A chain copolymer from $WCl_2(PMe_2Ph)_4$ and $[TlOCH_2CF_3]_4$

Helmut Rothfuss, Kirsten Folting and Kenneth G. Caulton*

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405 (USA)

(Received January 29, 1993; revised April 26, 1993)

Abstract

A combination of $WCl_2(PMe_2Ph)_4$ and $[TlOCH_2CF_3]_4$ crystallize from hexane solution as a 1:1 material whose structure shows it to be an alternating chain copolymer. The link between the W- and Tl-containing monomers is composed of weak Tl/Cl interactions between otherwise not significantly distorted *trans*-WCl_2P_4 octahedra and Tl_4O_4 cubes. The compound crystallizes as two distinct polymorphs, which differ in the Tl/Cl bond lengths and also the conformation of the phenyl substituents in the $W(PMe_2Ph)_4$ substructure. Electronic spectral data support the idea that a Tl/W adduct persists in hexane solution, and it is suggested that the binding force in both solid and solution is a weak charge transfer complexation.

Introduction

Reagents MOR are commonly used for the replacement of halide ligands in MX_mL_n. The impact of the identity of the monovalent metal in MOR on the efficiency of this metathesis reaction has been little studied and very little of a systematic and predictable character is available to aid in intelligent selection of the particular MOR reagent. Such reactions can sometimes be driven to completion by the combined choice of metal ion and solvent (e.g. the product NaCl is only poorly soluble in THF), but the most universal approach to the use of (in)solubility to promote reaction involves the choice M = Tl.

We report here results of a study which are remarkable for the insight it provides on the steps which *precede* precipitation of TlCl in such an apparently simple halide metathesis reaction.

Experimental

All manipulations were carried out under an atmosphere of dry argon. Solvents were dried over alkali metal/benzophenone and freshly distilled before use. All glassware was vigorously flame dried and silylated with $HN(SiMe_3)_2$.

Synthesis

To 105.1 mg (0.13 mmol) $WCl_2(PMe_2Ph)_4$ [1] in 20 ml of hexanes, toluene was slowly added while stirring until all the $WCl_2(PMe_2Ph)_4$ was dissolved. Careful addition of 159.0 mg (0.52 mmol) $TlOCH_2CF_3$ in 30 ml toluene caused precipitation of a small amount of metallic thallium. The stirring was stopped after ~30 s and the precipitate was allowed to settle. Filtering the reaction mixture through Celite yielded a yellow solution. After removal of the solvent under vacuum, 2 ml of hexanes were added to precipitate $WOCl_2(PMe_2Ph)_3$. The solution was decanted into a new flask and kept at −20 °C. After 2 days, yellow and orange crystals formed. These were recrystallized from hexanes to again give yellow and orange crystals. Both crystal forms are polymorphs of the chemical composition $[WCl_2(PMe_2Ph)_4]\cdot[(TlOCH_2CF_3)_4]\cdot\frac{1}{2}n\text{-}C_6H_{14}$.

The determination of the proportion of thallium in the above initial precipitate was carried out by redox titration [2]. For this purpose, the precipitate was separated and carefully washed with toluene. After drying, the solid was weighed and subsequently dissolved in concentrated HCl. Titration with $KMnO_4$ solution (~0.005 F, standardized against $Na_2C_2O_4$) showed the precipitate to be >98% thallium metal.

X-ray structure determinations

$[WCl_2(PMe_2Ph)_4][Tl(OCH_2CF_3)]_4\cdot 0.5n$-hexane, α-isomer

A small, well-formed crystal was selected using standard inert atmosphere handling techniques [3a]. The crystal was affixed to a glass fiber using silicone grease. It was then transferred to the goniostat where it was cooled to -160 °C for characterization (Table 1) and data collection ($6<2\theta<45°$). A systematic search of a

---

*Author to whom correspondence should be addressed.

TABLE 1. Crystallographic data for $[WCl_2(PMe_2Ph)_4][TlOCH_2CF_3]_4 \cdot \frac{1}{2}$hexane

	α-Isomer	β-Isomer
Chemical formula	$C_{40}H_{52}Cl_2F_{12}O_4P_4Tl_4W$, $0.5C_6H_{14}$	$C_{40}H_{52}Cl_2F_{12}O_4P_4Tl_4W$, $0.5C_6H_{14}$
a (Å)	14.890(2)	14.441(4)
b (Å)	15.326(2)	18.876(6)
c (Å)	14.184(2)	11.286(3)
α (°)	93.35(0)	102.47(2)
β (°)	114.45(0)	103.85(2)
γ (°)	81.21(0)	93.34(2)
V (Å^3)	2911.75	2896.82
Z	2	2
Formula weight	2064.05	2064.05
Space group	$P\bar{1}$	$P\bar{1}$
T (°C)	−160	−157
λ (Å)	0.71069	0.71069
ρ_{calc} (g cm^{-3})	2.354	2.366
μ(Mo Kα) (cm^{-1})	134.3	134.99
R	0.0426	0.0653
R_w	0.0421	0.0660

limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than $\bar{1}$). The choice of the triclinic space group $P\bar{1}$ (No. 2) was confirmed by the subsequent solution and refinement of the structure. An absorption correction was carried out. Plots of the four standard reflections measured every 400 reflections showed no significant variations. The structure was solved using direct methods (MULTAN-78) and Fourier techniques. The initial E-map indicated the presence of five heavy atoms, one W and four Tl. The remaining non-hydrogen atoms were located in successive difference Fourier maps phased with already known atoms. The full-matrix least-squares refinement was completed using anisotropic thermal parameters on all W, Tl, Cl, P and F atoms; the remaining non-hydrogen atoms were refined using isotropic thermal parameters. Hydrogen atoms were introduced in fixed calculated positions. One CF_3 group showed disorder in the fluorine atoms (F(65) through F(70)); these atoms were refined using isotropic thermal parameters once the individual occupancies had been refined. The total number of variables was 394 (including the scale factor and an overall isotropic extinction parameter). The asymmetric unit contains one molecule of $W(PMe_2Ph)_4Cl_2$, one molecule of $[TlOCH_2CF_3]_4$, as well as one-half molecule of n-hexane located at a center of symmetry (C(71) through C(73)). The final difference map was essentially featureless, the largest peak being a Tl residual of 2 e/Å^3. The results of the structure determinations are shown in Tables 2 and 3 and Figs. 1–3.

$[WCl_2(PMe_2Ph)_4][Tl(OCH_2CF_3)]_4 \cdot 0.5$n-hexane, β-isomer

A small, well-formed crystal was selected using standard inert atmosphere handling techniques [3a]. The crystal was affixed to a glass fiber using silicone grease and was transferred to the goniostat. When the crystal was cooled to −157 °C for characterization and data collection (Table 1, $6 < 2\theta < 45°$), the color changed from orange to yellow. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than $\bar{1}$). The choice of the centrosymmetric space group $P\bar{1}$ (No. 2) was confirmed by the subsequent solution and refinement of the structure. The structure was solved using direct methods (MULTAN-78) and Fourier techniques. The five heavy atoms were located in the initial E-map and the remaining non-hydrogen atoms were located in successive difference Fourier maps phased with the already located atoms. The full-matrix least-square refinement was completed using anisotropic thermal parameters on all W, Tl, Cl, P and F atoms, while the remaining non-hydrogen atoms were refined using isotropic thermal parameters. Hydrogen atoms were introduced in fixed, calculated positions. The total number of variables was 397 (including the scale factor and an overall isotropic extinction parameter). The asymmetric unit contains one molecule of $WCl_2(PMe_2Ph)_4$, one molecule of $(TlOCH_2CF_3)_4$, as well as one-half molecule of n-hexane at a center of symmetry (C(68) through C(70)). No disorder was observed. The final difference map contained several Tl and W residuals of about 3 e/Å^3; otherwise it was featureless. The results of the structure determination are shown in Tables 4 and 5 and Figs. 3 and 4.

Results

Our original intent was the replacement of chloride ligands in $WCl_2(PMe_2Ph)_4$ with substituents of higher

TABLE 2. Fractional coordinates and isotropic thermal parameters[a] for [α-WCl$_2$(PMe$_2$Ph)$_4$][TlOCH$_2$CF$_3$]$_4$ $\frac{1}{2}$n-C$_6$H$_{14}$

	$10^4\ x$	$10^4\ y$	$10^4\ z$	$10\ B_{iso}$
W(1)	1869(1)	2510(1)	2427(1)	10
Cl(2)	1883(4)	2472(4)	707(4)	14
Cl(3)	1798(4)	2539(4)	4119(4)	16
P(4)	176(4)	3395(4)	1828(4)	15
C(5)	−367(16)	3764(14)	467(17)	17(4)
C(6)	60(17)	4447(16)	2473(19)	25(5)
C(7)	−861(16)	2967(14)	1957(17)	16(4)
C(8)	−776(16)	2812(15)	2959(17)	20(4)
C(9)	−1550(18)	2509(16)	3096(19)	26(5)
C(10)	−2388(16)	2308(15)	2262(17)	19(4)
C(11)	−2453(18)	2468(16)	1280(19)	26(5)
C(12)	−1729(18)	2798(16)	1127(19)	25(5)
P(13)	3564(4)	1629(4)	3324(5)	17
C(14)	3598(17)	737(16)	4160(18)	24(5)
C(15)	4157(17)	1026(16)	2534(18)	25(5)
C(16)	4560(16)	2176(15)	4287(17)	19(4)
C(17)	5546(16)	2120(14)	4329(17)	16(4)
C(18)	6273(17)	2528(15)	5091(18)	22(5)
C(19)	6065(19)	3000(17)	5838(20)	31(5)
C(20)	5121(18)	3044(16)	5848(19)	28(5)
C(21)	4393(15)	2643(14)	5091(16)	15(4)
P(22)	1055(4)	1156(4)	1832(4)	14
C(23)	−12(16)	1212(15)	578(17)	19(4)
C(24)	536(17)	734(16)	2652(18)	23(5)
C(25)	1776(15)	131(14)	1590(16)	14(4)
C(26)	2051(16)	122(15)	762(17)	19(4)
C(27)	2615(17)	−597(16)	579(18)	22(5)
C(28)	2929(19)	−1334(17)	1199(20)	30(5)
C(29)	2667(18)	−1331(17)	2029(19)	28(5)
C(30)	2083(16)	−608(15)	2239(17)	20(4)
P(31)	2631(4)	3888(4)	2695(4)	13
C(32)	2647(18)	4557(16)	3793(19)	27(5)
C(33)	2021(17)	4692(16)	1611(18)	23(5)
C(34)	3912(15)	3879(14)	2793(16)	15(4)
C(35)	4128(14)	3408(13)	1992(15)	10(4)
C(36)	5068(17)	3386(15)	2001(18)	21(4)
C(37)	5774(17)	3814(16)	2730(18)	23(5)
C(38)	5542(15)	4266(14)	3524(16)	14(4)
C(39)	4593(14)	4288(13)	3508(15)	11(4)
Tl(40)	2390(1)	3407(1)	8740(1)	17
Tl(41)	1535(1)	1115(1)	8091(1)	20
Tl(42)	612(1)	2847(1)	5867(1)	20
Tl(43)	3370(1)	1800(1)	7011(1)	24
O(44)	3076(11)	1788(10)	8665(11)	19(3)
C(45)	3749(15)	1490(14)	9657(16)	14(4)
C(46)	4794(17)	1402(16)	9749(18)	22(5)
F(47)	5462(10)	1145(10)	10724(11)	36
F(48)	4995(10)	780(9)	9119(11)	32
F(49)	5054(11)	2135(10)	9553(12)	41
O(50)	847(11)	2707(10)	7753(11)	19(3)
C(51)	105(15)	2975(14)	8136(16)	14(4)
C(52)	−941(19)	2906(18)	7358(20)	30(5)
F(53)	−1027(11)	2108(11)	6909(13)	47
F(54)	−1581(10)	3088(10)	7749(11)	35
F(55)	−1197(11)	3463(11)	6533(11)	40
O(56)	2300(11)	3272(10)	6914(11)	19(3)
C(57)	2585(17)	3906(15)	6464(18)	21(4)
C(58)	1984(17)	4797(16)	6377(18)	23(5)
F(59)	2189(9)	5375(8)	5862(9)	23
F(60)	2166(10)	5161(9)	7328(10)	28
F(61)	1014(9)	4795(9)	5924(11)	32
O(62)	1695(11)	1345(10)	6465(12)	20(3)
C(63)	1387(24)	785(23)	5593(26)	54(7)
C(64)	1810(26)	−119(24)	5836(28)	56(7)
F(65)	1521(14)	−693(12)	5035(15)	51(4)
F(66)	2561(34)	−464(25)	6660(30)	50(8)
F(67)	1879(39)	−493(28)	6609(33)	47(8)
F(68)	1119(26)	−373(21)	6332(25)	49(7)
F(69)	2693(43)	−17(39)	5630(51)	68(10)
F(70)	2870(34)	−283(32)	6344(42)	55(9)
C(71)	5002(17)	4670(16)	9551(18)	24(5)
C(72)	6082(20)	4472(19)	9562(22)	37(6)
C(73)	6008(19)	3868(18)	8628(20)	33(5)

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given in ref. 3b.

TABLE 3. Selected bond distances (Å) and angles (°) for [α-WCl$_2$(PMe$_2$Ph)$_4$][TlOCH$_2$CF$_3$]$_4$·$\frac{1}{2}$n-C$_6$H$_{14}$

Tl(40)–Cl(2)	3 600(5)
Tl(41)–Cl(2)	4.025(5)
Tl(42)–Cl(3)	3.567(5)
Tl(43)–Cl(3)	3 920(5)
Tl(40)–O(44)	2.548(15)
Tl(40)–O(50)	2 512(14)
Tl(40)–O(56)	2.534(15)
Tl(41)–O(44)	2.464(14)
Tl(41)–O(50)	2.489(15)
Tl(41)–O(62)	2.466(15)
Tl(42)–O(50)	2.567(15)
Tl(42)–O(56)	2.499(14)
Tl(42)–O(62)	2.566(15)
Tl(43)–O(44)	2.561(14)
Tl(43)–O(56)	2.530(15)
Tl(43)–O(62)	2.485(14)
W(1)–Cl(2)	2.445(5)
W(1)–Cl(3)	2.443(5)
W(1)–P(4)	2.496(6)
W(1)–P(13)	2.512(6)
W(1)–P(22)	2.493(6)
W(1)–P(31)	2 484(6)
O(44)–C(45)	1.399(25)
O(50)–C(51)	1.419(24)
O(56)–C(57)	1.397(26)
O(62)–C(63)	1.41(3)
O(44)–Tl(40)–O(50)	76.9(5)
O(44)–Tl(40)–O(56)	77.7(5)
O(50)–Tl(40)–O(56)	76.1(5)
O(44)–Tl(41)–O(50)	78.9(5)
O(44)–Tl(41)–O(62)	76.4(5)
O(50)–Tl(41)–O(62)	79.1(5)
O(50)–Tl(42)–O(56)	75.7(4)
O(50)–Tl(42)–O(62)	75.8(5)
O(56)–Tl(42)–O(62)	77 5(5)
O(44)–Tl(43)–O(56)	77.5(5)
O(44)–Tl(43)–O(62)	74.3(5)
O(56)–Tl(43)–O(62)	78.5(5)

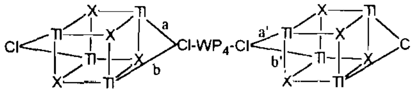
(*continued*)

TABLE 3 (*continued*)

Cl(2)–W(1)–Cl(3)	178.07(18)
Cl(2)–W(1)–P(4)	93.56(18)
Cl(2)–W(1)–P(13)	96.06(19)
Cl(2)–W(1)–P(22)	83.92(18)
Cl(2)–W(1)–P(31)	86.07(18)
Cl(3)–W(1)–P(4)	85.03(19)
Cl(3)–W(1)–P(13)	85.36(19)
Cl(3)–W(1)–P(22)	94.72(18)
Cl(3)–W(1)–P(31)	95.23(18)
P(4)–W(1)–P(13)	170.38(19)
P(4)–W(1)–P(22)	88.49(19)
P(4)–W(1)–P(31)	90.26(19)
P(13)–W(1)–P(22)	92.49(20)
P(13)–W(1)–P(31)	90.43(19)
P(22)–W(1)–P(31)	169.82(19)
Tl(40)–O(44)–Tl(41)	100.4(5)
Tl(40)–O(44)–Tl(43)	100.2(5)
Tl(40)–O(44)–C(45)	109.8(12)
Tl(41)–O(44)–Tl(43)	102.9(5)
Tl(41)–O(44)–C(45)	111.0(11)
Tl(43)–O(44)–C(45)	128.8(12)
Tl(40)–O(50)–Tl(41)	100.7(5)
Tl(40)–O(50)–Tl(42)	102.5(5)
Tl(40)–O(50)–C(51)	111.7(11)
Tl(41)–O(50)–Tl(42)	100.7(5)
Tl(41)–O(50)–C(51)	112.3(12)
Tl(42)–O(50)–C(51)	125.6(12)
Tl(40)–O(56)–Tl(42)	103.9(5)
Tl(40)–O(56)–Tl(43)	101.4(5)
Tl(40)–O(56)–C(57)	122.8(13)
Tl(42)–O(56)–Tl(43)	100.0(5)
Tl(42)–O(56)–C(57)	115.6(12)
Tl(43)–O(56)–C(57)	110.0(12)
Tl(41)–O(62)–Tl(42)	101.4(5)
Tl(41)–O(62)–Tl(43)	105.1(6)
Tl(41)–O(62)–C(63)	124.6(16)
Tl(42)–O(62)–Tl(43)	99.4(5)
Tl(42)–O(62)–C(63)	106.0(16)
Tl(43)–O(62)–C(63)	116.4(15)
O(44)–C(45)–C(46)	110.4(17)
O(50)–C(51)–C(52)	114.1(18)
O(56)–C957)–C(58)	113.3(18)
O(62)–C(63)–C(64)	113.1(28)

π-donor ability such as alkoxides. Since we found no reaction with potassium alkoxides (t-butoxide or 2,2,2-fluoroethoxide) at ambient temperature*, we investigated $TlOCH_2CF_3$. Reaction with $WCl_2(PMe_2Ph)_4$ occurred immediately, evident by the formation of a black precipitate. This solid was established to be metallic thallium. Simultaneously, corresponding amounts of trifluoroethanol, PMe_2Ph and $W(O)Cl_2(PMe_2Ph)_3$ were observed**. Evidently, traces of surface water† react with Tl(I) and W(II), as represented in eqn. (1). Despite our efforts to exclude any surface water or hydroxide groups on the glass wall, all reactions started with precipitation of small amounts of thallium metal. Therefore, stirring was halted as soon as the reaction components were well mixed (~30 s). After the precipitate settled, the clear yellow solution was filtered through Celite. Solvent was removed and the residue treated with hexanes to remove $W(O)Cl_2(PMe_2Ph)_3$, which is insoluble in hexanes. The resulting solution was allowed to stand for 48 h at −20 °C, forming yellow and orange crystals. These were recrystallized from hexanes at −20 °C to give crystals of two distinct morphologies: yellow needles (α) and orange cuboids (β). Both were identified by single crystal X-ray diffraction as distinct polymorphs of the same composition of matter, $[WCl_2(PMe_2Ph)_4][(TlOCH_2CF_3)_4]\cdot\frac{1}{2}n\text{-}C_6H_{14}$. The two are similar in being one-dimensional infinite coordination copolymers composed of alternating octahedral *trans*-$WCl_2(PMe_2Ph)_4$ and cubane $(TlOCH_2CF_3)_4$ tetramer building blocks. For each, the crystallographic repeat unit is $[WCl_2(PMe_2Ph)_4][(TlOCH_2CF_3)_4]\cdot\frac{1}{2}n\text{-}C_6H_{14}$. To a first approximation each chloride has weak interactions with two different Tl centers (**A**).

$$WCl_2(PMe_2Ph)_4 + \tfrac{1}{2}[(TlOCH_2CF_3)_4] + H_2O \longrightarrow$$
$$2CF_3CH_2OH + W(O)Cl_2(PMe_2Ph)_3 + 2Tl + PMe_2Ph \qquad (1)$$



X = OCH_2CF_3

A

While the Tl/Cl distances (3.567–4.025 Å in α and 3.667–3.727 Å in β) are longer than those in TlCl (3.32 Å) they are generally shorter than the sum of the van der Waals radii (3.90 Å)††. In finer detail, the distances *a* and *b* are sufficiently different that the approximate

---

*No reaction occurred from 25 up to 85 °C. At this temperature, orthometallation of $WCl_2(PMe_2Ph)_4$ was observed in $^{31}P\{^1H\}$ NMR. The introduction of an alkoxide ligand did not take place.

**To determine the organic products, the reaction was carried out once in deuterated benzene. After completion of the reaction, all volatiles were collected and investigated by ^1H NMR and GC/MS. Both spectroscopic methods indicated as sole organic products free dimethylphenylphosphine and trifluoroethanol. ^1H NMR of the non-volatile material revealed besides the two starting compounds the formation of $W(O)Cl_2(PMe_2Ph)_3$. The oxo compound was also detected by $^{31}P\{^1H\}$ NMR. See ref. 4.

†Use of unflamed glassware as well as adding traces of water to a solution of $WCl_2(PMe_2Ph)_4$ and $[(TlOCH_2CF_3)_4]$ leads to complete conversion to thallium metal and $W(O)Cl_2(PMe_2Ph)_3$. Pure $WCl_2(PMe_2Ph)_4$ is stable to water for short periods of time. See ref. 5.

††Tl/Cl distances have been reported as 3.88 Å in $[TlS_2CNEt_2]_2 \cdot CHCl_3$ [6a] and 2.98 Å in $[TlPt_3(CO)_3(PCy_3)_3][Rh(C_8H_{12})Cl_2]$ [6b].

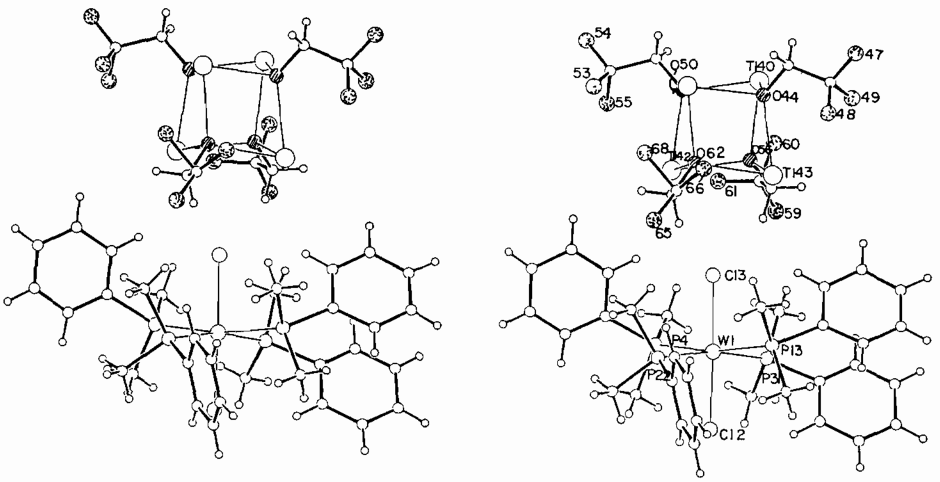


Fig. 1. Stereo ORTEP drawing of the repeat unit of the α-polymorph of the copolymer, showing selected atom labelling. Oxygen is hatched and fluorine stippled.

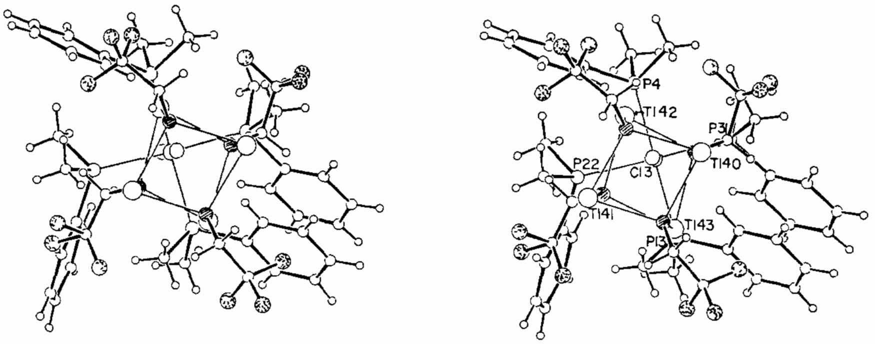
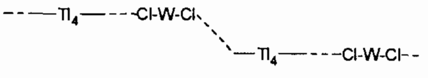


Fig. 2. Stereo ORTEP drawing viewed nearly down the Cl–W–Cl line, showing the offset of the Tl_4O_4 cubes in the α-polymorph

C_2 axis of the *trans* WCl_2P_4 unit does not coincide with the approximate S_4 axis of the $(TlOR_f)_4$ cube. Thus, the chain polymer is (to different degrees in the α- and β-polymorphs) 'stepped' (**B**). In the β form, one Tl/Cl separation is so long (4.630 Å) that it is preferable to say that only one Tl/Cl interaction exists (Tl42–Cl3).



B

Thallium centers also show contacts with fluorines of the CF_3 groups. For any Tl, the number of such interactions varies from two to six (3.118–4.350 Å)*. Moreover, certain of these are actually 'intermolecular' (i.e. to another $(TlOR_f)_4$ cube). Thallium thus shows no strongly preferred coordination number for these weak Tl/F interactions, but the number of these does correlate inversely with the number and strength of the Tl/Cl interactions: a lengthening of the Tl/Cl distance increases the number of Tl/F interactions. These do not perturb the Tl/O distances, however. All CF_3 groups bend away from the nearest WCl_2P_4 unit, to minimize repulsion.

While crystalline $[WCl_2P_4][(TlOR_f)_4]\cdot\frac{1}{2}n\text{-}C_6H_{14}$ is made up of interacting subunits, these subunits have structures which are not significantly different from those of *trans*-$WCl_2(PMePh_2)_4$ [8a] and of $(TlOSiPh_3)_4$ [8b]. In particular, bond lengths and angles involving W and Tl show no significant changes in the coordination polymer from their values in the pure compounds. As is evident from Table 6, bond lengths and angles differ only insignificantly between the α- and β-polymorphs. The distortion from a regular cubane structure for $Tl_4(OR_f)_4$ keeps all 12 Tl/O distances identical (to within 7σ), but involves compressing the O–Tl–O angles and expanding the Tl–O–Tl angles. The resultant shape has four protruding corners and four depressed corners. The structures of two siloxides of thallium are known, and both are cubane tetramers with Tl/O distances within 0.02 Å of those reported here. Angles O–Tl–O and Tl–O–Tl in these siloxides are all within 1° of

---

*The Tl/F distances in solid TlF are four at 2.58 Å and two at 3.53 Å [7a]. Tl/F distances as short as 3.068(8) Å have been reported in $Tl_2Zr[OCH(CF_3)_2]_6$ [7b].

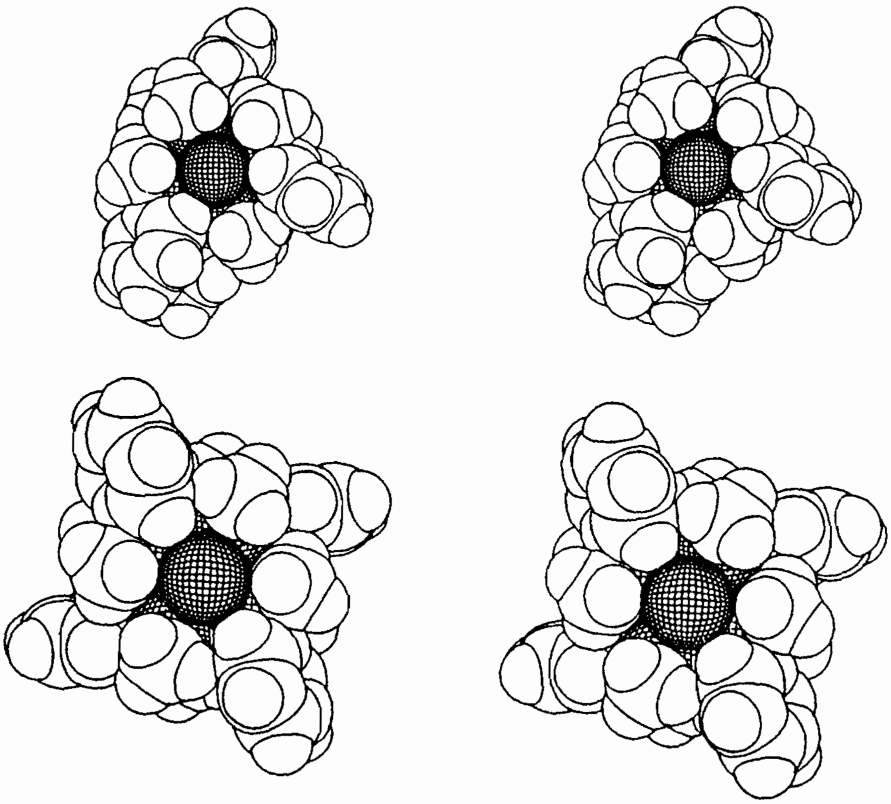
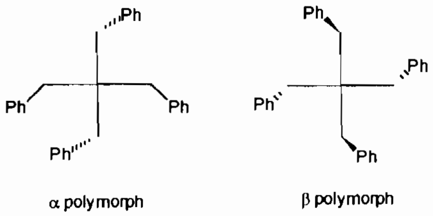


Fig. 3. Stereo space-filling drawings of the $WCl_2(PMe_2Ph)_4$ units in the α- (above) and β- (below) polymorphs

those reported here (i.e. the cubes show similar angular distortion) and only the angles Tl–O–Si (112.7(7)–121.8(10))° in $Tl_4[(OSiMe_2)_2O]_4)$ [8b] span a much smaller range than we report here (106.0(16)–130.3(19)°). This greater spread in $(Tl\text{-}OCH_2CF_3)_4$ may be tied in with attractive Tl/F interactions.

The polymorphs α and β show an additional difference in the stereochemistry of substituents on the phosphine ligands. These differ as shown below and are accompanied by a modest alteration in the orientation of the OR_f groups.



α polymorph β polymorph

The phenyl substituent locations in the α-polymorph yield no (approximate) molecular symmetry, while the idealized symmetry, including these substituents, for the β-polymorph is S_4. The lower symmetry conformer shows one pair of phenyls stacked face-to-face within the molecular repeat unit. An integral part of the WCl_2P_4 substructure of each polymorph is a puckering or ruffling of the WP_4 unit so that the phosphorus nuclei lie alternatively above and below the mean WP_4 plane. This phenomenon is quite general for $M(PMe_2Ph)_4$ and $M(PMePh_2)_4$ structures [9] and is symptomatic of a very crowded molecule.

It is of interest to know whether the interaction of $(TlOR_f)_4$ with WCl_2P_4 persists in solution. To that end, we have compared the Vis–UV spectra of the individual pure compounds, dissolved in hexane, to a hexane solution containing equimolar (4:1 Tl:W) reagents. The solution containing both compounds is not the simple sum of the pure components. This permits the conclusion that some interaction persists in solution. There is, however, no new single band in the range 200–800 nm which could be assigned as a charge transfer excitation. Instead, the two UV bands (226 and 262 nm) of $(TlOR_f)_4$ are changed in the 4:1 mixture: one band (262 nm) is absent whereas the second stays in its original position. All changes are deep into the UV, which is why there is no color visible to the eye for the solution containing the 4:1 mixture.

The interaction can also be shown to persist in C_6D_6 solvent at 25 °C by the change of the OCH_2 chemical shift in the OR_f moiety from 3.67 ppm (pure $TlOR_f)_4$ in benzene) to 3.97 ppm in the 4:1 Tl:W solution in benzene.

TABLE 4. Fractional coordinates and isotropic thermal parameters[a] for $[WCl_2(PMe_2Ph)_4][Tl(OCH_2CF_3)]_4$ $\frac{1}{2}$n-C_6H_{14}, β-isomer

	10^4 x	10^4 y	10^4 z	10 B_{iso}
W(1)	6580(1)	2525(1)	4999(1)	10
Cl(2)	4848(5)	2369(4)	4858(8)	19
Cl(3)	8300(5)	2673(5)	5144(7)	19
P(4)	6513(6)	1170(4)	4722(8)	16
C(5)	7692(22)	826(17)	5074(29)	17(6)
C(6)	5883(21)	817(16)	5786(28)	15(6)
C(7)	5869(20)	532(15)	3291(26)	11(5)
C(8)	4904(22)	545(17)	2807(29)	17(6)
C(9)	4347(23)	64(18)	1730(31)	22(6)
C(10)	4785(25)	−474(20)	1105(34)	29(7)
C(11)	5735(24)	−525(19)	1574(33)	26(7)
C(12)	6265(21)	−46(16)	2607(28)	15(5)
P(13)	6378(5)	2360(4)	2670(7)	16
C(14)	7025(23)	1670(17)	1950(30)	20(6)
C(15)	5161(26)	2154(20)	1638(34)	30(7)
C(16)	6870(19)	3137(14)	2105(25)	7(5)
C(17)	6259(22)	3565(17)	1474(29)	17(6)
C(18)	6670(24)	4139(18)	1096(32)	25(7)
C(19)	7662(24)	4275(18)	1326(31)	24(7)
C(20)	8255(24)	3858(18)	1947(32)	24(6)
C(21)	7808(22)	3284(17)	2288(29)	17(6)
P(22)	6420(6)	3864(4)	5241(8)	17
C(23)	7411(22)	4409(17)	5033(29)	19(6)
C(24)	5395(25)	4057(19)	4108(33)	28(7)
C(25)	6185(22)	4454(17)	6647(29)	17(6)
C(26)	5356(23)	4252(17)	6966(30)	20(6)
C(27)	5107(24)	4652(19)	8010(33)	26(7)
C(28)	5710(24)	5293(18)	8748(32)	24(6)
C(29)	6528(23)	5495(18)	8452(30)	22(6)
C(30)	6744(23)	5066(18)	7385(31)	22(6)
P(31)	7090(6)	2691(4)	7328(7)	13
C(32)	7846(24)	3564(18)	8201(31)	23(6)
C(33)	6152(22)	2686(17)	8151(29)	18(6)
C(34)	7878(22)	2074(17)	8049(30)	20(6)
C(35)	7544(23)	1597(17)	8695(30)	21(6)
C(36)	8177(24)	1130(19)	9180(32)	26(7)
C(37)	9104(27)	1145(20)	9121(35)	32(7)
C(38)	9444(24)	1642(19)	8502(32)	25(7)
C(39)	8804(24)	2081(18)	7993(31)	24(6)
Tl(40)	2664(1)	3267(1)	4864(1)	21
Tl(41)	2518(1)	1216(1)	4227(1)	25
Tl(42)	705(1)	2132(1)	5970(1)	25
Tl(43)	316(1)	2130(1)	2522(1)	19
O(44)	2125(13)	2163(10)	3040(17)	12(4)
C(45)	2675(31)	2136((24)	2131(41)	45(9)
C(46)	2286(26)	1572(20)	960(34)	29(7)
F(47)	2222(21)	904(13)	1186(23)	59
F(48)	2864(16)	1579(16)	173(22)	56
F(49)	1421(15)	1650(16)	364(21)	55
O(50)	2536(18)	2285(14)	6025(24)	36(5)
C(51)	3218(26)	2265(20)	7065(35)	31(7)
C(52)	3190(29)	2856(22)	8170(38)	37(8)
F(53)	3215(22)	3520(13)	7960(24)	69
F(54)	2375(17)	2788(15)	8532(21)	53
F(55)	3888(16)	2854(16)	9176(21)	56
O(56)	882(15)	3011(11)	4608(20)	21(4)
C(57)	394(23)	3618(18)	4752(30)	21(6)
C(58)	654(28)	4112(21)	6006(37)	34(8)
F(59)	138(15)	4697(12)	6138(20)	40

(*continued*)

TABLE 4 (*continued*)

	10^4 x	10^4 y	10^4 z	10 B_{iso}
F(60)	517(19)	3784(13)	6912(21)	52
F(61)	1573(15)	4393(13)	6412(24)	52
O(62)	743(16)	1257(12)	3907(21)	25(4)
C(63)	263(25)	576(19)	3871(33)	27(7)
C(64)	−512(28)	295(21)	2692(37)	34(8)
F(65)	−1198(13)	739(11)	2576(22)	40
F(66)	−947(14)	−355(11)	2565(26)	50
F(67)	−234(18)	273(12)	1622(23)	49
C(68)	91(26)	4721(20)	417(34)	30(7)
C(69)	677(31)	4147(23)	48(40)	44(9)
C(70)	856(36)	3615(28)	927(48)	61(11)

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given in ref. 3b.

TABLE 5. Selected bond distances (Å) and angles (°) for [β-$WCl_2(PMe_2Ph)_4][TlOCH_2CF_3]_4\cdot\frac{1}{2}$n-$C_6H_{14}$

Tl(40)–Cl(2)	3.667(6)
Tl(41)–Cl(2)	3.727(6)
Tl(42)–Cl(3)	3.639(6)
Tl(43)–Cl(3)	4.630(6)
Tl(40)–O(44)	2.526(19)
Tl(40)–O(50)	2 513(25)
Tl(40)–O(56)	2 525(21)
Tl(41)–O(44)	2.469(18)
Tl(41)–O(50)	2.527(26)
Tl(41)–O(62)	2.509(22)
Tl(42)–O(56)	2.534(21)
Tl(42)–O(62)	2.563(22)
Tl(43)–O(44)	2.531(18)
Tl(43)–O(56)	2.491(21)
Tl(43)–O(62)	2.512(22)
W(1)–Cl(2)	2.464(7)
W(1)–Cl(3)	2.446(7)
W(1)–P(4)	2.503(8)
W(1)–P(13)	2.523(8)
W(1)–P(22)	2.512(8)
W(1)–P(31)	2.498(8)
O(44)–C(45)	1.44(5)
O(50)–C(51)	1 35(4)
O(56)–C(57)	1.38(4)
O(62)–C(63)	1.41(4)
O(44)–Tl(40)–O(50)	79.8(7)
O(44)–Tl(40)–O(56)	75.4(6)
O(50)–Tl(40)–O(56)	76.1(7)
O(44)–Tl(41)–O(50)	80.6(7)
O(44)–Tl(41)–O(62)	74.7(7)
O(50)–Tl(41)–O(62)	80.7(8)
O(56)–Tl(42)–O(62)	78 3(7)
O(44)–Tl(43)–O(56)	75.9(6)
O(44)–Tl(43)–O(62)	73.6(6)
O(56)–Tl(43)–O(62)	80.0(7)
Cl(2)–W(1)–Cl(3)	179.63(26)
Cl(2)–W(1)–P(4)	86.54(26)
Cl(2)–W(1)–P(13)	95.30(25)
Cl(2)–W(1)–P(22)	86.19(27)
Cl(2)–W(1)–P(31)	94.80(26)

(*continued*)

TABLE 5 (*continued*)

Cl(3)-W(1)-P(4)	93.11(26)
Cl(3)-W(1)-P(13)	84.86(25)
Cl(3)-W(1)-P(22)	94.15(27)
Cl(3)-W(1)-P(31)	85 04(25)
P(4)-W(1)-P(13)	89.56(27)
P(4)-W(1)-P(22)	172.72(27)
P(4)-W(1)-P(31)	89.9(3)
P(13)-W(1)-P(22)	90 66(26)
P(13)-W(1)-P(31)	169.84(25)
P(22)-W(1)-P(31)	91.13(27)
Tl(40)-O(44)-Tl(43)	102.3(7)
Tl(40)-O(44)-C(45)	112.9(20)
Tl(41)-O(44)-Tl(43)	105.9(7)
Tl(41)-O(44)-C(45)	110.5(20)
Tl(43)-O(44)-C(45)	124.0(20)
Tl(40)-O(50)-Tl(41)	96 7(9)
Tl(40)-O(50)-C(51)	121.2(22)
Tl(41)-O(50)-C(51)	111.3(21)
Tl(40)-O(56)-Tl(42)	105.9(7)
Tl(40)-O(56)-Tl(43)	103.4(8)
Tl(40)-O(56)-C(57)	115.6(18)
Tl(42)-O(56)-Tl(43)	98.1(7)
Tl(42)-O(56)-C(57)	116.8(18)
Tl(43)-O(56)-C(57)	114.9(18)
Tl(41)-O(62)-Tl(42)	100.6(8)
Tl(41)-O(62)-Tl(43)	105.3(8)
Tl(41)-O(62)-C(63)	111 9(18)
Tl(42)-O(62)-Tl(43)	96 8(7)
Tl(42)-O(62)-C(63)	107 2(19)
Tl(43)-O(62)-C(63)	130.3(19)
O(44)-C(45)-C(46)	114.(3)
O(50)-C(51)-C(52)	112 (3)
O(56)-C(57)-C(58)	116.0(28)
O(62)-C(63)-C(64)	112.(3)

Discussion

One remarkable feature of the reaction and crystallization reported here is that the same composition of matter crystallizes simultaneously as two distinct polymorphs. We do not understand the controlling factors of this phenomenon except that highly *crowded* subunits (i.e. $WCl_2(PMe_2Ph)_4$) may quite generally have *several* conformers of comparable energy, and these may be slow to interconvert.

The results reported here are noteworthy because they show that the metal ion in an MOR reagent can take an active role in anionic ligand metathesis reaction. It serves as an electrophile (i.e. the Tl/Cl interactions observed here in the intact reagents) which can avoid the energetically costly formation of separated ions (eqn. (2)) followed by capture of free halide by Tl^+ (eqn. (3)). Instead, the reaction becomes molecular and perhaps even closer to concerted: the observation here of Tl/Cl interactions between the reagent *molecules* [10] indicates that the next step in the metathesis reaction could be site exchange of chloride and OR_f (eqn. (4)). In the present case, however, this metathesis

$$ClP_4W\text{-}Cl\cdots Tl_4(OR_f)_4 \longrightarrow ClP_4W\text{-}\overset{R_f}{O}\cdots Tl_4Cl(OR_f)_3 \qquad (4)$$

has not been observed to occur. Given the demonstration of halide/electrophile interactions between the intact reagents, it is clear that the choice of the metal M in an MOR reagent will influence not only the overall reaction thermodynamics, but also its mechanism.

$$L_nWCl \rightleftharpoons L_nW^+ + Cl^- \qquad (2)$$

$$Cl^- + Tl^+ \longrightarrow TlCl\downarrow \qquad (3)$$

While these results establish the presence of Tl/Cl interactions, they also reveal one reason why rapid production of W/OR_f bonds does not follow: the alkoxides have all of their nucleophilicity 'masked' by being triply bridging. With no lone pairs available, there is no way that the alkoxide can take an active (i.e. S_N2) role in displacing chloride*. Thus, molecular alkoxide aggregates containing μ_3-OR groups may have suppressed reactivity and may have to rely on the Cl/OR interchange mechanism portrayed in eqn. (4).

The formation of a polymer, rather than a simpler binary 'molecular pair', warrants comment. This originates in the bifunctional nature of each reagent: the tungsten is a *di*chloride reagent, and the $(TlOR_f)_4$ cube has multiple electrophilic Tl_2 faces. We feel that there may be an additional phenomenon operative for chain formation, however. The strongly reducing character of W(II), augmented by the presence of four donor phosphine ligands, raises the possibility of a charge transfer interaction [12]. This is reinforced by the fact that any cluster undergoes redox chemistry more easily than a monometal center, in part because electron transfer is delocalized over more metal centers. Consequently, no single metal (in the $(TlOR_f)_4$ aggregate) undergoes full electron transfer. The CF_3 group of course improves the electron acceptor character of the thallium aggregate. We therefore propose that there is fractional charge transfer in $[WCl_2(PMe_2Ph)_4]$-$[(TlOR_f)_4]$ and that the alternating sign of the charge in the chain polymer represents a stable energy state because it avoids the energy cost of creating the dipole which would be present in a molecular pair $[WCl_2(PMe_2Ph)_4^{\delta+}][(TlOR_f)_4^{\delta-}]$.

This charge transfer conjecture is further supported by the fact that solutions which give rise to the chain copolymer form thallium metal as soon as they contact a fresh glass wall. In any event, the reaction studied here is *not* one which leads to halide/alkoxide metathesis,

---

*The reactivity of $WCl_2(PMePh_2)_4$ (note the bulkier phosphines) with allyl alcohol relies on predissociation of phosphine to permit coordination of the alcohol [11]

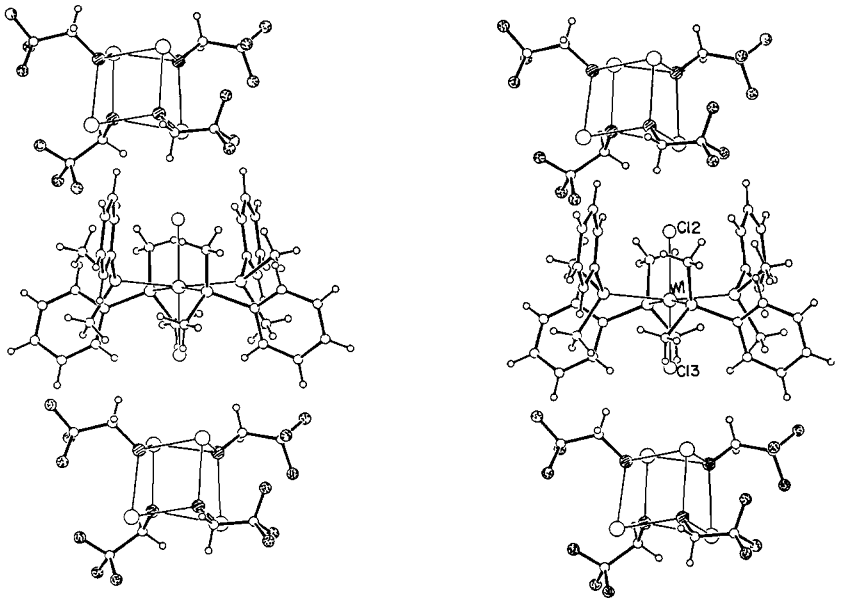


Fig. 4. Stereo ORTEP drawing of the repeat unit plus one additional $(TlOCH_2CF_3)_4$ unit of the β-polymorph, showing selected atom labelling. Oxygen is hatched and fluorine stippled.

TABLE 6. Comparison of structural parameters of two polymorphs of $[WCl_2(PMe_2Ph)_4][TlOCH_2CF_3]_4 \cdot \frac{1}{2}n\text{-}C_6H_{14}$

	α	β
Tl–O	2.464(14)–2.567(15)	2.469(18)–2.563(22)
∠O–Tl–O	74.3(5)–79.1(5)	73.6(6)–80.7(8)
∠Tl–O–Tl	99.4(5)–128.8(12)	96.7(9)–105.9(9)
∠Tl–O–C	106.0(16)–128.8(12)	107.2(19)–130.3(19)
W–Cl	2.443(5)–2.445(5)	2 446(7)–2.464(7)
W–P	2.484(6)–2.512(6)	2 498(8)–2.523(8)
cis ∠P–W–P	88.49(19)–92.49(20)	89.56(27)–91.13(27)
Small ∠Cl–W–P	83.92(18)–86.07(18)	84.86(25)–86.54(26)
Large ∠Cl–W–P	93.56(18)–96.06(19)	93 11(26)–95.30(25)

but rather electron transfer. While this is a common occurrence with silver(I) reagents, the present study serves as a reminder that *intended* thallium metathesis reagents can also display electron transfer.

Acknowledgement

This work was supported by the US National Science Foundation.

References

1 P.R. Sharp, J.C. Bryan and J.M. Mayer, *Inorg. Synth., 28* (1990) 330.

2 R.S. Beale, A.W. Hutchison and G.C. Chandlee, *Ind Eng Chem. Anal., 13* (1941) 240

3 (a) J.C. Huffman, L.N. Lewis and K.G. Caulton, *Inorg. Chem*, *19* (1980) 2755; (b) W.C. Hamilton, *Acta Crystallogr., 12* (1959) 609.

4 A.V. Butcher, J Chatt, G.J. Leigh and P.L. Richards, *J Chem. Soc, Dalton Trans.*, (1972) 1064; K. Yoon, G. Parkin, D.L. Hughes and G.J. Leigh, *J. Chem. Soc., Dalton Trans.*, (1992) 769.

5 B. Bell, J. Chatt and G.J. Leigh, *J. Chem. Soc., Dalton Trans*, (1972) 2492

6 (a) S. Hong and P. Jennische, *Acta Chem. Scand., Ser. A, 32* (1978) 313; (b) O.J. Ezomo, D.M.P. Mingos and I.D. Williams, *J Chem Soc., Chem Commun*, (1987) 924.

7 (a) N.W. Alcock, *Acta Crystallogr., Sect. A, 25* (1969) 101; (b) J.A. Samuels, J.W. Zwanziger, E.B. Lobkovsky and K.G. Caulton, *Inorg. Chem*, *31* (1992) 4046.

8 (a) F. Su, J.C. Bryan, S. Jang and J.M. Mayer, *Polyhedron, 8* (1989) 1261; (b) S. Harvey, M.F. Lappert, C. Raston, B.W. Skelton, G. Srivastava and A.H. White, *J. Chem. Soc, Chem Commun.*, (1988) 1216.

9 K.G. Caulton and E.G. Lundquist, *Inorg. Chim. Acta, 159* (1989) 23; A.J. Deeming, S. Doherty, J.E. Marshall and N.I. Powell, *Polyhedron, 10* (1991) 1857; *J. Chem. Soc., Chem. Commun.*, (1989) 1351.

10 C. Bianchini, D. Masi, K. Linn, C. Mealli, M. Peruzzini and F. Zanobini, *Inorg. Chem., 31* (1992) 4036.

11 P.R. Sharp, *Organometallics, 3* (1984) 1217; L.M. Atagi, S.C. Critchlow and J.M. Mayer, *J. Am. Chem. Soc., 114* (1992) 1483.

12 J.K. Kochi, *Acta Chem. Scand., 44* (1990) 409.