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Reinvestigation of *mer,trans*-(Acetonitrile)trichlorobis(triphenylphosphine)rhenium(III)

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Abstract

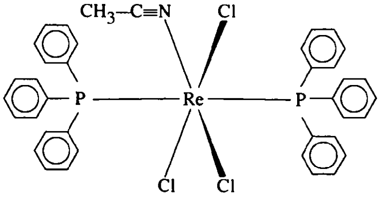
The crystals of (*OC*-6-13)-(acetonitrile-*N*)trichlorobis(triphenylphosphine-*P*)rhenium(III), $[ReCl_3(C_2H_3N)(C_{18}H_{15}P)_2]$, contain distorted octahedral molecules in which the phosphine ligands are *trans* with respect to one another and the Cl ligands adopt a meridional arrangement. In contrast to the isostructural $[OsCl_3(PPh_3)_2(CH_3CN)]$ complex, where the Os—Cl distances do not differ greatly, the Re—Cl bond *trans* to the nitrile ligand [2.393 (2) Å] is appreciably longer than the mutually *trans* Re—Cl bonds [2.344 (2) and 2.350 (2) Å].

Comment

For our studies of Re–ligand multiply bonded compounds, we required a convenient route to complexes of the type Cp′ReL_2X_2 (where Cp′ is cyclopentadienyl and its alkyl-substituted derivatives). A recent report has shown that $[ReCl_3(PPh_3)_2]$, generated *in situ* from $[ReOCl_3(PPh_3)_2]$ and PPh_3, undergoes a direct metathetic reaction with the triazenido anion Li(*R*N—N=N*R*) to give *trans*-$[ReCl_2(PPh_3)_2$(*R*N—N—N*R*)], in which the triazenido ligand acts as a bidentate ligand (Rossi *et al.*, 1982). This finding prompted us to explore the reaction of the Cp′ anions with *mer*-$[ReCl_3(PPh_3)_2(CH_3CN)]$ as a more direct route to the desired Cp′ReL_2X_2 compounds.

Addition of Cp′Li to a THF solution of $[ReCl_3(PPh_3)_2(CH_3CN)]$ yielded a dark green solid. Surprisingly, the ^{1}H NMR and IR spectra of the solid were virtually identical to the corresponding spectra of the orange rhenium precursor (Pearson & Beauchamp, 1995) and contained no signals attributable to the Cp′ ligand. The same dark green solid was obtained when the reaction was repeated in refluxing toluene or when *trans*-$[ReOCl_3(PPh_3)_2]$ and PPh_3 were used instead of $[ReCl_3(PPh_3)_2(CH_3CN)]$.

We undertook an X-ray diffraction study of the dark green crystals and discovered that the compound was in fact $[ReCl_3(PPh_3)_2(CH_3CN)]$, (I), whose structure had been reported previously by Drew, Tisley & Walton (1970), but it had been refined only to 7.7% and no atomic coordinates were provided. In order to compare the structural parameters obtained for the dark green crystals with those of the orange precursor, we recrystallized the orange solid prepared according to Rouschias & Wilkinson (1967) from CH_2Cl_2/Et_2O and subjected it to an X-ray diffraction study under similar conditions. The structures refined to R = 0.0367 (green) and 0.0371 (orange). At this point, the possibility was considered that the green material could show substitutional disorder resulting from the replacement of some $[ReCl_3(PPh_3)_2(CH_3CN)]$ by, for instance, $[ReOCl_2(PPh_3)_2(CH_3CN)]$. Parkin (1993) has recently described a number of systems of this type, *e.g.* $[MoOCl_2(PR_3)_3]/[MoCl_3(PR_3)_3]$. Analysis of distances and angles, displacement ellipsoids and electron-density contours, however, revealed no anomalies. Careful microscopic examination eventually showed that the green material actually consisted of an orange core covered with an amorphous dark green crust; the specimen appeared uniformly opaque under normal illumination, but some orange light was transmitted through the middle of the crystal when a more powerful light source was used. The results obtained with a green specimen are described here.



(I)

Our unit-cell parameters and space group correspond to those reported by Drew *et al.* (1970). The related $[OsCl_3(PPh_3)_2(CH_3CN)]$ compound studied by Parkes, Payne & Sherman (1980) is isostructural, since the cell parameters are the same as ours after their $P2_1/c$ unit cell is converted to $P2_1/n$.

The overall structure reported earlier is confirmed by the present study. The low steric requirement of CH_3CN is reflected by a general displacement of the *cis* ligands to its side. The effect is particularly significant for the Re—Cl bonds; Cl1—Re—Cl2 171.37 (6), N1—Re—Cl1 85.98 (15), N1—Re—Cl2 85.41 (15), Cl1—Re—Cl3 94.41 (6) and Cl2—Re—Cl3 94.20 (6)°. Very similar distortions are found in the Os^{III} complex, but the bond lengths in the two compounds show interesting differences. The Re—P1, Re—P2, Re—N1 and Re—Cl3 bonds are 0.029–0.055 Å longer than the corresponding bonds in the aforementioned Os^{III} compound, which is consistent with the *ca* 0.05 Å difference in their covalent radii (Huheey, 1972). In contrast, Re—Cl1 and Re—Cl2 are *ca* 0.015 Å shorter. Thus, whereas the three Os—Cl bonds do not differ appreciably, the mutually *trans* Re—Cl distances [2.344 (2) and 2.350 (2) Å] are very significantly less than the unique Re—Cl bond *trans* to CH_3CN [2.393 (2) Å]. A similar pattern was recently noted for a series of $[ReCl_3L_2(PPh_3)]$ complexes, where *L* is pyridine, 3-picoline or 1-methylimidazole [mutually *trans* Re—Cl, mean 2.369 Å; unique Re—Cl, mean 2.390 Å, σ = 0.004 Å (Pearson & Beauchamp, 1997)]. These differences are not well understood, but they are likely to result from different *d*-orbital occupancies in the d^4 Re^{III} and d^5 Os^{III} centers.

The two phosphine ligands are crystallographically independent, but the torsion angles listed in Table 1 indicate very similar conformations. They are similarly rotated about the Re—P bond, so that the P1—C11 and P2—C41 bonds are exactly above and below the Re—N1 bond, respectively. The Re—P—C11 and Re—P—C41 angles on this side are also *ca* 9° smaller than the other Re—P—C angles. The corresponding phenyl rings are roughly parallel to the $ReCl_3(CH_3CN)$ plane and the nitrile ligand is sandwiched between these π-electron systems. The two remaining rings of each phosphine ligand are closer to the upright orientation and require more space near the $ReCl_3(CH_3CN)$ plane, but staggered orientations with respect to the underlying Re—Cl bonds minimize steric hindrance.

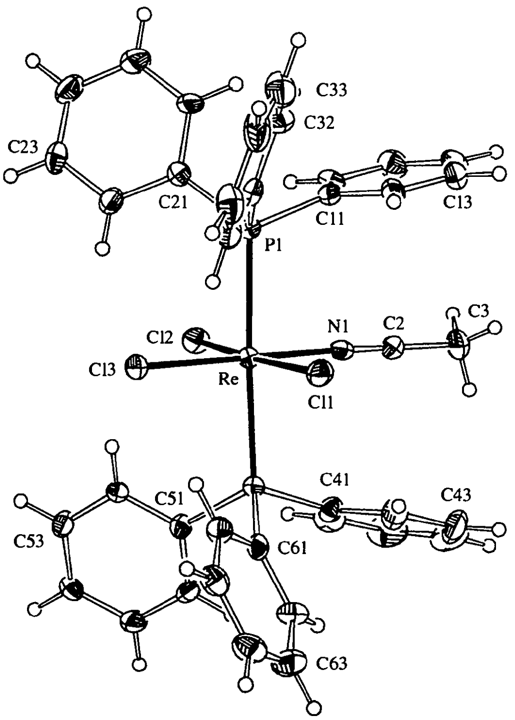


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title molecule. Displacement ellipsoids correspond to 40% probability.

Experimental

Addition of Cp′Li (1.00 mmol) to a THF solution (100 ml) of $[ReCl_3(PPh_3)_2(CH_3CN)]$ (1.00 mmol) caused an immediate color change from orange to deep green. Refluxing the reaction mixture for several hours followed by filtration and evaporation of the solvent gave a dark green solid.

Crystal data

$[ReCl_3(C_2H_3N)(C_{18}H_{15}P)_2]$
M_r = 858.15
Monoclinic
$P2_1/n$
a = 9.988 (2) Å
b = 15.154 (5) Å
c = 23.193 (7) Å
β = 90.31 (2)°
V = 3510.4 (17) Å^3
Z = 4
D_x = 1.624 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 22.5–25.0°
μ = 9.77 mm^{-1}
T = 223 (2) K
Parallelepiped
0.30 × 0.06 × 0.05 mm
Green/orange

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration
T_{min} = 0.251, T_{max} = 0.652
25 391 measured reflections
6648 independent reflections
4699 reflections with $I > 2\sigma(I)$

R_{int} = 0.063
θ_{max} = 69.83°
$h = -12 \rightarrow 12$
$k = -18 \rightarrow 18$
$l = -28 \rightarrow 28$
5 standard reflections
frequency: 30 min
intensity variation: 5.8%

Refinement

Refinement on F^2
$R(F)$ = 0.0367
$wR(F^2)$ = 0.0839
S = 0.865
6648 reflections
408 parameters
H atoms riding (*SHELXL*93 defaults; C—H 0.93–0.98 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.002
$\Delta\rho_{max}$ = 0.898 e Å^{-3}
$\Delta\rho_{min}$ = −1.844 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.000197 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Re—N1	2.068 (5)	C2—C3	1.462 (8)
Re—Cl1	2.344 (2)	P1—C11	1.820 (6)
Re—Cl2	2.350 (2)	P1—C21	1.829 (6)
Re—Cl3	2.393 (2)	P1—C31	1.835 (6)
Re—P1	2.459 (2)	P2—C41	1.809 (6)
Re—P2	2.463 (2)	P2—C61	1.831 (6)
N1—C2	1.127 (7)	P2—C51	1.835 (6)

N1—Re—Cl1	85.98 (15)	C2—N1—Re	177.2 (5)
N1—Re—Cl2	85.41 (15)	N1—C2—C3	179.8 (7)
Cl1—Re—Cl2	171.37 (6)	C11—P1—C21	104.3 (3)
N1—Re—Cl3	179.58 (15)	C11—P1—C31	104.0 (3)
Cl1—Re—Cl3	94.41 (6)	C21—P1—C31	101.0 (3)
Cl2—Re—Cl3	94.20 (6)	C11—P1—Re	107.6 (2)
N1—Re—P1	90.03 (13)	C21—P1—Re	120.2 (2)
Cl1—Re—P1	89.54 (5)	C31—P1—Re	118.1 (2)
Cl2—Re—P1	89.87 (5)	C41—P2—C61	102.8 (3)
Cl3—Re—P1	90.14 (5)	C41—P2—C51	104.9 (3)
N1—Re—P2	87.89 (13)	C61—P2—C51	100.4 (3)
Cl1—Re—P2	88.10 (5)	C41—P2—Re	111.3 (2)
Cl2—Re—P2	92.17 (5)	C61—P2—Re	118.2 (2)
Cl3—Re—P2	91.96 (5)	C51—P2—Re	117.4 (2)
P1—Re—P2	176.96 (5)		

N1—Re—P1—C11	−1.4 (3)	N1—Re—P2—C41	0.1 (3)
Cl2—Re—P1—C21	32.1 (3)	Cl1—Re—P2—C61	32.8 (2)
Cl3—Re—P1—C21	−62.1 (3)	Cl3—Re—P2—C61	−61.6 (2)
Cl1—Re—P1—C31	−32.5 (2)	Cl2—Re—P2—C51	−35.4 (2)
Cl3—Re—P1—C31	61.9 (2)	Cl3—Re—P2—C51	58.9 (2)
Re—P1—C11—C12	−86.3 (5)	Re—P2—C41—C42	77.8 (5)
Re—P1—C21—C22	33.9 (6)	Re—P2—C51—C52	−19.2 (6)
Re—P1—C31—C36	−22.8 (6)	Re—P2—C61—C66	36.3 (5)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed, Hall, Pippy & Huber, 1973). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1219). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aqua(2,2′-bipyridyl-*N*,*N*′)trichloromanganese(III)

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Abstract

In the structure of $[MnCl_3(C_{10}H_8N_2)(H_2O)]$, the Mn^{III} atom has a distorted octahedral coordination. In the basal plane, the metal atom is coordinated to the bipyridyl ligand and two Cl atoms. The apical positions are occupied by a Cl atom and an aqua ligand. In the crystal, polymeric chains are formed *via* $H_2O\cdots Cl$ hydrogen bonds.

Comment

Manganese complexes have received considerable attention in recent years due to the presence of manganese centres in biological systems (Weighardt, 1989). The complexation behaviour of 2,2′-bipyridine (bpy) or bpy-related ligands with Mn ions gives rise to a wide variety of coordination complexes depending on the nature of the bpy ligand, the oxidation state of the Mn ion and the nature of the other coordinating ligands. Mn^{II} complexes with bpy-type ligands are well known. There are over 100 structures of this type in the Cambridge Structural Database (Allen & Kennard, 1993). If we look for mononuclear Mn complexes involving bpy and Cl ligands, the number is rapidly reduced to six, two of which form polymers. The majority are Mn^{II} complexes, for example, $[MnCl(bpy)_2(H_2O)]ClO_4$ (Chen, Shi, Mak & Luo, 1995), $[Mn(bpy)_2Cl_2]$ (Lumme & Lindell, 1988) or *catena*-bis[μ_2-Cl–bpy–Mn^{II}] (Lubben, Meetsma & Feringa, 1995). Mn^{III} structures with bpy are rarer. The structure of the title compound, (I), can be

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