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# THE CRYSTAL AND ELECTRONIC STRUCTURE OF THE COMPLEX [ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>]

# J. O. DZIĘGIELEWSKI\* and B. MACHURA

Department of Inorganic and Radiation Chemistry, Institute of Chemistry, University of Silesia, 9th Szkolna Str., 40-006 Katowice, Poland

and

# T. J. BARTCZAK\*

X-Ray Crystallography Group, Institute of General and Ecological Chemistry, Technical University of Łódź, 116<sup>th</sup> Żeromskiego Str., Łódź, Poland

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**Abstract**—The crystallographic structure of the complex *trans*-[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] was determined and the spectroscopic characterization of the complex was established. Its electronic structure was also investigated ( $10Dq = 17,889 \text{ cm}^{-1}$ ,  $Ds = -4091 \text{ cm}^{-1}$ ,  $D\tau = 136 \text{ cm}^{-1}$ ,  $B = 473 \text{ cm}^{-1}$ ,  $C = 2175 \text{ cm}^{-1}$ ). Copyright © 1996 Elsevier Science Ltd

Complexes of the formula  $[Re(Hal)_4(PPh_3)_2]$ (Hal = Cl, Br or I and L = tertiary monophosphines or tertiary monoarsines) have been known for a long time,<sup>1-9</sup> but their crystallographic and electronic structures have not yet been defined. The complex  $[ReCl_4(PPh_3)_2]$  has been obtained in various ways, namely as a result of (HPPh<sub>3</sub>)<sub>2</sub>[ReCl<sub>6</sub>] pyrolysis;<sup>3</sup> the reaction of HCl with [Re- $H_3(PPh_3)_4$ ;<sup>4</sup> reduction of the trans-[ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] with a boiling solution of titanous chloride in HCl;<sup>5</sup> or as a result of [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] disproportionation in HCl.<sup>6</sup> Other methods of  $[\text{ReCl}_4(\text{PPh}_3)_2]$  synthesis involved the oxidation of [ReCl<sub>3</sub>(CH<sub>3</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>] by halogen-containing solvents  $(e.g. CCl_4)^7$ or the reaction of [ReCl<sub>4</sub>(MeCN)<sub>2</sub>] with PPh<sub>3</sub>.<sup>8</sup>

The authors<sup>10</sup> have observed the formation of  $[\text{ReCl}_4(\text{PPh}_3)_2]$  in the reaction:

 $[\text{ReOCl}_3(\text{PPh}_3)_2] + \text{NOCl} \rightarrow$ 

$$[\operatorname{ReCl}_4(\operatorname{PPh}_3)_2] + \operatorname{NO}_2$$

as a by-product (~5% yield) during the synthesis of  $[Re(NO)_2Cl_2(PPh_3)_2]$ :

$$[\text{ReOCl}_3(\text{PPh}_3)_2] + 4\text{NO} \rightarrow$$

 $[\operatorname{Re}(\operatorname{NO})_2\operatorname{Cl}_2(\operatorname{PPh}_3)_2] + \operatorname{NOCl} + \operatorname{NO}_2.$ 

The goal of this paper, apart from the introduction of a new synthetic method, was to determine the crystallographic and electronic structure of the complex  $[\text{ReCl}_4(\text{PPh}_3)_2]$ .

# **EXPERIMENTAL**

 $[\text{ReOX}_3(\text{PPh}_3)_2]^{11}$  and  $[\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^7$  were obtained according to literature methods. Gaseous NO was purified by passing through the washers with concentrated KOH solution and with solid NaOH.

All solvents were of the highest purity and were distilled before reactions. Trans-[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] was obtained via two independent methods.

## Method 1

Trans-[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] was only a by-product in this method. NO was passed through a vigorously

<sup>\*</sup>Authors to whom correspondence should be addressed: J.O.D. (synthesis and spectroscopy) and T.J.B. (X-ray crystallography).

stirred solution of  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  (0.850 g; 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) under argon. The synthesis was carried out during 4–5 h, and the colour of the reacting solution changed gradually from bright green to maroon. The resulting solution was evaporated to half its volume and a maroon precipitate of  $[\text{Re}(\text{NO})_2\text{Cl}_2(\text{PPh}_3)_2]$  was formed by adding 15 cm<sup>3</sup> of ethanol.<sup>10</sup> A small amount of carmine-red  $[\text{ReCl}_4(\text{PPh}_3)_2]$  was obtained from the filtrate (0.02 g; 0.0235 mmol).

An increase in the reaction time (7-8 h) leads to a significant increase of the yield of *trans*-[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.100 g; 0.12 mmol). *Trans*-[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] monocrystals were obtained from CH<sub>2</sub>Cl<sub>2</sub> solution. Found: C, 50.7; H, 3.51. Calc.: C, 50.7; H, 3.5%. Gaseous NOCl was detected in the reacting system and estimated using the literature method.<sup>12</sup>

#### Method 2

This is a literature method.<sup>7</sup> A suspension of  $[ReCl_3(CH_3CN)(PPh_3)_2]$  (0.500 g; 0.58 mmol) in  $CH_2Cl_2$  (15 cm<sup>3</sup>) and  $CCl_4$  (15 cm<sup>3</sup>) was boiled in air for 20 min. Crystals of *trans*- $[ReCl_4(PPh_3)_2]$  were obtained (yield 92%; 0.46 g; 0.54 mmol).

Solubility, IR and UV-vis spectra and magnetic moments of the complexes obtained by both methods are identical.

#### X-ray diffraction measurements

X-ray diffraction measurements were performed on a Kuma KM-4 diffractometer, using a crystal with dimensions  $0.21 \times 0.21 \times 0.49$  mm. Mo- $K_{\alpha}$ radiation ( $\lambda = 0.71073$  Å) was monochromated with a graphite monochromator. Final values of the lattice parameters were determined from 99 reflections in the range  $5 < \theta < 15^{\circ}$ . Diffraction intensities were measured at 293 K within the region  $3.0 < 2\theta < 60.0^{\circ}$  via the  $\omega$ -2 $\theta$  scan technique. Index ranges were  $-1 \le h \le 13$ ,  $-1 \le k \le 17$ ,  $-1 \leq l \leq 29$ . The crystal stability during the data collection was checked by measuring three standard reflections (200, -1 - 12, 11 - 4) after every 100 measurements; no significant changes of their intensities were detected. An empirical absorption correction ( $\psi$ -scan) was applied. Maximum and minimum transmission coefficients were 0.759 and 0.602, respectively. The structure was solved by the heavy atom method. All non-hydrogen atoms were refined anisotropically by the full-matrix leastsquares procedure with the weighting scheme  $w = 1/[\sigma^2(F_o)^2 + (0.2P)^2 + P]$ , where  $P = (F_o^2 + P)^2 + P$  $2F_c^2$ )/3. The hydrogen atoms were found in a difference Fourier synthesis or positioned theoretically, and were refined in a riding model with the C—H distance fixed at 0.96 Å. Weighted agreement factors  $R_w$  and goodness-of-fit S were based on  $F^2$ . The conventional R factor was based on F. The calculations were performed using the programs SHELXTL<sup>13</sup> and SHELXL-93<sup>14</sup> on a PC486D4 personal computer.

#### Physical measurements

Absorption bands were recorded using a Beckman 5240 spectrophotometer. Magnetic susceptibilities were measured at 296 K by the Faraday method, using  $Hg[Co(SCN)_4]$  as the calibrant. The elemental analyses were performed on an EA 1108 CHNS Fisons Instruments.

#### **RESULTS AND DISCUSSION**

### Crystal structure

The accurate cell parameters, crystal data and details concerning the structure refinement are given in Table 1. The unique rhenium atom lies on a centre of symmetry. Therefore, the atoms Re, Cl(1), Cl(2) and symmetry equivalents of the two chlorine atoms lie in one plane by the requirements of symmetry. The coordination around the rhenium atom (Fig. 1) is a square bipyramid extended along the Re-P bonds [2.5696(8) Å]. The Re-Cl bonds are slightly but significantly different : Re-Cl(1) = 2.3203(8) and Re-Cl(2) = 2.3300(8)Å (Table 2).

The molecular structure of  $[\text{ReCl}_4(\text{PPh}_3)_2]$ , omitting hydrogen atoms attached to the aromatic rings, is given in Fig. 2. The  $\text{ReCl}_4P_2$  core of the  $[\text{ReCl}_4(\text{PPh}_3)_2]$  molecule has  $D_{4h}$  symmetry. The principal distances and angles are listed in Table 2.

#### Electronic transitions

Table 3 presents the absorption bands together with their characteristics, based on Fig. 3. On the grounds of the absorption bands gathered in Table 3, Dq, Ds,  $D\tau$ , B and C were estimated. Based on Dq (17,889 cm<sup>-1</sup>), Ds (-4091 cm<sup>-1</sup>) and  $D\tau$  (136 cm<sup>-1</sup>), the orbital energies were calculated (Fig. 3). Based on B (473 cm<sup>-1</sup>) and C (2175 cm<sup>-1</sup>), the pairing energy was calculated (15,136 cm<sup>-1</sup>).

The data of Fig. 3 and Table 3 are consistent with the results contained in Table 2 and Fig. 2, because they confirm the structure of *trans*-[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] as an elongated square bipyramid with the electron configuration  $(b_{2g})^1(e_g)^2$ . Such a configuration is also confirmed by the magnetic moment  $\mu_{\text{eff}} = 3.62 \ \mu_{\text{B}}$ , corresponding to three un-

| Empirical formula                           | $C_{36}H_{30}Cl_4P_2Re$                              |
|---|--|
| Formula weight                              | 852.54   |
| Temperature                                 | 293 K  |
| Wavelength                                  | 0.71073 Å  |
| Crystal system                              | monoclinic   |
| Space group                                 | $P2_1/n$   |
| Unit cell dimensions                        | a = 9.343(1)  Å                                      |
|   | $b = 21.003(2) \text{ Å } \beta = 117.44(1)^{\circ}$ |
|   | c = 9.633(1) Å                                       |
| Volume                                      | 1677.6(3) Å <sup>3</sup>                             |
| Ζ   | 2  |
| Density (calculated)                        | $1.688 \text{ Mg m}^{-3}$                            |
| Absorption coefficient                      | 4.061 mm <sup>-1</sup>                               |
| <i>F</i> (000)                              | 838  |
| Reflections collected                       | 5631   |
| Independent reflections                     | 4631 ( $R_{\rm int} = 0.0212$ )                      |
| Refinement method                           | Full-matrix least-squares on $F^2$                   |
| Data/restraints/parameters                  | 4576/0/196   |
| Goodness-of-fit on $F^2$                    | 1.124  |
| $R_{\rm obs} \left[ I > 2\sigma(I) \right]$ | $R = 0.0275, R_{\rm w} = 0.0623$                     |
| R <sub>all</sub>                            | $R = 0.0366, R_{\rm w} = 0.0745$                     |
| Largest diff. peak and hole                 | 1.232 and $-0.645 \text{ e} \text{ Å}^{-3}$          |

Table 1. Crystal data and structure refinement for [ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>]



Fig. 1. The coordination around the rhenium atom.

paired electrons. A small deviation of  $\mu_{eff}$  in comparison with 3.88  $\mu_{B}$  is caused by a weak spin-orbit

coupling  $(\lambda = 299.6 \text{ cm}^{-1})$ . In the case of the ReCl<sub>6</sub><sup>2-</sup> ion, the spin-orbit coupling is strong



Fig. 2. The molecular structure of  $[ReCl_4(PPh_3)_2]$  (hydrogen atoms are omitted for clarity).



Fig. 3. The molecular orbitals diagram for  $[\text{ReCl}_4(\text{PPh}_3)_2]$ .

 $(\lambda = 3000 \text{ cm}^{-1})$ ,<sup>15</sup> and this causes the degenerate electronic ground state, having the ground term,  $\Gamma_8$ , not  ${}^4A_{2g}$ .

The existence of three unpaired electrons (in spite

of the energy level  $b_{2g}$  being lower than  $e_g$  by the value  $\Delta = 12,954$  cm<sup>-1</sup>) results from the fact that the pairing energy  $P > \Delta$ .

The results of this paper confirm the fact that the

| Re—Cl(1)     | 2.3203(8) | Cl(1)—Re— $Cl(2)$    | 89.11(3) |
|--------------|-----------|----------------------|----------|
| Re-Cl(2)     | 2.3300(8) | Cl(1)—Re—P(1)        | 92.80(3) |
| Re-P(1)      | 2.5696(8) | Cl(2)—Re—P(1)        | 92.85(3) |
| P(1)C(7)     | 1.810(3)  | C(7) - P(1) - C(1)   | 105.3(2) |
| P(1) - C(1)  | 1.821(3)  | C(7) - P(1) - C(13)  | 105.8(1) |
| P(1) - C(13) | 1.826(3)  | C(1) - P(1) - C(13)  | 101.3(1) |
|              |           | C(7) - P(1) - Re     | 110.8(1) |
|              |           | C(1) - P(1) - Re     | 93.9(2)  |
|              |           | C(13) - P(1) - Re    | 114.8(1) |
|              |           | C(6) - C(1) - P(1)   | 123.7(3) |
|              |           | C(2) - C(1) - P(1)   | 119.0(3) |
|              |           | C(12) - C(7) - P(1)  | 122.5(3) |
|              |           | C(8) - C(7) - P(1)   | 118.7(3) |
|              |           | C(14) - C(13) - P(1) | 118.2(2) |
|              |           |                      |          |

Table 2. Important bond lengths (Å) and angles (°) for [ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>]

Table 3. Band positions, molar extinction coefficients and assignments

| Assignments  |  |  |
|--|--|--|
| Character of the transition                        |  |  |
| ${}^{4}A_{2a} \rightarrow {}^{2}E_{a}$             |  |  |
| ${}^{4}A_{2a}^{^{3}} \rightarrow {}^{4}A_{1a}^{3}$ |  |  |
| ${}^{4}E_{a} \rightarrow {}^{4}A_{1a}$             |  |  |
| $d \rightarrow p$                                  |  |  |
| typical charge transfer                            |  |  |
| typical charge transfer                            |  |  |
|  |  |  |

[ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] prepared has  $D_{4h}$  symmetry, which is energetically preferred compared to the complex with  $C_{2r}$  symmetry. The compound with *cis* configuration may be obtained using bidentate ligands instead of monodentate ones.<sup>10</sup>

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