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Competitive ligand C–H bond activations: ring- and phosphine-metallated forms of $(C_5Me_5)Ta(PMe_3)_2$

Vernon C. Gibson*, Terence P. Kee¹

Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE (UK)

Steven T. Carter, Robert D. Sanner²

Department of Chemistry, George M. Bateman Physical Sciences Centre, Arizona State University, Tempe, AZ 85287, USA

and William Clegg

Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU (UK)

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Abstract

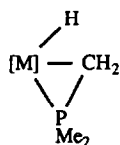
The reduction of $(\eta-C_5H_5)TaCl_4$ with sodium sand in neat trimethylphosphine gives a mixture of products from which $(\eta-C_5H_5)_2Ta(H)PMe_3$ (**1**) may be isolated in low yield and $(\eta-C_5H_5)Ta(PMe_3)_2(H)(\eta^2-CH_2PMe_2)$ (**2**) may be identified by NMR spectroscopy. Treatment of $(\eta-C_5Me_5)TaCl_4$ under similar conditions affords $(\eta-C_5Me_5)Ta(PMe_3)(H)_2(\eta^2-CHPMe_2)$ (**3**) which has been characterized spectroscopically and by an X-ray diffraction study. When a more conventional sodium amalgam/tetrahydrofuran reducing medium is used, $(\eta-C_5Me_5)TaCl_4$ reacts with excess trimethylphosphine to give $(\eta^7-C_5Me_5)(CH_2)_2Ta(H)_2(PMe_3)_2$ (**4**) in which two ring methyl C–H bonds have been cleaved. **4** has been characterized spectroscopically and by an X-ray diffraction study. Complexes **3** and **4** do not undergo interconversion readily under thermal conditions, and dynamic NMR studies on **3** provide no evidence for reversible hydrogen migrations. Investigations into use of other reducing media show that the ratio of the isomers obtained is highly dependent upon reducing agent and solvent.

Introduction

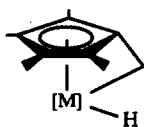
Trimethylphosphine and pentamethylcyclopentadienyl ligands have played an important role in the development of intermolecular C–H activation systems (1). This is partly due to their strong electron releasing properties which confer a high

¹ Present address: School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK.

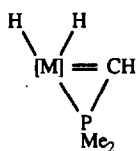
² Present address: Lawrence Livermore National Laboratory, Livermore, CA 94550, USA.



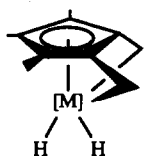
I



II



III



IV

electron density on the metal center and also their reduced proclivity for intramolecular cyclometallations, compared with, for example, aryl phosphines [2]. However, in certain situations, activations of the C–H bonds of either PMe_3 or $\eta^5\text{-C}_5\text{Me}_5$ (Cp^*) can occur to give ligand systems of types I and II. For trimethylphosphine, this was first observed in $\text{Fe}(\text{PMe}_3)_4$ which was shown by Muetterties to exist in equilibrium with its cyclometallated form $\text{Fe}(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)_3$ [3]. Analogous Ru [4], Os [4], Mo [5] and W [6] systems have since been investigated, and competitive PMe_3 cyclometallations have been seen during hydrocarbon activations using $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{PMe}_3)_3$ [1e].

Although activation of the ring methyl substituents has not been observed to date for this rhenium complex, there are a number of other examples where this does occur to give $\eta^6\text{-1,2,3,4-tetramethylfulvene}$ (or $\eta^5, \eta^1\text{-C}_5\text{Me}_4\text{CH}_2$) complexes; these include $\text{Cp}^*(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{TiMe}$ which results from the thermal decomposition of $\text{Cp}_2^*\text{TiMe}_2$ [7], $\text{Cp}^*(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{WH}$ which forms during photolysis of Cp_2^*WH_2 [8], $\text{Cp}^*(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{TiH}$, observed in solutions of Cp_2^*Ti [9], $\text{Cp}^*(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{ZrPh}$ formed upon thermolysis of $\text{Cp}_2^*\text{ZrPh}_2$ [10], and $\text{Cp}^*(\eta^5, \eta^1\text{-C}_5\text{Me}_4\text{CH}_2)\text{HfCH}_2\text{C}_6\text{H}_5$ formed as an intermediate in the thermal decomposition of $\text{Cp}_2^*\text{Hf}(\text{CH}_2\text{C}_6\text{H}_5)_2$ [11].

Activation of a second C–H bond of either C_5Me_5 or PMe_3 to give ligand systems of types III and IV are relatively rare: examples of the $\eta^2\text{-CHPMe}_2$ ligand are presently restricted to the tantalum complexes $\text{Ta}(\text{PMe}_3)_3(\eta^2\text{-CH}_2\text{PMe}_2)(\eta^2\text{-CHPMe}_2)$ [6], $\text{Ta}(\text{PMe}_3)_4\text{Cl}(\eta^2\text{-CHPMe}_2)$ [12], $\text{Ta}(\text{PMe}_3)_2(\eta\text{-C}_4\text{H}_6)(\eta^2\text{-CHPMe}_2)$ [12] and $\text{Ta}(\text{PMe}_3)_2(\text{H})_2(\eta^2\text{-CH}_2\text{PMe}_2)(\eta^2\text{-CHPMe}_2)$ [12], and here it is generally found that the abstracted hydrogens are lost from the metal center. This is also true for the few compounds arising by activation of two adjacent ring methyl substituents to give the $\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2$ ligand e.g. $\text{Cp}^*\text{W}(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2)$ which results upon prolonged photolysis of Cp_2^*WH_2 [8], $[\text{Cp}^*\text{Re}(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2)]\text{[BF}_4\text{]}$ which is generated upon photolysis of $[\text{Cp}_2^*\text{ReH}_2]\text{[BF}_4\text{]}$ [13], $\text{Cp}^*\text{Ti}(\eta^7\text{-}$

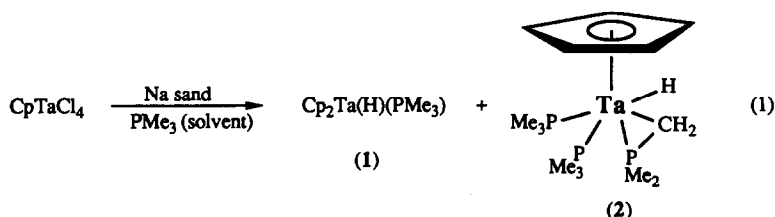
$C_5Me_3(CH_2)_2$ [14] obtained from the thermolysis of Cp_2^*TiR ($R = H, Me$), and $Cp^*Ta(H)(\eta^7-C_5Me_3(CH_2)_2)$ formed as the kinetic product upon thermolysis of $Cp_2^*Ta(=CH_2)(H)$ [15].

In this paper we describe the preparation, and spectroscopic and crystallographic characterization of two isomers of general formula $(C_5Me_5)Ta(PMe_3)_2$ in which two C–H bonds have been cleaved to give ligand systems of type III or IV. Preliminary accounts of this work have appeared [16].

Results and discussion

1. The reaction of $CpTaCl_4$ with sodium in neat PMe_3

Sodium sand in neat trimethylphosphine has been found to completely dehalogenate transition metal halides and thereby facilitate the synthesis of PMe_3 -rich complexes [6]. Somewhat surprisingly, the treatment of $CpTaCl_4$ with excess sodium sand in neat PMe_3 affords, as the major component, the orange crystalline bent-sandwich complex $Cp_2Ta(H)(PMe_3)$ (**1**) in low yield (eq. 1).



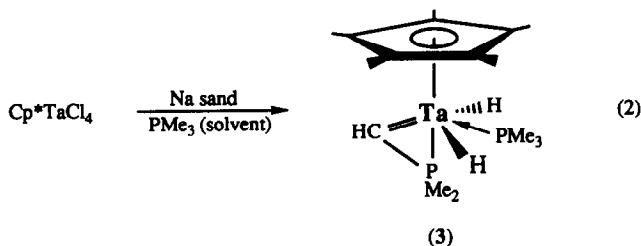
The spectroscopic data for **1** are comparable with analogous niobium and tantalum compounds containing other tertiary phosphine ligands [17]. In particular, the hydride ligand gives a doublet resonance at $\delta -9.39$ ppm ($^2J(\text{PH}) = 20.8$ Hz) in the ^1H NMR spectrum, while a doublet at $\delta 1.07$ ppm ($^2J(\text{PH}) = 7.0$ Hz) is attributable to the PMe_3 methyl hydrogens; the Cp ring hydrogens occur as a singlet at $\delta 4.39$ ppm. A band at 1700 cm^{-1} in the infrared spectrum is characteristic of the Ta–H stretching vibration.

There is also strong spectroscopic evidence for the formation of a half-sandwich derivative of general formula $CpTa(PMe_3)_3$ (**2**) in which one of the PMe_3 ligands has been cyclometallated to give a ligand system of type I. A ^1H NMR of the crude product mixture reveals doublet resonances at $\delta 1.82$ and 1.42 ppm attributable to diastereotopic PMe_2 methyls and signals at $\delta 0.44$ and -0.48 ppm due to diastereotopic methylene hydrogens of the cyclometallated PMe_3 ligand. A resonance at $\delta -69.51$ ppm in the ^{31}P NMR spectrum is also consistent with the phosphorus atom of the 3-membered metallacycle [4,6,18]. Other ^1H NMR resonances confirm the presence of the hydride ($\delta -3.02$), PMe_3 (doublets at $\delta 1.05$ and 1.07 ppm) and Cp ($\delta 4.40$ ppm) ligands. However, attempts to isolate this product from the mixture were unsuccessful due to its solubility in the oily pentane extracts.

2. The reaction of Cp^*TaCl_4 with sodium in neat PMe_3 : synthesis and spectroscopic characterization of $(\eta-C_5Me_5)Ta(PMe_3)(H)_2(\eta^2-CHPMe_2)$ (**3**)

The reaction of Cp^*TaCl_4 with sodium sand in neat PMe_3 gave an orange pentane extract from which colorless crystals of $(\eta-C_5Me_5)Ta(PMe_3)(H)_2(\eta^2-CHPMe_2)$ (**3**) were obtained in 46% yield. NMR studies and an X-ray structural investigation (*vide infra*) confirmed that activation of PMe_3 C–H bonds had

occurred but had not resulted in the formation of the usual $M(H)(\eta^2-CH_2PMe_2)$ moiety. Rather, a double metallation had taken place, with the metal inserting into two C–H bonds of a metal-bound PMe_3 methyl substituent to give the $Ta(H)_2(\eta^2-CHPMe_2)$ grouping (eq. 2).



NMR data for **3** are shown in Table 1 and the proton and carbon spectra are reproduced in Fig. 1.

The resonance at δ 9.19 ppm in the 1H NMR spectrum is characteristic of the metallacycle methine hydrogen (for comparison, the chemical shifts of these protons in other $\eta^2-CHPMe_2$ complexes occur in the range δ 8–10 ppm [6,11,19]). Resolution enhancement of this signal reveals a ddt pattern due to $^1H-^{31}P$ couplings with the metallacycle and bound PMe_3 phosphorus nuclei ($J(PH) = 3.3$ and 2.2 Hz respectively) and a small coupling to the equivalent hydride ligands ($J(HH) = 0.7$ Hz). The methyls of the metallacycle PMe_2 unit occur as a doublet at δ 1.44 ppm with a $^2J(PH)$ coupling of 10.2 Hz; this is significantly larger than is usually observed for a normal PMe_3 ligand, possibly reflecting a rehybridization of the metallacycle phosphorus leading to increased *s*-character in the P–C(methyl) bonds. The equivalent hydride ligands give a doublet of doublet resonance at δ 3.87 ppm; this relatively high frequency metal–hydride shift is not unusual for d^0 Ta^V complexes [20]. The signals attributable to the Cp^* ring methyl hydrogens and the PMe_3 methyls are unexceptional, occurring at δ 2.18 and 1.41 ppm respectively. The latter resolves into a doublet of doublets with a small long-range coupling (0.7 Hz) to the metallacycle phosphorus nucleus. The ^{31}P NMR spectrum gives two signals, at δ -24.9 and -112.4 ppm due to the PMe_3 and $\eta^2-CHPMe_2$ ligands respectively. The unusually low frequency shift of the latter is typical for the phosphorus of this metallacycle which, to date, have been found in the range δ -112 to -140 ppm [6,11,19]. The carbon of the metallacycle is found at δ 192.1 ppm, consistent with the shifts noted for other $\eta^2-CHPMe_2$ complexes [6,11,19].

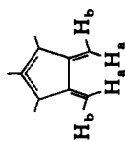
3. The molecular structure of $Cp^*Ta(PMe_3)(H)_2(\eta^2-CHPMe_2)$ (**3**)

Colorless crystals of **3** were obtained by slow cooling of a saturated petroleum ether solution to ca. $-60^\circ C$. The crystal data are summarized in Table 2 and atomic parameters are listed in Table 3. The molecular structure is illustrated in Fig. 2 and 3, and selected bond distances and angles are given in Table 4.

Analysis of the crystallographic data reveals η^5 -coordination of the C_5Me_5 ligand with a plane of symmetry passing through the ring centroid (RC) and atoms C(23), P(1) and P(2) (Fig. 3). The rms deviation from this plane is ≈ 0.005 Å with the tantalum atom lying approximately 0.015 Å out of this plane. The two metal hydride ligands and the metallacycle hydrogen were not detected in the structure determination, but the presence of a single hydrogen on C(23) and two equivalent

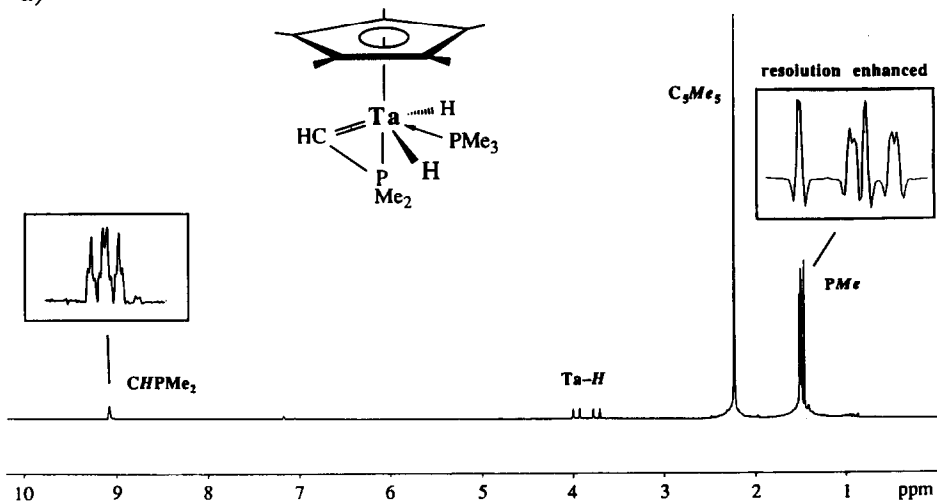
Table 1
NMR data for 3 and 4 ^a

Compound	Assignment	Chemical shifts (ppm), multiplicity, coupling constants (Hz)		
		¹ H	¹³ C	³¹ P
3	CHPMe ₂	9.19 (ddt, ² J(P ² H) 3.3, ³ J(P ¹ H) 2.2, ³ J(HH) 0.7)	192.1 (dd, ¹ J(P ² C) 53.2, ² J(P ¹ C) 9.6, ¹ J(CH) 171.0)	
	Ta-H	3.87 (dd, ² J(P ² H) 17.9, ² J(P ¹ H) 54.9)	12.6 (q, ¹ J(CH) 126.5)	
	C ₅ (CH ₃) ₅	2.18 (s)	108.8 (s)	
	P ² (CH ₃) ₂	1.44 (d, ² J(P ² H) 10.2)	20.93 (dd, ¹ J(P ² C) 22.8, ³ J(P ¹ C) 2.4)	-112.4 (d, ² J(PP) 57.2)
	P ¹ (CH ₃) ₃	1.41 (dd, ² J(P ¹ H) 6.4, ⁴ J(P ² H) 0.7)	24.24 (dd, ¹ J(P ¹ C) 21.0, ³ J(P ² C) 9.6)	-24.9 (d, ² J(PP) 57.2)
		1.86 (s)	11.9 (q, ¹ J(CH) 126.5)	
4	C ₅ Me ₂ Me(CH ₂) ₂	1.97 (s)	13.1 (q, ¹ J(CH) 126.5)	
	C ₅ Me ₂ Me(CH ₂) ₂	2.64 (dd, ² J(PH) 25.7 ^b , ² J(PH) 55.9 ^c)		
	Ta-H	1.32 (d, ² J(PH) 7.0 ^b)		
	P(CH ₃) ₃	1.14 (d, ² J(PH) 6.7 ^c)		
	C ₃ Me ₂ Me(CH ₂) ₂		21.5 (qd, ¹ J(CH) 130.2, ¹ J(PC) 22.8)	-14.6 ^d (d, ² J(PP) 28.3)
	C ₃ Me ₂ Me(CH ₂) ₂		24.0 (qd, ¹ J(CH) 129.6, ¹ J(PC) 22.1)	-27.8 ^d (d, ² J(PP) 28.3)
	H _a	1.30 (dd, ³ J(PH) 4.9 ^b , ² J(H _a H _b) 2.7)	123.8, 113.5, 105.2 (s)	
	H _b	2.66 (m, ³ J(PH) 3.0 ^b , ³ J(PH) 2.0 ^c , ² J(H _a H _b) 2.7)	45.0 (tdd, ¹ J(CH) 151.1, ² J(PC) 8.8, 4.4)	



^a Benzene-d₆, 298 K. ^b Coupling to the phosphorus atom which resonates at -27.8 ppm. ^c Coupling to the phosphorus atom which resonates at -14.6 ppm. ^d Assignment of these ³¹P resonances to the PMe₃ proton signals are arbitrary.

a)



b)

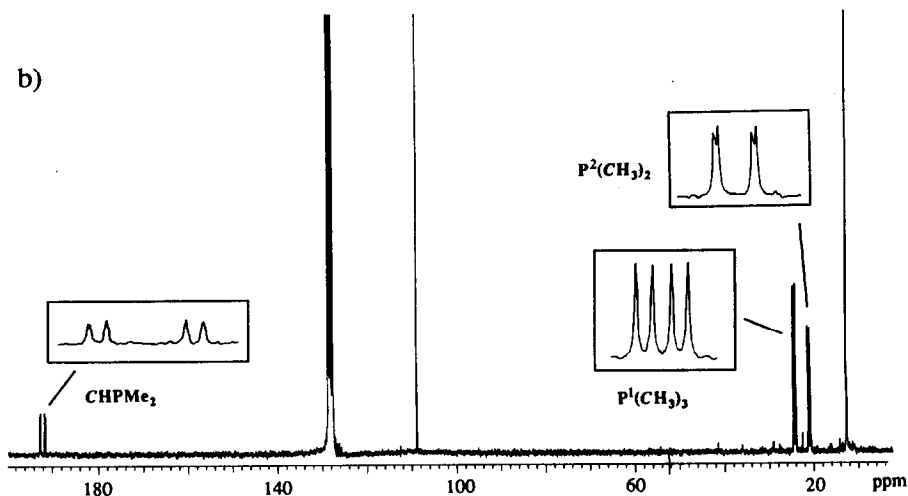


Fig. 1. (a) ^1H NMR spectrum (250 MHz, C_6D_6) and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (62.9 MHz, C_6D_6) of 3.

metal-hydride ligands is clearly indicated by NMR spectroscopy (see Table 1 and Fig. 1). On the basis of these observations, the established geometry of the other ligands around the metal center, and consideration of the remaining available space, the two hydride ligands are most reasonably positioned either side of the pseudo mirror plane as shown in equation 2. A consideration of the $\eta^5\text{-C}_5\text{Me}_5$ ring shows it to be unexceptional, with average values for inter-ring carbon-carbon, ring carbon-ring methyl and ring carbon-tantalum distances within the ranges found for other Cp^*Ta complexes [21,22a,24b,33].

The Ta-P(1) bond length of 2.59 Å is within the range of $\text{Ta}^{\text{V}}\text{-PMe}_3$ distances observed previously (ca. 2.51–2.60 Å) [22], and the PMe_3 methyls are staggered with respect to the ($\eta^5\text{-C}_5\text{Me}_5$) methyl groups, to relieve close contacts.

Table 2

Crystal data for Cp*Ta(PMe₃)₂(η²-CHPMe₂) (3)

Molecular formula	C ₁₆ H ₃₃ P ₂ Ta
<i>M</i>	468.3
Crystal system	orthorhombic
Crystal size (mm)	0.50 × 0.50 × 0.50
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.131(1)
<i>b</i> (Å)	13.399(1)
<i>c</i> (Å)	16.518(2)
<i>V</i> (Å ³)	2020.9
<i>Z</i>	4
<i>D</i> _c (g cm ⁻³)	1.539
<i>F</i> (000)	928
<i>μ</i> (mm ⁻¹)	5.52
2θ range (°)	3–50
Max. indices <i>h</i> , <i>k</i> , <i>l</i>	10, 15, 19
No. reflections measured	3901
No. of unique reflections	3549
No. of observed reflections	3177
<i>R</i> _{int}	0.115
transmission factors	0.018–0.042
Weighting parameters	34, 84, 149, –90, 65, –188
Extinction parameter <i>x</i>	3.4(1) × 10 ⁻⁷
Parameters refined	173
Max. Shift (esd)	0.006
Max. final electron density difference (e Å ⁻³)	1.66
Final <i>R</i>	0.033
Final <i>R</i> _w	0.030
Goodness of fit	1.06

Table 3

Atomic coordinates (×10⁴) for 3

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ta	5572(1)	5283(1)	6698(1)
P(1)	6867(2)	4607(2)	5414(1)
C(11)	5798(19)	3813(14)	4710(8)
C(12)	8439(20)	3771(14)	5592(11)
C(13)	7619(20)	5516(14)	4732(9)
P(2)	8134(2)	5582(2)	7141(2)
C(21)	9398(12)	4652(12)	7611(7)
C(22)	9313(13)	6650(10)	6890(14)
C(23)	6565(8)	5838(9)	7683(6)
C(30)	3128(7)	4531(5)	6566(6)
C(31)	3386(6)	4717(8)	7375(4)
C(32)	3432(7)	5778(7)	7491(5)
C(33)	3326(6)	6241(6)	6706(7)
C(34)	3105(8)	5473(7)	6143(6)
C(35)	2847(11)	3513(10)	6196(10)
C(36)	3436(10)	3963(9)	8053(6)
C(37)	3453(9)	6310(8)	8284(7)
C(38)	3247(9)	7332(7)	6566(9)
C(39)	2796(12)	5619(12)	5243(8)

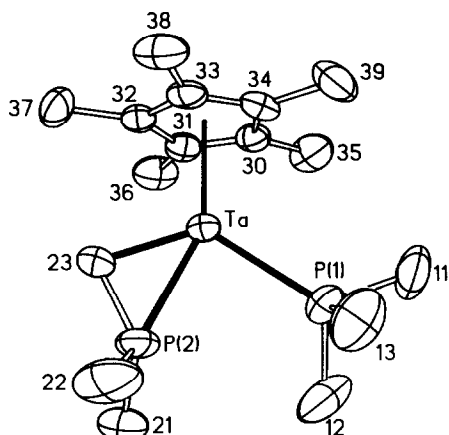


Fig. 2. Molecular structure of **3** with thermal ellipsoids at 40% probability level (hydrogen atoms not included).

To date, the $M(\text{CHPMe}_2)$ metallaheterocycle has been observed exclusively in tantalum complexes, two of which have been subjected to X-ray analysis; their metallacycle parameters along with those of **3** are collected in Table 5.

The tantalum–carbon distances are considerably shorter than those found for tantalum alkyls and for the Ta–C single bond of the $\text{Ta}(\eta^2\text{-CH}_2\text{PMe}_2)$ metallacycle [6]. Indeed, they are more comparable to the Ta=C bonds of 18 electron alkylidene complexes [23], and therefore, on the basis of the structural data, it would not seem unreasonable to formulate $\text{Ta}(\text{CHPMe}_2)$ with a tantalum–carbon double bond. However, a further notable feature of the metallacycle is a significantly shortened P–C bond length of 1.72 Å, ca. 0.1 Å shorter than P–C distances in normal PMe_3 ligands (typically 1.82–1.86 Å) [21,22c]. This suggests that there may also be a significant contribution from a bonding form with P–C double bond character. Significantly, Ta–C(alkyne) distances for complexes with substantial π (perpendicu-

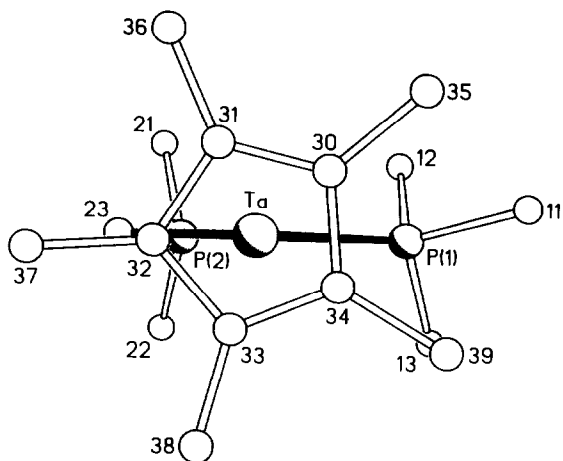


Fig. 3. View of **3** along the ring centroid–tantalum vector.

Table 4
Bond lengths (Å) and angles (deg) for **3**

Ta–P(1)	2.592(2)	Ta–P(2)	2.483(2)
Ta–C(23)	2.005(10)	Ta–C(30)	2.459(7)
Ta–C(31)	2.411(7)	Ta–C(32)	2.443(7)
Ta–C(33)	2.419(6)	Ta–C(34)	2.445(7)
P(1)–C(11)	1.854(17)	P(1)–C(12)	1.845(19)
P(1)–C(13)	1.796(17)	P(2)–C(21)	1.868(14)
P(2)–C(22)	1.838(14)	P(2)–C(23)	1.723(8)
C(30)–C(31)	1.380(12)	C(30)–C(34)	1.442(12)
C(30)–C(35)	1.516(15)	C(31)–C(32)	1.435(15)
C(31)–C(36)	1.509(15)	C(32)–C(33)	1.441(14)
C(32)–C(37)	1.492(15)	C(33)–C(34)	1.401(13)
C(33)–C(38)	1.482(12)	C(34)–C(39)	1.527(16)
P(1)–Ta–P(2)	82.4(1)	P(1)–Ta–C(23)	126.0(2)
P(2)–Ta–C(23)	43.6(2)	P(1)–Ta–C(30)	101.4(2)
P(2)–Ta–C(30)	161.3(2)	C(23)–Ta–C(30)	129.4(3)
P(1)–Ta–C(31)	130.3(2)	P(2)–Ta–C(31)	134.0(2)
C(23)–Ta–C(31)	96.6(3)	C(30)–Ta–C(31)	32.9(3)
P(1)–Ta–C(32)	153.9(2)	P(2)–Ta–C(32)	123.5(2)
C(23)–Ta–C(32)	80.0(3)	C(30)–Ta–C(32)	55.5(3)
C(31)–Ta–C(32)	34.4(3)	P(1)–Ta–C(33)	125.2(3)
P(2)–Ta–C(33)	135.4(2)	C(23)–Ta–C(33)	100.5(4)
C(30)–Ta–C(33)	56.5(2)	C(31)–Ta–C(33)	57.5(3)
C(32)–Ta–C(33)	34.5(3)	P(1)–Ta–C(34)	98.6(2)
P(2)–Ta–C(34)	164.0(2)	C(23)–Ta–C(34)	133.0(3)
C(30)–Ta–C(34)	34.2(3)	C(31)–Ta–C(34)	56.2(3)
C(32)–Ta–C(34)	55.7(3)	C(33)–Ta–C(34)	33.5(3)
Ta–P(1)–C(11)	118.3(5)	Ta–P(1)–C(12)	115.9(6)
C(11)–P(1)–C(12)	99.2(8)	Ta–P(1)–C(13)	116.8(6)
C(11)–P(1)–C(13)	101.4(7)	C(12)–P(1)–C(13)	102.4(8)
Ta–P(2)–C(21)	126.6(4)	Ta–P(2)–C(22)	127.7(5)
C(21)–P(2)–C(22)	104.6(6)	Ta–P(2)–C(23)	53.3(2)
C(21)–P(2)–C(23)	115.5(5)	C(22)–P(2)–C(23)	116.7(6)
Ta–C(23)–P(2)	83.1(4)	Ta–C(30)–C(31)	71.6(4)
Ta–C(30)–C(34)	72.4(4)	C(31)–C(30)–C(34)	108.2(8)
Ta–C(30)–C(35)	123.9(5)	C(31)–C(30)–C(35)	125.6(9)
C(34)–C(30)–C(35)	126.1(9)	Ta–C(31)–C(30)	75.5(4)
Ta–C(31)–C(32)	74.1(4)	C(30)–C(31)–C(32)	108.3(8)
Ta–C(31)–C(36)	122.0(5)	C(30)–C(31)–C(36)	127.1(10)
C(32)–C(31)–C(36)	124.3(8)	Ta–C(32)–C(31)	71.6(4)
Ta–C(32)–C(33)	71.9(4)	C(31)–C(32)–C(33)	107.7(4)
Ta–C(32)–C(37)	126.2(5)	C(31)–C(32)–C(37)	126.2(8)
C(33)–C(32)–C(37)	125.9(9)	Ta–C(33)–C(32)	73.7(4)
Ta–C(33)–C(34)	74.3(4)	C(32)–C(33)–C(34)	106.9(7)
Ta–C(33)–C(38)	124.3(5)	C(32)–C(33)–C(38)	124.7(10)
C(34)–C(33)–C(38)	127.9(10)	Ta–C(34)–C(30)	73.4(4)
Ta–C(34)–C(33)	72.2(4)	C(30)–C(34)–C(33)	108.7(8)
Ta–C(34)–C(39)	123.3(6)	C(30)–C(34)–C(39)	125.9(10)
C(33)–C(34)–C(39)	125.3(10)		

lar) donation, i.e. 4 electron donor ligands, lie in the range 2.06–2.08 Å [24]. These features will be discussed in more detail later. Consideration of the tantalum–phosphorus distances in the [Ta(CHPME₂)] moiety (Table 5) shows them to be, in all

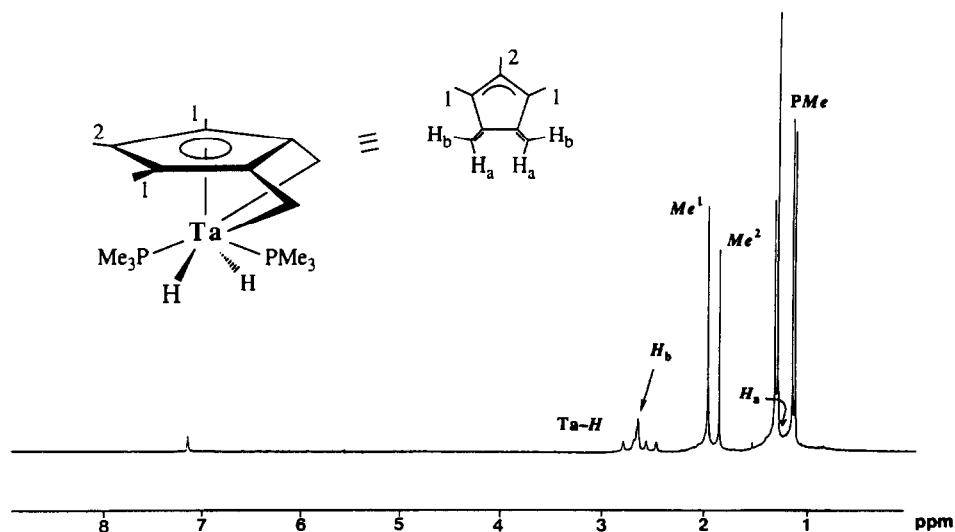


Fig. 4. ^1H NMR spectrum (250 MHz, C_6D_6) of **4**.

cases, shorter by ca. 0.1 Å than the Ta–PMe₃ distances in the same complex possibly reflecting a change in phosphorus hybridization to give an increase in % s-character in the Ta–P bond. Support for this is provided by consideration of the angles Ta–P(2)–C(21) (126.6(4)°) and Ta–P(2)–C(22) (127.7(5)°) which are considerably larger than those for the Ta–PMe₃ ligand (average 117.2°).

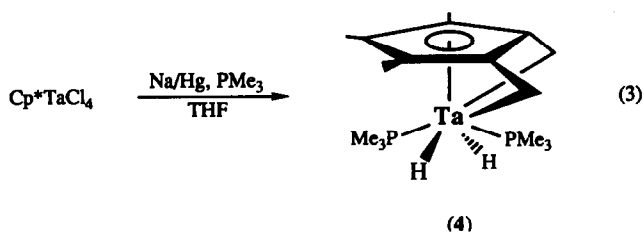
4. The reaction of Cp^*TaCl_4 with sodium amalgam and PMe_3 in THF solvent: synthesis and spectroscopic characterization of $(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_3)_2$ (4**)**

The reduction of Cp^*TaCl_4 with a more conventional sodium amalgam/tetrahydrofuran reducing medium in the presence of excess trimethylphosphine gives a colorless crystalline product of identical stoichiometry to **3**. The IR spectrum clearly shows the presence of metal-bound hydride ligands ($\nu(\text{Ta-H})$ 1635 cm^{-1}) but NMR and an X-ray structure analysis (*vide infra*) showed that activation of two C–H bonds on adjacent ring methyls had occurred to give $(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_3)_2$ (**4**) (eq. 3). A small amount (< 20%) of **3** is also formed in this reaction (by ^1H NMR) but may be readily separated from **4** by selective crystalliza-

Table 5

Compound	[Ta(CHPMe ₂)] metallacycle bond parameters						Ref.
	Ta–C	Ta–P	C–P	C–Ta–P	Ta–C–P	C–P–Ta	
3	2.005(10)	2.483(2)	1.723(8)	43.6(2)	83.1(4)	53.3(3)	this work
Ta(PMe ₃) ₃ (CH ₂ PMe ₂)- (CHPMe ₂)	2.015(4)	2.516(1)	1.716(5)	42.75(13)	84.39(19)	52.86(14)	6
Ta($\eta\text{-C}_4\text{H}_6$)(CHPMe ₂)- (PMe ₃) ₂ Cl	2.026(3)	2.495(1)	1.704(4)	42.72(10)	85.51(14)	53.77(12)	12

tion at low temperature. NMR data for **4** are collected in Table 1 and the proton spectrum is reproduced in Fig. 4.



The singlets at δ 1.97 and 1.86 ppm are attributable to the remaining ring methyls and the doublets at δ 1.32 and 1.14 ppm are due to the inequivalent phosphine ligands. The two equivalent hydride ligands occur as a doublet of doublet resonance at δ 2.64 ppm, coincident with one of the diastereotopic hydrogens of the methylene groups, at δ 2.66 ppm; at 250 MHz, the second methylene hydrogen is hidden beneath the high frequency P–Me resonance. These signals may be resolved at 360 MHz thus allowing an assignment of the methylene hydrogens by difference nOe experiments. Specifically, irradiation of the signal at δ 1.97 ppm (Me^1) led to a significant enhancement (3.4%) of the signal at δ 2.66 ppm and had no detectable effect on the signal at δ 1.30 ppm. The 2.66 ppm resonance is therefore assigned to the *exo*-methylene hydrogens H_b . The phosphorus nuclei of the inequivalent PMe_3 ligands resonate at δ -14.6 and δ -27.8 , shifts that are quite normal for coordinated PMe_3 ligands. In the ^{13}C NMR spectrum, the equivalent methylene carbons are located at δ 45.0 ppm.

5. The molecular structure of $(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_3)_2$ (**4**)

Colorless crystals of **4** were grown from a saturated light petroleum ether solution cooled to -35°C . The crystal data are summarized in Table 6 and atomic parameters are listed in Table 7. The molecular structure is illustrated in Figs. 5 and 6, and selected bond distances and angles are given in Table 8.

The molecule possesses a crystallographic mirror plane (Fig. 6) containing the tantalum atom, P(1), P(2) and C(31) and bisecting the C_5 ring through the C(33)–C(33') bond. The hydride ligands, which were located in the structure determination, are symmetrically displaced on either side of the mirror plane at a distance of 1.735(42) Å from the tantalum center. This is expectedly shorter than the Ta–H bond lengths found in the Ta^{III} complex $\text{TaCl}_2\text{H}_2(\text{PMe}_3)_4$ (1.94(11) Å [25]), but is comparable with the Ta–H distance established by neutron diffraction in the Ta^{V} species Cp_2TaH_3 [26]. The rather large esd value for the Ta–H distance in **4** precludes a more detailed comparison.

The tantalum–phosphorus distances, at 2.567(1) Å [P(1)] and 2.568(1) Å [P(2)], are within the range expected for Ta– PMe_3 complexes [21] and the two phosphine ligands subtend an angle of $100.1(1)^\circ$ to the metal center. The most intriguing feature of the molecular structure is the coordination of the C_7 fragment. Figure 5 shows that the tantalum atom is displaced from C(31) towards the C(33)–C(33') edge (0.44 Å from the ring centroid as determined by a normal from the ring plane through the metal atom). This distortion results in an elongated Ta–C(31) bond length of 2.569(5) Å (c.f. an average ring carbon–tantalum distance in **4** of 2.429(8) Å) and a significantly shortened Ta–C(33) distance of 2.172(3) Å. The ring slippage

Table 6

Crystal data for $(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_3)_2$ (**4**)

Molecular formula	$\text{C}_{16}\text{H}_{33}\text{P}_2\text{Ta}$
<i>M</i>	468.3
Crystal system	orthorhombic
Crystal size (mm)	$0.25 \times 0.30 \times 0.30$
space group	<i>Pnma</i>
<i>a</i> (Å)	11.2309(6)
<i>b</i> (Å)	11.9809(5)
<i>c</i> (Å)	14.4881(7)
<i>V</i> (Å ³)	1949.5
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.595
<i>F</i> (000)	928
μ (mm ⁻¹)	5.73
2 θ range (°)	3–60
Max. indices <i>h</i> , <i>k</i> , <i>l</i>	15, 16, 20
No. reflections measured	8915
No. of unique reflections	2972
No. of observed reflections	2635
<i>R</i> _{int}	0.019
transmission factors	0.11–0.16
Weighting parameters	9, 29, 8, –23, 19, –65
Extinction	negligible
Parameters refined	116
Max. shift (esd)	0.016
Max. final electron density	
difference (e Å ⁻³)	1.33
Final <i>R</i>	0.025
Final <i>R</i> '	0.019
Goodness of fit	0.97

Table 7

Atomic coordinates ($\times 10^4$) for **4**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ta	1661(1)	2500	594(1)
H	1471(36)	3804(34)	93(30)
P(1)	2399(1)	2500	–1083(1)
C(11)	1331(7)	2500	–2022(5)
C(12)	3317(5)	3690(4)	–1433(3)
P(2)	–600(1)	2500	324(1)
C(21)	–1261(6)	2500	–824(5)
C(22)	–1402(3)	3679(3)	833(4)
C(31)	3881(4)	2500	1020(4)
C(32)	3285(3)	3460(3)	1334(2)
C(33)	2307(3)	3109(3)	1913(2)
C(34)	5065(5)	2500	537(6)
C(35)	3681(5)	4647(4)	1195(4)
C(36)	1179(4)	3660(4)	1886(3)
H(36a)	596(51)	3314(45)	2319(41)
H(36b)	1174(52)	4438(54)	1760(41)

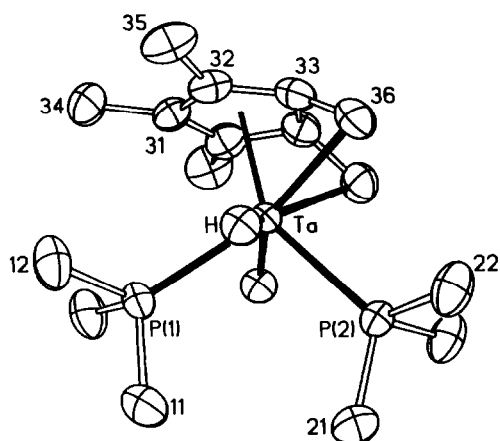


Fig. 5. Molecular structure of **4** with thermal ellipsoids at 40% probability level (hydrogen atoms not included).

is caused by interaction of the tantalum atom with the two adjacent ring-methylene carbon atoms C(36) and C(36'). The Ta–C(36) distance is more than 1 Å shorter than the metal–methyl distance found in $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}$ compounds [21,22a,24b,33], partially due to the 0.44 Å ring displacement. They are also bent below the plane of the ring as seen in the structures of related fulvene complexes [10,27]. The inter ring–carbon distance C(31)–C(32), at 1.407(5) Å, is relatively short, while C(33)–C(33') is elongated at 1.460(8) Å; the C(ring)–C(methylene) bond lengths are 1.429(6) Å; the implications of these distances for the bonding of the $\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2$ ligand are discussed in the following section.

6. Discussion

The formation of $\text{Cp}_2\text{Ta}(\text{H})(\text{PMe}_3)_2$ upon sodium sand reduction of CpTaCl_4 clearly arises by a Cp-ring transfer. Such a process is not common but has been

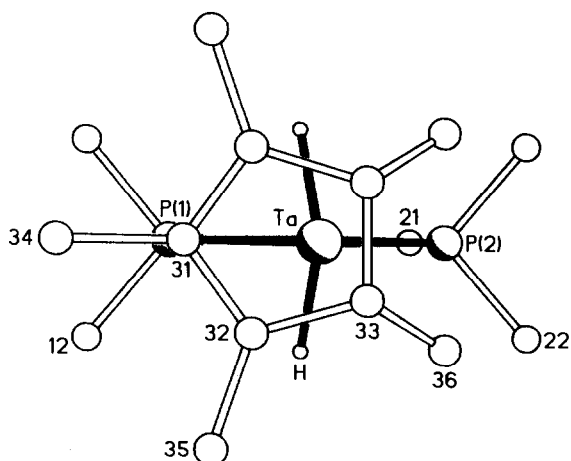


Fig. 6. View of **4** along the normal to the C_5 ring plane through the metal atom.

Table 8

Bond lengths (Å) and angles (deg) for **4**

Ta–H	1.735(42)	Ta–P(1)	2.567(1)
Ta–P(2)	2.568(1)	Ta–C(31)	2.569(5)
Ta–C(32)	2.409(4)	Ta–C(33)	2.172(3)
Ta–C(36)	2.394(4)	P(1)–C(11)	1.814(8)
P(1)–C(12)	1.831(5)	P(2)–C(21)	1.822(8)
P(2)–C(22)	1.830(4)	C(31)–C(32)	1.407(5)
C(31)–C(34)	1.502(8)	C(32)–C(33)	1.445(5)
C(32)–C(35)	1.503(6)	C(33)–C(36)	1.429(6)
C(33)–C(33')	1.460(8)	C(36)–H(36a)	0.997(58)
C(36)–H(36b)	0.949(65)		
H–Ta–P(1)	69.2(14)	H–Ta–P(2)	79.4(13)
P(1)–Ta–P(2)	100.1(1)	H–Ta–C(31)	102.7(13)
P(1)–Ta–C(31)	85.1(1)	P(2)–Ta–C(31)	174.8(1)
H–Ta–C(32)	81.3(14)	P(1)–Ta–C(32)	100.2(1)
P(2)–Ta–C(32)	144.7(1)	C(31)–Ta–C(32)	32.6(1)
H–Ta–C(33)	96.1(14)	P(1)–Ta–C(33)	136.5(1)
P(2)–Ta–C(33)	117.7(1)	C(31)–Ta–C(33)	57.6(2)
C(32)–Ta–C(33)	36.3(1)	H–Ta–C(36)	77.1(14)
P(1)–Ta–C(36)	144.4(1)	P(2)–Ta–C(36)	84.0(1)
C(31)–Ta–C(36)	91.8(1)	C(32)–Ta–C(36)	63.0(1)
C(33)–Ta–C(36)	36.1(1)	H–Ta–H'	128.4(28)
C(32)–Ta–H'	135.2(13)	C(33)–Ta–H'	135.4(14)
C(36)–Ta–H'	145.3(14)	C(32)–Ta–C(32')	57.1(2)
C(33)–Ta–C(32')	61.0(1)	C(36)–Ta–C(32')	95.7(1)
C(33)–Ta–C(33')	39.3(2)	C(36)–Ta–C(33')	65.3(1)
C(36)–Ta–C(36')	71.0(2)	Ta–P(1)–C(11)	119.8(3)
Ta–P(1)–C(12)	116.4(2)	C(11)–P(1)–C(12)	99.5(2)
C(12)–P(1)–C(12')	102.3(3)	Ta–P(2)–C(21)	122.8(2)
Ta–P(2)–C(22)	115.2(1)	C(21)–P(2)–C(22)	99.6(2)
C(22)–P(2)–C(22')	101.0(3)	Ta–C(31)–C(32)	67.4(2)
Ta–C(31)–C(34)	138.3(4)	C(32)–C(31)–C(34)	124.9(2)
C(32)–C(31)–C(32')	109.8(4)	Ta–C(32)–C(31)	80.0(2)
Ta–C(32)–C(33)	62.9(2)	C(31)–C(32)–C(33)	108.1(3)
Ta–C(32)–C(35)	128.0(3)	C(31)–C(32)–C(35)	126.2(4)
C(33)–C(32)–C(35)	125.3(4)	Ta–C(33)–C(32)	80.8(2)
Ta–C(33)–C(36)	80.5(2)	C(32)–C(33)–C(36)	121.6(4)
Ta–C(33)–C(33')	70.4(1)	C(32)–C(33)–C(33')	106.9(2)
C(36)–C(33)–C(33')	117.5(3)	Ta–C(36)–C(33)	63.5(2)
Ta–C(36)–H(36a)	113.5(32)	C(33)–C(36)–H(36a)	111.9(32)
Ta–C(36)–H(36b)	114.9(35)	C(33)–C(36)–H(36b)	117.7(35)
H(36a)–C(36)–H(36b)	121.6(47)		

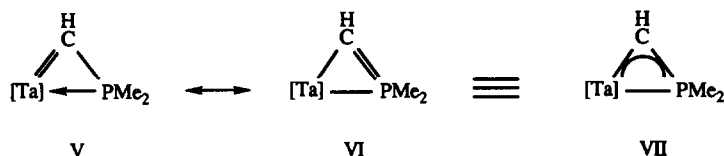
The prime denotes an atom related by the crystallographic mirror plane.

observed on at least one other occasion for tantalum [28]. **1** presumably arises by a competitive displacement of Cp in favour of a chloride ligand from a chloro-phosphine intermediate; the resulting NaCp presumably then reacts with an earlier intermediate to generate the bis(cyclopentadienyl) fragment. Independent evidence for the feasibility of this process is provided by the formation of Cp⁺CpTaCl₂ upon treatment of Cp⁺TaCl₃(PMe₃) with NaCp [29].

If this is somewhat unexpected, the exceptional selectivity observed in the formation of **3** and **4** is perhaps more surprising. Not only are C–H activations

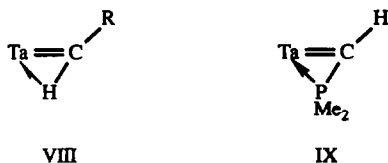
between ring and phosphine methyls differentiated, but multiple C–H bond scissions result with unprecedented site selectivity for multi-step reductions of this type. The hydrogens are abstracted exclusively either from the same methyl of the phosphine, or from adjacent methyls on the Cp* ring. This site selectivity must arise due to the close proximity of the methylene hydrogens and the adjacent ring methyls to the metal center in the putative 16 electron intermediates $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)]$ and $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ta}(\text{H})(\text{PMe}_3)_2]$.

We noted earlier that the bond lengths in the $[\text{Ta}(\text{CHPMe}_2)]$ metallacycle clearly indicate multiple bond character not only between tantalum and carbon, but also between carbon and phosphorus, thus leading to the conclusion that both forms V and VI contribute to the delocalized bonding picture shown in VII (below).



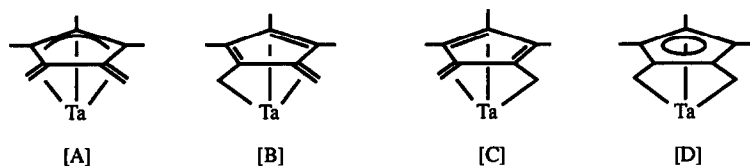
The CHPMe_2 ligand in V may be regarded as a phosphino-carbene contributing 4 electrons to the metal ligand bonding whilst VI is a λ^5 -phospha-acetylene, again donating 4 electrons, and is closely related to the metallacyclopropene bonding form of an acetylene ligand. The spectroscopic data also show consistencies with both representations. For example, the high frequency ^{13}C shift of the $[\text{Ta}(\text{CHPMe}_2)]$ carbon (δ 192.1 ppm) is close to the region typical of early transition metal alkylidenes (δ 220–280 ppm for tantalum alkylidenes [30]) and also close to shifts observed for the carbons of 4 electron acetylene ligands, e.g. $\text{Ta}(\text{CO})_2(\text{PhC}\equiv\text{CH})(\text{I})(\text{PMe}_3)_2$ [24a] (δ 197.3 ppm) and $\text{Ta}(\text{CO})_2(\text{HC}\equiv\text{CH})(\text{I})(\text{PMe}_3)_2$ [24a] (δ 198.3 ppm); the ^{13}C shift for the methine carbon in the directly related complex $\text{Cp}^*\text{TaCl}_2(\eta^2\text{-HC}\equiv\text{CPh})$ occurs at δ 215.0 ppm [24b]. Also, the shift of the metallacycle methine hydrogen (δ 9.19 ppm) is consistent with both the high frequency shifts of 18 electron d^0 tantalum alkylidenes (e.g. δ 10.22 ppm in $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$ [23a] and δ 10.86 ppm in $\text{Cp}_2\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})$ [23b]) and acetylenic hydrogens (e.g. $\text{Cp}^*\text{TaCl}_2(\eta^2\text{-HC}\equiv\text{CPh})$ (δ 11.89 ppm) [31], $\text{Ta}(\text{CO})_2(\text{PhC}\equiv\text{CH})(\text{I})(\text{PMe}_3)_2$ (δ 11.9 ppm) [24a] and $\text{Ta}(\text{CO})_2(\text{HC}\equiv\text{CH})(\text{I})(\text{PMe}_3)_2$ (δ 11.9 ppm) [24a]). The $J(\text{C}_\alpha\text{H})$ coupling constant of 171 Hz is more in agreement with 4 electron acetylene ligands (c.f. 183 Hz for $\text{Cp}^*\text{TaCl}_2(\eta^2\text{-HC}\equiv\text{CPh})$ and 189 Hz for $\text{Cp}^*\text{TaCl}_2(\eta^2\text{-HC}\equiv\text{CH})$ [24b]) than alkylidene ligands (c.f. 132 Hz for $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$ [23a] and 127 Hz for $\text{Cp}_2\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})$ [23b]) and is also comparable with the reported $^1J(\text{CH})$ value for the triply-bridging methylidyne ligand in $\text{H}_3\text{Os}_3(\text{CO})_9(\text{CH})$ [32] (171 Hz).

An additional important phenomenon has been recognised to operate in electronically unsaturated alkylidene complexes which may have structural and spectroscopic implications for 3. Within the $\text{M}=\text{CHR}$ moiety, a rehybridization of the C_α atom may occur resulting in an increased $\text{Ta}-\text{C}_\alpha-\text{C}_\beta$ angle and a reduced $\text{Ta}-\text{C}_\alpha-\text{H}_\beta$ angle (VIII below).



Similar observations have also been reported for electronically saturated tantalocene complexes; the reason here presumably due to unfavourable steric interactions between a Cp ring and the C_α -alkyl substituent [23]. It appears, however, that in electronically unsaturated complexes the reasons for the distortion are primarily electronic [33] and reminiscent of the $CH \cdots M$ agostic interactions [34] in electronically unsaturated alkyls. As the $Ta-C_\alpha-C_\beta$ angle increases, so the alkylidene ligand more resembles a hydrogen-bridged alkylidyne and consequently the $Ta-C_\alpha$ distances are intermediate between those of saturated alkylidene and alkylidyne compounds. There are striking similarities between these distorted, or *agostic*, alkylidenes and the metallacycle in **3** (see IX above); thus, the relatively short $Ta=C$ distance in **3**, even when compared with those of saturated alkylidene complexes may be partly due to a rehybridization of C_α upon coordination of the PMe_2 moiety to the metal center thus increasing the $Ta-C_\alpha-H_\alpha$ angle and leading to a certain degree of $Ta-C$ triple bond character in the $Ta(\eta^2-CHPMe_2)$ metallacycle (H_α was not located in the X-ray analysis but the $Ta-C_\alpha-H_\alpha$ angle is not anticipated to be too dissimilar to the corresponding angle of $145(3)^\circ$ found in $Ta(PMe_3)_3(\eta^2-CH_2PMe_2)(\eta^2-CHPMe_2)$ [6]).

The ring system in **4** is most conveniently represented as a normal cyclopentadienyl ring with two additional sp^3 -type methylene bridges to the metal (D, below). However, NMR and X-ray data suggest that the fused η^4 -butadiene/ η^3 -allyl bonding form (A) is a more appropriate representation [35*].



In particular, the 1H NMR spectrum shows a *geminal* $^1H-^1H$ coupling constant of 2.7 Hz between the diastereotopic ring methylene hydrogens, within the range expected for *geminal* hydrogen atoms attached to sp^2 -hybridized carbon (typically 0–3 Hz [36]) rather than sp^3 -hybridized carbon (12–15 Hz [36]). *Geminal* $^1H-^1H$ coupling constants of 1.8 and 4.4 Hz have been reported for $Cp^*(C_5Me_3(CH_2)_2)W$ [8] and $Cp^*(C_5Me_3(CH_2)_2)Ti$ [9] respectively, whereas a value of 6.59 Hz was found for $Cp^*(C_5Me_4CH_2)ZrPh$ [10], which was proposed to contain a predominantly sp^2 -hybridized C_α atom. The methylene carbons resonate at δ 45.0 ppm in the ^{13}C spectrum with a C–H coupling constant of 151.1 Hz which is also consistent with sp^2 -hybridized carbon (typically 150–160 Hz [37]). Quite similar $^1J(CH)$ values have been reported for $Cp^*(C_5Me_4CH_2)WH$ (151.3 Hz) [8], $Cp^*(C_5Me_4CH_2)TiMe$ (150 Hz) [9], $Cp^*(C_5Me_3(CH_2)_2)W$ (152 Hz) [8] and $Cp^*(C_5Me_3(CH_2)_2)Ti$ (160 Hz) [13] while the more sp^3 -hybridized C_α atom of $Cp^*(C_5Me_4CH_2)ZrPh$ [10] gives a $^1J(CH)$ coupling of 144.8 Hz. It should be noted that the available spectroscopic data cannot, however, rule out contributions from the equivalent η^7 -heptatrienyl anions in B and C.

The bond distances $C(31)-C(32)$ (1.407(5) Å), $C(33)-C(33')$ (1.460(8) Å) and $C(\text{ring})-C(\text{methylene})$ (1.429(6) Å) in the $\{Ta(C_5Me_3(CH_2)_2)_2\}$ moiety [16b] are also in accord with the fused η^4 -butadiene/ η^3 -allyl bonding mode.

* Reference number with asterisk indicates a note in the list of references.

The configurational stability of 3 and 4

Since **3** and **4** differ only in the site of activation of their ligand C–H bonds, it seemed possible that they could interconvert via a common intermediate such as the 14 electron fragment $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2]$ arising by regeneration of the classical C_5Me_5 and PMe_3 ligands. It has already been shown that products containing this fragment can be obtained by treatment of **3** or **4** with, for example, carbon monoxide [16b,19], thus demonstrating the viability of the reverse metal-to-carbon hydrogen migrations, at least on the timescale of a chemical reaction. However, double resonance experiments on **3** give no indication of magnetization transfer between the metal hydride and metallacycle methine site to 360 K, suggesting that any migration processes must occur at a rate slower than $1/T_1$ (where T_1 is the longitudinal relaxation time of the methine hydrogen). Similar observations have been reported for $\text{Ta}(\text{H})_2(\eta^2\text{-CHPMe}_2)(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)_2$ [12]. Above 360 K, both **3** and **4** decompose to give several unidentifiable species along with enhancement of the signal due to protio benzene; this suggests that activation of C_6D_6 is accompanying their decomposition. Amongst the products observed upon warming **4** is a small amount of **3** suggesting that the latter may be thermodynamically more stable, but the reaction is far from clean; conversely, **4** is not observed upon decomposition of **3**. There is also no evidence for formation of a mixed ligand-metallated species such as $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ta}(\text{H})_2(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)]$, another plausible intermediate for their interconversion. Thus, it would appear that the 14 electron species $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2]$ is not readily attainable from **3** or **4** although it can be trapped-out in the presence of other 2 electron donor ligands, presumably facilitated by stabilization of intermediate 16 electron species such as $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)]$ and $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ta}(\text{H})(\text{PMe}_3)_2]$.

Preparations of 3 and 4 with other reducing media

The intriguing selectivity found in the formation of **3** and **4** must clearly arise due to the reducing medium (solvent and reducing agent) since all other conditions (temperature, reaction time) are similar in the two reactions. Therefore, we have investigated other reducing media in an attempt to identify any overridingly important factors influencing the selectivities observed. It is likely that the reduction follows the pathway $\text{Cp}^*\text{TaCl}_4(\text{PMe}_3) \rightarrow \text{Cp}^*\text{TaCl}_3(\text{PMe}_3) \rightarrow \text{Cp}^*\text{TaCl}_2(\text{PMe}_3)_2$ since yellow and purple-red solutions of $\text{Cp}^*\text{TaCl}_4(\text{PMe}_3)$ and $\text{Cp}^*\text{TaCl}_3(\text{PMe}_3)$ are clearly discernable during the early stages of reaction, and moreover we have found that $\text{Cp}^*\text{TaCl}_2(\text{PMe}_3)_2$ may be converted to either **3** or **4** with the same degree of selectivity using sodium metal/neat PMe_3 or $\text{Na}/\text{Hg}/\text{THF}$ in the presence of PMe_3 respectively.

Investigations into reductions of $\text{Cp}^*\text{TaCl}_2(\text{PMe}_3)_2$ under differing conditions of solvent and reducing agent [38*] showed that very strong reducing agents such as potassium metal or sodium/potassium alloy lead to pentane insoluble products, possibly due to further reduction of **3** or **4** to anionic organo-tantalum species. Weaker reducing agents such as zinc and aluminum, however, are found not to completely dehalogenate $\text{Cp}^*\text{TaCl}_2(\text{PMe}_3)_2$ in either THF or neat PMe_3 . Sodium sand reductions in neat PMe_3 invariably yield **3** as the sole pentane soluble product whereas reductions in ethereal solvents with either sodium sand, sodium amalgam or sodium naphthalenide produce mixtures of **3** and **4** whose composition is strongly dependent upon the reducing agent [39*]. The degree of intimate mixing of the

reagents may be important since a higher yield of **4** (ca. 95%) is obtained with the homogeneous reductant sodium naphthalenide in THF. However, given the many inter-related factors which could influence the individual reduction steps along the reaction pathway, and the likely heterogeneous nature of the reduction steps using metallic sodium, or sodium amalgam, a clear idea of the mechanism beyond $\text{Cp}^*\text{TaCl}_2(\text{PMe}_3)_2$ is likely to prove difficult to ascertain.

Experimental

All manipulations of air and/or moisture sensitive materials were performed on a conventional vacuum/inert atmosphere (nitrogen or argon) line by standard Schlenk and cannula techniques, or in an nitrogen- or argon-filled dry box.

The following solvents were dried by prolonged reflux over a suitable drying agent and were freshly distilled and deoxygenated prior to use (drying agent in parentheses): toluene (sodium metal), petroleum ether (b.p. 40–60 °C and 100–120 °C, lithium aluminium hydride and sodium respectively), and tetrahydrofuran (sodium benzophenone ketyl). Benzene- d_6 and toluene- d_8 were dried by vacuum distillation from phosphorus(V) oxide and stored over activated 4 Å molecular sieves.

Elemental analyses were performed by the microanalytical services of this department. Infrared spectra were recorded on Perkin–Elmer 577 and 457 grating spectrophotometers using either KBr or CsI windows. Absorptions are abbreviated as: s (strong), m (medium), w (weak), br (broad), sp (sharp), sh (shoulder). Mass spectra were recorded on a VG 7070E Mass Spectrometer. NMR spectra were recorded on the following instrument, at the frequencies listed, unless stated otherwise: Bruker AC 250, ^1H (250.13 MHz), ^{13}C (62.90 MHz), ^{31}P (101.26 MHz). The following abbreviations have been used for signal multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), qnt (quintet), m (multiplet). Chemical shifts are quoted to the following references, unless stated otherwise: ^{31}P (dilute aq. H_3PO_4 , 0 ppm); ^{13}C (C_6D_6 , 128.0 ppm); ^1H (C_6D_6 , 7.15 ppm).

The following chemicals were prepared by published procedures: PMe_3 [6b], NaCp [40], $^n\text{Bu}_3\text{SnCp}$ [41], CpTaCl_4 [28], Cp^*TaCl_4 [29], Cp^*H [42] and $^n\text{Bu}_3\text{SnCp}^*$ [43]. All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of $\text{Cp}^\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$ (**3**)*

Trimethylphosphine (25 mL) was condensed on to a mixture of Cp^*TaCl_4 (3.0 g, 6.6 mmol) and sodium sand (1.0 g, 43.5 mmol) in a 150 mL thick-walled 'rotoflo' glass ampoule, cooled to -78°C . The mixture was warmed to room temperature with stirring and one atmosphere of argon was introduced. Within 15 min, the PMe_3 solution had adopted a yellow coloration which gradually darkened to deep brown with continued stirring for 4 d. The ampoule was then degassed and excess PMe_3 was condensed into a receiving vessel to leave a brown residue. Extraction with petroleum ether (80 mL, b.p. 40–60 °C) followed by filtration afforded a light orange solution which was concentrated to 20 mL and cooled to -78°C . The resulting colorless crystals were collected and dried *in vacuo*. Yield 1.4 g (46%). Further purification may be achieved by vacuum sublimation at 75–80 °C (5×10^{-3} torr). Anal. Found: C, 40.94; H, 7.15. $\text{C}_{16}\text{H}_{33}\text{P}_2\text{Ta}$ calcd.: C, 41.03; H, 7.12%. IR (Nujol, CsI, cm^{-1}): 3030 m, 1710 s, 1650 s, br, 1485 m, 1420 m, 1300 m, sp, 1280 s,

sp, 1033 m, 962 s, br, 925 s, br, 870 m, 860 m, 845 m, 830 m, 783 w, 730 m, 722 s, 686 s, 670 m, 655 m, 586 w, 375 m, 347 m, 330 w. Mass spectrum m/e (EI, 70 eV): 468 $[M]^+$, 466 $[M - H_2]^+$, 390 $[M - H_2 - PMe_3]^+$.

Preparation of $(\eta^7-C_5Me_5(CH_2)_2)Ta(H)_2(PMe_3)_2$ (**4**)

Trimethylphosphine (0.43 g, 5.7 mmol) and tetrahydrofuran (THF) (25 mL) were condensed into a 150 mL 'rotoflo' glass ampoule containing Cp^*TaCl_4 (0.5 g, 1.09 mmol) and sodium amalgam (20 g, 0.5% w/w, 4.35 mmol) cooled to $-196^\circ C$. The mixture was allowed to warm to room temperature with stirring, once the solvent had liquified, and one atmosphere of argon was admitted. During stirring for a further 24 h, the color of the THF solution changed from yellow to deep brown. The volatile components were then removed under reduced pressure and the residue was extracted with petroleum ether (25 mL, b.p. $40-60^\circ C$) to afford an orange-brown solution. Concentration of this solution to ca. 10 mL followed by cooling to $-78^\circ C$ for 24 h gave colorless crystals which were collected and dried *in vacuo*. Yield 0.33 g (65%). Further purification may be achieved by slow vacuum sublimation at $75-80^\circ C$ (5×10^{-3} torr). Anal. Found: C, 40.99; H, 7.16. $C_{16}H_{33}P_2Ta$ calcd.: C, 41.03; H, 7.12%. IR (Nujol, CsI, cm^{-1}): 3055 m, 1635 s, br, 1430 s, 1413 s, 1342 s, 1303 m, 1297 m, 1287 s, 1278 s, 1270 m, 1092 m, 1077 w, 1024 m, 948 s, br, 930 sh, 872 m, 855 m, 845 m, 837 s, 782 w, 733 s, 720 s, 703 m, 675 m, 668 m, 650 m, br, 610 m, 420 m, 363 m, 345 m, 310 w, 277 w. Mass spectrum m/e (CI^+ , isobutane carrier gas): 468 $[M]^+$ (weak), 466 $[M - 2H]^+$, 407 $[M - PMe_2]^+$, 390 $[M - 2H - PMe_3]^+$.

X-Ray crystallography

Crystal data for compounds **3** and **4** are summarized in Tables 2 and 6 respectively. Measurements were made with a Stoe-Siemens four-circle diffractometer and graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 295 K. Unit cell parameters were refined from 2θ values ($20-25^\circ$) of 32 reflections measured at $\pm\omega$ to minimize systematic errors. Intensities were measured by an on-line profile fitting method [44], and scan parameters for each reflection were automatically selected. An intensity decay of approximately 5% for both data sets was observed by monitoring three standard reflections at regular intervals, and was corrected during data reduction. The data set for compound **3** consisted of one unique quadrant ($h \leq 0, k \geq 0$), together with some equivalent reflections ($h > 0$); for compound **4**, three octants of data ($+++$, $---$, $--+$) were collected. Semi-empirical absorption corrections were applied, based on measurement of sets of equivalent reflections at a range of azimuthal angles [45]. Data with $|F_o| > 4\sigma_c(F_o)$ were considered as 'observed'; σ_c was based on counting statistics only.

The structures were determined by Patterson and difference syntheses, and refined to a minimum of $\sum w\Delta^2$, with $\Delta = |F_o| - |F_c|$. SHELXTL [45] and locally written computer programs were employed, and atomic scattering factors were taken from ref. 46. The weighting scheme was $w^{-1} = \sigma^2(F_o) = \sigma_c^2(F_o) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$, where $G = F_o/F_{max}$ and $H = \sin \theta / \sin \theta_{max}$; the parameters A were derived from analysis of the data [47]. The isotropic extinction parameter x is defined by $Fc' = Fc / (1 + xF_c^2 / \sin^2 \theta)^{1/4}$. The weighted R factor, $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$.

The 'absolute structure' of **3** was determined by refinement of the parameter $\eta = 1.15(3)$ [48]. Attempted refinement of **4** in the alternative, non-centrosymmetric,

space group $Pn2_1a$ ($Pna2_1$ in a different orientation) was unsuccessful, and the centrosymmetric $Pnma$ was accepted as correct.

A table of thermal parameters and tests of observed and calculated structure factors are available from the authors.

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