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Reduction of pentachlorotantalum in pure trimethylphosphine: the synthesis of compounds containing the Ta-η^2-$CHPMe_2$ group: crystal structure of [Ta(η^2-$CHPMe_2$)(η-C_4H_6)(PMe_3)$_2$Cl] *

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Abstract

Reduction by sodium sand of $TaCl_5$ in liquid PMe_3 proceeds in the sequence [Ta(PMe_3)$_2$$Cl_5$], [Ta($PMe_3$)$_3$$Cl_4$], [Ta($PMe_3$)$_3$$Cl_3$], [Ta($PMe_3$)$_4$$Cl_2$], [Ta($\eta^2$-$CHPMe_2$)($PMe_3$)$_4$Cl], [Ta($\eta^2$-$CHPMe_2$)($\eta^2$-$CH_2PMe_2$)($PMe_3$)$_3$]. The compound [Ta($\eta^2$-$CHPMe_2$)($PMe_3$)$_4$Cl] reacts with cyclopentadiene and butadiene giving [Ta(η-C_5H_5)$_2$(PMe_3)Cl] and [Ta(η^2-$CHPMe_2$)(η-C_4H_6)(PMe_3)$_2$Cl], respectively. The crystal structure of [Ta(η^2-$CHPMe_2$)(η-C_4H_6)(PMe_3)$_2$Cl] has been determined. The compound [Ta(η^2-$CHPMe_2$)(η^2-CH_2PMe_2)(PMe_3)$_3$] reacts with dihydrogen giving [Ta(η^2-$CHPMe_2$)(η^2-CH_2PMe_2)(PMe_3)$_2$$H_2$].

We have reported that reduction using sodium sand of the halides $MoCl_5$, WCl_6, $ReCl_5$ and $TaCl_5$ in pure trimethylphosphine as a reactive solvent can lead to the one-pot synthesis of the highly electron-rich derivatives [Mo(PMe_3)$_5$$H_2$] [1] [W($\eta^2$-$CH_2PMe_2$)($PMe_3$)$_4$H] [2], [Re($PMe_3$)$_5$H] [1] and [Ta($\eta^2$-$CHPMe_2$)($\eta^2$-$CH_2PMe_2$)($PMe_3$)$_3$] [2], respectively. Clearly these reactions proceed by multiple steps. Here we describe a detailed study of the reaction and intermediates leading to [Ta(η^2-$CHPMe_2$)(η^2-CH_2PMe_2)(PMe_3)$_3$] (**1**).

There have been several tertiaryphosphine(halogeno)tantalum compounds described previously which are relevant to the work described below.

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* Dedicated to Professor L. Sacconi in recognition of his outstanding contribution to organometallic chemistry.

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Known tertiaryphosphinechloro derivatives of tantalum(V) include [Ta(PPh$_3$)Cl$_5$] [3], [Ta(PPh$_2$Me)$_2$Cl$_5$] [4] and [Ta(PMe$_3$)$_2$Cl$_5$] [5]. Reduction of tantalum pentachloride in the presence of the appropriate phosphine gives [Ta(PPhMe$_2$)$_2$Cl$_4$], [Ta(PEt$_3$)$_2$Cl$_4$], and [Ta(PMe$_3$)$_3$Cl$_4$], whose crystals structures have been determined [6]. These three compounds are green in solution but crystallise as red or orange solids. The dimer [TaCl$_4$(PMe$_3$)$_2$]$_2$ has been described [7]. The only characterised example of mononuclear tertiaryphosphinechloro derivatives of tantalum(III) is [Ta(PMe$_3$)$_3$Cl$_3$] [8], which was prepared by reduction of TaCl$_5$ in tetrahydrofuran (thf) using sodium amalgam in the presence of trimethylphosphine. It forms red, paramagnetic crystals and readily dimerises with loss of trimethylphosphine giving [Ta(PMe$_3$)$_2$Cl$_2$(μ-Cl)]$_2$ [9]. Reduction of tantalum pentachloride with a stoichiometric amount of sodium amalgam in diethyl ether with excess trimethylphosphine gives the brown crystalline tantalum (II) compound [*trans*-Ta(PMe$_3$)$_4$Cl$_2$] [3], whose crystal structure has been determined. The related mononuclear tertiaryphosphinechloro derivative of tantalum(II) namely, [Ta(dmpe)$_2$Cl$_2$] has been described [10]. Whilst tantalum(I) carbonylphosphine halides have been reported [10], as far as we are aware, there are no known simple tertiary phosphine-tantalum(I) halides.

Results and discussion

When a mixture of pentachlorotantalum, sodium sand and an excess of trimethylphosphine was stirred for 4–5 d a sequence of distinct colour changes was observed. The initial reaction mixture was bright yellow which gave a green precipitate and a pale green solution. Next the green precipitate redissolved giving a deep orange-red solution which slowly turned dark brown. After a further 24 h the brown solution became red (when viewed by transmitted light) and green (when viewed by reflected light). Continued stirring slowly discharged the red component and finally a clear emerald solution developed. No further changes occurred and pure **1** was isolated from the emerald solution.

We presume that the yellow colour of the initial mixture is due to the compound [Ta(PMe$_3$)$_2$Cl$_5$] and that the subsequent green precipitate is [Ta(PMe$_3$)$_2$Cl$_4$].

When the reaction was stopped at the stage where the orange-red solution predominated a red crystalline solid (**2**) can be isolated by crystallization from pentane at −4 °C. Comparison of the ^{1}H NMR spectrum with that reported [8] for [Ta(PMe$_3$)$_3$Cl$_3$] (**2**) showed them to be identical. After separation of **2** the mother liquor was concentrated and cooled to −25 °C to give dark orange crystals which, by comparison with the previously reported ^{1}H NMR data, were shown to be [Ta(PMe$_3$)$_4$Cl$_2$] (**3**). The compounds **2** and **3** were synthesised using literature methods and their reduction using sodium sand in liquid trimethylphosphine gave **1**. When TaCl$_5$ was stirred in neat trimethylphosphine with activated magnesium turnings for eight days, brown crystals of [Ta(PMe$_3$)$_2$Cl$_4$] (**4**) were isolated in high yield.

Sattelberger has described [3] the synthesis of **3** using TaCl$_5$, three equivalents of sodium amalgam and five equivalents of trimethylphosphine in diethyl ether. Repeating this reaction but using seven equivalents of sodium amalgam in diethyl ether together with an excess of trimethylphosphine gave, even after prolonged stirring, only **3**. It appears that a stronger reducing agent such as sodium metal is required to remove the two chlorine atoms of **4** and form **1**.

As noted earlier, a red colour is observed just prior to the formation of **1**. The reduction of $TaCl_5$ (4 g) using sodium sand (2 g) in neat trimethylphosphine was stopped when the first green colouring due to **1** appeared. An extremely air- and water-sensitive dark brown oil **5** was isolated from the reaction mixture but repeated attempts to obtain crystals were unsuccessful.

However, detailed spectroscopic studies and the formation of derivatives strongly suggest the oil to be the compound $[Ta(\eta^2\text{-}CHPMe_2)(PMe_3)_4Cl]$ (**5**). The NMR data for **5**, and the other new compounds, are given in Table 1. The ^1H NMR spectrum of **5** at room temperature shows a broad singlet at 9.56 ppm assignable to a carbene hydrogen. The equivalent hydrogen occurs at 9.46 ppm in the ^1H NMR spectrum of **1**. In the region 1–2 ppm there is a large broad singlet at 1.40 ppm due to four trimethylphosphine ligands and the methyls of the PMe_2 group. The broad nature of the bands suggested fluxional behaviour. The ^1H NMR spectrum at −70 °C showed that the fluxionality of the molecule has been partially reduced. The signal assigned to the terminal trimethylphosphine hydrogens appears as a virtual triplet and the hydrogen of the carbene is seen as a doublet of quintets. The doublet structure is assigned to coupling with the ^{31}P nucleus of the adjacent PMe_2 group (J(P–H) 2.4 Hz) and the quintet structure to coupling with four apparently equivalent PMe_3 (J(P–H) 5.6 Hz). The ^{31}P NMR spectrum of **5** also shows fluxionality at r.t. which is partially reduced at −45 °C.

The ^{13}C NMR spectra of **5** provides strong evidence for the proposed structure. At r.t. the fully ^1H-coupled ^{13}C NMR spectrum showed a doublet of doublets at 187.8 ppm with J(C–P) 73 and J(C–H) 161 Hz. The downfield chemical shift is characteristic for a carbene carbon and the band shows couplings to both the adjacent phosphorus (73 Hz) and the hydrogen (161 Hz). The spectrum showed a quartet (J 127 Hz) of broad signals at 25.6 ppm. On cooling to −45 °C fine structure was observed in these signals. The $^{13}C\{^1H\}$ NMR spectrum at −45 °C shows that the band at 25.6 ppm has resolved into three lines, presumably due to overlapping signals from the methyl groups of the $Ta(\eta^2\text{-}CHPMe_2)$ group and those of the PMe_3 ligands. In addition to the large coupling to the adjacent ^{31}P nucleus of the PMe_2 group (J(P–C) 73 Hz), the resonance due to the carbene carbon at 187.8 ppm shows a further quintet fine structure, which may be assigned to coupling to four, apparently equivalent, trimethylphosphine ligands. We note that a close analogue to **5** namely, $[Ta(CHCMe_3)(PMe_3)_4Cl]$, also showed apparent equivalence of the PMe_3 ligands [11].

The compound **5** was treated with cyclopentadiene giving dark crystals of $[Ta(\eta\text{-}C_5H_5)_2(PMe_3)Cl]$ (**6**). The data characterising **6** are given in Table 1. Bis-η-cyclopentadienyltantalum compounds $[Ta(\eta\text{-}C_5H_5)_2LX]$ are well-known [12]. The formation of **6** may be envisaged to proceed via the stepwise substitution of the four PMe_3 ligands giving two η-cyclopentadiene groups followed by stepwise transfer of *endo*-hydrogens to the $Ta\text{-}\eta^2\text{-}CHPMe_2$ group forming a PMe_3 group.

Treatment of **5** with butadiene gave air-sensitive, black needle-shaped crystals of $[Ta(\eta\text{-}C_4H_6)(\eta^2\text{-}CHPMe_2)(PMe_3)_2Cl]$ (**7**) whose crystal structure has been determined. The molecular structure of **7** is shown in Fig. 1 and selected distances and angles are in Table 2.

If each ligand around tantalum is assumed to occupy one site, the central metal

Table 1

Analytical and spectroscopic data

Compound [a]	NMR [b]
5 Brown oil	^{1}H [c], −70 °C: 9.46 [quin of d, 1H, J(P–H) 5.6, J(P–H) 2.4, P–CH=Ta], 140 [vt, 36H, J'(P–H) 4.8, 4PMe$_3$], 1.33 [d, J(P–H) 7, PMe$_2$].
	^{31}P [c], −95 °C: −24.3 [d, 4P, J(P–P) 10, TaPMe$_3$], −139.6 [quin, 1P, J(P–P) 9, TaPMe$_2$].
	^{13}C [c], −45 °C: 187.8 [ddquin, J_d(C–H) 161, J_d(P–C) 73, J_{qin}(P–C) 10, P–CH=Ta], 25.6 [q of m, J'(P–C) 127, 4PMe$_3$ and PMe$_2$].
6 Dark red	^{1}H: 4.04 [d, 10H, J(P–H) 2, 2η-C$_5$H$_5$], 0.95 [d, 9H, J(P–H) 8, PMe$_3$].
C, 34.9 (34.9); H, 4.4 (4.4);	^{13}C, off resonance decoupled: 89.8 [d, J(P–C)2, 2η-C$_5$], 18.8 [q, J(P–C) 26, PMe$_3$].
Cl, 8.2 (8.4) [d]	^{31}P: −37.2 [s, TaPMe$_3$].
7 Black [e] C, 31.2 (31.4); H, 6.1 (6.4)	^{1}*H*: 8.85 [d, 1H, J(P–H) 19, P=CH], 5.76 [m, 6 lines, 1H, H$_a$ or H$_b$], 4.56 [m, 1H, H$_b$ or H$_a$], 1.56 [br, 1H, H$_c$], 1.44 [d, 9H, J(P–H) 7, PMe$_3$], 1.38 [d, 9H, 8, PMe$_3$], 1.24 [d, 9H, J(P–H) 7, PMe$_3$], 1.12 [d, 9H, J(P–H) 8, PMe$_3$], 0.92 [m, 1H, H$_e$ or H$_f$], 0.08 [m, 1H, H$_f$ or H$_e$], H$_d$ is obscured.
	^{13}C: 173.1 [dddd, J(C–P) 13, 32, 50, J(C–H) 158, Ta=CH–P], 114.7 [d, J(C–H) 159, diene =CH], 86.6 [d, J(C–H) 161, diene CH], 44.6 [dt, J(C–P) 12, J(C–H) 150, diene CH$_2$], 44.0 [t, J(C–H) 146, diene CH$_2$], 16.1 [dq, J(C–P) 19,6, J(C–H) 132, P$_A$Me$_3$], 15.3 (dq, J(C–P) 25, J(C–H) 130, P$_C$Me], 14.5 [dq, J(C–P) 25, J(C–H) 125, P$_B$Me$_3$], 14.4 [dq, J(C–P) 19, J(C–H) 128, P$_C$Me].
	^{31}P: −10.5 [dd, J(P$_A$ − P$_B$) 45, J(P$_A$ − P$_C$) 23, P$_A$Me$_3$], −18.6 [dd, P$_B$Me$_3$], −118.2 [dd, J(P$_C$ − P$_A$) 23, J(P$_C$ − P$_B$) 43, P$_C$Me$_3$].
8 White m/e 484 [M^+] [f]	^{1}H: 8.10 [ddt, 1H, J(P–H) 13, 16, 7, Ta=CH], 5.48 [m, 1H, TaH], 3.37 [m, 1H, TaH], 1.60 [d, 3H, J(P–H) 7, PMe], 1.58 [d, 9H, J(P–H) 7, PMe$_3$], 1.56 [d, 3H, J(P–H) 6, PMe], 1.49 [d, 9H, J(P–H) 8, PMe$_3$], 1.31 [d, 3H, J(P–H) 8, PMe], 1.24 [d, 3H, J(P–H) 8, PMe], −0.44 [m, 1H, 1H ofTaCH$_2$], −0.70 [m, 1H, 1 H of TaCH$_2$].
	^{13}C{^{1}H}: 170 [m, Ta=CH], 24.4 [dd, J(C–P) 9, 25, PMe$_3$], 23.5 [dd, J(C–P) 10, 20, PMe$_3$], 23.1 [d, J(C–P) 18, PMe$_3$], 17.9 [d, J(C–P) 18, PMe], 16.2 [d, J(C–P) 16, PMe], 15.4 [d, J(C–P) 11, PMe], −2.6 [m, Ta-CH$_2$].
	^{31}P: −10.1 [ddd, J(P–P) a,b 37; a,c 68; a,d 24, P$_a$Me$_3$], −14.6 [ddd, J(P–P) b,a 37; b,c 35; b,d 50, P$_b$Me$_3$], −59.3 [ddd, J(P–P) c,a 68; c,b 35; c,d 19, P$_c$–CH–Ta], −124.0 [ddd, J(P–P) d,a 24; d,b 50; d,c, 19, P$_d$–CH=Ta].

[a] Microanalytical data given as: Found (calc.) in %. [b] Given as: chemical shift (δ) (multiplicity, relative intensity, J in Hz, assignment). In bezene-d_6 at r.t., unless otherwise stated. [d] m/e for ^{35}Cl: 422 [M^+], 346 [$M^+ - PMe_3$]. [c] Toluene-d_8. [e] Yellow solution. [f] m/e, 408 [$M^+ - PMe_3$].

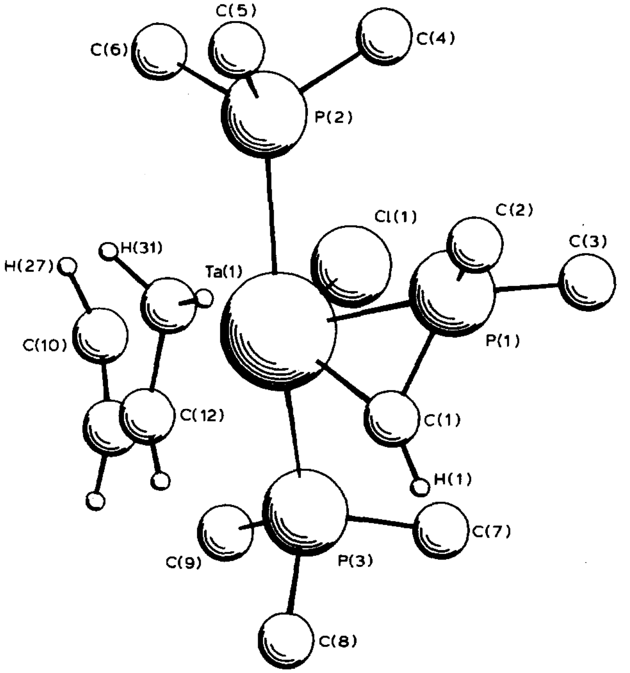


Fig. 1. Molecular structure of 7. Hydrogens in calculated positions have been omitted for clarity.

has a distorted trigonal bipyramidal coordination geometry. P(2) and P(3) are approximately axial (P(2)–Ta(1)–P(3) 150.85(3)°) and the η^2-CHPMe$_2$ ligand is in an equatorial position. This is the second example of this ligand coordinated to tantalum and the observed geometry is close to that found for η^2-CHPMe$_2$ in [Ta(η^2-CH$_2$PMe$_2$)(η^2-CHPMe$_2$)(PMe$_3$)$_3$] [1]. Ta(1), P(1) and C(1) form a bonded triangle with H(1) virtually coplanar (0.08 Å out of the plane). C(2) and C(3) are respectively 1.411 and 1.452 Å and below the TaPC plane. The Ta–C(1) distance of 2.026(3) Å is close to that (2.015(4) Å) in **1** again indicative of a Ta=C double bond (Ta=CH$_2$ 2.026(10) Å in Ta(η^5-C$_5$H$_5$)$_2$(=CH$_2$)(CH$_3$) [13]. P(1)–C(1) is short (1.704(4) Å) in comparison with the average P–Me bond length of 1.821 Å suggesting multiple bond character.

The Ta–P(1) bond is markedly shorter than for P(2) or P(3) but comparison with **1** shows this may be because the latter two phosphine ligands are sterically crowded. Even so, the Ta–P distances are all within the range observed in a series of TaCl$_n$(PR$_3$)$_m$ compounds [14]. The Ta–Cl bond of 2.516(1) Å is also long and reflects the electron-rich nature of the metal centre.

The butadiene ligand appears tipped so that C(13) is closer to tantalum and C(11) furthest away. The terminal C–C bonds are longer than the central, as found for other tantalum-butadiene complexes [15], and the actual values are, within experimental error, the same as those seen in [Hf(η-C$_4$H$_6$)$_2$(dmpe)] (dmpe = bis(dimethylphosphino)ethane) [16]. This may be attributed to a greater contribution of the σ-1,4-η^2-2,3-C$_4$H$_6$ representation of bonding in contrast with [Mo(η-C$_4$H$_6$)$_3$ [17], where the η^2,η^2-1,3-diene form predominates. C(10)–C(13) are approximately coplanar and the tantalum lies 1.857 Å out of this plane. The hydrogen

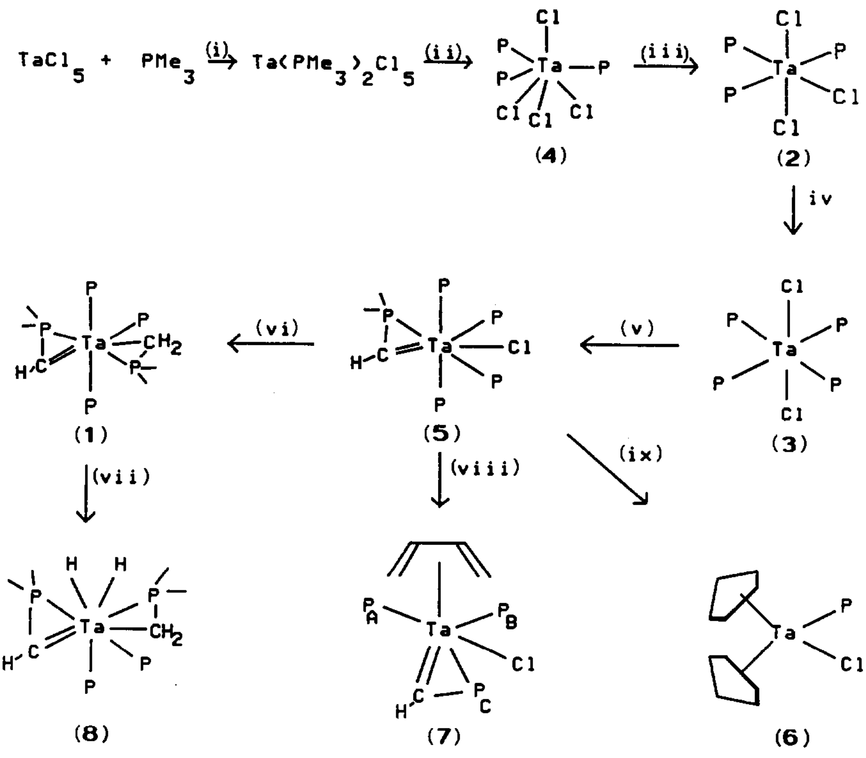
Table 2

Selected bond lengths (Å) and angles (°)

Ta(1)–P(1)	2.495(1)	P(1)–Ta(1)–P(2)	81.68(3)
Ta(1)–P(2)	2.638(1)	P(1)–Ta(1)–P(3)	106.80(3)
Ta(1)–P(3)	2.599(1)	P(2)–Ta(1)–P(3)	150.85(3)
Ta(1)–Cl(1)	2.516(1)	P(1)–Ta(1)–Cl(1)	92.60(4)
Ta(1)–C(1)	2.026(3)	P(2)–Ta(1)–Cl(1)	75.20(4)
Ta(1)–C(10)	2.353(4)	P(3)–Ta(1)–Cl(1)	76.57(4)
Ta(1)–C(11)	2.402(4)	P(1)–Ta(1)–C(1)	42.72(10)
Ta(1)–C(12)	2.354(4)	P(2)–Ta(1)–C(1)	123.21(10)
Ta(1)–C(13)	2.283(4)	P(3)–Ta(1)–C(1)	74.17(10)
		Cl(1)–Ta(1)–C(1)	110.84(11)
P(1)–C(1)	1.704(4)		
P(1)–C(2)	1.828(4)	Ta(1)–C(1)–P(1)	83.51(14)
P(1)–C(3)	1.826(4)	Ta(1)–P(1)–C(1)	53.77(12)
		Ta(1)–P(1)–C(1)	129.05(16)
		Ta(1)–P(1)–C(3)	126.80(17)
		C(1)–P(1)–C(2)	116.2(2)
		C(1)–P(1)–C(3)	115.5(2)
		C(2)–P(1)–C(3)	103.2(2)
P(2)–C(4)	1.822(5)	Ta(1)–P(2)–C(4)	116.42(2)
P(2)–C(5)	1.807(5)	Ta(1)–P(2)–C(5)	118.2(2)
P(2)–C(6)	1.824(6)	Ta(1)–P(2)–C(6)	115.9(2)
		C(4)–P(2)–C(5)	100.4(3)
		C(4)–P(2)–C(6)	102.4(3)
		C(5)–P(2)–C(6)	101.0(3)
P(3)–C(7)	1.816(5)	Ta(1)–P(3)–C(7)	113.5(2)
P(3)–C(8)	1.820(5)	Ta(1)–P(3)–C(8)	117.0(2)
P(3)–C(9)	1.825(5)	Ta(1)–P(3)–C(9)	118.5(2)
		C(7)–P(3)–C(8)	101.6(2)
		C(7)–P(3)–C(9)	101.0(2)
		C(8)–P(3)–C(9)	102.7(3)
		Ta(1)–C(1)–P(1)	83.51(14)
C(1)–H(1)	0.95(4)	Ta(1)–C(1)–H(1)	150(3)
		P(1)–C(1)–H(1)	126(3)
C(10)–C(11)	1.415(7)	C(10)–C(11)–C(12)	120.8(4)
C(11)–C(12)	1.365(7)	C(11)–C(12)–C(13)	117.9(4)
C(12)–C(13)	1.448(6)		
C(10)–H(26)	0.95(4)	C(11)–C(10)–H(26)	119(4)
C(10)–H(27)	0.97(4)	C(11)–C(10)–H(27)	125(3)
C(11)–H(28)	0.95(4)	C(10)–C(11)–H(28)	124(3)
C(12)–H(29)	0.95(4)	C(12)–C(11)–H(28)	115(3)
C(13)–H(30)	0.98(3)	C(11)–C(12)–H(29)	117(3)
C(13)–H(31)	1.01(3)	C(13)–C(12)–H(29)	125(3)
		C(12)–C(13)–H(30)	117(3)
		C(12)–C(13)–H(31)	114(3)

atoms, which were located, lie *syn* 0.6 Å out of the butadiene plane away from tantalum, *anti* 0.15 Å towards tantalum and those on C(11) and C(12) almost in plane.

The NMR spectra of **7** are consistent with the solid state structure (Table 1). The internal hydrogens of the butadiene ligand appear at δ 5.76 and 4.56, and *anti*-hy-



Scheme 1. P = PMe_3. (i) Dissolve $TaCl_5$ in pure PMe_3. (ii) $TaCl_5$ with sodium sand in excess of PMe_3 at r.t. for 15 h. (iii) $TaCl_5$ with sodium sand in excess of PMe_3 at r.t. for 40 h. (iv) $TaCl_5$ with magnesium turnings in excess of PMe_3 at r.t. for 8 d, 64%. (v) $TaCl_5$ with sodium sand in excess of PMe_3 at r.t. for 4 d, 64%. (vi) $TaCl_5$ with sodium sand in an excess of PMe_3 at r.t. for 5 d. (vii) Dihydrogen at 2 atm and r.t. for 1 h, 39% from **1**. (viii) Butadiene at r.t. for 12 h, 16% base on $TaCl_5$. (ix) Cyclopentadiene at r.t. for 12 h, 19% based on $TaCl_5$.

drogens are at δ 0.92 and 0.08. One of the *syn*-hydrogens is a broad doublet at δ 1.65 but the other *syn*-hydrogen is obscured by the PMe_3 resonances. The ^{13}C NMR spectrum, however, further establishes the presence of an η-butadiene group with two doublets at δ 114.7, J(C–H) 158 and δ 86.6, J(C–H) 159; a doublet of triplets at δ 44.6, J(C–H) 150, J(P–C) 12 and a triplet at δ 44.0, J(C–H) 146. The metallacycle is characterized by a downfield doublet (J(P—H) 19) at δ 8.85 in the ^1H NMR and a downfield doublet of doublets of doublets of doublets at δ 173.1 ppm with J(C–H) 158 and J(P–C) 50, 32, 13 in the ^{13}C NMR spectrum.

Double resonance and magnetization transfer experiments showed that the three pairs of hydrogens H_a and H_b, H_c and H_d, and H_e and H_f (see Fig. 3) undergo pairwise exchange. The kinetics of this exchange was investigated by magnetization transfer experiments (Fig. 2). A double exponential fit of the magnetization vs. time curve provides the value for K_{298} 1.870 s^{-1} and the activation energy for the process $\Delta G^{\ddagger}$ 71.4 kJ mol^{-1} using the Eyring equation.

A mechanism involving only rotation about the tantalum butadiene centroid axis can be discounted since it does not result in the observed pairwise exchange. A possible mechanism for the exchange is shown in Fig. 3.

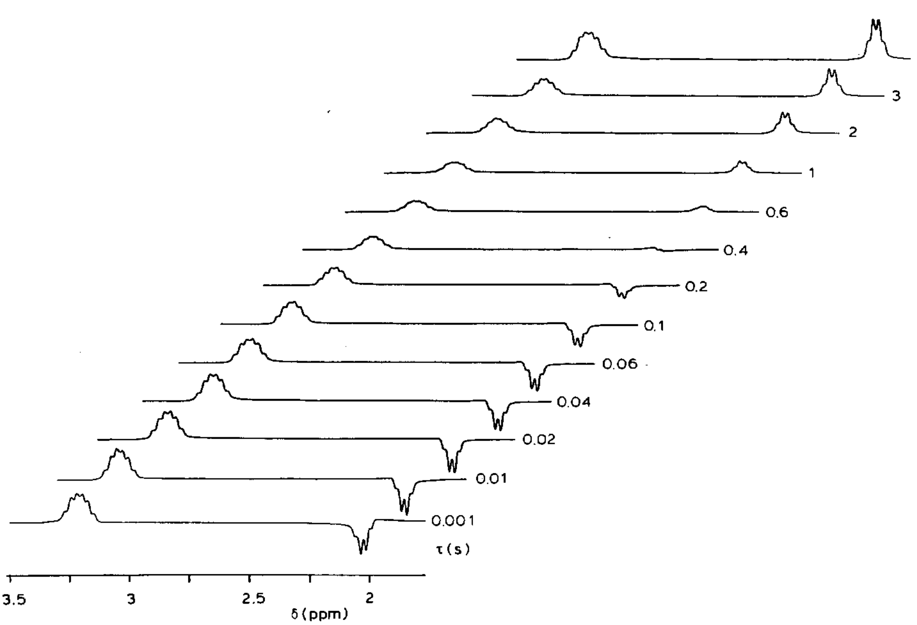


Fig. 2. Magnetisation transfer experiment on the H_a and H_b atoms of the η-butadiene ligand of 7.

The second step of rotation of the η-butadiene ligand about the ligand–metal axis may be assumed to be fast compared to the first step, which is, therefore, rate limiting. Values of $\Delta G^{\ddagger}$ 40–60 kJ mol^{-1} have been reported previously for the rotation of butadiene ligands [18]. The σ^2-1,4-η^2-2,3-C_4H_6 representation used in Scheme 1 is supported by the alternation in the C–C bond lengths in the crystal structure determination.

A solution of **1** in petroleum ether reacted rapidly with dihydrogen (2 atm.) to give a colourless solution, from which white crystals **8** could be sublimed at 50 °C. The compound is highly air and water sensitive and samples stored at r.t. showed decomposition after 12 h. This sensitivity precluded microanalysis and **8** has been characterised spectroscopically. A mass spectrum showed a highest ion peak at $m/e = 484$, corresponding to $[Ta(\eta^2\text{-}CHPMe_2)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2H_2]$ (**8**), and a peak at $m/e = 408$ ($M^+ - PMe_3$). The ^1H NMR spectrum of **8** shows a complex band at δ 8.1 ppm assignable to the CH=Ta hydrogen with primary coupling to four inequivalent ^{31}P nuclei and with partially resolved finer coupling. The bands assigned to the Ta-CH_2 hydrogens occur at −0.44 and −0.70 ppm. The coupling

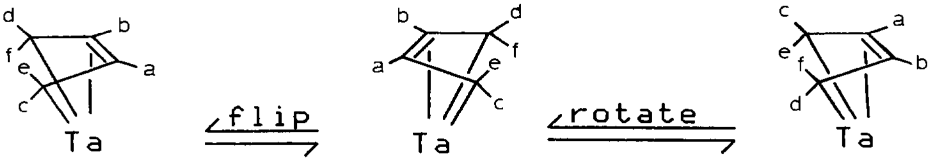


Fig. 3. Proposed mechanism for the fluxionality of the n-butadiene group of 7.

patterns are too complex to be simply rationalised. The doublets of relative intensity 3 at δ 1.60, 1.56, 1.31 and 1.24 may be assigned to the methyl groups bound to the two metallacycle phosphorus atoms. The two complex signals at 5.48 and 3.37 ppm may be assigned to inequivalent Ta-H hydrogens. $^1H-^1H$ decoupling experiments are complicated by ^{31}P couplings. For example, irradiation at one of the hydride signals produces changes in the other multiplets and shows both hydrides are connected in the molecule and that there is strong coupling of the carbene hydrogen to the hydride at 3.3 ppm. Unfortunately, the chemical shift range of the ^{31}P NMR spectrum was sufficiently large to preclude the observation of a phosphorus decoupled ^1H NMR spectrum and selective ^{31}P decoupling experiments were of little value because the multiplets remained highly complex. Consequently detailed evaluation of coupling constants in the ^1H NMR spectrum was not undertaken.

The ^{31}P NMR spectrum of **8** shows four distinct signals which supports the assignment of **8** as a tetrakisphosphine species. Characteristic shifts of the metallacycle phosphines, namely P-CH_2-Ta at -59.3 and P-CH=Ta at -124.0 ppm, provide further evidence that reaction of **1** with H_2 did not disrupt either of the two metallacycles. The structure proposed for **8** contains no unique *trans*- or *cis*-relationships. This limits any deductions that can be made concerning the phosphorus–phosphorus coupling constants, although we note there are two large and four small values. The ^{13}C NMR spectral data are in agreement with the ^1H and ^{31}P spectra but provides no further information towards assigning a structure. Spin-inversion transfer experiments on the hydride signals in **8** did not show transfer to any other site at room temperature and higher temperatures could not be used because of decomposition.

The reactions described above and the structures proposed for the new compounds **5**, **7** and **8** are shown in Scheme 1.

Experimental

All preparations and reactions described were carried out under an atmosphere or argon using standard Schlenk vessels, and vacuum-line technique, or in an inert atmosphere box. Argon was purified by passage through a gas drying column containing BASF catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of argon. Solvents were pre-dried over molecular sieves and then distilled from potassium (toluene, benzene, thf, cyclohexane), sodium-potassium alloy (pentane, 40–60 °C petroleum ether, diethyl ether), or phosphorus pentoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for NMR were stored over activated molecular sieves or a potassium film and were transferred by vacuum distillation.

Elemental analyses were performed by the Analysis Department in this laboratory, or in the case of very air-sensitive materials, by Analytische Laboratorien, 5270 Gummersbach, 1 Elbach, W. Germany.

Infrared spectra were recorded on a Pye Unicam SP2000 double beam, grating spectrophotometer, or on a Perkin–Elmer 1510 FT interferometer. NMR spectra were recorded on the following instruments: ^1H NMR: 300 MHz, Bruker WH-300; ^{13}C NMR: 62.8 MHz, Bruker AM-250; ^{31}P NMR: 101.2 MHz, Bruker AM-250. Abbreviations used in multiplicities are; (s) singlet, (d) doublet, t (triplet), q (quartet), (quin) quintet, (sex) sextet, (m) multiplet, (vt) virtual triplet, (br) broad. Spectra were referenced internally using the residual solvent resonance (^{1}H, ^{13}C) relative to tetramethylsilane (= 0 ppm), or, externally using trimethylphosphate in D_2O (^{31}P). All chemical shifts are quoted in (ppm), and coupling constants in hertz (Hz).

Synthesis of $[Ta(\eta^2\text{-}CHPMe_2)(\eta^2\text{-}CH_2PMe_3)(PMe_2)_3]$ *(1)*

$TaCl_5$ (2.0 g, 5.6 mmol) and sodium sand (2.0 g, 87 mmol) were placed in an ampoule equipped with a magnetic stirrer bar. This was cooled to −196 °C and PMe_3 (50 cm^3) was trap-trap distilled into the ampoule. On warming to r.t. a deep yellow solution developed. The mixture was stirred for 5 d. After 15 h the yellow colour was replaced by a green precipitate in a pale green solution. After a further 40 h the solution has become deep red. The large quantities of grey precipitate, presumably sodium chloride, which formed in the reaction made stirring inefficient. Over the next 20 h the solution turned dark brown. Slowly the dark brown colour was lost, to be replaced by a dark solution which appeared green when viewed by reflected light and red when viewed by transmitted light. Over the last 36 h the solution became more pale and the red component disappeared to leave a clear, emerald green solution. The PMe_3 was then removed by trap-trap distillation to give a dark solid. This was extracted with light petroleum ether (b.p. 40–60 °C, 80 cm^3) and the extract was filtered giving a green solution. Solvent was removed under reduced pressure to give green crystals which were dried in vacuo. Yield, 80 mg, 0.14 mmol, 2.5%.

Isolation of $[Ta(PMe_3)_3Cl_3]$ *(2) and* $[Ta(PMe_3)_4Cl_2]$ *(3)*

$TaCl_5$ (4.0 g, 11.4 mmol) and sodium sand (2.0 g, 87 mmol) in an ampoule were cooled to −196 °C and PMe_3 (60 cm^3) was trap-trap distilled into the ampoule. The mixture was warmed to r.t. and stirred for 50 h. On allowing the mixture to settle the solution was a deep orange. The PMe_3 was removed by trap-trap distillation to leave a sticky dark brown residue. This was extracted with petroleum ether (40–60 °C, 150 cm^3) giving a deep red solution which was filtered and the filtrate was reduced in volume to 50 cm^3. Cooling to −4 °C gave ca. 2 g of red crystals which were isolated and dried in vacuo. By comparison of the ^{1}H and ^{31}P NMR spectra these were shown to be $[Ta(PMe_3)_3Cl_3]$. The mother liquor was reduced in volume to 20 cm^3 and cooled to −25 °C overnight to give a small quantity of dark orange crystals. These were isolated and dried in vacuo. The ^{1}H NMR spectrum showed the product to be $[Ta(PMe_3)_4Cl_2]$.

Alternative syntheses $[Ta(PMe_3)_4Cl_2]$ *(3)*

Procedure A. A mixture of sodium amalgam (0.7% w/w, 67 mmol), PMe_3 (8.39 g, 110 mmol) and thf (150 cm^3) at −30 °C was treated with a slurry of $TaCl_5$ (8.06 g, 22.5 mmol) in thf (10 cm^3) at −30 °C. The mixture was warmed to r.t. and stirred vigourously. After 12 h the solution had turned brown, accompanied by large amounts of precipitate. The solution was filtered through a bed of Celite and the residue was washed with diethyl ether (6 × 100 cm^3). The filtrate and washings were combined and the solvent was removed under reduced pressure giving a brown solid. This was extracted with diethyl ether (500 cm^3). The resulting brown extract was concentrated to 200 cm^3. Cooling to −25 °C for 12 h gave brown crystals which were separated and dried in vacuo. Yield, 5.8 g, 10.4 mmol, 43%.

Procedure B. A modification of the reported method [3] was used. A slurry of $TaCl_5$ (3.57 g, 9.9 mmol) in diethyl ether (30 cm^3) was cooled to −30 °C. Sodium amalgam (0.6%, 50 mmol) was added to a solution of PMe_3 (5.3 g, 70 mmol) in diethyl ether (150 cm^3) and the mixture was cooled to −30 °C. The $TaCl_5$ slurry was added quickly while stirring the amalgam vigorously. No reaction was observed at this temperature but on warming to r.t. a green colour was observed. After stirring for 30 h the solution was yellow-brown. The solution was decanted and the residues were washed with diethyl ether (3×60 cm^3). These were combined and filtered through a bed of Celite. The solvent was removed under reduced pressure to give a yellow-brown solid. This was extracted with petroleum ether (40–60 °C, 200 cm^3) to give a deep yellow brown extract which was was filtered and the filtrate was cooled to −25 °C. Brown crystals separated and were collected and dried in vacuo. Comparison of the ^1H NMR spectrum with that of an authentic sample showed the product to be $[Ta(PMe_3)_4Cl_2]$ (3). Yield, 1.0 g, 1.7 mmol, 18%.

Procedure C. PMe_3 (50 cm^3) was distilled onto $TaCl_5$ (2.0 g, 56 mmol) and activated magnesium turnings (2.0 g, 74 mmol). The mixture was warmed to r.t. and stirred for 8 d until a deep red-brown colour in the solution persisted. During this reaction the solids formed made the reaction very viscous and stirring was difficult. Excess PMe_3 was distilled from the ampoule and the residue was extracted with petroleum ether (40–60 °C, 200 cm^3) to give a brown-red solution. This was filtered and the filtrate was concentrated to 20 cm^3. Cooling to 4 °C for 12 h gave a large quantity of brown crystals which were isolated and dried in vacuo. By comparison with the ^1H NMR spectrum of an authentic sample this was identified as $[Ta(PMe_3)_4Cl_2]$ (3). Yield 2 g, 32.6 mmol, 64%.

Synthesis of 1 from $[Ta(PMe_3)_3Cl_3]$ (2)

The compound $[Ta(PMe_3)_3Cl_3]$ (2.0 g, 3.9 mmol) and sodium sand (2.0 g, 87 mmol) was cooled to −78 °C and PMe_3 (45 cm^3) was trap-trap distilled onto the mixture. On warming to r.t. the solution developed a dark brown colour. The mixture was stirred for 70 h giving an emerald solution. The PMe_3 was distilled from the product giving a dark residue. This was extracted with petroleum ether (40–60 °C, 100 cm^3) and the emerald extract was filtered. The solvent was removed from the filtrate under reduced pressure giving dark green crystals which were dried in vacuo. The ^1H NMR spectrum showed the product to be $[Ta(\eta^2\text{-}CHPMe_2)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$. Yield, 100 mg, 0.17 mmol, 4.3%.

Synthesis of 1 from $[Ta(PMe_3)_4Cl_2]$ (3)

The compound $[Ta(PMe_3)_4Cl_2]$ (0.5 g, 0.9 mmol) and sodium sand (2 g, 87 mmol) were cooled to −78 °C and PMe_3 (50 cm^3) was trap-trap distilled onto the mixture. On warming to r.t. the solution was dark orange-brown. The mixture was stirred for 12 h giving an emerald solution. The PMe_3 was distilled from the reaction mixture and the residual solid was extracted with petroleum ether (40–60 °C, 100 cm^3). The emerald green extract was filtered and solvent was removed from the filtrate, under reduced pressure, giving green crystals. The ^1H NMR spectrum showed the product to be $[Ta(\eta^2\text{-}CHPMe_2)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$. Yield, 50 mg, 0.1 mmol, 10%.

Synthesis of [Ta(η^2-CHPMe$_2$)(PMe$_3$)$_4$Cl] (5)

PMe_3 (50 cm^3) was distilled onto a mixture of $TaCl_5$ (4.0 g, 11 mmol) and sodium sand (2 g, 87 mmol). The reaction was warmed to r.t. and stirred for 4 d. After allowing the reaction to settle out the solution appeared red-green. The excess of PMe_3 was distilled from the mixture and the residue was extracted with petroleum ether (40–60 ° C, 150 cm^3). The resulting dark extract was filtered and solvent was removed from the filtrate under reduced pressure. Attempts to crystallise the resulting dark brown oil were unsuccessful.

Synthesis of [Ta(η-C$_5$H$_5$)$_2$(PMe$_3$)Cl] (6)

$TaCl_5$ (4 g, 11.2 mmol) and sodium sand (2 g, 87 mmol) were stirred in PMe_3 (50 cm^3) for 4 d. On allowing the reaction to settle the solution was the red-green colour previously described. The PMe_3 was distilled from the reaction and the residue was extracted with petroleum ether (40–60 ° C, 150 cm^3). The resulting solution was filtered and the filtrate was concentrated to 50 cm^3. The concentrate was cooled (to -196 ° C) and cyclopentadiene (0.9 g, 14 mmol) was distilled onto it. On warming to r.t. the solution had become dark brown and a large quantity of dark crystalline material was deposited. The solution was decanted and the crystalline material was dried in vacuo. This was extracted with toluene (100 cm^3) giving a dark red solution. After filtration the solution was reduced to 20 cm^3 and petroleum ether (100–120 ° C, 60 cm^3) added. Cooling to -25 ° C gave black needle crystals which were isolated and dried in vacuo. Yield, 0.9 g, 2.1 mmol, 19% based on $TaCl_5$.

Synthesis of [TaCl(η^2-CHPMe$_2$)(η-C$_4$H$_6$)(PMe$_3$)$_2$] (7)

$TaCl_5$ (4 g, 11.2 mmol) and sodium sand (2 g, 87 mmol) were stirred in PMe_3 (50 cm^3) for 4 d. The PMe_3 was distilled from the reaction and the residue extracted with petroleum ether (40–60 ° C, 150 cm^3). The resulting red-green solution was filtered and reduced to 40 cm^3. This was cooled to -196 ° C and butadiene (4.9 g, 92 mmol) was trap-trap distilled into the reaction vessel. The mixture was warmed to r.t. and after 5 min the solution was pale red and a flocculent brown solid had precipitated. The reaction was stirred overnight but no further change was observed. The mixture was filtered and solvent was removed from the filtrate under reduced pressure. The residue was extracted with petroleum ether (40–60 ° C, 80 cm^3) to give a pale orange solution. This was concentrated to 30 cm^3 and cooled to -40 ° C for 12 h giving large black needle-shaped crystals. These were isolated and dried in vacuo. Yield, 0.6 g, 1.8 mmol, 16% based on $TaCl_5$.

Synthesis of [Ta(η^2-CHPMe$_2$)(η^2-CH$_2$PMe$_2$)(PMe$_3$)$_2$H$_2$] (8)

The compound **1** (300 mg, 0.53 mmol) in pentane (30 cm^3) was treated with dihydrogen at 2 atm. After 30 min the initially green solution became pale yellow and deposited a flocculant brown solid. After 1 h, the reaction mixture was filtered giving a colourless filtrate from which solvent was removed under reduced pressure. The residual colourless oil was distilled onto a cold probe (77 K) at 10^{-2} torr and 50 ° C giving a white compound. On warming to r.t. the product melted to an air-sensitive oily solid, which was very soluble in pentane. Yield, 100 mg, 39%.

Crystal structure determination

Crystal data for 7. $C_{13}H_{31}ClP_3Ta$, $M = 496.7$, monoclinic, a 15.583(2), b

9.631(3), c 26.127(4) Å, β 91.85(1)°, U 3919.4 Å^3, space group $I2/c$, $Z = 8$, D_c 1.68 Mg m^{-3}, (Mo-$K_{\alpha 1}$) 0.70930 Å, μ(Mo-K_α) 62.73 cm^{-1}, $F(000) = 1952$, crystal dimensions 0.65 × 0.14 × 0.20 mm.

Data collection of processing

A crystal of **7** was sealed under nitrogen in Lindemann glass capillary mounted on an Enraf-Nonius CAD4 diffractometer, the cell dimensions obtained by least squares from the positions of 25 carefully centred reflections. Data collection was in ω–2θ scan mode with scan width $(0.95 + 0.35 \tan\theta)$° and ω scan speed range 0.87–5.49° min^{-1}. 7715 reflections were measured ($1 \leqslant \theta \leqslant 27.5$°), 4490 unique (emerging $R = 0.014$ after absorption correction [19] (max, min correction 1.54, 1.0)) giving 3613 observed ($I > 3\sigma(I)$).

Structure analysis and refinement

Solution was by the heavy-atom method. Refinement by full matrix least-squares with all non-hydrogen atoms anisotropic. Hydrogen atoms were located and were included in calculated positions on phosphines; those on C(1) and the butadiene ligand (C(10)–C(13)) were allowed to refine with soft positional restraints [20] while the remainder were recalculated between cycles of refinement (U[iso] 0.06 Å^2).

Corrections were made for anomalous dispersion [21] and isotropic extinction [22]. A Chebsyshev weighting scheme [23] was applied where $w = 1/1\sum_{r=1}^{n} A_r T_r(X)$ and $X = F_o/|F_o|_{\max}$; T_r is the polynomial function with coeffi-

Table 3

Fractional atomic coordinates for **7**

Atom	x	y	z
Ta(1)	0.172940(8)	0.46799(1)	0.137235(5)
P(1)	0.14019(6)	0.3497(1)	0.05391(3)
P(2)	0.31923(6)	0.3334(1)	0.12875(4)
P(3)	0.08515(7)	0.6974(1)	0.13651(4)
Cl(1)	0.27193(7)	0.6397(1)	0.09687(5)
C(1)	0.0683(2)	0.4321(4)	0.0911(1)
C(2)	0.1199(3)	0.1658(5)	0.0412(2)
C(3)	0.1519(4)	0.4225(6)	−0.0100(2)
C(4)	0.3695(3)	0.3438(7)	0.0668(2)
C(5)	0.3194(3)	0.1477(5)	0.1385(2)
C(6)	0.4062(3)	0.3864(7)	0.1729(3)
C(7)	0.0734(3)	0.7760(5)	0.0735(2)
C(8)	−0.0261(3)	0.6864(5)	0.1554(2)
C(9)	0.1263(4)	0.8437(5)	0.1742(2)
C(10)	0.2174(4)	0.5339(6)	0.2207(2)
C(11)	0.1282(3)	0.5082(5)	0.2231(1)
C(12)	0.0939(3)	0.3855(5)	0.2062(1)
C(13)	0.1521(3)	0.2799(4)	0.1885(2)
H(1)	0.010(2)	0.448(5)	0.083(2)
H(26)	0.238(4)	0.626(4)	0.226(2)
H(27)	0.262(3)	0.469(5)	0.231(2)
H(28)	0.088(3)	0.573(5)	0.235(2)
H(29)	0.033(2)	0.379(5)	0.205(2)
H(30)	0.127(3)	0.197(4)	0.172(2)
H(31)	0.203(2)	0.262(5)	0.213(2)

cients, A_r, of 53.2, 71.6, and 26.1 to give satisfactory agreement analyses. At convergence

$$R(\Sigma || F_o| - |F_c|| / \Sigma |F_o|) = 0.019 \text{ and}$$

$$R' \left\{ = \left[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(|F_o|)^2 \right]^{1/2} \right\} = 0.022.$$

Solution and refinement used the Oxford CRYSTALS system [24] on the VAX 11/750 computer of the Chemical Crystallography Laboratory, Oxford University. Scattering factors were taken from International Tables for X-ray Crystallography [25]. Fractional coordinates are given in Table 3.

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