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Synthesis and characterization of rhenium polyhydrides stabilized by the tripodal ligand $MeC(CH_2PPh_2)_3$ *,**

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Abstract

The reaction of $CH_3C(CH_2PPh_2)_3$ (triphos) with $[Re(O)Cl_3(PPh_3)_2]$ in THF at reflux temperature yields $[(\eta^2\text{-triphos})Re(O)Cl_3]$ (**3**). Compound **3** is transformed into $[(\eta^2\text{-triphos})ReH_7]$ (**4**) by treatment with $LiAlH_4$ in refluxing THF. The reaction of $[Re(MeCN)Cl_3(PPh_3)_2]$ with triphos in refluxing toluene gives *fac*-$[(\eta^3\text{-triphos})ReCl_3]$ (**5**) in excellent yield. Complex **5** is converted to the classical pentahydride $[(\eta^3\text{-triphos})ReH_5]$ (**6**) by treatment with $NaBH_4$ at room temperature. The reductive elimination of H_2 from **6** is promoted by monodentate ligands such as PPh_3 and CO, giving substitution products of the formula $[(\eta^3\text{-triphos})ReH_3(L)]$ (L = PPh_3 (**7**) or CO (**8**)). All the rhenium polyhydrides obtained have been characterized by spectroscopic techniques including IR and multinuclear variable-temperature NMR analysis. A detailed study of the spin-lattice relaxation time (T_1) at variable temperature has shown that T_1 cannot be used unambiguously to discriminate between classical and non-classical structures of rhenium polyhydrides.

1. Introduction

Among transition-metal polyhydrides, rhenium compounds are extensively studied because of their intriguing structural chemistry and their use in both catalytic and stoichiometric reactions [1–12].

In spite of the huge amount of literature data, there are several important questions in the chemistry of rhenium polyhydride complexes which still need to be addressed. In particular, there is lack of a reliable spectroscopic criterion to distinguish classical ($M\text{-}H_x$) from non-classical ($M\text{-}\eta^2\text{-}H_2$ or $M\text{-}\eta^3\text{-}H_3$) structures [13–15].

In order to contribute to the understanding of the solution structure of rhenium polyhydrides, we started a project directed to the synthesis and spectroscopic characterization of rhenium polyhydrides containing tripodal polyphosphine coligands which have recently been found to be suitable ligands for the stabilization of a large variety of either classical and non-classical polyhydride metal complexes [16–24]. Tripodal polyphosphine ligands also appear appropriately structured for NMR studies, as they exhibit readily distinguishable ^{31}P NMR patterns and confer on the resulting metal complexes with a precise stoichiometry and stereochemistry [25–29].

Here we report the synthesis and the spectroscopic characterization of a family of rhenium polyhydrides stabilized by the potentially tridentate ligand triphos (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$).

As we completed our work, a paper by Walton and coworkers appeared in the literature [30], which describes the electrochemical and chemical properties of

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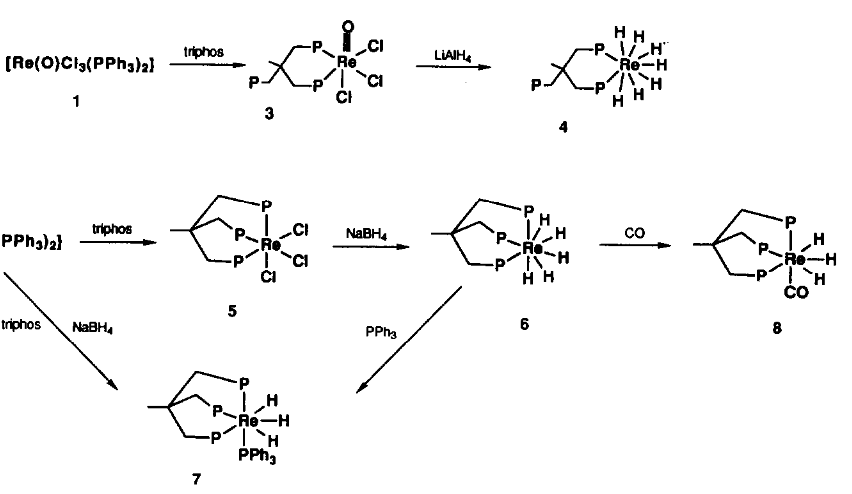


Scheme 1.

some rhenium complexes with triphos, including a pentahydride complex also prepared by us. Accordingly, only the results that do not overlap with those reported by Walton are discussed in the present paper.

2. Experimental details

2.1. General procedures

Tetrahydrofuran (THF) and dichloromethane were purified just prior to use by distillation under dinitrogen over $LiAlH_4$ and P_2O_5, respectively. The aromatic hydrocarbons, C_6H_6 and C_7H_8, were dried over sodium and distilled under argon just prior to use. All the other solvents and chemicals were reagent grade and, unless otherwise stated, were used as received. Deuterated solvents for NMR measurements (Janssen and Aldrich) were dried over a molecular sieve. Literature methods were used for the preparation of triphos (1,1,1-tris(diphenylphosphinomethyl)ethane) [31] and of the rhenium starting products $[Re(O)Cl_3(PPh_3)_2]$ (**1**) [32] and $[Re(MeCN)Cl_3(PPh_3)_2]$ (**2**) [33].

Infrared spectra of samples mulled in Nujol between KBr plates were recorded on a Perkin–Elmer 577 spectrophotometer. NMR spectra were recorded on either Varian VXR 300 or Bruker AC200P spectrometers operating at 299.94 and 200.13 MHz (^1H) and at 121.42 and 81.01 MHz (^{31}P), respectively. Peak positions are relative to tetramethylsilane as an external reference (^1H) or to external 85% H_3PO_4 ($^{31}P\{^1H\}$) with downfield values positive. Proton NMR spectra with selective decoupling of the ^{31}P resonances were recorded on the Bruker instrument equipped with a 5-mm inverse probe and a BFX-5 Bruker amplifier. The 2D-COSY NMR experiment on **5** was performed with the Varian's pulse sequence using the Varian instrument. A delay of 2 s was used between acquisi-

TABLE 1. Selected IR and $^{31}P\{^1H\}$ NMR spectral data for the complexes

Compound	Solvent	Temperature (K)	$^{31}P\{^1H\}$ [a]			IR [c]	
			Pattern [b]	δ (ppm)	J(PP) (Hz)	ν(Re–H) (cm^{-1})	Other (cm^{-1})
3	CD_2Cl_2	294	A_2M	δ_A −32.62 δ_M −27.61	J_{AM} 3.9		982s ν(Re=O)
4	C_6D_6	294	A_2M	δ_A 0.40 δ_M −27.94	J_{AM} 2.7	1960s, br 1909s	
6	C_6D_6	293	A_3 [d]	δ_A 8.47		1950–1900br	
7	CD_2Cl_2	293	A_3X [d]	δ_A 3.90 δ_X 45.35	J_{AX} 28.3	1963m,br 1925m,br 1881m,br	
8	CD_2Cl_2	188	A_2M	δ_A −1.27 δ_M −3.94	J_{AM} 18.3	1961m 1923s	1854vs ν(C≡O)

[a] At 81.01 MHz. Chemical shift values are relative to 85% H_3PO_4 with positive values being downfield from the standard. [b] P_A and P_M refer to the triphos phosphorus atoms, whereas P_X denotes the PPh_3 in complex **7**. [c] Key: s, strong; m, medium; br, broad. [d] The fluxional process that averages the triphos phosphorus atoms could not be frozen at any accessible temperature (see text).

TABLE 2. Selected ^1H NMR spectral data [a]

Compound	Solvent	Temperature (K)	NMR data [b] (δ, integral, assignment, J) [c]
3	CD_2Cl_2	294	0.86 (s, 3H, CH_3)
			3.67 (m, 2H, $CH_{2(coord)}$)
			3.26 (m, 2H, $CH_{2(coord)}$)
			2.67 (d, 2H, $CH_{2(uncoord)}$, $^2J(HP_M)$ 2.4)
4	C_6D_6	294	0.89 (s, 3H, CH_3)
			3.30 (m, 2H, $CH_{2(coord)}$)
			2.70 (m, 2H, $CH_{2(coord)}$)
			2.24 (d, 2H, $CH_{2(uncoord)}$, $^2J(HP_M)$ 2.0)
			−5.36 (t, 7H, ReH, $^2J(HP)$ 15.0)
5 [d]	CD_2Cl_2	294	5.87 (s, 3H, CH_3)
			8.30 (s, 6H, CH_2)
6	C_7D_8	293	1.46 (q, 3H, CH_3, $^4J(HP)$ 2.4)
			2.45 (br s, 6H, CH_2)
			−6.35 (q, 5H, ReH, $^2J(HP)$ 6.2)
7	CD_2Cl_2	293	1.44 (q, 3H, CH_3, $^4J(HP)$ 2.7)
			2.28 (br s, 6H, CH_2)
			−7.20 (dq, 3H, ReH, $^2J(HP_{PPh_3})$ 37.8, $^2J(HP_{triphos})$ 18.4)
8	CD_2Cl_2	293	1.46 (q, 3H, CH_3, $^4J(HP)$ 2.4)
			2.28 (br s, 6H, CH_2)
			−6.08 (q, 3H, ReH, $^2J(HP)$ 11.2)

[a] The resonance due to the aromatic hydrogen atoms of the triphos ligand and of the PPh_3 ligand in complex **7** are not reported. [b] Chemical shifts (δ) are in ppm relative to TMS. Coupling constants are in Hz. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [c] The suffixes coord and uncoord denote the methylene protons of the coordinated and uncoordinated arms of the triphos ligand, respectively. [d] The complex is paramagnetic.

tions. A 2D Fourier transformation gave a 2D-spectrum with adequate signal-to-noise ratio after *ca.* 3 h of data collection. The spin-lattice relaxation times (T_1) were measured at different temperatures with the inversion-recovery sequence at 299.94 MHz. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyzer.

2.2. Synthesis of the complexes

All reactions and manipulations were routinely performed under argon unless otherwise stated, using standard Schlenk-tube techniques. The solid complexes were collected on sintered glass-frits and washed with ethanol and light petroleum ether before being dried under a stream of argon.

The reactions described in this paper are summarized in Scheme 1. Selected IR absorptions and $^{31}P\{^1H\}$ NMR spectral data are reported in Table 1, while selected ^1H NMR resonances are gathered in Table 2.

2.3. Preparation of [(η^2-triphos)Re(O)Cl_3] (3)

$[Re(O)Cl_3(PPh_3)_2]$ (0.84 g, 1.01 mmol) was suspended in benzene (50 mL) and the resulting slurry was heated under reflux for 1 h with vigorous stirring. The Re^V compound dissolved completely and produced a green solution which was cooled to room temperature. Solid triphos (0.62 g, 1.00 mmol) was added and the solution was stirred at reflux temperature for 1 h during which time it turned light blue. Evaporation of the solvent to half-volume, and addition of hot ethanol gave a light-blue precipitate which was recrystallized from CH_2Cl_2/EtOH. Prolonged reaction times do not increase the yield of **3**, neither did they produce the green product that Davis and Fergusson formulated as a seven-coordinate isomer of **3** in which triphos was suggested to act as a tridentate ligand [34]. Yield 93%. Anal. Found: C, 52.54; H, 4.17; Cl, 11.27. $C_{41}H_{39}Cl_3OP_3Re$ calc.: C, 52.76; H, 4.21; Cl, 11.40%.

2.4. Preparation of [(η^2-triphos)ReH_7] (4)

Solid $LiAlH_4$ (2.00 g, 52.70 mmol) was added in small portions to a well-stirred suspension of **3** (1.00 g, 1.07 mmol) in THF (150 mL). The reaction mixture was gently heated under reflux for 24 h and then cooled to *ca.* 0°C. The excess of $LiAlH_4$ was hydrolyzed by careful addition of a mixture of THF/H_2O (50 mL, 3/1 v/v) through a pressure-equalizing dropping funnel. The slurry was filtered to remove all the hydrolysis products and a clear pale orange solution was obtained. Addition of ethanol/hexane (200 mL, 1/1 v/v) and concentration of the mixture under a brisk current of argon gave pale orange microcrystals of **4**, which were washed with hexane (2 × 20 mL) and dried under argon. Yield 40%. Anal. Found: C, 59.94; H, 5.67. $C_{41}H_{46}P_3Re$ calc.: C, 60.19; H, 5.67%.

2.5. Preparation of [(η^3-triphos)$ReCl_3$] (5)

A slight excess of solid triphos (1.00 g, 1.60 mmol) was added under stirring to a hot suspension of the Re^{III} precursor **2** (0.76 g, 0.90 mmol) in toluene (40 mL). The mixture was brought to reflux temperature and then stirred for 1 h. During this time it changed from orange-yellow to light yellow and **5** separated as a yellow-green microcrystalline product. Precipitation of **5** was completed by cooling the mixture to room temperature. The crude product was recrystallized from CH_2Cl_2/EtOH. Yield 97%. Anal. Found: C, 53.49; H, 4.16; Cl, 11.50. $C_{41}H_{39}Cl_3P_3Re$ calc.: C, 53.67; H, 4.29; Cl, 11.59%.

2.6. Preparation of [(η^3-triphos)ReH_5] (6)

A solution of $NaBH_4$ (0.50 g, 13.21 mmol) in ethanol (30 mL) was added at 0°C (ice-bath) during 5 min to a well-stirred suspension of **5** (0.50 g, 0.54 mmol) in THF (50 mL). While stirring for 3 h at 0°C, it changed gradually from yellow-green to deep yellow and finally to light yellow. The cooling bath was removed and the solvent slowly evaporated in a stream of argon to yield pale-yellow crystals which were filtered off and then washed with ethanol, water, absolute ethanol, and, finally, petroleum ether before being dried under argon. Yield 85%. Anal. Found: C, 60.03; H, 5.41. $C_{41}H_{44}P_3Re$ calc.: C, 60.35; H, 5.44%.

2.7. Preparation of [(η^3-triphos)Re(PPh_3)H_3] (7)

2.7.1. Method A

A stoichiometric amount of solid triphos (0.22 g, 0.35 mmol) was added with stirring to a hot suspension of **2** (0.30 g, 0.35 mmol) in THF (30 mL). The mixture was heated at reflux for 1 h and then $NaBH_4$ (0.30 g, 7.90 mmol) in boiling ethanol (20 mL) was added. The resulting pale-yellow solution was further heated at reflux for 1 h, cooled to room temperature, and concentrated under dinitrogen to yield **7** as pale-yellow microcrystals. Yield 60%.

2.7.2. Method B

Solid PPh_3 (0.12 g, 0.48 mmol) was added to a THF (30 mL) solution of the pentahydride **6** (0.20 g, 0.24 mmol). The solution was gently heated to *ca.* 40°C and stirred for 15 min. Addition of ethanol (20 mL) and concentration under dinitrogen gave **7**. Yield 84%. Anal. Found: C, 65.80; H, 5.22. $C_{59}H_{57}P_4Re$ calc.: C, 65.84; H, 5.34%.

2.8. Preparation of [(η^3-triphos)Re(CO)H_3] (8)

A stream of CO was bubbled for 20 min throughout a hot solution (50°C) of **6** (0.20 g, 0.24 mmol) in THF (30 mL). The resulting colourless solution was cooled to room temperature and ethanol was added (30 mL) until **8** began to separate as an off-white microcrystalline solid. Yield 75%. Anal. Found: C, 59.86; H, 5.19. $C_{42}H_{42}OP_3Re$ calc.: C, 59.89; H, 5.03%.

3. Results and discussion

3.1. Synthesis and characterization of [(η^2-triphos)Re(O)Cl_3] (3)

The reaction between [Re(O)Cl_3(PPh_3)$_2$] (**1**) and triphos in refluxing benzene provides a new and very simple method for the high-yield synthesis of the light-blue Re^V oxo-halide complex [(η^2-triphos)Re(O)Cl_3] (**5**). In general, the crude product of the reaction is sufficiently pure for preparative purposes; however, recrystallization from CH_2Cl_2/EtOH affords analytically pure samples.

A compound exhibiting comparable chemico-physical properties to **3** was synthesized in the early seventies by Davis and Fergusson by reaction of $KReO_4$, triphos and hypophosphorous acid in ethanol-concentrated hydrochloric acid [34]. Indeed, the spectroscopic (IR and ^1H NMR) data of **3** agree well with those reported in the literature (see Tables 1 and 2). The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2/CH_2Cl_2), not reported previously, exhibits a first order A_2M splitting pattern with a small $^4J(PP)$ coupling of 3.9 Hz. The chemical shift of the M portion of the spectrum (−27.21 ppm) falls in the usual range of free phosphines and therefore indicates the presence of a dangling phosphine arm of the triphos ligand, as inferred by Davis and Fergusson from conductivity measurements on the quaternization product obtained by treatment with CH_3I [34]. Indeed, several examples of metal complexes with triphos acting as a *dihapto* ligand are known and have been characterized, both in the solid state (X-ray diffraction analysis) and in solution (NMR spectroscopy) [35,36].

The two coordinated phosphorus atoms are magnetically equivalent and resonate in the high-field region of the spectrum (−32.62 ppm), as expected for a phosphine complex of a third row transition metal. In conclusion, a structure can be assigned to **3** in which the metal atom is octahedrally coordinated by three chlorides, an oxo group and two phosphorus atoms of triphos.

3.2. Synthesis and characterization of [(η^2-triphos)Re(H)$_7$] (4)

The oxo-halide complex **3** has been found to be a suitable precursor for the preparation of the polyhydride complex [(η^2-triphos)Re(H)$_7$] (**4**) by treatment in refluxing THF with an excess of $LiAlH_4$, followed by hydrolysis at 0°C. The new heptahydride complex **4**, isolated as pale-orange diamagnetic microcrystals, has been characterized by elemental analysis and spectroscopic techniques.

The IR spectrum of **4** shows a series of strong broad absorptions in the 1960–1900 cm^{-1} region which are typical of ν(Re–H) modes. A broad, medium intensity band at *ca.* 830 cm^{-1} may be assigned to the Re–H deformation mode [3]. The $^{31}P\{^1H\}$ NMR spectrum displays an A_2M splitting pattern with a J(PP) of 2.7 Hz. The low intensity signal appears as a narrow triplet at δ −27.94 and matches the chemical shift found for the uncoordinated phosphine donor in the Re^V complex **3**. In contrast, the other doublet resonance, which is assigned to the two equivalent rhenium-bonded ^{31}P nuclei, is at lower field (δ 0.40 ppm) as compared to the corresponding signal of the oxo-chloride complex **3**. This is consistent with the different *trans* influence exerted by the hydride and chloride ligands [33]. The $^{31}P\{^1H\}$ NMR spectrum of **4** does not change within the temperature window of toluene-d_8, thus indicating the absence of any dynamic process involving the phos-

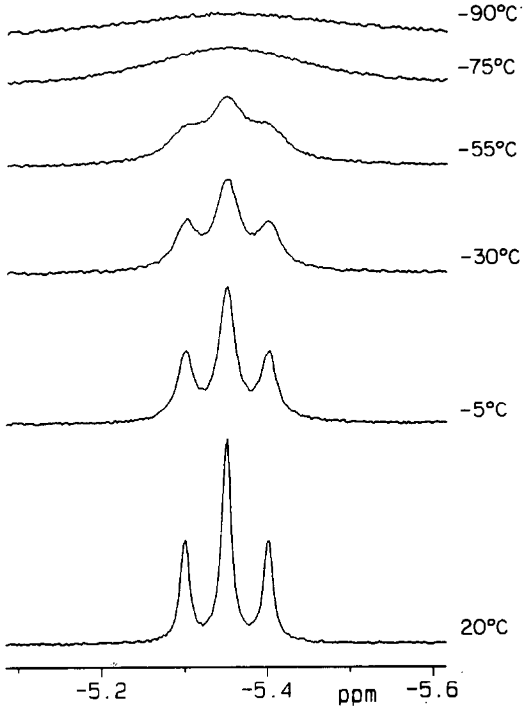
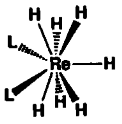


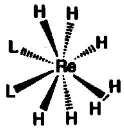
Fig. 1. Variable-temperature ^1H NMR spectrum of **4** (hydride region) in toluene-d_8 (299.94 MHz, TMS reference).

phorus atoms of triphos and also a remarkable robustness of the complex toward dihydrogen loss.

The ^1H NMR spectrum of **4** (C_6D_6, 20°C) shows a triplet resonance at -5.36 ppm (J(HP) = 15.0 Hz) in the hydride region. Accurate integration of this resonance (polyphosphine signals as internal standard) allows one to fix the hydride hydrogen number as seven. Variable-temperature ^1H NMR spectra of **4** in C_7D_8 at 300 MHz in the hydride region are shown in Fig. 1. At room temperature, the seven hydrides are equivalent, indicating a rapid exchange process. As the temperature is decreased, the triplet resonance broadens until at 75°C no discernible J(PP) is observed. At the lowest accessible temperature (-90°C) the signal is almost completely collapsed, implying a decoalescence process at even lower temperatures [37*].

Complex **4** belongs to the well known and widely studied family of rhenium polyhydrides of formula $[ReH_7L_2]$ [1] (L = PR_3 or AsR_3) for which either the classical nine-coordinate tricapped trigonal prismatic form $[Re(H)_7L_2]$ (**I**), or the non-classical structures $[Re(\eta^2\text{-}H_2)(H)_5L_2]$ (eight-coordinate dodecahedron) (**II**) and $[Re(\eta^2\text{-}H_2)_2(H)_3L_2]$ (seven-coordinate pentagonal bipyramid) (**III**) have been proposed on the basis of ^1H NMR relaxation times (T_1), [6a,38a,39,40] electrochemical studies [41,42], X-ray [43] and neutron diffraction analyses [44]. Recently, *ab initio* calculations on the model complex $[ReH_7(PH_3)_2]$ have suggested that the classical structure **I** is more stable by 2–4 kcal/mol than the nonclassical dodecahedral form **II**, whereas the seven-coordinate structure **III** is still energetically unfavoured by *ca.* 7–10 kcal/mol as compared to **I** [45].


I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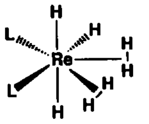
III

In light of the ^1H and $^{31}P\{^1H\}$ NMR evidence only, it is not possible to assign a structure to **4**. Accordingly, variable-temperature measurements of the spin-lattice relaxation time were carried out by using the standard inversion-recovery-sequence at 300 MHz field in C_7D_8 [46,39]. At room temperature, when the fast motion regime is attained, the narrow triplet resonance exhibits a relatively short T_1 value of 74 ms. On lowering the temperature, the T_1 value steadily decreases going through a minimum value of *ca.* 45 ms at *ca.* -30°C. Scaling this datum to the 250 MHz spectrometer field, which is the "reference magnetic field" used by Crabtree and coworkers [39], a very short value of *ca.* 37 ms was calculated at an estimated temperature of -27°C. For a further decrease in temperature, the T_1 value increases, and at *ca.* -75°C it becomes longer than 140 ms. The $T_{1(\min)}$ value is apparently low and may well indicate the contribution of $\eta^2\text{-}H_2$ ligands to the overall relaxation mechanism. However, low $T_{1(\min)}$ values in polyhydride complexes of high coordination number are not always reliable criteria for the presence of an $\eta^2\text{-}H_2$ ligand [38,39,40c,42,47]. Indeed, we have found that there is no significant difference in the average H–H separation calculated from the $T_{1(\min)}$ values of **4** assuming either the classical formulation **I** or the non-classical structures **II** and **III**. As an example, by using the simplified equations proposed by Hamilton and Crabtree [40c,48], the calculated H–H distance ranges, independently of the selected non-classical tautomers **II** or **III**, from 1.07 to 1.35 Å for the two limiting cases of rapid spinning or no rotation of the molecular hydrogen ligands, respectively [40].

One reason which has been invoked to account for the unusually short relaxation times of rhenium polyhydrides is the dipolar metal contribution to the relaxation of coordinated hydrogen ligands (MHDD mechanism). Such a contribution should be particularly significant for metal nuclei with high γ and I values, such as

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* Reference number with asterisk indicates a note in the list of references.

cobalt and rhenium [47d,49]. Moreover, as pointed out by Luo and Crabtree [40], the short $T_{1(\min)}$ values for rhenium heptahydrides could also be a consequence of severe crowding around the metal, and the metal is here surrounded by as many as seven ligands. Obviously the use of a conformationally restrictive ligand such as triphos might help in closing up the H ··· H non-bonding contacts, which may be responsible for the low $T_{1(\min)}$ value in **4**. In keeping with this hypothesis, Brammer *et al.* have recently reported a low-temperature neutron diffraction study on $[ReH_7(Ptol_3)_2]$ (containing two sterically demanding tri-*p*-tolylphosphine) in which a short H ··· H contact of 1.357(7) Å has been found [44b]. Such a value is intermediate between those of coordinated η^2-H_2 ligands ($r_{H\cdots H} <$ 1.1 Å), and of classical hydrides ($r_{H\cdots H} \geqslant 1.6$ Å) [50].

3.3. Synthesis and characterization of $[(\eta^3\text{-triphos})ReCl_3]$ (5)

The straightforward reaction of $[Re(MeCN)Cl_3(PPh_3)_2]$ (**2**) with triphos in refluxing toluene provides a convenient method for the synthesis of the octahedral Re^{III} complex $[(\eta^3\text{-triphos})ReCl_3]$ (**5**) where triphos is a *trihapto* ligand. Complex **5**, which constitutes a key starting material for the synthesis of rhenium(III) complexes with triphos, is obtained as a yellow-green microcrystalline product in almost quantitative yield.

Complex **5** has previously been synthesized through alternative reactions in lower yields [34,51]. However, the ^1H NMR data reported in the literature are evidently incorrect. Complex **5** is paramagnetic with a μ_{eff} (1.8 μ_B), well below the value expected for a high-spin d^4 Re^{III} ion [51]. A similar reduction of μ_{eff} has previously been observed in other Re^{III} derivatives and has been interpreted as a consequence of a large spin-orbit coupling [32,52,53]. The second-order paramagnetism which usually affects $[ReX_3L_3]$ complexes does not allow one to detect any $^{31}P\{^1H\}$ NMR resonance in a spectral window of 100,000 Hz centred at 81.15 MHz, probably as a consequence of rapid ^{31}P relaxation, but this does not much affect the ^1H NMR spectrum (Fig. 2) [54]. Indeed, **5** exhibits a Knight-shifted proton NMR spectrum with sharp resonances like those observed in diamagnetic complexes and with only some of the proton signals at unusually large chemical shifts. The resonances at 5.87 (3H) and 8.30 ppm (6H) are singlets and are assigned to the methyl and methylene protons of the triphos backbone, respectively. These resonances show no resolvable coupling to the three magnetically equivalent triphos phosphorus atoms. The signal at 10.14 ppm (12H), which is the most low-field shifted is a broad doublet and, in keeping with the literature data, is assignable to the *ortho*-phenyl protons of the phosphine [54]. The remaining two absorptions at 8.50 (12H) and 6.96 ppm (6H) are triplets and are assigned to the *meta*- and *para*-protons of the six diphenylphosphino groups, re-

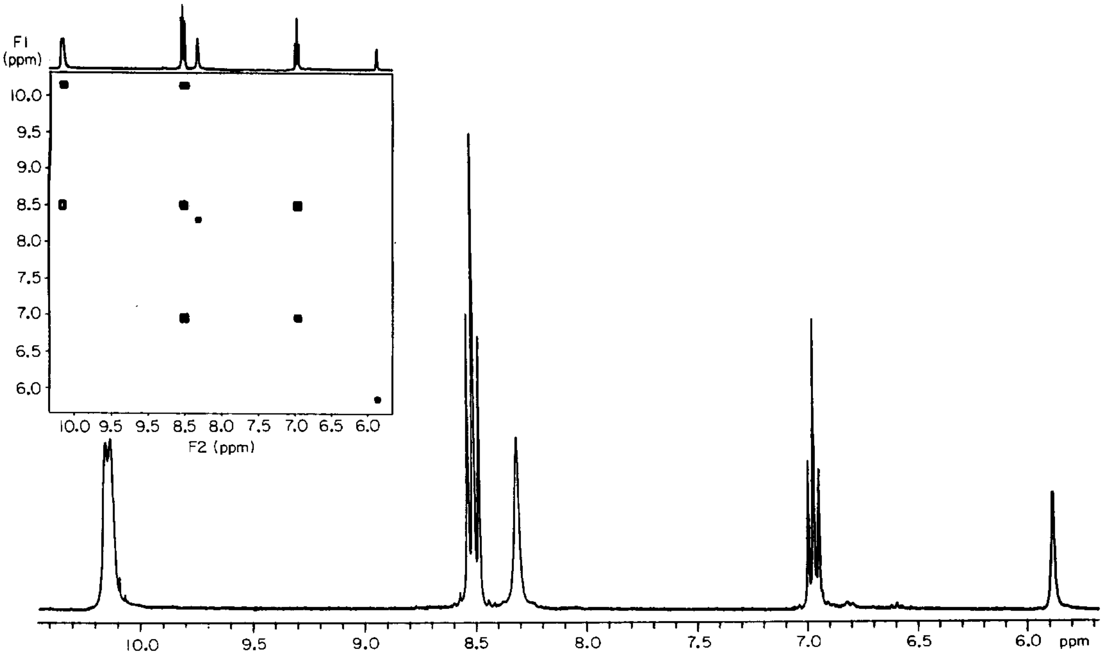


Fig. 2. ^1H NMR spectrum of **5** in CD_2Cl_2 (299.94 MHz, 21°C, TMS reference) including a plot of the 2D-COSY NMR spectrum (top left corner).

spectively. The proposed coupling network has been unambiguously confirmed by a 2D-COSY NMR spectrum (Fig. 2).

Mononuclear rhenium(III) complexes of the formula $[ReX_3L_3]$, where X is a halide and L is a tertiary phosphine, form an extensive class of compounds which invariably possess a *meridional* configuration [1] as ascertained by X-ray crystal structure determinations and IR studies [42,55]. Even in complexes containing polydentate ligands which may adopt either *fac*- or *mer*-configurations, the only observed stereoisomer is the meridional one. As an example, the complexes $[ReCl_3\{PhP(CH_2CH_2PPh_2)_2\}]$ and $[ReCl_3\{PhN(CH_2CH_2PPh_2)_2\}]$, recently described by Crabtree *et al.*, have been assigned a *mer*-configuration [56] although both the tridentate ligands are endowed with sufficient flexibility to stabilize either *fac*- and *mer*-stereoisomers [57]. The peculiar stereochemical requirements of triphos, which, in octahedral complexes, invariably cap a triangular face of the coordination polyhedron, are responsible for the stabilization of *fac*-octahedral Re^{III} complexes. To the best of our knowledge, **5** represents the first octahedral phosphine Re^{III} complex adopting a *facial*-stereochemistry [58*]. A single crystal X-ray diffraction analysis by Walton and coworkers has recently confirmed the *fac*-stereochemistry adopted by the triphos ligand in complex **5** [30].

3.4. Synthesis and characterization of $[(\eta^3\text{-triphos})Re(H)_5]$ (6)

Treatment of **5** in THF at *ca.* 0°C with an excess of $NaBH_4$ in ethanol yields the rhenium(V) pentahydride complex $[(\eta^3\text{-triphos})Re(H)_5]$ (**6**), which can be isolated as a cream solid. Complex **6**, which has been prepared independently by Walton *et al.* by a slightly different procedure [30], exhibits chemico-physical properties consistent with those of the known pentahydride complexes of the formula $[ReH_5L_3]$ ($L = PR_3$ or AsR_3) [1].

The $^{31}P\{^1H\}$ NMR spectrum in THF-d_8 at room temperature consists of a very broad singlet resonance centred at *ca.* 8.8 ppm ($w_{1/2} = 180$ Hz) [59*], that indicates the magnetic equivalence of the three phosphorus atoms. As the temperature is decreased, this broad hump becomes narrower, but no slow exchange spectrum was observed, even at −90°C ($w_{1/2} \approx 20$ Hz). The ^1H NMR spectrum (THF-d_8) in the high field region exhibits a broad quartet (δ −6.35) integrating as five protons. As it has been commonly found in rhenium polyhydride complexes, the five hydride ligands in **6** are magnetically equivalent at room temperature as a consequence of rapid exchange [3,56,60]. As the temperature is decreased, the hydride resonance becomes sharper (at −40°C, δ −6.40, J(HP) 6.6 Hz) and then, below −60°C, broadens significantly. Nevertheless, no decoalescence was obtained, even at the lowest accessible temperature (−90°C).

Since the NMR data do not allow one unambiguously to assign the solution structure of **6**, we decided to carry out variable temperature T_1 measurements. Indeed, in spite of the ambiguity in using the T_1 criterion to determine the presence of nonclassical η^2-H_2 ligands in rhenium polyhydrides, it appears that the T_1 analysis for **6** unequivocally points to a genuine classical structure. A plot of ln T_1 *vs.* $1000/T$ (curve a in Fig. 3) is a well defined "V" curve which gives an estimated minimum value of 240 ms at *ca.* −54°C. This value, scaled to 200 ms for a 250 MHz field, is higher than the $T_{1(\min)}$ values of 78 and 83 ms found for the classical polyhydride $[ReH_5\{PhX(CH_2CH_2PPh_2)_2\}]$ (X = N or P), respectively [56]. Also, it is worth mentioning that classical structures have been established for the strictly related monophosphine

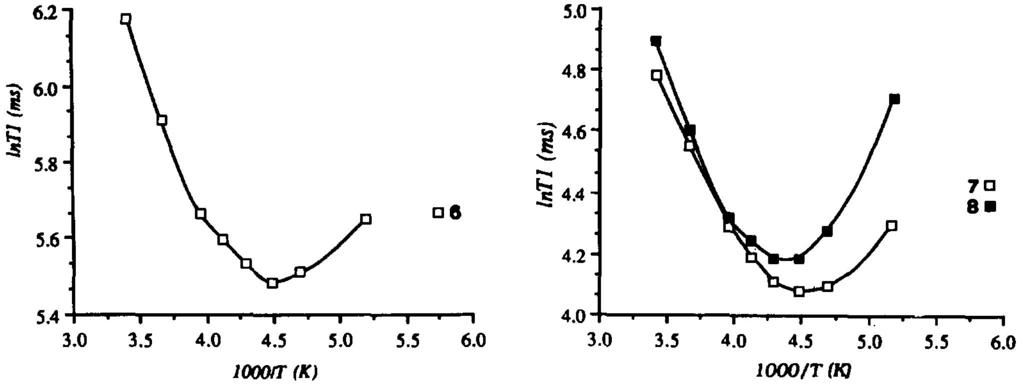


Fig. 3. Plot of ln T_1 *vs.* $1000/T$ for $[(\eta^3\text{-triphos})ReH_5]$ (6), $[(\eta^3\text{-triphos})Re(PPh_3)H_3]$ (7) and $[(\eta^3\text{-triphos})Re(CO)H_3]$ (8).

complexes [ReH$_5$(PPh$_3$)$_3$] [61a,b] and [ReH$_5$(PMePh$_2$)$_3$] [61c] by means of X-ray and neutron diffraction studies.

3.5. Synthesis and characterization of the trihydrides [(η^3-triphos)-Re(PPh$_3$)(H)$_3$] (7) and [(η^3-triphos)-Re(CO)(H)$_3$] (8)

In an effort to get preliminary information on the reactivity of **6**, we have found that, in contrast to the generally observed inertness of Re^{V} pentahydrides [10a], the complex is fairly reactive toward monodentate donors such as PPh$_3$ and CO. These reagents readily induce dihydrogen elimination to give the stable Re^{III} trihydrides [(η^3-triphos)Re(L)H$_3$] (L = PPh$_3$, **7**; CO, **8**). Reaction of **6** with triphenylphosphine occurs in THF at *ca.* 40°C and gives **7** in excellent yield. The same compound can be prepared, although in a lower yield, by the one-pot reaction of **2** with NaBH$_4$ in refluxing THF in the presence of triphos. Complex **7** is obtained as air-stable, off-white crystals, whose chemico-physical properties are in excellent agreement with those reported in the literature [30]. In particular, the proton NMR spectrum of **7** at 20°C in CD$_2$Cl$_2$ shows a narrow doublet of quartets at -7.20 ppm indicating rapid fluxionality in solution. The coupling constant to the PPh$_3$ phosphorus atom ($J(\mathrm{HP}_{\mathrm{PPh}_3}) = 37.8$ Hz) is significatively larger than that to the three equivalent P atoms of triphos ($J(\mathrm{HP}_{\mathrm{triphos}}) = 18.4$ Hz). As the temperature is decreased, the hydride signal broadens, but the decoalescence of this resonance could not be obtained even at the lowest attainable temperature (-90°C). In a similar way, the ^{31}P{^{1}H} NMR spectrum, which consists of a first order A$_3$X splitting pattern at room temperature, cannot be frozen out, confirming that a low-energy scrambling of the hydride ligands also occurs at very low temperature.

The novel carbonyl complex [(η^3-triphos)Re(CO)(H)$_3$] (**8**) can be synthesized as air-stable off-white crystals by reaction of carbon monoxide (1 atm, 20 min) with **6** in warm THF (40°C). The IR spectrum of **8** contains a very strong ν(CO) absorption at 1854 cm^{-1} and two broad and weaker ν(Re–H) bands at 1961 and 1923 cm^{-1}. The ^{1}H NMR spectrum of **8** (CD$_2$Cl$_2$, 20°C) exhibits a binomial quartet for the hydride resonance (δ -6.08, J(HP) 11.2 Hz) integrating as three protons. Again, decreasing the temperature causes significant broadening of the resonance, but the slow-motion regime cannot be observed even at -90°C. In contrast, the complete decoalescence of the phosphorus resonances is observed at -85°C. At this temperature the ^{31}P{^{1}H} NMR spectrum consists of a well resolved first-order A$_2$M pattern, indicating that the fluxional process which averages the chemical environment of the phosphorus atoms of triphos has been slowed down significantly. On increasing the temperature, the two signals lose their multiplicity and then coalesce into a broad hump centred at the weighted averaged position (at 20°C, δ -2.1) of the slow-exchange regime. The lower fluxionality exhibited by **8** as compared to **7** is attributed to the presence of the π-acceptor CO ligand that, by diminishing the electron density on the metal, favours a stronger coordination of the *trans* phosphorus atom.

TABLE 3. Variable-temperature ^{1}H NMR relaxation time (T_1) measurements on the hydride resonance of rhenium polyhydride complexes **6**–**8** at 300 MHz

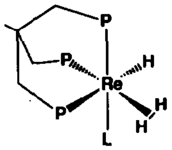
T (°C)	T_1 (ms)		
	6 [a]	**7** [b]	**8** [b]
20	485	134	120
0	370	100	95
−20	287	75	74
−30	270	70	67
−40	253	66	61
−50	240	66	59
−60	246	72	60
−80	282	111	74

[a] In THF-d_8. [b] In CD$_2$Cl$_2$.

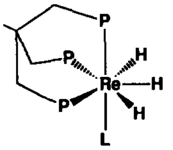
Variable-temperature longitudinal relaxation (T_1) measurements on complexes **7** and **8** (Table 3) do not provide conclusive evidence for the solution structure of the two complexes. Indeed, plots of ln T_1 *vs.* $1000/T$ (see curves b and c in Fig. 3), have a well defined "V" shape from which quite similar $T_{1(\mathrm{min})}$ values for the two complexes (*ca.* 66 and 60 ms, respectively) can be calculated. Again, these values, although intrinsically short, suffer from the uncertainty which affects T_1 measurements on rhenium polyhydrides. Values as short as 60 ms (50 ms at 250 MHz) may be the consequence of an efficient rhenium–hydride dipole–dipole relaxation mechanism and thus may well account for classical hydride formulations.

Re^{III} hydrides of the general formula [ReH$_3$(L)(PR$_3$)$_3$], like **7** and **8**, have been widely studied [62] and their solution NMR properties have been compared and contrasted with those of the isoelectronic cationic Os^{II} complexes [OsH$_3$(L)$_4$]$^+$ (L = monodentate or bidentate phosphines) for which the existence of both classical trihydride species and nonclassical hydride-dihydrogen tautomers has been recognized [48,49,63]. In addition, Morris and coworkers have recently described the osmium trihydride complex *trans*-[Os(H $\cdots$ H)H(depe)$_2$] (depe = PEt$_2$CH$_2$CH$_2$PEt$_2$) as lying on the borderline between classical and nonclassical structure [63].

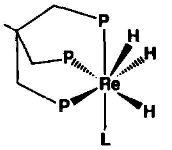
In conclusion, no definitive coordination stereochemistry can be assigned to **7** and **8**, which may be formulated either as nonclassical six-coordinate octahedral hydride-molecular hydrogen complexes (IV) or as classical seven-coordinate trihydride complexes. In the latter case, two different structures are consistent with the spectral analysis: a pentagonal bipyramid (V) and a monocapped octahedron (VI) with a hydride ligand capping one of the triangular faces of the coordination polyhedron. Indeed, a structure of type V has been proposed for $[ReH_3(dppe)_2]$ on the basis of solution NMR studies [63], while a pentagonal bipyramidal geometry has been authenticated in the solid state by X-ray methods for $[ReH_3(dppe)_2]$ [64] (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[ReH_3(PPh_3)_4]$ [42].



IV



V



VI

4. Conclusions

We have prepared and characterized a family of rhenium polyhydrides stabilized by the stereochemically restrictive ligand triphos. This tripodal polyphosphine may act either as a bidentate ligand, thus allowing coordination of as many as seven hydrides to rhenium as in $[(\eta^2\text{-triphos})ReH_7]$ (**4**), or it may cap one face of the coordination polyhedron to form the Re^V complex $[(\eta^3\text{-triphos})ReH_5]$ (**6**). The latter compound reacts with monodentate donors to yield substitution products via reductive elimination of H_2.

The T_1 criterion is not a reliable tool for distinguishing definitively between classical and non-classical tautomers of rhenium polyhydrides. Only in case of the pentahydride **6** does the long $T_{1(\min)}$ value (240 ms) unambiguously indicate the presence of a genuine classical pentahydride species in solution.

Complexes **4** and **6**–**8** are highly reactive and their chemistry is presently being studied. In particular, reactions with different electrophiles are under investigation, as they are expected to produce new examples of cationic polyhydride complexes containing either classical and non-classical H_2 ligands [9b,62], with potential applications in catalytic reactions [65].

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