Synthesis and Characterisation of Half-sandwich Tantalum Compounds in Oxidation States (I)—(V): Tertiary Phosphine, Acetylene, Butadiene, Carbonyl, and Oxo Derivatives. *X*-Ray Crystal Structures of $[Ta(C_5Me_5)Cl_3(PMe_3)]$ and $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$†

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The half-sandwich tertiary phosphine tantalum compounds $[Ta(C_5H_5)Cl_3(PMe_3)]$ (**3**), $[Ta(C_5H_5)Cl_2(PMe_3)_3]$ (**6**), $[Ta(C_5Me_5)Cl_2(PMe_3)_2]$ (**7**) and $[Ta(C_5Me_5)Cl_3(dmpe)]$ (**5**) (dmpe = $Me_2PCH_2CH_2PMe_2$) have been prepared by treatment of $[Ta(C_5R_5)Cl_4]$ (R = H or Me) with magnesium in tetrahydrofuran (thf) in the presence of the phosphine. Compounds (**3**), (**6**), and (**7**) decompose in chlorocarbons to give the tetrachlorides $[Ta(C_5R_5)Cl_4(PMe_3)]$. Compound (**7**) also decomposes in hydrocarbon solvents to give a mixture of products from which $[Ta(C_5Me_5)Cl_3(PMe_3)]$ (**4**) may be crystallized selectively. The *X*-ray crystal structure of (**4**) has been determined in the orthorhombic space group $P2_12_12_1$ and reveals a four-legged piano-stool geometry. Compound (**7**) reacts with RC≡CPh (R = H or Ph) to give the known acetylene complexes $[Ta(C_5Me_5)Cl_2(\eta^2\text{-}RC{\equiv}CPh)]$ [R = Ph (**9**) or H (**10**)] and with butadiene to give $[Ta(C_5Me_5)Cl_2(\eta\text{-}C_4H_6)]$ (**11**). By contrast, (**6**) reacts with butadiene to give the η^2-butadiene complex $[Ta(C_5H_5)Cl_2(PMe_3)_2(\eta^2\text{-}C_4H_6)]$ (**12**) which is unstable in the absence of an excess of butadiene but does not eliminate PMe_3 upon prolonged heating at elevated temperatures to form the known compound $[Ta(C_5H_5)Cl_2(\eta\text{-}C_4H_6)]$. Carbon monoxide reacts with compounds (**6**) and (**7**) to give $[Ta(C_5H_5)Cl_2(CO)(PMe_3)_2]$ (**13**) and $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$ (**14**), respectively. The *X*-ray structure of (**14**) reveals a pseudo octahedral geometry with mutually *trans* ring and phosphine ligands and a *cis*-dichloro/*cis*-dicarbonyl ligand arrangement. There is also a considerable ring-slip distortion present in the C_5Me_5 ring. Reduction of (**14**) with sodium amalgam in thf in the presence of PMe_3 affords *cis*-$[Ta(C_5Me_5)(CO)_2(PMe_3)_2]$ (**15**) in 61% yield. Although stable indefinitely at room temperature, (**15**) converts upon warming at 100 °C to the *trans* isomer. The reaction has been monitored by ^1H n.m.r. spectroscopy giving a pseudo first-order rate constant of $9.9(1) \times 10^{-5}$ s^{-1}. Reduction of (**14**) with sodium amalgam in the presence of CO (1.5 atm) gives $[Ta(C_5Me_5)(CO)_4]$ (**17**) in 65% yield. Complex (**17**) can also be obtained in 47% yield in a one-pot reaction by treatment of $[Ta(C_5Me_5)Cl_4]$ with 4 equivalents of sodium amalgam in the presence of 1 equivalent of PMe_3. The oxide $[Ta(C_5Me_5)(O)Cl_2]$ (**18**) has been obtained by treatment of (**7**) with CO_2. A dimeric structure with bridging oxo ligands is suggested on the basis of i.r. spectroscopy and mass spectrometry.

Since the late 1970s, half-sandwich compounds of the heavier Group 5 elements, niobium and tantalum, have been readily accessible through treatment of the metal pentahalides with cyclopentadienyl-tin [1–3] and -silicon [4] reagents. A considerable derivative chemistry, particularly for niobium in its mid- to low-oxidation states, has been developed by Green,[2,5] Leigh,[6] and more recently by Royo[7] and Curtis and their co-workers.[8] By comparison, the chemistry of the analogous half-sandwich tantalum system has received much less attention.[6,8]

Here we describe the synthesis of a series of half-sandwich tantalum compounds containing tertiary phosphine ligands and the use of some of these compounds to prepare both new and known low- to mid-valent half-sandwich tantalum species. There has also been a growing interest in high-valent half-sandwich chemistry and we describe the use of the tantalum(III) trimethylphosphine derivative $[Ta(C_5Me_5)Cl_2(PMe_3)_2]$ to prepare the half-sandwich tantalum(V) oxide $[Ta(C_5Me_5)(O)Cl_2]$, a previously unknown heavy metal analogue of $[V(C_5H_5)(O)Cl_2]$.[9] Some of the results arising from this work have been communicated.[10,11]

Results and Discussion

Phosphine–Chloride Derivatives.—The simple adducts $[Ta(C_5R_5)Cl_4(PMe_3)]$ [R = H (**1**) or Me (**2**)] are the most readily accessible half-sandwich PMe_3 derivatives arising by direct interaction of $[Ta(C_5R_5)Cl_4]$ with trimethylphosphine. Sanner *et al.*[12] have shown that $[Ta(C_5Me_5)Cl_4(PMe_3)]$ (**2**) may be obtained in good yield by treatment of $[Ta(C_5Me_5)Cl_4]$

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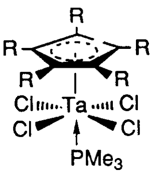
† Trichloro(η^5-pentamethylcyclopentadienyl)(trimethylphosphine)-tantalum(IV) and dicarbonyldichloro(η^5-pentamethylcyclopentadienyl)(trimethylphosphine)tantalum(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. units employed: atm = 101 325 Pa, eV ≈ 1.6×10^{-19} J.



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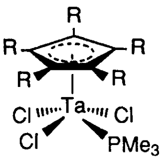
R = Me (2)



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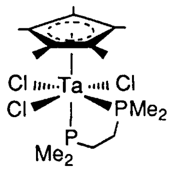
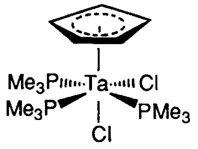
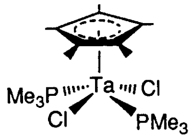


(5)



(6)



(7)

with PMe_3 in CH_2Cl_2 while the analogous C_5H_5 derivative has been prepared by a related procedure using tetrahydrofuran (thf) as a solvent.[6] The purple tantalum(IV) compounds $[Ta(C_5R_5)Cl_3(PMe_3)]$ [R = H (3) or Me (4)] are obtained upon reduction of (1) or (2), respectively, with a half molar equivalent of magnesium in the presence of PMe_3 [equation (1)].

$$[Ta(C_5R_5)Cl_4] + \tfrac{1}{2}Mg \xrightarrow[\text{thf}]{PMe_3} [Ta(C_5R_5)Cl_3(PMe_3)] + \tfrac{1}{2}MgCl_2 \quad (1)$$

R = H (3) or Me (4)

Compound (4) has been described previously[13a] and an analogous procedure has been adopted here for the preparation of (3). There was no evidence for the formation of $[Ta(C_5H_5)Cl_3(PMe_3)_2]$ when (3) was prepared in the presence of an excess of PMe_3 in contrast to the analogous niobium system.[7b] Consistent with tantalum(IV) d^1 metal centres neither (3) nor (4) gives signals in the ^1H or ^{31}P n.m.r. spectra at ambient temperature. Compound (3) also appears to lose co-ordinated PMe_3 more readily than (4) leading to variable elemental analyses, an effect which has been noted for other labile PMe_3 complexes.[14] Despite their instability in solution, these half-sandwich tantalum(IV) metal fragments have been found to be synthetically useful: for example, (4) has been employed in the synthesis of bent-sandwich compounds containing pentamethylcyclopentadienyl ligands,[13a] where it is assumed that the trimethylphosphine, although co-ordinating only weakly to $[Ta(C_5Me_5)Cl_3]$, prevents oligomerisation or disproportionation of this fragment. This is supported by a crystal structure determination on $[Ta(C_5Me_5)Cl_3(PMe_3)]$ (4) (see below) which shows it to be mononuclear with a four-legged piano-stool geometry.

The 1,2-bis(dimethylphosphino)ethane (dmpe) tantalum(IV) derivative $[Ta(C_5Me_5)Cl_3(dmpe)]$ (5) may be prepared as a purple crystalline solid in 60% yield by treatment of $[Ta(C_5Me_5)Cl_4]$ with magnesium (0.5 equivalent) in the presence of dmpe. The presence of the chelating diphosphine leads to a less labile co-ordination sphere and inert atmosphere toluene solutions of (5) show no evidence for decomposition over 48 h at room temperature. Moreover, solid samples show no sign of hydrolysis upon exposure to moist air for 3—4 min, unlike (3) which decomposes completely within the same period of time. Magnetic susceptibility measurements on compound (5) in $[^2H_6]$benzene, following a modification of the method described by Evans,[15] give an effective magnetic moment ($\mu_{eff.}$) of 1.5, consistent with the d^1 metal centre of (5) (theoretical spin-only value = 1.73) and within the range (1.41—1.69) observed for several niobium(IV) analogues of (5).[7b] Thus, (5) is presumed to be isostructural to $[Nb(C_5H_5)Cl_3(dppe)]$[16] [dppe = 1,2-bis(diphenylphosphino)ethane] which possesses a pseudo-octahedral geometry with a meridional arrangement of halogen atoms lying *cis* to the C_5H_5 ring.

Reduction of $[Ta(C_5H_5)Cl_4]$ with one equivalent of magnesium in the presence of four equivalents of PMe_3 gives red crystals of $[Ta(C_5H_5)Cl_2(PMe_3)_3]$ (6) in 30% yield [equation (2)]. The preparation of this compound has also been reported[8] recently by the treatment of $[Ta(C_5H_5)Cl_4]$ with sodium amalgam in toluene in the presence of PMe_3.

$$[Ta(C_5H_5)Cl_4] + Mg \xrightarrow[\text{thf}]{\text{excess } PMe_3} [Ta(C_5H_5)Cl_2(PMe_3)_3] + MgCl_2 \quad (2)$$

(6)

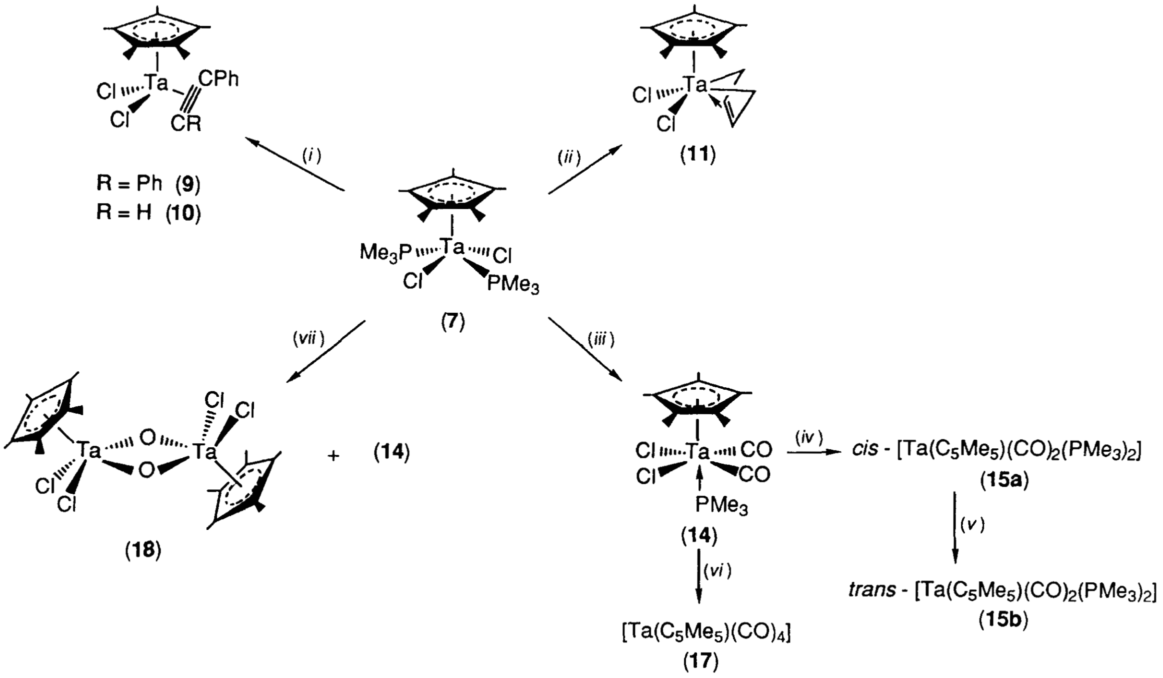
By contrast, when $[Ta(C_5Me_5)Cl_4]$ is treated with 1 equivalent of magnesium in thf, in the presence of 3.5 equivalents of PMe_3, the resulting dark red solution gives a compound (7) in which only two PMe_3 ligands are bound to the metal [equation (3)].

$$[Ta(C_5Me_5)Cl_4] + Mg \xrightarrow[\text{thf}]{\text{excess } PMe_3} [Ta(C_5Me_5)Cl_2(PMe_3)_2] + MgCl_2 \quad (3)$$

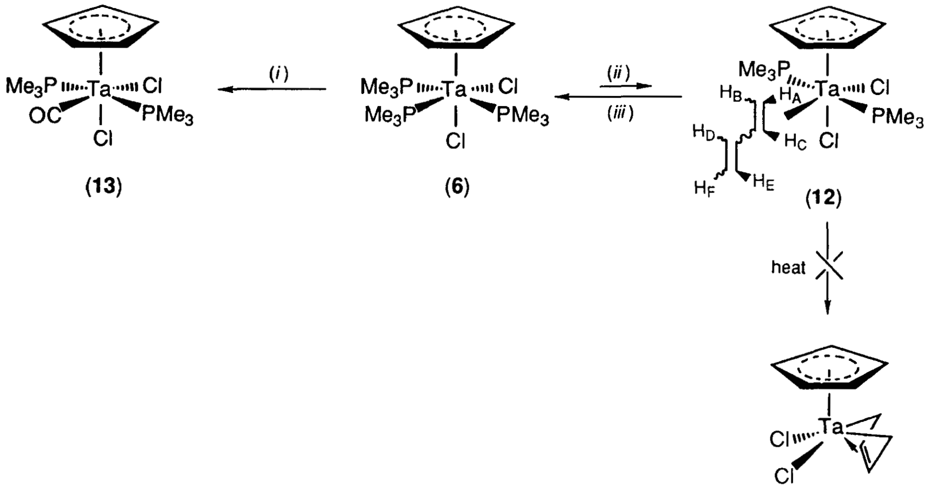
(7)

This stoicheiometry is supported by elemental analyses and by reactions of (7) with a variety of substrates which lead to displacement of either one or two PMe_3 ligands (see below). The 250-MHz ^1H n.m.r. spectrum ($[^2H_6]$benzene) of (7) is entirely different to that of (6); no signals due to (7) are observed in the usual region (*i.e.* δ 12—0) at room temperature, suggesting the complex to be paramagnetic. Instead, contact-shifted resonances are found at δ 91.45 and 20.56 (0.037 mol dm^{-3} solution) in the ratio 15:18 due to the ring and phosphine methyls, respectively. No signals were observed in the $^{31}P-\{^1H\}$ spectrum at room temperature. A solution magnetic moment, $\mu_{eff.}$, of 2.1 ($[^2H_6]$benzene, 0.037 mol dm^{-3}) supports the presence of a d^2, tantalum(III) metal centre. The observed effective magnetic moment is somewhat lower than those reported for the half-sandwich vanadium(III) complexes $[V(C_5H_5)Cl_2(PR_3)_2]$ which possess $\mu_{eff.}$ values of *ca.* 2.8[17] (theoretical spin only value = 2.83). A possible explanation for this discrepancy is partial solution decomposition (for which there is some evidence as indicated below) or a spin equilibrium with the singlet ($S = 0$) state. Similar suggestions have been offered to explain the complex solution behaviour of $[TaBr_3(PMe_2Ph)_3]$[18] which has a $\mu_{eff.}$ of 0.37 at 298 K in CD_2Cl_2 (0.035 mol dm^{-3}).

The paramagnetism of (7) argues against a dimeric structure in solution. Such a formulation would presumably contain bridging chloro ligands allowing tantalum to achieve an 18-electron valence configuration, and in the absence of a readily accessible lowest-unoccupied molecular orbital (l.u.m.o.) would be expected to be diamagnetic. Complex (7) is therefore likely to be monomeric in solution with a four-legged 'piano-stool' arrangement of ligands. A *trans* displacement of the PMe_3 ligands is anticipated to be favoured on steric grounds {similar to *trans*-$[V(C_5H_5)Cl_2(PMe_3)_2]$ which has been characterised crystallographically}.[17] Attempts to grow crystals of (7) suitable for an *X*-ray structure determination, from either light petroleum or toluene, however, result in decomposition to a mixture of products from which $[Ta(C_5Me_5)Cl_3(PMe_3)]$ (4) crystallizes preferentially. The formation of (4) and (7) most likely results from a disproportionation reaction presumably



Scheme 1. Reagents and conditions: (*i*) PhC_2R (1 equiv.), toluene, 2 weeks, 25 °C; (*ii*) C_4H_6 (1 equiv.), C_6D_6, 1 h, 25 °C; (*iii*) CO (1 atm), toluene, 3 h, 25 °C; (*iv*) Na(Hg) (2 equiv.), PMe_3 (2 equiv.), thf, 24 h, 25 °C; (*v*) 100 °C, several hours; (*vi*) Na(Hg) (2 equiv.), CO ($\approx$1.5 atm), thf, 24 h, 25 °C; (*vii*) CO_2 (1 atm), toluene, 16 h, 25 °C



Scheme 2. Reagents and conditions: (*i*) CO (1 atm), toluene, 1 h, 25 °C; (*ii*) C_4H_6 (5 equiv.), C_6D_6, 25 °C; (*iii*) PMe_3 (1 equiv.), C_6D_6, 25 °C

also affording a tantalum(II) species. Solutions of (**7**) in [$^2H_6$]benzene invariably contain a significant quantity of free PMe_3 and signals attributable to a diamagnetic species are observable in the ^1H n.m.r. spectrum. Although these solutions are stable at room temperature over many weeks in sealed tubes, removal of the solvent and consequently of the liberated PMe_3 results in the formation of (**4**) as noted before. These observations suggest that a solution equilibrium exists between (**7**) and monophosphine derivative (**8**) [equation (4)].

$$\underset{(\mathbf{7})}{[Ta(C_5Me_5)Cl_2(PMe_3)_2]} \rightleftharpoons \underset{(\mathbf{8})}{[Ta(C_5Me_5)Cl_2(PMe_3)]} + PMe_3 \quad (4)$$

The latter is more likely to exist as a dimer and may be responsible for the disproportionation process. Relevant to this is the observation by Messerle and co-workers[19] that [{$Ta(C_5Me_5)Cl_2$}$_2$] reacts with PMe_3 to give a mixture of products of which only complex (**4**) was identified. Further support for the formation of a dimeric monophosphine species is provided by the recent isolation of the stable analogue [{$Ta(C_5H_5)Cl_2(PMe_2Ph)$}$_2$].[20] During the course of these studies on the formation and reactivity of (**7**), no evidence has been obtained for the existence of [$Ta(C_5Me_5)Cl_2(PMe_3)_3$] despite a recent report to the contrary.[21]

Complexes (**3**), (**4**), (**6**), and (**7**) react with chlorocarbon solvent at room temperature to form, ultimately, the corresponding tetrachloride adducts [$Ta(C_5R_5)Cl_4(PMe_3)$] (R = H or Me) which may be identified by comparison of their ^1H n.m.r. spectra with those of authentic samples. The C_5Me_5 derivatives react more rapidly with chlorocarbons at room temperature, (**4**) and (**7**) undergoing complete transformation within 30 min whereas (**3**) and (**6**) take several hours. A possible explanation for this may lie in the greater electron releasing properties of C_5Me_5 over those of C_5H_5,[22] which would be expected to lead to destabilisation of the lower oxidation state half-sandwich halides.

Reactions of the Tantalum(III) *Phosphine Derivatives* (**6**) *and* (**7**).—Complexes (**6**) and (**7**) react cleanly with a variety of substrates to give tantalum derivatives in oxidation states ranging from (I) to (V). Some of the derivative chemistry developed is shown in Schemes 1 and 2.

Reactions with Phenylacetylenes.—Complex (**7**) reacts with equimolar amounts of diphenylacetylene or phenylacetylene in toluene solvent as shown in Scheme 1 to give the orange complexes $[Ta(C_5Me_5)Cl_2(\eta^2\text{-}PhC{\equiv}CPh)]$ (**9**) and $[Ta(C_5Me_5)Cl_2(\eta^2\text{-}PhC{\equiv}CH)]$ (**10**), respectively, which have been obtained previously by treatment of $[Ta(C_5Me_5)Cl_2(\eta^2\text{-olefin})]$ with $PhC{\equiv}CR$ (R = Ph or H)[23] and more recently $[Ta(C_5Me_5)Cl_2(\eta^2\text{-}PhC{\equiv}CPh)]$ has been isolated from the reaction of $[\{Ta(C_5Me_5)Cl(CO)_2\}_2(\mu\text{-}Cl)_2]$ with $PhC{\equiv}CPh$.[8] In the reactions of (**7**) with acetylenes, no diamagnetic intermediates or organometallic by-products are observed by ^1H n.m.r. spectroscopy which also showed that 2 equivalents of PMe_3 are displaced cleanly.

Reactions with Butadiene.—The reaction between (**7**) and butadiene (1 equivalent) proceeds smoothly at room temperature to give the previously reported complex $[Ta(C_5Me_5)Cl_2(\eta\text{-}C_4H_6)]$[24] (**11**) in high yield. By contrast complex (**6**) (Scheme 2) reacts with butadiene at room temperature to afford an equilibrium mixture of (**6**) and a single product arising by displacement of one PMe_3 ligand ($K_{eq.} \ll 1$). The product has been characterised as $[Ta(C_5H_5)Cl_2(PMe_3)_2(\eta^2\text{-}C_4H_6)]$ (**12**) by ^1H n.m.r. spectroscopy and represents a rare example of an η^2-butadiene species. Attempts to isolate (**12**) were unsuccessful due to its lack of stability in the absence of excess of butadiene. The butadiene ligand gives rise to six distinct multiplets attributable to the hydrogens of non-co-ordinated [δ 5.79 (H_D), 4.66 (H_E), and 4.53 (H_F)] and co-ordinated [δ 3.20 (H_C), 1.90 (H_A), and 1.4—1.0 (H_B) (obscured by PMe_3 resonances)] olefinic bonds. The ^1H n.m.r. data for the butadiene ligand in (**12**) bear close similarity to the butadiene signals observed for $[Ta(C_5Me_5)_2H(\eta^2\text{-}C_4H_6)]$[25] and are very different to those for the η^4-butadiene ligand in $[Ta(C_5R_5)Cl_2(\eta^4\text{-}C_4H_6)]$(R = H or Me).[24] Complex (**12**) may be heated for several hours at 70 °C in a sealed tube without conversion to the known $[Ta(C_5H_5)Cl_2(\eta^4\text{-}C_4H_6)]$, reflecting a reduced propensity for PMe_3 dissociation from the C_5H_5 derivative.

Reactions with Carbon Monoxide.—Complex (**6**) reacts cleanly with carbon monoxide (*ca.* 1 atm) in toluene over 1 h at room temperature to afford $[Ta(C_5H_5)Cl_2(CO)(PMe_3)_2]$ (**13**) in 87% yield. Complex (**13**) has been isolated previously in low yield as an impure thf solvate.[6] N.m.r. data on the thf-free compound suggest (**13**) to be isostructural with the crystallographically characterised derivative, $[Ta(C_5H_5)Cl_2(CO)(PMe_2Ph)_2]$.[6] Further phosphine substitution does not occur in the presence of excess carbon monoxide; no reaction was observed over 24 h at 70 °C by ^1H n.m.r. spectroscopy. By contrast, treatment of (**7**) with an excess of carbon monoxide (*ca.* 1 atm) leads to rapid formation of the dicarbonyl compound $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$ (**14**), presumably *via* the monocarbonyl analogue of (**13**). No intermediates were observed, however, when the reaction was monitored by ^1H n.m.r. spectroscopy, suggesting that they are too short-lived under the reaction conditions employed. This is consistent with the observations of Mayer and Bercaw[26] who reported that the monocarbonyl complex $[Ta(C_5Me_5)H_2(CO)(PMe_3)_2]$ is stable in solution whereas substitution of one of the hydride ligands for a chloro group leads to an equilibrium with the dicarbonyl complex $[Ta(C_5Me_5)HCl(CO)_2(PMe_3)]$. It was proposed that this resulted from replacing hydrogen with the more sterically demanding and π-basic chloride ligand. For complex (**14**), containing two chloride ligands, this trend may be accentuated to the extent that $[Ta(C_5Me_5)Cl_2(CO)(PMe_3)_2]$ is not observable. An i.r. spectrum of (**14**) confirms the presence of ligated carbon monoxide (three bands are observed rather than the two anticipated, at 1 988, 1 900, and 1 880 cm^{-1}, possibly due to solid-state splitting of one of the bands) and of PMe_3 ligands (975, 960, and 745 cm^{-1}). The 250 MHz ^1H n.m.r. spectrum ([$^2H_6$]benzene) shows a doublet resonance at δ 1.26 [^2J(PH) = 9.8 Hz] attributable to a single PMe_3 ligand. Assuming complex (**14**) possesses a pseudo-octahedral geometry, several geometrical isomers are possible. However, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum gives a single carbonyl resonance at 238.1 p.p.m. [^2J(PC) = 25.2 Hz] indicating that the carbon monoxide ligands possess equivalent solution environments. Fluxionality, involving the rapid interconversion of two or more isomers, is unlikely as similar pseudo-octahedral complexes, $[M(C_5R_5)Cl_2L_3]$, have generally been shown to retain their solid-state structures in solution.[6,7b] Furthermore, a semi-quantitative analysis[27] of the i.r. bands attributable to the symmetric and anti-symmetric carbonyl stretching modes at 1 988 and 1 880 cm^{-1} respectively (CH_2Cl_2 solution) gave an OC–M–CO bond angle of *ca.* 100° suggesting a *cis* displacement of the carbonyl ligands. Only the *cis*-dichloro, *cis*-dicarbonyl isomer shown in Scheme 1 is consistent with all of these observations. The solid-state structure of complex (**14**) was subsequently established by a single crystal *X*-ray structure determination.

Table 1. Selected spectroscopic data for *cis*- and *trans*-$[Ta(C_5Me_5)(CO)_2(PMe_3)_2]$

	$[Ta(C_5Me_5)(CO)_2(PMe_3)_2]$	
	trans	*cis*
I.r. (Nujol, cm^{-1})	1 842, $\nu_{sym.}$(CO), 1 750, $\nu_{asym.}$(CO)	1 822, $\nu_{sym.}$(CO), 1 732, $\nu_{asym.}$(CO)
^1H N.m.r. (C_6D_6, δ)	1.90 (s, C_5Me_5), 1.35 [m, 18 H, J(PH) 6.4 Hz, 2 PMe_3]	1.93 (s, C_5Me_5), 1.13 [m, 18 H, J(PH) 6.4 Hz, 2 PMe_3]
^{13}C N.m.r. (C_6D_6, δ)	278.1 [t, ^2J(PC) 19.5 Hz, 2 CO]	278.1 [d, ^2J(PC) 22.9 Hz, 2 CO]

Formation and Isomerisation of cis-$[Ta(C_5Me_5)(CO)_2(PMe_3)_2]$ (**15a**).—Reduction of (**14**) with sodium amalgam (2 equivalents) in thf solvent in the presence of PMe_3 affords *cis*-$[Ta(C_5Me_5)(CO)_2(PMe_3)_2]$ (**15a**) in 61% yield. The *trans* isomer, (**15b**), prepared by treatment of $[Ta(C_5Me_5)H_4(PMe_3)_2]$ with carbon monoxide, has been reported previously by Mayer and Bercaw.[26] There is no evidence for the formation of this isomer from the reaction of CO with complex (**14**). For comparative purposes, the principal spectroscopic data for the two isomers are collected in Table 1. They are readily distinguishable by both their i.r. and n.m.r. spectra: the equivalent carbonyl ligands of (**15b**) give a triplet resonance at 278.1 p.p.m. [^2J(PC) = 19.5 Hz] in the ^{13}C n.m.r. spectrum due to coupling to the two equivalent ^{31}P nuclei, while the carbonyls of (**15a**) give a doublet resonance [^2J(PC) = 22.9 Hz] at the same chemical shift (278.1 p.p.m.). Thus, the carbonyl ligands of the *cis* isomer (**15a**) couple strongly to only one ^{31}P nucleus, a behaviour similar to that observed for *cis*-$[Ta(C_5Me_5)(CO)_2(dmpe)]$.[26]

A semi-quantitative analysis[27] of the symmetric and anti-symmetric ν(CO) bands in the Nujol spectrum of complex **(15a)** gave a OC–M–CO angle of 97° consistent with a *cis* dicarbonyl ligand geometry. Also, the ν(CO) bands for **(15a)** occur to low frequency of those for **(15b)** consistent with enhanced $d\pi$–π^* back donation to the carbonyl ligands in the *cis* isomer. With regard to the apparent selective formation of **(15a)** and **(15b)**, it is perhaps of some significance that the relative dispositions of the two carbonyl ligands of $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$ and the phosphine ligands of $[Ta(C_5Me_5)H_4(PMe_3)_2]$ are retained in the products.

The *cis* isomer does not convert to the *trans* isomer over many months at room temperature (by ^1H n.m.r. spectroscopy on sealed samples in $[^2H_6]$benzene). However, conversion does occur at an elevated temperature, and above 70 °C the rate is sufficently rapid to monitor conveniently by ^1H n.m.r. spectroscopy. Significantly, **(15a)** is converted to **(15b)** suggesting that the *trans* form is favoured thermodynamically. This may be rationalised primarily on steric grounds since the relatively bulky PMe_3 ligands will prefer to occupy *trans*-orientated positions as observed for $[M(C_5H_5)X_2(PMe_3)_2]$ compounds.[17]

Two general types of mechanism have been postulated to account for the isomerisation of $[M(C_5H_5)(CO)_2LX]$ compounds:[28] either ligand dissociation, or an intramolecular pseudo-rotation of the metal-bound ligands. Of these two possibilities, the experimental observations provide some support for carbon monoxide dissociation since $[Ta(C_5Me_5)(CO)_3(PMe_3)]$ **(16)** is formed during the thermolysis of **(15a)** [equation (5)].

$$\underset{\textbf{(15a)}}{cis\text{-}[Ta(C_5Me_5)(CO)_2(PMe_3)_2]} + CO \longrightarrow \underset{\textbf{(16)}}{[Ta(C_5Me_5)(CO)_3(PMe_3)]} + PMe_3 \quad (5)$$

Although the conversion **(15a)** to **(16)** is slow at ambient temperature ($t_{\frac{1}{2}}$ *ca.* 7 d at 25 °C), the rate is appreciable at 70 °C. Consequently, it has not proved possible to monitor the isomerization process in the presence of an excess of CO gas. Dissociation of PMe_3 may be discounted as the rate of *cis* to *trans* conversion is independent of added PMe_3. An expression for the rate of loss of **(15a)** **(A)** can be constructed [equation (6), where $c_1 = k_1 - (k_1k_{-1}/k_{-1} + k_2)$ and $c_2 = (k_{-1}k_{-2}/k_{-1} + k_2)$] allowing for the side reactions with CO shown in equations (9) and (10). The postulated intermediate $[Ta(C_5Me_5)(CO)(PMe_3)_2]$ **(B)** [equation (7)] is assumed to exist in a low steady-state concentration, and being co-ordinatively unsaturated would be expected to be short-lived in the presence of donor molecules. Indeed, no intermediates were observed when the isomerization was monitiored by ^1H n.m.r. spectroscopy.

$$\frac{-d[(\mathbf{A})]}{dt} = (c_1 + k_3[CO])[(\mathbf{A})] - c_2[(\mathbf{C})] - k_{-3}[(\mathbf{D})][PMe_3] \quad (6)$$

$$\underset{\textbf{(A)}}{cis\text{-}[Ta(C_5Me_5)(CO)_2(PMe_3)_2]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\textbf{(B)}}{[Ta(C_5Me_5)(CO)(PMe_3)_2]} + CO \quad (7)$$

$$\underset{\textbf{(B)}}{[Ta(C_5Me_5)(CO)(PMe_3)_2]} + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\textbf{(C)}}{trans\text{-}[Ta(C_5Me_5)(CO)_2(PMe_3)_2]} \quad (8)$$

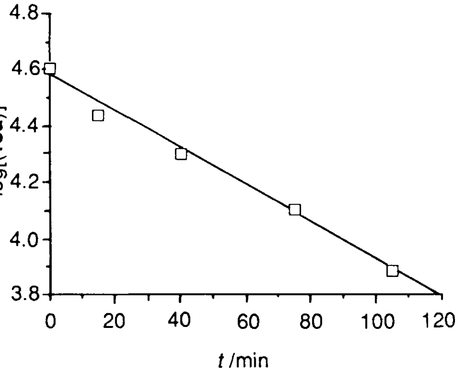


Figure 1. Plot of log [**(15a)**] *vs.* *t* (100 °C, C_6D_6)

$$\underset{\textbf{(A)}}{cis\text{-}[Ta(C_5Me_5)(CO)_2(PMe_3)_2]} + CO \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\textbf{(D)}}{[Ta(C_5Me_5)(CO)_3(PMe_3)]} + PMe_3 \quad (9)$$

$$\underset{\textbf{(C)}}{trans\text{-}[Ta(C_5Me_5)(CO)_2(PMe_3)_2]} + CO \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{\textbf{(D)}}{[Ta(C_5Me_5)(CO)_3(PMe_3)]} + PMe_3 \quad (10)$$

During the early stages of conversion, the concentration of $[Ta(C_5Me_5)(CO)_3(PMe_3)]$ **(D)** remains low and first-order kinetics are obeyed (Figure 1). This is consistent with the low initial concentrations of **(C)**, **(D)**, and PMe_3: thus it is reasonable to expect $k_{-1} \approx k_2 \gg k_1, k_3$. The observed pseudo first-order rate constant ($k_{obs.}$) may then be approximated to k_1 which from Figure 1 is evaluated to be $9.9(1) \times 10^{-5}$ s^{-1}. This is significantly smaller than $k_{cis\rightarrow trans}$ for $[Mo(C_5H_5)(CO)_2LR]$ complexes which can range in value from *ca.* 0.2 s^{-1} (−56 °C) for R = H, L = $P(OPh)_3$, to *ca.* 0.4 s^{-1} (123 °C) for R = Cl, L = $P(OMe)_3$[28] and which have been shown to isomerize *via* non-dissociative mechanisms. Thus, it would appear that the activation barrier for the intramolecular ligand rearrangement in $[Ta(C_5Me_5)(CO)_2(PMe_3)_2]$ must be comparable, at least, to the tantalum–carbonyl bond dissociation energy.

$[Ta(C_5Me_5)(CO)_4]$ **(17)**.—The reduction of $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$ **(14)** by sodium amalgam (2.5 equivalents) in thf solution under *ca.* 1.5 atm of CO gives a dark orange solution from which $[Ta(C_5Me_5)(CO)_4]$ **(17)** may be isolated in 65% yield. The supernatant solution was found to contain $[Ta(C_5Me_5)(CO)_3(PMe_3)]$ **(16)** by n.m.r. spectroscopy: a singlet at δ 1.85 is attributable to the C_5Me_5 ring hydrogens and a doublet resonance at δ 1.03 [^2J(PH) = 8.1 Hz] is due to the methyls of a single metal-bound PMe_3 ligand. Complexes **(16)** and **(17)** are separated readily by fractional crystallization. It is likely that the two compounds are formed by competing pathways since **(16)** does not react with CO to give **(17)** under the conditions employed. The success of this reaction in giving **(17)** in reasonable yield prompted us to attempt a direct 'one-pot' synthesis. Thus, the reaction of $[Ta(C_5Me_5)Cl_4]$ with 4 equivalents of sodium amalgam in the presence of 1 equivalent of PMe_3 affords **(17)** cleanly in 47% yield. This mild synthetic procedure offers an alternative to the forcing conditions reported previously.[22] While the precise role of the co-ordinated PMe_3 remains obscure, an important influence may be the co-ordinative stabilization of mononuclear intermediates {both $[Ta(C_5Me_5)Cl_3(PMe_3)]$ and $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$

Table 2. Crystal data for complexes (**4**) and (**14**)*

	(**4**)	(**14**)
Molecular formula	$C_{13}H_{24}Cl_3PTa$	$C_{15}H_{24}Cl_2O_2PTa$
M	498.6	519.2
Crystal size/mm	0.20 × 0.35 × 0.40	0.20 × 0.25 × 0.40
a/Å	8.330 6(4)	9.876(1)
b/Å	14.289(1)	12.122(1)
c/Å	15.145(1)	15.567(1)
U/Å^3	1 802.8	1 863.6
D_c/g cm^{-3}	1.837	1.850
F(000)	964	1 008
μ/mm^{-1}	6.55	6.21
Max. indices h, k, l	9, 16, 18	11, 14, 18
No. of reflections measured	4 321	15 106
No. of unique reflections	3 172	3 295
No. of observed reflections	2 648	3 164
R_{int}	0.027	0.033
Transmission factors	0.061—0.098	0.076—0.110
Weighting parameters	38, 88, −24, −107, 77, −132	15, −214, 346, 25, −29, 73
Extinction parameters x	4.2(6) × 10^{-7}	9.8(8) × 10^{-7}
Parameters refined	164	215
Max. shift/e.s.d.	0.002	0.056
Max. final electron density difference/e Å^{-3}	1.23	2.96
Final R	0.033	0.033
Final R'	0.027	0.024
Goodness of fit	1.11	1.09

* Details in common: orthorhombic; space group, $P2_12_12_1$; $Z = 4$; 2θ range, 3—50°.

Table 3. Atomic co-ordinates (× 10^4) for complex (**4**)

Atom	x	y	z
Ta	2 549(1)	3 540(1)	2 570(1)
Cl(1)	430(3)	3 435(2)	3 639(2)
Cl(1)	3 775(3)	4 859(2)	1 857(2)
Cl(3)	387(3)	3 876(2)	1 549(2)
P	3 867(3)	4 393(2)	3 908(2)
C(1)	2 770(21)	5 488(9)	4 047(11)
C(2)	3 698(15)	3 872(10)	5 005(7)
C(3)	5 939(14)	4 805(9)	3 838(11)
C(4)	3 435(17)	1 970(5)	2 198(7)
C(5)	3 424(13)	2 433(6)	1 571(5)
C(6)	4 841(11)	2 689(7)	1 999(6)
C(7)	4 698(11)	2 420(7)	2 883(6)
C(8)	3 247(14)	1 967(7)	3 010(7)
C(9)	822(14)	1 493(11)	1 988(14)
C(10)	3 177(23)	2 513(13)	571(9)
C(11)	6 344(18)	3 136(11)	1 605(12)
C(12)	6 083(15)	2 387(10)	3 521(10)
C(13)	2 751(21)	1 481(10)	3 839(9)

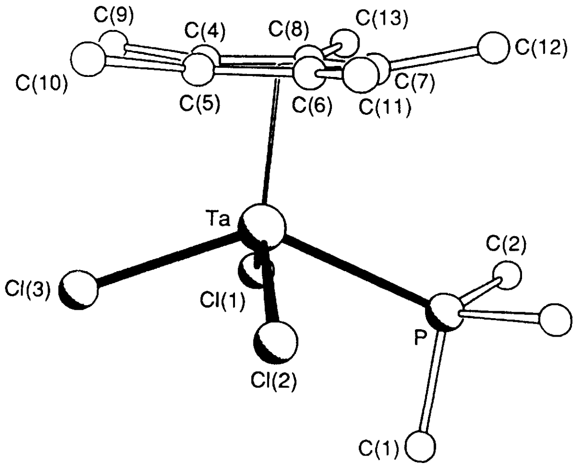


Figure 2. The molecular structure of complex (**4**)

have been found to be mononuclear by *X*-ray diffraction studies}. Further, the effect of co-ordinated PMe_3 on the reduction potentials of the intermediates may facilitate a more controlled conversion from the tantalum(v) starting material to the tantalum(i) product.

[$Ta(C_5Me_5)(O)Cl_2$] (**18**).—A saturated toluene solution of (**7**) reacts with CO_2 (1 atm) to give the half-sandwich oxide (**18**) in 40% yield. A likely dimeric structure with *trans* orientated C_5Me_5 ligands is shown in Scheme 1, although a higher nuclearity species cannot be ruled out unequivocally in the absence of an *X*-ray structure determination. A strong, broad absorption at 675 cm^{-1} in the i.r. spectrum is assignable to the Ta–O–Ta vibrations of bridging oxo ligands and its chemical ionisation (c.i.) mass spectrum gives an envelope at *m*/*z* 805 (^{35}Cl) corresponding to a dimeric formulation (no higher mass fragments are observed). Unfortunately, the low solubility of (**18**) and its instability in solution[11] have prevented an accurate molecular weight determination. Nevertheless, this aggregated form contrasts with the vanadium analogue [$V(C_5Me_5)(O)Cl_2$] which has been shown to be monomeric[29] while both monomeric and oxo-bridged dimeric formulations for [$Re(C_5Me_5)(O)Cl_2$] have been reported.[30] The reaction described here involves a formal dissociation of CO_2 into 'O' and 'CO'; the formation of the latter is confirmed by the observation of (**14**) as a by-product: this reaction type has been observed on previous occasions,[31] presumably proceeding *via* a η^2-CO_2 intermediate. Attempts to obtain (**18**) by reactions of (**7**) with other potential sources of oxygen atoms, *e.g.* NO, Me_3NO, N_2O, Me_2SO, or H_2O were unsuccessful; all afforded intractable mixtures. The reactivity and stability of (**18**) will be reported separately.

Molecular Structure of [$Ta(C_5Me_5)Cl_3(PMe_3)$] (**4**).—Red prisms of [$Ta(C_5Me_5)Cl_3(PMe_3)$] were obtained from a saturated toluene solution of (**7**), cooled to −35 °C for 24 h. The

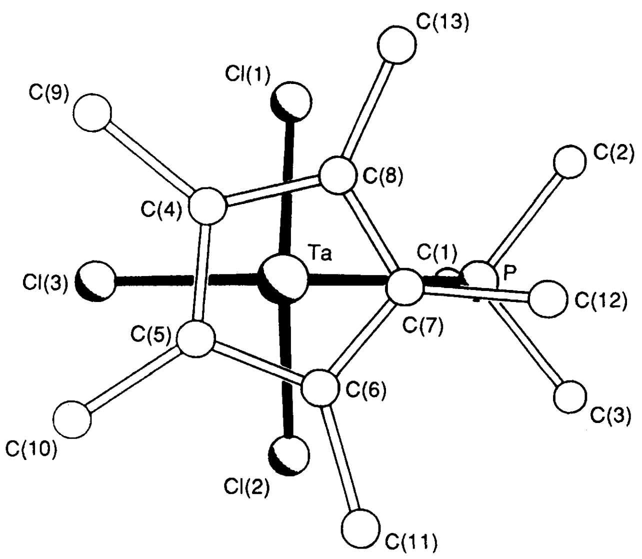


Figure 3. View of complex (**4**) along the ring centroid–tantalum vector

Table 4. Bond lengths (Å) and angles (°) for complex (**4**): X = centre of ring; Z = point in best plane of ring where normal from tantalum intersects

Ta–Cl(1)	2.400(3)	Cl(1)–Ta–Cl(2)	131.8(1)
Ta–Cl(2)	2.395(3)	Cl(1)–Ta–Cl(3)	83.8(1)
Ta–Cl(3)	2.416(3)	Cl(2)–Ta–Cl(3)	83.1(1)
Ta–P	2.608(3)	Cl(1)–Ta–P	79.2(1)
		Cl(2)–Ta–P	78.7(1)
Ta–C(4)	2.325(9)	Cl(3)–Ta–P	135.8(1)
Ta–C(5)	2.319(10)		
Ta–C(6)	2.424(9)	Ta–P–C(1)	104.0(4)
Ta–C(7)	2.448(9)	Ta–P–C(2)	119.3(4)
Ta–C(8)	2.390(10)	Ta–P–C(3)	119.4(4)
P–C(1)	1.843(13)	C(1)–P–C(2)	103.6(6)
P–C(2)	1.827(11)	C(1)–P–C(3)	103.8(6)
P–C(3)	1.846(11)	C(2)–P–C(3)	104.6(6)
C(4)–C(5)	1.474(14)	X–Ta–Cl(1)	104.6
C(4)–C(8)	1.423(14)	X–Ta–Cl(2)	113.1
C(4)–C(9)	1.517(15)	X–Ta–Cl(3)	114.3
C(5)–C(6)	1.383(14)	X–Ta–P	109.9
C(5)–C(10)	1.548(15)		
C(6)–C(7)	1.397(13)	Z–C(4)–C(9)	5.8
C(6)–C(11)	1.487(16)	Z–C(5)–C(10)	4.7
C(7)–C(8)	1.418(14)	Z–C(6)–C(11)	2.5
C(7)–C(12)	1.526(16)	Z–C(7)–C(12)	11.0
C(8)–C(13)	1.521(16)	Z–C(8)–C(13)	7.3
C–Ta	2.053		

crystal data are given in Table 2 and atomic parameters are listed in Table 3. Views of complex (**4**) are shown in Figures 2 and 3. Selected bond distances and angles are given in Table 4. The complex is monomeric, possessing a distorted, four-legged 'piano-stool' geometry typical of $[M(C_5R_5)L_3L']$ compounds.[32–35] As in these (**4**) contains a pseudo mirror plane passing through P, Ta, and Cl(3) and is geometrically similar to the 18-electron complexes $[M(C_5H_5)(CO)_3X]$[32–35] (M = Mo or W; X = halide or alkyl) in which the unique ligand X lies beneath a ring carbon atom and the carbonyl ligand *trans* to X lies beneath a C–C bond of the ring (Figure 3). As in other η^5-C_5Me_5 complexes,[36] all of the ring-methyl carbon atoms are bent away from the mean ring plane and the tantalum atom, in this case by an average of *ca.* 6° (Table 4). However, the C(7)–C(12) bond is displaced considerably further from the ring plane (11°), presumably as a result of unfavourable steric interaction with the PMe_3 ligand. Also, the PMe_3 ligand is orientated with one methyl substituent *exo* and two methyls *endo* to the C_5Me_5 ring (Figure 2), thus avoiding close contacts between PMe_3 and ring methyl substituents.

The tantalum–ring carbon distances range quite widely from 2.319(10) [Ta–C(5)] to 2.448(9) Å [Ta–C(7)] with ΔM = 0.13 Å (ΔM = difference between longest and shortest distances). Comparative values of ΔM and ΔR (corresponding difference for inter-ring carbon–carbon distances) are given in Table 5. The range of tantalum–carbon distances appears to be caused by a tilting of the η^5-C_5Me_5 ring, bringing atoms C(4) and C(5) closer to the metal [2.325(9) and 2.319(10) Å respectively]. This type of behaviour has also been observed in the 18-electron complexes $[M(C_5H_5)(CO)_3X]$ (M = Mo or W; X = halide or alkyl)[35] and explained on the basis of maximising overlap between the metal d_{xy} orbital and the unoccupied C_5H_5 π orbital of suitable symmetry.[37]

The vector from tantalum, normal to the ring is displaced from the ring centroid by 0.159 Å in a direction towards the C(4)–C(5) edge. Significantly, the C(4)–C(5) distance is the longest inter-ring distance [1.474(14) Å]. Thus, the ring distortions found in $[Ta(C_5Me_5)Cl_3(PMe_3)]$ (**4**) probably arise due to a combination of electronic factors and the steric influence of the relatively bulky PMe_3 ligand.

The tantalum–chlorine distances of 2.400(3) [Cl(1)], 2.395(3) [Cl(2)], and 2.416(3) Å [Cl(3)] are within the range found for other Ta^{IV}–Cl distances and correlate well with the formal valence electron count of the metal, such that those complexes with lower formal electron counts have the shorter tantalum–chlorine distances[38–42] presumably as a result of increased ligand-to-metal, $p\pi$–$d\pi$ interactions. Significantly, it is the chlorine atom [Cl(3)] lying opposite to the phosphine [Cl(3)–Ta–P = 135.8(1)°] that gives the longest Ta–Cl bond, presumably the result of the *trans* influence of the PMe_3 ligand.[43]

The phosphorus–carbon bond lengths within the PMe_3 ligand are normal, 1.827(11)—1.846(11) Å.[44] The C–P–C angles of 104.0(3)° (average) are all less than the tetrahedral value of

Table 5. ΔM (difference between longest and shortest Ta–C distances) and ΔR (comparative difference between longest and shortest inter-ring C–C distances) values

Compound	ΔR/Å	ΔM/Å	Ref.
$[Ta(C_5Me_5)(CHPh)(CH_2Ph)_2]$	0.05	0.08	*a*
$[Ta(C_5Me_5)(CPh)(PMe_3)_2Cl]$	0.03	0.12	*b*
$[Ta(C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)]$	0.01	0.04	36
$[Ta(C_5Me_5)Cl_2(\eta^2\text{-}PhC{\equiv}CPh)]$	0.03	0.03	23
$[Ta(C_5Me_5)H_4(PMe_3)_2]$	0.05	0.07	44
$[Ta(C_5Me_5)Cl_3(PMe_3)]$	0.09 ± 0.02	0.13	This work

[a] L. W. Messerle, P. Jennische, R. R. Schrock, and G. Stucky, *J. Am. Chem. Soc.*, 1980, **102**, 6744. [b] M. R. Churchill and W. J. Youngs, *Inorg. Chem.*, 1979, **18**, 171.

Table 6. Atomic co-ordinates (× 10^4) for complex (**14**)

Atom	*x*	*y*	*z*
Ta	7 395(1)	7 636(1)	7 702(1)
C(1)	6 985(7)	5 968(5)	7 586(5)
O(1)	6 761(6)	5 052(3)	7 529(4)
C(2)	5 497(6)	7 693(8)	8 279(5)
O(2)	4 510(4)	7 760(7)	8 624(4)
P	5 680(2)	7 439(2)	6 354(1)
C(3)	3 878(6)	7 374(9)	6 567(6)
C(4)	5 823(10)	8 499(7)	5 572(5)
C(5)	5 929(11)	6 210(8)	5 709(6)
Cl(1)	8 893(2)	7 623(3)	6 404(1)
Cl(2)	7 017(2)	9 623(1)	7 311(1)
C(6)	7 729(6)	6 937(5)	9 119(4)
C(7)	7 767(7)	8 152(5)	9 153(4)
C(8)	8 956(6)	8 490(5)	8 717(4)
C(9)	9 632(5)	7 572(6)	8 416(4)
C(10)	8 882(7)	6 598(5)	8 642(4)
C(11)	6 817(11)	7 212(6)	9 653(6)
C(12)	6 941(10)	8 851(7)	9 732(6)
C(13)	9 450(10)	9 671(5)	8 724(6)
C(14)	11 013(6)	7 538(7)	7 974(4)
C(15)	9 433(9)	5 431(5)	8 586(6)

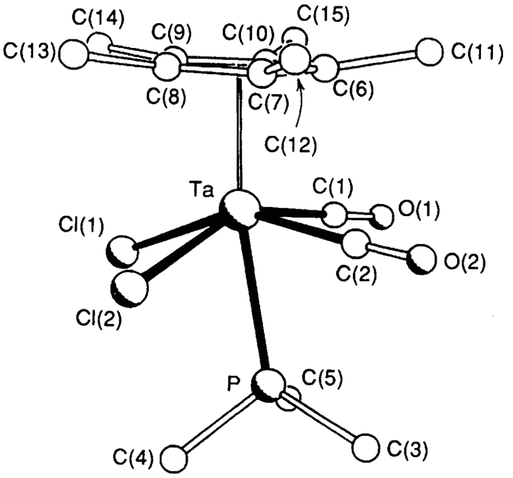


Figure 4. The molecular structure of complex (**14**)

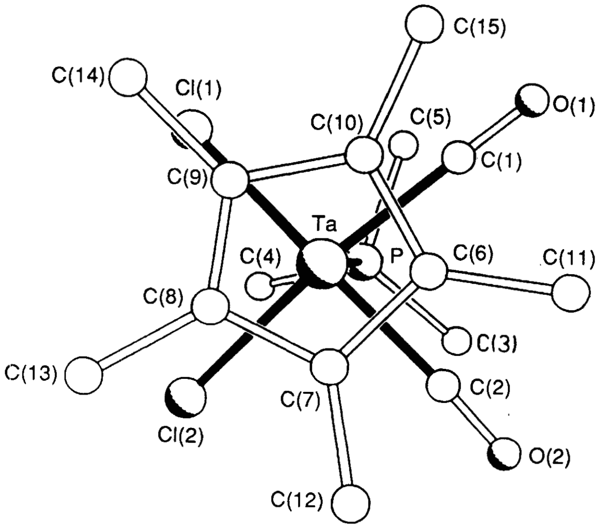
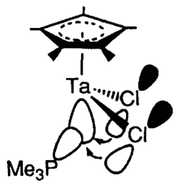


Figure 5. View of complex (**14**) along the ring centroid–tantalum vector

109.5°, as expected upon co-ordination of PMe$_3$ to a metal centre.[45] Finally, the tantalum–phosphorus bond length of 2.608(3) Å is within the range usually found for Ta^{IV}–PMe$_3$ complexes.[39,42]

Molecular Structure of [Ta(C$_5$Me$_5$)Cl$_2$(CO)$_2$(PMe$_3$)] (**14**).—Purple prisms of [Ta(C$_5$Me$_5$)Cl$_2$(CO)$_2$(PMe$_3$)] (**14**) were obtained by cooling a saturated toluene solution to −35 °C for several days. The crystal data are given in Table 2 and atomic parameters are listed in Table 6. The molecular structure is illustrated in Figures 4 and 5 and selected bond distances and angles are given in Table 7. If the η^5-C$_5$Me$_5$ ligand is assumed to occupy a single co-ordination site, the molecule may be described as a distorted octahedron with the ring and phosphine ligands lying mutually *trans* (ring centroid–Ta–P = 170.9°). The chloro and carbonyl ligands also adopt a mutually *trans* orientation resulting in a *cis*-dichloro/*cis*-dicarbonyl arrangement as suggested by the n.m.r. and i.r. data. The Ta–ring centroid distance of 2.094 Å is comparable to those reported for other Ta(C$_5$Me$_5$) complexes and is, as expected, slightly longer than that found for complex (**4**) (2.053 Å) due to the more electron rich nature of the metal centre in (**14**). Although the average inter-ring carbon–carbon and carbon–tantalum distances of 1.426(16) and 2.419(18) Å, respectively, are normal,[44] the individual values cover quite a large range, with ΔR = 0.096 and ΔM = 0.101 Å (*cf.* Table 5) which again represents a considerable ring slippage.

The vector from tantalum, normal to the η^5-C$_5$Me$_5$ ring is displaced 0.118 Å from the ring centroid towards ring carbon atoms C(6) and C(7) (Figure 5). Consequently, the Ta–C(6) and Ta–C(7) distances of 2.386(6) and 2.373(6) Å, respectively, are significantly shorter than the other Ta–ring carbon distances [av. 2.446(6) Å]. The ring slippage also results in an elongated C(6)–C(7) bond [1.475(9) Å] and a shortened C(8)–C(9) distance [1.379(9) Å]. Similar, although much larger distortions have been noted in half-sandwich oxo-rhenium systems,[46] and correlated with the strong *trans* influence of the oxo ligand. A similar effect may operate in (**14**) as Figure 5 indicates the PMe$_3$ ligand to be directed approximately *trans* (X–Ta–P = 163.4°) to the C(8)–C(9) bond [X = midpoint of C(8)–C(9)]. Another interesting feature of this molecule is the distortion of the axial PMe$_3$ ligand away from collinearity with the ring centroid tantalum vector. This has also been observed in the pseudo-isoelectronic complex, [Re(C$_5$Me$_5$)Cl$_4$(PMe$_3$)][47] although no explanation was offered. It is possible that the distortion arises to maximize overlap between the Ta(C$_5$Me$_5$)Cl$_2$(CO)$_2$ l.u.m.o. (d_{z^2}), and the PMe$_3$ σ-donor orbital and $p\pi$ interactions with chlorine lone pairs (see below).



The distortion also results in an expanded ring centroid–Ta–Cl angle of 109.4° compared to a ring centroid–Ta–CO angle of 98.3° (av.). Inter-ligand steric interactions between the halides, the ring methyls and the PMe$_3$ ligand are likely to accentuate this distortion.

The tantalum–chlorine bond distances of 2.504(2) [Cl(1)] and 2.512(2) Å [Cl(2)] are *ca.* 0.1 Å longer than those of (**4**) presumably due to the lower tantalum oxidation state and electronic saturation of (**14**). Furthermore, the distances are somewhat longer than those of many other tantalum(III) chloro complexes,[39,47–51] reflecting the electron rich nature of (**14**) and

Table 7. Bond lengths (Å) and angles (°) for complex (**14**): X = midpoint of C(8)–C(9); Y = ring centroid; Z = point in plane of ring where normal from tantalum intersects

Ta–Cl(1)	2.504(2)	Cl(1)–Ta–Cl(2)	84.2(1)
Ta–Cl(2)	2.512(2)		
		Cl(1)–Ta–P	75.2(1)
Ta–P	2.707(2)	Cl(2)–Ta–P	78.7(1)
		C(1)–Ta–C(2)	83.9(3)
Ta–C(1)	2.070(6)		
Ta–C(2)	2.079(7)	C(1)–Ta–P	74.0(2)
Ta–C(6)	2.386(7)	C(2)–Ta–(P)	76.9(2)
Ta–C(7)	2.373(6)		
Ta–C(8)	2.438(6)	C(1)–Ta–Cl(1)	92.2(2)
Ta–C(9)	2.474(6)	C(1)–Ta–Cl(2)	152.4(2)
Ta–C(10)	2.426(6)	C(2)–Ta–Cl(1)	151.8(2)
		C(2)–Ta–Cl(2)	86.5(3)
C(1)–O(1)	1.136(7)		
C(2)–O(2)	1.117(8)	Ta–C(1)–O(1)	179.5(8)
		Ta–C(2)–O(2)	176.1(7)
P–C(3)	1.812(7)		
P–C(4)	1.776(9)	Ta–P–C(3)	118.4(3)
P–C(5)	1.812(10)	Ta–P–C(4)	114.7(3)
		Ta–P–C(5)	114.6(3)
C(6)–C(7)	1.475(9)		
C(6)–C(10)	1.420(9)	C(3)–P–C(4)	103.6(5)
C(6)–C(11)	1.508(11)	C(3)–P–C(5)	101.5(5)
C(7)–C(8)	1.417(9)	C(4)–P–C(5)	101.8(4)
C(7)–C(12)	1.481(11)		
C(8)–C(9)	1.379(9)	Ta–C(6)–C(7)	71.5(3)
C(8)–C(13)	1.513(10)		
C(9)–C(10)	1.438(9)	X–Ta–P	163.4
C(9)–C(14)	1.528(8)		
C(10)–C(15)	1.518(9)	Y–Ta–C(1)	97.7
		Y–Ta–C(2)	98.9
X–Ta	2.537		
Y–Ta	2.094	Y–Ta–P	170.9
Z–Ta	2.091	Y–Ta–Cl(1)	109.3
Y–Z	0.118	Y–Ta–Cl(2)	109.4

the fact that the chlorine atoms are displaced mutually *trans* to strongly *trans*-influencing carbonyl ligands with angles Cl(1)–Ta–C(2) and Cl(2)–Ta–C(1) of 151.8(2) and 152.4(2)° respectively. Similarly, the electron rich nature of the tantalum atom in (**14**) results in a significantly longer tantalum–phosphorus bond [2.707(2) Å] than is usually found in Ta^{III}–PMe_3 complexes (typically lying in the range 2.51—2.67 Å).[36,39,41,49,52] The two carbon monoxide ligands are essentially linear [Ta–C(1)–O(1) = 179.5(8), Ta–C(2)–O(2) = 176.1(7)°] with tantalum–carbon distances of 2.070(6) [C(1)] and 2.079(7) Å [C(2)]. These are, as expected, longer than the tantalum–carbon distance in $[Ta(C_5H_5)Cl_2(PMe_2Ph)_2(CO)]$·thf [2.01(2) Å][6] since in the latter complex only one carbonyl ligand is available to accept π-charge density from tantalum. This is also reflected in the carbon–oxygen distances of (**14**) being shorter than that in $[Ta(C_5H_5)Cl_2(PMe_2Ph)_2(CO)]$·thf {1.136(7) and 1.117(8) Å for (**14**) *cf.* 1.20(2) Å for $[Ta(C_5H_5)Cl_2(PMe_2Ph)_2(CO)]$·thf}.

Conclusion

A number of half-sandwich tantalum compounds containing highly basic trimethylphosphine groups have been synthesized, and the ready displacement of these ligands has been exploited to prepare both new and known half-sandwich complexes in a range of oxidation states. The tantalum(III) phosphine derivatives are found to be particularly useful synthetic precursors and should allow convenient access to many more half-sandwich tantalum species.

Experimental

General.—All manipulations of air and/or moisture sensitive materials were performed on a conventional vacuum/inert atmosphere (nitrogen or argon) line using standard Schlenk and cannula techniques, or in an inert atmosphere (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), light petroleum (b.p. 40—60 lithium aluminium hydride; 100—120 °C, sodium), tetrahydrofuran (sodium diphenylketyl), dichloromethane (calcium hydride), 1,2-dichloroethane (calcium hydride), acetonitrile (calcium hydride), and diethyl ether (lithium aluminium hydride). The following n.m.r. solvents were dried by vacuum distillation from a suitable drying agent (in parentheses) and stored over activated 4 Å molecular sieves: $[^2H_6]$benzene (P_2O_5), $[^2H_8]$toluene (P_2O_5), $[^2H_1]$chloroform (P_2O_5), $[^2H_8]$tetrahydrofuran (sodium diphenylketyl), and $[^2H_3]$acetonitrile (calcium hydride).

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), or sh (shoulder). Mass spectra were recorded on a VG 7070E mass spectrometer, n.m.r. spectra were recorded on the following instruments, at the frequencies listed, unless stated otherwise: Bruker AC 250, ^1H (250.13 MHz), ^{13}C (62.90 MHz), ^{31}P (101.26 MHz); Varian EM 360L, ^1H (60 MHz); Hitachi Perkin-Elmer R-24(B), ^1H (60 MHz). The following abbreviations have been used for band multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), qnt (quintet), vct (virtually coupled triplet), and m (multiplet). Chemical shifts (δ) are quoted to the following references, unless stated otherwise: ^{31}P (dilute aqueous, H_3PO_4, 0 p.p.m.); ^{13}C (C_6D_6, 128.0 p.p.m.); ^1H (C_6D_6, 7.15 and $CDCl_3$, 7.24).

The following chemicals were prepared by previously published procedures: $[Na(C_5H_5)]$,[53] $[Sn(C_5H_5)Bu^n{}_3]$,[54] $Si(C_5Me_5)Me_3$,[55] $[Ta(C_5H_5)Cl_4]$,[2] $[Ta(C_5Me_5)Cl_4]$,[13] C_5Me_5H,[56] and $[Sn(C_5Me_5)Bu^n{}_3]$.[12] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations.—$[Ta(C_5H_5)Cl_3(PMe_3)]$ (**3**). Trimethylphosphine (0.16 g, 2.1 mmol) was vacuum condensed from a graduated cold finger onto a mixture of $[Ta(C_5H_5)Cl_4]$ (0.4 g, 1.04 mmol), magnesium turnings (12.48 mg, 0.52 mmol), and thf (25 cm^3) cooled to −196 °C in a 'Rotoflo' glass ampoule (150 cm^3 capacity). The mixture was allowed to warm to room temperature, whereupon 1 atm of nitrogen was introduced into the vessel. Stirring was maintained at this temperature until all the magnesium had been consumed (4 h). The volatiles were removed under reduced pressure and the residue was extracted into toluene (50 cm^3), containing a little trimethylphosphine (0.1 cm^3), to afford a purple solution. Filtration followed by concentration (*ca.* 8 cm^3) and cooling (−78 °C) afforded purple crystals of $[Ta(C_5H_5)Cl_3(PMe_3)]$. Yield, 0.30 g (68%) (Found: C, 21.90; H, 3.60. $C_8H_{14}Cl_3PTa$ requires C, 22.40; H, 3.30%). I.r. (Nujol, KBr, cm^{-1}): 3 090w, 1 428m, 1 414m, 1 300m, 1 283m, 1 029w, 1 010w, 955s br, 870 (sh), 850 (sh), 840m, 832m, 819s, 737m, and 670w. ^1H N.m.r. (250 MHz, $[^2H_6]$benzene, 298 K): no signals between δ +200 and −200. Mass spectrum [electron ionization (e.i.), 70 eV, ^{35}Cl]: m/z 351 $[M - PMe_3]^+$ and 316 $[M - PMe_3 - Cl]^+$.

$[Ta(C_5Me_5)Cl_3(dmpe)]$ (**5**). 1,2-Bis(dimethylphosphino)ethane (0.20 g, 1.33 mmol) was added, *via* a syringe against a counterflow of nitrogen, to a suspension of $[Ta(C_5Me_5)Cl_4]$ (0.4 g, 0.87 mmol) and magnesium turnings (0.01 g, 0.44 mmol) in thf (30 cm^3) at room temperature. The mixture was stirred to give initially a yellow solution which darkened through orange to deep purple-brown after all the magnesium had been consumed (6 h). The volatiles were removed and the residue was extracted with toluene (60 cm^3) to afford a purple solution. Filtration, followed by concentration to 5 cm^3 and cooling to −60 °C, afforded purple crystals, which were collected, washed with light petroleum (b.p. 40—60 °C) (2 × 4 cm^3) and dried *in vacuo*. Yield, 0.3 g (60%) (Found: C, 33.25; H, 5.55. $C_{16}H_{31}Cl_3P_2Ta$ requires C, 33.55; H, 5.45%). I.r. (Nujol, CsI, cm^{-1}): 1 430m, 1 420m, 1 300m, 1 290s, 1 148m, 1 095w, 1 075w, 1 030m, 1 010w, 970s, 955s, 945s, 880w, 870w, 850w, 805w, 750m, 740m, 730m, 710m, 660m, 353m, 290s (sh), 280s, and 265s. ^1H N.m.r. (250 MHz, [$^2H_6$]benzene, 298 K): no signals between δ +200 and −200. Mass spectrum (e.i., 70 eV, ^{35}Cl): *m*/*z* 420 [*M* − dmpe − H]$^+$ and 386 [*M* − dmpe − Cl]$^+$. Magnetic moment ([$^2H_6$]benzene, 298 K): $\mu_{eff.}$ = 1.5 (Evans' method).[15]

[$Ta(C_5H_5)Cl_2(PMe_3)_3$] (**6**). Trimethylphosphine (2.74 g, 36 mmol) was vacuum condensed onto a mixture of [$Ta(C_5H_5)Cl_4$] (3.5 g, 9.0 mmol), magnesium turnings (0.22 g, 9.0 mmol), and thf (50 cm^3) frozen at −196 °C in a thick-walled 'Rotoflo' glass ampoule (150 cm^3 capacity). The mixture was allowed to warm to room temperature, whereupon 1 atm of nitrogen was admitted. Stirring was maintained at room temperature for 12 h by which time all of the magnesium had been consumed. The volatiles were removed under reduced pressure and the residue was extracted with toluene (100 cm^3). After filtration, the red solution was concentrated to 20 cm^3 and cooled to −78 °C to afford red crystals, which were collected, washed with light petroleum (b.p. 40—60 °C) (2 × 5 cm^3) and dried *in vacuo*. Two further toluene extractions (2 × 50 cm^3) of the crude residue afforded a combined yield of 1.44 g (30%) (Found: C, 30.90; H, 5.40. $C_{14}H_{32}Cl_2P_3Ta$ requires C, 30.85; H, 5.95%). I.r. (Nujol, CsI, cm^{-1}): 3 090w, 1 440m br, 1 416s, 1 308m, 1 300m (sh), 1 289m, 1 278m, 1 270m, 1 107w, 1 068w, 993m, 945s br, 866m, 839m br, 831m, 806m, 775m, 759m, 720s, 710s, 703s, 660m, 379w, 352m, 295m, and 260s. N.m.r. (250 MHz, [$^2H_6$]benzene, 296 K): ^1H, δ 4.13 [m, 5 H, $^3J(PH)$ = 3.5, 2.7, C_5H_5],* 1.20 [vct, 18 H, *J*(PH) = 3.3, 2*trans*-PMe_3], and 1.11 [d, 9 H, $^2J(PH)$ = 6.7 Hz, PMe_3]; ^{31}P (broad-band decoupled), δ −26.46 (s, PMe_3) and −29.79 p.p.m. (s, 2*trans*-PMe_3); ^{13}C (broad-band decoupled), δ 88.65 (s, C_5H_5), 24.01 [d, $^1J(PC)$ = 21.9, PMe_3], and 16.83 p.p.m. [vct, *J*(PC) = 10.3 Hz, 2*trans*-PMe_3].

[$Ta(C_5Me_5)Cl_2(PMe_3)_2$] (**7**). Trimethylphosphine (2.03 g, 26.7 mmol) was condensed onto [$Ta(C_5Me_5)Cl_4$] (3.5 g, 7.63 mmol), magnesium turnings (0.18 g, 7.63 mmol), and thf (40 cm^3) frozen at −196 °C. Upon warming to room temperature, 1 atm of argon was introduced. After stirring for 1 h at ambient temperature the thf solution had developed a red coloration. The mixture was stirred for a further 9 h by which time all the magnesium had been consumed. Removal of the volatile components under reduced pressure and extraction of the brown residue into light petroleum (b.p. 40—60 °C) (80 cm^3) afforded a deep cherry-red solution. Filtration, followed by concentration under reduced pressure (20 cm^3) and cooling to −78 °C afforded red crystals. Repeated extractions of the crude residue, followed by crystallisation as above, gave a combined yield of 2.7 g (66%) (Found: C, 35.00; H, 6.05. $C_{16}H_{33}Cl_2P_2Ta$ requires C, 35.65; H, 6.05%). I.r. (Nujol, CsI, cm^{-1}): 1 425m, 1 300m, 1 286m, 1 280m (sh), 1 028m, 951s br, 844m, 731s, 667m, 415w, 355m, 336m (sh), and 277m. ^1H N.m.r. (250 MHz, [$^2H_6$]benzene, 0.037 mol dm^{-3}, 298 K): δ 91.45 (s, 15 H, C_5Me_5) and 20.56 (s, 18 H, $2PMe_3$). Magnetic moment ([$^2H_6$]benzene, 298 K): $\mu_{eff.}$ = 2.1 (Evans' method).[15]

[$Ta(C_5Me_5)Cl_2(\eta^2\text{-}PhC{\equiv}CPh)$] (**9**). Toluene (30 cm^3) was added to a weighed mixture of [$Ta(C_5Me_5)Cl_2(PMe_3)_2$] (0.4 g, 0.74 mmol) and diphenylacetylene (0.13 g, 0.74 mmol) at room temperature. The mixture was stirred for 2 weeks to give an orange solution which was filtered, concentrated (10 cm^3) and cooled to −78 °C to afford the product as orange crystals. Yield, 0.27 g (65%) (Found: C, 51.00; H, 4.60. $C_{24}H_{25}Cl_2Ta$ requires C, 51.00; H, 4.45%). I.r. (Nujol, CsI, cm^{-1}): 3 080w, 3 050w, 1 644w, 1 593w, 1 570w, 1 442s, 1 270w br, 1 176m, 1 160m, 1 073m, 1 030m, 940m, 925m, 840w, 788m, 769s, 717m, 710m, 692s, 608w, 553w, 520w, 390m, 345s, and 330s. N.m.r. (250 MHz, [$^2H_6$]benzene, 298 K): ^1H, δ 7.78 [d, 4 H, $^3J(H_oH_m)$ = 7.7, aryl H_o], 7.23 [dd, 4 H, $^3J(H_oH_m)$] = 7.7, $^3J(H_mH_p)$ = 7.14, aryl H_p], 7.04 [t, 2 H, $^3J(H_mH_p)$ = 7.14 Hz, aryl H_p] and 1.82 (s, 15 H, C_5Me_5); ^{13}C (broad band decoupled), δ 222.00 (s, $PhC{\equiv}CPh$), 141.60 (s, Ph–C_{ipso}), 130.29 (s, Ph–C), 128.84 (s, Ph–C), 128.60 (s, Ph–C), 120.95 (s, C_5Me_5), and 11.78 p.p.m. (s, C_5Me_5). Mass spectrum (e.i., 70 eV, ^{35}Cl): *m*/*z* 564 [*M*]$^+$, 528 [*M* − Cl − H]$^+$, and 386 [*M* − Ph_2C_2]$^+$.

[$Ta(C_5H_5)Cl_2(CO)(PMe_3)_2$] (**13**). A thick-walled glass 'Rotoflo' ampoule containing [$Ta(C_5H_5)Cl_2(PMe_3)_3$] (0.2 g, 0.37 mmol) in toluene (30 cm^3) was evacuated and cooled to −78 °C. One atmosphere of carbon monoxide was introduced into the vessel at this temperature. The mixture was allowed to warm to room temperature and stirred for 1 h. The excess of carbon monoxide was vented off carefully and the mixture was filtered. Removal of the solvent under reduced pressure afforded pure [$Ta(C_5H_5)Cl_2(CO)(PMe_3)_2$] as pink crystals, which were washed with light petroleum (b.p. 40—60 °C, 5 cm^3) and dried *in vacuo*. Yield, 0.16 g (87%) (Found: C, 29.00; H, 4.50. $C_{12}H_{23}Cl_2OP_2Ta$ requires C, 29.00; H, 4.65%). I.r. (Nujol, CsI, cm^{-1}): 3 080w, 1 890s br, 1 432m, 1 420m, 1 303m, 1 280m, 1 117w, 1 070w, 1 006m, 950s br, 861m, 846m, 838m, 829m, 820m, 810m, 737m, 729s, 670m, 600w, 523m, 500m, 356m, and 273s. N.m.r. (250 MHz, [$^2H_6$]benzene, 298 K): ^1H, δ 4.44 [t, 5 H, $^3J(PH)$ = 2.5, C_5H_5] and 1.19 [vct, 18 H, *J*(PH) = 4.1 Hz, $2PMe_3$]; ^{31}P (broad-band decoupled), δ −28.10 p.p.m. (s, $2PMe_3$); ^{13}C (broad-band decoupled), δ 247.76 [s, CO, $^2J(PC)$ unresolved], 89.75 (s, C_5H_5), and 16.41 p.p.m. [vct, *J*(PC) = 10.1 Hz, $2PMe_3$].

[$Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)$] (**14**). A thick-walled glass 'Rotoflo' ampoule was charged with [$Ta(C_5Me_5)Cl_2(PMe_3)_2$] (0.2 g, 0.37 mmol) and toluene (30 cm^3). The resulting red toluene solution was degassed at −78 °C and 1 atm of carbon monoxide was introduced into the vessel at this temperature. The mixture was warmed to room temperature with stirring to give a purple solution. After stirring for a further 3 h the solution was filtered, concentrated to 5 cm^3 and cooled in a solid CO_2 acetone slush bath to afford purple crystals. These were collected, washed with cold light petroleum (b.p. 40—60 °C) (2 × 5 cm^3), and dried *in vacuo*. Yield, 0.18 g (94%) (Found: C, 34.65; H, 4.65. $C_{15}H_{24}Cl_2O_2PTa$ requires C, 34.70; H, 4.65%). I.r. (Nujol, KBr, cm^{-1}): 1 988s, 1 900s, 1 880s, 1 428w, 1 305w, 1 290m sp, 1 283m sp, 975s, 960m, 745m, 483m, and 465m. N.m.r. (250 MHz, [$^2H_6$]benzene, 298 K): 1.75 (s, 15 H, C_5Me_5) and 1.26 [d, 9 H, $^2J(PH)$ = 9.8 Hz, PMe_3]; ^{31}P (broad-band decoupled), δ −26.60 p.p.m. (s, PMe_3); ^{13}C (broad-band decoupled), δ 238.10 [d, $^2J(PC)$ = 25.2, 2CO], 104.83 (s, C_5Me_5), 14.99 [d, $^1J(PC)$ = 27.0 Hz, PMe_3], and 11.28 (s, C_5Me_5).

cis-[$Ta(C_5Me_5)(CO)_2(PMe_3)_2$] (**15a**). Trimethylphosphine (0.15 g, 1.9 mmol) and thf (30 cm^3) were condensed onto a mixture of [$Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)$] (0.5 g, 0.96 mmol) and sodium amalgam (11.1 g amalgam, 0.5% w/w, 2.4 mmol) cooled to −196 °C in a 150-cm^3 'Rotoflo' glass ampoule. The mixture was warmed to room temperature and 1 atm of argon

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* Coupling pattern is a poorly resolved dt and the quoted *J* values are approximate; values obtained in [$^2H_8$]toluene.

was introduced. After stirring at room temperature for 24 h an orange-brown solution was formed. Removal of the volatiles under reduced pressure, followed by extraction into toluene (50 cm^3) and filtration afforded an orange-red solution. Concentration (10 cm^3) and cooling of this solution to −78 °C gave orange crystals. Yield, 0.3 g (61%) (Found: C, 41.00; H, 6.80. $C_{18}H_{33}O_2P_2Ta$ requires C, 41.20; H, 6.35%). I.r. (Nujol, KBr, cm^{-1}): 1 822s, 1 732s, 1 440m, 1 306w, 1 298w, 1 287m, 1 280m, 1 025w, 960s, 941s, 855w, 843w, 715w, 665m. N.m.r. (250 MHz, [$^2H_6$]benzene, 298 K): ^{1}H, δ 1.93 (s, 15 H, C_5Me_5) and 1.13 [vct, 18 H, J(PH) = 6.4 Hz, 2PMe$_3$]; ^{31}P (broad-band decoupled), δ 15.97 p.p.m. (s, 2PMe$_3$); ^{13}C (broad-band decoupled), δ 278.11 [d, ^2J(PC) = 22.9 Hz, 2CO], 104.47 (s, C_5Me$_5$), 22.96 (m, 2PMe$_3$), and 12.40 p.p.m. (s, C$_5$$Me_5$). Mass spectrum (c.i., isobutane carrier gas): m/z 525 $[M + H]^+$, 497 $[M - CO + H]^+$, 468 $[M - 2CO]^+$, 449 $[M - PMe_3 + H]^+$, 421 $[M - PMe_3 - CO + H]^+$, 391 $[M - 2CO - PMe_3 - H]^+$, and 373 $[M - 2PMe_3 + H]^+$.

$[Ta(C_5Me_5)(CO)_4]$ (**17**). (*a*) *From* $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$. Tetrahydrofuran (40 cm^3) was vacuum transferred onto a mixture of $[Ta(C_5Me_5)Cl_2(CO)_2(PMe_3)]$ (0.5 g, 0.96 mmol) and sodium amalgam (11.1 g, 0.5% w/w, 2.4 mmol) in a 150-cm^3 'Rotoflo' glass ampoule cooled to −78 °C. One atmosphere of carbon monoxide was then introduced and the mixture was allowed to warm to room temperature with stirring. After 24 h, the colour had changed from purple to orange-brown. The volatile components were removed under reduced pressure and the residue was extracted into toluene (80 cm^3). Filtration of the resulting orange solution, followed by concentration to 10 cm^3 and cooling to −78 °C, afforded $[Ta(C_5Me_5)(CO)_4]$ as orange crystals. Yield, 0.26 g (65%).

(*b*) *From* $[Ta(C_5Me_5)Cl_4]$. Trimethylphosphine (0.084 g, 1.1 mmol) was condensed onto a mixture of $[Ta(C_5Me_5)Cl_4]$ (0.5 g, 1.1 mmol), sodium amalgam (22.5 g amalgam, 0.5% w/w, 4.95 mmol), and thf (40 cm^3) cooled in a methanol slush bath (−94 °C) in a thick-walled 150-cm^3 'Rotoflo' glass ampoule. One atmosphere of carbon monoxide was then introduced into the vessel. Upon warming to room temperature and stirring for 1 h, the solution turned red-brown. At this point, the carbon monoxide atmosphere was replenished at −94 °C. Continued stirring at room temperature for a further 20 h resulted in further changes in colour from purple to brown and finally orange-brown. The subsequent work-up procedure is identical to that described in (*a*) and gave $[Ta(C_5Me_5)(CO)_4]$ in 47% yield (0.22 g). The filtrate from this crystallisation contained a second complex, formulated as $[Ta(C_5Me_5)(CO)_3(PMe_3)]$ in *ca.* 7% yield (^{1}H n.m.r.) (Found: C, 39.70; H, 3.65. $C_{14}H_{15}O_4Ta$ requires C, 39.25; H, 3.55%). I.r. (thf solution, CsI, cm^{-1}): 2 020s sp and 1 905s br. ^{1}H N.m.r. (250 MHz, [$^2H_1$]chloroform, 298 K): 2.14 (s, C_5Me_5). Mass spectrum (e.i., 70 eV): m/z 428 $[M]^+$, 400 $[M - CO]^+$, 370 $[M - 2CO - 2H]^+$, 342 $[M - 3CO - 2H]^+$, and 314 $[M - 4CO - 2H]^+$.

$[Ta(C_5Me_5)(O)Cl_2]$ (**18**). A thick-walled, 150-cm^3 glass 'Rotoflo' ampoule, containing a saturated toluene solution (25 cm^3) of $[Ta(C_5Me_5)Cl_2(PMe_3)_2]$ (0.5 g, 0.93 mmol) was cooled to −78 °C and evacuated. One atmosphere of carbon dioxide was introduced into the vessel and the mixture was allowed to warm to room temperature. After stirring for 16 h, a suspension of yellow microcrystals was in evidence. These were separated by filtration, collected and dried *in vacuo*. Further recrystallisation was unnecessary. Yield, 0.15 g (40%) (Found: C, 29.60; H, 3.85. $C_{10}H_{15}Cl_2OTa$ requires C, 30.00; H, 3.75%). I.r. (Nujol, CsI, cm^{-1}): 1 430m, 1 070w, 1 025m, 803w, 675s br, 610w, 598m, 550m, 436m, 387s, 330s, 310s, 291s. ^{1}H N.m.r. (250 MHz, [$^2H_6$]benzene, 298 K): δ 2.22 (s, C_5Me_5). Mass spectrum (c.i., isobutane carrier gas, ^{35}Cl): m/z 805 $[M_2 + H]^+$, 769 $[M_2 - Cl]^+$, and 403 $[M + H]^+$.

X-*Ray Crystallography*.—Crystal data for complexes (**4**) and (**14**) are summarised in Table 2. All measurements were made at room temperature (295 K) on a Stoe–Siemens diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å). Crystals were sealed in Lindemann glass capillary tubes. Cell parameters were refined from 2θ values (20—25°) of 32 reflections measured at ±ω to minimise systematic errors. Intensity data were collected in a ω—θ scan mode covering a range 0.51 below α_1 to 0.51° above α_2 [0.68° for (**14**)]. No significant variation was observed in the intensities of three standard reflections checked periodically. The data set for (**4**) consisted of the unique octant with all indices positive, a second octant with h negative, and some equivalent reflections with negative k; a whole sphere of data was collected for (**14**). Semi-empirical absorption corrections were applied.[57]

For structure determination, observed data were taken as those with $F > 4\sigma_c(F)$, where σ_c is based on counting statistics only. The structures were solved from Patterson and difference syntheses,[58] and refined by blocked-cascade least-squares methods to minimise $\Sigma w\Delta^2$, with $\Delta = |F_o| - |F_c|$ and $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$ $(G = F_o/F_{max.},\ H = \sin\theta/\sin\theta_{max.})$.[58] An isotropic extinction parameter x was refined, whereby $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were located in a difference synthesis for (**14**), and were refined subject to constraints: C–H 0.96 Å, H–C–H 109.5°, U(H) = 1.2 U_{eq}(C). No H atoms were located for (**4**), presumably because of torsional disorder of the methyl groups.

The absolute structure was determined by refinement of the η parameter.[59] The value of 0.97(4) for (**4**) indicates the correct hand; for (**14**), the value of 0.45(5) indicates that the structure may be partially twinned. Scattering factors were taken from ref. 60 The largest peaks in the final difference syntheses were close to the Ta atoms.

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

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