6. C<sub>23</sub>H<sub>31</sub>O<sub>7</sub>P<sub>2</sub>Re **2b** and **2b-fac** requires C, 41.4; H, 4.7%).

**fac,cis-[ReH(CO)<sub>3</sub>{PPh<sub>2</sub>(OEt)}] 2c-fac.** This complex was prepared exactly like **2b** by irradiation at room temperature for 40 min of a solution of [Re(CO)<sub>3</sub>] in toluene containing a slight excess of PPh<sub>2</sub>(OEt). After evaporation of the solvent, the oil obtained was chromatographed on a silica gel column, obtaining exclusively the *fac,cis* isomer as a white crystalline solid; yield  $\geq 60\%$  (Found: C, 50.7; H, 4.15. C<sub>31</sub>H<sub>31</sub>O<sub>5</sub>P<sub>2</sub>Re **2c** requires C, 50.9; H, 4.3%).

**mer,trans-[ReH(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}] 2a.** This complex was prepared exactly like the related compound **2b**, obtaining exclusively the *mer,trans* isomer; yield  $\geq 60\%$  (Found: C, 30.0; H, 5.6. C<sub>15</sub>H<sub>31</sub>O<sub>9</sub>P<sub>2</sub>Re requires C, 29.85; H, 5.2%).

**cis,mer-[ReH(CO)<sub>2</sub>L<sub>3</sub>] 3 and cis,mer-[ReH(CO)L<sub>4</sub>] 4 [L = PPh(OEt)<sub>2</sub> b or PPh<sub>2</sub>(OEt) c].** To a solution of [ReH(CO)<sub>3</sub>] (5 mmol, 1.64 g) in toluene (30 cm<sup>3</sup>) was added an excess of the appropriate phosphine (35 mmol) and the reaction mixture was irradiated at room temperature for about 45 h. The solvent was removed under reduced pressure giving an oil which was chromatographed on a silica gel column (70 × 4 cm) using a mixture of light petroleum (b.p. 40–60 °C), diethyl ether and benzene (10:1:1) as eluent. Evaporation to dryness of the first fraction eluted (400 cm<sup>3</sup>) and treatment of the resulting oil with ethanol (3 cm<sup>3</sup>) allowed us to obtain the monocarbonyls **4** in low yield ( $\geq 5\%$  for **4b**, traces for **4c**). From the second fraction eluted (700 cm<sup>3</sup>), after removal of the solvent and treatment with ethanol, white microcrystals of the dicarbonyls **3** were obtained; yield  $\geq 40\%$  (Found: C, 45.75; H, 5.6. C<sub>32</sub>H<sub>46</sub>O<sub>8</sub>P<sub>3</sub>Re

**3b** requires C, 45.9; H, 5.5. Found: C, 56.35; H, 5.1. C<sub>44</sub>H<sub>46</sub>O<sub>5</sub>-P<sub>3</sub>Re **3c** requires C, 56.6; H, 5.0. Found: C, 49.00; H, 6.0. C<sub>41</sub>H<sub>61</sub>O<sub>9</sub>P<sub>4</sub>Re **4b** requires C, 48.85; H, 6.1%).

**cis,mer-[ReH(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}] 3a.** This compound was prepared like the related **3** by treating [ReH(CO)<sub>3</sub>] (5 mmol, 1.64 g) in toluene (30 cm<sup>3</sup>) with an excess of P(OEt)<sub>3</sub> (35 mmol, 5.8 cm<sup>3</sup>) and irradiating the resulting solution for about 12 h. Chromatographic separation on silica gel, using light petroleum (b.p. 40–60 °C)–diethyl ether (10:1), allowed the separation of **3a** (first eluted, yield  $\geq 60\%$ ) as a white solid from the tricarbonyl [ReH(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}] **2a** (second eluted, yield  $\geq 10\%$ ) (Found: C, 32.6; H, 6.3. C<sub>20</sub>H<sub>46</sub>O<sub>11</sub>P<sub>3</sub>Re requires C, 32.4; H, 6.25%).

**trans-[ReH(CO){P(OEt)<sub>3</sub>}] 4a.** This compound was also prepared like the related **4b** by irradiating a [ReH(CO)<sub>3</sub>] solution (5 mmol, 1.64 g in 30 cm<sup>3</sup> of toluene) containing an excess of P(OEt)<sub>3</sub> (35 mmol, 5.8 cm<sup>3</sup>) for about 40 h. Removal of the solvent under reduced pressure gave an oil which was triturated with ethanol (5 cm<sup>3</sup>). By vigorous stirring of the resulting solution a white solid separated which was crystallised from CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and ethanol (7 cm<sup>3</sup>); yield  $\geq 65\%$  (Found: C, 34.05; H, 7.3. C<sub>25</sub>H<sub>61</sub>O<sub>13</sub>P<sub>4</sub>Re requires C, 34.1; H, 7.0%).

**[Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>4</sub>L]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 5, [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>3</sub>L<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 6 and [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 7 [L = P(OEt)<sub>3</sub> a, PPh(OEt)<sub>2</sub> b, PPh<sub>2</sub>(OEt) c or PPh<sub>2</sub>(OMe) d].** These complexes were prepared in CD<sub>2</sub>Cl<sub>2</sub> solution at low temperature (–80 °C) by protonation with HBF<sub>4</sub>·Et<sub>2</sub>O of the corresponding hydride, but they were not isolated as solids owing to the easy loss of hydrogen above 220 K for **5** and above 250–280 K for **6** and **7**. A typical preparation involved the addition by microsyringe of HBF<sub>4</sub>·Et<sub>2</sub>O (0.02 mmol, 2.9 μl) to a solution of the appropriate hydride (0.02 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 cm<sup>3</sup>) placed into a 5 mm NMR tube and cooled to –80 °C. The tube was shaken to complete the reaction and then the NMR spectra (<sup>1</sup>H and <sup>31</sup>P) were registered. [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>4</sub>{PPh<sub>2</sub>(OMe)}]<sup>+</sup> **5d**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 193 K) 7.45 (10 H, m, Ph), 3.59 (3 H, d, CH<sub>3</sub>) and –3.75 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 198 K) 122.98 (s). [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}]<sup>+</sup> **6a**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 4.13 (12 H, br, CH<sub>2</sub>), 1.41 (18 H, t, CH<sub>3</sub>) and –4.6 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 105.5 (s). [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>3</sub>{PPh(OEt)<sub>2</sub>}]<sup>+</sup> **6b**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 7.64 (10 H, m, Ph), 3.98 (8 H, m, br, CH<sub>2</sub>), 1.42 (12 H, t, CH<sub>3</sub>) and –4.3 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 119.19 (s). [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>3</sub>{PPh<sub>2</sub>(OMe)}<sub>2</sub>]<sup>+</sup> **6d**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 7.52 (20 H, m, Ph), 3.3 (6 H, t, CH<sub>2</sub>) and –3.9 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 123.1 (s). [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}]<sup>+</sup> **7a**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 4.02 (18 H, m, CH<sub>2</sub>), 1.36, 1.21 (27 H, t, CH<sub>3</sub>) and –5.02 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) A<sub>2</sub>B spin system, δ<sub>A</sub> 112.2, δ<sub>B</sub> 110.8, J<sub>AB</sub> = 42.6 Hz. [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>2</sub>{PPh(OEt)<sub>2</sub>}]<sup>+</sup> **7b**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 7.60–7.10 (15 H, m, Ph), 3.77, 3.50 (12 H, m, CH<sub>2</sub>), 1.30, 1.15 (18 H, t, CH<sub>3</sub>) and –4.5 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) AB<sub>2</sub> spin system, δ<sub>A</sub> 131.4, δ<sub>B</sub> 129.5, J<sub>AB</sub> = 27.5 Hz. [Re(η<sup>2</sup>-H<sub>2</sub>)(CO)<sub>2</sub>{PPh<sub>2</sub>(OEt)}<sub>3</sub>]<sup>+</sup> **7c**: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) 7.70–7.20 (30 H, m, Ph), 3.60–3.10 (6 H, m, CH<sub>2</sub>), 1.22, 1.02 (9 H, t, CH<sub>3</sub>) and –3.55 (2 H, br, η<sup>2</sup>-H<sub>2</sub>); δ<sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 203 K) AB<sub>2</sub> spin system, δ<sub>A</sub> 106.2, δ<sub>B</sub> 103.5, J<sub>AB</sub> = 27.5 Hz.

**[Re(η<sup>2</sup>-HD)(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> 6a<sub>1</sub> and [Re(η<sup>2</sup>-HD)(CO)<sub>3</sub>{PPh(OEt)<sub>2</sub>}]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> 6b<sub>1</sub>, [Re(η<sup>2</sup>-HD)(CO)<sub>2</sub>L<sub>3</sub>]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> [L = P(OEt)<sub>3</sub> 7a<sub>1</sub>, PPh(OEt)<sub>2</sub> 7b<sub>1</sub> or PPh<sub>2</sub>(OEt) 7c<sub>1</sub>].** These isotopomers were prepared in a NMR tube exactly like **6** and **7** using CF<sub>3</sub>CO<sub>2</sub>D as the protonating agent.

**[ReH<sub>2</sub>(CO){P(OEt)<sub>3</sub>}]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 8\*a and [Re(η<sup>2</sup>-H<sub>2</sub>)(CO){P(OEt)<sub>3</sub>}]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 8a.** These derivatives were also prepared only in CD<sub>2</sub>Cl<sub>2</sub> solution by protonation at low temperature (–80 °C) with HBF<sub>4</sub>·Et<sub>2</sub>O of the hydride [ReH(CO){P(OEt)<sub>3</sub>}]<sub>4</sub>. A mixture of **8\*a** and **8a** was always obtained, the <sup>1</sup>H and <sup>31</sup>P

NMR spectra being as follows:  $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2, 203 \text{ K})$  3.97 (qnt), 3.54 (qnt), 24 H,  $\text{CH}_2$ ), 1.34, 1.31, 1.27, 1.22 (36 H, t,  $\text{CH}_3$ ),  $-5.60$  (br) and  $-6.17$  (qnt) (2 H,  $\text{H}_2$ );  $\delta_{\text{P}}(\text{CD}_2\text{Cl}_2, 203 \text{ K})$  117.5 (s, br).

**[ReH(D)(CO){P(OEt)<sub>3</sub>]<sub>4</sub>]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> 8\*a<sub>1</sub> and [Re( $\eta^2$ -HD)(CO){P(OEt)<sub>3</sub>]<sub>4</sub>]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> 8a<sub>1</sub>.** These isotopomers were prepared exactly like the related complexes **8\*a** and **8a** using  $\text{CF}_3\text{CO}_2\text{D}$  as the protonating agent.

**[ReH<sub>2</sub>(CO){PPh(OEt)<sub>2</sub>]<sub>4</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 8\*b and [Re( $\eta^2$ -H<sub>2</sub>)(CO){PPh(OEt)<sub>2</sub>]<sub>4</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> 8b.** These compounds were prepared only in  $\text{CD}_2\text{Cl}_2$  solution at low temperature ( $-80^\circ\text{C}$ ) by protonation with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  of the hydride  $[\text{ReH}(\text{CO})\text{L}_4]$ . The method was exactly the same as that used for the related derivatives **8\*a** and **8a** and, also in this case, a mixture of **8\*b** and **8b** was always obtained, with <sup>1</sup>H and <sup>31</sup>P NMR data as follows:  $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2, 273 \text{ K})$  7.60–7.20 (20 H, m, Ph), 3.60 (16 H, m,  $\text{CH}_2$ ), 1.24, 1.21 (24 H, t,  $\text{CH}_3$ ),  $-4.75$  (br) and  $-5.18$  (qnt) (2 H,  $\text{H}_2$ );  $\delta_{\text{P}}(\text{CD}_2\text{Cl}_2, 273 \text{ K})$  133.5 (s) and 142.0 (s).

**[ReH(D)(CO){PPh(OEt)<sub>2</sub>]<sub>4</sub>]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> 8b\*a<sub>1</sub> and [Re( $\eta^2$ -HD)(CO){PPh(OEt)<sub>2</sub>]<sub>4</sub>]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> 8b<sub>1</sub>.** These isotopomers were prepared exactly like the related complexes **8\*b** and **8b** using  $\text{CF}_3\text{CO}_2\text{D}$  as the protonating agent.

**[ReH<sub>2</sub>(CO){PPh(OEt)<sub>2</sub>]<sub>4</sub>]BPh<sub>4</sub> 8\*b-BPh<sub>4</sub>.** An equimolar amount of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.1 mmol, 14  $\mu\text{l}$ ) was added to a suspension of  $[\text{ReH}(\text{CO})\{\text{PPh}(\text{OEt})_2\}_4]$  (0.1 mmol, 0.100 g) in ethanol (3  $\text{cm}^3$ ) cooled to  $-80^\circ\text{C}$ . The reaction mixture was brought to  $0^\circ\text{C}$  and stirred for about 2 h. An excess of  $\text{NaBPh}_4$  (0.2 mmol, 0.068 g) in ethanol (2  $\text{cm}^3$ ) was added giving a white solid which was filtered off and crystallised from  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) and ethanol (3  $\text{cm}^3$ ); yield  $\geq 65\%$ ;  $\Lambda_{\text{M}} = 51.9 \text{ S cm}^2 \text{ mol}^{-1}$  (Found: C, 58.7; H, 6.3.  $\text{C}_{65}\text{H}_{82}\text{BO}_9\text{P}_4\text{Re}$  requires C, 58.8; H, 6.2%).

**[Re( $\eta^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(CO)<sub>3</sub>{PPh<sub>2</sub>(OEt)<sub>2</sub>]<sub>2</sub>] 9c.** To a suspension of  $[\text{ReH}(\text{CO})_3\{\text{PPh}_2(\text{OEt})_2\}_2]$  (0.2 mmol, 0.146 g) in ethanol (5  $\text{cm}^3$ ) cooled to  $-80^\circ\text{C}$  an equimolar amount of  $\text{CF}_3\text{SO}_3\text{H}$  was added and the reaction mixture, brought to room temperature, was stirred for 2 h. The white solid obtained was filtered off and crystallised from ethanol; yield  $\geq 60\%$  (Found: C, 43.95; H, 3.6.  $\text{C}_{32}\text{H}_{30}\text{F}_3\text{O}_8\text{P}_2\text{ReS}$  requires C, 43.7; H, 3.4%).

**[Re(CO)<sub>2</sub>L<sub>3</sub>]BPh<sub>4</sub> 10 [P = P(OEt)<sub>3</sub> a or PPh<sub>2</sub>(OEt) c].** To a solution of the hydride  $[\text{ReH}(\text{CO})_2\text{L}_3]$  **3** (0.2 mmol) in ethanol (ca. 5  $\text{cm}^3$ ) cooled to  $-80^\circ\text{C}$  an equimolar amount of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.2 mmol, 29  $\mu\text{l}$ ) was added and the reaction mixture, brought to room temperature, stirred for 2 h. An excess of  $\text{NaBPh}_4$  (0.3 mmol, 0.10 g) in ethanol (3  $\text{cm}^3$ ) was added and the white solid obtained was filtered off and crystallised from  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) and ethanol (7  $\text{cm}^3$ ); yield  $\geq 85\%$ ;  $\Lambda_{\text{M}} = 55.1$  for **10a**, 53.6  $\text{S cm}^2 \text{ mol}^{-1}$  for **10c** (Found: C, 50.1; H, 6.3.  $\text{C}_{44}\text{H}_{65}\text{BO}_{11}\text{P}_3\text{Re}$  **10a** requires C, 49.9; H, 6.2. Found: C, 65.0; H, 5.3.  $\text{C}_{68}\text{H}_{65}\text{BO}_5\text{P}_3\text{Re}$  **10c** requires C, 65.2; H, 5.2%).

**[Re(CO){P(OEt)<sub>3</sub>]<sub>4</sub>]BPh<sub>4</sub> 11a.** This compound was prepared exactly like the related complex **10a** by protonation with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  of  $[\text{ReH}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]$ ; yield  $\geq 80\%$ ;  $\Lambda_{\text{M}} = 54.0 \text{ S cm}^2 \text{ mol}^{-1}$  (Found: C, 49.25; H, 6.6.  $\text{C}_{49}\text{H}_{80}\text{BO}_{13}\text{P}_4\text{Re}$  requires C, 49.1; H, 6.7%).

**mer,trans-[Re(C≡CPh)(CO)<sub>3</sub>L<sub>2</sub>] 12 [L = P(OEt)<sub>3</sub> a, PPh(OEt)<sub>2</sub> b or PPh<sub>2</sub>(OEt) c].** To a solution of the appropriate hydride  $[\text{ReH}(\text{CO})_3\text{L}_2]$  (0.60 mmol) in toluene (10  $\text{cm}^3$ ) cooled to  $-80^\circ\text{C}$  a slight excess of triflic acid (0.66 mmol, 58.4  $\mu\text{l}$ ) was added and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of  $\text{Li}^+[\text{PhC}\equiv\text{C}]^-$  (2.4 mmol, 1.28  $\text{cm}^3$  of a 1.88  $\text{mol dm}^{-3}$  solution in thf) was added to the resulting solution and, after 2 h of stirring, the solvent was removed

under reduced pressure. The oil obtained was triturated with ethanol (2  $\text{cm}^3$ ) at  $0^\circ\text{C}$  until a pale yellow solid separated (2–3 h), which was filtered off and dried under vacuum; yield  $\geq 70\%$  (Found: C, 48.4; H, 4.5.  $\text{C}_{31}\text{H}_{35}\text{O}_7\text{P}_2\text{Re}$  **12b** requires C, 48.5; H, 4.6. Found: C, 56.1; H, 4.3.  $\text{C}_{39}\text{H}_{35}\text{O}_5\text{P}_2\text{Re}$  **12c** requires C, 56.3; H, 4.2%).

**trans-[Re(C≡CPh)(CO){P(OEt)<sub>3</sub>]<sub>4</sub>] 13a.** An excess of  $\text{Li}^+[\text{PhC}\equiv\text{C}]^-$  (1.6 mmol, 0.85  $\text{cm}^3$  of a 1.88  $\text{mol dm}^{-3}$  solution in thf) was added to a solution of  $[\text{Re}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$  **11a** (0.4 mmol, 0.48 g) in thf (15  $\text{cm}^3$ ) and the reaction mixture stirred for 2 h. The solvent was evaporated to dryness leaving an oil which was triturated with ethanol (2  $\text{cm}^3$ ) until a pale yellow solid separated, which was filtered off and dried under vacuum; yield  $\geq 65\%$  (Found: C, 40.6; H, 6.9.  $\text{C}_{33}\text{H}_{65}\text{O}_{13}\text{P}_4\text{Re}$  requires C, 40.45; H, 6.7%).

**cis,mer-[Re(4-MeC<sub>6</sub>H<sub>4</sub>CN)(CO)<sub>2</sub>{PPh(OEt)<sub>2</sub>]<sub>2</sub>]BPh<sub>4</sub> 14b and cis,mer-[Re(4-MeC<sub>6</sub>H<sub>4</sub>NC)(CO)<sub>2</sub>{PPh(OEt)<sub>2</sub>]<sub>2</sub>]BPh<sub>4</sub> 15b.** An equivalent amount of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.2 mmol, 29  $\mu\text{l}$  of a 54% solution) was added to a suspension of  $[\text{ReH}(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_2]$  (0.2 mmol, 0.167 g) in ethanol (4  $\text{cm}^3$ ) cooled to  $-80^\circ\text{C}$ . The reaction mixture was slowly brought to room temperature and stirred for 30 min. An excess of *p*-toluonitrile in one case and *p*-tolyl isocyanide in the other (0.3 mmol) was added to the resulting solution, which was stirred for 1 h and then an excess of  $\text{NaBPh}_4$  (0.4 mmol, 0.137 g) in ethanol (2  $\text{cm}^3$ ) was added. A white solid slowly separated, which was filtered off and crystallised from ethanol; yield  $\geq 60\%$ ;  $\Lambda_{\text{M}} = 49.5$  for **14b**, 52.8  $\text{S cm}^2 \text{ mol}^{-1}$  for **15b** (Found: C, 60.2; H, 5.8; N, 1.0.  $\text{C}_{64}\text{H}_{72}\text{BO}_8\text{P}_3\text{Re}$  **14b** requires C, 60.4; H, 5.7; N, 1.1. Found: C, 60.5; H, 5.7; N, 1.2.  $\text{C}_{64}\text{H}_{72}\text{BO}_8\text{P}_3\text{Re}$  **15b** requires C, 60.4; H, 5.7; N, 1.1%).

**trans-[Re(4-MeC<sub>6</sub>H<sub>4</sub>NC)(CO){P(OEt)<sub>3</sub>]<sub>4</sub>]BPh<sub>4</sub> 16a.** This complex can be prepared exactly like the related compound **15** or by treating the unsaturated compound  $[\text{Re}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$  **11a** with isocyanide. A typical preparation involved the addition of an excess of 4-MeC<sub>6</sub>H<sub>4</sub>NC (1 mmol, 117  $\mu\text{l}$ ) to a solution of  $[\text{Re}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$  (0.4 mmol, 0.48 g) in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). After 2 h of stirring, the solvent was removed under reduced pressure giving an oil which was treated with ethanol (3  $\text{cm}^3$ ). By cooling the resulting solution to  $-25^\circ\text{C}$ , white microcrystals of the compound were obtained, which were filtered off and dried under vacuum; yield  $\geq 80\%$ ;  $\Lambda_{\text{M}} = 52.6 \text{ S cm}^2 \text{ mol}^{-1}$  (Found: C, 52.2; H, 6.8; N, 1.1.  $\text{C}_{57}\text{H}_{87}\text{BO}_{13}\text{P}_4\text{Re}$  requires C, 52.05; H, 6.7; N, 1.1%).

### Crystallography

**[ReH(CO)<sub>4</sub>{PPh<sub>2</sub>(OMe)}<sub>2</sub>] 1d.** Crystallographic measurements were performed at 203 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  0.710 73 Å) using a colourless prismatic crystal of approximate dimensions 0.60 × 0.50 × 0.40 mm. Cell constants were determined from the setting angles of 25 reflections ( $\theta$  range 7–15°) by the  $\omega$  scan technique. Of 4321 reflections collected in the  $\theta$  range 3–26°, 3563 independent reflections, after  $\psi$ -scan absorption correction (maximum, minimum 0.9920, 0.5656), 3235 with  $I > 2\sigma(I)$  were observed. No correction for crystal decomposition was required. The structure was solved by Patterson and Fourier-difference techniques. Refinement of  $F^2$ , by full-matrix least-squares techniques, was made with 273 independent parameters. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were isotropically refined at positions obtained from Fourier-difference techniques.

**[ReH(CO)<sub>3</sub>{PPh<sub>2</sub>(OMe)}<sub>2</sub>] 2d.** A colourless prismatic crystal (0.50 × 0.30 × 0.10 mm) was analysed at 203 K as above. Cell parameters were obtained from setting angles of 25 reflections



**Table 1** Infrared and NMR data for the rhenium complexes

Compound	IR <sup>a</sup>		<sup>1</sup> H NMR <sup>b,c</sup>		Spin system	<sup>31</sup> P- <sup>{1</sup> H} NMR <sup>b,d</sup>	<sup>13</sup> C- <sup>{1</sup> H} NMR <sup>b,c</sup>	
	$\tilde{\nu}/\text{cm}^{-1}$	Assign-ment	$\delta$ (J/Hz)	Assign-ment		$\delta$ (J/Hz)	$\delta$ (J/Hz)	Assign-ment
<b>1c</b> <i>cis</i> -[ReH(CO) <sub>4</sub> {PPh <sub>2</sub> (OEt)}]	2080m 1985s 1959s	v(CO)	3.57 (qnt) <sup>e</sup> 0.99 (t) −4.95 (d) <i>J</i> <sub>PH</sub> = 20	CH <sub>2</sub> CH <sub>3</sub> ReH		111.5 (s) <sup>e</sup>		
<b>1d</b> <i>cis</i> -[ReH(CO) <sub>4</sub> {PPh <sub>2</sub> (OMe)}]	2083s 1967s (br)	v(CO)	3.43 (d) −5.59 (d) <i>J</i> <sub>PH</sub> = 24	CH <sub>3</sub> ReH		133.0 (s)	189.21 (d) <i>J</i> <sub>CP</sub> = 7.3 189.16 (d) <i>J</i> <sub>CP</sub> = 11.4 189.12 (d) <i>J</i> <sub>CP</sub> = 47 54.5 (d)	CO    CH <sub>3</sub>
<b>2a</b> <i>mer,trans</i> -[ReH(CO) <sub>3</sub> {P(OEt) <sub>3</sub> } <sub>2</sub> ]	2020w 1945s 1927s	v(CO)	3.97 (m) <sup>f</sup> 1.50 (t) −6.25 (t) <i>J</i> <sub>PH</sub> = 24	CH <sub>2</sub> CH <sub>3</sub> ReH		130.5 (s) <sup>f</sup>		
<b>2b</b> <i>mer,trans</i> -[ReH(CO) <sub>3</sub> {PPh(OEt) <sub>2</sub> } <sub>2</sub> ]	2020w 1951s 1926s	v(CO)	3.95 (m) <sup>e</sup> 3.69 (m) 1.07 (t) −5.54 (t) <i>J</i> <sub>PH</sub> = 22	CH <sub>2</sub> CH <sub>3</sub> ReH		143.0 (s) <sup>e</sup>		
<b>2b-fac</b> <i>fac,cis</i> -[ReH(CO) <sub>3</sub> {PPh(OEt) <sub>2</sub> } <sub>2</sub> ]	2026s 1961s 1913s	v(CO)	3.80 (m) <sup>e</sup> 3.50 (m) 1.00 (t) −5.00 (t) <i>J</i> <sub>PH</sub> = 18	CH <sub>2</sub> CH <sub>3</sub> ReH		141.3 (s) <sup>e</sup>		
<b>2c</b> <i>mer,trans</i> -[ReH(CO) <sub>3</sub> {PPh <sub>2</sub> (OEt)} <sub>2</sub> ]	2040w 1946s 1926s	v(CO)	3.83 (m) 1.31 (t) −5.80 (t) <i>J</i> <sub>PH</sub> = 20	CH <sub>2</sub> CH <sub>3</sub> ReH		130.9 (s)	196.2 (t) <i>J</i> <sub>CP</sub> < 1 194.9 (t) <i>J</i> <sub>CP</sub> = 10.2 63.4 (br) 16.2 (br)	CO   CH <sub>2</sub> CH <sub>3</sub>
<b>2c-fac</b> <i>fac,cis</i> -[ReH(CO) <sub>3</sub> {PPh <sub>2</sub> (OEt)} <sub>2</sub> ]	1943s 1928s 1915s	v(CO)	3.91 (m) <sup>f</sup> 1.17 (t) −5.27 (t) <i>J</i> <sub>PH</sub> = 20	CH <sub>2</sub> CH <sub>3</sub> ReH		115.5 (s) <sup>f</sup>		
<b>2d</b> <i>mer,trans</i> -[ReH(CO) <sub>3</sub> {PPh <sub>2</sub> (OMe)} <sub>2</sub> ]	2034w 1931s (br)	v(CO)	3.51 (t) <sup>g</sup> −5.85 (t) <i>J</i> <sub>PH</sub> = 20	CH <sub>3</sub> ReH		137.1 (s) <sup>g</sup>	195.8 (t) <sup>g</sup> <i>J</i> <sub>CP</sub> = 5.9 194.4 (t) <i>J</i> <sub>CP</sub> = 10.4 77.6 (d)	CO   CH <sub>3</sub>
<b>3a</b> <i>cis,mer</i> -[ReH(CO) <sub>2</sub> {P(OEt) <sub>3</sub> } <sub>3</sub> ]	1958s 1893s	v(CO)	4.07 (m) <sup>f</sup> 1.22 (t) $\delta_X$ −6.39 A <sub>2</sub> BX <i>J</i> <sub>AX</sub> = 32.5 <i>J</i> <sub>BX</sub> = 25.6	CH <sub>2</sub> CH <sub>3</sub> ReH	A <sub>2</sub> B	$\delta_A$ 135.6 <sup>f</sup>  $\delta_B$ 133.9 <i>J</i> <sub>AB</sub> = 46.0	198.3 (t of d) <sup>f</sup> <i>J</i> <sub>CP</sub> = 10 197.1 (t of d) <i>J</i> <sub>CP</sub> = 8 60.9 (t), 60.8 (t), 16.2 (t), 16.1 (t)	CO   CH <sub>2</sub> CH <sub>3</sub>
<b>3b</b> <i>cis,mer</i> -[ReH(CO) <sub>2</sub> {PPh(OEt) <sub>2</sub> } <sub>3</sub> ]	1953s 1894s	v(CO)	3.95 (m) <sup>e</sup> 3.70 (m) 3.40 (m) 1.11 (t) 1.02 (t) $\delta_X$ −5.36 AB <sub>2</sub> X <i>J</i> <sub>AX</sub> = 30.0 <i>J</i> <sub>BX</sub> = 23.0	CH <sub>2</sub> CH <sub>3</sub> ReH	AB <sub>2</sub>	$\delta_A$ 146.2 <sup>e</sup> $\delta_B$ 145.8 <i>J</i> <sub>AB</sub> = 33.0		
<b>3c</b> <i>cis,mer</i> -[ReH(CO) <sub>2</sub> {PPh <sub>2</sub> (OEt)} <sub>3</sub> ]	1937s 1882s	v(CO)	4.00 (m) <sup>f</sup> 3.74 (m) 3.45 (qnt) 1.09 (t) 0.98 (t) $\delta_X$ −4.50 AB <sub>2</sub> X <i>J</i> <sub>AX</sub> = 32.6 <i>J</i> <sub>BX</sub> = 20.2	CH <sub>2</sub> CH <sub>3</sub> ReH	AB <sub>2</sub>	$\delta_A$ 116.1 <sup>f</sup> $\delta_B$ 113.5 <i>J</i> <sub>AB</sub> = 30.8		
<b>4a</b> <i>trans</i> -[ReH(CO){P(OEt) <sub>3</sub> } <sub>4</sub> ]	1876s	v(CO)	4.11 (m) <sup>f</sup> 1.27 (t) −7.08 (qnt) <i>J</i> <sub>PH</sub> = 25	CH <sub>2</sub> CH <sub>3</sub> ReH		136.6 (s) <sup>f</sup>		

Table 1 (Contd.)

Compound	IR <sup>a</sup>		<sup>1</sup> H NMR <sup>b,c</sup>		Spin system	<sup>31</sup> P- <sup>{1</sup> H} NMR <sup>b,d</sup>	<sup>13</sup> C- <sup>{1</sup> H} NMR <sup>b,c</sup>	
	$\tilde{\nu}/\text{cm}^{-1}$	Assign-ment	$\delta(\text{J/Hz})$	Assign-ment		$\delta(\text{J/Hz})$	$\delta(\text{J/Hz})$	Assign-ment
<b>4b</b> <i>cis,mer</i> -[ReH(CO){PPh(OEt) <sub>2</sub> }] <sub>4</sub>	1862s	v(CO)	3.80 (m) <sup>e</sup> 3.40 (m) 1.08 (t)	CH <sub>2</sub> CH <sub>3</sub> ReH		147.2 (s) <sup>e</sup>		
<b>8*b</b> -BPh <sub>4</sub> [ReH <sub>2</sub> (CO){PPh(OEt) <sub>2</sub> }] <sub>4</sub> -BPh <sub>4</sub>	1959s	v(CO)	3.62 (m) 0.99 (t) -6.05 (qnt) <i>J</i> <sub>PH</sub> = 24	CH <sub>2</sub> CH <sub>3</sub> ReH	A <sub>4</sub> A <sub>2</sub> B <sub>2</sub>	147.0 (s) $\delta_A$ 152.7 <sup>h</sup> $\delta_B$ 146.6 <i>J</i> <sub>AB</sub> = 40.3		
<b>8*b</b> [ReH <sub>2</sub> (CO){PPh(OEt) <sub>2</sub> }] <sub>4</sub> <sup>+</sup>			-5.18 (qnt)	ReH		141.0 (s)		
<b>9c</b> [Re( $\eta^1$ -OSO <sub>2</sub> CF <sub>3</sub> )(CO) <sub>3</sub> {PPh <sub>2</sub> (OEt)} <sub>2</sub> ]	2070w 1962s 1930s	v(CO)	3.69 (qnt) 1.23 (t)	CH <sub>2</sub> CH <sub>3</sub>		108.3 (s)		
<b>10a</b> [Re(CO) <sub>2</sub> {P(OEt) <sub>3</sub> }] <sub>3</sub> BPh <sub>4</sub>	1326m 1991s 1895s	v(tf <sup>-</sup> ) <sup>i</sup> v(CO)	4.07 (m) 1.33 (t)	CH <sub>2</sub> CH <sub>3</sub>		118.9 (s, br)		
<b>10c</b> [Re(CO) <sub>2</sub> {PPh <sub>2</sub> (OEt)} <sub>3</sub> ]BPh <sub>4</sub>	1966s 1885s	v(CO)	1.30 (t) 3.45 (m) 3.24 (qnt) 1.04 (t)	CH <sub>2</sub> CH <sub>3</sub>	AB <sub>2</sub>	$\delta_A$ 115.1 $\delta_B$ 113.1 <i>J</i> <sub>AB</sub> = 31.6		
<b>11a</b> [Re(CO){P(OEt) <sub>3</sub> ]BPh <sub>4</sub>	1868s	v(CO)	0.82 (t) 3.98 (m) 1.22 (t)	CH <sub>2</sub> CH <sub>3</sub>		123.7 (s), 122.9 (s, br)		
<b>12b</b> <i>mer,trans</i> -[Re(C≡CPh)(CO) <sub>3</sub> {PPh(OEt) <sub>2</sub> }] <sub>2</sub>	2101m 2042w 1950s 1933s	v(C≡C) v(CO)	4.20 (m) 3.95 (m) 1.33 (t)	CH <sub>2</sub> CH <sub>3</sub>		129.5 (s)	190.5 (t) <i>J</i> <sub>CP</sub> = 8 190.2 (t) <i>J</i> <sub>CP</sub> = 11 113.1 (t) 99.4 (t) <i>J</i> <sub>CP</sub> = 16 63.3 (t) 16.4 (t)	CO C <sub>β</sub> C <sub>α</sub>
<b>12c</b> <i>mer,trans</i> -[Re(C≡CPh)(CO) <sub>3</sub> {PPh <sub>2</sub> (OEt)} <sub>2</sub> ]	2098m 2036w 1947s 1927s	v(C≡C) v(CO)	3.91 (m) 1.28 (t)	CH <sub>2</sub> CH <sub>3</sub>		100.0 (s)	191.07 (t) <i>J</i> <sub>CP</sub> = 10 190.91 (t) <i>J</i> <sub>CP</sub> = 6 116.9 (t) <i>J</i> <sub>CP</sub> = 2.5 101.8 (t) <i>J</i> <sub>CP</sub> = 15 63.0 (t) 16.3 (t)	CO C <sub>β</sub> C <sub>α</sub> CH <sub>2</sub> CH <sub>3</sub>
<b>13a</b> <i>trans</i> -[Re(C≡CPh)(CO){P(OEt) <sub>3</sub> }] <sub>4</sub>	2084m 1845m	v(C≡C) v(CO)	4.15 (m) 1.23 (t)	CH <sub>2</sub> CH <sub>3</sub>		119.0 (s)		
<b>14b</b> <i>cis,mer</i> -[Re(4-MeC <sub>6</sub> H <sub>4</sub> CN)(CO) <sub>2</sub> {PPh(OEt) <sub>2</sub> }] <sub>3</sub> BPh <sub>4</sub>	2259m 1987s 1908s	v(CN) v(CO)	3.95 (m) 2.38 (s) 1.36 (t) 1.35 (t)	CH <sub>2</sub> <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> POCH <sub>2</sub> CH <sub>3</sub>	A <sub>2</sub> B	$\delta_A$ 136.3 $\delta_B$ 135.2 <i>J</i> <sub>AB</sub> = 31.5		
<b>15b</b> <i>cis,mer</i> -[Re(4-MeC <sub>6</sub> H <sub>4</sub> CN)(CO) <sub>2</sub> {PPh(OEt) <sub>2</sub> }] <sub>3</sub> BPh <sub>4</sub>	2149s 1996s 1940s	v(CN) v(CO)	3.99 (m) <sup>j</sup> 2.35 (s) 1.38 (t) 1.37 (t)	CH <sub>2</sub> <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> POCH <sub>2</sub> CH <sub>3</sub>	A <sub>2</sub> B	$\delta_A$ 130.7 <sup>j</sup> $\delta_B$ 129.9 <i>J</i> <sub>AB</sub> = 30.4	193.5 (q) 189.3 (m) 148.0 (m) 63.5 (t) 63.4 (t) 21.5 (s) 16.3 (t) 16.2 (t)	CO CN CH <sub>2</sub> <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> POCH <sub>2</sub> CH <sub>3</sub>
<b>16a</b> <i>trans</i> -[Re(4-MeC <sub>6</sub> H <sub>4</sub> CN)(CO){P(OEt) <sub>3</sub> }] <sub>4</sub> BPh <sub>4</sub>	2131s 1942s	v(CN) v(CO)	4.15 (qnt) <sup>j</sup> 2.36 (s) 1.32 (t)	CH <sub>2</sub> <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> POCH <sub>2</sub> CH <sub>3</sub>		114.4 (s) <sup>j</sup>		

<sup>a</sup> In KBr pellets. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>, at 25 °C. <sup>c</sup> Phenyl proton and carbon resonances are omitted. <sup>d</sup> Positive shift downfield from 85% H<sub>3</sub>PO<sub>4</sub>. <sup>e</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>f</sup> In CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>. <sup>g</sup> In CDCl<sub>3</sub>. <sup>h</sup> At -80 °C. <sup>i</sup> tf<sup>-</sup> = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. <sup>j</sup> In (CD<sub>3</sub>)<sub>2</sub>CO.

the ligands, with a *mer,trans* geometry in the compound **2d**. The hydride ligands are always *trans* to a carbonyl ligand with H-Re-C angles of 171(3)° for **1d** and 173(2)° for **2d** showing the deviation from the idealised geometry. The Re-H distances of 1.60(8) Å in **1d** and 1.70(6) Å in **2d** agree, within experimental error, with those obtained for terminal H-Re bonds and may be compared to M-H terminal distances for other third-row metals.<sup>16</sup> The Re-P distance in **1d** [Re-P(1) 2.405(2) Å] is

slightly longer than those **2d** [Re-P(1) 2.3775(14), Re-P(2) 2.3804(14) Å]. The Re-C bond distances lie within the range 1.94–2.00 Å, showing no significant difference from the other known rhenium(t) compounds. The extent of the octahedral distortion can be clearly estimated for **1d** and **2d** from the analysis of bond angles, particularly C(1)-Re-P(1) in **1d** and P(2)-Re-P(1), C(2)-Re-P(1) and C(2)-Re-P(2) in **2d** (Table 3).

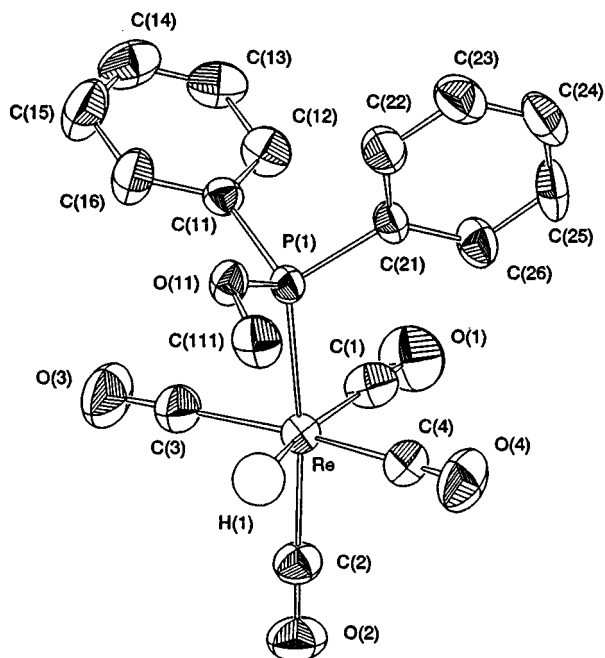


Fig. 1 An ORTEP plot with the atom-numbering scheme used for  $[\text{ReH}(\text{CO})_4\{\text{PPh}_2(\text{OMe})\}]$  **1d**. Thermal ellipsoids at 40% probability

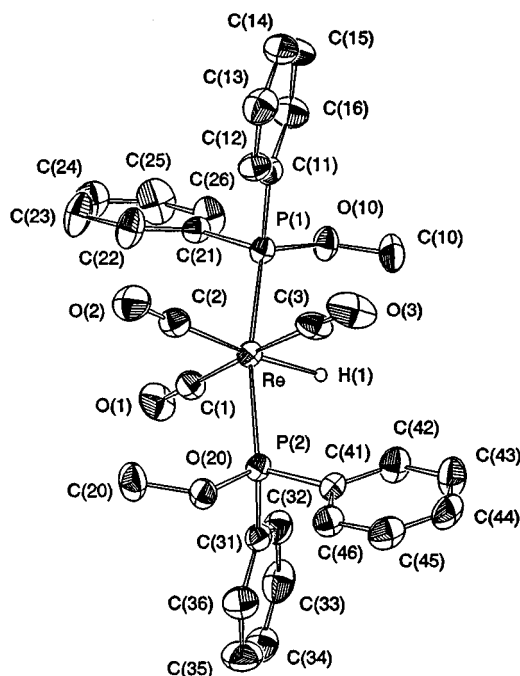
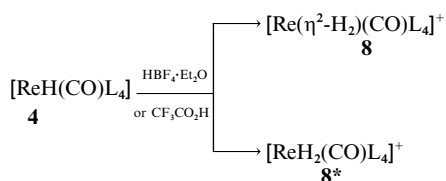


Fig. 2 An ORTEP plot with the atom-numbering scheme used for  $[\text{ReH}(\text{CO})_3\{\text{PPh}_2(\text{OMe})\}_2]$  **2d**. Thermal ellipsoids at 40% probability

### Preparation and characterisation of $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})\text{L}_4]^+$ and $[\text{ReH}_2(\text{CO})\text{L}_4]^+$ cations

The reaction of the monohydride  $[\text{ReH}(\text{CO})\text{L}_4]$  **4** with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  or  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CD}_2\text{Cl}_2$  at  $-80^\circ\text{C}$  proceeds to give a mixture of the molecular hydrogen complex  $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})\text{L}_4]^+$  **8** and the dihydride  $[\text{ReH}_2(\text{CO})\text{L}_4]^+$  **8\***, as shown in Scheme 2.



Scheme 2 L = P(OEt)<sub>3</sub> **a** or PPh(OEt)<sub>2</sub> **b**

Table 2 Crystal data and structure refinement for  $[\text{ReH}(\text{CO})_4\{\text{PPh}_2(\text{OMe})\}]$  **1d** and  $[\text{ReH}(\text{CO})_3\{\text{PPh}_2(\text{OMe})\}_2]$  **2d**

	<b>1d</b>	<b>2d</b>
Empirical formula	$\text{C}_{17}\text{H}_{14}\text{O}_5\text{PRe}$	$\text{C}_{29}\text{H}_{27}\text{O}_5\text{P}_2\text{Re}$
<i>M</i>	515.45	703.65
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$ (no. 14)
<i>a</i> /Å	8.498(7)	8.629(2)
<i>b</i> /Å	9.706(8)	30.720(11)
<i>c</i> /Å	11.5359(10)	10.617(2)
$\alpha$ /°	83.84(6)	
$\beta$ /°	88.46(6)	91.290(10)
$\gamma$ /°	74.28(8)	
<i>U</i> /Å <sup>3</sup>	910.7(11)	2813.7(13)
<i>Z</i>	2	4
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.880	1.661
$\mu$ /mm <sup>-1</sup>	6.781	4.469
<i>F</i> (000)	492	1384
$\theta$ Range for data collection/°	3.05 to 25.94	3.08 to 26.94
Index ranges	$-1 \leq h \leq 10$ , $-11 \leq k \leq 11$ , $-14 \leq l \leq 14$	$0 \leq k \leq 39$ , $-13 \leq l \leq 13$
Reflections collected	4321	7309
Independent reflections	3563	6085
<i>R</i> <sub>int</sub>	0.0349	0.0238
Data, restraints, parameters	3562, 0, 273	6081, 0, 442
Goodness of fit on <i>F</i> <sup>2</sup>	1.063	1.075
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0334, 0.0828	0.0329, 0.0597
(all data)	0.0392, 0.0862	0.0656, 0.0754
Largest Δ <i>F</i> peak and hole/e Å <sup>-3</sup>	2.048, -1.492	0.588, -0.527

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

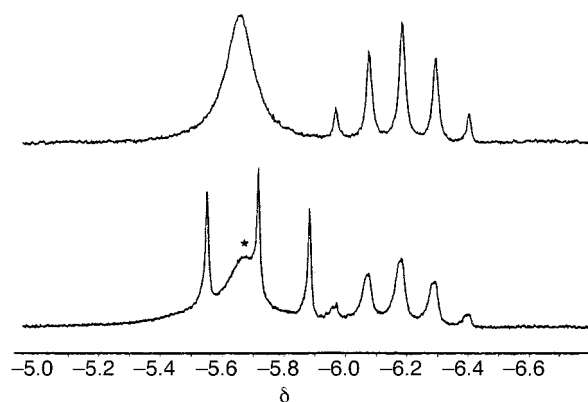
$[\text{ReH}(\text{CO})_4\{\text{PPh}_2(\text{OMe})\}]$ <b>1d</b>			
Re–H(1)	1.60(8)	P(1)–C(11)	1.815(5)
Re–C(2)	1.962(6)	P(1)–C(21)	1.820(6)
Re–C(1)	1.970(8)	O(1)–C(1)	1.137(9)
Re–C(4)	1.972(7)	O(2)–C(2)	1.125(8)
Re–C(3)	2.004(7)	O(3)–C(3)	1.122(9)
Re–P(1)	2.405(2)	O(4)–C(4)	1.139(8)
P(1)–O(11)	1.614(4)	O(11)–C(111)	1.440(7)
H(1)–Re–C(2)	83(3)	C(1)–Re–C(3)	94.2(3)
H(1)–Re–C(1)	171(3)	C(4)–Re–C(3)	168.1(3)
C(2)–Re–C(1)	95.5(3)	H(1)–Re–P(1)	88(3)
H(1)–Re–C(4)	74(3)	C(2)–Re–P(1)	170.2(2)
C(2)–Re–C(4)	90.6(3)	C(1)–Re–P(1)	94.3(2)
C(1)–Re–C(4)	97.5(3)	C(4)–Re–P(1)	89.0(2)
H(1)–Re–C(3)	95(3)	C(3)–Re–P(1)	88.0(2)
C(2)–Re–C(3)	90.4(3)		
$[\text{ReH}(\text{CO})_3\{\text{PPh}_2(\text{OMe})\}_2]$ <b>2d</b>			
Re–H(1)	1.70(6)	P(1)–O(10)	1.620(4)
Re–C(2)	1.943(6)	P(1)–C(21)	1.818(5)
Re–C(3)	1.966(6)	P(1)–C(11)	1.828(6)
Re–C(1)	1.977(6)	O(10)–C(10)	1.422(8)
Re–P(1)	2.3775(14)	P(2)–O(20)	1.622(4)
Re–P(2)	2.3804(14)	P(2)–C(41)	1.820(5)
C(1)–O(1)	1.131(6)	P(2)–C(31)	1.837(6)
C(2)–O(2)	1.152(6)	O(20)–C(20)	1.438(8)
C(3)–O(3)	1.131(7)		
H(1)–Re–C(2)	173(2)	C(3)–Re–P(1)	91.6(2)
H(1)–Re–C(3)	83(2)	C(1)–Re–P(1)	88.3(2)
C(2)–Re–C(3)	91.03(3)	H(1)–Re–P(2)	84(2)
H(1)–Re–C(1)	93(2)	C(2)–Re–P(2)	98.8(2)
C(2)–Re–C(1)	93.3(2)	C(3)–Re–P(2)	88.6(2)
C(3)–Re–C(1)	175.6(3)	C(1)–Re–P(2)	90.4(2)
H(1)–Re–P(1)	83(2)	P(1)–Re–P(2)	166.27(5)
C(2)–Re–P(1)	94.9(2)		

The <sup>1</sup>H NMR spectra of the reaction mixture show, in the hydride region, a broad signal at δ –5.6 (**8a**) and at –4.85 (**8b**) and a sharp quintet at δ –6.16 (**8\*a**) and at –5.18 (**8\*b**), as shown in Fig. 3 for complexes **8a** and **8\*a**. Variable-temperature

**Table 4** Proton NMR data in the hydride region for selected rhenium complexes

Compound	<i>T</i> /K	$\delta(\text{M-H}_2)^a$	$T_{1(\text{min})}/\text{ms}$	$\delta(\text{M-H})^a$	$T_{1(\text{min})}/\text{ms}$	$J_{\text{HD}}/\text{Hz}$	$T^b/\text{K}$
<b>1d</b> [ReH(CO) <sub>4</sub> {PPh <sub>2</sub> (OMe)}]	203			-5.72 (d) <sup>c</sup>	334		
<b>2c</b> [ReH(CO) <sub>3</sub> {PPh <sub>2</sub> (OEt)} <sub>2</sub> ]	200			-6.03 (t) <sup>c</sup>	250		
<b>2d</b> [ReH(CO) <sub>3</sub> {PPh <sub>2</sub> (OMe)} <sub>2</sub> ]	211			-6.05 (t) <sup>c</sup>	223		
<b>3b</b> [ReH(CO) <sub>2</sub> {PPh(OEt) <sub>2</sub> } <sub>3</sub> ]	196			-5.86 (m)	140		
<b>5d</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>4</sub> {PPh <sub>2</sub> (OMe)}] <sup>+</sup>	211	-3.7 (br) <sup>c</sup>	9.0				220
<b>6a</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>3</sub> {P(OEt) <sub>3</sub> } <sub>2</sub> ] <sup>+</sup>	186	-4.6 (br)	3.0				245
<b>6a<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO) <sub>3</sub> {P(OEt) <sub>3</sub> } <sub>2</sub> ] <sup>+</sup>	193	-4.95 (t)				30	
<b>6b</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>3</sub> {PPh(OEt) <sub>2</sub> } <sub>2</sub> ] <sup>+</sup>	198	-4.3 (br)	3.5				245
<b>6b<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO) <sub>3</sub> {PPh(OEt) <sub>2</sub> } <sub>2</sub> ] <sup>+</sup>	203	-4.65 (t)				31	
<b>6c</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>3</sub> {PPh <sub>2</sub> (OEt)} <sub>2</sub> ] <sup>+</sup>	230	-4.0 (br) <sup>c</sup>	7.0				253
<b>6d</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>3</sub> {PPh <sub>2</sub> (OMe)} <sub>2</sub> ] <sup>+</sup>	215	-3.9 (br) <sup>c</sup>	7.0				243
<b>7a</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>2</sub> {P(OEt) <sub>3</sub> } <sub>3</sub> ] <sup>+</sup>	190	-5.0 (br)	5.0				273
<b>7a<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO) <sub>2</sub> {P(OEt) <sub>3</sub> } <sub>3</sub> ] <sup>+</sup>	193	-5.21 (t)				33	
<b>7b</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>2</sub> {PPh(OEt) <sub>2</sub> } <sub>3</sub> ] <sup>+</sup>	203	-4.5 (br)	5.5				279
<b>7b<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO) <sub>2</sub> {PPh(OEt) <sub>2</sub> } <sub>3</sub> ] <sup>+</sup>	203	-4.65 (t)				33	
<b>7c</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO) <sub>2</sub> {PPh <sub>2</sub> (OEt)} <sub>3</sub> ] <sup>+</sup>	208	-3.6 (br)	4.0				258
<b>7c<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO) <sub>2</sub> {PPh <sub>2</sub> (OEt)} <sub>3</sub> ] <sup>+</sup>	223	-3.80 (t)				33	
<b>8a</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO){P(OEt) <sub>3</sub> } <sub>4</sub> ] <sup>+</sup>	198	-5.6 (br)	10				270
<b>8a<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO){P(OEt) <sub>3</sub> } <sub>4</sub> ] <sup>+</sup>	256	-5.66 (t)				33	
<b>8*a</b> [ReH <sub>2</sub> (CO){P(OEt) <sub>3</sub> } <sub>4</sub> ] <sup>+</sup>	193			-6.16 (qnt)	98		270
<b>8*a<sub>1</sub></b> [ReH(D)(CO){P(OEt) <sub>3</sub> } <sub>4</sub> ] <sup>+</sup>	256	-6.12 (qnt of d)				2.1	
<b>8b</b> [Re( $\eta^2$ -H <sub>2</sub> )(CO){PPh(OEt) <sub>2</sub> } <sub>4</sub> ] <sup>+</sup>	207	-4.85 (br)	7.5				276
<b>8b<sub>1</sub></b> [Re( $\eta^2$ -HD)(CO){PPh(OEt) <sub>2</sub> } <sub>4</sub> ] <sup>+</sup>	203	-5.05 (t)				32.5	
<b>8*b</b> [ReH <sub>2</sub> (CO){PPh(OEt) <sub>2</sub> } <sub>4</sub> ] <sup>+</sup>	193			-5.18 (qnt)	120		
<b>8*b-BPh<sub>4</sub></b> [ReH <sub>2</sub> (CO){PPh(OEt) <sub>2</sub> } <sub>4</sub> ]BPh <sub>4</sub>	208			-6.24 (m)	124		>298

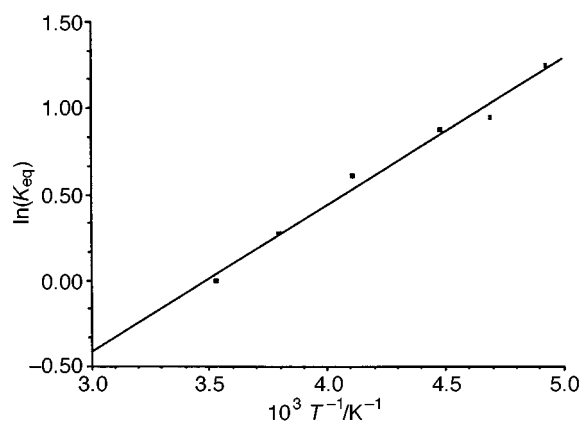
<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 200 MHz. <sup>b</sup> Limit for thermal stability. <sup>c</sup> At 400 MHz.



**Fig. 3** Proton NMR spectra in the high-field region at 243 K in CD<sub>2</sub>Cl<sub>2</sub> of an equilibrium mixture of [Re( $\eta^2$ -H<sub>2</sub>)(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]<sup>+</sup> **8a** and [ReH<sub>2</sub>(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]<sup>+</sup> **8\*a** (top), and their isotopomers [Re( $\eta^2$ -HD)(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]<sup>+</sup> **8a<sub>1</sub>** and [ReH(D)(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]<sup>+</sup> **8\*a<sub>1</sub>**. The signal indicated by the asterisk (\*) is due to an impurity of **8a**

$T_1$  measurements in CD<sub>2</sub>Cl<sub>2</sub> (Table 4) give a short  $T_{1(\text{min})}$  value (10 ms at 198 K for **8a** and 7.5 ms at 207 K for **8b**, at 200 MHz) for the broad signal characteristic of a  $\eta^2$ -H<sub>2</sub> complex,<sup>17</sup> while a  $T_{1(\text{min})}$  of 98 ms at 193 K (**8\*a**) and 120 ms at 193 K (**8\*b**), at 200 MHz, measured on the quintet is consistent with a classical dihydride [ReH<sub>2</sub>(CO)L<sub>4</sub>]<sup>+</sup> cation. Support for this attribution comes from the spectra of the isotopomers [Re( $\eta^2$ -HD)(CO)L<sub>4</sub>]<sup>+</sup> **8a<sub>1</sub>**, **8b<sub>1</sub>** and [ReH(D)(CO)L<sub>4</sub>]<sup>+</sup> **8\*a<sub>1</sub>** obtained by protonation with CF<sub>3</sub>CO<sub>2</sub>D of [ReH(CO)L<sub>4</sub>] and shown in Fig. 3. The broad signal attributed to the  $\eta^2$ -H<sub>2</sub> ligand is replaced by a triplet in the isotopomer spectra, with large  $J_{\text{HD}}$  values of 32.5 Hz, unequivocally consistent with the non-classical structure. A quintet of doublets replaces, instead, the signal of the dihydride, whose  $J_{\text{HD}}$  value of 2.1 Hz strongly confirms the classical structure of the [ReH(D)(CO)L<sub>4</sub>]<sup>+</sup> cation.

The two complexes [Re( $\eta^2$ -H<sub>2</sub>)(CO)L<sub>4</sub>]<sup>+</sup> **8** and [ReH<sub>2</sub>(CO)L<sub>4</sub>]<sup>+</sup> **8\*** are in tautomeric equilibrium, which is temperature dependent and, at higher temperatures, is shifted towards the classical **8\*** compound. The temperature dependence of the equilibrium constant was studied by integration of the <sup>1</sup>H NMR hydride resonances of the two tautomers in the temper-



**Fig. 4** Plot of  $\ln(K_{\text{eq}})$  vs.  $1/T$  for the equilibrium between [ReH<sub>2</sub>(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]<sup>+</sup> **8\*a** and [Re( $\eta^2$ -H<sub>2</sub>)(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]<sup>+</sup> **8a** in CD<sub>2</sub>Cl<sub>2</sub>. See Table 5 and text for explanations

ature range 203–283 K. Only in the case of the P(OEt)<sub>3</sub> complexes **8a** and **8\*a**, however, does the separation of the signals allow the determination of the  $K_{\text{eq}}$  whose values are reported in Table 5. A plot of  $\ln(K_{\text{eq}})$  vs.  $1/T$  is linear (Fig. 4) and gives the thermodynamic parameters  $\Delta H = 1.71 \pm 0.10$  kcal mol<sup>-1</sup> and  $\Delta S = -6.0 \pm 0.4$  cal K<sup>-1</sup> mol<sup>-1</sup> for the conversion of the dihydride into the dihydrogen complex. These values are slightly different from those previously reported for the equilibrium between classical and non-classical rhenium hydrides of the type<sup>18</sup> [ReH<sub>2</sub>(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> and [Re( $\eta^2$ -H<sub>2</sub>)(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> and for the equilibrium<sup>19</sup> between [ReH<sub>4</sub>(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> and [ReH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> and probably reflect the influence of the phosphite ligands on the stability of the classical and non-classical hydride complexes.

The [Re( $\eta^2$ -H<sub>2</sub>)(CO)L<sub>4</sub>]<sup>+</sup> derivatives are thermally unstable and the loss of H<sub>2</sub> takes place therefore at -5 to 0 °C, preventing the separation of the products in the solid state. However, when the protonation reaction of the PPh(OEt)<sub>2</sub> derivative **4b** was carried out in ethanol instead of CH<sub>2</sub>Cl<sub>2</sub> a white solid was obtained after precipitation with the BPh<sub>4</sub><sup>-</sup> anion, the IR and NMR spectra of which and analytical data support its formulation as the dihydride species [ReH<sub>2</sub>(CO){PPh(OEt)<sub>2</sub>}<sub>4</sub>]BPh<sub>4</sub>



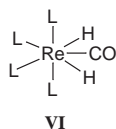
**Table 5** Thermodynamic parameters for the equilibrium between  $[\text{ReH}_2(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$  **8\*a** and  $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$  **8a** in  $\text{CD}_2\text{Cl}_2^a$

<i>T</i> /K	<i>K</i> <sub>eq</sub> <sup>b</sup>
203	3.49
213	2.59
223	2.40
243	1.83
263	1.32
283	0.99
$\Delta H - 1.71 \pm 0.10 \text{ kcal mol}^{-1c}$	$\Delta S - 6.0 \pm 0.4 \text{ cal K}^{-1} \text{ mol}^{-1d}$

<sup>a</sup> Determined by <sup>1</sup>H NMR integration of the hydride resonances of complexes **8\*a** and **8a**. <sup>b</sup> Defined as  $[\mathbf{8a}]/[\mathbf{8*a}]$ . <sup>c</sup> Calculated from the slope of the plot of  $\ln(K_{\text{eq}})$  vs.  $1/T$ . <sup>d</sup> Calculated from the intercept of the plot in *c*.

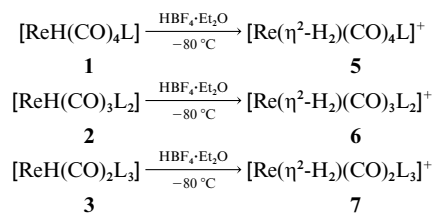
**8\*b-BPh<sub>4</sub>**. The <sup>1</sup>H NMR spectra show, in fact, a well resolved quintet in the hydride region at  $\delta -6.05$  (25 °C,  $\text{CD}_2\text{Cl}_2$ ) with a  $T_{1(\text{min})}$  value (200 MHz) of 124 ms at 208 K, suggesting the classical nature of the species. The infrared spectrum shows only one  $\nu(\text{CO})$  band at  $1959 \text{ cm}^{-1}$ , while the <sup>31</sup>P-<sup>1</sup>H NMR spectrum shows a slightly broad singlet near  $\delta 147$  at room temperature. The values of the chemical shift for both the protons and the <sup>31</sup>P nuclei of **8\*b-BPh<sub>4</sub>** compound are, however, different from those observed for the corresponding  $[\text{ReH}_2(\text{CO})\text{L}_4]^+$  **8\*b** cations prepared in  $\text{CH}_2\text{Cl}_2$  solution (see Table 1). Furthermore, this complex is stable in solution and no evidence of formation of the tautomer  $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})\text{L}_4]^+$  was observed. These different properties shown by the two hydrides obtained by protonation of  $[\text{ReH}(\text{CO})\{\text{PPh}(\text{OEt})_2\}_4]$  **4b** with  $\text{HBF}_4$  in two different solvents (dichloromethane and ethanol) may be explained on the basis of the existence of two isomers with different geometries, only one of which is in tautomeric equilibrium with the  $\eta^2\text{-H}_2$  derivatives. Support for this hypothesis comes from variable-temperature <sup>1</sup>H and <sup>31</sup>P NMR data of the two  $[\text{ReH}_2(\text{CO})\text{L}_4]^+$  species: while the proton and <sup>31</sup>P spectra of the cation **8\*b** prepared in  $\text{CD}_2\text{Cl}_2$  remain unchanged between 0 and  $-90$  °C, the spectra of the solid sample  $[\text{ReH}_2(\text{CO})\text{L}_4]\text{BPh}_4$  **8\*b-BPh<sub>4</sub>** are temperature dependent and the slightly broad singlet at  $\delta 147.0$  which appears at room temperature in the <sup>31</sup>P spectrum becomes a well resolved  $\text{A}_2\text{B}_2$  multiplet at  $-70$  °C, consistent with the presence of two by two magnetically equivalent phosphite ligands. Also the <sup>1</sup>H spectrum changes as the temperature is lowered and the quintet observed at room temperature turns into a complicated multiplet at  $-80$  °C due to the coupling with the non-equivalent phosphine ligands.

The structure of seven-co-ordinate complexes can be discussed in terms of a pentagonal bipyramid, a monocapped octahedron or a capped trigonal prismatic geometry.<sup>19,20</sup> Our <sup>1</sup>H and <sup>31</sup>P NMR spectra of both 'isomers' do not allow us to assign a geometry in solution. However, previous X-ray data on seven-co-ordinate rhenium complexes<sup>21</sup> and the magnetic inequivalence of the phosphorus nuclei allow us to propose the geometry **VI** for the solid derivative  $[\text{ReH}_2(\text{CO})\{\text{PPh}(\text{OEt})_2\}_4]\text{BPh}_4$  **8\*b-BPh<sub>4</sub>**, while no hypothesis may be made for the species **8\*b** prepared in  $\text{CD}_2\text{Cl}_2$ .



### Preparation of other $\eta^2\text{-H}_2$ complexes

Protonation reactions of the other carbonyl compounds  $[\text{ReH}(\text{CO})_2\text{L}_3]$  **3**,  $[\text{ReH}(\text{CO})_3\text{L}_2]$  **2** and  $[\text{ReH}(\text{CO})_4\text{L}]$  **1** with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  also proceed easily at  $-80$  °C but give, in contrast to the monocarbonyls  $[\text{ReH}(\text{CO})\text{L}_4]$  **4**, only the dihydrogen



**Scheme 3** L = P(OEt)<sub>3</sub> **a**, PPh(OEt)<sub>2</sub> **b**, PPh<sub>2</sub>(OEt) **c** or PPh<sub>2</sub>(OMe) **d**

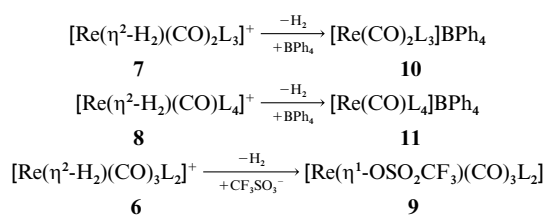
complexes  $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{L}_3]^+$  **7**,  $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_3\text{L}_2]^+$  **6** and  $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_4\text{L}]^+$  **5**, as shown in Scheme 3. The  $\eta^2\text{-H}_2$  complexes were fairly stable in solution at low temperature, but were not isolated as solids owing to the easy loss of dihydrogen. Loss of dihydrogen, in the case of the tetracarbonyls **5** and of the tricarbonyls **6**, begins at temperatures lower than  $-30$  to  $-50$  °C, while the dicarbonyls are stable until  $0$  °C. In every case the <sup>1</sup>H NMR spectra of solutions in  $\text{CD}_2\text{Cl}_2$  containing **5**, **6** or **7** exhibit a single broad resonance in the hydride region, between  $\delta -3.6$  and  $-5.21$ , with  $T_{1(\text{min})}$  values of 3–9 ms (200 and 400 MHz, Table 4), consistent<sup>17</sup> with the proposed formulation. This assignment is further supported by the <sup>1</sup>J<sub>HD</sub> values of 30–33 Hz found for the isotopomers **6a**, **6b**, **7a**, **7b**, **7c**, **8a** and **8b**, which confirm the presence of an authentic  $\eta^2\text{-H}_2$  ligand in the rhenium complex.

Protonation of our rhenium hydrides **1–4** allowed us to obtain a series of cationic dihydrogen and/or dihydride complexes with different phosphite: carbonyl ratios, which enables a comparison between them and also to related rhenium  $\eta^2\text{-H}_2$  derivatives previously reported.<sup>3f,14,15c,e,18,22</sup> First our  $\eta^2\text{-H}_2$  cationic complexes are all thermally unstable and their easy loss of hydrogen does not seem to be influenced by the nature of the anion and the use of  $\text{HBF}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{CF}_3\text{CO}_2\text{H}$  as the protonating agent does not influence the stability of the derivatives. Furthermore, only dihydrogen complexes were obtained with the carbonyl:phosphite ratio 4:1, 3:2 and 2:3, while a tautomeric equilibrium between  $\eta^2\text{-H}_2$  and dihydride was observed in the protonation of  $[\text{ReH}(\text{CO})\text{L}_4]$  with a CO:P ratio 1:4. This result is not surprising taking into account the lesser  $\pi$ -acceptor properties of the phosphites as compared to the carbonyl ligand, which make the rhenium a more electron-rich metal centre in  $[\text{ReH}(\text{CO})\text{L}_4]$  than in the other  $[\text{ReH}(\text{CO})_{5-n}\text{L}_n]$  ( $n = 2, 3, 4$ ) complexes, therefore favouring the homolytic cleavage of  $\text{H}_2$  resulting in the dihydride species. In addition, also other factors probably affect the homolytic cleavage of a  $\text{H}_2$  ligand, but the related  $\pi$ -acceptor properties of the ancillary ligands seem to play an important role, as shown by the existence of dihydrides or an equilibrium between dihydride and dihydrogen species in other monocarbonyl complexes.<sup>18,22b</sup>

A comparison among our  $\eta^2\text{-H}_2$  complexes **5**, **6**, **7**, **8** shows that, although the spectroscopic properties ( $T_{1(\text{min})}$  and <sup>1</sup>J<sub>HD</sub>) are rather similar, the stability to the loss of  $\text{H}_2$  varies greatly, according to the carbonyl:phosphite ratio and the nature of the phosphite ligands. As shown in Table 4, the temperature limit of stability increases with the number of 'phosphines' in the complexes, with the monocarbonyls **8** being the most stable. The nature of the phosphite also influences the stability of the complexes and the results show that the phosphonite PPh(OEt)<sub>2</sub> is that which most stabilises the  $\eta^2\text{-H}_2$  derivatives among the phosphites used. However, despite the known properties<sup>4</sup> of the PPh(OEt)<sub>2</sub> ligand in stabilising dihydrogen complexes, no rhenium  $\eta^2\text{-H}_2$  complexes can be isolated in the solid state, owing to the easy loss of  $\text{H}_2$ . This instability of the  $\eta^2\text{-H}_2$  complexes of rhenium is rather unexpected, when taking into account that the strictly comparable manganese complexes<sup>4e</sup>  $[\text{Mn}(\eta^2\text{-H}_2)(\text{CO})\text{L}_4]\text{BPh}_4$  are stable at room temperature and can be isolated as solids. Generally, the dihydrogen complexes of the third-row transition metals are more stable than those corresponding to the first row and our results, therefore, show

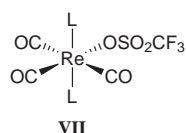
how the stability of the dihydrogen complexes depends on a balance of factors which are not yet completely established.

The evolution of H<sub>2</sub> from complexes **5–8** results in the disappearance of the η<sup>2</sup>-H<sub>2</sub> resonance at δ –3.6 to –5.21 and the formation of formally 16-electron complexes which, in the case of the compounds [Re(CO)<sub>2</sub>L<sub>3</sub>]BPh<sub>4</sub> **10** and [Re(CO)L<sub>4</sub>]BPh<sub>4</sub> **11**, can be isolated as white solids and characterised (Scheme 4).



Scheme 4

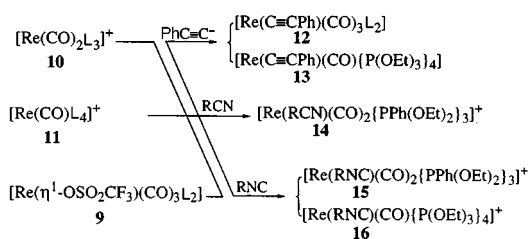
Evolution of H<sub>2</sub> from complexes containing the CF<sub>3</sub>SO<sub>3</sub><sup>–</sup> anion affords the η<sup>1</sup>-triflate complex which, in the case of [Re(η<sup>1</sup>-OSO<sub>2</sub>CF<sub>3</sub>)(CO)<sub>3</sub>{PPh<sub>2</sub>(OEt)}<sub>2</sub>] **9c**, was obtained as a solid with a *mer,trans* geometry **VII**, as was established in solution by IR and NMR data (Table 1).



The unsaturated complexes **10** and **11** are white solids, stable in the air, diamagnetic, 1:1 electrolytes and probably are stabilised by an agostic interaction<sup>23</sup> between the electron-deficient rhenium centre and a C–H bond of the ethyl (or phenyl) group of one phosphite ligand. Unfortunately, in the temperature range between +20 and –90 °C, the <sup>1</sup>H and <sup>31</sup>P NMR data do not give any information to support this hypothesis and no suitable crystals for a X-ray determination were obtained. Therefore, the presence of an agostic bond must remain as a hypothesis supported by the numerous precedents.<sup>3g,15e,24–26</sup>

### Reactivity

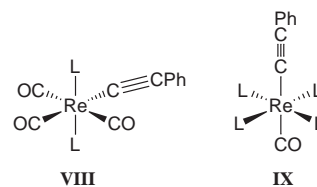
Some studies on the properties of the unsaturated complexes are reported in Scheme 5. Both the unsaturated complexes **10**



Scheme 5 L = P(OEt)<sub>3</sub> **a**, PPh(OEt)<sub>2</sub> **b** or PPh<sub>2</sub>(OEt) **c**; R = 4-MeC<sub>6</sub>H<sub>4</sub>

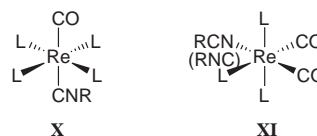
and **11** and the triflate compound **9** react with a variety of small donor molecules to give a series of neutral or cationic rhenium complexes the spectroscopic data for which are reported in Table 1. The acetylide complexes **12**, **13** were obtained as white or pale yellow solids soluble in polar and non-polar solvents, where they behave as non-electrolytes. The infrared and NMR spectra confirm the presence of the acetylide ligand and suggest the geometries **VIII** and **IX** for the complexes in solution. The characteristic ν(C≡C) of the acetylide ligand is, in fact, present as a medium-intensity band at 2084–2101 cm<sup>–1</sup> in the infrared spectra of complexes **12** and **13**, while in the <sup>13</sup>C NMR spectra the C<sub>α</sub> and C<sub>β</sub> signals are clearly assigned (between δ 99 and 177) on the basis of the multiplicity of the signals and by the

J<sub>CP</sub> values (Table 1). Furthermore, in the temperature range between +30 and –90 °C the <sup>31</sup>P-<sup>1</sup>H NMR spectra of the [Re(C≡CPh)(CO)<sub>3</sub>L<sub>2</sub>] **12** compounds show only one sharp singlet, while the ν(CO) bands are two strong and one of weak intensity, consistent with a *mer,trans* geometry **VIII**. A *trans*



geometry **IX** can be proposed, instead, for the monocarbonyl [Re(C≡CPh)(CO)L<sub>4</sub>] **13** derivative, on the basis of the presence of only one ν(CO) band and only one singlet in the <sup>31</sup>P-<sup>1</sup>H NMR spectra.

By treating the unsaturated complexes **10**, **11** with the appropriate ligand the new monoisocyanide **15**, **16** and the mononitrile complexes **14** can be prepared; these were isolated as pale yellow solids, stable in the air, diamagnetic and 1:1 electrolytes. The infrared spectra show only one ν(CN) band at 2259 cm<sup>–1</sup> for the nitrile **14** and at 2131 or 2149 cm<sup>–1</sup> for the isocyanide complexes. Furthermore, only one ν(CO) band at 1942 cm<sup>–1</sup> was observed for the complex [Re(4-MeC<sub>6</sub>H<sub>4</sub>NC)(CO){P(OEt)<sub>3</sub>}<sub>4</sub>]BPh<sub>4</sub> **16a**, the <sup>31</sup>P-<sup>1</sup>H NMR spectrum of which shows a sharp singlet suggesting magnetic equivalence of the four phosphite ligands, as in the *trans* geometry **X**.



The infrared spectra of both the dicarbonyl complexes **14b** and **15b** show two strong ν(CO) bands suggesting a *cis* arrangement of the two carbonyl ligands. These two CO groups, however, are not magnetically equivalent, as indicated by the <sup>13</sup>C NMR spectrum of [Re(4-MeC<sub>6</sub>H<sub>4</sub>NC)(CO)<sub>2</sub>{PPh(OEt)<sub>2</sub>}<sub>3</sub>]BPh<sub>4</sub> **15b**, which shows at δ 193.5 and at 189.3 two multiplets due to two non-equivalent carbonyl carbon atoms. Furthermore, the <sup>31</sup>P-<sup>1</sup>H NMR spectrum shows an A<sub>2</sub>B multiplet (Table 1) indicating that two phosphites are magnetically equivalent and different from the third. On this basis a *cis,mer* geometry of type **XI** can reasonably be proposed for the dicarbonyl **14b** and **15b** compounds.

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