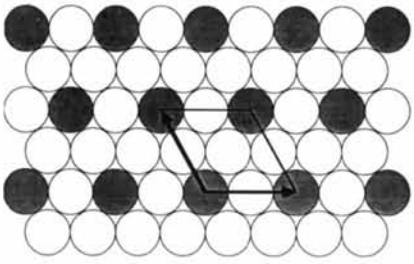
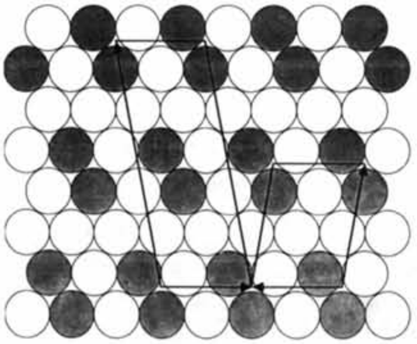
distortion of the uniform sphere structure, c will equal $a \times 7^{1/2}$ with a monoclinic angle of 100.9°. The observed values of $c/(a \times 7^{1/2})$ (0.973) and β [98.01 (1)°] are in excellent agreement with this ideal while the deviation in the ratio $b/a(\frac{2}{3})^{1/2}$ (0.743) strongly reflects the presence of the lower-symmetry piperidinium cation.



(III)



(IV)

A more perfunctory analysis of the system is made by classifying it as a distorted variant of the $CsNiCl_3$ structure. Here a loosely defined aggregate of two piperidinium cations and a chloride anion comprise the 'monocation' of the structure. Distortions and characteristics of the isomorphic α-picolinium trichloronickelate structure (Bond & Willett, 1992; Bond, 1990) are, then, applicable to the description of the bis(piperidinium) tetrachloronickelate structure. Indeed, the average geometry of the inorganic chain is practically identical in the two structures: Ni—Cl (mean) = 2.42 (2) Å, Ni—Cl—Ni (mean) = 79 (1)°, Ni···Ni distance = 3.0716 (4) Å compared to 2.42 (3) Å, 78 (1)° and 3.040 (1) Å, respectively, for the α-picolinium salt. These chains have a nearest-neighbor distance of 10.17 Å compared to 9.37 Å in the α-picolinium derivative or 9.11 Å in the tetramethylammonium derivative, leading us to believe that this new class of A_2NiCl_4 compounds should prove to be good examples of one-dimensional magnetic systems.

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Structure of *trans*-$[Re(CO)_4(PPh_3)I]$

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Abstract. (*OC*-6-23)-Tetracarbonyliodo(triphenylphosphine)rhenium, $[ReI(C_{18}H_{15}P)(CO)_4]$, M_r = 687.4, monoclinic, $P2_1/c$, $a = 9.344$ (3), $b = 19.17$ (5), $c = 12.604$ (4) Å, $\beta = 90.13$ (2)°, $V = 2258$ (1) Å^3, $Z = 4$, $D_x = 2.0224$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 88.2$ cm^{-1}, $F(000) = 1287.8$, $T = 293$ K, $R = 0.042$

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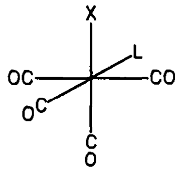
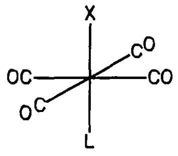
for 3482 unique reflections. The PPh_3 group and I atom were observed to be in a *trans* arrangement with the CO groups bending, on average, towards the I atom.

Introduction. The substitution chemistry of *cis*-$[Re(CO)_4LX]$ (1) (L = Group 15 donor ligand; X = Cl, Br, I) has been well documented (Wilkinson, Stone & Abel, 1982). Since the *trans*-$[Re(CO)_4LX]$ (2) complexes cannot be prepared by conventional procedures, *i.e.* by substitution of $[Re(CO)_5X]$ with L (Singleton, Moelwyn-Hughes & Garner, 1970; Moelwyn-Hughes, Garner & Gordon, 1971; Jolly & Stone, 1965; Freni, Giusto & Romiti, 1967), their chemistry has, until recently, not been explored. Studies on the halogen cleavage reactions of $[Re_2(CO)_8L_2]$ have now permitted the maximization of the yield of (2) and an exploration of the chemistry of the *trans* complex is now possible (Ingham & Coville, 1992). Previous studies on *cis* and *trans* isomers of $[Re(CO)_2L_3Br]$ (3), (4) (Reimann & Singleton, 1973) would suggest that the CO ligands in (2) should be readily displaced by incoming ligands to yield novel disubstituted isomers. To our surprise, we have found that the CO ligands in (2) are quite unreactive. To assist with an understanding of the substitution chemistry of (2), an X-ray crystal structure determination of *trans*-$[Re(CO)_4(PPh_3)I]$ (5) has been undertaken.



(1)



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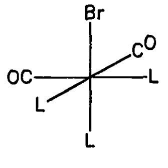

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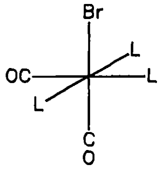

(4)

Experimental. *trans*-$[Re(CO)_4(PPh_3)I]$ was obtained from the reaction between *diax*-$[Re(CO)_4(PPh_3)]_2$ and I_2 (Ingham & Coville, 1992). *trans*-$[Re(CO)_4(PPh_3)I]$ was purified by column chromatography and pale-yellow crystals suitable for X-ray analysis were obtained by slow crystallization of the materials from mesitylene at 273 K.

Crystal 0.4 × 0.5 × 0.4 mm, systematic absences established space group $P2_1/c$, Enraf–Nonius CAD-4 four-circle diffractometer. Mo $K\alpha$ graphite-monochromated radiation, ω–2θ scan [scan width $(0.60–0.35\tan\theta)^\circ$, scan speed max. 5.49° min^{-1}, min. 60 s per reflection], $2.5 < \theta < 27^\circ$, h −11 to 11, k −1 to 24, l −1 to 16, cell constants from least-squares refinements of the θ values of 25 general reflections, with $11 \le \theta \le 19^\circ$, 5326 intensities measured, 3482 reflections with $F > 3\sigma(F)$.

Lorentz–polarization and empirical absorption corrections (North, Phillips & Mathews, 1968) were applied (min. 0.7682; max. 0.9994). Linear and approximate isotropic crystal decay was minor and no correction was made for this during processing. Patterson (Re, Mo atoms) and difference Fourier techniques were employed to solve the structures using normal heavy-atom procedures. Full-matrix least-squares refinement (*SHELX*82; Sheldrick, 1982) with all non-H atoms anisotropic and H atoms in calculated positions was performed. The weighting scheme used was $w = K\sigma^2(F)$. Final R and wR are 0.042 and 0.037. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and anomalous-dispersion corrections for Re, I and P from Cromer & Liberman (1970) were made. Residual electron density in the final difference maps was within 1.26 and −1.44 e Å^{-3}.

Discussion. The stereochemistry of the title complex is shown in a *SCHAKAL* plot (Keller, 1988) (Fig. 1) which also shows the numbering scheme used in this analysis. Table 1* contains the positional and thermal parameters and Table 2 selected bond length and angle data for *trans*-$[Re(CO)_4(PPh_3)I]$.

The main points of significance relating to the title compound are:

(1) The I atom is in a position *trans* to the phosphine ligand. The only previously reported structures, $[Re(CO)_4LX]$ [L = PEt_3, X = Cl (Bucknor, Cotton, Falvello, Reid & Schmulbach, 1986); L = dtdp (dtdp = *cis*-3,4-dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3,-diazaphosphole-*P*), X = Br (Baccolini, Busetto, Contessa, Albano & De Martin, 1984)] contain the phosphine ligand in the *cis* position, with respect to the halogen. These products were obtained by direct thermal reaction of the monomer, $[Re(CO)_5X]$, with the ligand, L. The only other equivalent structures reported containing a phosphine ligand in a *trans* position to a substituent are found when the phosphine is *trans* to a metal fragment as in $Br_2Sn[Re(CO)_4(PPh_3)]_2$ (Preut & Haupt,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55688 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0414]

1983) and $[Re_2(CO)_8(PMe_2Ph)_2]$ (Harris, Boeyens & Coville, 1985).

(2) The carbonyl ligands in $[Re(CO)_4(PPh_3)I]$ bend, on average, towards the iodine ligand ($X—M—CO < 90°$). This bending away from the phosphine ligand could be related to steric influences or an electronic influence (Elian & Hoffmann, 1975).

(3) The *M*—CO bond lengths in (5) [1.971 (11) Å] are shorter than the equivalent bond lengths in $[Re(CO)_5I]$ [2.021 (14) Å] (Russel & Ruff, 1982; Cotton & Daniels, 1983). The *M*—CO bond lengths in (5) are also comparable to the *cis* *M*—CO bond lengths observed in *cis*-$[Re(CO)_4(dtdp)Br]$. This suggests that the phosphine ligand *trans* to *X* is not expected to enhance the reactivity of the CO ligands in (1) relative to the *cis* CO ligands in (2).

(4) The *M*—CO bond lengths in (5) are of the same order as for the CO ligands *cis* to Cl and PEt_3 in $[Re(CO)_4(PEt_3)Cl]$ [1.974 (12) Å]. However, in the latter structure the *M*—CO bond lengths *trans* to PEt_3 [1.952 (14) Å] and *trans* to Cl [1.922 (16) Å] are shorter.

(5) The *M*—P bond length is dependent on whether the phosphine ligand is *cis* or *trans* to *X*, as is evident from the range of *M*—P bond lengths observed in some related structures: *cis* *d*(*M*—P): 2.484 (3) Å ($X = Cl$, $L = PEt_3$), 2.475 (5) Å ($X = Br$, $L =$ dtdp); *trans* *d*(*M*—P): 2.398 (2) Å ($X = I$, $L = PPh_3$), 2.421 (7) Å $\{SnBr_2[Re(CO)_4(PPh_3)]\}$, 2.349 (5) Å $\{[Re(CO)_4PMe_2Ph]\}$.

(6) The *M*—I bond length in $[Re(CO)_5I]$ [2.779 (2) Å] does not change on replacement of a *trans* CO by PPh_3 [2.880 (1) Å].

In conclusion, the decrease in the *M*—CO bond lengths of $[Re(CO)_5I]$ on replacing a CO ligand by a phosphine ligand results in a decrease in the reactivity of the substituted complexes. No significant differences are observed in the *M*—CO bond lengths when the phosphine ligand is in a *cis* or a *trans* position relative to *X*. This can account for the similar reactivities of the isomeric complexes (1) and (2).

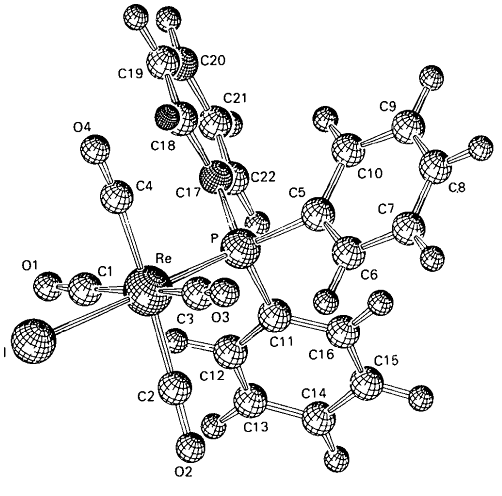

Fig. 1. A *SCHAKAL* plot of *trans*-$[Re(CO)_4(PPh_3)I]$ showing the stereochemistry and numbering system used.

Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* Re, $\times 10^4$ *for others*) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (5)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
Re	21094 (4)	10972 (2)	38179 (3)	41
I	392 (1)	1490	5534 (1)	71
P	3427 (3)	691 (1)	2309 (2)	40 (1)
O1	− 546 (8)	276 (4)	3055 (6)	75 (2)
O2	3248 (10)	− 131 (5)	5210 (6)	89 (3)
O3	4375 (11)	2071 (6)	4775 (7)	172 (4)
O4	948 (12)	2444 (4)	2856 (6)	84 (3)
C1	429 (11)	559 (5)	3339 (7)	50 (2)
C2	2815 (11)	312 (6)	4662 (8)	54 (3)
C3	3591 (14)	1697 (7)	4426 (9)	89 (4)
C4	1408 (13)	1983 (7)	3161 (7)	58 (3)
C5	5100 (9)	1143 (5)	1979 (7)	42 (2)
C6	6096 (10)	1278 (5)	2778 (8)	55 (3)
C7	7372 (11)	1606 (6)	2537 (9)	67 (3)
C8	7633 (12)	1812 (6)	1538 (10)	64 (3)
C9	6709 (12)	1698 (6)	739 (9)	56 (3)
C10	5411 (10)	1358 (5)	935 (7)	52 (3)
C11	3969 (10)	− 221 (5)	2423 (6)	43 (2)
C12	2978 (12)	− 712 (6)	2655 (9)	61 (3)
C13	3249 (14)	− 1403 (6)	2712 (10)	71 (4)
C14	4641 (15)	− 1619 (7)	2610 (9)	64 (4)
C15	5724 (15)	− 1119 (7)	2405 (10)	64 (4)
C16	5344 (11)	− 443 (6)	2285 (8)	59 (3)
C17	2424 (9)	710 (5)	1051 (6)	50 (2)
C18	1722 (11)	1323 (5)	752 (7)	52 (3)
C19	982 (11)	1360 (6)	− 215 (7)	55 (3)
C20	986 (11)	817 (7)	− 866 (7)	78 (3)
C21	1659 (11)	191 (6)	− 573 (7)	78 (3)
C22	2362 (10)	143 (5)	374 (7)	56 (2)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *for* (5)

Re—I	2.800 (1)	Re—P	2.398 (2)
Re—C1	1.973 (11)	P—C5	1.836 (9)
Re—C2	1.957 (12)	P—C11	1.824 (9)
Re—C3	1.955 (12)	P—C17	1.840 (8)
Re—C4	1.999 (13)		
P—Re—I	175.1 (1)	Re—P—C5	117.7 (3)
P—Re—C1	89.8 (3)	Re—P—C11	113.1 (3)
P—Re—C2	90.5 (3)	Re—P—C17	114.5 (3)
P—Re—C3	97.9 (3)		
P—Re—C4	96.7 (3)		

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Synthesis and Structure of (Acetato-*O*,*O*′)(perchlorato-*O*)(2,2′:6′2″-terpyridine-*N*,*N*′,*N*″)copper(II)

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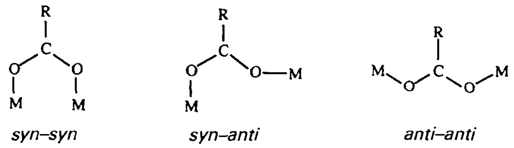
Abstract. (Acetato-*O*,*O*′)(perchlorato-*O*)(2,2′:6′,2″-terpyridine-*N*,*N*′,*N*″)copper(II), [Cu(ClO$_4$)(CH$_3$CO$_2$)(C$_{15}$H$_{11}$N$_3$)], $M_r = 455.32$, triclinic, $P\bar{1}$, $a = 11.010$ (3), $b = 10.791$ (3), $c = 8.356$ (2) Å, $\alpha = 83.56$ (2), $\beta = 86.11$ (2), $\gamma = 64.67$ (2)°, $V = 891.4$ (7) Å^3, $Z = 2$, $D_x = 1.696$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 14.66$ cm^{-1}, $F(000) = 462$, $T = 298$ K, final $R = 0.062$ and $wR = 0.066$ for 1011 reflections with $I \geq 2.5\sigma(I)$. The structure consists of discrete neutral [Cu(terpy)(CH$_3$COO)(ClO$_4$)] units (terpy = 2,2′:6′,2″-terpyridine). The coordination environment around Cu$^{\text{II}}$ ions is distorted 4 + 2 octahedral. The equatorial plane is composed of the three N atoms of the terpyridine ligand and one O atom of the acetate group, whereas the apical positions are occupied by the other O atom of the acetate ligand and one O atom of the perchlorate anion.

Introduction. Since the determination of the crystal structure of copper(II) acetate monohydrate (van Niekerk & Schoening, 1953), carboxylate-containing Cu$^{\text{II}}$ complexes have been exhaustively investigated from both structural and magnetic viewpoints (Wilkinson, Gillard & McCleverty, 1987; Kato & Muto, 1988). These studies have identified three structural types of carboxylate O-atom coordination, *i.e.* unidentate, chelating and bridging. We are interested in the last coordination mode because our current research work deals with the chemical and structural effects that govern exchange-coupling interactions in polynuclear species (Lloret, Julve, Faus, Solans, Journaux & Morgenstern-Badarau, 1990). In this respect, the ability of simple carboxylates to form bridging ligands is well established (Mehrotra & Bohra, 1983), the most important types being *syn–syn*, *syn–anti* and *anti–anti*.



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