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Hydride and dihydrogen dicarbonylrhenium(I) complexes with phosphites, phosphonites and phosphinites

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ABSTRACT

Photoirradiation of a toluene solution of [ReH(CO)$_3$(L)] [S. Bolaño, J. Bravo, R. Carballo, S. García-Fontán, U. Abram, E.M. Vázquez-López, Polyhedron 18 (1999) 1431–1436] [L = 1,2-bis(diphenylphosphinoxy)ethane] in the presence of PPh$_n$(OR)$_{3-n}$ (n = 0, 1; R = Me, Et) leads to the replacement of a CO ligand by the corresponding monodentate phosphite or phosphonite ligand to give new hydride compounds of formula [ReH(CO)$_2$(L)(L′)] [L′ = P(OMe)$_3$ (**1**); P(OEt)$_3$ (**2**); PPh(OMe)$_2$ (**3**); PPh(OEt)$_2$ (**4**)]. Protonation of compounds **1**–**4** in CD_2Cl_2, with $HBF_4.OMe_2$ or with $HOOCCF_3$ at 193 K in a NMR tube, gave the corresponding dihydrogen complexes. When the temperature was increased from 193 to 293 K, the η^2-H_2 ligand was replaced by OMe_2 or $^-OOCCF_3$ groups (depending on the acid employed) to give new stable complexes and the loss of H_2 gas.

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1. Introduction

Organorhenium chemistry has expanded markedly in recent decades and rhenium hydrido complexes, stabilized with phosphorus-containing co-ligands, play an important role in this field [2]. Among these phosphorus-containing co-ligands, phosphines (PR_3) are very commonly used because their electronic and steric properties can be easily tuned by changing the nature of the R groups, which in turn modifies the properties of the complex. By contrast, compounds resulting from a sequential substitution of the alkyl R groups of the phosphine by alkoxy groups [PR$_n$(OR)$_{3-n}$; n = 0 (phosphites), n = 1 (phosphonites), n = 2 (phosphinites)] have not been investigated to the same extent [3], although their weaker σ-donor and stronger π-acceptor nature [4] – in comparison to the phosphines – must influence the properties of the complex. On the other hand, the chemistry of transition metal complexes bearing dihydrogen as a ligand is very relevant in different research fields, including the design of hydrogen storage materials, in catalysis involving hydrogen bonds and in the action of several enzymes in biology [5]. We have previously reported on the synthesis and properties of hydrido rhenium compounds bearing different mono- and bidentate phosphonites, phosphinites and phosphites [6]. In this paper, we report the synthesis and properties of new hydridodicarbonylrhenium(I) complexes bearing different phosphite, phosphonite and phosphinite ligands.

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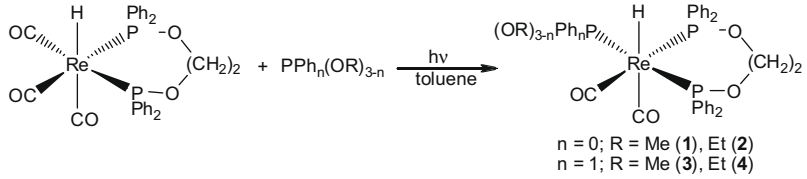
2. Results and discussion

2.1. Hydride complexes

Photoirradiation of a toluene solution of [ReH(CO)$_3$(L)] [1] [L = 1,2-bis(diphenylphosphinoxy)ethane] with a 150 W medium-pressure Hg lamp for 36 h, in the presence of PPh$_n$(OR)$_{3-n}$ (n = 0, 1; R = Me, Et), leads to replacement of a CO ligand by the corresponding monodentate phosphite or phosphonite ligand to give new hydride compounds of formula [ReH(CO)$_2$(L)(L′)] [L′ = P(OMe)$_3$ (**1**); P(OEt)$_3$ (**2**); PPh(OMe)$_2$ (**3**); PPh(OEt)$_2$ (**4**)] (Scheme 1).

The new hydrides are air-stable white solids at room temperature. The IR spectra show two strong bands at 1943–1947 and 1885–1893 cm^{-1}, which are assigned to ν_{sym}(CO) and ν_{asym}(CO), respectively, and are consistent with two CO ligands in a mutually *cis* disposition [7]. The ν(Re–H) band is observed as a medium intensity band at about 1830 cm^{-1}, except for compound **1** in which it is probably obscured by the much more intense ν(CO) bands [8]. The $^{31}P\{^1H\}$ NMR spectra show an AMX pattern for compounds **1–3** and an ABM pattern for **4**. The J values (two of around 30 Hz and one about 240 Hz for each compound) were obtained by simulation [9] (Fig. 1). These values are consistent with an octahedral geometry in which the monodentate phosphorous ligand (L′) is *trans* with respect to one phosphorus donor atom of the bidentate diphosphinite ligand (L), as shown in Scheme 1, with the three P atoms being magnetically different.

At room temperature, the ^1H NMR spectra of the complexes each show, at high field, a signal corresponding to an AMXY spin



Scheme 1.

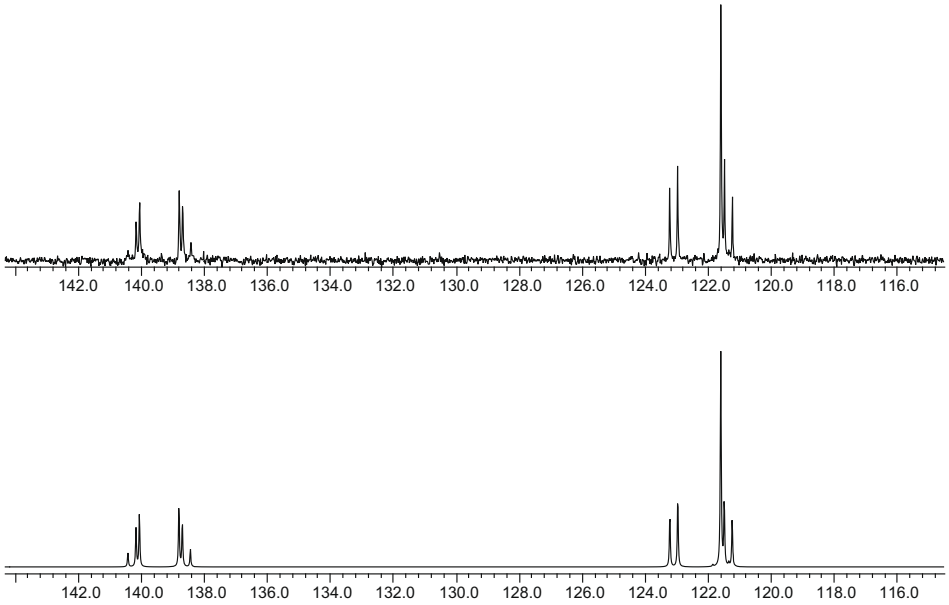


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum (experimental, top; simulated, bottom) of compound **1**.

system in which the hydrido nucleus (A) couples to the three magnetically different phosphorus nuclei (all located in *cis* positions with respect to the hydride proton). The similarity of the three coupling constants precluded their experimental measurement, except in the case of compound **2** in which the signal appears as quite a well resolved double doublet of doublets (Fig. 2). The coordination of the bidentate diphosphinite ligand to the metal makes the four methylenic protons of that ligand magnetically different in all cases. This is clearly observed in the case of compound **2**, which shows three well resolved multiplets that integrate as one proton each in the region 3.79–4.37 ppm (the fourth methylenic proton signal is located underneath the signal due to the $-CH_2-$ group corresponding to the three ethoxy groups of L′, which integrates as seven protons) (Fig. 3). Variable temperature NMR experiments carried out between 193 and 293 K for compounds **1**–**4** did not show any significant modification in the signals. Longitudinal

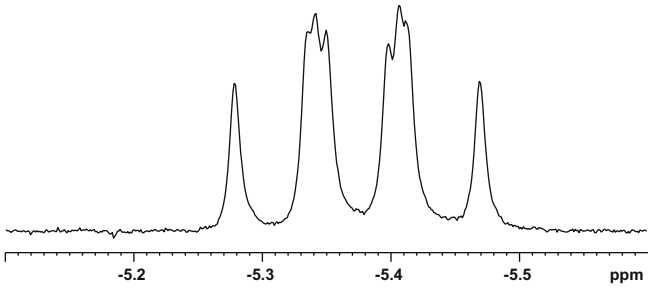


Fig. 2. Partial (hydride region) ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 293 K) of compound **2**.

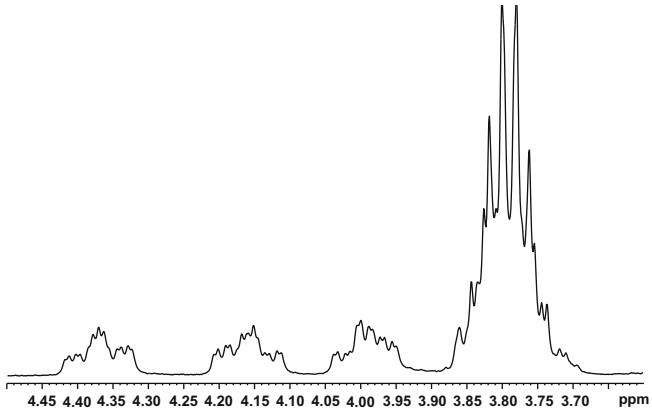


Fig. 3. Partial (methylenic protons of L and L′ ligands) ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 293 K) of compound **2**.

relaxation time values of the hydride resonance were measured in CD_2Cl_2 solutions at 400 MHz by the inversion-recovery method at different temperatures. The $T_{1(min)}$ values obtained for the compounds (Table 1) are similar to those reported for other rheniumhydridecarbonyl compounds bearing these types of phosphorous ligand [1,6a]. The $^{13}C\{^{1}H\}$ NMR spectra of all complexes show two well resolved signals at low field (198–199 ppm). The signal at ~198 ppm appears as a double doublet of doublets with a J_{CP} value of approximately 50 Hz, which is much higher than the other two coupling constants (7 and 12 Hz, approximately). These signals correspond to the carbonyl group *trans* to one of the P nuclei and *cis* to the other two, which are not equivalent to

Table 1
$T_{1(min)}$ values for complexes **1**–**4**.

Compound	$T_{1(min)}$/ms	T(K)
[ReH(CO)$_2$(L){P(OMe)$_3$}] (**1**)	256	211
[ReH(CO)$_2$(L){P(OEt)$_3$}] (**2**)	213	218
[ReH(CO)$_2$(L){PPh(OMe)$_2$}] (**3**)	260	223
[ReH(CO)$_2$(L){PPh(OEt)$_2$}] (**4**)	230	218

each other. The other signal at ~199 ppm is a quartet due to coupling of a carbonyl group to three *cis* phosphorus nuclei with similar J_{CP} values (Fig. 4).

2.2. Dihydrogen complexes

Protonation of compounds 1–4 in CD_2Cl_2 with $HBF_4.OMe_2$ or with $HOOCCF_3$ at 193 K in an NMR tube gave the corresponding dihydrogen complexes [10], as evidenced by the presence of a new broad singlet at lower field (~−4 ppm) than that of the hydride ligand of the precursor complex. Measurement at various temperatures of the spin lattice relaxation time (T_1) of the new hydride resonance (Table 2) gave minimum values of 8–10 ms at 224–236 K (400 MHz). On the basis of these observations, the compounds are formulated as dihydrogen complexes [11]. When the temperature was progressively increased to ambient temperature, stable complexes were obtained. The compounds obtained at ambient temperature are different depending on the acid employed (Scheme 2).

The conversion was monitored by recording the $^{31}P\{^1H\}$ and ^1H NMR spectra as the temperature was increased from 193 to 293 K. The $^{31}P\{^1H\}$ NMR spectra show, at the lowest temperature attainable, three new signals that differ from those of the hydride compound – these signals may be assigned to the new dihydrogen complex. When the temperature was increased, the broad signal at high field in the ^1H NMR spectra, corresponding to the η^2-H_2 ligand, lost intensity and, simultaneously, a singlet at 4.6 ppm, corresponding to free H_2 gas [12], was observed. The elimination of the H_2 ligand must give rise to a very reactive unsaturated cationic complex. These highly electrophilic unsaturated cationic complexes are stabilized in many cases through the coordination of solvent molecules and/or by agostic interactions [13]. In our case, when $HBF_4{\cdot}OMe_2$ was used as the protonation agent, a signal was observed in the ^1H NMR spectrum at 3.5–4.0 ppm that integrated to approximately six protons. This observation seems to indicate that the free coordination site is probably occupied by the dimethyl ether present in the acidic solution added. On the other hand, when trifluoroacetic acid was employed, the vacant

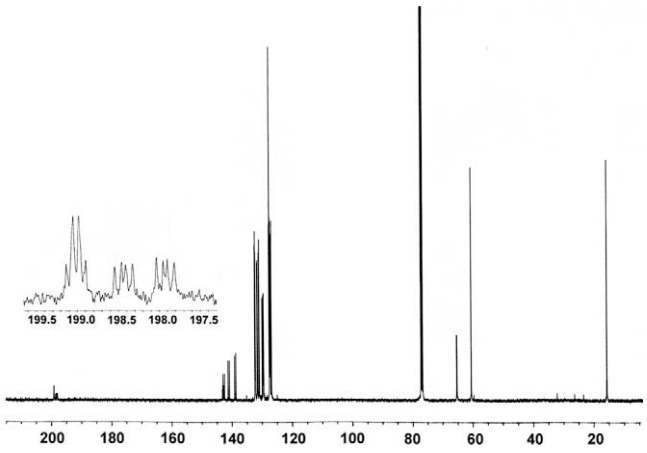


Fig. 4. $^{13}C\{^1H\}$ NMR spectrum of compound **2**.

Table 2
$T_{1(min)}$ and δ values (in CD_2Cl_2 at 400 MHz) of the η^2-H_2 signal of the dihydrogen complexes.

Compound	$T_{1(min)}$/ms	δ (H_2)/ppm	T^a/K
[Re(η^2-H_2)(CO)$_2$(L){P(OMe)$_3$}]BF_4	10 at 236 K	−4.14	243
[Re(η^2-H_2)(CO)$_2$(L){P(OEt)$_3$}]BF_4	9 at 224 K	−4.34	263
[Re(η^2-H_2)(CO)$_2$(L){PPh(OMe)$_2$}]BF_4	10 at 231 K	−3.70	283
[Re(η^2-H_2)(CO)$_2$(L){PPh(OEt)$_2$}]BF_4	8 at 236 K	−3.78	253

[a] Limit for thermal stability.

coordination site was occupied by the CF_3COO^- ligand. This fact was confirmed by the coincidence of the spectral features with those of the trifluoroacetate compounds obtained in an alternative way, i.e., by treating the analogous bromide derivatives [ReBr(CO)$_2$LL′] with silver trifluoroacetate (see Supporting information) [14]. On the other hand, the three signals in the $^{31}P\{^1H\}$ spectrum were gradually replaced by a new set of three signals (Fig. 5) that remained unchanged at room temperature for several weeks. These signals were assigned to a new complex in which the free coordination site formed by the loss of the dihydrogen ligand is occupied by OMe_2 or CF_3COO^- (depending on the acid used in the protonation experiment). It is noteworthy that the dihydrogen complexes obtained by using the acid HBF_4 showed a slightly higher thermal stability (approximately 10°) than those obtained with $HOOCCF_3$. This is probably due to the greater nucleophilic character of the trifluoroacetate anion in comparison with that of OMe_2. In accordance with compounds bearing similar ligands [15], the temperature limit of stability of the dihydrogen compounds depends, not only on the nature of the phosphorus-containing ligand, but also on the carbonyl: P-ligand ratio. Thus, the temperature limit of stability of the dihydrogen compounds [243–283 K; carbonyl: phosphite ratio 2:3 (see Table 2)] is greater than the precursor compound (233 K; carbonyl: phosphite ratio 3:2) [1].

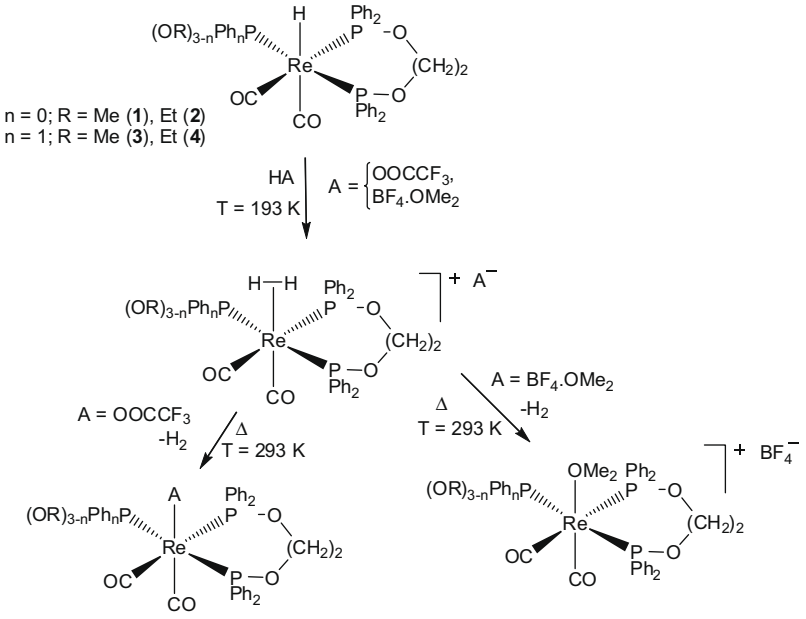
3. Experimental

3.1. General methods and instrumentation

Synthetic work was carried out under a dry argon atmosphere using standard Schlenk techniques. All solvents were purified by conventional procedures [16] and distilled prior to use. Monodentate phosphites and phosphonites (Aldrich) were used as received. Photoirradiation was carried out with a 150 W medium-pressure Hg lamp for 36 h. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker ARX-400 spectrometer operating at frequencies of 400, 100 and 161 MHz, respectively; the spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions as indicated, using the solvent as the internal lock. ^1H and $^{13}C\{^1H\}$ signals are referred to internal TMS and those of $^{31}P\{^1H\}$ to 85% H_3PO_4; downfield shifts (δ in ppm) are considered positive. Low-temperature measurements were made by cooling the probe with a stream of cold N_2 (g) from a liquid N_2 boil off evaporator. NMR spectra were simulated using gNMR 5.1 [9]. T_1 relaxation times for the hydridic resonances of complexes were measured in dichloromethane-d_2 as a function of temperature at 400 MHz using a standard inversion-recovery methodology. IR spectra (KBr disc) were recorded on a Bruker VECTOR IFS 28 FT apparatus, and mass spectra on a Micromass Autospec M LSIMS (FAB^+) system. Microanalyses were carried out on a Fisons model EA 1108 elemental analyzer.

3.2. Synthesis of complexes *cis,mer*-[ReH(CO)$_2$(L)L′; [L = $Ph_2POCH_2CH_2OPPh_2$; L′ = $P(OMe)_3$ (**1**), $P(OEt)_3$ (**2**), $PPh(OMe)_2$ (**3**), $PPh(OEt)_2$ (**4**)]

An excess of the appropriate phosphite or phosphonite was added to a solution of [ReH(CO)$_3$(L)] (0.1 g, 0.14 mmol) in toluene (15 mL) in 1:3 molar ratio. The reaction mixture was irradiated



Scheme 2.

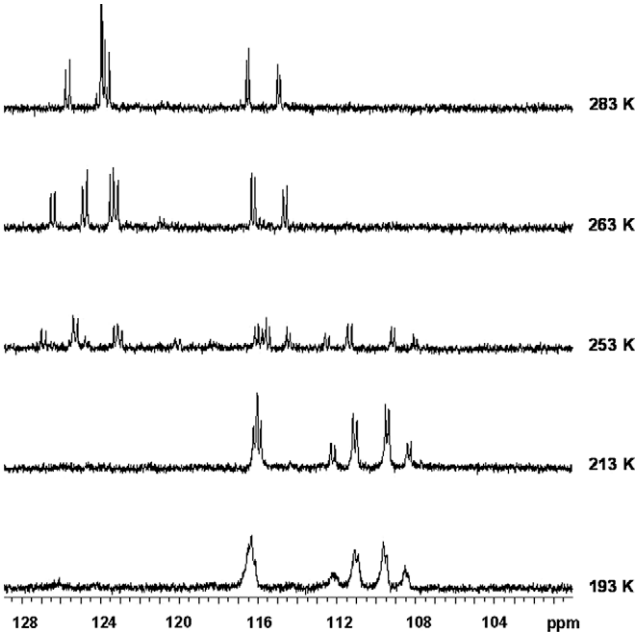
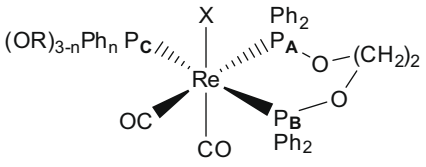


Fig. 5. Modification of the $^{31}P\{^1H\}$ NMR spectrum of $[Re(\eta^2\text{-}H_2)(CO)_2(L)\{P(OEt)_3\}]^+ BF_4^-$ on increasing the temperature from 193 to 283 K

with UV light for about 36 h. The solvent was removed under reduced pressure to give an oil, which was treated with methanol (3 mL) to afford a white product. The solid was filtered off, washed with methanol, dried under vacuum, and recrystallized from 2:10 (v/v) CH_2Cl_2/MeOH by slow evaporation.

Labelling scheme:



Compound ***1****:* Yield ⩾ 35%. Anal. Calc. for $C_{31}H_{34}O_7P_3Re$: C, 46.61; H, 4.29. Found: C, 46.82; H, 4.35%. MS (*m*/*z*, referred to the most abundant isotopes): 798, [M]; 767, [M−OCH_3]; 736, [M−2OCH_3]. IR (KBr, cm^{-1}): ν_{CO} = 1944 (vs), 1885 (vs). ^1H NMR (400 MHz, CD_2Cl_2): δ −5.46 (ddd, 1H, $^2J_{PH}$ = 23, 26 and 28 Hz, ReH), 3.31 (d, 9H, $^3J_{HP}$ = 12 Hz, CH_3), 3.87 [m, 1H, $(CH_2)_2$], 4.11 [m, 3H, $(CH_2)_2$], 7.22–7.85 (m, 20H, Ph). $^{31}P\{^1H\}$NMR (161 MHz, $CDCl_3$) (see labelling scheme): δ 122.4 (dd, P_A, $^2J_{(PA,PB)}$ = 40 Hz, $^2J_{(PA,PC)}$ = 30 Hz), 123.7 (dd, P_B, $^2J_{(PB,PA)}$ = 40 Hz, $^2J_{(PB,PC)}$ = −234 Hz), 140.4 (dd, P_C, $^2J_{(PC,PA)}$ = 30 Hz, $^2J_{(PC,PB)}$ = −234 Hz). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 51.7 (d, $^2J_{(C,PC)}$ = 3 Hz, CH_3), 65.4 [s,br; $(CH_2)_2$], 65.5 [s,br; $(CH_2)_2$], 126.9–142.0 (Ph), 198.0 (ddd, $^2J_{(C,PB)}$ = 8 Hz, $^2J_{(C,PC)}$ = 13 Hz, $^2J_{(C,PA)}$ = 50 Hz, CO), 198.9 (q, $^2J_{(C,P)}$ = 8 Hz, CO).

Compound ***2*** *:* Yield ⩾ 31%. Anal. Calc. for $C_{34}H_{40}O_7P_3Re$: C, 48.56; H, 4.80. Found: C, 48.44; H, 4.72%. MS (*m*/*z*, referred to the most abundant isotopes): 840, [M]; 795, [M−OCH_2CH_3]; 739, [M−2CO−OCH_2CH_3]. IR (KBr, cm^{-1}): ν_{CO} = 1943 (vs), 1893 (vs). ^1H NMR (400 MHz, CD_2Cl_2): δ −5.37 (ddd, 1H, $^2J_{PH}$ = 23, 25 and 28 Hz, ReH), 1.07 (t, 9H, $^3J_{HP}$ = 7 Hz, CH_3), 3.79 [m, 6H (L) + 1H (L′), CH_2], 3.99 [m, 1H, $(CH_2)_2$], 4.15 [m, 1H, $(CH_2)_2$], 4.37 [m, 1H, $(CH_2)_2$], 7.25–7.83 (m, 20H, Ph). $^{31}P\{^1H\}$NMR (161 MHz, $CDCl_3$) (see labelling scheme): δ 120.9 (dd, P_A, $^2J_{(PA,PB)}$ = 40 Hz, $^2J_{(PA,PC)}$ = 31 Hz), 126.0 (dd, P_B, $^2J_{(PB,PA)}$ = 40 Hz, $J_{(PB,PC)}$ = 230 Hz), 134.2 (dd, P_C, $^2J_{(PC,PA)}$ = 31 Hz, $^2J_{(PC,PB)}$ = 230 Hz). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 15.7 (d, $^3J_{(C,PC)}$ = 6 Hz, CH_3), 60.5 (d, $^2J_{(C,PC)}$ = 3 Hz, CH_2), 65.3 [s, $(CH_2)_2$], 65.4 [s, $(CH_2)_2$], 126.9–142.5 (Ph), 198.3 (ddd, $^2J_{(C,PB)}$ = 8 Hz, $^2J_{(C,PC)}$ = 13 Hz, $^2J_{(C,PA)}$ = 51 Hz, CO), 199.1 (q, $^2J_{(C,P)}$ = 8 Hz, CO).

Compound ***3*** *:* Yield ⩾ 36%. Anal. Calc. for $C_{36}H_{36}O_6P_3Re$: C, 51.24; H, 4.30. Found: C, 51.12; H, 4.25%. MS (*m*/*z*, referred to the most abundant isotopes): 844, [M]; 754, [M−CO−2OCH_3]. IR (KBr, cm^{-1}): ν_{CO} = 1945 (vs), 1891 (vs). ^1H NMR (400 MHz, CD_2Cl_2): δ −5.07 (dt, 1H, $^2J_{PH}$ = 23 Hz, $^2J_{PH}$ = 29 Hz, Re–H), 3.21 (d, 3H, $^3J_{HP}$ = 12 Hz, CH_3), 3.26 (d, 3H, $^3J_{HP}$ = 12 Hz, CH_3), 3.92 [m, 1H, $(CH_2)_2$], 4.13 [m, 3H, $(CH_2)_2$], 7.20–7.92 (m, 25H, C_6H_5). $^{31}P\{^1H\}$NMR (161 MHz, CD_2Cl_2) (see labelling scheme): δ 123.5 (dd, P_B, $^2J_{(PB,PA)}$ = 41 Hz, $^2J_{(PB,PC)}$ = −199 Hz), 123.3 (dd, P_A, $^2J_{(PA,PB)}$ = 41 Hz, $^2J_{(PA,PC)}$ = 26 Hz), 150.6 (dd, P_C, $^2J_{(PC,PA)}$ = 26 Hz, $^2J_{(PC,PB)}$ = −199 Hz). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 52.0 (d,

$^2J_{(C,PC)}$ = 6 Hz, CH_3), 52.7 (d, $^2J_{(C,PC)}$ = 5 Hz, CH_3), 65.3 [s,br; $(CH_2)_2$], 65.5 [s,br; $(CH_2)_2$], 126.9–143.0 (Ph), 198.3 (ddd, $^2J_{(CE,PB)}$ = 7 Hz, $^2J_{(CE,PC)}$ = 12 Hz, $^2J_{(CE,PA)}$ = 48 Hz, CO), 199.6 (q, $^2J_{(C,B)}$ = 7 Hz, CO).

Compound ***4****:* Yield ⩾ 39%. Anal. Calc. for $C_{38}H_{40}O_6P_3Re$: C, 52.28; H, 4.62. Found: C, 52.01; H, 4.43%. MS (*m*/*z*, referred to the most abundant isotopes): 872, [M]. IR (KBr, cm^{-1}): ν_{CO} = 1947 (vs), 1892 (vs). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.16 (dt, 1H, $^2J_{PH}$ = 23 and 29 Hz, ReH), 0.82 (t, 3H, $^4J_{HP}$ = 7 Hz, CH_3), 1.01 (t, 3H, $^4J_{HP}$ = 7 Hz, CH_3), 3.36 (m, 2H, CH_2), 3.52 [m, 1H, $(CH_2)_2$], 3.80 [m, 2H + 1H, $(CH_2)_2$], 4.06 [m, 1H, $(CH_2)_2$], 4.12 [m, 1H, $(CH_2)_2$], 7.18–7.77 (m, 25H, Ph). ^{31}P{^{1}H}NMR (161 MHz, $CDCl_3$) (see labelling scheme): δ 121.2 (dd, P_A, $^2J_{(PA,PB)}$ = 28 Hz, $^2J_{(PA,PC)}$ = 40 Hz), 126.5 (dd, P_B, $^2J_{(PB,PA)}$ = 40 Hz, $^2J_{(PB,PC)}$ = 199 Hz), 143.8 (dd, P_C, $^2J_{(PC,PA)}$ = 28 Hz, $^2J_{(PC,PB)}$ = 199 Hz). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 15.7 (d, $^3J_{(C,PC)}$ = 6 Hz, CH_3), 15.8 (d, $^3J_{(C,PC)}$ = 6 Hz, CH_3), 61.3 (d, $^2J_{(C,PC)}$ = 7 Hz, CH_2), 62.0 (d, $^2J_{(C,PC)}$ = 4 Hz, CH_2), 65.2 [s,br; $(CH_2)_2$], 65.5 [s,br; $(CH_2)_2$], 126.9–142.6 (Ph), 198.3 (ddd, $^2J_{(C,PB)}$ = 9 Hz, $^2J_{(C,PC)}$ = 11 Hz, $^2J_{(C,PA)}$ = 51 Hz, CO), 199.6 (q, $^2J_{(C,P)}$ = 7 Hz, CO).

3.3. Protonation reactions

Hydrido compounds **1–4** were protonated by following a procedure described in the literature for similar compounds [17]. A typical experiment involved the addition by syringe of a slight excess of $HBF_4.Me_2O$ (35.0 μmol, 2.9 μl of *ca.* 85% solution in Me_2O) to a cooled (193 K) and degassed solution of [ReH(CO)$_2$(L){P(OMe)$_3$}] (33.8 μmol, 27.0 mg) in dry CD_2Cl_2, (0.5 cm^3) placed in a 5 mm NMR tube sealed with septum cap. After transferring the tube to the spectrometer probe the ^{1}H and ^{31}P NMR spectra were recorded in the temperature range 193 to 293 K and T_1 values were measured.

[Re(η^2-H$_2$)(CO)$_2$(L){P(OMe)$_3$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 193 K): δ −4.14 [s, br, 2H, Re(η^2-H$_2$)], 3.46 (d, 9H, $^3J_{HP}$ = 11 Hz, CH_3), 3.87–4.30 [m, 4H, $(CH_2)_2$], 7.15–7.72 (m, 20H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 193 K) (see labelling scheme): δ 117.4 (dd, P_A, $^2J_{(PA,PB)}$ = 30 Hz, $^2J_{(PA,PC)}$ = 27 Hz), 109.0 (dd, P_B, $^2J_{(PB,PC)}$ = 183 Hz), 113.6 (dd, P_C).

[Re(OMe$_2$)(CO)$_2$(L){P(OMe)$_3$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 263 K): δ 3.29 [s, br, ∼6H, OMe_2], 3.57 (d, 9H, $^3J_{HP}$ = 10 Hz, CH_3), 4.05–4.27 [m, 4H, $(CH_2)_2$], 7.26–7.76 (m, 20H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 263 K) (see labelling scheme): δ 124.3 (dd, P_A, $^2J_{(PA,PB)}$ = 34 Hz, $^2J_{(PA,PC)}$ = 36 Hz), 119.6 (dd, P_B, $^2J_{(PB,PC)}$ = 273 Hz), 124.0 (dd, P_C).

[Re(η^2-H$_2$)(CO)$_2$(L){P(OEt)$_3$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 193 K): δ −4.34 [s, br, 2H, Re(η^2-H$_2$)], 0.82 (s, br, 9H, CH_3), 3.50–4.17 [m, 10H, (CH_2) (L+L′)], 6.67–8.03 (m, 20H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 193 K) (see labelling scheme): δ 116.3 (dd, P_A, $^2J_{(PA,PB)}$ = 28 Hz, $^2J_{(PA,PC)}$ = 33 Hz), 109.1 (dd, $J_{(PB,PC)}$ = 180 Hz), 111.6 (dd, P_C).

[Re(OMe$_2$)(CO)$_2$(L){P(OEt)$_3$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 1.16 (t, 9H, $^3J_{HP}$ = 7 Hz, CH_3), 3.54 [s, br, ∼6H, OMe_2], 3.95–4.10 [m, 7H, (CH_2) (L+L′)], 4.12–4.45 (m, 3H, CH_2, L′) 7.32–7.87 (m, 20H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 293 K) (see labelling scheme): δ 123.9 (dd, P_A, $^2J_{(PA,PB)}$ = 37 Hz, $^2J_{(PA,PC)}$ = 36 Hz), 115.8 (dd, P_B, $^2J_{(PB,PC)}$ = 273 Hz), 124.5 (dd, P_C).

[Re(η^2-H$_2$)(CO)$_2$(L){PPh(OMe)$_2$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 193 K): δ −3.70 [s, br, 2H, Re(η^2-H$_2$)], 3.65 (s, br, 6H, CH_3), 3.80–4.30 [m, 4H, (CH_2) (L)], 7.10–8.00 (m, 25H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 193 K) (see labelling scheme): δ 111.9 (dd, P_A, $^2J_{(PA,PB)}$ = 32 Hz, $^2J_{(PA,PC)}$ = 24 Hz), 115.0 (dd, $J_{(PB,PC)}$ = 150 Hz), 134.0 (dd, P_C).

[Re(OMe$_2$)(CO)$_2$(L){PPh(OMe)$_2$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 283 K): δ 3.20 [s, br, ∼6H, OMe_2], 3.50 (d, 3H, $^3J_{HP}$ = 11 Hz, CH_3), 3.61 (d, 3H, $^3J_{HP}$ = 11 Hz, CH_3), 4.00–4.40 [m, 4H, (CH_2) (L)], 7.40–8.00 (m, 25H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 283 K) (see labelling scheme): δ 123.4 (dd, P_A, $^2J_{(PA,PB)}$ = 36 Hz, $^2J_{(PA,PC)}$ = 41 Hz), 124.0 (dd, $J_{(PB,PC)}$ = 245 Hz), 140.9 (dd, P_C).

[Re(η^2-H$_2$)(CO)$_2$(L){PPh(OEt)$_2$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 193 K): δ −3.78 [s, br, 2H, Re(η^2-H$_2$)], 0.95 (s, br, 3H, CH_3), 1.06 (s, br, 3H, CH_3), 3.47–4.20 [m, 8H, (CH_2) (L+L′)], 7.02–8.03 (m, 25H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 193 K) (see labelling scheme): δ 111.9 (dd, P_A, $^2J_{(PA,PB)}$ = 34 Hz, $^2J_{(PA,PC)}$ = 24 Hz), 115.6 (dd, $J_{(PB,PC)}$ = 144 Hz), 126.9 (dd, P_C).

[Re(OMe$_2$)(CO)$_2$(L){PPh(OEt)$_2$}]$^+$ BF_4^-. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 1.16 (t, 3H, $^3J_{HP}$ = 7 Hz, CH_3), 1.22 (t, 3H, $^3J_{HP}$ = 7 Hz, CH_3), 3.54 [s, br, ∼6H, OMe_2], 3.73–4.41 [m, 8H, (CH_2) (L+L′)], 7.14–7.96 (m, 25H, Ph). ^{31}P{^{1}H}NMR (161 MHz, CD_2Cl_2, 293 K) (see labelling scheme): δ 123.0 (dd, P_A, $^2J_{(PA,PB)}$ = 37 Hz, $^2J_{(PA,PC)}$ = 30 Hz), 125.0 (dd, P_B, $^2J_{(PB,PC)}$ = 230 Hz), 136.2 (dd, P_C).

4. Conclusions

New air-stable hydrides of formula [ReH(CO)$_2$(L)(L′)] [L′ = P(OMe)$_3$ (**1**); P(OEt)$_3$ (**2**); PPh(OMe)$_2$ (**3**); PPh(OEt)$_2$ (**4**)], have been synthesized and characterized. Protonation of compounds 1–4 with $HBF_4.OMe_2$ or with $HOOCCF_3$ at low temperature resulted on formation of products containing a dihydrogen ligand. The dihydrogen complexes obtained by using the acid HBF_4 showed higher thermal stability (approximately 10°) than those obtained with $HOOCCF_3$. This is probably due to the greater nucleophilic character of the trifluoroacetate anion in comparison with that of OMe_2. In accordance with other rhenium hydrides bearing similar ligands, the temperature limit of stability of the dihydrogen compounds depends on the nature of the phosphite ligand and on the carbonyl: phosphite ratio, increasing with the number of phosphorus ligands.

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Appendix A. Supplementary material

Characterization data for trifluoroacetate complexes [Re(OOCCF$_3$)(CO)$_2$LL′]; [L = 1,2-bis(diphenylphosphinoxy)ethane, L′ = PPh$_n$(OR)$_{3-n}$ (n = 0, 1; R = Me, Et)].

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.038.

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