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

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Hydride complexes [ReH(CO)$_4$L] **1**, [ReH(CO)$_3$L$_2$] **2**, [ReH(CO)$_2$L$_3$] **3** and [ReH(CO)L$_4$] **4** [L = P(OEt)$_3$ **a**, PPh(OEt)$_2$ **b**, PPh$_2$(OEt) **c** or PPh$_2$(OMe) **d**] were prepared by treating [ReH(CO)$_5$] with the appropriate phosphite under UV irradiation or reflux. The complexes were characterised by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and by crystal structure determinations of **1d** and **2d**. Protonation of the monocarbonyls [ReH(CO)L$_4$] **4** in CD$_2$Cl$_2$ with HBF$_4$·Et$_2$O resulted in an equilibrium mixture of the classical dihydride complexes [ReH$_2$(CO)L$_4$]$^+$BF$_4^-$ and their non-classical tautomers [Re(η^2-H$_2$)(CO)L$_4$]$^+$BF$_4^-$. The dihydride [ReH$_2$(CO){PPh(OEt)$_2$}$_4$]BPh$_4$ was also isolated as a solid by protonation of [ReH(CO){PPh(OEt)$_2$}$_4$] in ethanol. Thermally unstable [Re(η^2-H$_2$)(CO)$_4$L]$^+$, [Re(η^2-H$_2$)(CO)$_3$L$_2$]$^+$ and [Re(η^2-H$_2$)(CO)$_2$L$_3$]$^+$ **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)$_2$L$_3$]BPh$_4$ and [Re(CO)L$_4$]BPh$_4$ **11** and the triflate [Re(η^1-OSO$_2$CF$_3$)(CO)$_3$L$_2$] were obtained from the η^2-H$_2$ derivatives by evolution of H$_2$. The new complexes [Re(C≡CPh)(CO)$_3$L$_2$], [Re(C≡CPh)(CO)L$_4$] **13**, [Re(4-MeC$_6$H$_4$CN)(CO)$_2$L$_3$]BPh$_4$, [Re(4-MeC$_6$H$_4$NC)(CO)$_2$L$_3$]BPh$_4$ and [Re(4-MeC$_6$H$_4$NC)(CO)L$_4$]BPh$_4$ were prepared by treating the triflate compounds or the unsaturated compounds [Re(CO)$_2$L$_3$]BPh$_4$ and [Re(CO)L$_4$]BPh$_4$ with Li$^+$C≡CPh$^-$ or with the appropriate ligand.

Since the initial discovery of the first transition metal dihydrogen complexes[1] 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.[2] 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.[2,3] 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$_2$ 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^2-H$_2$ compounds.

We have previously reported[4] 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,[5] describing the synthesis and the protonation reaction of new polyhydrides of the type ReH$_3$L$_4$, ReH$_5$L$_3$ and Re$_2$H$_8$L$_4$. 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$^{\mathrm{I}}$ containing phosphites as ancillary ligands. The crystal structures of two hydrides and the characterisation of the new η^2-H$_2$ complexes are also reported.

Experimental

All synthetic work was carried out under an appropriate atmosphere (H$_2$, 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)$_2$, PPh$_2$(OEt) and PPh$_2$(OMe) were prepared by the method of Rabinowitz and Pellon.[6] The complex [Re$_2$(CO)$_{10}$] was from Pressure Chemical Co. (Pittsburgh) and used as received, HBF$_4$·Et$_2$O (54% solution), triflic acid, CF$_3$CO$_2$H, CF$_3$CO$_2$D and phenylacetylene were Aldrich products, used without further purification. Lithium phenylacetylide Li$^+$[PhC≡C]$^-$ was prepared by treating a slight excess of phenylacetylene (40 mmol, 4.4 cm^3) with lithium (35 mmol, 0.24 g) in tetrahydrofuran (thf) (10 cm^3). *p*-Tolyl isocyanide was obtained by the phosgene method of Ugi *et al.*[7] 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 (^{1}H, ^{13}C, ^{31}P) on a Bruker AC200 or AMX400 spectrometer at temperatures varying between +30 and −90 °C, unless otherwise noted. Proton and ^{13}C spectra are referred to internal tetramethylsilane, while ^{31}P-{^{1}H} chemical shifts are reported with respect to 85% H$_3$PO$_4$, with downfield shifts considered positive. Proton T_1 values were measured in CD$_2$Cl$_2$ 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^{-3} mol dm^{-3} solutions of the complexes in MeNO$_2$ at 25 °C was measured with a Radiometer CDM 83 instrument.

Preparation of the complexes

The hydride [ReH(CO)$_5$] was prepared as previously reported.[8]

***cis*-[ReH(CO)$_4$L] 1 [L = PPh$_2$(OEt) c or PPh$_2$(OMe) d].** To a solution of [ReH(CO)$_5$] (2.5 mmol, 0.82 g) in thf (20 cm^3) 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^3) until a white solid separated. The product was filtered off and crystallised from dichloromethane (2 cm^3) and ethanol or methanol (4 cm^3); yield ⩾60% (Found: C, 41.1; H, 3.1. $C_{18}H_{16}O_5PRe$ **1c** requires C, 40.8; H, 3.05. Found: C, 39.5; H, 2.8. $C_{17}H_{14}O_5PRe$ **1d** requires C, 39.6; H, 2.9%).

mer**,*****trans*****-[ReH(CO)$_3$L$_2$] 2 [L = PPh$_2$(OEt) c or PPh$_2$(OMe) d].** An excess of the appropriate phosphine (12 mmol) was added to a solution of [ReH(CO)$_5$] (5 mmol, 1.64 g) in thf (30 cm^3) 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^3). A white solid slowly separated which was filtered off and crystallised from CH_2Cl_2 (4 cm^3) and ethanol or methanol (10 cm^3); yield ⩾90% for **2c**, ⩾45% for **2d** (Found: C, 51.0; H, 4.2. $C_{31}H_{31}O_5P_2Re$ **2c** requires C, 50.9; H, 4.3. Found: C, 49.0; H, 4.1. $C_{29}H_{27}O_5P_2Re$ **2d** requires C, 49.5; H, 3.9%).

mer**,*****trans*****- and *****fac*****,*****cis*****-[ReH(CO)$_3${PPh(OEt)$_2$}$_2$] 2b and 2b-*****fac*****.** A slight excess of diethoxyphenylphosphine (12 mmol, 2.4 cm^3) was added to a solution of [ReH(CO)$_5$] (5 mmol, 1.64 g) in toluene (30 cm^3) 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^3) was evaporated to dryness leaving an oil which was treated with ethanol (5 cm^3). By cooling the resulting solution to −25 °C white crystals of the *mer*,*trans* complex **2b** were obtained; yield ⩾60%. From the second fraction eluted (500 cm^3), after evaporation of the solvent and treatment with ethanol, the *fac*,*cis* isomer **2b-*fac*** was obtained; yield ⩾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. $C_{23}H_{31}O_7P_2Re$ **2b** and **2b-*fac*** requires C, 41.4; H, 4.7%).

fac**,*****cis*****-[ReH(CO)$_3${PPh$_2$(OEt)}$_2$] 2c-*****fac*****.** This complex was prepared exactly like **2b** by irradiation at room temperature for 40 min of a solution of [Re(CO)$_5$] in toluene containing a slight excess of PPh$_2$(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 ⩾60% (Found: C, 50.7; H, 4.15. $C_{31}H_{31}O_5P_2Re$ **2c** requires C, 50.9; H, 4.3%).

mer**,*****trans*****-[ReH(CO)$_3${P(OEt)$_3$}$_2$] 2a.** This complex was prepared exactly like the related compound **2b**, obtaining exclusively the *mer*,*trans* isomer; yield ⩾60% (Found: C, 30.0; H, 5.6. $C_{15}H_{31}O_9P_2Re$ requires C, 29.85; H, 5.2%).

cis**,*****mer*****-[ReH(CO)$_2$L$_3$] 3 and *****cis*****,*****mer*****-[ReH(CO)L$_4$] 4 [L = PPh(OEt)$_2$ b or PPh$_2$(OEt) c].** To a solution of [ReH(CO)$_5$] (5 mmol, 1.64 g) in toluene (30 cm^3) 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^3) and treatment of the resulting oil with ethanol (3 cm^3) allowed us to obtain the monocarbonyls **4** in low yield (⩾5% for **4b**, traces for **4c**). From the second fraction eluted (700 cm^3), after removal of the solvent and treatment with ethanol, white microcrystals of the dicarbonyls **3** were obtained; yield ⩾40% (Found: C, 45.75; H, 5.6. $C_{32}H_{46}O_8P_3Re$ **3b** requires C, 45.9; H, 5.5. Found: C, 56.35; H, 5.1. $C_{44}H_{46}O_5P_3Re$ **3c** requires C, 56.6; H, 5.0. Found: C, 49.00; H, 6.0. $C_{41}H_{61}O_9P_4Re$ **4b** requires C, 48.85; H, 6.1%).

cis**,*****mer*****-[ReH(CO)$_2${P(OEt)$_3$}$_3$] 3a.** This compound was prepared like the related **3** by treating [ReH(CO)$_5$] (5 mmol, 1.64 g) in toluene (30 cm^3) with an excess of P(OEt)$_3$(35 mmol, 5.8 cm^3) 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 ⩾60%) as a white solid from the tricarbonyl [ReH(CO)$_3${P(OEt)$_3$}$_2$] **2a** (second eluted, yield ⩾10%) (Found: C, 32.6; H, 6.3. $C_{20}H_{46}O_{11}P_3Re$ requires C, 32.4; H, 6.25%).

trans**-[ReH(CO){P(OEt)$_3$}$_4$] 4a.** This compound was also prepared like the related **4b** by irradiating a [ReH(CO)$_5$] solution (5 mmol, 1.64 g in 30 cm^3 of toluene) containing an excess of P(OEt)$_3$ (35 mmol, 5.8 cm^3) for about 40 h. Removal of the solvent under reduced pressure gave an oil which was triturated with ethanol (5 cm^3). By vigorous stirring of the resulting solution a white solid separated which was crystallised from CH_2Cl_2 (3 cm^3) and ethanol (7 cm^3); yield ⩾65% (Found: C, 34.05; H, 7.3. $C_{25}H_{61}O_{13}P_4Re$ requires C, 34.1; H, 7.0%).

[Re(η^2-H$_2$)(CO)$_4$L]$^+$BF$_4$$^-$ 5, [Re(η^2-H$_2$)(CO)$_3$L$_2$]$^+$BF$_4$$^-$ 6 and [Re(η^2-H$_2$)(CO)$_2$L$_3$]$^+$BF$_4$$^-$ 7 [L = P(OEt)$_3$ a, PPh(OEt)$_2$ b, PPh$_2$(OEt) c or PPh$_2$(OMe) d]. These complexes were prepared in CD_2Cl_2 solution at low temperature (−80 °C) by protonation with $HBF_4 \cdot Et_2O$ 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 $HBF_4 \cdot Et_2O$ (0.02 mmol, 2.9 μl) to a solution of the appropriate hydride (0.02 mmol) in CD_2Cl_2 (0.5 cm^3) 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 (^1H and ^{31}P) were registered. [Re(η^2-H$_2$)(CO)$_4${PPh$_2$(OMe)}]$^+$ **5d**: δ_H(CD_2Cl_2, 193 K) 7.45 (10 H, m, Ph), 3.59 (3 H, d, CH_3) and −3.75 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 198 K) 122.98 (s). [Re(η^2-H$_2$)(CO)$_3${P(OEt)$_3$}$_2$]$^+$**6a**: δ_H(CD_2Cl_2, 203 K) 4.13 (12 H, br, CH_2), 1.41 (18 H, t, CH_3) and −4.6 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 203 K) 105.5 (s). [Re(η^2-H$_2$)(CO)$_3${PPh(OEt)$_2$}$_2$]$^+$ **6b**: δ_H(CD_2Cl_2, 203 K) 7.64 (10 H, m, Ph), 3.98 (8 H, m, br, CH_2), 1.42 (12 H, t, CH_3) and −4.3 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 203 K) 119.19 (s). [Re(η^2-H$_2$)(CO)$_3${PPh$_2$(OMe)}$_2$]$^+$ **6d**: δ_H(CD_2Cl_2, 203 K) 7.52 (20 H, m, Ph), 3.3 (6 H, t, CH_3) and −3.9 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 203 K) 123.1 (s). [Re(η^2-H$_2$)(CO)$_2${P(OEt)$_3$}$_3$]$^+$ **7a**: δ_H(CD_2Cl_2, 203 K) 4.02 (18 H, m, CH_2), 1.36, 1.21 (27 H, t, CH_3) and −5.02 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 203 K) A_2B spin system, δ_A 112.2, δ_B 110.8, $J_{AB} = 42.6$ Hz. [Re(η^2-H$_2$)(CO)$_2${PPh(OEt)$_2$}$_3$]$^+$ **7b**: δ_H(CD_2Cl_2, 203 K) 7.60–7.10 (15 H, m, Ph), 3.77, 3.50 (12 H, m, CH_2), 1.30, 1.15 (18 H, t, CH_3) and −4.5 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 203 K) AB_2 spin system, δ_A 131.4, δ_B 129.5, $J_{AB} = 27.5$ Hz. [Re(η^2-H$_2$)(CO)$_2${PPh$_2$(OEt)}$_3$]$^+$ **7c**: δ_H(CD_2Cl_2, 203 K) 7.70–7.20 (30 H, m, Ph), 3.60–3.10 (6 H, m, CH_2), 1.22, 1.02 (9 H, t, CH_3) and −3.55 (2 H, br, η^2-H$_2$); δ_P(CD_2Cl_2, 203 K) AB_2 spin system, δ_A 106.2, δ_B 103.5, $J_{AB} = 27.5$ Hz.

[Re(η^2-HD)(CO)$_3${P(OEt)$_3$}$_2$]$^+$CF$_3$CO$_2$$^-$ 6a$_1$ and [Re(η^2-HD)(CO)$_3${PPh(OEt)$_2$}$_2$]$^+$CF$_3$CO$_2$$^-$ 6b$_1$, [Re(η^2-HD)(CO)$_2$L$_3$]$^+$CF$_3$CO$_2$$^-$ [L = P(OEt)$_3$ 7a$_1$, PPh(OEt)$_2$ 7b$_1$ or PPh$_2$OEt 7c$_1$]. These isotopomers were prepared in a NMR tube exactly like **6** and **7** using CF_3CO_2D as the protonating agent.

[ReH$_2$(CO){P(OEt)$_3$}$_4$]$^+$BF$_4$$^-$ 8*a and [Re(η^2-H$_2$)(CO){P(OEt)$_3$}$_4$]$^+$BF$_4$$^-$ 8a. These derivatives were also prepared only in CD_2Cl_2 solution by protonation at low temperature (−80 °C) with $HBF_4 \cdot Et_2O$ of the hydride [ReH(CO){P(OEt)$_3$}$_4$]. A mixture of **8*a** and **8a** was always obtained, the ^1H and ^{31}P

NMR spectra being as follows: δ_H(CD_2Cl_2, 203 K) 3.97 (qnt), 3.54 (qnt), 24 H, CH_2), 1.34, 1.31, 1.27, 1.22 (36 H, t, CH_3), −5.60 (br) and −6.17 (qnt) (2 H, H_2); δ_P(CD_2Cl_2, 203 K) 117.5 (s, br).

$[ReH(D)(CO)\{P(OEt)_3\}_4]^+CF_3CO_2^-$ 8*a$_1$ and $[Re(\eta^2\text{-}HD)(CO)\{P(OEt)_3\}_4]^+CF_3CO_2^-$ 8a$_1$. These isotopomers were prepared exactly like the related complexes **8*a** and **8a** using CF_3CO_2D as the protonating agent.

$[ReH_2(CO)\{PPh(OEt)_2\}_4]^+BF_4^-$ 8*b and $[Re(\eta^2\text{-}H_2)(CO)\{PPh(OEt)_2\}_4]^+BF_4^-$ 8b. These compounds were prepared only in CD_2Cl_2 solution at low temperature (−80 °C) by protonation with $HBF_4{\cdot}Et_2O$ of the hydride $[ReH(CO)L_4]$. 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 ^1H and ^{31}P NMR data as follows: δ_H(CD_2Cl_2, 273 K) 7.60–7.20 (20 H, m, Ph), 3.60 (16 H, m, CH_2), 1.24, 1.21 (24 H, t, CH_3), −4.75 (br) and −5.18 (qnt) (2 H, H_2); δ_P(CD_2Cl_2, 273 K) 133.5 (s) and 142.0 (s).

$[ReH(D)(CO)\{PPh(OEt)_2\}_4]^+CF_3CO_2^-$ 8b*$_1$ and $[Re(\eta^2\text{-}HD)(CO)\{PPh(OEt)_2\}_4]^+CF_3CO_2^-$ 8b$_1$. These isotopomers were prepared exactly like the related complexes **8*b** and **8b** using CF_3CO_2D as the protonating agent.

$[ReH_2(CO)\{PPh(OEt)_2\}_4]BPh_4$ 8*b-BPh$_4$. An equimolar amount of $HBF_4{\cdot}Et_2O$ (0.1 mmol, 14 μl) was added to a suspension of $[ReH(CO)\{PPh(OEt)_2\}_4]$ (0.1 mmol, 0.100 g) in ethanol (3 cm^3) cooled to −80 °C. The reaction mixture was brought to 0 °C and stirred for about 2 h. An excess of $NaBPh_4$ (0.2 mmol, 0.068 g) in ethanol (2 cm^3) was added giving a white solid which was filtered off and crystallised from CH_2Cl_2 (2 cm^3) and ethanol (3 cm^3); yield ⩾65%; Λ_M = 51.9 S cm^2 mol^{-1} (Found: C, 58.7; H, 6.3. $C_{65}H_{82}BO_9P_4Re$ requires C, 58.8; H, 6.2%).

$[Re(\eta^1\text{-}OSO_2CF_3)(CO)_3\{PPh_2(OEt)\}_2]$ 9c. To a suspension of $[ReH(CO)_3\{PPh_2(OEt)\}_2]$ (0.2 mmol, 0.146 g) in ethanol (5 cm^3) cooled to −80 °C an equimolar amount of CF_3SO_3H 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 ⩾60% (Found: C, 43.95; H, 3.6. $C_{32}H_{30}F_3O_8P_2ReS$ requires C, 43.7; H, 3.4%).

$[Re(CO)_2L_3]BPh_4$ 10 [P = $P(OEt)_3$ a or $PPh_2(OEt)$ c]. To a solution of the hydride $[ReH(CO)_2L_3]$ **3** (0.2 mmol) in ethanol (*ca.* 5 cm^3) cooled to −80 °C an equimolar amount of $HBF_4{\cdot}Et_2O$ (0.2 mmol, 29 μl) was added and the reaction mixture, brought to room temperature, stirred for 2 h. An excess of $NaBPh_4$ (0.3 mmol, 0.10 g) in ethanol (3 cm^3) was added and the white solid obtained was filtered off and crystallised from CH_2Cl_2 (2 cm^3) and ethanol (7 cm^3); yield ⩾85%; Λ_M = 55.1 for **10a**, 53.6 S cm^2 mol^{-1} for **10c** (Found: C, 50.1; H, 6.3. $C_{44}H_{65}BO_{11}P_3Re$ **10a** requires C, 49.9; H, 6.2. Found: C, 65.0; H, 5.3. $C_{68}H_{65}BO_5P_3Re$ **10c** requires C, 65.2; H, 5.2%).

$[Re(CO)\{P(OEt)_3\}_4]BPh_4$ 11a. This compound was prepared exactly like the related complex **10a** by protonation with $HBF_4{\cdot}Et_2O$ of $[ReH(CO)\{P(OEt)_3\}_4]$; yield ⩾80%; Λ_M = 54.0 S cm^2 mol^{-1} (Found: C, 49.25; H, 6.6. $C_{49}H_{80}BO_{13}P_4Re$ requires C, 49.1; H, 6.7%).

***mer,trans*-$[Re(C{\equiv}CPh)(CO)_3L_2]$ 12 [L = $P(OEt)_3$ a, $PPh(OEt)_2$ b or $PPh_2(OEt)$ c].** To a solution of the appropriate hydride $[ReH(CO)_3L_2]$ (0.60 mmol) in toluene (10 cm^3) cooled to −80 °C a slight excess of triflic acid (0.66 mmol, 58.4 μl) was added and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of $Li^+[PhC{\equiv}C]^-$ (2.4 mmol, 1.28 cm^3 of a 1.88 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 cm^3) at 0 °C until a pale yellow solid separated (2–3 h), which was filtered off and dried under vacuum; yield ⩾70% (Found: C, 48.4; H, 4.5. $C_{31}H_{35}O_7P_2Re$ **12b** requires C, 48.5; H, 4.6. Found: C, 56.1; H, 4.3. $C_{39}H_{35}O_5P_2Re$ **12c** requires C, 56.3; H, 4.2%).

***trans*-$[Re(C{\equiv}CPh)(CO)\{P(OEt)_3\}_4]$ 13a.** An excess of $Li^+[PhC{\equiv}C]^-$ (1.6 mmol, 0.85 cm^3 of a 1.88 mol dm^{-3} solution in thf) was added to a solution of $[Re(CO)\{P(OEt)_3\}_4]BPh_4$ **11a** (0.4 mmol, 0.48 g) in thf (15 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 cm^3) until a pale yellow solid separated, which was filtered off and dried under vacuum; yield ⩾65% (Found: C, 40.6; H, 6.9. $C_{33}H_{65}O_{13}P_4Re$ requires C, 40.45; H, 6.7%).

***cis,mer*-$[Re(4\text{-}MeC_6H_4CN)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ 14b and *cis,mer*-$[Re(4\text{-}MeC_6H_4NC)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ 15b.** An equivalent amount of $HBF_4{\cdot}Et_2O$ (0.2 mmol, 29 μl of a 54% solution) was added to a suspension of $[ReH(CO)_2\{PPh(OEt)_2\}_3]$ (0.2 mmol, 0.167 g) in ethanol (4 cm^3) cooled to −80 °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 $NaBPh_4$ (0.4 mmol, 0.137 g) in ethanol (2 cm^3) was added. A white solid slowly separated, which was filtered off and crystallised from ethanol; yield ⩾60%; Λ_M = 49.5 for **14b**, 52.8 S cm^2 mol^{-1} for **15b** (Found: C, 60.2; H, 5.8; N, 1.0. $C_{64}H_{72}BO_8P_3Re$ **14b** requires C, 60.4; H, 5.7; N, 1.1. Found: C, 60.5; H, 5.7; N, 1.2. $C_{64}H_{72}BO_8P_3Re$ **15b** requires C, 60.4; H, 5.7; N, 1.1%).

***trans*-$[Re(4\text{-}MeC_6H_4NC)(CO)\{P(OEt)_3\}_4]BPh_4$ 16a.** This complex can be prepared exactly like the related compound **15** or by treating the unsaturated compound $[Re(CO)\{P(OEt)_3\}_4]BPh_4$ **11a** with isocyanide. A typical preparation involved the addition of an excess of $4\text{-}MeC_6H_4NC$ (1 mmol, 117 μl) to a solution of $[Re(CO)\{P(OEt)_3\}_4]BPh_4$ (0.4 mmol, 0.48 g) in CH_2Cl_2 (10 cm^3). After 2 h of stirring, the solvent was removed under reduced pressure giving an oil which was treated with ethanol (3 cm^3). By cooling the resulting solution to −25 °C, white microcrystals of the compound were obtained, which were filtered off and dried under vacuum; yield ⩾80%; Λ_M = 52.6 S cm^2 mol^{-1} (Found: C, 52.2; H, 6.8; N, 1.1. $C_{57}H_{87}BO_{13}P_4Re$ requires C, 52.05; H, 6.7; N, 1.1%).

Crystallography

$[ReH(CO)_4\{PPh_2(OMe)\}]$ 1d. Crystallographic measurements were performed at 203 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 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 (θ range 7–15°) by the ω scan technique. Of 4321 reflections collected in the θ range 3–26°, 3563 independent reflections, after ψ-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.

$[ReH(CO)_3\{PPh_2(OMe)\}_2]$ 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 (θ range 9–13°). A total of 7309 reflections were collected in the θ range 3–27°. Of 6085 independent reflections, after ψ-scan absorption correction (maximum, minimum 0.999, 0.892) 4531 with $I > 2\sigma(I)$ were considered observed. No correction for crystal decomposition was required. The structure was solved by direct methods and Fourier-difference techniques as above.

Scattering factors and anomalous dispersion corrections were taken from ref. 9. Most calculations were performed with SHELXS 86[10] and SHELXL 93.[11] Figures were plotted with ZORTEP.[12]

CCDC reference number 186/962.

See http://www.rsc.org/suppdata/dt/1998/2071/ for crystallographic files in .cif format.

Results and Discussion

Preparation and characterisation of classical hydride complexes

A series of mixed phosphite–carbonyl complexes of the type $[\mathrm{ReH(CO)_{5-\mathit{n}}L_{\mathit{n}}}]$ **1**–**4** ($n = 1, 2, 3, 4$) were prepared by thermal or photochemical substitution of the carbonyl ligands in the $[\mathrm{ReH(CO)_5}]$ species with the appropriate phosphite, as shown in Scheme 1. The reaction of $[\mathrm{ReH(CO)_5}]$ with an equimolar amount of phosphite proceeds to give the tetracarbonyls $[\mathrm{ReH(CO)_4L}]$ **1** which can be isolated as solids only in the case of $\mathrm{PPh_2(OR)}$ (R = Et **c** and Me **d**) ligands. With an excess of phosphite, instead, the reaction afforded exclusively the tricarbonyl compounds $[\mathrm{ReH(CO)_3L_2}]$ **2** which were isolated as white solids in high yields. Irradiation of $[\mathrm{ReH(CO)_5}]$ solutions containing an excess of the appropriate phosphite caused the sequential substitution of the carbonyl ligands, allowing the synthesis of all the hydride complexes **1**–**4** which, after chromatographic separation, were obtained as solids and characterised. However, the monocarbonyls $[\mathrm{ReH(CO)L_4}]$ **4c** and **4d** were formed only in very small amounts and were not isolated. Good analytical data were obtained for all the hydride complexes, which are white or pale yellow solids, diamagnetic and non-electrolyte. The IR and NMR spectra (Table 1) confirm the proposed formulation and suggest for the compounds **1**–**4** the presence in solution of the geometries **I**–**V** which are similar to those found, in some cases, in the solid state (see below).

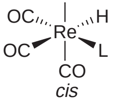
$$[\mathrm{ReH(CO)_5}] + \mathrm{L} \xrightarrow[\text{heat}]{\text{thf}} \underset{\mathbf{1}}{[\mathrm{ReH(CO)_4L}]} + \mathrm{CO}$$

$$[\mathrm{ReH(CO)_5}] \xrightarrow[\text{heat}]{\text{excess L}} \underset{\mathbf{2}}{[\mathrm{ReH(CO)_3L_2}]}$$

$$[\mathrm{ReH(CO)_5}] \xrightarrow[h\nu]{\mathrm{L}} \underset{\mathbf{1}}{[\mathrm{ReH(CO)_4L}]} \xrightarrow[h\nu]{\mathrm{L}} \underset{\mathbf{2}}{[\mathrm{ReH(CO)_3L_2}]}$$

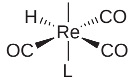
$$\xrightarrow[h\nu]{\mathrm{L}} \underset{\mathbf{3}}{[\mathrm{ReH(CO)_2L_3}]} \xrightarrow[h\nu]{\mathrm{L}} \underset{\mathbf{4}}{[\mathrm{ReH(CO)L_4}]}$$

Scheme 1 L = $\mathrm{P(OEt)_3}$ **a**, $\mathrm{PPh(OEt)_2}$ **b**, $\mathrm{PPh_2(OEt)}$ **c** or $\mathrm{PPh_2(OMe)}$ **d**



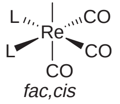
cis

I



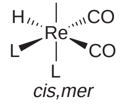
mer,trans

II



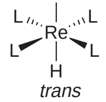
fac,cis

III



cis,mer

IV



trans

V

The IR spectra of the tetracarbonyls **1** show two strong bands and one of medium intensity, in agreement with a *cis* geometry **I**, confirmed in the solid state for **1d**. Both the *fac*,*cis* and *mer*,*trans* isomers were obtained for the tricarbonyls $[\mathrm{ReH(CO)_3L_2}]$ containing the $\mathrm{PPh(OEt)_2}$ **2b** and the $\mathrm{PPh_2(OEt)}$ **2c** ligands, while the *mer*,*trans* complex was exclusively obtained in the cases of **2a** and of **2d**. Diagnostic for the differentiation of the two isomers are the IR spectra, which show three bands with weak, strong and strong intensities, as the frequency decreases, for the *cis*,*mer* isomers, while three bands of strong and of comparable intensity are observed in the spectra of the *fac*,*cis* derivatives. In the temperature range between −80 and +30 °C the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectra of both the isomers of the tricarbonyl $[\mathrm{ReH(CO)_3L_2}]$ **2** compounds appear as only one sharp singlet, suggesting the magnetic equivalence of the two phosphite ligands. The hydride pattern also confirms the equivalence of the two phosphites showing, for both the isomers, a sharp triplet consistent with the two geometries **II** and **III**. The only isomer obtained for the compounds **2a** and **2d** contains a meridional arrangement of the three carbonyl ligands, with the two phosphites in *trans* position (*mer*,*trans* geometry **II**), as confirmed by the IR and NMR spectra of the two derivatives and by the crystal structure determination of **2d**.

However, a *cis*,*mer* geometry **IV** seems to be suggested instead by the spectroscopic data of the dicarbonyl $[\mathrm{ReH(CO)_2L_3}]$ **3** complexes. Two ν(CO) bands are observed in the IR spectra at 1958–1882 $\mathrm{cm^{-1}}$, consistent with two CO ligands in a mutually *cis* position. These two CO groups, however, are not magnetically equivalent, as shown by the $^{13}\mathrm{C}$ NMR spectra of the derivative $[\mathrm{ReH(CO)_2\{P(OEt)_3\}_3}]$ **3a**, which show two multiplets at δ 198.3 and 197.1 attributed to the carbonyl carbon atoms of two inequivalent CO ligands. The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectra show an $\mathrm{A_2B}$ or $\mathrm{AB_2}$ multiplet, while the hydride signal appears, in the proton spectra, as a multiplet easily simulable as the X part of an $\mathrm{A_2BX}$ or $\mathrm{AB_2X}$ spectrum (X = H), consistent with two phosphines being magnetically equivalent and different from the third. A type **IV** geometry for compounds **3** seems therefore to be consistent with the reported data.

Finally, a *trans* geometry **V** can be assigned to the monocarbonyl compounds $[\mathrm{ReH(CO)L_4}]$ **4** on the basis of the presence, between −80 and +30 °C, of a sharp singlet in the $^{31}\mathrm{P}$ NMR spectra.

Mixed carbonyl–phosphine complexes of rhenium have often been obtained by substituting CO ligands in $[\mathrm{ReX(CO)_5}]$ (X = halide or H) precursors, but include mainly a halogen derivative.[13] Only recently $[\mathrm{ReH(CO)_3(PR_3)_2}]$ ($\mathrm{PR_3 = PPh_3}$ or $\mathrm{PPh_2Pr^i}$) derivatives were prepared from $[\mathrm{ReH(CO)_5}]$ species.[14] The related hydrides can be obtained, in some cases, from the halide by treatment with $\mathrm{LiAlH_4}$ or sodium. However, they generally contain phosphine or phosphine–carbonyl as ligands,[13–15] with the rhenium(I) hydrides with phosphite as coligands being rather scarce. The thermal and the photochemical decarbonylation of $[\mathrm{ReH(CO)_5}]$ in the presence of 'phosphite' allows the synthesis of a series of mono-, di-, tri- and tetra-substituted $[\mathrm{ReH(CO)_{5-\mathit{n}}P_{\mathit{n}}}]$ complexes together with a systematic investigation using $\mathrm{P(OEt)_3}$, $\mathrm{PPh(OEt)_2}$, $\mathrm{PPh_2(OEt)}$ and $\mathrm{PPh_2(OMe)}$ as a ligand.

Crystal structures of $[\mathrm{ReH(CO)_4\{PPh_2(OMe)\}}]$ 1d and $[\mathrm{ReH(CO)_3\{PPh_2(OMe)\}_2}]$ 2d

Crystals suitable for X-ray analysis were obtained for both complexes by recrystallisation from $\mathrm{CH_2Cl_2}$–MeOH solution. The crystallographic data and the final *R* indices for the two compounds **1d** and **2d** are summarised in Table 2, selected bond distances and angles in Table 3. The ORTEP drawings of the compounds, along with the numbering schemes adopted, are shown in Figs. 1 and 2.

In both structures the terminal hydride ligand was located from an analysis of the Fourier-difference map. The two hydride compounds have a distorted octahedral disposition of

Table 1 Infrared and NMR data for the rhenium complexes

Compound	IR[a]		^{1}H NMR[b,c]			^{31}P-{^{1}H} NMR[b,d]	^{13}C-{^{1}H} NMR[b,c]	
	ṽ/cm^{-1}	Assignment	δ(*J*/Hz)	Assignment	Spin system	δ(*J*/Hz)	δ(*J*/Hz)	Assignment
1c *cis*-[ReH(CO)$_4${PPh$_2$(OEt)}]	2080m	ν(CO)	3.57 (qnt)[e]	CH$_2$		111.5 (s)[e]		
	1985s		0.99 (t)	CH$_3$				
	1959s		−4.95 (d)	ReH				
			J_{PH} = 20					
1d *cis*-[ReH(CO)$_4${PPh$_2$(OMe)}]	2083s	ν(CO)	3.43 (d)	CH$_3$		133.0 (s)	189.21 (d)	CO
	1967s (br)		−5.59 (d)	ReH			J_{CP} = 7.3	
			J_{PH} = 24				189.16 (d)	
							J_{CP} = 11.4	
							189.12 (d)	
							J_{CP} = 47	
							54.5 (d)	CH$_3$
2a *mer,trans*-[ReH(CO)$_3${P(OEt)$_3$}$_2$]	2020w	ν(CO)	3.97 (m)[f]	CH$_2$		130.5 (s)[f]		
	1945s		1.50 (t)	CH$_3$				
	1927s		−6.25 (t)	ReH				
			J_{PH} = 24					
2b *mer,trans*-[ReH(CO)$_3${PPh(OEt)$_2$}$_2$]	2020w	ν(CO)	3.95 (m)[e]	CH$_2$		143.0 (s)[e]		
	1951s		3.69 (m)					
	1926s		1.07 (t)	CH$_3$				
			−5.54 (t)	ReH				
			J_{PH} = 22					
2b-*fac* *fac,cis*-[ReH(CO)$_3${PPh(OEt)$_2$}$_2$]	2026s	ν(CO)	3.80 (m)[e]	CH$_2$		141.3 (s)[e]		
	1961s		3.50 (m)					
	1913s		1.00 (t)	CH$_3$				
			−5.00 (t)	ReH				
			J_{PH} = 18					
2c *mer,trans*-[ReH(CO)$_3${PPh$_2$(OEt)}$_2$]	2040w	ν(CO)	3.83 (m)	CH$_2$		130.9 (s)	196.2 (t)	CO
	1946s		1.31 (t)	CH$_3$			J_{CP} <1	
	1926s		−5.80 (t)	ReH			194.9 (t)	
			J_{PH} = 20				J_{CP} = 10.2	
							63.4 (br)	CH$_2$
							16.2 (br)	CH$_3$
2c-*fac* *fac,cis*-[ReH(CO)$_3${PPh$_2$(OEt)}$_2$]	1943s	ν(CO)	3.91 (m)[f]	CH$_2$		115.5 (s)[f]		
	1928s		1.17 (t)	CH$_3$				
	1915s		−5.27 (t)	ReH				
			J_{PH} = 20					
2d *mer,trans*-[ReH(CO)$_3${PPh$_2$(OMe)}$_2$]	2034w	ν(CO)	3.51 (t)[g]	CH$_3$		137.1 (s)[g]	195.8 (t)[g]	CO
	1931s (br)		−5.85 (t)	ReH			J_{CP} = 5.9	
			J_{PH} = 20				194.4 (t)	
							J_{CP} = 10.4	
							77.6 (d)	CH$_3$
3a *cis,mer*-[ReH(CO)$_2${P(OEt)$_3$}$_3$]	1958s	ν(CO)	4.07 (m)[f]	CH$_2$	A$_2$B	δ$_A$ 135.6[f]	198.3	CO
	1893s						(t of d)[f]	
			1.22 (t)	CH$_3$		δ$_B$ 133.9	J_{CP} = 10	
			δ$_X$ −6.39	ReH		J_{AB} = 46.0	197.1	
			A$_2$BX				(t of d)	
			J_{AX} = 32.5				J_{CP} = 8	
			J_{BX} = 25.6				60.9 (t),	CH$_2$
							60.8 (t)	
							16.2 (t),	CH$_3$
							16.1 (t)	
3b *cis,mer*-[ReH(CO)$_2${PPh(OEt)$_2$}$_3$]	1953s	ν(CO)	3.95 (m)[e]	CH$_2$	AB$_2$	δ$_A$ 146.2[e]		
	1894s		3.70 (m)			δ$_B$ 145.8		
			3.40 (m)			J_{AB} = 33.0		
			1.11 (t)	CH$_3$				
			1.02 (t)					
			δ$_X$ −5.36	ReH				
			AB$_2$X					
			J_{AX} = 30.0					
			J_{BX} = 23.0					
3c *cis,mer*-[ReH(CO)$_2${PPh$_2$(OEt)}$_3$]	1937s	ν(CO)	4.00 (m)[f]	CH$_2$	AB$_2$	δ$_A$ 116.1[f]		
	1882s		3.74 (m)			δ$_B$ 113.5		
			3.45 (qnt)			J_{AB} = 30.8		
			1.09 (t)	CH$_3$				
			0.98 (t)					
			δ$_X$ −4.50	ReH				
			AB$_2$X					
			J_{AX} = 32.6					
			J_{BX} = 20.2					
4a *trans*-[ReH(CO){P(OEt)$_3$}$_4$]	1876s	ν(CO)	4.11 (m)[f]	CH$_2$		136.6 (s)[f]		
			1.27 (t)	CH$_3$				
			−7.08 (qnt)	ReH				
			J_{PH} = 25					

Table 1 (*Contd.*)

	IR[a]		^{1}H NMR[b,c]			^{31}P-{^{1}H} NMR[b,d]	^{13}C-{^{1}H} NMR[b,c]	
Compound	$\tilde{\nu}$/cm^{-1}	Assignment	δ(*J*/Hz)	Assignment	Spin system	δ(*J*/Hz)	δ(*J*/Hz)	Assignment
4b *cis*,*mer*-[ReH(CO){PPh(OEt)$_2$}$_4$]	1862s	ν(CO)	3.80 (m)[e] 3.40 (m) 1.08 (t) −5.68 (qnt) J_{PH} = 24	CH$_2$ CH$_3$ ReH		147.2 (s)[e]		
8*b-BPh$_4$ [ReH$_2$(CO){PPh(OEt)$_2$}$_4$]BPh$_4$	1959s	ν(CO)	3.62 (m) 0.99 (t) −6.05 (qnt) J_{PH} = 25	CH$_2$ CH$_3$ ReH	A$_4$ A$_2$B$_2$	147.0 (s) δ$_A$ 152.7[h] δ$_B$ 146.6 J_{AB} = 40.3		
8*b [ReH$_2$(CO){PPh(OEt)$_2$}$_4$]$^+$			−5.18 (qnt)	ReH		141.0 (s)		
9c [Re(η^1-OSO$_2$CF$_3$)(CO)$_3${PPh$_2$(OEt)}$_2$]	2070w 1962s 1930s 1326m	ν(CO) ν(tf$^-$)[i]	3.69 (qnt) 1.23 (t)	CH$_2$ CH$_3$		108.3 (s)		
10a [Re(CO)$_2${P(OEt)$_3$}$_3$]BPh$_4$	1991s 1895s	ν(CO)	4.07 (m) 1.33 (t) 1.30 (t)	CH$_2$ CH$_3$		118.9 (s, br)		
10c [Re(CO)$_2${PPh$_2$(OEt)}$_3$]BPh$_4$	1966s 1885s	ν(CO)	3.45 (m) 3.24 (qnt) 1.04 (t) 0.82 (t)	CH$_2$ CH$_3$	AB$_2$	δ$_A$ 115.1 δ$_B$ 113.1 J_{AB} = 31.6		
11a [Re(CO){P(OEt)$_3$]BPh$_4$	1868s	ν(CO)	3.98 (m) 1.22 (t)	CH$_2$ CH$_3$		123.7 (s), 122.9 (s, br)		
12b *mer*,*trans*-[Re(C≡CPh)(CO)$_3${PPh(OEt)$_2$}$_2$]	2101m 2042w 1950s 1933s	ν(C≡C) ν(CO)	4.20 (m) 3.95 (m) 1.33 (t)	CH$_2$ CH$_3$		129.5 (s)	190.5 (t) J_{CP} = 8 190.2 (t) J_{CP} = 11 113.1 (t) 99.4 (t) J_{CP} = 16 63.3 (t) 16.4 (t)	CO C$_β$ C$_α$ CH$_2$ CH$_3$
12c *mer*,*trans*-[Re(C≡CPh)(CO)$_3${PPh$_2$(OEt}$_2$]	2098m 2036w 1947s 1927s	ν(C≡C) ν(CO)	3.91 (m) 1.28 (t)	CH$_2$ CH$_3$		100.0 (s)	191.07 (t) J_{CP} = 10 190.91 (t) J_{CP} = 6 116.9 (t) J_{CP} = 2.5 101.8 (t) J_{CP} = 15 63.0 (t) 16.3 (t)	CO C$_β$ C$_α$ CH$_2$ CH$_3$
13a *trans*-[Re(C≡CPh)(CO){P(OEt)$_3$}$_4$]	2084m 1845m	ν(C≡C) ν(CO)	4.15 (m) 1.23 (t)	CH$_2$ CH$_3$		119.0 (s)		
14b *cis*,*mer*-[Re(4-MeC$_6$H$_4$CN)(CO$_2$){PPh(OEt)$_2$}$_3$]BPh$_4$	2259m 1987s 1908s	ν(CN) ν(CO)	3.95 (m) 2.38 (s) 1.36 (t) 1.35 (t)	CH$_2$ *p*-C*H*$_3$C$_6$H$_4$ POCH$_2$C*H*$_3$	A$_2$B	δ$_A$ 136.3 δ$_B$ 135.2 J_{AB} = 31.5		
15b *cis*,*mer*-[Re(4-MeC$_6$H$_4$NC)(CO)$_2${PPh(OEt)$_2$}$_3$]BPh$_4$	2149s 1996s 1940s	ν(CN) ν(CO)	3.99 (m)[j] 2.35 (s) 1.38 (t) 1.37 (t)	CH$_2$ *p*-C*H*$_3$C$_6$H$_4$ POCH$_2$C*H*$_3$	A$_2$B	δ$_A$ 130.7[j] δ$_B$ 129.9 J_{AB} = 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$_2$ *p*-*C*H$_3$C$_6$H$_4$ POCH$_2$*C*H$_3$
16a *trans*-[Re(4-MeC$_6$H$_4$NC)(CO){P(OEt)$_3$}$_4$]BPh$_4$	2131s 1942s	ν(CN) ν(CO)	4.15 (qnt)[j] 2.36 (s) 1.32 (t)	CH$_2$ *p*-C*H*$_3$C$_6$H$_4$ POCH$_2$C*H*$_3$		114.4 (s)[j]		

[a] In KBr pellets. [b] In CD$_2$Cl$_2$, at 25 °C. [c] Phenyl proton and carbon resonances are omitted. [d] Positive shift downfield from 85% H$_3$PO$_4$. [e] In C$_6$D$_6$. [f] In CD$_3$C$_6$D$_5$. [g] In CDCl$_3$. [h] At −80 °C. [i] tf$^-$ = CF$_3$SO$_3$$^-$. [j] In (CD$_3$)$_2$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.[16] 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(I) 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).

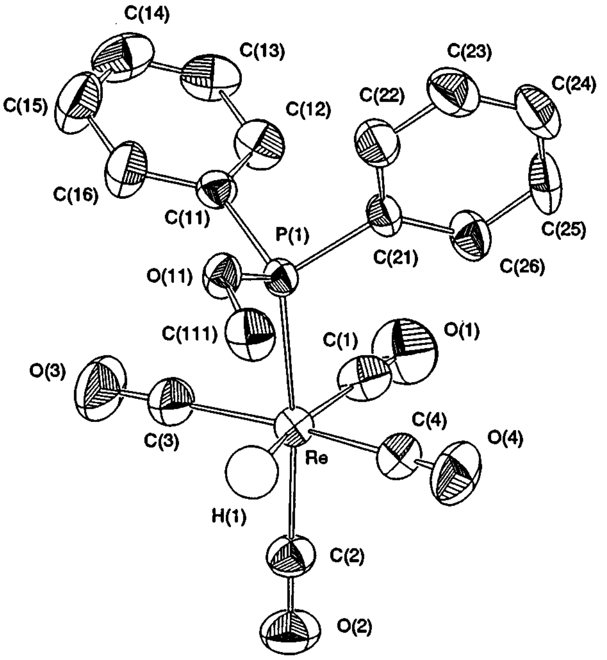


Fig. 1 An ORTEP plot with the atom-numbering scheme used for [ReH(CO)$_4${PPh$_2$(OMe)}] **1d**. Thermal ellipsoids at 40% probability

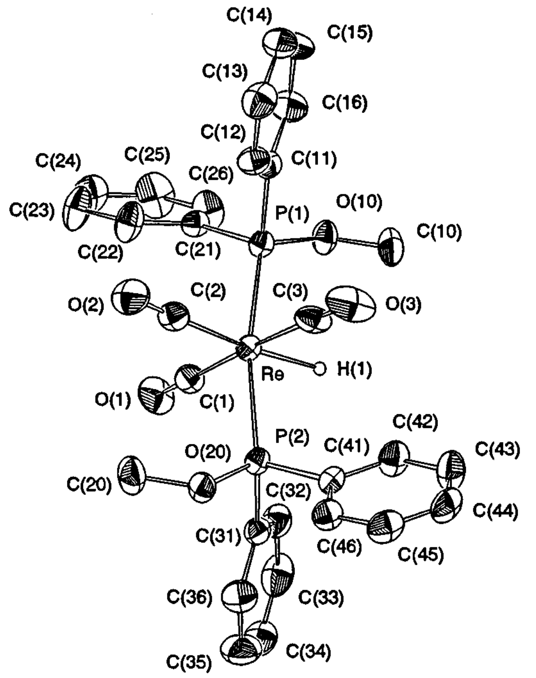
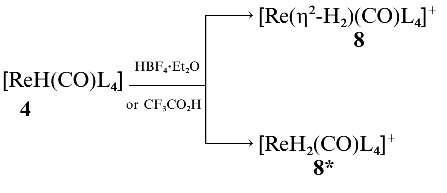


Fig. 2 An ORTEP plot with the atom-numbering scheme used for [ReH(CO)$_3${PPh$_2$(OMe)}$_2$] **2d**. Thermal ellipsoids at 40% probability

Preparation and characterisation of [Re(η^2-H$_2$)(CO)L$_4$]$^+$ and [ReH$_2$(CO)L$_4$]$^+$ cations

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



Scheme 2 L = P(OEt)$_3$ **a** or PPh(OEt)$_2$ **b**

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

	1d	**2d**
Empirical formula	$C_{17}H_{14}O_5PRe$	$C_{29}H_{27}O_5P_2Re$
M	515.45	703.65
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$ (no. 14)
a/Å	8.498(7)	8.629(2)
b/Å	9.706(8)	30.720(11)
c/Å	11.5359(10)	10.617(2)
α/°	83.84(6)	
β/°	88.46(6)	91.290(10)
γ/°	74.28(8)	
U/Å^3	910.7(11)	2813.7(13)
Z	2	4
D_c/Mg m^{-3}	1.880	1.661
μ/mm^{-1}	6.781	4.469
F(000)	492	1384
θ Range for data collection/°	3.05 to 25.94	3.08 to 26.94
Index ranges	$-1 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$, $-14 \leqslant l \leqslant 14$	$-1 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 39$, $-13 \leqslant l \leqslant 13$
Reflections collected	4321	7309
Independent reflections	3563	6085
R_{int}	0.0349	0.0238
Data, restraints, parameters	3562, 0, 273	6081, 0, 442
Goodness of fit on F^2	1.063	1.075
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0334, 0.0828	0.0329, 0.0597
(all data)	0.0392, 0.0862	0.0656, 0.0754
Largest Δ*F* peak and hole/e Å^{-3}	2.048, −1.492	0.588, −0.527

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

[ReH(CO)$_4${PPh$_2$(OMe)}] **1d**			
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)		
[ReH(CO)$_3${PPh$_2$(OMe)}$_2$] **2d**			
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 ^{1}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	T/K	δ(M–H$_2$)[a]	$T_{1(\text{min})}$/ms	δ(M–H)[a]	$T_{1(\text{min})}$/ms	J_{HD}/Hz	T^b/K
1d $[ReH(CO)_4\{PPh_2(OMe)\}]$	203			−5.72 (d)[c]	334		
2c $[ReH(CO)_3\{PPh_2(OEt)\}_2]$	200			−6.03 (t)[c]	250		
2d $[ReH(CO)_3\{PPh_2(OMe)\}_2]$	211			−6.05 (t)[c]	223		
3b $[ReH(CO)_2\{PPh(OEt)_2\}_3]$	196			−5.86 (m)	140		
5d $[Re(\eta^2\text{-}H_2)(CO)_4\{PPh_2(OMe)\}]^+$	211	−3.7 (br)[c]	9.0				220
6a $[Re(\eta^2\text{-}H_2)(CO)_3\{P(OEt)_3\}_2]^+$	186	−4.6 (br)	3.0				245
6a$_1$ $[Re(\eta^2\text{-}HD)(CO)_3\{P(OEt)_3\}_2]^+$	193	−4.95 (t)				30	
6b $[Re(\eta^2\text{-}H_2)(CO)_3\{PPh(OEt)_2\}_2]^+$	198	−4.3 (br)	3.5				245
6b$_1$ $[Re(\eta^2\text{-}HD)(CO)_3\{PPh(OEt)_2\}_2]^+$	203	−4.65 (t)				31	
6c $[Re(\eta^2\text{-}H_2)(CO)_3\{PPh_2(OEt)\}_2]^+$	230	−4.0 (br)[c]	7.0				253
6d $[Re(\eta^2\text{-}H_2)(CO)_3\{PPh_2(OMe)\}_2]^+$	215	−3.9 (br)[c]	7.0				243
7a $[Re(\eta^2\text{-}H_2)(CO)_2\{P(OEt)_3\}_3]^+$	190	−5.0 (br)	5.0				273
7a$_1$ $[Re(\eta^2\text{-}HD)(CO)_2\{P(OEt)_3\}_3]^+$	193	−5.21 (t)				33	
7b $[Re(\eta^2\text{-}H_2)(CO)_2\{PPh(OEt)_2\}_3]^+$	203	−4.5 (br)	5.5				279
7b$_1$ $[Re(\eta^2\text{-}HD)(CO)_2\{PPh(OEt)_2\}_3]^+$	203	−4.65 (t)				33	
7c $[Re(\eta^2\text{-}H_2)(CO)_2\{PPh_2(OEt)\}_3]^+$	208	−3.6 (br)	4.0				258
7c$_1$ $[Re(\eta^2\text{-}HD)(CO)_2\{PPh_2(OEt)\}_3]^+$	223	−3.80 (t)				33	
8a $[Re(\eta^2\text{-}H_2)(CO)\{P(OEt)_3\}_4]^+$	198	−5.6 (br)	10				270
8a$_1$ $[Re(\eta^2\text{-}HD)(CO)\{P(OEt)_3\}_4]^+$	256	−5.66 (t)				33	
8*a $[ReH_2(CO)\{P(OEt)_3\}_4]^+$	193			−6.16 (qnt)	98		270
8*a$_1$ $[ReH(D)(CO)\{P(OEt)_3\}_4]^+$	256	−6.12 (qnt of d)				2.1	
8b $[Re(\eta^2\text{-}H_2)(CO)\{PPh(OEt)_2\}_4]^+$	207	−4.85 (br)	7.5				276
8b$_1$ $[Re(\eta^2\text{-}HD)(CO)\{PPh(OEt)_2\}_4]^+$	203	−5.05 (t)				32.5	
8*b $[ReH_2(CO)\{PPh(OEt)_2\}_4]^+$	193			−5.18 (qnt)	120		
8*b-BPh$_4$ $[ReH_2(CO)\{PPh(OEt)_2\}_4]BPh_4$	208			−6.24 (m)	124		>298

[a] In CD_2Cl_2 at 200 MHz. [b] Limit for thermal stability. [c] At 400 MHz.

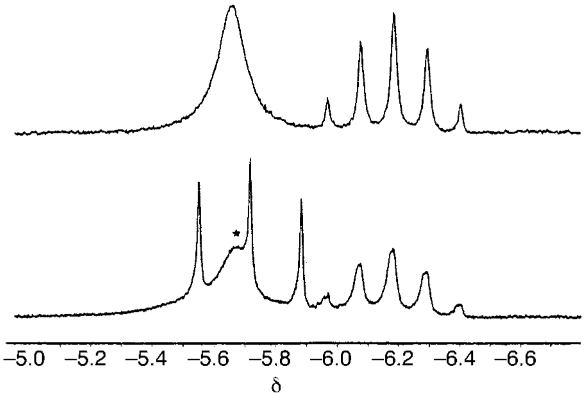


Fig. 3 Proton NMR spectra in the high-field region at 243 K in CD_2Cl_2 of an equilibrium mixture of $[Re(\eta^2\text{-}H_2)(CO)\{P(OEt)_3\}_4]^+$ **8a** and $[ReH_2(CO)\{P(OEt)_3\}_4]^+$ **8*a** (top), and their isotopomers $[Re(\eta^2\text{-}HD)(CO)\{P(OEt)_3\}_4]^+$ **8a$_1$** and $[ReH(D)(CO)\{P(OEt)_3\}_4]^+$ **8*a$_1$**. The signal indicated by the asterisk (*) is due to an impurity of **8a**

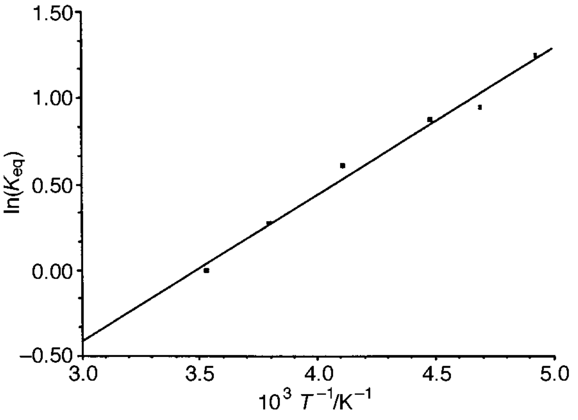


Fig. 4 Plot of ln (K_{eq}) *vs.* 1/T for the equilibrium between $[ReH_2(CO)\{P(OEt)_3\}_4]^+$ **8*a** and $[Re(\eta^2\text{-}H_2)(CO)\{P(OEt)_3\}_4]^+$ **8a** in CD_2Cl_2. See Table 5 and text for explanations

T_1 measurements in CD_2Cl_2 (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 η^2-H_2 complex,[17] 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 $[ReH_2(CO)L_4]^+$ cation. Support for this attribution comes from the spectra of the isotopomers $[Re(\eta^2\text{-}HD)(CO)L_4]^+$ **8a$_1$**, **8b$_1$** and $[ReH(D)(CO)L_4]^+$ **8*a$_1$** obtained by protonation with CF_3CO_2D of $[ReH(CO)L_4]$ and shown in Fig. 3. The broad signal attributed to the η^2-H_2 ligand is replaced by a triplet in the isotopomer spectra, with large J_{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_{HD} value of 2.1 Hz strongly confirms the classical structure of the $[ReH(D)(CO)L_4]^+$ cation.

The two complexes $[Re(\eta^2\text{-}H_2)(CO)L_4]^+$ **8** and $[ReH_2(CO)L_4]^+$ **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 ^1H NMR hydride resonances of the two tautomers in the temperature range 203–283 K. Only in the case of the $P(OEt)_3$ complexes **8a** and **8*a**, however, does the separation of the signals allow the determination of the K_{eq} whose values are reported in Table 5. A plot of ln (K_{eq}) *vs.* 1/T is linear (Fig. 4) and gives the thermodynamic parameters $\Delta H = 1.71 \pm 0.10$ kcal mol^{-1} and $\Delta S = -6.0 \pm 0.4$ cal K^{-1} mol^{-1} 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[18] $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ and $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ and for the equilibrium[19] between $[ReH_4(CO)(PMe_2Ph)_3]^+$ and $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$ and probably reflect the influence of the phosphite ligands on the stability of the classical and non-classical hydride complexes.

The $[Re(\eta^2\text{-}H_2)(CO)L_4]^+$ derivatives are thermally unstable and the loss of H_2 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 $PPh(OEt)_2$ derivative **4b** was carried out in ethanol instead of CH_2Cl_2 a white solid was obtained after precipitation with the BPh_4^- anion, the IR and NMR spectra of which and analytical data support its formulation as the dihydride species $[ReH_2(CO)\{PPh(OEt)_2\}_4]BPh_4$

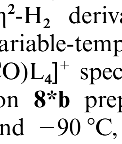
Table 5 Thermodynamic parameters for the equilibrium between $[ReH_2(CO)\{P(OEt)_3\}_4]^+$ **8*a** and $[Re(\eta^2-H_2)(CO)\{P(OEt)_3\}_4]^+$ **8a** in CD_2Cl_2[a]

T/K	K_{eq}[b]
203	3.49
213	2.59
223	2.40
243	1.83
263	1.32
283	0.99
ΔH −1.71 ± 0.10 kcal mol^{-1}[c]	ΔS −6.0 ± 0.4 cal K^{-1} mol^{-1}[d]

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

8*b-BPh$_4$. The ^1H NMR spectra show, in fact, a well resolved quintet in the hydride region at δ −6.05 (25 °C, CD_2Cl_2) with a $T_{1(min)}$ value (200 MHz) of 124 ms at 208 K, suggesting the classical nature of the species. The infrared spectrum shows only one ν(CO) band at 1959 cm^{-1}, while the ^{31}P-$\{^1H\}$ NMR spectrum shows a slightly broad singlet near δ 147 at room temperature. The values of the chemical shift for both the protons and the ^{31}P nuclei of **8*b-BPh$_4$** compound are, however, different from those observed for the corresponding $[ReH_2(CO)L_4]^+$ **8*b** cations prepared in CH_2Cl_2 solution (see Table 1). Furthermore, this complex is stable in solution and no evidence of formation of the tautomer $[Re(\eta^2-H_2)(CO)L_4]^+$ was observed. These different properties shown by the two hydrides obtained by protonation of $[ReH(CO)\{PPh(OEt)_2\}_4]$ **4b** with 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 η^2-H_2 derivatives. Support for this hypothesis comes from variable-temperature ^1H and ^{31}P NMR data of the two $[ReH_2(CO)L_4]^+$ species: while the proton and ^{31}P spectra of the cation **8*b** prepared in CD_2Cl_2 remain unchanged between 0 and −90 °C, the spectra of the solid sample $[ReH_2(CO)L_4]BPh_4$ **8*b-BPh$_4$** are temperature dependent and the slightly broad singlet at δ 147.0 which appears at room temperature in the ^{31}P spectrum becomes a well resolved A_2B_2 multiplet at −70 °C, consistent with the presence of two by two magnetically equivalent phosphite ligands. Also the ^1H 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.

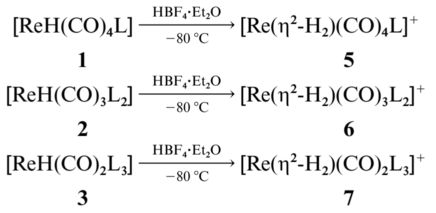
The structure of seven-co-ordinate complexes can be discussed in terms of a pentagonal bipyramid, a monocapped octahedron or a capped trigonal prismatic geometry.[19,20] Our ^1H and ^{31}P NMR spectra of both 'isomers' do not allow us to assign a geometry in solution. However, previous X-ray data on seven-co-ordinate rhenium complexes[21] and the magnetic inequivalence of the phosphorus, nuclei allow us to propose the geometry **VI** for the solid derivative $[ReH_2(CO)\{PPh(OEt)_2\}_4]BPh_4$ **8*b-BPh$_4$**, while no hypothesis may be made for the species **8*b** prepared in CD_2Cl_2.



VI

Preparation of other η^2-H_2 complexes

Protonation reactions of the other carbonyl compounds $[ReH(CO)_2L_3]$ **3**, $[ReH(CO)_3L_2]$ **2** and $[ReH(CO)_4L]$ **1** with $HBF_4{\cdot}Et_2O$ also proceed easily at −80 °C but give, in contrast to the monocarbonyls $[ReH(CO)L_4]$ **4**, only the dihydrogen cations $[Re(\eta^2-H_2)(CO)_2L_3]^+$ **7**, $[Re(\eta^2-H_2)(CO)_3L_2]^+$ **6** and $[Re(\eta^2-H_2)(CO)L_4]^+$ **5**, as shown in Scheme 3. The η^2-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 ^1H NMR spectra of solutions in CD_2Cl_2 containing **5**, **6** or **7** exhibit a single broad resonance in the hydride region, between δ −3.6 and −5.21, with $T_{1(min)}$ values of 3–9 ms (200 and 400 MHz, Table 4), consistent[17] with the proposed formulation. This assignment is further supported by the $^1J_{HD}$ values of 30–33 Hz found for the isotopomers **6a$_1$**, **6b$_1$**, **7a$_1$**, **7b$_1$**, **7c$_1$**, **8a$_1$** and **8b$_1$** which confirm the presence of an authentic η^2-H_2 ligand in the rhenium complex.



Scheme 3 L = $P(OEt)_3$ **a**, $PPh(OEt)_2$ **b**, $PPh_2(OEt)$ **c** or $PPh_2(OMe)$ **d**

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 η^2-H_2 derivatives previously reported.[3f,14,15c,e,18,22] First our η^2-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 HBF_4, CF_3SO_3H or CF_3CO_2H 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 η^2-H_2 and dihydride was observed in the protonation of $[ReH(CO)L_4]$ with a CO : P ratio 1 : 4. This result is not surprising taking into account the lesser π-acceptor properties of the phosphites as compared to the carbonyl ligand, which make the rhenium a more electron-rich metal centre in $[ReH(CO)L_4]$ than in the other $[ReH(CO)_{5-n}L_n]$ (n = 2, 3, 4) complexes, therefore favouring the homolytic cleavage of H_2 resulting in the dihydride species. In addition, also other factors probably affect the homolytic cleavage of a H_2 ligand, but the related π-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.[18,22b]

A comparison among our η^2-H_2 complexes **5**, **6**, **7**, **8** shows that, although the spectroscopic properties ($T_{1(min)}$ and $^1J_{HD}$) are rather similar, the stability to the loss of 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 $PPh(OEt)_2$ is that which most stabilises the η^2-H_2 derivatives among the phosphites used. However, despite the known properties[4] of the $PPh(OEt)_2$ ligand in stabilising dihydrogen complexes, no rhenium η^2-H_2 complexes can be isolated in the solid state, owing to the easy loss of H_2. This instability of the η^2-H_2 complexes of rhenium is rather unexpected, when taking into account that the strictly comparable manganese complexes[4e] $[Mn(\eta^2-H_2)(CO)L_4]BPh_4$ 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_2 from complexes **5**–**8** results in the disappearance of the η^2-H_2 resonance at δ −3.6 to −5.21 and the formation of formally 16-electron complexes which, in the case of the compounds $[Re(CO)_2L_3]BPh_4$ **10** and $[Re(CO)L_4]BPh_4$ **11**, can be isolated as white solids and characterised (Scheme 4).

$$[Re(\eta^2\text{-}H_2)(CO)_2L_3]^+ \xrightarrow[+BPh_4]{-H_2} [Re(CO)_2L_3]BPh_4$$

7 **10**

$$[Re(\eta^2\text{-}H_2)(CO)L_4]^+ \xrightarrow[+BPh_4]{-H_2} [Re(CO)L_4]BPh_4$$

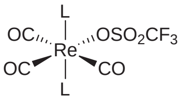
8 **11**

$$[Re(\eta^2\text{-}H_2)(CO)_3L_2]^+ \xrightarrow[+CF_3SO_3^-]{-H_2} [Re(\eta^1\text{-}OSO_2CF_3)(CO)_3L_2]$$

6 **9**

Scheme 4

Evolution of H_2 from complexes containing the $CF_3SO_3^-$ anion affords the η^1-triflate complex which, in the case of $[Re(\eta^1\text{-}OSO_2CF_3)(CO)_3\{PPh_2(OEt)\}_2]$ **9c**, was obtained as a solid with a *mer,trans* geometry **VII**, as was established in solution by IR and NMR data (Table 1).

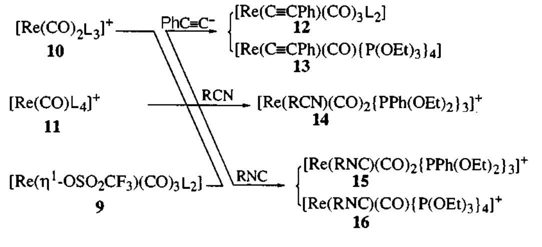


VII

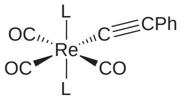
The unsaturated complexes **10** and **11** are white solids, stable in the air, diamagnetic, 1 : 1 electrolytes and probably are stabilised by an agostic interaction[23] between the electron-deficient rhenium centre and a C–H bond of the ethyl (or phenyl) group of one phosphite ligand. Unfortunately, in the temperature range between +20 and −90 °C, the ^1H and ^{31}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.[3g,15e,24–26]

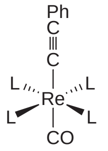
Reactivity

Some studies on the properties of the unsaturated complexes are reported in Scheme 5. Both the unsaturated complexes **10** 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^{-1} in the infrared spectra of complexes **12** and **13**, while in the ^{13}C NMR spectra the C_α and C_β signals are clearly assigned (between δ 99 and 177) on the basis of the multiplicity of the signals and by the J_{CP} values (Table 1). Furthermore, in the temperature range between +30 and −90 °C the ^{31}P-$\{^1H\}$ NMR spectra of the $[Re(C{\equiv}CPh)(CO)_3L_2]$ **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 $[Re(C{\equiv}CPh)(CO)L_4]$ **13** derivative, on the basis of the presence of only one ν(CO) band and only one singlet in the ^{31}P-$\{^1H\}$ NMR spectra.



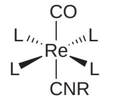
Scheme 5 L = $P(OEt)_3$ **a**, $PPh(OEt)_2$ **b** or $PPh_2(OEt)$ **c**; R = 4-MeC_6H_4

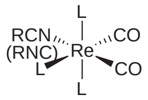




VIII **IX**

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^{-1} for the nitrile **14** and at 2131 or 2149 cm^{-1} for the isocyanide complexes. Furthermore, only one ν(CO) band at 1942 cm^{-1} was observed for the complex $[Re(4\text{-}MeC_6H_4NC)(CO)\{P(OEt)_3\}_4]BPh_4$ **16a**, the ^{31}P-$\{^1H\}$ NMR spectrum of which shows a sharp singlet suggesting magnetic equivalence of the four phosphite ligands, as in the *trans* geometry **X**.





X **XI**

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 ^{13}C NMR spectrum of $[Re(4\text{-}MeC_6H_4NC)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ **15b**, which shows at δ 193.5 and at 189.3 two multiplets due to two non-equivalent carbonyl carbon atoms. Furthermore, the ^{31}P-$\{^1H\}$ NMR spectrum shows an A_2B 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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