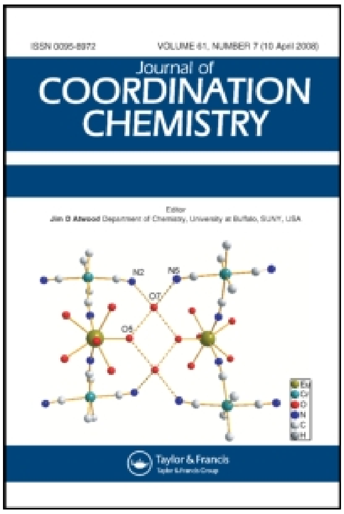

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FORMATION OF COORDINATED *t*-$Bu_2P(H)O$ *via* REACTION OF *t*-Bu_2PCl WITH ETHANOLIC ReO_4^-. SYNTHESIS AND STRUCTURE OF *trans*-$ReOCl_2$ (OEt){*t*-Bu_2 P(OEt)}{*t*-Bu_2 P(H)O}

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FORMATION OF COORDINATED *t*-$Bu_2P(H)O$ *via* REACTION OF *t*-Bu_2PCl WITH ETHANOLIC ReO_4^-. SYNTHESIS AND STRUCTURE OF *trans*-$ReOCl_2(OEt)\{t\text{-}Bu_2P(OEt)\}\{t\text{-}Bu_2P(H)O\}$

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Reaction of *t*-Bu_2PCl with $KReO_4$ (3:1) in ethanol at room temperature results in the formation of *trans*-$ReOCl_2(OEt)\{t\text{-}Bu_2P(OEt)\}\{t\text{-}Bu_2P(H)O\}$ in 65% yield. The structure of this purple, hexane-soluble crystalline material has been determined by X-ray crystallography. The compound crystallizes in the space group $P2_1/n$ with $a = 12.762$ (5), $b = 15.919$ (4), $c = 15.103(2)$ Å, $\beta = 109.34(5)°$, and $Z = 4$. The structure was refined to $R = 0.066$ ($R_w = 0.071$) for 1968 independent reflections. The molecular structure consists of a rhenium atom in a distorted octahedral geometry. Two Cl atoms are *trans* to each other as are the Re=O and Re-O-Et units. The Re=O and Re-O-Et lengths (1.69(2) and 1.85(2) Å) and the geometry about the ethoxide oxygen atom indicate a considerable degree of M–O multiple bonding for both of these units. The *t*-$Bu_2P(H)O$ and *t*-$Bu_2P(OEt)$ units are mutually *trans* and behave as neutral, two-electron donors to the Re(V) center.

Keywords: rhenium, phosphine, phosphine oxide, complex, structure

INTRODUCTION

As part of a study of the reactions of chlorophosphines (R_2PCl) with a variety of oxometallate species, we have investigated the reactions of potassium perrhenate ($KReO_4$) with di-tertbutylchlorophosphine (*t*-Bu_2PCl). At room temperature in THF, toluene and diethylether reactions occur readily; however, we have so far been unable to isolate a pure compound from the resulting reaction mixtures. In contrast, the reaction of *t*-Bu_2PCl with $KReO_4$ in ethanol (3:1) produces a bright purple solution from which the purple, crystalline, hexane-soluble Re(V) species *trans*-$ReOCl_2(OEt)\{t\text{-}Bu_2P(OEt)\}\{t\text{-}Bu_2P(H)O\}$ (**1**) may be isolated in 65% yield as follows.

$$KReO_4 + 3t\text{-}Bu_2PCl \xrightarrow{EtOH} ReOCl_2(OEt)\{t\text{-}Bu_2P(OEt)\}\{t\text{-}Bu_2P(H)O\} + \text{other products}$$

The formation of *t*-$Bu_2P(OEt)$ can be readily accounted for from the interaction of *t*-Bu_2PCl with EtOH. However, a complex mechanism must occur to allow for the overall formation of (**1**), and it is surprising that it is formed in such a high yield. An interesting feature of (**1**) is the formation of the coordinated *t*-$Bu_2P(H)O$ unit. Also formed in the reaction in *ca* 15% yield is free *t*-$Bu_2P(H)O$. Although a variety of Re(V) oxide complexes are known, relatively few structural characterizations of these species have been reported.[1,2] In this paper, we describe the synthesis, characterization and X-ray crystal structure of (**1**).

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EXPERIMENTAL

All reactions were performed under nitrogen or vacuum. Hexane was dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Ethanol was distilled from magnesium ethoxide under nitrogen prior to use.

Potassium perrhenate ($KReO_4$)[3] and bis-*t*-butylphosphoruschloride[4] were prepared by the literature methods. Instruments: IR, Perkin Elmer 1330; NMR, Varian EM-390 ^1H, 90 MHz, Varian FT-80 (^{31}P, 32.348 MHz). Melting points were determined in sealed capillaries under nitrogen (1 atm) and are uncorrected.

Trans-ReOCl$_2$(OEt){t-Bu$_2$P(OEt)}{t-Bu$_2$P(H)O} (**1**)

Bis-*t*-butylphosphoruschloride (0.98 cm^3, 6.35 mmol) was added to a solution of $KReO_4$ (1.0 g, 6.33 mmol) in 40 cm^3 ethanol at -78°C. The mixture turned purple with a white precipitate after being warmed slowly to room temperature for three hours. The solution was decanted and volatile materials were removed from it under vacuum. The

TABLE I
Crystal Data for (**1**).

Description of Crystal	(**1**)
Colour	Purple
Habit	Brick
Max. crystal dimension (mm)	0.25 × 0.23 × 0.23
Unit Cell	
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell parameters:	
a(Å)	12.762(5)
b(Å)	15.919(4)
c(Å)	15.103(3)
β(deg.)	109.34(5)
U(Å^3)	2895.2(5)
Molecules per unit cell	4
Formula	$C_{20}H_{47}Cl_2O_4P_2Re$
Molecular weight (g mol^{-1})	670.65
Calculated density (g cm^{-3})	1.539
μ-calc. (cm^{-1})	45.70
Data Collection	
Radiation (Å)	MoK_α(0.71073)
Scan technique	$\theta/20$
Scan width (deg)	$0.8 + 0.35 \tan \theta$
Range of indices (h, k, l)	0 to 14, 0 to 16, −17 to 17
2θ range (deg)	3.0° to 48.0°
No. reflections measured	2277
Standard reflections:	
intensity	$6\ 1\ 2,\ \bar{2}\ 8\ 3$
orientation	$2\ 8\ 1,\ 4\ \bar{7}\ 1$
Decay of standards	< 3.0%
Min. % transmission	37.72
Max. % transmission	46.05
Average % transmission	41.88
Structure Determination	
No. reflections used ($I > 3\ \sigma(I)$)	1968
No. parameters varied	247
Data/parameter ratio	8.0
Shift to error ratio	1.49
E.s.d. of an observation of unit weight	8.33
R	0.066
R_w	0.071

residue was extracted into hexane (40 cm^3), and the resulting blue solution was evaporated under vacuum to *ca.* half the volume (20 cm^3). Cooling (-30°C) yielded purple crystals which were collected and dried under vacuum. Also formed is *t*-$Bu_2P(H)O$[5] (*ca* 15%) which cocrystallizes with (**1**). The two compounds may be separated manually and further batches of *t*-$Bu_2P(H)O$ may be isolated from the supernatant liquid left from the first crystallization. Yield: 1.50 g (65%). M.P. 98–101°C (dec.). NMR: $^1H(C_6D_6$, δ values rel. Me_4Si at 90 MHz), δ 4.29 m, (2 H, P-O-CH_2-CH_3), δ 3.96, q, (2 H, $^3J_{H-H}$ = 8 Hz, O-CH_2-CH_2), δ 1.46, d, (18 H, J_{P-H} = 10 Hz, *t-Bu*$_2$P), δ 1.33, t, (3 H, $^3J_{H-H}$ = 8 Hz, O-CH_2-CH_3), δ 1.13, d, (18 H, J_{P-H} = 12 Hz, *t-Bu*$_2$P). The P-*H* and P-O-CH_2-CH_3 resonances were not observed and may be obscured by other peaks. $^{31}P\{^1H\}$, (in C_6D_6, ambient temperature, rel. 85% H_3PO_4(aq.)), δ 131.64 s, [*t*-Bu_2*P*(OCH_2CH_3)], δ 74.45 s, (*t*-Bu_2*P*(H)O). ^{31}P, (C_6D_6, ambient temperature), the δ 74.45 peak splits into a doublet, $^1J_{P-H}$ = 435 Hz. IR (nujol mull, KBr): 2720w, 2340w, 1465s, 1395m, 1375s, 1350w, 1195w, 1185w, 1100s, 1075s, 1030s, 1015s, 955s, 935s, 920s, 815m, 745m, 720w, 645w, 620m, 585s, (cm^{-1}).

X-Ray Crystallography

Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoK_α radiation. Data were collected by the $\theta/2\theta$ scan technique at

TABLE II
Bond Lengths (Å) and Angles (°) for (**1**).

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
Re	Cl1	2.389(8)	P2	C9	1.83(3)	C9	C10	1.59(5)
Re	Cl2	2.397(8)	P2	C13	1.90(4)	C9	C11	1.59(4)
Re	P2	2.406(7)	O1	C19	1.40(4)	C9	C12	1.57(4)
Re	O1	1.85(2)	O4	C17	1.46(3)	C13	C14	1.57(4)
Re	O2	1.69(2)	C1	C2	1.54(5)	C13	C15	1.58(4)
Re	O3	2.18(2)	C1	C3	1.51(5)	C13	C16	1.50(4)
P1	O3	1.50(1)	C1	C4	1.57(4)	C17	C18	1.54(5)
P1	C1	1.79(3)	C5	C6	1.57(4)	C19	C20	1.25(7)
P1	C5	1.82(3)	C5	C7	1.62(4)			
P2	O4	1.61(2)	C5	C8	1.55(4)			

Atom 1	*Atom 2*	*Atom 3*	*Angle*	*Atom 1*	*Atom 2*	*Atom 3*	*Angle*
Cl1	Re	Cl2	171.0(3)	Re	P2	O4	116.2(8)
Cl1	Re	P2	96.8(3)	Re	P2	C9	109.9(9)
Cl1	Re	O1	91.0(6)	Re	P2	C13	116.5(8)
Cl1	Re	O2	91.8(6)	O4	P2	C9	98(1)
Cl1	Re	O3	86.0(5)	O4	P2	C13	103(1)
Cl2	Re	P2	91.7(3)	C9	P2	C13	103(1)
Cl2	Re	O1	85.5(6)	C9	P2	C13	111(1)
Cl2	Re	O2	90.5(6)	Re	O1	C19	151(3)
Cl2	Re	O3	85.3(5)	Re	O3	P1	137(1)
P2	Re	O1	93.3(5)	P2	O4	C17	124(2)
P2	Re	O2	94.5(6)	O4	C17	C18	106(3)
P2	Re	O3	174.7(4)	O1	C19	C20	119(4)
O1	Re	O2	171.4(8)				
O1	Re	O3	82.1(6)				
O2	Re	O3	89.9(7)				
O3	P1	C1	110(1)				
O3	P1	C5	109(1)				
C1	P1	C5	118(2)				

Numbers in parentheses are estimated standard deviations.

23 ± 2°C. Details of the standard data collection methods are as described in reference 6. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS.[7] A crystal of (**1**) was mounted in a thin-walled glass capillary tube under nitrogen. Unit cell parameters were obtained by carefully centering 25 refractions having 2θ values between 22.0° and 24.0°. The space group was uniquely determined by systematic absences as $P2_1/n$. Details of crystal data parameters and other relevant information are collected in Table 1. Key bond lengths and angles are in Table 2 and positional parameters in Table 3. The data were corrected for Lorentz and polarization effects and a numerical absorption correction was made using a ψ scan method. The structure was solved and refined by direct methods (MULTAN)[8] and by successive cycles of least-squares refinement followed by difference Fourier maps. A non-Poisson contribution weighting scheme was used in the least squares refinement with an experimental instability factor P of 0.07.[9] All non-hydrogen atoms except for C(3), C(5) and C(10) were refined anisotropically. Hydrogen atoms were not located. The highest peak in the final difference Fourier was 1.05 $e\text{Å}^{-3}$ located 1.136 Å from Re.

RESULTS AND DISCUSSION

Synthesis

Bis-*t*-butylphosphoruschloride (t-Bu_2PCl) reacts with an ethanolic solution of

TABLE III
Positional parameters and estimated standard deviations for (**1**).

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
Re	0.53389(8)	0.15025(8)	0.76946(7)	2.73(2)
Cl1	0.4088(5)	0.2659(6)	0.7199(5)	4.9(2)
Cl2	0.6358(6)	0.0233(6)	0.8243(5)	4.8(2)
P1	0.2860(5)	0.0449(6)	0.6878(4)	3.5(2)
P2	0.7022(5)	0.2283(5)	0.7921(4)	3.1(2)
O1	0.539(1)	0.165(1)	0.8926(9)	3.5(4)
O2	0.518(1)	0.124(1)	0.6574(9)	3.8(5)
O3	0.388(1)	0.076(1)	0.762(1)	3.5(4)
O4	0.814(1)	0.189(1)	0.865(1)	4.7(5)
C1	0.165(2)	0.067(2)	0.719(2)	5.4(8)
C2	0.160(2)	0.010(2)	0.800(2)	7(1)
C3	0.172(3)	0.156(3)	0.753(2)	7.3(9)*
C4	0.055(2)	0.054(3)	0.634(3)	9(1)
C5	0.310(2)	−0.063(2)	0.658(2)	3.9(6)*
C6	0.394(2)	−0.058(2)	0.603(2)	5.5(9)
C7	0.196(2)	−0.104(2)	0.588(2)	6(1)
C8	0.362(2)	−0.113(2)	0.750(2)	5.6(9)
C9	0.741(2)	0.223(2)	0.686(2)	5.1(8)
C10	0.765(2)	0.127(2)	0.671(2)	5.4(7)*
C11	0.853(2)	0.274(2)	0.702(2)	5.0(8)
C12	0.653(3)	0.255(2)	0.593(2)	6(1)
C13	0.704(2)	0.341(2)	0.834(2)	4.9(8)
C14	0.645(2)	0.340(2)	0.910(1)	5.4(6)
C15	0.828(2)	0.370(2)	0.884(2)	5.7(9)
C16	0.646(2)	0.400(2)	0.756(2)	4.4(8)
C17	0.825(2)	0.161(2)	0.960(2)	4.5(8)
C18	0.911(3)	0.089(3)	0.983(3)	8(1)
C19	0.531(3)	0.132(3)	0.977(2)	12(1)
C20	0.445(4)	0.146(5)	0.996(4)	17(2)

Starred atoms were refined with isotropic thermal parameters. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \text{gamma}) \times B(1, 2) + ac(\cos \text{beta}) \times B(1, 3) + bc (\cos \text{alpha}) \times B(2, 3)]$.

potassium perrhenate (3:1) over a period of several hours to give a bright purple solution and a white precipitate. From the mixture, purple crystals of *trans*-ReOCl$_2$(OEt){*t*-Bu$_2$P(OEt)}{*t*-Bu$_2$P(H)O} (**1**) can be isolated by evaporation to dryness and crystallization from hexane in *ca* 65% yield. In addition, moderate yields of the phosphine oxide *t*-Bu$_2$P(H)O[5] (*ca* 15%) may be isolated and the two products may be separated by careful fractional crystallization from hexane (−20°C).

IR spectroscopic data for (1) give evidence for the presence of the P-H group ($\nu_{\text{P-H}}$ = 2340 cm^{-1}, *w*). The NMR data (^{1}H and ^{31}P) are in accord with the solid state structure as determined by X-ray crystallography. Thus the ^{1}H NMR spectrum has two doublets at δ 1.46 ($J_{\text{P-H}}$ = 10 Hz) and δ 1.13 ($J_{\text{P-H}}$ = 12 Hz) which are assigned to the two sets of *t-Bu*$_2$P protons. Two sets of resonances are observed at δ 4.29 and δ 3.96 and are assigned to the P-O-*CH*$_2$-CH$_3$ and Re-O-*CH*$_2$-CH$_3$ protons, respectively. The P-O-CH$_2$-*CH*$_3$ resonance is probably obscured by *t-Bu*$_2$P resonances while the Re-O-CH$_2$-*CH*$_3$ peak is at δ 1.33. The unique P-*H* can also not be assigned with certainty. The ^{31}P{^{1}H} NMR shows two sharp singlets at δ 131.64 and δ 74.45, and the latter is split into a doublet ($^1J_{\text{P-H}}$ = 435 Hz) in the ^{31}P spectrum.

X-Ray Structure of (1)

A view of the molecule is shown in Figure 1 and bond lengths and angles are presented in Table II. The coordination geometry about Re is essentially octahedral with roughly *trans*-chloride atoms. The stereochemistry is similar to that found in other Re(V) oxo analogues such as ReI$_2$O(OMe)(PPh$_3$)$_2$[2] ReI$_2$O(OEt)(PPh$_3$)$_2$[2] and ReCl$_3$O(PEt$_2$Ph)$_2$.[10]

The Re-O(oxide) and Re-O(alkoxo) distances (1.69 (2) Å and 1.85 (2) Å) are similar to those found in ReI$_2$O(OEt)(PPh$_3$)$_2$ (1.715 (9) Å and 1.880 (9) Å) and ReI$_2$O(OMe)(PPh$_3$)$_2$ (1.698 (5) Å and 1.859 (5) Å). The short Re-O (oxide) distance suggests a considerable degree of triple bond character due to O ⟶ Re π bonding. The Re-O (alkoxo) distance

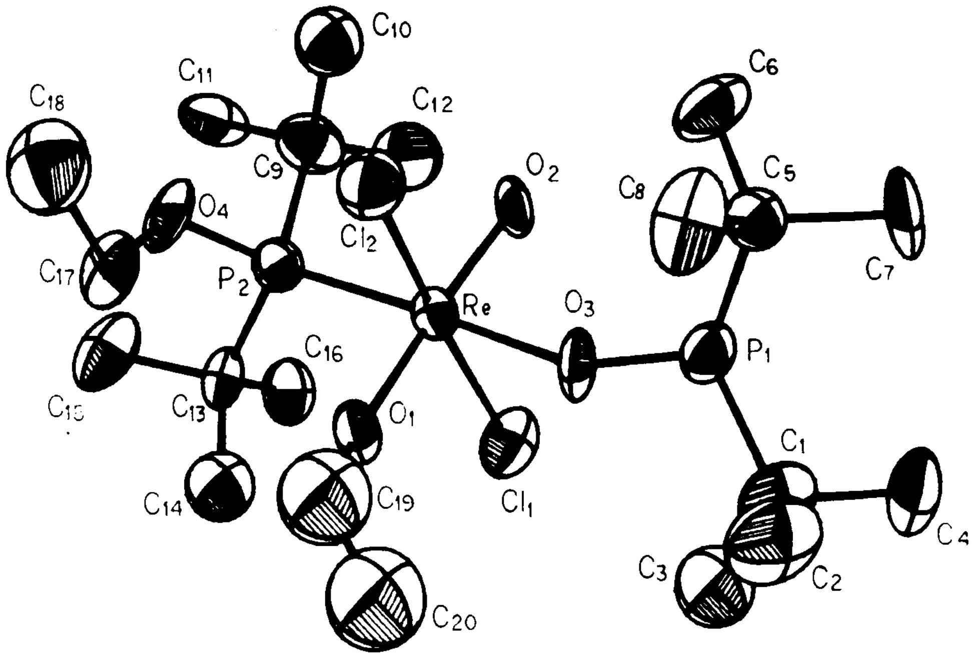

FIGURE 1. ORTEP view of (1).

and Re-O(1)-C(19) angle of 151(3)° also indicate appreciable double bond character.[11,12] In contrast, the Re-O ($P(H)Bu^t_2$) distance (2.18 (2) Å) indicates that the phosphine oxide ligand behaves as a normal two-electron donor to Re. The Re-Cl bond distances are similar (2.389 (8) Å and 2.397 (8) Å) and can be compared to a Re-Cl distance of 2.377 (2) Å in $ReNCl_2(PPh_3)_2$,[12] 2.38 Å in $[Re_2OCl_{10}]^{4-}$[13] and 2.44 Å (av.) in $ReCl_3O(PEt_2Ph)_2$.[10] Lastly, the Re-P distance for the $P(OCH_2CH_3)(t\text{-}Bu)_2$ group 2.406 (7) Å is typical for Re(V) - P(phosphine) interactions.[5,10,12]

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of thermal parameters and observed and calculated structure factors have been deposited with the editor and are available on request.

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