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Rhenium-(III) and -(V) hydride complexes with modified poly(pyrazolyl)borates

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The hydrides $[ReH_2\{\kappa^3\text{-}(OR)(\mu\text{-}OR)B(pz)_2\}(PPh_3)_2]$ (R = Me **1** or Et **2**) and $[ReH_4\{\kappa^3\text{-}(H)(\mu\text{-}OR)B(3,5\text{-}Me_2pz)_2\}(PPh_3)]$ (R = Me **3** or Et **4**) have been obtained by treating $[ReOCl_3(PPh_3)_2]$ with $Na[H_2B(pz)_2]$ or $Na[H_2B(3,5\text{-}Me_2pz)_2]$ in alcohols (ROH, R = Me or Et) at room temperature. The same type of reaction with $Na[Ph_2B(pz)_2]$, using methanol as solvent, gave $[ReO(OMe)\{\kappa^2\text{-}Ph_2B(OMe)(pz)\}_2]$ **5**, although in a very low yield. The characterization of the new compounds involved IR and ^1H NMR spectroscopies, $^{31}P\text{-}\{^1H\}$ NMR, variable temperature ^1H and ^{31}P NMR studies, T_1 and $J_{H\text{-}D}$ measurements. The crystal structures of the complexes **1**, **4** and **5** were also determined. The structural parameters of the hydride ligands in **1** and **4** have not been obtained, but were tentatively assigned by X-ray diffraction associated with molecular orbital calculations of *ab initio* and extended Hückel type.

Introduction

Transition metal polyhydride complexes have received considerable attention due to their interesting structures and reactivities.[1,2] Most of the hydrides described for rhenium are stabilized by phosphines, with fewer containing cyclopentadienyls or poly(pyrazolyl)borates.[3–6] To the best of our knowledge, so far, all these complexes have been prepared using as starting materials $[ReH_7(PPh_3)_2]$ or $[Re(O)Cl_2L]$ [L = $C_5Me_5^-$ or $HB(pz)_3^-$].

As part of our ongoing work on the chemistry of rhenium with poly(pyrazolyl)borates,[7] we found a novel route to new hydride complexes of Re^{III} or Re^{V}, which involves the use of $[Re(O)Cl_3(PPh_3)_2]$[8] and dihydrobis(pyrazolyl)borates. In this work we report the synthesis of $[ReH_2\{\kappa^3\text{-}(OR)(\mu\text{-}OR)B(pz)_2\}(PPh_3)_2]$ (R = Me **1** or Et **2**) and $[ReH_4\{\kappa^3\text{-}(H)(\mu\text{-}OR)B(3,5\text{-}Me_2pz)_2\}(PPh_3)]$ (R = Me **3** or Et **4**) obtained by treating $[Re(O)Cl_3(PPh_3)_2]$ with $Na[H_2B(pz)_2]$ or $Na[H_2B(3,5\text{-}Me_2pz)_2]$ in methanol or/and in ethanol. The study of these compounds included, in some cases, X-ray diffraction analysis, molecular orbital calculations of *ab initio* and extended Hückel (EHMO) type, variable temperature ^1H and ^{31}P NMR, T_1 and $J_{H\text{-}D}$ measurements. The crystal structure of $[ReO(OMe)\{\kappa^2\text{-}Ph_2B(\mu\text{-}OMe)(pz)\}_2]$ **5** is also described; the complex was obtained from $[Re(O)Cl_3(PPh_3)_2]$ and $Na[Ph_2B(pz)_2]$ in methanol.

Experimental

General procedures

The reactions were carried under a nitrogen atmosphere by using standard Schlenk techniques or dry glove-boxes. Solvents were dried, degassed and distilled prior to use, according to described procedures. The compounds $[Re(O)Cl_3(PPh_3)_2]$, $Na[H_2B(pz)_2]$, $Na[Ph_2B(pz)_2]$ and $Na[H_2B(3,5\text{-}Me_2pz)_2]$ were prepared as described previously.[8–10] The ^1H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^1H chemical shifts were referenced with the residual solvent resonance relative to tetramethylsilane and the ^{31}P chemical shifts with external 85% H_3PO_4 solution. The NMR samples were prepared in $CDCl_3$, or toluene-d_8, dried and distilled prior to use. The IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrometer. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer automatic analyser.

Syntheses

$[ReH_2\{\kappa^3\text{-}(OMe)(\mu\text{-}OMe)B(pz)_2\}(PPh_3)_2]$ 1. To a suspension of $[Re(O)Cl_3(PPh_3)_2]$ (800 mg, 0.96 mmol) in methanol were added 815 mg (4.8 mmol) of $Na[H_2B(pz)_2]$ dissolved in the minimum volume of methanol. After the addition was complete, the mixture was stirred for 24 h at room temperature. It was centrifuged and the insoluble yellow solid separated, washed several times with methanol and finally extracted with toluene. The toluene solution was evaporated to dryness, and the yellow solid **1** washed with *n*-hexane and dried *in vacuo* (150 mg, 0.16 mmol, 20% yield). Slow diffusion of methanol into a saturated solution of **1** in toluene led to single crystals suitable for X-ray analysis (Found: C, 57.4; H, 4.5; N, 6.1. Calc. for $C_{44}H_{44}BN_4O_2P_2Re$: C, 57.5; H, 4.8; N, 6.1%). IR (cm^{-1}): 3052w, 2966w, 2938w, 2833w, 2052vw [ν(Re–H)], 1933w [ν(Re–H)], 1583vw, 1501vw, 1477m, 1458w, 1431s, 1403m, 1387m, 1302m, 1263s, 1243s, 1204w, 1181w, 1138w, 1087s, 1048s, 1013s, 977w, 927w, 880vw, 856w, 812s, 759s, 739s, 696s, 634w, 614w, 548s, 516s, 454w, 434w and 419w. ^1H NMR (toluene-d_8): δ 3.23 (3 H, s, OCH_3), 3.51 (3 H, s, OCH_3), 5.67 [2 H, t, ^3J = 1.9, H(4)], 7.46 [2 + 2 H, br, H(3/5)], 6.87 (18 H, m, *m*- + *p*-H of PPh_3), 7.56 (12 H, m, *o*-H of PPh_3) and −5.96 (2 H, t, $^2J_{P\text{-}H}$ = 46.6 Hz, Re-H). $^{31}P\text{-}\{^1H\}$ NMR (toluene-d_8): δ 46.8.

$[ReH_2\{\kappa^3\text{-}(OEt)(\mu\text{-}OEt)B(pz)_2\}(PPh_3)_2]$ 2. This compound has been prepared as above for **1**, using ethanol as solvent. The characterization of **2** was only made by ^1H, ^{31}P NMR and IR spectroscopies, due to the very low yield of the reaction (*ca.* 5% yield). IR (cm^{-1}): 3050w, 2940w, 2057vw [ν(Re–H)], 1970vw [ν(Re–H)], 1478m, 1432s, 1405w, 1297w, 1259m, 1227m, 1181w, 1089s, 1040s, 803s, 743s, 695s, 622vw and 517s. ^1H NMR (toluene-d_8): δ 1.13 (3 H, t, ^3J = 6.4, OCH_2CH_3), 1.27 (3 H, t, ^3J = 6.4, OCH_2CH_3), 3.68 (2 H, q, ^3J = 6.4, OCH_2CH_3), 3.98 (2 H, q, ^3J = 6.4, OCH_2CH_3), 5.69 [2 H, t, ^3J = 1.9, H(4)], 6.89 (18 H, m, *m*- + *p*-H of PPh_3), 7.46–7.49 [4 H, br, H(3/5)], 7.56

(12 H, m, *o*-H of PPh_3) and −6.08 (2 H, t, $^2J_{P\text{-}H} = 46.2$ Hz, Re-H). $^{31}P\text{-}\{^1H\}$ NMR (toluene-d_8): δ 45.1.

[$ReH_4\{\kappa^3$-(H)(μ-OMe)B(3,5-$Me_2pz)_2\}(PPh_3)$] 3. To a suspension of [$Re(O)Cl_3(PPh_3)_2$] (500 mg, 0.6 mmol) in methanol–ethanol (1 : 2) was added 680 mg (3.0 mmol) of Na[H_2B(3,5-$Me_2pz)_2$] dissolved in the minimum volume of methanol–ethanol (1 : 2). The reaction mixture was stirred for 24 h at room temperature, and after this time an insoluble yellow solid was separated by centrifugation, recrystallized from toluene–methanol and dried under vacuum leading to complex **3** (90 mg, 0.16 mmol, 25% yield) (Found: C, 50.2; H, 5.6; N, 8.1. Calc. for $C_{29}H_{37}BN_4OPRe$: C, 50.8; H, 5.4; N, 8.2%). IR (KBr, cm^{-1}): 3040w, 2935m, 2450s [ν(B-H)], 2063m [ν(Re–H)], 2020m [ν(Re–H)], 1975s [ν(Re–H)], 1582w, 1537s, 1479s, 1452w, 1430s, 1818 (sh), 1384s, 1358w, 1301w, 1262s, 1212m, 1178s, 1151m, 1075s, 1057s, 1034s, 998 (sh), 975 (sh), 918m, 895s, 863m, 842w, 805s, 770s, 768w, 756m, 696m, 688w, 702s, 650w, 540s, 518s, 506 (sh), 460w and 445m. ^1H NMR (toluene-d_8): δ 2.02 (6 H, s, CH_3), 2.21 (6 H, s, CH_3), 3.15 (3 H, s, OCH_3), 5.52 [2 H, s, H(4)], 7.00 (9 H, m, *m*- + *p*-H of PPh_3), 7.58 (6 H, m, *o*-H of PPh_3) and −4.85 (4 H, d, $^2J_{P\text{-}H} = 27.3$ Hz, ReH). $^{31}P\text{-}\{^1H\}$ NMR (toluene-d_8): δ 46.6.

[$ReH_4\{\kappa^3$-(H)(μ-OEt)B(3,5-$Me_2pz)_2\}(PPh_3$] 4. To a suspension of [$Re(O)Cl_3(PPh_3)_2$] (500 mg, 0.6 mmol) in ethanol was added Na[H_2B(3,5-$Me_2pz)_2$] (680 mg, 3.0 mmol) dissolved in the minimum volume of ethanol. The system was stirred for 24 h at room temperature. After centrifugation, a yellow-greenish solid was separated, dissolved in dichloromethane and transferred to a chromatography column charged with silica gel. Elution with CH_2Cl_2 gave a yellow fraction from which complex **4** was recovered (250 mg, 60% yield). Slow diffusion of *n*-hexane into a saturated solution of **4** in toluene led to single crystals suitable for X-ray analysis (Found: C, 51.5; H, 5.6; N, 7.9. Calc. for $C_{30}H_{39}BN_4OPRe$: C, 51.5; H, 5.6; N, 8.0%) IR (KBr, cm^{-1}): 3035w, 2910w, 2445m [ν(B-H)], 2049w [ν(Re–H)], 2000m [ν(Re–H)], 1950w [ν(Re–H)], 1584w, 1560w, 1535m, 1452w, 1431s, 1429m, 1380m, 1360 (sh), 1303w, 1263m, 1211m, 1185m, 1167m, 1093s, 1055m, 1028 (sh), 999w, 981w, 920m, 795m, 781m, 770w, 749m, 700s, 543s, 521s and 445w. ^1H NMR (toluene-d_8): δ 0.65 (3 H, t, $^3J = 6.9$, OCH_2CH_3), 2.05 (6 H, s, CH_3), 2.19 (6 H, s, CH_3), 3.59 (2 H, q, $^3J = 6.9$, OCH_2CH_3), 5.55 [2 H, s, H(4)], 7.00 (9 H, m, *m*- + *p*-H of PPh_3), 7.60 (6 H, m, *o*-H of PPh_3) and −4.76 (4 H, d, $^2J_{P\text{-}H} = 27.3$ Hz, ReH). $^{31}P\text{-}\{^1H\}$ NMR (toluene-d_8): δ 46.1.

[ReO(OMe)$\{\kappa^2$-Ph_2B(μ-OMe)(pz)$\}_2$] 5. To a suspension of [$Re(O)Cl_3(PPh_3)_2$] (500 mg, 0.6 mmol) in methanol was added Na[$Ph_2B(pz)_2$] (390 mg, 1.2 mmol). After overnight reaction at room temperature a brown solution was obtained. This solution was vacuum dried and the remaining solid analysed by IR and ^1H NMR spectroscopies. The presence of species containing the core $[Re{=}O]^{3+}$ and Hpz was detected, but no hydride species were present. Recrystallization of this solid from CH_2Cl_2–hexane resulted in the formation of green crystals, which were identified as complex **5** by X-ray diffraction analysis and by ^1H NMR spectroscopy. The complex is not formed during the recrystallization, as indicated by ^1H NMR spectroscopy of the crude product, but it is obtained in a very low yield (*ca.* 5%). ^1H NMR ($CDCl_3$): δ 2.65 (3 H, s, OCH_3), 4.21 (6 H, s, $BOCH_3$), 6.60 [2 H, t, $^3J = 1.9$, H(4)], 7.25 (12 H, m, *m*+*p*-H of Ph), 7.34 (8 H, m, *o*-H of Ph), 7.67 [2 H, d, $^3J = 2.3$, H(3/5)] and 8.15 [2 H, d, $^3J = 2.3$ Hz, H(3/5)].

X-Ray crystallographic analysis

X-Ray data were collected from yellow crystals of complexes **1** and **4** and from a green crystal of **5**. The crystals were mounted in thin-walled glass capillaries within a nitrogen filled glovebox. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-Kα radiation, using an ω–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $16.3 < 2\theta < 31.7$ for **1**, $19.7 < 2\theta < 34.2$ for **4** and $15.7 < 2\theta < 31.8$ for **5**. The crystal data are summarized in Table 1. The data were corrected[11] for Lorentz-polarization effects, for linear decay (no decay was observed for **4**) and empirically for absorption. The heavy atom positions were located by Patterson methods using SHELXS 86.[12] The remaining atoms were located in successive Fourier-difference maps and refined by least squares on F^2 using SHELXL 93.[13] For **5** a dichloromethane solvent molecule of crystallization was also located in the Fourier-difference map. The two carbons of the ethoxide group in **4** were found to be disordered over two different positions with 0.54 and 0.46 occupancies. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms not attached to the metal atom were included in calculated positions, constrained to ride at fixed distances of the parent carbon atom with group U_{iso} values assigned. The structural parameters for the hydride ligands were obtained by MO calculations, and introduced in the molecular structure after the last Fourier-difference cycle. The final Fourier-difference synthesis revealed electron densities between +4.67 and −3.15 e $Å^{-3}$ for **1,** 1.07 and −0.89 e $Å^{-3}$ for **4** and 0.88 and −0.96 e $Å^{-3}$ for **5** near the rhenium atom. Atomic scattering factors and anomalous dispersion terms were as in SHELXL 93.[13] The ORTEP drawings were made with ORTEP II[14a] or ORTEX[14b] and all the calculations were performed on a Dec α3000 computer.

CCDC reference number 186/1365.

See http://www.rsc.org/suppdata/dt/1999/1293/ for crystallographic files in .cif format.

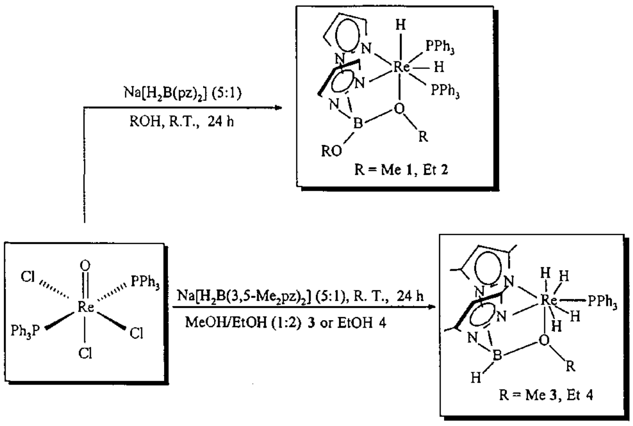
MO Calculations

Combined *ab initio* and extended Hückel calculations were carried out on model complexes. *Ab initio* calculations were performed at the Hartree–Fock level with a LANL2MB basis set using the GAUSSIAN94/DFT program.[15a] Extended Hückel[15b–d] type calculations with modified H_{ij}[16] were also carried out. The basis set for the metal atoms consisted of *n*s, *n*p and (*n* − 1)d orbitals. The s and p orbitals were described by single Slater type wavefunctions, and d orbitals were taken as contracted linear combinations of two Slater type wavefunctions. Standard parameters were used for all atoms. The refined crystal structures of complexes **1** and **4** without hydride ligands were used as starting models for all calculations. The EHMO calculations and drawings were made with CACAO.[15e] In all *ab initio* calculations the phosphines were replaced by PH_3 groups with the hydrogens pointing in the same spatial direction as the phenyl groups of the real complexes. In complex **4** the 3,5-Me groups were replaced by hydrogens.

Results and discussion

Synthesis of the complexes and spectroscopic data

The rhenium(III) hydrides **1** and **2** have been prepared by treating [$ReOCl_3(PPh_3)_2$] with Na[$H_2B(pz)_2$] at room temperature, in the molar ratio 1 : 5, in methanol or ethanol, respectively. When the same reaction is done using Na[H_2B(3,5-$Me_2pz)_2$] the compounds **3** and **4** are obtained (Scheme 1). Complexes **1**–**4** precipitate from the reaction mixture and are obtained, upon appropriate work-up, as crystalline yellow solids in yields which go from low to moderate (**1**, 20; **2**, 5; **3**, 25; **4**, 60%). All the complexes have been fully characterized, except **2** that has been characterized only by ^1H, ^{31}P NMR and IR spectroscopies, due to the very low yield of the reaction. They are air stable and very soluble in aromatic solvents, as well as in THF and CH_2Cl_2.



Scheme 1

This synthetic process is a novel route to prepare rhenium hydride complexes which is reproducible, and different from others previously described to prepare hydrides of Re^{III} or Re^{V} with anionic stabilizing ligands,[3–6] although some of the complexes described in this work are obtained with disappointing yields.

The importance of the B–H bonds in the preparation of the hydrides **1**–**4** was confirmed by treating [ReOCl$_3$(PPh$_3$)$_2$] with Na[Ph$_2$B(pz)$_2$] in methanol. In this reaction no hydrides were formed. The IR and ^{1}H NMR spectra of the crude product, before recrystallization, showed clearly that compound **5** was present as well as some other oxo-species. By recrystallization the only complex that we have been able to characterize was [ReO(OMe){κ^2-Ph$_2$B(μ-OMe)(pz)}$_2$] **5**.

Other d-transition metal complexes with modified poly(pyrazolyl)borates co-ordinated in a κ^3-*N*,*N*,*O* fashion have also been described but were obtained by insertion of aldehydes or ketones into the B–H bond of the corresponding dihydrobis(pyrazolyl)borate complexes.[17–19] With modified [Ph$_2$B(pz)$_2$] ligands, as far as we know, there is only one d-transition metal complex.[20]

In the IR spectra of complexes **1** and **2** a very broad and relatively weak band assigned to *ν*(Re–H) appears in the 1933–2057 cm^{-1} range [*ν*(M–H) stretching vibrations 1500–2300 cm^{-1}].[1,2,21] No *ν*(B–H) stretching vibrations appear in the spectra of **1** and **2**; for **3** and **4** one relatively simple band assigned to the remaining B–H bond appears at 2450 and at 2445 cm^{-1}, respectively. In the spectra of **4** and **3** *ν*(Re–H) appears in the ranges 1950–2049 and 1975–2063 cm^{-1}, respectively.[1,2,21] The frequency of the *ν*(B–H) and *ν*(Re–H) stretching vibrations of **3** and **4** compares well with those exhibited by the analogous [ReH$_4${HB(pz)$_3$}(PPh$_3$)].[6]

The ^{1}H NMR spectra of complexes **1** and **2** present two resonances of relative intensity 4:2 in the range δ 7.46–7.49 [H(3)/H(5)] and 5.67–5.69 [H(4)], respectively, due to the modified poly(pyrazolyl)borates. In both complexes the two alkoxide groups co-ordinated to the boron atom are magnetically different and appear as two resonances of equal intensity at δ 3.51 and 3.23 for **1** and as four resonances of relative intensities 2:2:3:3 at δ 3.98, 3.68, 1.27 and 1.13 for **2**. For **3** and **4** one resonance is observed for the H(4) proton of the pyrazolyl rings and two resonances for the corresponding methyl groups, with relative intensities 2:6:6, and in the ranges δ 5.52–5.55 and 2.02–2.19, respectively. The protons of the co-ordinated B–OMe appear as a singlet at δ 3.15 for **3**, and in the case of **4** the B–OEt protons appear as a quartet at δ 3.59 (CH$_2$) and as a triplet at δ 0.65 (CH$_3$). The hydrides in **1** and **2** appear as a triplet at δ −5.96 ($J_{\text{P-H}}$ = 46.6) and at −6.08 ($J_{\text{P-H}}$ = 46.2 Hz), respectively. These resonances integrate for two hydrogen atoms on one scan or using large repetition delays. For **3** and **4** the metal bound hydrogen atoms appear as doublets at δ −4.85 and at −4.76, respectively, with coupling constants of $J_{\text{P-H}}$ = 27.3 Hz and integrating for four hydrogen atoms. The equivalency of the two phosphines in **1** and **2** and the number of hydrides co-ordinated to the rhenium in **1**–**4** were confirmed by ^{31}P-{^{1}H(selective)} NMR spectra. For **1** and **2** a triplet was observed at δ 46.8 ($J_{\text{P-H}}$ = 46.6) and at 45.1 ($^3J_{\text{P-H}}$ = 46.2 Hz) respectively, and for **3** and **4** as a quintuplet at δ 46.6 ($^3J_{\text{P-H}}$ = 27.3) and at 46.1 ($^3J_{\text{P-H}}$ = 27.3 Hz), respectively. The values found in the hydride region for **3** and **4** compare with those described for the classical hydride [ReH$_4${HB(pz)$_3$}(PPh$_3$)].[6]

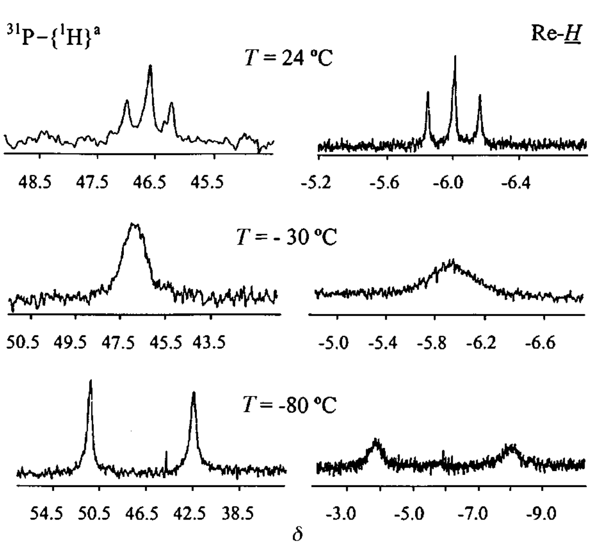


Fig. 1 Variable temperature ^{1}H (in the ReH region) and ^{31}P NMR spectra for complex **1**. ^{a} At 24 °C the ^{31}P {^{1}H selective} one.

Variable temperature ^{1}H and ^{31}P NMR studies have been done for complexes **3** and **4**, but no static spectra could be obtained, despite the broadening of the resonance due to the hydrides and due to the H(4) protons of the pyrazolyl rings. However, for **1** it was possible to slow down the rate of the dynamic process responsible for the spectrum obtained at room temperature (r.t.) and at −80 °C a static spectrum was obtained. Its pattern indicates that the two pyrazolyl rings, the two phosphines and the two hydrides are magnetically different. The two alkoxide groups are not affected by the temperature, as they always appear as two independent resonances. Fig. 1 shows the ^{1}H NMR spectra of **1** at different temperatures, in the area of the hydrides, and variable temperature ^{31}P NMR spectra. Using the different coalescence temperatures [H(4), T_c = −75 °C; Re–H, −55 °C; PPh$_3$, −45 °C] and the respective peak separation obtained from the static spectra, the following activation energies were found:[22] $\Delta G_{T_c}^{\ddagger}$ = 38.6 ± 2.0 kJ mol^{-1} based on ^{1}H NMR and 40.6 ± 1.0 kJ mol^{-1} based on ^{31}P NMR. The values are comparable and must be related to the same dynamic process, that probably is an intramolecular non-dissociative process which does not involve scrambling of the alkoxide groups.[21,23]

Measurements of T_1 were done for complex **1** at different temperatures but the calculation of T_1(min) was not possible. We observed a decrease in T_1 values with the temperature but due to the broadening and coalescence of the resonance we were not able to get a typical V-shaped curve and to determine the minimum value. However, as referred to above, for **1** a static spectrum (Fig. 1) was obtained with two ReH resonances of equal intensity and integrating for one hydrogen atom each. Below the coalescence temperature (T_c = −55 °C) the T_1 values for each resonance are of the same magnitude and relatively high (−65 °C, T_1 = 228; 211; −80 °C, T_1 = 2130, 2440 ms). These results led us to assume that, at least at low temperature, we must have a classical structure,[24] analogous to the one assigned in the solid state (see below).

Table 1 Crystallographic data for complexes **1**, **4** and **5**

	1	**4**	**5**
Formula	$C_{44}H_{44}BN_4O_2P_2Re$	$C_{30}H_{39}BN_4OPRe$	$C_{33}H_{35}B_2N_4O_4Re{\cdot}CH_2Cl_2$
M	919.78	699.63	844.40
Crystal size/mm	0.43 × 0.11 × 0.05	0.62 × 0.34 × 0.16	0.36 × 0.25 × 0.21
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	11.625(2)	9.8554(7)	11.274(1)
b/Å	12.683(3)	11.035(1)	13.007(1)
c/Å	15.885(4)	14.868(2)	13.350(1)
α/°	96.65(2)	107.354(7)	100.639(7)
β/°	100.20(2)	91.229(5)	100.376(8)
γ/°	115.54(2)	100.002(5)	108.309(7)
U/Å^3	2030.6(8)	1515.3(3)	1766.1(2)
Z	2	2	2
T/K	293	293	293
D_c/g cm^{-3}	1.504	1.533	1.588
μ(Mo-Kα)/mm^{-1}	3.11	4.09	3.63
F(000)	924	700	840
No. reflections measured	6692	6841	8934
No. unique reflections (R_{int})	6370 (0.0241)	6579 (0.0228)	8504 (0.0147)
$R1^a$	0.0748 (0.0618)	0.0485 (0.0286)	0.0484 (0.0347)
$wR2^a$	0.1845 (0.1560)	0.0944 (0.0703)	0.0838 (0.0736)

[a] The values in parentheses were calculated for data with $I > 2\sigma(I)$ only.

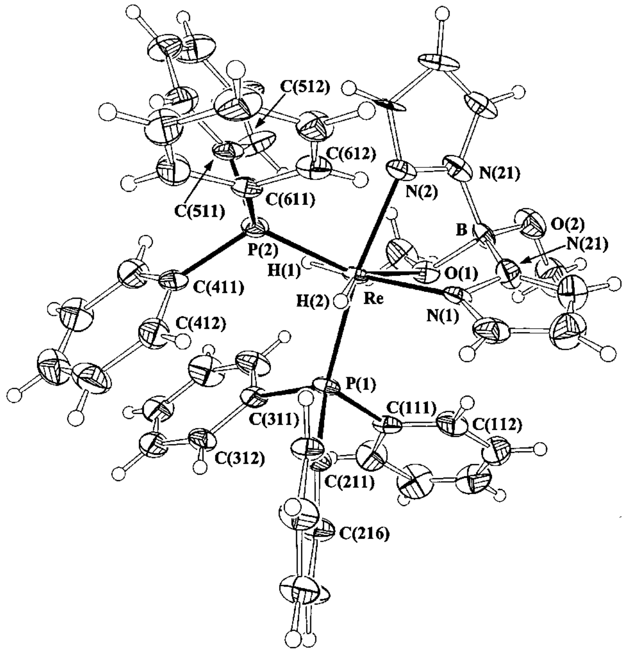


Fig. 2 An ORTEP[14a] drawing of complex **1** with atom numbering scheme. The hydride ligands were not located; their structural parameters were calculated. Thermal ellipsoids are drawn at the 40% probability level.

For complexes **3** and **4** T_1 measurements were also made and a typical behaviour was found with a well defined minimum. The T_1(min) values found at 300 MHz were: **3**, 60; **4**, 57 ms. These values are relatively low and, although as the same magnitude as the values found for other rhenium polyhydrides, are not conclusive by themselves in terms of classical *versus* non-classical.[25] For **4** the isotopomers $[ReH_{4-n}D_n\{\kappa^3\text{-}(D)(\mu\text{-}OEt)B(3,5\text{-}Me_2pz)_2\}(PPh_3)]$ ($n = 1$–3) were prepared using $Na[D_2B(3,5\text{-}Me_2pz)_2]$. The ^{1}H NMR spectrum obtained for the isotopomeric mixture presents three separate and equally spaced doublet resonances in the hydride region, which are high field shifted (−20 ppb per D), with a constant value for $^2J_{P-H}$ (27 Hz). The H–D coupling was not resolved but, based on the half-height width of the several hydride resonances, J_{H-D} must be less than 2 Hz for all the isotopomers. These data strongly suggest a classical structure for **4**, and as a consequence for **3** which has similar spectroscopic characteristics.[26]

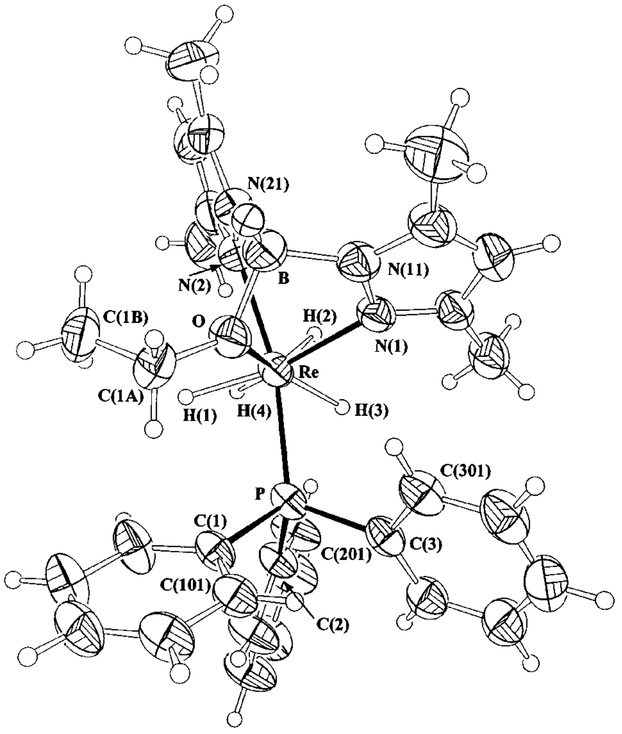


Fig. 3 An ORTEP[14a] drawing of complex **4** with atom numbering scheme. Details as in Fig. 2.

Molecular structures of complexes 1 and 4 and hydride assignment

Diffraction data did not allow us to obtain structural parameters for the hydride ligands in complexes **1** and **4**. The crystal structures of these two compounds were solved and refined by standard crystallographic methods, up to the point where only the hydride ligands in the co-ordination sphere were missing. The ORTEP diagrams, including calculated hydrides (see below), are shown in Figs. 2 and 3 and bond distances and angles are shown in Tables 2 and 3.

In complex **1** the Re–P bond distances are 2.319(2) and 2.272(3) Å, with an P–Re–P angle of 102.95(9)° indicating a *cis* position for the PPh_3 ligands. The two Re–N bonds are significantly different, 2.149(8) and 2.233(8) Å, the longest being the one *trans* to the PPh_3 ligand [P(1)–Re–N(2) angle of 166.9(2)°]

Table 2 Selected bond distances (Å) and angles (°) for complex **1**[a]

Re–N(1)	2.149(8)	Re–P(1)	2.319(2)
Re–N(2)	2.233(8)	Re–P(2)	2.272(3)
Re–O(1)	2.239(7)	O(1)–B	1.486(13)
O(2)–B	1.419(13)	N(11)–B	1.532(14)
N(21)–B	1.55(2)	Re–H(1)	1.69[a]
Re–H(2)	1.66[a]		
P(2)–Re–P(1)	102.95(9)	N(1)–Re–N(2)	79.5(3)
P(1)–Re–N(1)	96.7(2)	P(1)–Re–N(2)	166.9(2)
P(2)–Re–O(1)	143.5(2)	N(1)–Re–P(2)	134.7(2)
P(2)–Re–N(2)	88.3(2)	O(1)–Re–N(2)	73.1(3)
O(1)–Re–N(1)	73.4(3)	O(1)–Re–P(1)	93.8(2)
H(1)–Re–H(2)	133.6	H(2)–Re–P(1)	80.5
H(1)–Re–P(1)	82.5	H(2)–Re–P(2)	70.0
H(1)–Re–P(2)	72.3	H(2)–Re–N(1)	73.7
H(1)–Re–N(1)	151.4	H(2)–Re–N(2)	110.0
H(1)–Re–N(2)	94.8	H(2)–Re–O(1)	145.6
H(1)–Re–O(1)	78.1		

[a] Hydride ligands were not located; their structural parameters were calculated.

Table 3 Selected bond distances (Å) and angles (°) for complex **4**[a]

Re–N(1)	2.183(4)	Re–P	2.319(1)
Re–N(2)	2.167(4)	Re–O	2.246(3)
O–B	1.478(6)	N(11)–B	1.520(7)
N(21)–B	1.551(9)	Re–H(1)	1.66[a]
Re–H(2)	1.64[a]	Re–H(3)	1.65[a]
Re–H(4)	1.65[a]		
N(1)–Re–P	103.0(1)	N(2)–Re–P	164.0(1)
P–Re–O	92.7(1)	N(1)–Re–N(2)	82.5(2)
N(2)–Re–O	74.0(2)	N(1)–Re–O	73.9(1)
H(1)–Re–H(2)	117.7	H(2)–Re–H(3)	53.8
H(1)–Re–H(3)	122.6	H(2)–Re–H(4)	66.2
H(1)–Re–H(4)	55.6	H(2)–Re–N(1)	82.2
H(1)–Re–N(1)	154.4	H(2)–Re–N(2)	73.7
H(1)–Re–N(2)	87.9	H(2)–Re–P	121.6
H(1)–Re–P	80.8	H(2)–Re–O	141.9
H(1)–Re–O	80.7	H(3)–Re–H(4)	76.1
H(3)–Re–N(1)	81.6	H(4)–Re–N(1)	148.0
H(3)–Re–N(2)	126.7	H(4)–Re–N(2)	92.7
H(3)–Re–P	69.3	H(4)–Re–P	90.2
H(3)–Re–O	145.5	H(4)–Re–O	135.1

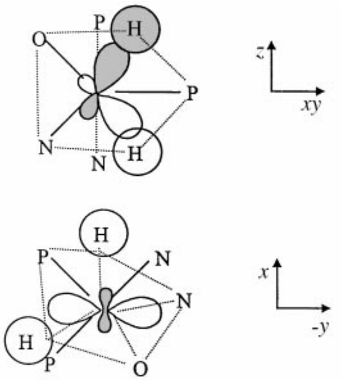
[a] Hydride ligands were not located; their structural parameters were calculated.

and this *trans* Re–P bond shows the longest Re–P distance. The two Re–N bond distances are longer than the corresponding values found in $[ReCl_2\{\kappa^3\text{-}B(pz)_4\}(PPh_3)]$ [range: 2.095(8)–2.112(8) Å].[27] These data must reflect the geometrical constraints of the modified poly(pyrazolyl)borate and the steric bulk of the two phosphine ligands. The mean Re–P distance of 2.295(3) Å is comparable to the mean values found in similar rhenium(III) dihydrides where the PPh_3 ligands are also in a *cis* position: 2.318(1) Å in $[Re(\eta^5\text{-}C_5H_5)H_2(PPh_3)_2]$, 2.324(3) Å in $[Re(\eta^5\text{-}C_9H_7)H_2(PPh_3)_2]$ and 2.353(7) Å in $[Re(\eta^4\text{-}C_4H_5S)H_2(PPh_3)_2]$.[5,28] Within the $[(OMe)_2B(pz)_2]^-$ ligand, the two B–O bond lengths are different, 1.49(1) and 1.42(1) Å, the longest being the one involved in the B–O(1) ··· Re interaction.

In complex **4** the two Re–N bond distances are almost identical, 2.183(4) and 2.167(4) Å, with an average of 2.175(4) Å. The N–Re–N bond angle of 82.5(2)° is larger than the value of 79.5° observed in **1**, probably due to the larger steric requirements of the two PPh_3 ligands in the latter. The Re–P bond distance of 2.319(1) Å is shorter than the corresponding bond distance of 2.346(1) Å in $[Re(\eta^5\text{-}C_5H_5)H_4(PPh_3)]$,[5a] and than the mean value of 2.391(1) Å observed in the eight-co-ordinated $[ReH_4(hqn)(PPh_3)_2]$ (hqn = 2-hydroxyquinolinolate)[29] where the two PPh_3 ligands are in a *trans* position.

In order to assign the structural parameters of the hydride ligands and to get some information about the co-ordination geometry around the rhenium, molecular orbital calculations of *ab initio* and extended Hückel type have been performed.[15d,30] The EHMO calculations were used to predict the structural parameters of the hydrides linked to the metal centre, based on the positional parameters determined by X-ray diffraction for $[Re\{\kappa^3\text{-}(OMe)(\mu\text{-}OMe)B(pz)_2\}(PPh_3)_2]^{2+}$ and for $[Re\{\kappa^3\text{-}(H)(\mu\text{-}OEt)B(3,5\text{-}Me_2pz)_2\}(PPh_3)]^{4+}$. Inspection of the frontier orbitals, Fig. 4, showed that, for these two complexes, the *two* and the *four* lower unoccupied MOs are essentially constituted by metal centred AOs.[15d] Since hydrides are donor ligands the *two* or the *four* LUMOs in the rhenium(III) and -(V) fragments were assigned to two or to four hydrogens which were positioned at the maximum charge density determined by the topological analysis of the squared wavefunctions of each lower unoccupied orbital, at a fixed Re–H distance of 1.65 Å. One of the pitfalls in this assumption is the possibility of two of the hydrides occupying the same orbital, in a non-classical arrangement, leaving one of the empty orbitals unused. To avoid such errors, additional *ab initio* optimizations, at the Hartree–Fock level using a LANL2MB basis set, were carried out from starting classical and non-classical structures which were obtained from the EHMO calculations.

For complex **1** two different structures were obtained, both classical, showing a capped octahedron or C_s-3 : 2 : 2[31] geometry, Fig. 5(a) and 5(b), the latter being energetically favourable by 17 kJ mol^{-1}. However if an optimization is carried out with the heavy atoms frozen at their crystallographic positions we obtain the geometry in Fig. 5(c) which is structurally closer to that in 5(a). To rationalize this trend we can go back to the EHMO calculated hybrids, Fig. 4(a). The LUMO, apart from some density that is spread over the ligand atoms, is essentially $x^2 - y^2$ (51%) and LUMO-1 is a mixture of xz (35%) and yz (23%) and lies in the bisecting plane of the N–Re–P angle. If the LUMO and LUMO-1 orbitals are to be used in σ bonds with a single s orbital of a hydride, our solid state based model complexes should suffer major stereochemical distortions due to the bulkiness of the phosphines. In fact the optimized structure in Fig. 5(b), where this steric hindrance is to be expected, has one of the phosphines distorted from its crystallographic position. If instead of making two σ bonds the empty orbitals interact with the symmetric (σ bond) and antisymmetric (π bond) combination of the 1s orbitals, as depicted in Scheme 2, we can optimize a structure [Fig. 5(a)] similar to the observed one [Fig. 5(c)].



Scheme 2

While in the dihydride all the optimized geometries are classical, in the tetrahydride we were able to find local energy minima, nearly isoenergetic (the difference is *ca.* 3 kJ mol^{-1}), for both classical and non-classical structures, Fig. 6(a) and 6(b) respectively. The classical nature of Fig. 6(a) is confirmed by the *ab initio* overlap populations between hydrogens, smaller than 0.03 e [Fig. 6(a)], compared with 0.3 e in the non-classical Fig. 6(b). The co-ordination geometry in Fig. 6(a) is dodecahedral

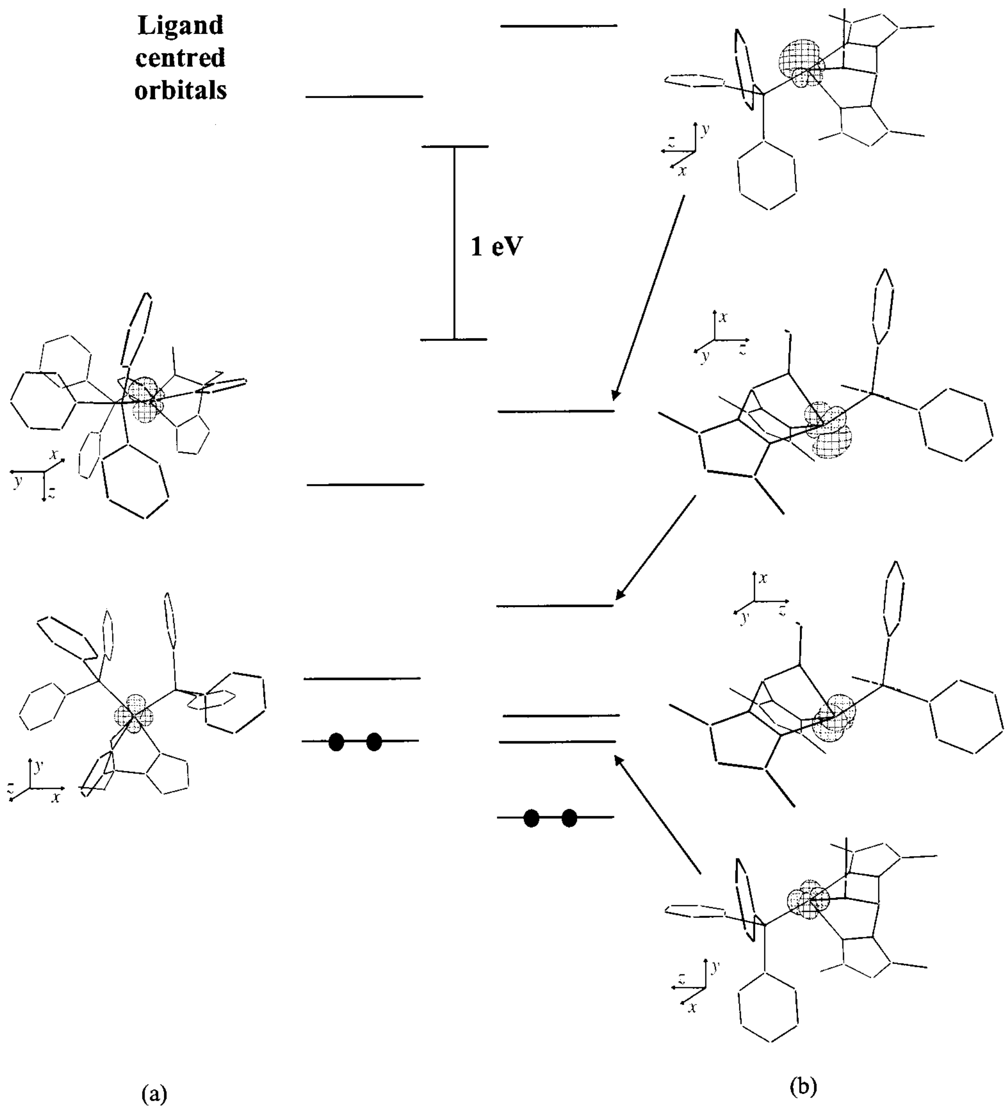


Fig. 4 Simplified MO diagrams for complexes **1** (a) and **4** (b). The drawings for the metal centred orbitals only represent the rhenium contribution. The skeleton of the molecule is included as a visual aid.

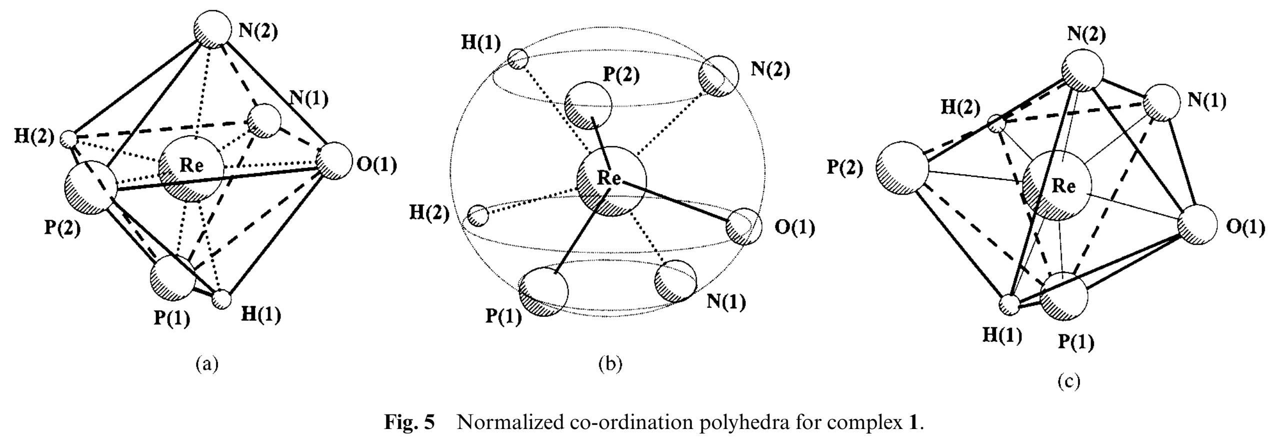
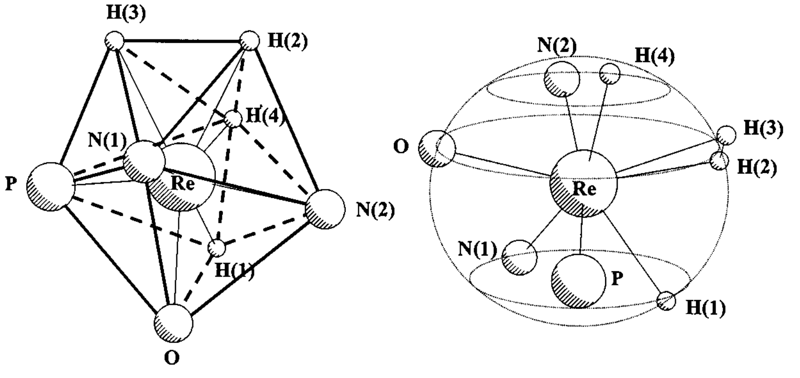


Fig. 5 Normalized co-ordination polyhedra for complex **1**.

while that in 6(b) can be considered as C_s-3:2:2 seven-co-ordinated.[31] Both structures were optimized with all the heavy atoms frozen at their crystallographic positions. The existence of these two types of *ab initio* structures can, again, be explained using the EHMO original hybrids, Fig. 4(b). Each pair of hydrogen atoms H2/H3 and H1/H4 can make a single strong σ bond with the LUMO-2 (-35% xz, 25% x^2-y^2) or LUMO-3 (36% yz, 12% s, 11% y) orbitals in a non-classic dihydrogen conformation [shorter H···H distance, *e.g.* H2···H3 in Fig. 6(b)]. Alternatively, these spatially extended hybrids can make a less strong σ bond with the symmetric combination of 1s orbitals of two classic hydrides [larger H···H distance, *e.g.* H1···H4 in Fig. 6(a)] and, in addition, the LUMO (-42% z^2, -15% xy) or LUMO-1 (-36% x^2-y^2, -10% xz) orbital can make a weaker π interaction with the antisymmetric combination of 1s orbitals.

Using the formulae given by Desrosiers *et al.*[25b] and the cartesian coordinates for $H_{hydride}$, P and Re, we calculated



(a) (b)

Fig. 6 Normalized co-ordination polyhedra for complex **4**.

Table 4 Selected bond distances (Å) and angles (°) for complex **5**

Re–N(1)	2.055(4)	Re–O(1)	1.693(3)
Re–N(2)	2.062(3)	Re–O(2)	1.857(3)
Re–O(3)	2.100(3)	Re–O(4)	2.122(3)
O(2)–C(2)	1.362(7)	O(3)–C(3)	1.431(5)
O(4)–C(4)	1.433(5)	N(11)–B(1)	1.585(6)
B(1)–O(3)	1.538(5)	B(2)–O(4)	1.543(5)
N(21)–B(2)	1.574(6)	av. B–C	1.609(7)
O(3)–B(1)	1.538(5)	O(4)–B(2)	1.543(5)
O(1)–Re–O(2)	176.4(1)	O(1)–Re–O(3)	93.1(1)
O(2)–Re–O(3)	85.5(1)	O(2)–Re–O(4)	87.6(1)
O(3)–Re–O(4)	101.1(1)	N(1)–Re–N(2)	102.9(1)
O(1)–Re–N(1)	93.1(2)	O(1)–Re–N(2)	93.0(2)
O(2)–Re–N(1)	89.9(1)	O(2)–Re–N(2)	88.4(1)
O(3)–Re–N(1)	77.6(1)	O(4)–Re–N(2)	78.2(1)
Re–O(2)–C(2)	175.9(4)	Re–O(3)–C(3)	122.1(3)
Re–O(4)–C(4)	119.8(3)	N(11)–B(1)–O(3)	100.2(3)
C(5)–B(1)–C(6)	115.8(4)	N(21)–B(2)–O(4)	100.9(3)
C(7)–B(2)–C(8)	114.0(4)		

T_1(min) as 57 and 6 ms (300 MHz) for the classical and non-classical structures, respectively. In these calculations only $H_{hydride}\cdots H_{hydride}$, $P\cdots H_{hydride}$ and Re–$H_{hydride}$ dipole–dipole interactions were considered. Comparing theoretical with experimental T_1(min) values found for complex **4**, we assigned the structure in Fig. 6(a) as the one observed in the solid state. We believe that our results indicate that the structure of **4** in solution, at temperatures close to those corresponding to T_1(min), must be similar to the one found in the solid state.†

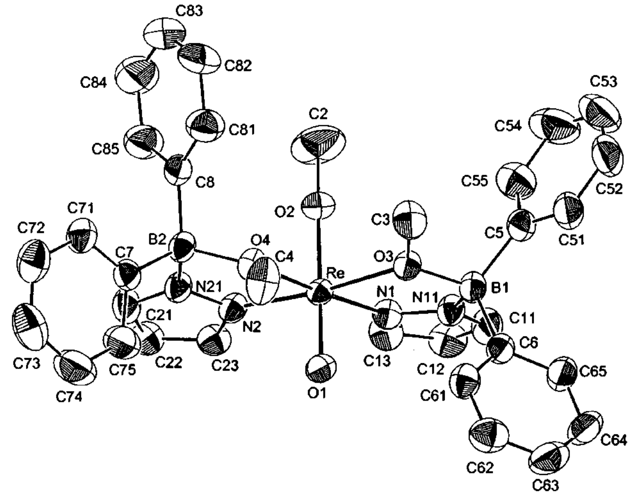


Fig. 7 An ORTEP[14a] drawing of complex **5** with atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

Molecular structure of complex 5

An ORTEP view of the structure of complex **5** is shown in Fig. 7. Selected bond distances and angles are listed in Table 4. Compound **5** is monomeric and the co-ordination geometry about the rhenium center is approximately octahedral, with the two bidentate modified poly(pyrazolyl)borates lying in the equatorial plane and the oxo and methoxide ligands occupying the axial positions. This geometry accounts for the ^{1}H NMR data obtained (see Experimental section).

As can be seen in the values of the angles around the rhenium atom, a distortion from the regular octahedral geometry is observed, with the Re atom 0.078 Å out of the equatorial plane towards the axial oxo ligand. The two pyrazolyl rings are almost coplanar, with the N(2) pyrazolyl ring slightly tilted towards the oxo ligand. The two methoxide groups co-ordinated to the boron atoms are oriented differently, one pointing towards the Re=O bond and the other towards the Re–OMe bond. The angles around the boron atoms indicate a strong distortion from tetrahedral geometry. This distortion, which is observed mainly in the angles C(5)–B(1)–C(6) 115.8, C(7)–B(2)–C(8) 114.0, N(11)–B(1)–O(3) 100.2 and N(21)–B(2)–O(4) 100.9, must reflect the steric requirements of the phenyl groups and the small bite of the ligand.

The Re=O bond distance, 1.693(3) Å, is in the range normally found for monooxo complexes[27] and compares well with the values of the corresponding distances in previous structurally characterized monomeric oxo rhenium(v) complexes with κ^2- or κ^3-$[B(pz)_4]^-$.[32,33] The Re–O(2) bond distance and the Re–O(2)–C(2) bond angle are 1.857(3) Å and 175.9(4)°, respectively. The Re–O(2) bond distance is significantly shorter than the corresponding distance in $[ReO(OEt)(L)_2]$ (L = *o*-aminophenyldiphenylphosphine) [2.004(7) Å],[34] but compares with the values found in other rhenium(v) complexes: 1.896(5), 1.859(5) and 1.890(2) Å in $[ReO(acac)\{\kappa^2\text{-}B(pz)_4\}(OMe)]$, $[ReOI_2(OMe)(PPh_3)_2]$ and $[ReOCl_2(O^iPr)(PPh_3)_2]$, respectively.[33,35,36] In complexes with the core $[ReO(OR)]^{2+}$ a certain competition of the oxygen of the alkoxide group with the oxo ligand for the d_π orbitals of the metal has been invoked to explain the short Re–O bond distances and the large Re–O–C bond angles in the fragment $[O\text{–}Re\text{–}OR]^{2+}$.

Concluding remarks

We have shown that by treating $[ReOCl_3(PPh_3)_2]$ with dihydrobis(pyrazolyl)borates in alcohols it is possible to prepare hydride derivatives stabilized by modified poly(pyrazolyl)borates. The presence of the B–H bonds is essential for the

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† Pictures of the topological analysis and energies of the LUMOs obtained by EHMO calculations, *ab initio* optimized cartesian co-ordinates, orbital populations and energies are available from the authors.

formation of the hydride complexes whose oxidation state depends on the number of B–H bonds which are activated. The structures of **1** and **4** are the first examples of rhenium(III) and -(V) hydrides stabilized by modified poly(pyrazolyl)borates co-ordinated to the metal in a κ^3-*N*,*N*,*O* fashion. X-Ray diffraction data associated with combined EHMO and *ab initio* calculations were tentatively used to predict the structural parameters of the hydrides in **1** and **4**.

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