Reactions of Dichlorobis(2,3-dimethylbutane-2,3-diolato)-tungsten(VI) with Water and Alcohols†

Ari Lehtonen* **and Reijo Sillanpää**
Department of Chemistry, University of Turku, FIN-20500, Turku, Finland

A tungsten(VI) complex $[WCl_2(pin)_2]$ **1** [H_2pin = pinacol (2,3-dimethylbutane-2,3-diol)] reacted with water forming dimeric $[W_2O_3(pin)_2(Hpin)_2]$, but in the presence of tripropylamine $[(NPr_3H)_2Cl]_2[W_6O_{19}]$ **2** was formed. The reaction of **1** with H_2pin led to $[W(pin)_3]$ and with phenol (PhOH) to $[W(pin)_2(OPh)_2]$ **3**. The structures of complexes **2** and **3** were confirmed by X-ray methods. Compound **2** is made up of the known $[W_6O_{19}]^{2-}$ anion and two $[NPr_3H \cdots Cl^- \cdots HNPr_3]^+$ cations. Complex **3** is formed of monomeric $[W(pin)_2(OPh)_2]$ molecules in which the W atom is octahedrally surrounded by six oxygen atoms.

The chloro complexes of high-valent tungsten are known to react with molecules containing hydrogen donors, such as OH, NH_2 or SH groups, leading to the liberation of HCl and formation of new tungsten–ligand bonds.[1–3] These reactions are similar to those supposed to be involved in various catalytically interesting processes, *e.g.* in propylene ammoxidation and some enzymatic reactions.[4,5] Hydrogen donors can also mimic the hydroxyl groups of solid catalyst carriers, *e.g.* diols have been considered as soluble models for silica supports.[5]

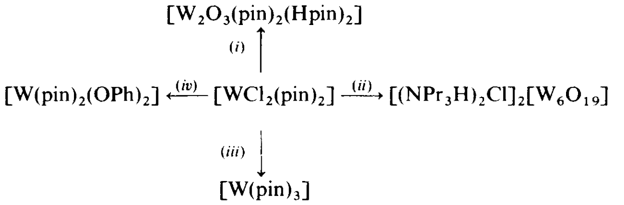
Organotungsten chlorides can react with water in organic solvents forming complexes containing terminal oxo ligands. The tungsten(V) complex $[W(\eta\text{-}C_5Me_5)Cl_4]$ undergoes hydrolysis of the metal chloride bonds to yield oxo complexes, with the final product being dependent on the base employed.[3] The reaction of $[WO(CH_2CMe_3)_3Cl]$ and an excess of water in the presence of NEt_3 leads to $[W_2O_3(CH_2CMe_3)_6]$.[6]

Reactions of high-valent chlorotungsten complexes with alcohols have been extensively studied. Silylated alcohols or a base are needed to displace the last halide ions, when hexa-alcoholato or -phenolato complexes are prepared from corresponding tungsten(VI) halides. However, the reaction of WCl_6 with H_2bino (1,1′-binaphthol) leads readily to $[W(bino)_3]$.[7] The complex $[W(\eta\text{-}C_5Me_5)(OMe)_3Cl]$ does not react with further alcohol in the presence of NEt_3, unlike the analogous phenolato complex in the reaction with additional phenol.[8] These observations indicate that chloro ligands are more easily replaced by phenols than alcohols and easier by one bifunctional than by two monofunctional alcoholate ligands.

Recently we described the synthesis and crystal structure of *cis*-$[WCl_2(pin)_2]$ **1** (H_2pin = pinacol, 2,3-dimethylbutane-2,3-diol).[9] This complex is stable in the solid state and is a suitable starting material for other new tungsten(VI) compounds. In this paper we report the reactions of **1** with water, alcohols and other selected hydrogen donors. Also the crystal structure of $[W(pin)_2(OPh)_2]$ is described.

Results and Discussion

The reactions of complex **1** studied are shown in Scheme 1.



$$\begin{tikzcd}
 & {[W_2O_3(pin)_2(Hpin)_2]} & \\
{[W(pin)_2(OPh)_2]} & {[WCl_2(pin)_2]} \arrow[l, "(iv)"'] \arrow[u, "(i)"] \arrow[r, "(ii)"] \arrow[d, "(iii)"] & {[(NPr_3H)_2Cl]_2[W_6O_{19}]} \\
 & {[W(pin)_3]} &
\end{tikzcd}$$

Scheme 1 (*i*) Water–EtOH + tetrahydrofuran (thf); (*ii*) water + NPr_3–thf; (*iii*) $H_2pin–CHCl_3$; (*iv*) 2 $PhOH–CH_2Cl_2$

Reactions with Water.—Crystals of $[W_2O_3(pin)_2(Hpin)_2]$ are formed when complex **1** is dissolved in EtOH–thf and the solution allowed to stand in the presence of atmospheric moisture [equation (1)]. We had earlier prepared the same

$$2[WCl_2(pin)_2] + 3\,H_2O \longrightarrow [W_2O_3(pin)_2(Hpin)_2] + 4\,HCl \quad (1)$$

compound by the hydrolysis of $[W(eg)(pin)_2]$ [H_2eg = ethylene glygol (ethane-1,2-diol)].[10] In the hydrolysis reaction of **1** the chloride ligands are replaced by hydroxyl groups and the subsequent condensation reaction involving these groups produces compounds with W–O–W bridges and terminal W=O bonds in addition to products such as HCl.

Hydrolysis of complex **1** in thf solution containing NPr_3 as a base leads to the formation of **2** [equation (2)]. Compound **2**

$$6\,[WCl_2(pin)_2] + 19\,H_2O + 4\,NPr_3 \longrightarrow [W_6O_{19}]^{2-} + 4\,NPr_3H^+ + 2\,Cl^- + 10\,HCl + 12\,H_2pin \quad (2)$$

is formed of $[NPr_3H \cdots Cl \cdots HNPr_3]^+$ cations and $[W_6O_{19}]^{2-}$ anions. The hexatungstate anion $[W_6O_{19}]^{2-}$ has also been prepared from the oxotungsten(VI) alcoholate complex, $[WO(OMe)_4]$, *i.e.* by hydrolysis in a methanol solution containing NR_4OH (R = Et, Pr or Bu)[11] and by non-aqueous reaction with $[WO_4]^{2-}$.[12]

Reactions with Alcohols.—The reaction of complex **1** with 1 equivalent of H_2pin [equation (3)] in chloroform solution was

$$[WCl_2(pin)_2] + H_2pin \longrightarrow [W(pin)_3] + 2\,HCl \quad (3)$$

monitored by ^1H NMR spectroscopy. It occurred nearly quantitatively at room temperature during 1 h. However, simple aliphatic alcohols like ethanol or propan-2-ol do not show any

---

† *Supplementary data available:* see instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, issue 1, pp. xxv–xxx.

reactivity. This is in accord with our earlier observations that the formation and stabilities of the tungsten(VI) diolato complexes are achieved by the chelate effect. Differently from the aliphatic alcohols, the more acidic phenol[13] reacts with **1** forming $[W(pin)_2(OPh)_2]$ **3** but reaction (4) is clearly slower

$$[WCl_2(pin)_2] + 2PhOH \longrightarrow [W(pin)_2(OPh)_2] + 2HCl \quad (4)$$

than the one with H_2pin. Quantitative reaction is achieved in a few hours if an excess of PhOH is used and the liberated HCl is removed by a nitrogen flow. Complex **3** is very soluble in common organic solvents and can be sublimed at 60 °C (0.5 mmHg, *ca.* 67 Pa). Crystallization from the minimum volume of hexane at −18 °C leads to yellow single crystals.

The reaction of complex **3** with H_2pin was also monitored by ^1H NMR spectroscopy. Since PhOH does not substitute the diolate ligands from $[W(eg)(pin)_2]$,[14] we expected that the chelate effect would facilitate the ligand displacement and $[W(pin)_3]$ would be formed. However, no reaction was observed at room temperature during 1 week. Displacement reactions with diols have been studied for $[VO(OR)_3]$ (R = Me, Et or Pr^i) complexes, and the reaction rates are known to be dependent on the steric bulk of the alcoholate ligands.[15] The chelate effect is obviously not the only factor which controls the diolate–alcoholate displacement, but also steric effects and some kinetic inertness limit these reactions.

Table 1 Selected bonding distances (Å) and angles (°) for complex **3**

W–O(1)	1.900(5)	O(1)–C(2)	1.448(9)
W–O(2)	1.908(5)	O(2)–C(3)	1.45(1)
W–O(3)	1.920(5)	O(3)–C(8)	1.444(9)
W–O(4)	1.889(5)	O(4)–C(9)	1.462(9)
W–O(5)	1.884(5)	O(5)–C(13)	1.36(1)
W–O(6)	1.916(6)	O(6)–C(19)	1.35(1)
O(1)–W–O(2)	78.0(2)	O(3)–W–O(4)	77.8(2)
O(1)–W–O(3)	89.4(2)	O(4)–W–O(5)	160.2(2)
O(1)–W–O(4)	99.2(2)	O(4)–W–O(6)	89.1(2)
O(1)–W–O(5)	91.6(2)	O(5)–W–O(6)	84.9(3)
O(1)–W–O(6)	163.6(2)	W–O(1)–C(2)	119.8(5)
O(2)–W–O(3)	163.2(2)	W–O(2)–C(3)	120.5(5)
O(2)–W–O(4)	93.2(2)	W–O(3)–C(8)	119.5(5)
O(2)–W–O(5)	105.3(2)	W–O(4)–C(9)	120.2(5)
O(2)–W–O(6)	87.4(2)	W–O(5)–C(13)	144.5(5)
O(3)–W–O(5)	85.8(2)	W–O(6)–C(19)	138.6(5)
O(3)–W–O(6)	106.2(2)		

Other Reactions.—Substitution of the chloride ligands was attempted by use of benzoic acid, but no reaction occurred in CH_2Cl_2 solution at room temperature, not even in the presence of base. Refluxing of a toluene solution of complex **1** and $PhCO_2H$ led to a blue sticky solid and the formation of HCl.

When complex **1** was treated with 3 equivalents of aniline a red solution was formed and $PhNH_2{\cdot}HCl$ precipitated. The filtered red solution lightened in a few hours. After drying *in vacuo* a residue containing red and yellow solids was found. Redissolving the residue in hydrocarbon or chlorinated solvents led to lightening of the solution colour and deposition of red and yellow powders on cooling. A similar mixture was obtained if Li(NHPh) was used instead of $PhNH_2$. Unfortunately, no good spectroscopic data or satisfactory elemental analyses of these solids were obtained. However, the ^1H NMR spectrum of the red residue in $CDCl_3$ showed several signals at δ 1.30–1.42 and a multiplet at δ 7.0–7.8. The ratio of the methyl and phenyl protons was *ca.* 7 : 1. A similar spectrum has been reported for $[W_2(NHPh)_2(\mu\text{-}pin)(pin)_4]$.[16]

The reaction of the complex **1** with H_2S was examined in an attempt to prepare sulfido complexes corresponding to the dimeric oxo complex. However, when a H_2S flow was passed over a CH_2Cl_2 solution of **1** a black oil was formed in 1 minute. The oil was insoluble in common organic solvents and water.

Structure of Complex **3**.—The main structural parameters of complex **3** are shown in Table 1. The structure comprises monomeric molecules in which the central tungsten atom is surrounded by six oxygen atoms (Fig. 1). The co-ordination around W^{VI} is closely similar to that found in $[W(diol)_3]$ complexes.[18,19] The bite angle O–W–O between two phenolate ligands is 84.9(3)°. This is slightly larger than that formed by 1,2-diols, but is clearly smaller than in the mixed-ligand tungsten(VI) aryloxo chloro complexes, in which the corresponding angles are nearly 90°.[20] The W–O distances vary from 1.884(5) to 1.920(5) Å and are of the same magnitude as those found for $[W(diol)_3]$ complexes. Differences between aliphatic and aromatic W–OR bond distances are insignificant, although related distances in $[WO(dmbino)(OBu^t)_2]$ (dmbino = 3,3′-dimethyl-1,1′-binaphtholate) have been found to differ by *ca.* 0.134 Å.[21] It seems that the rigidity of the diolate ligands dictates the geometry of their tungsten(VI) complexes.

Table 2 Crystal data and experimental details for compounds **2** and **3**

Compound	**2**	**3**
Formula	$C_{36}H_{88}Cl_2N_4O_{19}W_6$	$C_{24}H_{34}O_6W$
M_r	2055.12	602.38
Crystal dimensions/mm	0.20 × 0.15 × 0.25	0.20 × 0.20 × 0.15
Crystal appearance	Bright, prism	Yellow, plate
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a/Å	30.68(1)	7.799(2)
b/Å	12.531(2)	20.414(3)
c/Å	20.415(6)	15.740(2)
β/°	130.89(2)	98.05(2)
U/Å^3	5933(3)	2481.3(9)
Z	8	4
D_c/g cm^{-3}	2.301	1.612
μ/cm^{-1}	119.91	47.87
F(000)	3848	1200
R_{int}	0.075	0.083
Measured reflections	5599	4859
Unique reflections	5486	4509
Observed reflections	2686 [$I > 3\sigma(I)$]	2690 [$I > 2\sigma(I)$]
Minimum, maximum transmission coefficients	0.60, 1.00	0.78, 1.00
No. of parameters	304	280
Maximum, minimum $\Delta\rho$/e Å^{-3}	−1.045, 0.927	−0.55, 0.47

Table 3 Positional parameters for $[W(pin)_2(OPh)_2]$

Atom	x	y	z
W(1)	−0.019 41(4)	0.199 37(2)	0.126 33(2)
O(1)	−0.234 5(7)	0.154 4(3)	0.116 1(3)
O(2)	−0.065 1(6)	0.183 1(3)	0.005 9(3)
O(3)	0.002 0(7)	0.190 0(3)	0.248 7(3)
O(4)	0.131 7(7)	0.127 0(3)	0.146 5(3)
O(5)	−0.127 5(7)	0.280 0(3)	0.142 8(4)
O(6)	0.172 4(7)	0.252 0(3)	0.103 7(4)
C(1)	−0.446(1)	0.208 7(4)	0.014 9(6)
C(2)	−0.338(1)	0.147 4(4)	0.032 7(5)
C(3)	−0.201(1)	0.138 3(4)	−0.028 5(6)
C(4)	−0.122(1)	0.069 2(4)	−0.021 3(6)
C(5)	−0.462(1)	0.088 5(5)	0.036 2(6)
C(6)	−0.265(1)	0.154 6(5)	−0.120 9(6)
C(7)	0.137(1)	0.144 0(5)	0.382 3(6)
C(8)	0.070(1)	0.129 9(4)	0.288 3(5)
C(9)	0.212(1)	0.111 4(4)	0.233 7(5)
C(10)	0.258(1)	0.037 9(5)	0.235 2(6)
C(11)	−0.078(1)	0.081 2(4)	0.283 5(6)
C(12)	0.376(1)	0.152 8(5)	0.251 8(6)
C(13)	−0.172(1)	0.322 7(4)	0.202 8(6)
C(14)	−0.134(1)	0.388 6(5)	0.193 3(7)
C(15)	−0.181(1)	0.432 3(5)	0.253(1)
C(16)	−0.259(1)	0.412 6(7)	0.318 9(8)
C(17)	−0.295(1)	0.347 5(7)	0.328 5(7)
C(18)	−0.252(1)	0.301 8(5)	0.269 6(6)
C(19)	0.202(1)	0.313 4(4)	0.077 0(6)
C(20)	0.103(1)	0.342 9(5)	0.008 6(7)
C(21)	0.139(1)	0.404 6(6)	−0.016 2(7)
C(22)	0.275(2)	0.438 2(5)	0.024 4(8)
C(23)	0.378(1)	0.409 6(6)	0.091 2(8)
C(24)	0.343(1)	0.346 7(5)	0.118 0(7)

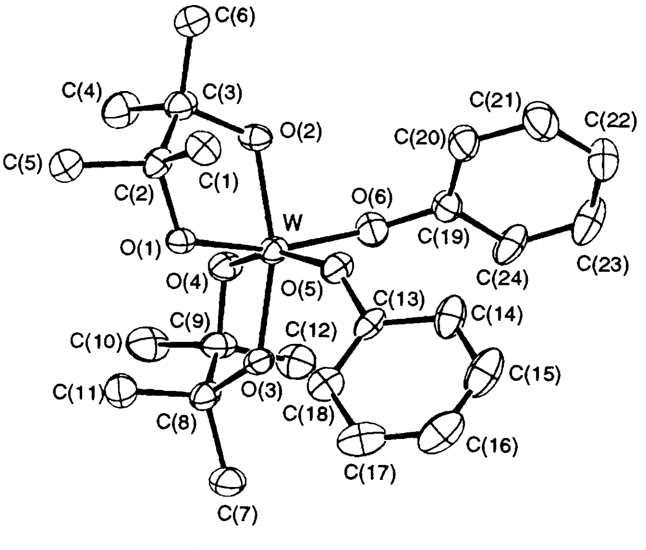


Fig. 1 An ORTEP[17] drawing of compound **3**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity

Nakamura and co-workers[22] have studied the relationship between W–O (aryl) distances and W–O–C angles.[21] They have shown that these parameters are correlated by a hyperbolic curve to a good approximation. In theory, it is possible that these values can reflect the degree of π donation to the metal. In complex **3** the W–O–C (aryl) angles are 144.5(5) and 138.6(5) ° and distances are 1.884(5) and 1.916(6) Å, respectively. The larger W–O–C angle is associated with the shorter W–O bond distance, which is consistent with Nakamura's observations. Anyway, the angular variation is not necessarily a reflection of the electronic properties of the W–O bond but may simply be caused by steric compression as shown to be the case for aryloxo complexes of Nb^V and Ta^V.[23]

Conclusion

The compound $[WCl_2(pin)_2]$ **1**, reacts with hydroxyl donors such as water , H_2pin and PhOH leading to the displacement of the chloride ligand and liberation of HCl. Reaction with water leads to an oxygen-bridged dimer, but in the presence of tripropylamine the product is hexatungstate anion. Although **1** reacts with diols and phenol, no reaction occurs with monovalent aliphatic alcohols.

Experimental

The compounds H_2pin (Aldrich) and PhOH (Merck) were used without further purification. Solvents were purified by standard methods and stored over 4 Å molecular sieves. The complex $[WCl_2(pin)_2]$ was prepared as described earlier.[9] The IR spectra were measured on a Mattson Galaxy FTIR spectrometer as Nujol mulls, ^1H and ^{13}C NMR spectra on a JEOL GSX-400 spectrometer in $CDCl_3$.

Hydrolysis of Complex **1**.—Complex **1** (100 mg, 0.21 mmol) was dissolved in EtOH–thf solution (5 cm^3 of each). The solution was kept in an open vessel for 3 d. During this period the solvent had decreased in volume to 5 cm^3 and 50 mg (55%) of $[W_2O_3(pin)_2(Hpin)_2]$ had precipitated. The ^1H NMR [δ_H 1.25–1.50(m)] and IR [960s (W=O) and 787s (W–O–W)] spectra were identical with those reported earlier.[10]

In the presence of base. Complex **1** (50.0 mg, 0.1 mmol) was dissolved in thf (4 cm^3) and tripropylamine (0.05 cm^3, 0.3 mmol) added. The mixture was allowed to stand in an open vessel for 2 d until the solvent had decreased in volume to 2 cm^3. It was then kept at −18 °C for 3 d until $[(NPr_3)_2Cl]_2[W_6O_{19}]$ **2** (20 mg, 60%) separated. It was washed with hexane and characterized by X-ray analysis.

Reaction of Complex **1** *with* H_2pin.—Complex **1** (25 mg, 0.05 mmol) and H_2pin (6 mg, 0.05 mmol) were dissolved in $CDCl_3$ (2 cm^3). The ^1H NMR spectrum of the reaction mixture was measured after 15, 30 and 60 mins. That after 60 min was equivalent to the spectrum of $[W(pin)_3]$ (δ_H 1.18 and 1.45).

Preparation of $[W(pin)_2(OPh)_2]$ **3**.—Complex **1** (100 mg, 0.21 mmol) in CH_2Cl_2 (10 cm^3) was treated with PhOH (50 mg, 0.53 mmol). The solution was stirred for 4 h under nitrogen. Removal of the dichloromethane, extraction with hexane (2 × 3 cm^3) and reduction of the solvent volume to 3 cm^3 led to a yellow solution. The complex $[W(pin)_2(OPh)_2]$ (105 mg, 80%) was precipitated as yellow crystals during 3 d at −18 °C (Found: C, 47.75; H, 5.60. $C_{24}H_{34}O_6W$ requires C, 47.85; H, 5.70%). NMR(solvent $CDCl_3$, standard $SiMe_4$): δ_H 1.18, 1.25, 1.34, 1.50, 6.85 (m), 6.92 (m) and 7.22 (m); δ_C 25.0 (m), 97.3, 97.8, 120.1, 122.0, 128.5 and 161.1.

Reaction of Complex **3** *with* H_2pin.—Complex **3** (25 mg, 0.05 mmol) and H_2pin (10 mg, 0.10 mmol) were dissolved in $CDCl_3$ (2 cm^3). The ^1H NMR spectrum of the mixture was measured after 0.5, 1 and 2 h and finally after 1 week. There was no indication of the formation of free PhOH.

Crystallography.—Details of the experimental techniques used are given in ref. 10. Reflections were measured on a Rikagu AFC 5S diffractometer using Mo-Kα radiation (λ = 0.7169 Å). Crystallographic data for compounds **2** and **3** are presented in Table 2. Data for **3** were corrected for absorption and also for decay (5%).

The structure of complex **2** was solved by the Patterson method and refined to $R(F) = 0.054$ and $wR(F^2) = 0.095$ $\{w = 1/[\sigma^2(F_o)^2 + (0.0249P)^2 + 25.000P], P = (F_o^2 + 2F_c^2)/3\}$ using the SHELXL 93 program system.[24] That of **3** was solved by the Patterson method and refined by subsequent Fourier syntheses to $R = 0.033$ and $R' = 0.036$ (heavy atoms anisotropic and hydrogen atoms in calculated positions with fixed parameters) using the TEXSAN-TEXRAY program system.[25] Fixed atomic coordinates for **3** are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Neste Foundation for financial support.

References

1 Z. Dori, *Prog. Inorg. Chem.*, 1981, **28**, 239.
2 W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777.
3 M. S. Rau, C. M. Kretz, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1993, **12**, 3447.
4 A. Cervilla, E. Llopis, A. Ribera, A. Doménech and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1994, 3511.
5 D. M.-T. Chan, W. C. Fulz, W. A. Nugent, D. C. Roe and T. H. Tulip, *J. Am. Chem. Soc.*, 1985, **107**, 251.
6 I. Feinstein-Jaffe, D. Gibson, S. J. Lippard, R. R. Schrock and A. Spool, *J. Am. Chem. Soc.*, 1984, **106**, 6305.
7 S. D. Dietz, N W. Eilerts, J. A. Heppert and M. D. Morton, *Inorg. Chem.*, 1993, **32**, 1698.
8 M. B. O'Regan, M. G. Vale, J. F. Payack and R. R. Schrock, *Inorg. Chem.*, 1992, **31**, 1112.
9 A. Lehtonen and R. Sillanpää, *Polyhedron*, 1995, **14**, 455.
10 A. Lehtonen and R. Sillanpää, *J. Chem. Soc., Dalton Trans.*, 1994, 2119.
11 K. F. Jahr, J. Fuchs and R. Oberhauser, *Chem. Ber.*, 1968, **101**, 477.
12 R. J. Errington, M. D. Kerlogue and D. G. Richards, *J. Chem. Soc., Chem. Commun.*, 1993, 649.
13 D. D. Perrin, *pK_a Prediction for Organic Acids and Bases*; Chapman and Hall, London, 1981.
14 A. Lehtonen and R. Sillanpää, *Polyhedron*, in the press.
15 D. C. Crans, R. A. Felty, H. Chen, H. Eckert and N. Das, *Inorg. Chem.*, 1994, **33**, 2427.
16 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, 1985, **4**, 999.
17 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, 1976.
18 J. Scherle and F. A. Schröder, *Acta Crystallogr., Sect. B*, 1974, **30**, 2772.
19 A. Lehtonen and R. Sillanpää, *Polyhedron*, 1994, **13**, 2519.
20 F. Quignard, M. Leconte, J.-M. Basset, L.-Y. Hsu, J. J. Alexander and S. G. Shore, *Inorg. Chem.*, 1987, **26**, 4272.
21 J. A. Heppert, S. D. Dietz, N. W. Eilerts, R. W. Henning, M. D. Morton and F. Takusagawa, *Organometallics*, 1993, **12**, 2565.
22 N. Kanehisa, Y. Kai, N. Kasai, H. Yasuda, Y. Nakayama and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1197.
23 B. D. Steffey, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1990, **9**, 963.
24 G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement. University of Göttingen, 1993.
25 TEXSAN-TEXRAY Structure Analysis Package, Version 5.0, Molecular Structure Corporation, Houston, TX, 1989.

Received 17*th March* 1995; *Paper* 5/01708D