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The synthesis, spectroscopic investigation, crystal and molecular structure of [ReCl₃(MeCN)(dppe)] complex

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Abstract

The [ReOCl₃(dppe)] complex reacts with acetonitrile in the presence of excess of triphenylphosphine to give a new monomeric nitrile rhenium(III) complex – [ReCl₃(MeCN)(dppe)] (1). This paper presents spectroscopic characterization, magnetochemical measurements, crystal and molecular structure for 1. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitrile transition metal complexes have been recognized as convenient substrates in the synthesis of organometallic derivatives for many years. R—C \equiv N ligand, which has weak σ donor and π acceptor ability can be readily displaced by other isoelectronic unsaturated ligands [1–5] or can be converted into other organic ligands in such chemical processes as insertion, nucleophilic and electrophilic attack [1,6–9].

The interest in nitrile compounds results also from structural aspects of coordinated R—C \equiv N molecules, which can interact with metal centers in several different ways, as: (i) terminal σ -bonded, η^1 -NCR, (ii) π -bonded, η^2 -NCR or (iii) bridging, σ , π -bonded, μ - η^1 , η^2 -NCR [1–9].

The finding that $[\text{ReCl}_3(\text{PPh}_3)_2]$, generated in situ from $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and PPh₃, undergoes a direct reaction with the triazenido anion Li(RN–N=NR) to give *trans*- $[\text{ReCl}_2(\text{PPh}_3)_2(\text{RN}-\text{N}-\text{NR})]$ [10] prompted us to explore the reaction of $[\text{ReOCl}_3(\text{dppe})]$ with acetonitrile in the presence of excess of triphenylphosphine as a direct route to the monomeric rhenium complex with acetonitrile and bis(diphenylophosphine)ethane in coordination sphere. Here we present the synthesis method of the novel nitrile rhenium(III) complex $[ReCl_3(MeCN)(dppe)]$ (1), its spectroscopic characterization, crystal and molecular structure.

2. Experimental

Triphenylphosphine, bis(diphenylophosphino)ethane (dppe) and ammonium perrhenate were purchased from Aldrich Chemical and used without further purification. Solvents were obtained from commercial sources and thoroughly deoxygenated prior to use. The reaction was performed under argon atmosphere. [ReOCl₃(dppe)] was prepared according to the literature method [11].

2.1. Preparation of $[ReCl_3(MeCN)(dppe)]$ (1)

Triphenylphosphine (5 g, 19 mmol) was added to a suspension of [ReOCl₃(dppe)] (1 g, 1.4 mmol) in tetrahydrofurane (50 ml) and acetonitrile (50 ml). The brownish-orange solution thus formed was refluxed for 4 h. The volume was condensed to 15 ml and upon slow cooling to room temperature brownish-orange microcrystalline precipitate was isolated. X-ray quality crystals were obtained by recrystallization from acetonitrile. Yield 70%.IR (KBr, cm⁻¹) 3062 (w), 2888 (w), 1485 (m),

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1434 (s), 1407 (m), 1312 (w), 1186 (w), 1161 (w), 1103 (s), 1027 (w), 996 (w) 871 (w), 801 (w), 782 (s), 743 (s), 692 (s), 647 (m), 526 (s), 513 (m), 477 (m).

Anal. found: C, 49.82; H, 3.75; N, 1.85. Calc. for $C_{28}H_{27}Cl_3NP_2Re$ (1): 45.94; H, 3.72; N, 1.91.

2.2. Physical measurements

UV–Vis spectra were recorded on a spectrophotometer Lab Alliance UV–Vis 8500 in the range 800–220 nm in deoxygenated dichloromethane solution. IR spectra were recorded as KBr pellets with a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm⁻¹. The magnetic susceptibility was determined with a superconducting quantum interference device (SQUID, Quantum Design) magnetometer. Elemental analyses (C H N) were performed on a Perkin–Elemer CHN-2400 analyzer.

2.3. Crystal structures determination and refinement

The X-ray intensity data were collected on a Kuma KM-4 diffractometer with $\omega - 2\theta$ scan mode. Details concerning crystal data and refinement are given in Table 1. Lorentz polarization, empirical absorption

Table 1Crystal data and structure refinement for 1

	1
Empirical formula	$C_{28}H_{27}Cl_3NP_2Re$
Formula weight	732.00
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.5270(10) Å
	b = 22.511(4) Å
	$\beta = 102.44(3)^{\circ}$
	c = 13.598(3) Å
Volume	$2847.8(9) \text{ Å}^{3}$
Ζ	4
Density (calculated)	1.707 Mg/m^3
Absorption coefficient	4.679 mm^{-1}
F(000)	1432
Crystal size	$0.26 \times 0.26 \times 0.13 \text{ mm}$
θ range for data collection	1.78–26.07°
Index ranges	$-11 \leq h \leq 0$
	$-27 \leq k \leq 0$
	$-16 \leq l \leq 16$
Reflections collected	5968
Independent reflections	5624 ($R_{\rm int} = 0.0384$)
Max. and min. transmission	0.5814 and 0.3759
Data/restraints/parameters	5624/0/318
Goodness-of-fit on F^2	1.240
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0495
	wR2 = 0.0932
R indices (all data)	R1 = 0.0949
	wR2 = 0.1206
Largest diff. peak and hole	1.592 and $-1.307 \text{ e } \text{\AA}^{-3}$

corrections were applied. The structures were solved by means of the Patterson and Fourier methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms of the phenyl rings were treated as "riding" on their parent carbon atoms [d(C-H) = 0.96 Å] and assigned isotropic temperature factors equal to 1.2 times the value of equivalent temperature factor of the parent carbon atom. SHELXL97 [12] and SHELXTL [13] programs were used for all the calculations.

3. Results and discussion

The $[ReCl_3(MeCN)(dppe)]$ complex has been prepared in high yield by use of the procedure shown in Eq. (1).

$$[\text{ReOCl}_3(\text{dppe})] + \text{MeCN} + \text{PPh}_3$$

$$\rightarrow [\text{ReCl}_3(\text{MeCN})(\text{dppe})] + \text{OPPh}_3 \qquad (1)$$

It can be assumed that the $[ReCl_3(dppe)]$ compound, generated from $[ReOCl_3(dppe)]$ and PPh₃ in the first step of the synthesis, reacts with MeCN to give $[ReCl_3(MeCN)(dppe)]$. The mass ratio of $[ReOCl_3(dppe)]$ and PPh₃ equal to 1:5 ensures the maximum yield of **1**. In the case of smaller excess of PPh₃, some unreacted starting material has been recovered from the reaction.

The rhenium atom in 1 is in a distorted octahedral environment with terminal N–C–CH₃ group [Re– N–C angle – 176.0(8)°] *trans* to one of the phosphorus atoms of the chelate ligand and three halide ligands in *meridional* geometry (Fig. 1). The departure from the ideal octahedron is induced mainly by the chelate ligand and partially by two weak intramolecular hydrogen bonds: C(6)–H(6A)…Cl(1) and C(18)–H(18A)… N(1) (D…A distance 3.646(12) and 3.392(14) Å and D–H…A angle 148.2° and 137.2°, respectively). The



Fig. 1. The molecular structure of **1**. The thermal ellipsoids are drawn at 50% probability level.

Table 2 Bond lengths (Å) and angles (°) for 1

Bond lengths		Angles	
Re(1) - N(1)	2.121(8)	N(1)— $Re(1)$ — $Cl(2)$	89.3(2)
Re(1) - P(1)	2.387(3)	N(1)— $Re(1)$ — $Cl(3)$	90.1(2)
Re(1) - P(2)	2.388(3)	Cl(2) - Re(1) - Cl(3)	175.22(9)
Re(1)- $Cl(1)$	2.452(2)	N(1) - Re(1) - P(1)	178.7(2)
Re(1)- $Cl(2)$	2.332(2)	Cl(2) - Re(1) - P(1)	90.46(10)
Re(1)- $Cl(3)$	2.334(2)	Cl(3) - Re(1) - P(1)	90.04(9)
N(1)-C(27)	1.105(12)	N(1) - Re(1) - P(2)	95.4(2)
C(27)-C(28)	1.475(15)	Cl(2) - Re(1) - P(2)	90.32(9)
P(1)-C(1)	1.813(10)	Cl(3) - Re(1) - P(2)	85.01(9)
P(1)-C(7)	1.810(12)	P(1) - Re(1) - P(2)	83.33(9)
P(1)-C(26)	1.869(12)	N(1) - Re(1) - Cl(1)	85.1(2)
P(2)-C(13)	1.882(10)	Cl(2)-Re(1)- $Cl(1)$	91.98(9)
P(2)-C(25)	1.811(11)	Cl(3)-Re(1)- $Cl(1)$	92.70(9)
P(2)-C(19)	1.844(10)	P(1) - Re(1) - Cl(1)	96.20(9)
		P(2) - Re(1) - Cl(1)	177.66(9)
		C(27) - N(1) - Re(1)	176.0(8)
		N(1)-C(27)-C(28)	177.9(12)

most important bond length and angles for 1 are reported in Table 2. The Re–N(nitrile) bond lengths of 2.121(8) Å in 1 agrees well with Re–N values found in rhenium complexes containing nitrile ligand in *trans* position to strong π -acceptor, but it is significantly longer than Re–N bond lengths found for complexes in which *trans* position to nitrile ligand is not occupied by π -acceptor. In [ReBr₃(NO)(MeCN)(PPh₃)] [14] and [NEt₄][ReBr₄(NO)(MeCN)] [15] with acetonitrile *trans* to nitrosyl group the Re–N(nitrile) bond lengths are equal to 2.156(7) and 2.153(11) Å, respectively, but in *mer-trans*-[ReCl₃(MeCN)(PPh₃)₂] the Re–N distance equals to 2.068(5) Å [16].

A clear *trans* effect of dppe ligand is also observed in the elongation of Re-Cl distance trans to phosphorus atom of the dppe ligand. The Re-Cl(1) bond *trans* to phosphine ligand at 2.452(2) Å is longer than the mutually trans Re-Cl bonds equal to 2.332(2) and 2.334(2) Å. The Re-P distances at 2.387(3) and 2.388(3) Å are considerably shorter than those found in the rhenium complexes with chelate phosphine ligands: 2.450(4), 2.456(4) and 2.480(4) Å in mer-[ReCl₃(dppm-P,P') (dppom-P)] [17] and 2.479(1) and 2.458(2) Å in trans- $[\text{ReCl(NO)(dppe)}_2]^{2+}$ [18]. The significant shortening of the C-N bond length [1.105(12) Å] in comparison with free acetonitrile [1.155 A] [19] is observed and it is expected upon coordination. The NC-CH₃ distance is within the range observed for other acetonitrile complexes [14-16].

The IR spectra of **1** is governed by the vibrations of the phosphine ligand. The $v(C \equiv N)$ vibration is absent, as already noted for other monomeric rhenium(III) nitrile complexes [20–22]. However, the absence of the characteristic strong v(Re=O) band at ~970 cm⁻¹ is clear indication that there is no oxo-Re(V) starting material left in **1** [11].

The complex 1 shows room temperature magnetic moment of 1.41 BM. This value is characteristic of mononuclear complexes with low-spin rhenium(III) (d⁴) ions in O_h field [23] and arises because of the large spin– orbit coupling ($\xi = 2500 \text{ cm}^{-1}$) [24]. The variation of the magnetic susceptibility with temperature of 1 in the solid state is shown in Fig. 2. Temperature-independent paramagnetism should be characteristic of d⁴ systems in octahedral environments [25] and has been confirmed for some of rhenium(III) and osmium(IV) halide complexes [24,26–28].

The positions and molar absorption coefficients of electronic bands for **1** and the electronic transitions assigned to the bands are shown in Table 3. The data of Table 3 prove a pseudo-octahedral configuration of complex **1**. Comparatively high values of molar extinction coefficient of the bands connected with intercombination electron transitions, result from high spin–orbital coupling ($\lambda = 3316 \text{ cm}^{-1}$). As a result of the coupling, term ${}^{3}T_{1}$ splits into singlet terms mixed with ${}^{3}T_{1}$. Because of this fact, intercombination electron transitions have to a certain degree the character of singlet–singlet transitions. Pure triplet ground state (${}^{3}T_{1}$) exists at very low



Fig. 2. The variation of the magnetic susceptibility with temperature for **1**.

Table	3							
Band	positions,	molar	absorpti	on coe	fficients	and	assignments	for 1

Band position (cm ⁻¹)	3	Assignment
14 025	32	$^3T_1 \rightarrow {}^5E$
22 625	195	${}^3T_1 \rightarrow {}^1T_2$
26 525	735	${}^{3}T_{1} \rightarrow {}^{3}E$
33 300	6575	${}^3T_1 \rightarrow {}^3T_2$
36630	12650	$\pi^0_{\mathrm{Cl}^-} \rightarrow 5 \mathrm{d}_{\mathrm{Re}}$
37 450	14 260	$\pi_{\text{Cl}^-}^0 \rightarrow 5d_{\text{Re}}$
38 315	14 300	$5d_{Re} \rightarrow \pi^*_{N\equiv C-R}$
43 100	71 630	$\pi^b_{C_6H_5} \rightarrow 3d_P; \ \pi \rightarrow \pi^*$

 $\varepsilon = \text{molar absorption coefficient } (\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}).$

temperature, and that is why $\mu_{eff} = 1.41$ BM is significantly lower than 2.83 BM, and the magnetic susceptibility does not depend on temperature. EPR signals of complex 1 at room temperature are not observed because of the same effect. The existence of π bond in Re—P_{dppe} group (proven by longer Re—Cl in *trans* position towards the phosphine ligand, in comparison with the other Re—Cl bonds), proves a transfer of electron density from 5d_{Re} to 3d_P. The transfer has no manifestation in the absorption bands. Identical Re—P(1) and Re—P(2) bond lengths show the comparable π -acceptor abilities of PPh₃ and N=C—Me.

The values of the 10 Dq ligand field parameter and Racah's parameters – *B* and *C*, calculated on the basis of the positions and molar extinction coefficients of electronic bands are equal to 2652, 431 and 1983 cm⁻¹, respectively.

Supplementary data

Supplementary data of [ReCl₃(MeCN)(dppe)] complex are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 203627.

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