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# $^1$H NMR study of monomeric chloro-rhenium(III) complexes with triarylphosphines and nitriles

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**Abstract**

$ReCl_3(RCN)(PR'_3)_2$ complexes (R = Me, Et, Ph; R' = Ph, *p*-tol, *m*-tol) give relatively narrow $^1$H NMR signals in spite of the presence of the paramagnetic Re(III) centre. The signals of one ligand are not greatly affected by changes in the other ligand. In all cases, the spectra are consistent with the *mer-trans* structure previously found in the solid state for $ReCl_3(MeCN)(PPh_3)_2$. For P(*m*-tol)$_3$, the preparation of the $ReOCl_3\{P(m\text{-tol})_3\}_2$ starting complex from $ReO_4^-$ required milder conditions than for $PPh_3$ and P(*p*-tol)$_3$, the standard method leading to the further reduced compound $ReCl_4\{P(m\text{-tol})_3\}_2$, whose crystal structure was determined by X-ray diffraction (monoclinic, $P2_1/c$, $a = 11.218$, $b = 18.204$, $c = 11.192$ Å, $\beta = 118.64°$, $R = 0.042$). The latter complex adopts the *trans* geometry with the Re atom sitting on a crystallographic inversion centre.

*Keywords:* Crystal structures; Rhenium complexes; Nitrile complexes; Phospine complexes; Paramagnetic complexes

## 1. Introduction

Our laboratory is currently investigating the preparation and properties of dinuclear Re(III) complexes containing purines as bridging ligands [1]. Re(III) monomers with purines coordinated via a specific site could be interesting not only as precursors for such dimeric systems, but also for the modelling of Re–DNA interactions and eventual applications of the $^{186}$Re and $^{188}$Re isotopes in radiotherapy [2]. Since Re(III) compounds often give relatively narrow $^1$H NMR signals despite their paramagnetism [3–7], this technique could be efficiently used to characterize complexes with these relatively complicated multidentate ligands, but it is generally difficult to draw structural conclusions from the large chemical shifts induced by the Re(III) centre. As a first step, we examined a set of closely related $ReCl_3(RCN)(PR'_3)_2$ compounds, which are being considered as starting materials for reactions with purines. $ReCl_3(RCN)(PPh_3)_2$ compounds with various nitriles have been reported by Rouschias and Wilkinson [8]. In the present study, compounds containing three nitriles (R = Me, Et, Ph) and three phosphines (R' = Ph, *m*-tol, *p*-tol) were prepared with the aim of determining how the $^1$H resonances of one ligand are affected by relatively minor changes in the other. While preparing the starting $ReOCl_3(PR'_3)_2$ complexes to be reacted with the nitriles, it was noticed that P(*m*-tol)$_3$ did not behave like $PPh_3$ and P(*p*-tol)$_3$: although the standard reaction with $ReO_4^-$ led to the expected yellow–green $ReOCl_3(PR'_3)_2$ compounds for the last two ligands, a brick red material was isolated with P(*m*-tol)$_3$. This product is also discussed in the present paper.

## 2. Experimental

### 2.1. Reactants and methods

$KReO_4$, $PPh_3$, P(*m*-tol)$_3$, P(*p*-tol)$_3$, MeCN, EtCN and PhCN were used as received from Aldrich. Both P(tol)$_3$ ligands were stored in the glovebox. Solvents were distilled over sodium.

All experiments were performed in an argon atmosphere using standard Schlenk techniques. $^1$H NMR spectra in $CDCl_3$ were recorded at 300 MHz on a Varian VXR-300 spectrometer (spectral width: 160 ppm; relaxation delay: 2.0 s). The residual solvent signal ($\delta$ 7.268 ppm) served as internal standard and the chemical shifts were converted to the usual TMS scale. The $^{31}$P NMR spectra were recorded at 121.42 MHz with the same instrument and 85% $H_3PO_4$ in $D_2O$ was used as external standard ($\delta$ 0 ppm). IR spectra (4000–250 cm$^{-1}$) were obtained as KBr pellets on a Perkin-

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Elmer 783 spectrophotometer. Magnetic moments were determined at room temperature with an Evans magnetic susceptibility balance (Johnson-Matthey), calibrated with $HgCo(SCN)_4$ ($\chi = 16.44 \times 10^{-6}$ c.g.s.e.m.u.). Corrections for diamagnetism were calculated from Pascal's constants [9]. UV–Vis spectra (250–800 nm) were recorded in $CH_2Cl_2$ solution with a Varian Cary 5E spectrophotometer.

### 2.2. Preparative work

#### 2.2.1. $ReOCl_3(PR'_3)_2$ complexes

The compounds with R′ = Ph and *p*-tol were prepared by the same procedure, which is a slight modification of the method published by Parshall et al. [10]. $KReO_4$ (2.0 g, 7 mmol) and excess phosphine (10 g) were refluxed in a mixture of conc. HCl (11.5 ml) and ethanol (116 ml). After 30 min, the mixture had turned green. The yellow–green solid was then filtered at 70 °C, washed with ethanol (25 ml), and finally washed with water to eliminate KCl. Yields of ~90% were obtained. The $^{31}P$ NMR data for the $PPh_3$ complex correspond to published results [11]. $^{31}P$ NMR: $\delta$ −15.8 ppm. The $^1H$ NMR spectrum shows a set of multiplets in the 7.2–7.6 ppm region. For the *p*-tol derivative: $^{31}P$ NMR: $\delta$ −18.6 ppm; $^1H$ NMR: 7.62(m) and 7.19(d) ring, 2.36(s) methyl, ppm.

For $P(m\text{-tol})_3$, while the reaction mixture was refluxed for 30 min, it gradually changed from green to brick red. The product was later shown to be a mixture of the desired $ReOCl_3\{P(m\text{-tol})_3\}_2$ compound with the red $ReCl_4\{P(m\text{-tol})_3\}_2$ complex (see below). If reaction time was limited to 5 min, the mixture remained green and pure $ReOCl_3\{P(m\text{-tol})_3\}_2$ was obtained (yield 60%). This green product shows a single $^{31}P$ NMR signal at −18.4 ppm as expected. The $^1H$ NMR spectrum contains multiplets at 7.55 and 7.29 ppm for the ring protons and a singlet at 2.31 ppm for the methyl group. The presence of the Re=O bond is confirmed by the IR $\nu(Re{=}O)$ band appearing at 969 $cm^{-1}$ [12].

#### 2.2.2. $ReCl_3(RCN)(PR'_3)_2$ (R = Me, Et, Ph; R′ = Ph, *p*-tol, *m*-tol)

$ReCl_3(MeCN)(PPh_3)_2$ was prepared as described by Rouschias and Wilkinson (method B) [8]. The same method was used for the remaining compounds. The appropriate $ReOCl_3(PR'_3)_2$ complex (2.6 g) and the nitrile (25 ml) were refluxed in toluene for 2 h with an excess of the corresponding phosphine. The solid was precipitated by addition of ethanol and purified by recrystallization in $CH_2Cl_2$/ethanol.

### 2.3. Crystal data for $ReCl_4\{P(m\text{-tol})_3\}_2$

$C_{42}H_{42}Cl_4P_2Re$, FW = 936.76, $a = 11.218(4)$, $b = 18.204(8)$, $c = 11.192(4)$ Å, $\beta = 118.64(3)°$, $V = 2005.9(1)$ Å$^3$, $F(000) = 934$, $Z = 2$, $D = 1.551$ g $cm^{-3}$, $\lambda$(Cu K$\alpha$) = 1.54178 Å, $T = 210$ K.

### 2.4. Crystallographic work

The bright red diamond-shaped plate used had the following dimensions between the indicated pairs of faces: 0.25 $(\bar{1}11 - 1\bar{1}\bar{1}) \times 0.21$ $(11\bar{1} - \bar{1}\bar{1}1) \times 0.04$ $(100 - \bar{1}00)$ mm. The X-ray work was done at 210 K on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu K$\alpha$ radiation. The automatic search procedure yielded a monoclinic primitive cell. The final cell parameters were obtained by refinement of 25 reflections ($20 < 2\theta < 25°$). Intensity data were collected by the $\omega/2\theta$ scan technique ($2\theta \leq 140°$). Orientation was monitored every 400 measurements and intensity was checked every hour with five standard reflections. Intensity fluctuations remained within ±2.4%. The whole sphere of 13 640 reflections was measured. These data were corrected for absorption (Gaussian integration, 10 × 10 × 10 grid, $\mu = 92.15$ $cm^{-1}$, transmission range: 0.15–0.71). Averaging yielded 3796 unique *hkl* and $\bar{h}kl$ reflections, of which 3119 with $I \geq 3\sigma(I)$ were retained for structure determination and refinement. The usual corrections for the effects of Lorentz and polarization were applied.

Monoclinic Laue symmetry and systematic absences (*h*0*l*, *l* odd; 0*k*0, *k* odd) unambiguously identified space group $P2_1/c$. The structure was solved by the heavy-atom method. From the Patterson map, the Re atom was found to sit on a crystallographic inversion centre and the origin was arbitrarily chosen. All other non-hydrogen atoms were found from successive $\Delta F$ maps. Refinement was done on $|F|$ by full-matrix least-squares procedures. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = 1/[\sigma^2(F) + 0.0002F^2]$. The non-hydrogen atoms were refined anisotropically. Hydrogens were fixed at idealized positions (C–H = 0.95 Å) with individual isotropic thermal parameters $U_{iso,H} = (U_{iso,C} + 0.01)$ Å$^2$. The general background in the $\Delta F$ map was within ±0.46 e Å$^{-3}$, with highest peaks of −1.9 and 1.7 e Å$^{-3}$ near Re. The final agreement factors were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.042$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.051$. The goodness-of-fit ratio was 2.13 for 225 parameters refined. All calculations were done with the NRCVAX system [13]. The refined coordinates are listed in Table 1. For thermal parameters and hydrogen coordinates see Section 4.

## 3. Results and discussion

### 3.1. Rhenium(III) compounds

All $ReCl_3(RCN)(PR'_3)_2$ complexes prepared here are paramagnetic with magnetic moments (Table 2) typical of low-spin Re(III) monomers [8]. Crystallographic work has shown that $ReCl_3(MeCN)(PPh_3)_2$ exists as the *mer-trans* isomer in the solid state [14]. Its IR spectrum exhibits bands at 314(w), 298(s) and 270(m) $cm^{-1}$, which probably correspond to the three active $\nu(Re\text{–}Cl)$ modes expected for this geometry. The remaining complexes should have the

Table 1
Refined coordinates and equivalent isotropic temperature factors (Å$^2$) for *trans*-$ReCl_4\{P(m\text{-tol})_3\}_2$

| Atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| Re | 0.00000 | 0.50000 | 0.50000 | 2.07(1) |
| Cl(1) | 0.02700(17) | 0.48763(9) | 0.30797(17) | 3.66(8) |
| Cl(2) | −0.19329(14) | 0.57326(8) | 0.38304(15) | 3.09(6) |
| P | −0.15794(14) | 0.38858(8) | 0.41901(14) | 2.14(6) |
| C(11) | −0.2677(5) | 0.3799(3) | 0.2355(5) | 2.3(2) |
| C(12) | −0.2866(6) | 0.4373(3) | 0.1453(5) | 2.4(3) |
| C(13) | −0.3707(6) | 0.4294(3) | 0.0060(6) | 2.7(3) |
| C(14) | −0.4384(6) | 0.3630(4) | −0.0424(6) | 3.1(3) |
| C(15) | −0.4210(7) | 0.3058(4) | 0.0455(6) | 3.2(3) |
| C(16) | −0.3349(6) | 0.3138(3) | 0.1843(6) | 2.8(3) |
| C(17) | −0.3862(8) | 0.4918(4) | −0.0882(7) | 3.7(3) |
| C(21) | −0.0730(5) | 0.2995(3) | 0.4609(5) | 2.4(3) |
| C(22) | 0.0229(6) | 0.2856(3) | 0.4180(6) | 2.9(3) |
| C(23) | 0.0856(7) | 0.2180(4) | 0.4361(7) | 3.8(3) |
| C(24) | 0.0522(8) | 0.1635(4) | 0.5014(7) | 4.2(4) |
| C(25) | −0.0412(8) | 0.1762(4) | 0.5467(8) | 4.1(4) |
| C(26) | −0.1030(7) | 0.2440(4) | 0.5271(7) | 3.3(3) |
| C(27) | 0.1883(9) | 0.2046(5) | 0.3864(10) | 5.8(5) |
| C(31) | −0.2744(6) | 0.3867(3) | 0.4891(6) | 2.3(3) |
| C(32) | −0.4134(6) | 0.3968(3) | 0.4056(6) | 2.4(3) |
| C(33) | −0.5039(6) | 0.3979(3) | 0.4578(6) | 2.9(3) |
| C(34) | −0.4522(7) | 0.3888(3) | 0.5972(6) | 3.1(3) |
| C(35) | −0.3143(7) | 0.3778(4) | 0.6815(6) | 3.2(3) |
| C(36) | −0.2246(6) | 0.3776(3) | 0.6284(6) | 2.7(3) |
| C(37) | −0.6541(7) | 0.4088(4) | 0.3667(8) | 4.0(4) |

same stereochemistry, since they show similar features in this region. A well separated band is observed in all cases at 270 cm$^{-1}$, whereas the two high-frequency components are usually not resolved, producing a strong, slightly broadened, peak near 300 cm$^{-1}$.

The IR spectra above 400 cm$^{-1}$ are mostly governed by the vibrations of the phosphines, which are not greatly affected by coordination. The most obvious effects of coordination are noted in two sets of bands between 400 and 550 cm$^{-1}$, due to substituent-sensitive modes of the phosphine aromatic rings [15,16]. Free $PPh_3$ shows three components at 510(m)/496(s)/487(vs) cm$^{-1}$, respectively. In the complexes, intensity varies in the opposite order (510(vs)/505(s,sh)/488(m) cm$^{-1}$) and the two high-frequency contributors are not always resolved. In the other region, where the free $PPh_3$ absorptions occur at 427(m)/416(m)/396(w) cm$^{-1}$, the two high-frequency components have moved to 447(m)/426(m) cm$^{-1}$ upon complexation. Similar effects are noted for $P(p\text{-tol})_3$: the 513(w)/504(s)/494(vs) cm$^{-1}$ system becomes a doublet at 508(vs)/492(s) cm$^{-1}$ in the complexes, whereas the higher-frequency band in the 406(m)/388(w) cm$^{-1}$ pair of the free ligand appears as a doublet displaced to 433(m)/421(m) cm$^{-1}$ in the complexes. The spectrum of $P(m\text{-tol})_3$ differs appreciably from those of the two other phosphines. In the 510–545 cm$^{-1}$ region, one of the several weak bands of the free ligand is displaced to ~550 cm$^{-1}$ and becomes much stronger. Also, the bands at 438(s) and 429(m) cm$^{-1}$ are displaced to ~465(s) and ~450(s) cm$^{-1}$ in the complexes. The $\nu(C{\equiv}N)$ vibrations are absent in all cases, as already noted for other rhenium(III)–nitrile complexes [8,17]. The absence of the characteristic strong $\nu(Re{=}O)$ band at ~969 cm$^{-1}$ is clear indication that there is no oxo–Re(V) starting material left in these samples.

Re(III) monomers with tertiary phosphines and arsines have been noted to give relatively narrow $^1$H NMR signals due to fast relaxation of the unpaired electrons [9,18,19]. A typical spectrum is given in Fig. 1 and the data for all compounds are listed in Table 3. Signals were assigned from comparisons with similar compounds and the $^1$H–$^1$H coupling patterns observed in most of the cases (Fig. 2) were used as extra evidence for assignments. The coupling constants are similar to those obtained in diamagnetic systems [20]. Couplings to $^{31}$P were not observed, as is usually the case in such systems [3,5].

The nitrile protons are the most affected in these complexes. The methyl group of MeCN appears as a singlet near 52 ppm, that is, at a surprisingly low field considering that its signal occurs at 8.8 ppm in $[Re(MeCN)Cl_2(Me_3\text{-tacn})]BPh_4$ (where tacn = triazacyclononane) [17]. For EtCN, the $CH_2$ group gives a quartet at ~40 ppm, whereas the triplet for the $CH_3$ group (~3.5 ppm) is not much displaced, because it is more distant from the Re centre. The protons of benzonitrile are assigned from integrations and couplings. Much smaller displacements are observed: with

Table 2
UV–Vis data and magnetic moments for the $ReCl_3(RCN)(PR'_3)_2$ complexes

| | $\lambda_{max}$ (nm) [a] | $\epsilon \times 10^{-3}$ (l mol$^{-1}$ cm$^{-1}$) | $\mu$ (BM) |
|---|---|---|---|
| $ReCl_3(MeCN)(PPh_3)_2$ | 435 | 2.25 | 1.60 |
| $ReCl_3(EtCN)(PPh_3)_2$ | 435 | 1.83 | 1.50 |
| $ReCl_3(PhCN)(PPh_3)_2$ | 352<br>401<br>432 | 5.50<br>3.65<br>3.75 | 1.70 |
| $ReCl_3(MeCN)\{P(m\text{-tol})_3\}_2$ | 440 | 1.63 | |
| $ReCl_3(EtCN)\{P(m\text{-tol})_3\}_2$ | 440 | 1.47 | |
| $ReCl_3(MeCN)\{P(p\text{-tol})_3\}_2$ | 446 | 1.59 | 1.41 |
| $ReCl_3(EtCN)\{P(p\text{-tol})_3\}_2$ | 444 | 1.60 | 1.36 |

[a] In $CH_2Cl_2$.

respect to the multiplet of free PhCN at ~7.5 ppm, the *meta* protons have shifted downfield, the *ortho* and *para* protons upfield. The phosphines exhibit a constant pattern which is virtually unaffected by the nature of the nitrile: the *ortho* protons appear around 14 ppm, downfield from the *meta* and *para* protons (8.4–8.7 ppm). Integration indicates that the multiplets near 8.7 for the $PPh_3$ complexes originate from both the *meta* and the *para* protons. Interestingly, the methyl signal of $P(p\text{-tol})_3$ (2.35 ppm) is virtually unaffected by complexation (~2.30 ppm), whereas that of $P(m\text{-tol})_3$ (2.32 ppm) undergoes a substantial downfield shift to (~2.80 ppm).

UV–Vis spectra (Table 2) of the complexes show a maximum around 440 nm, probably due to a charge tranfer transition. The very similar patterns indicate a similar structure for all complexes in solution. Two additional bands for the benzonitrile compound are likely due to transitions localized in the ligand $\pi$ system.

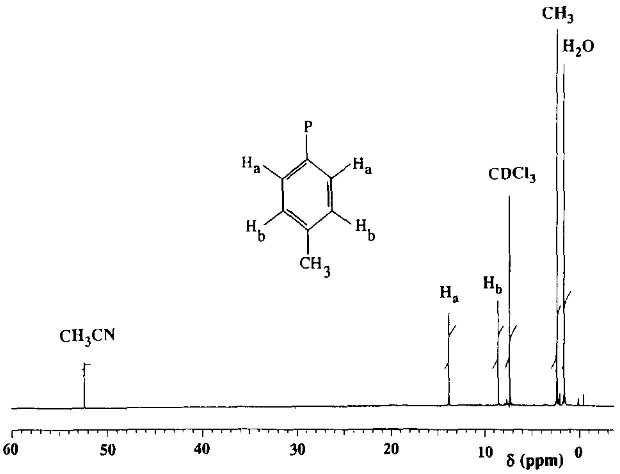

Fig. 1. $^1H$ NMR spectrum of $ReCl_3(MeCN)\{P(p\text{-tol})_3\}_2$ in $CDCl_3$.

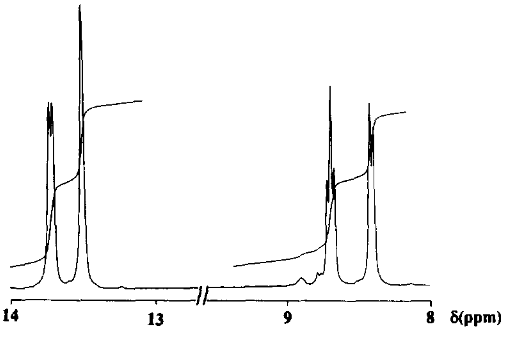

Fig. 2. Expanded view of the aromatic portion of the $^1H$ NMR spectrum of $ReCl_3(EtCN)\{P(m\text{-tol})_3\}_2$ showing the $^1H$–$^1H$ couplings.

### 3.2. $ReOCl_3\{P(m\text{-tol})_3\}_2$ and $ReCl_4\{P(m\text{-tol})_3\}_2$

The method used to prepare $ReOCl_3(PPh_3)_2$ from $ReO_4^-$ yielded the expected complex when applied to $P(p\text{-tol})_3$, but under the same conditions, $P(m\text{-tol})_3$ gave a brick red powder instead of the expected yellow–green product. From the $^1H$ NMR spectrum, this powder was suspected to contain two species: one of them showed signals in the normal range, whereas very large displacements typical of a paramagnetic species were observed for the other. The diamagnetic component presented two set of multiplets around 7.4 ppm for the aromatic phosphine protons and a peak at 2.31 ppm for the methyl group. The single $^{31}P$ NMR peak at −18.4 ppm was ascribed to $ReOCl_3\{P(m\text{-tol})_3\}_2$, since a signal is observed at the same place for the corresponding $PPh_3$ and $P(p\text{-tol})_3$ complexes. This was also supported by the presence of a strong IR $\nu(Re{=}O)$ peak at 971 $cm^{-1}$ [12]. As to the paramagnetic component, the $^1H$ NMR spectrum showed peaks which were assigned as follows: 23.73 and 20.80 (*ortho*), 10.99 (*para*), 8.35 (*meta*) and 4.96 (methyl) ppm. These assignments are based on those of the analogous com-

Table 3
$^1H$ NMR data for the $ReCl_3(RCN)(PR'_3)_2$ complexes

| | Phosphine | | | | Nitrile |
|---|---|---|---|---|---|
| | *ortho* | *meta* | *para* | methyl | |
| $ReCl_3(MeCN)(PPh_3)_2$ | 13.92(d) | 8.72(m) | | | 51.22(s) |
| $ReCl_3(EtCN)(PPh_3)_2$ | 13.87(d) | 8.68(m) | | | 38.92(q) $CH_2$ |
| | | | | | 3.41(t) $CH_3$ |
| $ReCl_3(PhCN)(PPh_3)_2$ | 14.09(d) | 8.61(m) | | | 10.44(t) *meta* |
| | | | | | 6.48(br) [b] *para* |
| | | | | | 5.39(d) *ortho* |
| $ReCl_3(MeCN)\{P(p\text{-tol})_3\}_2$ | 13.76(d) | 8.48(d) | | 2.31(s) | 52.25(s) |
| $ReCl_3(EtCN)\{P(p\text{-tol})_3\}_2$ | 13.71(d) | 8.44(d) | | 2.29(s) | 39.94(q) $CH_2$ |
| | | | | | 3.48(t) $CH_3$ |
| $ReCl_3(MeCN)\{P(m\text{-tol})_3\}_2$ | 13.57(s) H2 [a] | 8.72(t) H5 [a] | 8.46(d) | 2.83(s) | 52.03(s) |
| | 13.73(d) H6 [a] | | | | |
| $ReCl_3(EtCN)\{P(m\text{-tol})_3\}_2$ | 13.50(s) H2 [a] | 8.69(t) H5 [a] | | 2.79(s) | 39.59(q) $CH_2$ |
| | 13.71(d) H6 [a] | | 8.40(d) | | 3.48(t) $CH_3$ |

[a] Assuming that the methyl group occupies position 3.
[b] Unresolved multiplet.

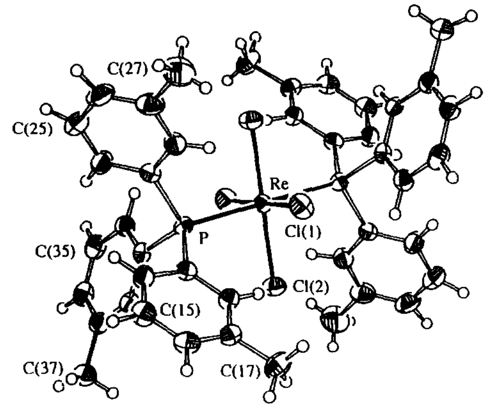

Fig. 3. ORTEP view of the $ReCl_4\{P(m\text{-tol})_3\}_2$ molecule. Ellipsoids correspond to 50% probability. Re occupies a crystallographic inversion centre. Atoms in the aromatic rings are assigned C(*ij*) symbols, where *i* is the ring number and *j* corresponds to sequential numbering aroung the ring, starting with *j* = 1 for the P-bonded carbon (*j* = 7 for methyl group).

plex with $PPh_2Et$ described by Over et al. [7], considering that the *ortho* protons on phenyl rings in similar compounds appear at much lower field than the *para* and *meta* protons [21]. In this case, the higher oxidation state seems to induce a larger displacement of the methyl protons than found with the previous Re(III) compounds. The $^{31}P$ NMR spectrum showed no signals besides that of $ReOCl_3\{P(m\text{-tol})_3\}_2$, in agreement with the fact that $^{31}P$ NMR signals are observed only exceptionnally for these paramagnetic complexes [6].

Recrystallization of the brick red mixture yielded pure bright red crystals, whose $^1H$ NMR signals coincide with those found above for the paramagnetic component. By X-ray diffraction, the crystals were found to contain discrete *trans*-$ReCl_4\{P(m\text{-tol})_3\}_2$ molecules (Fig. 3). The Re atom occupies a crystallographic inversion centre. Thus, all *trans* angles are equal to 180° by symmetry, and Table 4 shows that the *cis* angles are all close to 90°. The Re–P distance

Table 4
Interatomic distances (Å) and bond angles (°) in *trans*-$ReCl_4\{P(m\text{-tol})_3\}_2$

| | | | |
|---|---|---|---|
| *Distances* | | | |
| Re–Cl(1) | 2.321(2) | C(21)–C(26) | 1.386(8) |
| Re–Cl(2) | 2.339(2) | C(22)–C(23) | 1.383(9) |
| Re–P | 2.556(2) | C(23)–C(27) | 1.519(10) |
| P–C(11) | 1.826(5) | C(23)–C(24) | 1.387(11) |
| P–C(21) | 1.825(6) | C(24)–C(25) | 1.385(11) |
| P–C(31) | 1.818(6) | C(25)–C(26) | 1.381(10) |
| C(11)–C(12) | 1.397(8) | C(31)–C(32) | 1.394(8) |
| C(11)–C(16) | 1.389(8) | C(31)–C(36) | 1.391(8) |
| C(12)–C(13) | 1.389(8) | C(32)–C(33) | 1.393(8) |
| C(13)–C(17) | 1.501(9) | C(33)–C(37) | 1.506(9) |
| C(13)–C(14) | 1.392(9) | C(33)–C(34) | 1.390(9) |
| C(14)–C(15) | 1.381(9) | C(34)–C(35) | 1.387(10) |
| C(15)–C(16) | 1.389(8) | C(35)–C(36) | 1.393(9) |
| C(21)–C(22) | 1.396(8) | | |
| *Angles* | | | |
| Cl(1)–Re–Cl(2) | 91.98(6) | C(11)–C(16)–C(15) | 120.2(5) |
| Cl(1)–Re–Cl(2) [a] | 88.02(6) | P–C(21)–C(22) | 117.8(4) |
| Cl(1)–Re–P | 88.31(5) | P–C(21)–C(26) | 123.6(4) |
| Cl(1)–Re–P [a] | 91.69(5) | C(22)–C(21)–C(26) | 118.5(6) |
| Cl(2)–Re–P | 87.42(6) | C(21)–C(22)–C(23) | 122.2(6) |
| Cl(2)–Re–P [a] | 92.58(6) | C(22)–C(23)–C(27) | 120.7(7) |
| Re–P–C(11) | 116.5(2) | C(22)–C(23)–C(24) | 117.8(6) |
| Re–P–C(21) | 115.2(2) | C(27)–C(23)–C(24) | 121.5(6) |
| Re–P–C(31) | 112.4(2) | C(23)–C(24)–C(25) | 121.1(6) |
| C(11)–P–C(21) | 101.5(3) | C(24)–C(25)–C(26) | 120.1(6) |
| C(11)–P–C(31) | 104.3(3) | C(21)–C(26)–C(25) | 120.3(6) |
| C(21)–P–C(31) | 105.5(3) | P–C(31)–C(32) | 120.8(4) |
| P–C(11)–C(12) | 122.3(4) | P–C(31)–C(36) | 120.0(4) |
| P–C(11)–C(16) | 118.6(4) | C(32)–C(31)–C(36) | 119.1(5) |
| C(12)–C(11)–C(16) | 119.0(5) | C(31)–C(32)–C(33) | 121.8(5) |
| C(11)–C(12)–C(13) | 121.3(5) | C(32)–C(33)–C(37) | 121.4(6) |
| C(12)–C(13)–C(14) | 118.5(5) | C(32)–C(33)–C(34) | 118.2(5) |
| C(12)–C(13)–C(17) | 119.8(6) | C(37)–C(33)–C(34) | 120.3(6) |
| C(17)–C(13)–C(14) | 121.7(5) | C(33)–C(34)–C(35) | 120.7(6) |
| C(13)–C(14)–C(15) | 120.9(5) | C(34)–C(35)–C(36) | 120.5(5) |
| C(14)–C(15)–C(16) | 120.1(6) | C(31)–C(36)–C(35) | 119.6(5) |

[a] $-x, 1-y, 1-z$.

(2.556(2) Å) is longer than in the $PEt_3$ analogue (2.518(1) Å) [22]. This difference can be explained by steric hindrance from the bulky aromatic rings. The Re–Cl distances are not sensitive to this effect: they are comparable in the two compounds. The IR spectra show a strong, slightly split, $\nu$(Re–Cl) vibration centred at 320 $cm^{-1}$. A single IR-active $\nu$(Re–Cl) vibration of the $E_u$ type is predicted for a $D_{4h}$ coordination. The small splitting observed likely results from the complex occupying a site of crystallographic symmetry lower than $D_{4h}$.

As for the $ReOCl_3\{P(m\text{-tol})_3\}_2$ compound, it could be obtained by the method commonly used [9], provided refluxing was stopped after 5 min, before the mixture started to change from green to brown. The reasons for $P(m\text{-tol})_3$ leading to a more reduced complex than $P(p\text{-tol})_3$ and $PPh_3$ when reacted with $ReO_4^-$ are still unclear.

## 4. Supplementary material

Tables of anisotropic temperature factors, hydrogen parameters, distances to the least-squares planes and structure factor amplitudes for the crystal structure of $ReCl_4\{P(m\text{-tol})_3\}_2$ are available upon request from author A.L.B.

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