



New complexes of the $fac\text{-}\{(CO)_3Re^+\}$ fragment bearing a diaminediphosphine ligand

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ABSTRACT

The mono- and binuclear hydride compounds $fac\text{-}[ReH(CO)_3L]$ (**1a**) and $[\{ReH(CO)_4\}_2(\mu\text{-}L)]$ (**1b**) have been prepared by reaction of $[ReH(CO)_5]$ with $Ph_2PN(CH_3)(CH_2)_2N(CH_3)PPh_2$ (**L**) under UV light. Protonation reactions of the hydride compound **1a** with equimolar amounts of HSO_3CF_3 or HCl yielded the triflate or the chlorido compounds $fac\text{-}[Re(OSO_2CF_3)(CO)_3L]$ (**2**) and $fac\text{-}[ReCl(CO)_3L]$ (**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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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 $fac\text{-}\{(CO)_3Re^+\}$ fragment [2], to its photochemical properties [3] and to the introduction of the β^- emitting isotopes ^{188}Re and ^{186}Re 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 co-ligand 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, triflate and chlorido complexes of the $fac\text{-}\{(CO)_3Re^+\}$ fragment bearing a diaminediphosphine ligand, with the aim of analysing how the presence of nitrogen atoms (in-

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 , ^{31}P , ^{13}C and ^{19}F 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 $CDCl_3$ or CD_2Cl_2 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 $CFCl_3$ and those of $^{31}P\{^1H\}$ to 85% H_3PO_4 , with downfield shifts (δ in ppm) considered positive. Low-temperature measurements were made by cooling the probe with a stream of cold N_2 (g) from a liquid N_2 boil off evaporator. 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.

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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}) ν_{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 ≥ 10%. *Anal. Calc.* for C₃₆H₃₂N₂O₈P₂Re₂ (1054.98): C, 40.99; H, 3.06; N, 2.65. Found: C, 40.93; H, 3.10; N, 2.69%. FAB

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}) ν_{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(OSO₂CF₃)(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 μL, 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 C₃₂H₃₀F₃N₂O₆P₂Re (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–SO₂CF₃]. IR (cm^{–1}) ν_{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). ³¹P{¹H} NMR (CD₂Cl₂, ppm): δ 62.4 (s); ¹⁹F{¹H} 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}).

Table 1
Crystal data and structure refinement for compounds **1a**, **2**, and **3**.

	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 × 0.38 × 0.25	0.22 × 0.14 × 0.08	0.22 × 0.13 × 0.11
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)
c (Å)	30.210(2)	18.8577(13)	17.2456(11)
β (°)	94.6020(10)	105.070(1)	117.894(1)
V (Å 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
μ (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 ≤ h ≤ 13 –12 ≤ k ≤ 12 –39 ≤ l ≤ 37	–48 ≤ h ≤ 48 –13 ≤ k ≤ 11 –24 ≤ l ≤ 24	–16 ≤ h ≤ 33 –19 ≤ k ≤ 20 –22 ≤ l ≤ 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 > 2σ (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

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