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New complexes of the *fac*-{(CO)₃Re⁺} fragment bearing a diaminediphosphine ligand

Sandra Bolaño, Jorge Bravo*, Jesús Castro, Soledad García-Fontán**, Mª Carmen Marín

Departamento de Química Inorgánica, Universidade de Vigo, Lagoas-Marcosende, E-36310 Vigo, Spain

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1. Introduction

Rhenium coordination chemistry is a well established field [1], but a renewed interest has lately emerge due, particularly in the case of the fac-{(CO)₃Re⁺} fragment [2], to its photochemical properties [3] and to the introduction of the β^- emitting isotopes ¹⁸⁸Re and ¹⁸⁶Re in the field of diagnostic and therapeutic radiopharmaceuticals [4], being the above mentioned fragment, one of the most promising and developed organometallic cores for the labelling of biomolecules [5]. The metal centre (in the low oxidation state +I) is chemically highly inert and it permits the application of a broad variety of donor and acceptor atoms [6]. Besides, the [Re(CO)₃] core is exceedingly compact, displaying an almost spherical shape. If the octahedral coordination sphere is "closed" with an appropriate coligand system, the metal centre will be efficiently protected against further ligand attack or re-oxidation. On the other hand, such co-ligands are necessary to complete the coordination sphere of the metal and allow the tuning of both steric and electronic properties of the resulting labelled biomolecules. One of the areas we focus on in the field of rhenium coordination chemistry is the study of the influence of bidentate phosphinite co-ligands on the properties of different rhenium-carbonyl complexes [7]. In this paper we report on the synthesis and spectroscopic and diffractometric characterisation of the hydrido, triflato and chlorido complexes of the fac-{(CO)₃Re⁺} fragment bearing a diaminediphosphine ligand, with the aim of analysing how the presence of nitrogen atoms (in-

ABSTRACT

The mono- and binuclear hydride compounds fac-[ReH(CO)₃L] (**1a**) and [{ReH(CO)₄}₂(μ -L)] (**1b**) have been prepared by reaction of [ReH(CO)₅] with Ph₂PN(CH₃)(CH₂)₂N(CH₃)PPh₂ (**L**) under UV light. Protonation reactions of the hydride compound **1a** with equimolar amounts of HSO₃CF₃ or HCl yielded the triflato or the chlorido compounds fac-[Re(OSO₂CF₃)(CO)₃L] (**2**) and fac-[ReCl(CO)₃L] (**3**), respectively. The compounds have been characterised by elemental analysis, IR and NMR spectroscopic data, and mass spectrometry. Their structures have been confirmed by X-ray crystallography.

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stead of the oxygen atoms in the phosphinite ligands) influences on the properties of the complexes.

2. Experimental

2.1. General methods and instrumentation

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques. All the solvents were purified by conventional procedures [8] and distilled prior to use. The ligand *N*,*N*′-dimethyl-bis(diphenylphosphine)ethylenediamine (**L**) was prepared according to published methods [9]. Photoirradiation was carried out with a 150 W medium-pressure Hg lamp. The ¹H, ³¹P, ¹³C and ¹⁹F NMR (δ in ppm) spectra were obtained on a Bruker ARX-400 spectrometer operating at frequencies of 400, 161, 100, and 376 MHz, respectively; the spectra were recorded in CDCl₃ or CD₂Cl₂ solutions, as indicated, using the solvent as internal lock. 1H and $^{13}C\{^1H\}$ signals are referred to internal TMS, those of $^{19}F\{^1H\}$ to CFCl₃ and those of $^{31}P\{^1H\}$ to 85% H₃PO₄, with downfield shifts (δ in ppm) considered positive. Low-temperature measurements were made by cooling the probe with a stream of cold N₂ (g) from a liquid N_2 boil off evaporator. T_1 relaxation times for the hydridic resonances of complexes 1a and 1b were measured in dichloromethane- d_2 as a function of temperature at 400 MHz using a standard inversion-recovery methodology. IR spectra (KBr discs) were obtained on a Bruker VECTOR IFS 28 FT apparatus and mass spectra were recorded on Micromass Autospec MLSIMS (FAB⁺) system. Microanalyses were carried out on a Fisons Model EA 1108 elemental analyzer.





^{*} Corresponding author. Tel.: +34 986812275; fax: +34 986813798.

^{**} Corresponding author. Tel.: +34 986812275; fax: +34 986813798.

E-mail addresses: jbravo@uvigo.es (J. Bravo), sgarcia@uvigo.es (S. García-Fontán).

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2.2. Preparation of fac-[ReH(CO)₃L] (**1a**) and [{ReH(CO)₄}₂(μ -L)] (**1b**)

Ph₂PN(CH₃)(CH₂)₂N(CH₃)PPh₂ (L) (3 g, 6.72 mmol) was added to a solution of [ReH(CO)₅] (1 g, 3.06 mmol) in toluene (40 mL) and the reaction mixture was irradiated with UV light at room temperature for about 6 h. The solvent was then removed under reduced pressure to give a yellow oil which was chromatographed on a silica gel column (length 70 cm, diameter 4 cm) using a 10:2 mixture light petroleum (b.p. 40–60 °C) and diethyl ether as eluent. The first fraction eluted (30 mL) was evaporated to dryness leaving and oil which was treated with ethanol (3 mL). By cooling the resulting solution to -25 °C white crystals of the mononuclear compound **1a** were obtained. The binuclear compound **1b** was obtained from the second fraction eluted (30 mL), after evaporation of the solvent and treatment of the oily residue obtained with ethanol.

2.2.1. fac-[ReH(CO)₃L] (1a)

Yield ≥ 50%. *Anal.* Calc. for C₃₁H₃₁N₂O₃P₂Re (727.72): C, 51.16; H, 4.29; N, 3.85. Found: C, 51.12; H, 4.27; N, 3.84%. FAB MS: *m/z* (referred to the most abundant isotopes): 727 [M], 671 [M–2CO], 669 [M–H–2CO]. IR (cm⁻¹) v_{CO} : 2004 (s), 1921 (s), 1908 (s). ¹H NMR (CD₂Cl₂, ppm): δ –3.99 (t, 1H, *J*_{HP} = 23 Hz, ReH), 2.43 (t, 6H, *J*_{HP} = 4 Hz, –NCH₃), 3.10 (m, 2H, –CH₂), 3.82 (m, 2H, –CH₂), 7.14–7.91 (m, 20H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, ppm): δ 68.5 (s). ¹³C{¹H} NMR (CD₂Cl₂, ppm): δ 39.4 (s, –CH₃), 53.4 (s, –CH₂), 126.3–139.4 (m, Ph), 194.2 (t, *J*_{CP} = 6 Hz, CO_{cis}), 196.3 (m, CO_{trans}). Suitable crystals for X-ray structure analysis were obtained by slow evaporation of the solvent from a solution of **1a** in a 2:10 (v/v) CH₂Cl₂/EtOH mixture.

2.2.2. [{ $ReH(CO)_4$ }₂(μ -L)] (**1b**)

Yield \geq 10%. Anal. Calc. for $C_{36}H_{32}N_2O_8P_2Re_2$ (1054.98): C, 40.99; H, 3.06; N, 2.65. Found: C, 40.93; H, 3.10; N, 2.69%. FAB

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MS: *m*/*z* (referred to the most abundant isotopes): 1055 [M], 1053 [M–2H], 1025 [M–2H–CO], 997 [M–2H–2CO], 968 [M–2H–3CO], 940 [M–2H–4CO], 912 [M–2H–5CO]. IR (cm⁻¹) *v*_{CO}: 2077 (s), 1962 (s), 1940 (s). ¹H NMR (CD₂Cl₂, ppm): δ –5.35 (d, 2H, *J*_{HP} = 22 Hz, ReH), 2.49 (d, 6H, *J*_{HP} = 11 Hz, -NCH₃), 3.16 (m, 4H, -CH₂], 7.19–7.73 (m, 20H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, ppm): δ 72.5 (s). ¹³C{¹H} NMR (CDCl₃, ppm): δ 37.5 (s, -CH₃), 51.4 (t, *J*_{CP} = 6 Hz, -CH₂), 127.9–136.9 (m, Ph), 188.2 (d, *J*_{CP} = 46 Hz, *trans* CO–P), 189.2 (d, *J*_{CP} = 10 Hz, *trans* CO–H), 189.8 (d, *J*_{CP} = 7 Hz, *trans* CO–CO). Suitable crystals for X-ray structure analysis were obtained by slow evaporation of the solvent from a solution of **1b** in a 2:10 (v/v) CH₂Cl₂/EtOH mixture.

2.3. Preparation of $fac-[Re(OSO_2CF_3)(CO)_3L]$ (2)

To a solution of $[ReH(CO)_3L]$ (1a) (50 mg, 0.07 mmol) in CH₂Cl₂ (15 mL), cooled to -80 °C, an equimolar amount of HSO₃CF₃ (7 μ L, 0.07 mmol) in CH₂Cl₂ was added. The mixture was allowed to reach room temperature and was stirred for 1 h. The solvent was evaporated to dryness leaving an oil which was triturated with ethanol (2 mL) until a white solid separated off. This solid was filtered out, washed with ethanol and dried under vacuum. Suitable crystals for X-ray structure analysis were obtained by slow evaporation of the solvent from a solution of **2** in a 2:10 (v/v) CH₂Cl₂/ EtOH mixture. Yield: 94%. Anal. Calc. for C₃₂H₃₀SF₃N₂O₆P₂Re (875.78): C, 43.89; H, 3.45; N, 3.20. Found: C, 43.79; H, 3.39; N, 3.27%. FAB MS: m/z (referred to the most abundant isotopes): 876 [M], 819 [M-2CO], 727 [M-SO₃CF₃]. IR (cm⁻¹) v_{CO} : 2038 (s), 1959 (s), 1929 (s). ¹H NMR (CD₂Cl₂, ppm): δ 2.52 (t, 6H, J_{HP} = 4 Hz, -NCH₃), 3.15 (m, 2H, CH₂), 3.67 (m, 2H, -CH₂), 7.21-7.85 (m, 20H, Ph). ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, ppm): δ 62.4 (s); ${}^{19}F{}^{1}H{}$ NMR (CD₂Cl₂, ppm): δ -78.0 (s); ¹³C{¹H} NMR (CDCl₃, ppm): δ 39.3 (t, J_{CP} = 3 Hz, -CH₃), 51.7 (t, J_{CP} = 7 Hz, -CH₂), 125.3 (s, CF₃), 127.2–135.6 (m, Ph), 188.3 (t, J_{CP} = 6 Hz, CO_{cis}), 190.0 (m, CO_{trans}).

	1a	2	3
Empirical formula	C ₃₁ H ₃₁ N ₂ O ₃ P ₂ Re	$C_{32}H_{30}F_{3}N_{2}O_{6}P_{2}ReS$	C ₃₁ H ₃₀ ClN ₂ O ₃ P ₂ Re
Formula weight	727.72	875.78	762.16
Crystal size (mm)	$0.39 \times 0.38 \times 0.25$	$0.22\times0.14\times0.08$	$0.22\times0.13\times0.11$
T (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c	C2/c
a (Å)	10.5523(7)	37.306(3)	25.5482(16)
b (Å)	9.6130(6)	10.3552(7)	15.7749(10)
<i>c</i> (Å)	30.210(2)	18.8577(13)	17.2456(11)
β (°)	94.6020(10)	105.070(1)	117.894(1)
$V(\dot{A}^3)$	3054.6(3)	7034.4(9)	6142.8(7)
Z	4	8	8
D_{calc} (Mg m ⁻³)	1.582	1.654	1.648
$\mu (\mathrm{mm}^{-1})$	4.116	3.665	4.182
F(0 0 0)	1440	3456	3008
θ Range for data collection (°)	2.10-28.04	2.05-28.02	1.57-28.05
Index ranges	$-11 \leqslant h \leqslant 13$	$-48\leqslant h\leqslant 48$	$-16 \leqslant h \leqslant 33$
	$-12 \leqslant k \leqslant 12$	$-13 \leqslant k \leqslant 11$	$-19 \leqslant k \leqslant 20$
	$-39 \leqslant l \leqslant 37$	$-24 \leqslant l \leqslant 24$	$-22 \leqslant l \leqslant 22$
Reflections collected	18 423	19 103	17 537
Independent reflections (R_{int})	7161(0.0510)	7884(0.0878)	6955(0.0744)
Reflections observed (> 2σ)	5429	3389	3284
Data completeness	0.968	0.927	0.933
Maximum and minimum transmission	1.000 and 0.708	1.000 and 0.710	1.000 and 0.816
Data/restraints/parameters	7161/0/358	7884/0/426	6955/17/353
Goodness-of-fit (GOF) on F ²	0.911	0.689	0.812
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0311, wR_2 = 0.0530$	$R_1 = 0.0481, wR_2 = 0.0538$	$R_1 = 0.0499, wR_2 = 0.0618$
R indices (all data)	$R_1 = 0.0503, wR_2 = 0.0564$	$R_1 = 0.1626, wR_2 = 0.0708$	$R_1 = 0.1409, wR_2 = 0.0724$
Largest diff. peak and hole (e $Å^{-3}$)	0.922 and -1.212	1.036 and -0.932	1.531 and -0.776

Table 2

Crystal	data	and	structure	refinement	for	1b.	
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	1b
Empirical formula	C36H32N2O8P2Re2
Formula weight	1054.98
Crystal size (mm)	$0.28\times0.25\times0.16$
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.6370(6)
<i>b</i> (Å)	16.4673(12)
<i>c</i> (Å)	13.7691(10)
β (°)	104.5110(10)
$V(Å^3)$	1895.9(2)
Ζ	2
D_{calc} (Mg m ⁻³)	1.848
$\mu (\mathrm{mm}^{-1})$	6.514
F(0 0 0)	1012
θ Range for data collection (°)	1.97-28.04
Index ranges	$-9 \leqslant h \leqslant 11$
	$-21 \leqslant k \leqslant 21$
	$-16 \leqslant l \leqslant 18$
Reflections collected	11 563
Independent reflections (R _{int})	4455(0.0623)
Reflections observed (> 2σ)	3309
Data completeness	0.967
Maximum and minimum transmission	1.000 and 0.549
Data/restraints/parameters	4455/0/231
Goodness-of-fit (GOF) on F^2	0.895
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0319, wR_2 = 0.0583$
R indices (all data)	$R_1 = 0.0509, wR_2 = 0.0616$
Largest difference peak and hole (e $Å^{-3}$)	1.515 and -0.746

2.4. Preparation of $fac-[ReCl(CO)_3L]$ (3)

To a solution of $[ReH(CO)_3L]$ (**1a**) (0.15 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) cooled to -80 °C an equimolar amount of HCl was added and the reaction mixture, brought to room temperature, was stirred for 2 h. The solvent was evaporated to dryness leaving an oil which was triturated with ethanol (2 mL). The white solid obtained was filtered out and recrystallised from a mixture CH₂Cl₂/EtOH by slow evaporation of the solvent. Yield: 86%. *Anal.* Calc. for C₃₁H₃₀ClO₃P₂N₂Re (762.16): C, 48.85; H, 3.99; N, 3.67. Found: C, 48.80; H, 3.92; N, 3.52%. FAB MS: *m/z* (referred to the most abundant isotopes): 762, [M]; 734, [M–CO]; 699, [M–Cl–CO]. IR (cm⁻¹) v_{CO} : 2030 (vs), 1966 (m), 1932 (vs). ¹H NMR (CD₂Cl₂)

ppm): δ 2.52 (t, 6H, J_{HP} = 4 Hz, -NCH₃), 3.15 (m, 2H, -CH₂), 4.27 (m, 2H, -CH₂), 7.25-8.13 (m, 20H, Ph); ³¹P{¹H} NMR (CD₂Cl₂, ppm): δ 56.2 (s); ¹³C{¹H} NMR (CDCl₃, ppm): δ 39.3 (t, J_{CP} = 3 Hz, -CH₃), 52.5 (t, J_{CP} = 7 Hz, -CH₂), 127.1-136.6 (m, Ph), 187.2 (t, J_{CP} = 6 Hz, *cis* CO), 190.5 (m, *trans* CO). Suitable crystals for X-ray structure analysis were obtained by slow evaporation of the solvent from a solution of **3** in a 2:10 (v/v) CH₂Cl₂/EtOH mixture.

2.5. X-ray crystallographic analysis

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo K α radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART [10] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [11] for integration of intensity of reflections and scaling, and SADABS [12] for empirical absorption correction. The structures were solved and refined with the O^{scail} program [13] by direct methods (1a, 1b, and **2**) or by Patterson methods (**3**) and refined by a full-matrix least-squares based on F^2 [14]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters except in the case of those bonded to the metal (1a and 1b). In the case of compound 3 one of the phenyl groups is disordered over two positions with occupancy factor of 54:46%. Details of crystal data and structural refinement are given in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis and spectroscopic characterisation of fac-[ReH(CO)₃L] (**1a**) and [{ReH(CO)₄}₂(μ -L)] (**1b**)

Reaction of $[ReH(CO)_5]$ with $Ph_2PN(CH_3)(CH_2)_2N(CH_3)PPh_2$ (L) in 1:2 mole ratio gave a 2:1 mixture of two products that were subsequently separated by column chromatography. The mayor component was identified as the mononuclear compound *fac*-[ReH(CO)_3L] (**1a**) and the minor component as the binuclear compound [$[ReH(CO)_4]_2(\mu-L)$] (**1b**).

At 298 K, the ³¹P{¹H} NMR spectrum of **1a** displays a singlet at δ 68.5 ppm and the ¹H NMR spectrum displays a triplet at –3.99 ppm (J_{HP} = 23 Hz). The signals corresponding to the methylene protons of the bidentate ligand L appear as two multiplets



Fig. 1. Molecular structure of compound 1a.

(at 3.10 and 3.82 ppm) indicating their diastereotopic nature, as it was already observed for similar systems [9b]. The ${}^{13}C{}^{1}H$ spectrum shows, at low field, a triplet (194.2 ppm, $J_{CP} = 6$ Hz) assignable to the CO group located *cis* to both phosphorous nuclei, and a multiplet (196.3 ppm) corresponding to the other two CO groups, supporting the formulation of compound **1a** as the *fac* isomer of [ReH(CO)₃L]. The value of T_1 (min) found for the hydrido signal was 207 ms (227 K) at 400 MHz.

The room temperature ³¹P{¹H} NMR spectrum of the binuclear compound **1b** shows a singlet at 72.5 ppm, indicating the magnetic equivalence of the two phosphorous nuclei of the bridging ligand. The ¹H NMR spectrum of **1b** displays a doublet at high field (-5.35 ppm, J_{HP} = 22 Hz). The appearance of the methylene protons signal as a single narrow multiplet at 3.16 ppm suggests that in **1b** the environment of these nuclei is more uniform than in **1a**, probably due to the presence of the more restrictive chelating ligand in **1a**. In agreement with these results, the ¹³C{¹H} spectrum shows, at low field, three doublets attributable to the CO groups: one at 188.2 ppm (J_{CP} = 46 Hz) corresponding to the CO *trans* to P atom,



Fig. 2. Molecular structure of compound 2.

one at 189.2 ppm (J_{CP} = 10 Hz) that is assignable to CO *trans* to the H atom and one at 189.8 ppm (J_{CP} = 7 Hz) corresponding to the mutually *trans* CO groups (this signal integrates to approximately double than the previous one). Determination of the minimum spin-lattice relaxation time [T_1 (min)] for the hydrido nucleus at 400 MHz by the standard inversion-recovery method gave a value of 372 ms at 230 K. This value is significantly higher than that obtained for compound **1a**, possibly due to their having different numbers of P nuclei in the vicinity of the hydrido ligand [15]. This fact was already observed for similar rheniumhydridocarbonyl compounds bearing diphosphinites as supporting ligands [7c].

3.2. Synthesis and spectroscopic characterisation of fac-[$Re(OSO_2CF_3)$ (CO_3L] (2)

Protonation of the hydride [ReH(CO)₃L] (**1a**) with HSO₃CF₃ in 1:1 mole ratio leads to the formation of the triflate complex [Re(-OSO₂CF₃)(CO)₃L] (**2**), with releasing of H₂(g). Compound **2** was stable in solid state at room temperature. The IR spectrum shows three strong bands at 2038, 1959 and 1929 cm⁻¹ that can be assigned to the CO stretching vibrations. The ³¹P{¹H} NMR spectrum shows a single resonance indicating the magnetic equivalence of the two phosphorus nuclei. In keeping with the *fac* arrangement of the CO ligands, the ¹³C{¹H} spectrum shows two low-field signals assignable to the CO groups: a triplet corresponding to the CO group located *cis* to both phosphorous nuclei (189 ppm, $J_{CP} = 6$ Hz), and a multiplet (190 ppm) corresponding to the other two CO ligands.

3.3. Synthesis and spectroscopic characterisation of fac-[ReCl(CO)₃L] (3)

Reaction of fac-[ReH(CO)₃L] (**1a**) with an equimolar amount of HCl afforded fac-[ReCl(CO)₃L]. The new complex is stable in the solid state and in solution at room temperature, and was characterised by the usual spectroscopic techniques. The IR spectrum shows three strong v(CO) bands characteristic of the fac-Re^I(CO)₃ fragment [16] at 2030, 1966 and 1932 cm⁻¹. The ¹H NMR spectrum of 3 shows two multiplets located at 3.15 ppm and 4.27 ppm corresponding to the methylene protons of the bidentate ligand. The ¹³C{¹H} NMR spectrum shows two low field signals assignable to the CO groups: a triplet corresponding to the CO group located



Fig. 3. Molecular structure of compound 3.

Table 3	
Selected bond lengths (Å) and angles (°) for complexes 1a 2 and 3	

	1a	2	3
Re-A ^a	1.89(3)	2.230(4)	2.537(2)
Re-C(1)	1.955(4)	1.829(9)	1.858(9)
Re-C(2)	1.918(4)	1.902(8)	1.890(9)
Re-C(3)	1.927(4)	1.920(8)	1.897(8)
Re-P(1)	2.4532(9)	2.486(2)	2.457(2)
Re-P(2)	2.4595(9)	2.514(2)	2.498(2)
C(1)-O(1)	1.145(4)	1.201(8)	1.187(8)
C(2)-O(2)	1.150(4)	1.167(8)	1.168(8)
C(3)-O(3)	1.139(4)	1.164(8)	1.170(8)
P(1)-N(1)	1.663(3)	1.640(6)	1.6534
P(2)-N(2)	1.705(3)	1.697(6)	1.7015
S(1)-O(13)		1.401(6)	
S(1)-O(12)		1.415(5)	
S(1)-O(11)		1.468(4)	
C(1)-Re-A ^a	175.0(9)	176.9(3)	175.0(2)
C(2)–Re–A	82.6(9)	91.7(3)	84.8(2)
C(3)–Re–A	87.4(9)	92.0(3)	90.0(2)
A-Re-P(1)	89.4(9)	89.8(1)	90.18(7)
A-Re-P(2)	90.4(9)	94.1(1)	96.21(7)
C(1)-Re-P(1)	93.7(1)	91.9(2)	90.1(2)
C(1)-Re-P(2)	93.5(1)	88.4(3)	88.8(2)
C(2)-Re-P(1)	93.0(1)	90.9(2)	90.3(2)
C(2)-Re-P(2)	172.4(1)	173.9(3)	175.2(2)
C(3)-Re-P(1)	175.9(1)	177.8(2)	179.7(3)
C(3)-Re-P(2)	87.4(1)	88.0(2)	85.5(2)
C(1)-Re-C(2)	93.3(2)	85.7(3)	90.2(3)
C(1)-Re-C(3)	89.6(2)	86.3(3)	89.8(3)
C(2)-Re-C(3)	89.1(2)	90.1(3)	89.9(3)
P(1)-Re-P(2)	90.08(3)	90.83(7)	94.36(6)
O(1)-C(1)-Re(1)	173.9(4)	173.4(7)	176.9(8)
O(2)-C(2)-Re(1)	174.7(4)	175.9(8)	176.4(7)
O(3)-C(3)-Re(1)	178.5(4)	176.6(8)	178.3(8)
P(1)-N(1)-C(51)	121.0(3)	121.8(5)	115.2
P(1)-N(1)-C(52)	123.1(2)	123.7(5)	122.4
C(51)-N(1)-C(52)	115.8(3)	114.2(6)	122.0
P(2)-N(2)-C(53)	120.3(2)	122.7(4)	124.6
P(2)-N(2)-C(54)	117.7(2)	117.8(5)	118.8
C(53)-N(2)-C(54)	107.4(3)	108.0(6)	104.8

^a A represents the hydride atom (compound **1a**), the donor oxygen O(11) atom (compound **2**), or the chloride atom (compound **3**).

cis to both phosphorus nuclei (\sim 187 ppm; *J*_{CP} \sim 7 Hz), and a multiplet (\sim 190 ppm) corresponding to the other two CO ligands.

3.4. Description of the structures

Figs. 1–3 show ORTEP drawings of compounds 1a, 2, and 3 with the numbering scheme. Selected bond lengths and bond angles are listed in Table 3. All the compounds consist of a rhenium(I) atom in an octahedral environment, coordinated by three carbonyl ligands facially disposed and two phosphorous atoms from the bidentate *N*,*N*'-dimethyl-bis(diphenylphosphino)ethylenediamine ligand The remaining coordination position is occupied by a hydrido (compound **1a**), triflato (compound **2**) or chlorido (compound **3**) ligand. The Re-P bond lengths range from 2.4532(9) to 2.514(2) Å. For each compound the two distances are similar, with differences lower than 0.05 Å, being the average of these distances shorter for the hydrido compound (1a) and longer for the triflato compound (2). The Re–C bond lengths *trans* to the phosphorus atoms range from 1.891(9) to 1.927(4) Å. All these values are similar to those reported for the bromo derivative [ReBr(CO)₃{Ph₂PN(Me)CH₂CH₂(Me)-NPPh₂}] [9b] but, in contrast with what was observed in the bromo analogue, the shorter Re-P bond has, as expected, the longer Re-C bond trans to it.

The remaining Re–C bond lengths have values of 1.955(4) Å (for compound **1a**), 1.829(9) Å (for compound **2**), and 1.855(9) Å (for compound **3**), reflecting the π -donor ability of the anionic ligands *trans* to them (triflato > chlorido > hydrido).

The seven-membered chelate ring adopts, in all cases, a boat shape with P-Re-P angles ranging from 90.08(3)° to 94.32(6)°. Considering the equatorial plane as that described by the Re(1)-P(1)-P(2)-C(2)-C(3) atoms the chelate ring is twisted towards the anionic ligand in all cases. That plane is more regular in the case of the chlorido complex (3) [Rms deviation of 0.008 Å vs 0.034 and 0.037 Å for compounds **1a** and **2**, respectively]. The rhenium atom is located below this plane by 0.096(2) Å, for compound 1a, and above this plane by 0.012(3) and 0.072(3) Å, for compounds 2 and 3, respectively. This fact is probably due to the lower steric requirements of the hydride ligand. Remarkably, and in a similar way with what was reported for the related bromo complex [9b], each of the three complexes presents one of the nitrogen atoms, N(1), virtually planar [sum of angles of 359.9(3)°, 359.6° and $359.7(6)^{\circ}$ respectively], while the other one, N(2), is pyramidal [sum of angles: 345.4(3)°, 348.2° and 348.5(6)° respectively]. Also this is accompanied by a slight shortening of the P(1)-N(1) dis-



Fig. 4. Molecular structure of compound 1b.

Table 4

Selected bond lengths (Å) and angles (°) for 1b.

Re-C(1)	1.960(6)	Re-C(2)	1.962(6)
Re-C(3)	1.955(6)	Re-C(4)	1.948(5)
Re-H(1)	1.61(6)	Re-P(1)	2.443(1)
C(1)-O(1)	1.150(6)	C(2)-O(2)	1.137(6)
C(3)-O(3)	1.150(6)	C(4)-O(4)	1.143(6)
N(1) - P(1)	1.705(4)		
H(1)-Re-C(1)	83(2)	H(1)-Re-C(2)	174(2)
H(1)-Re-C(3)	93(2)	H(1)-Re-C(4)	83.8(2)
H(1)-Re-P(1)	87(2)	C(1)-Re-P(1)	89.2(1)
C(2) - Re - P(1)	96.6(1)	C(3)-Re-P(1)	90.6(1)
C(4) - Re - P(1)	170.9(2)	C(1)-Re- $C(2)$	92.3(2)
C(1)-Re- $C(3)$	175.7(2)	C(1)-Re- $C(4)$	89.6(2)
C(2)-Re- $C(3)$	92.0(2)	C(2)-Re- $C(4)$	92.4(2)
C(3)-Re- $C(4)$	89.9(2)	Re-C(1)-O(1)	177.8(4)
Re-C(2)-O(2)	177.8(5)	Re-C(3)-O(3)	177.7(5)
Re-C(4)-O(4)	178.1(6)	C(31)-N(1)-C(32)	112.0(3)
C(31)-N(1)-P(1)	114.3(3)	C(32)-N(1)-P(1)	114.7(3)

tances [1.663(3), 1.6534 and 1.640(6) Å] as compared to the P(2)–N(2) distances [1.705(3), 1.7015 and 1.697(6) Å]. This feature contrasts with what was observed for Pt(II) [17] or Pd(II) [18] complexes with a similar bidentate aminophosphine ligands where both nitrogen atoms are planar.

Fig. 4 shows the ORTEP drawing of the binuclear compound **1b**, with the numbering scheme. Selected bond lengths and bond angles are listed in Table 4.

Compound **1b** crystallised in the centro-symmetric $P2_1/c$ monoclinic space group with a symmetry centre situated in the midpoint of the carbon–carbon bond of the bidentate aminophosphine ligand *N*,*N*'-dimethyl-bis(diphenylphosphino)ethylenediamine. This ligand is bridging two identical (crystallographically imposed) [Re(CO)₄H] fragments. The coordination polyhedra are slightly distorted octahedra. The Re–C distances range from 1.948(5) to 1.962(6) Å. It is noteworthy the small differences between these distances, taking into account the different nature of the respective *trans* groups (CO, H or P). The Re–P(1) bond length [2.443(1) Å] is clearly shorter than those found for compounds **1a**, **2**, and **3**. This feature contrasts with that found for similar systems involving phosphinite ligands acting either as chelating or bridging ligands [7c] or other aminophosphine ligands [19].

The *cis* angles around the rhenium atom range from $83(2)^{\circ}$ to $96.6(2)^{\circ}$, showing a significant irregularity of the octahedron. The most important source of distortion is the position of the phosphorus atom, which is tilted towards the hydrido ligand; as a result, the phosphorus atom, instead of being in the plane defined by the C(1), C(3) and C(4) carbon atoms, is 0.22(1) Å out of this plane. The rhenium atom is located on the other side of this plane and at 0.073(4) Å from it. The sum of angles around the nitrogen atoms is $341(3)^{\circ}$, showing an important sp³ character for them. Consequently, the P–N distance [1.705(4) Å] is in good agreement with the values found for the pyramidal nitrogen atoms of the compounds **1a**, **2**, and **3** discussed above.

4. Conclusions

The mononuclear complexes fac-[ReA(CO)₃L] [A = H (1a), OTf (2), Cl (3); L = *N*,*N*'-dimethyl-bis(diphenylphosphino)ethylenediamine] and the binuclear compound [{ReH(CO)₄}₂(L)] (1b) have been synthesised and characterised. The spectroscopic parameters of the compounds do not exhibit significant differences when com-

Supplementary data

CCDC 760590–760593 contain the supplementary crystallographic data for compounds **1a**, **3**, **2**, and **1b**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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