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Synthesis, Characterization and Behavior in Solution of Tantalum(III) and Tantalum(IV) Halide, Hydride and Cyclopentadienyl Dimethylphenylphosphane Adducts

L. G. HUBERT-PFALZGRAF*, M. TSUNODA and J. G. RIESS

Laboratoire de Chimie de Coordination, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034 Nice, France

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Reduction of tantalum pentahalides Ta_2X_{10} (X = Cl, Br) by magnesium turnings in CH_2Cl_2 was investigated in the presence of various phosphanes, and found to be highly dependent on the ligand. In the case of phenyldimethylphosphane it led to tantalum(III) derivatives, $Ta_2X_6(PhPMe_2)_4$ (X = Cl, Br) and $[TaBr_3(PhPMe_2)]_n$ in high yields. These compounds are diamagnetic in the solid and in solution. The chloride is very stable, both in the solid and in solution, while spontaneous reduction of the metal was observed in solution for the bromo derivatives, yielding ionic species. Reaction between Me_3SnCp and $Ta_2Cl_6(PhPMe_2)_4$ led to $Cp_2Ta_2Cl_4(PhPMe_2)_2$, the first dimeric cyclopentadienyltantalum(III) derivative reported, while the addition of molecular hydrogen under normal pressure gave a stable hydride $Ta_2Cl_6(PhPMe_2)_4H_2$. All products were characterized by elemental analysis, IR, ^1H and ^{31}P spectroscopy, molecular weight data and mass spectrometry.

Introduction

Simple 'unprotected' tantalum trihalides have long been known to be insoluble, inert, often non-stoichiometric materials, with compositions ranging from $TaX_{2.9}$ to $TaX_{3.1}$ (X = Cl, Br), which probably have polymeric structures [1]. On the other hand, the *molecular* chemistry of derivatives of niobium and to an even larger extent of tantalum in their lower oxidation states is only recent, and still limited, in spite of the interesting reactivity patterns [2] and catalytic activity they have already been shown to display [2, 3]. In 1972 Kepert *et al.* obtained $[TaCl_3(CH_3CN)_2]_2$ [4], a compound whose formulation apparently corresponded to oxidation state 3 for the metal, but which was later shown by X-ray crystallography [5] to be a tantalum(V) compound having a 1,2-dimethyl–1,2-diimidoethene bridging ligand resulting from the reductive coupling of two acetonitrile molecules. The first true tantalum(III) halide adducts, $Ta_2X_6(SC_4H_8)_3$ (X = Cl, Br) were reported only in 1978 by Templeton and McCarley [6]. Schrock *et al.* then reported a monomeric tantalum(III) adduct, *trans-mer*-$TaCl_3(PMe_3)_2(C_2H_4)$, obtained by spontaneous reduction of an alkylidene [7]. Finally, the reduction of $TaCl_4(dmpe)_2$ by sodium amalgam or sodium naphthalenide gave directly a tantalum(II) compound $TaCl_2(dmpe)_2$, with no evidence for tantalum(III) derivatives [8].

We are currently investigating the molecular chemistry of niobium and tantalum in their low oxidation states [9, 10]. The convenient synthesis of $Nb_2Cl_6(PhPMe_2)_4$ by a one-step reduction of Nb_2Cl_{10} by magnesium in the presence of the ligand [9], has stimulated similar studies on the tantalum pentahalides. The recent account of the synthesis and characterization of $Ta_2Cl_6(PMe_3)_4$ by Sattelberger *et al.* [11] prompts us to report the preparation and characterization of $Ta_2X_6(PhPMe_2)_4$ (X = Cl, Br) and $[TaBr_3(PhPMe_2)]_n$; $Ta_2Cl_6(PhPMe_2)_4$ was further characterized as its cyclopentadienyl $Cp_2Ta_2Cl_4(PhPMe_2)_2$ and hydride $Ta_2Cl_6(PhPMe_2)_4H_2$ derivatives.

The new compounds were characterized by elemental analysis, infrared and NMR spectroscopy (^1H, ^{31}P, ^{13}C (Table I)), magnetic susceptibility measurements, and by mass spectrometry in the case of the more volatile cyclopentadienyl derivative.

Results and Discussion

Reduction of Tantalum(V) Chloride by Magnesium

The reaction between Ta_2Cl_{10} and an excess of phenyldimethylphosphane (ligand to metal ratio ⩾ 3)—in the absence of magnesium—in CH_2Cl_2 led to a tantalum(IV) derivative, as evidenced by EPR. When the reaction was conducted in the presence of an excess of magnesium turnings, the oxidation of

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*Author to whom all correspondence should be addressed.

TABLE I. Spectroscopic Data.

	IR (Nujol) νM–X, νM–P (cm^{-1})	NMR (in CH_2Cl_2, 25 °C)	
		δ^{31}P (ppm)	δ^{13}C (ppm)
$Ta_2Cl_6(PhPMe_2)_4$	350vs, 290m, 275m	75.6, $\underline{47.5}$[a]; 22.2	–
$[TaBr_3(PhPMe_2)_2]_n$	390s, 350sh, 320sh, 290s, 275s, 200w	20.6; 19.6 $\underline{-1.5}$ (J_{P-H}) = 528 Hz)	– –
$[TaBr_3(PhPMe_2)]_n$	380s, 360s, 290s, 280sh, 225vs, 215vs	68.8, 69.70 $\underline{-2}$ (J_{P-H} = 528 Hz)	–
$Cp_2Ta_2Cl_4(PhPMe_2)_2$	410sh, 340sh, 330s, 310s, 290sh, 280vs, 265sh, 255sh	23 ppm	124.3 (Cp) (J_{C-H} = 175 Hz; J_{C-P} = 4.7 Hz)
$Ta_2Cl_6(PhPMe_2)_4H_2$	395w, 300vs, 285sh, 255sh	[b]	–

[a] The main resonances are underlined. [b] The longer time required for ^{31}P measurements provoked extensive decomposition.

magnesium was observed,* and the reaction was complete after 3 days. The amount of $MgCl_2$ formed indicates a reduction of tantalum to its +3 oxidation state in a compound that is soluble in the reaction media. The isolation of this product in reproductible yields was very difficult, because of its tendency to form oils, and of its extreme air-sensitivity both in solution and in the solid state. We succeeded, however, by carefully avoiding moisture, in isolating a crystalline diamagnetic material. Its spectroscopic data (IR, ^{31}P, NMR) and elemental analysis are compatible with the formulation $Ta_2Cl_6(PhPMe_2)_4$. In addition, it was characterized by the less air-sensitive cyclopentadienyl and hydride derivatives (see below).

The influence of the phosphorus ligand on the course of the reduction reactions was also investigated, and it was found that the reducing ability of magnesium towards Ta_2Cl_{10} is indeed strongly dependent on the nature of the phosphorus ligand: only tantalum(V) adducts were obtained when the crowded PCy_3 (Cy = cyclohexyl) and $P(tBu)_3$ (tBu = tertiobutyl) phosphanes were used [13], while the previously reported tantalum(IV) adduct [8] $TaCl_4(dmpe)_2$ was obtained with 1,2-bis (dimethylphosphino)ethane. The choice of $PhPMe_2$ thus appears to be particularly suitable if one wants to achieve reduction to oxidation state 3 by magnesium.

The reactivity patterns of Ta_2X_{10} (X = Cl, Br) with respect to Mg in the presence of various phosphanes can be summarized as shown in Scheme 1.

Reactivity of $Ta_2Cl_6(PhPMe_2)_4$

Reaction between $Ta_2Cl_6(PhPMe_2)_4$, formed *in situ*, and trimethylcyclopentadienyltin in CH_2Cl_2 led to $Cp_2Ta_2Cl_4(PhPMe_2)_2$, which was isolated in 76% yield and fully characterized, thus confirming the identity of the parent tantalum(III) compound. The reaction illustrates an aspect of the reactivity of the latter compound as a dimer in which the dimeric form is maintained, which suggest the presence of a metal–metal interaction of bond order higher than one [12]. This compound appears to be the first dimeric Ta(III) cyclopentadienyl derivative reported so far.

$Ta_2Cl_6(PhPMe_2)_4$ dissolved in toluene reacts with molecular hydrogen (1 atm) at 25 °C to give, after 60 min, a blue slightly air-sensitive diamagnetic solid, in high yields. Elemental analyses are similar to those of the starting tantalum derivatives, but IR and quantitative ^{1}H NMR data are in agreement with the formation of $Ta_2Cl_6(PhPMe_2)_4H_2$, which corresponds formally to a tantalum(IV) adduct.

Characterization of the Chloride Derivatives

All compounds were found to be diamagnetic in the solid state and in solution; this may be due to a direct metal–metal interaction or to superexchange phenomena between halogen bridges, which in both cases implies at least dimeric structures. The extreme air-sensitivity of the various derivatives precluded molecular weight measurements in solution. Their solubility (and especially that of $Ta_2Cl_6(PhPMe_2)_4$, which is more soluble than its niobium analog) in common organic solvents such as benzene, dichloromethane, chloroform or acetonitrile, is however indicative of the absence of extensive metal–metal bonding. A molecular complexity of 2 was measured by vapor pressure osmometry for $[CpTaCl_2(PhPMe_2)]_2$ in benzene (M found 765, M calcd 455 for the monomer), suggesting also a dimeric structure for $Ta_2Cl_6(PhPMe_2)_4$ [12].

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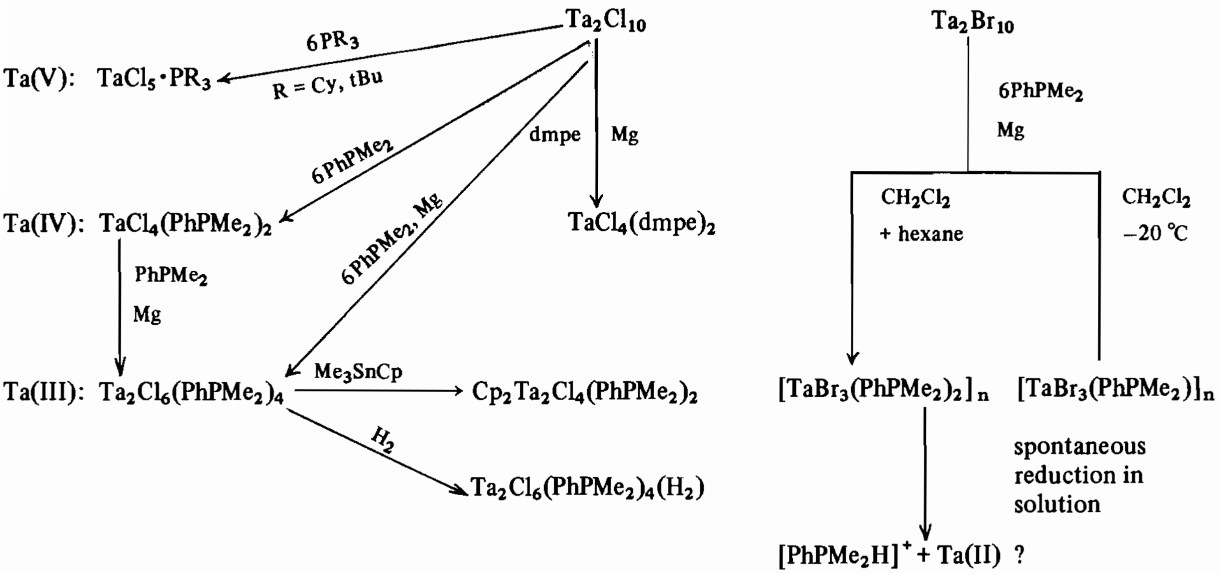
*Sometimes the magnesium turnings must be activated by adding a drop of mercury or small amounts of diethylether (less than one mol per mol of the metal chloride). Larger quantities lead to degradation of the ether as evidenced by the presence of a νOH stretching frequency of the final product [15].



Scheme 1. Reactivity of various phosphanes towards Ta_2X_{10} (X = Cl, Br) in CH_2Cl_2.

The IR spectra measured on the solid state exhibit the absorption bands of the ligand, while the presence of metal–halogen absorptions located between 400 and 200 cm^{-1} further supports a dimeric structure having bridging halogen atoms [14]. In the spectra of $Cp_2Ta_2Cl_4(PhPMe_2)_2$ can also be seen one of the absorption bands characteristic of the cyclopentadienyl ring at 3105 cm^{-1}, the other probably being masked by those of the phenyl group of the ligand. The reaction between $Ta_2Cl_6(PhPMe_2)_4$ and molecular hydrogen is confirmed by the appearance of an absorption at 1730 cm^{-1}, which can be attributed to a terminal νTa–H stretching [15].

The ^1H NMR spectra of $Ta_2Cl_6(PhPMe_2)_4$ in CH_2Cl_2 at room temperature show several doublets in the Me–P region, whose relative intensities were found to be dependent on dilution and temperature, thus indicating the presence of several distinct molecular species in the solution. This was no surprise, since the tendency of early transition metal derivatives to give complex mixtures of isomers in dynamic equilibrium in solution is well established [16]. Seven geometrical isomers can be drawn for $Ta_2Cl_4(\mu^2\text{-}Cl)_2(PhPMe_2)_4$ if one postulates an octahedral environment for the metal. The fact that the methyl groups may be diastereotopic in some of these isomers further complicates the analysis of the ^1H NMR spectra by giving doublets of signals displaying the same area. We therefore measured $^{31}P\{^1H\}$ NMR spectra, which were more informative. The free ligand (δ = −45 ppm) was never detected. Several singlets of concentration-dependent area, among which one, at δ = 47.5 ppm, is always largely predominant (*ca.* 60% total peak area), were found at room temperature, and attributed to distinct molecular species. The ligands appear to occupy equivalent positions in the predominant species. Thus the main isomer appears to display a structure different from that of $Ta_2Cl_6(PMe_3)_4$ in the solid or in solution [11].

The molecular constitution of solutions of $Cp_2Ta_2Cl_4 \cdot (PhPMe_2)_2$ was also investigated. It was less complex, since only one isomer could be detected, in solvents as different as chloroform, dichloromethane, toluene or acetonitrile. Thus its proton NMR spectra measured in $CDCl_3$ at room temperature show only one sharp cyclopentadienyl signal at 6.75 ppm (J_{CH} = 175 Hz), and one doublet at 2.15 ppm (J = 10 Hz) for the PMe_2 groups. No change in the spectra was observed by lowering the temperature down to −60 °C. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra confirm that only one isomer having equivalent cyclopentadienyl (δ = 124.3 ppm; J_{C-P} = 4.7 Hz) and phosphorus ligands ($\delta^{31}P$ = 23 ppm) was present. It is not known at present if the cyclopentadienyl groups are in *cis* or *trans* positions.

The hydride derivative shows a broad* singlet at δ = −3 ppm, in the ^1H NMR spectra at room temperature, which we assign, in agreement with the IR data and the integration ratios in the NMR, to a pair of chemically equivalent terminal hydride ligands. This means that $Ta_2Cl_6(PhPMe_2)_4$ exhibits a different reactivity pattern as compared to $Ta_2Cl_6(PMe_3)_4$ [11] towards molecular hydrogen.

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*Probably as a result of the large quadrupolar moment of the tantalum nuclei.

Reduction of Tantalum(V) Bromide by Magnesium

Since our aim was to produce a convenient starting material for developing the molecular chemistry of tantalum in its low oxidation states, and considering the difficulties we had met in the isolation of $Ta_2Cl_6(PhPMe_2)_4$, we also investigated the reactions of the more reducible Ta_2Br_{10} in similar conditions. The reduction of tantalum(V) to tantalum(III) by magnesium was also observed, but the stoichiometry of the product isolated was found to depend on the isolation procedure (Scheme 1). Thus green-yellow crystals which analysed as $TaBr_3(PhPMe_2)$ were obtained by precipitation on cooling the concentrated CH_2Cl_2 medium at –20 °C, while crystals of comparable color but of formula $TaBr_3(PhPMe_2)_2$ were isolated if the precipitation was induced at room temperature by adding hexane. The products are both highly air-sensitive, but their isolation, in nearly quantitative yields (92% and 97%, respectively), was favored with respect to their chloro analogs by lower solubilities.

Behavior in Solution of the Bromo Tantalum(III) Dimethylphenylphosphane Adducts

Once they have been isolated as crystalline diamagnetic solids, the bromo derivatives show properties that are definitely distinct from those of the chlorides: first, they become only sparingly soluble in the usual solvents, which may indicate the formation of tetramers of higher molecular weight clusters; secondly, they undergo spontaneous reduction of the metal in various protic solvents, as evidenced by the immediate formation of the phosphonium ion $PhPMe_2H^+$ in the ^{31}P NMR. Since the phosphonium ion was not detected in the infra-red spectra measured on solid $[TaBr_3(PhPMe_2)]_n$ or $[TaBr_3(PhPMe_2)_2]_n$, its formation indicates a change in the formal oxidation state of phosphorus upon dissolution, and therefore a spontaneous reduction of the tantalum species. Furthermore, the phosphorus spectrum measured on the reaction medium before isolation of the bromo derivatives shows different molecular species at 20.7, 21,5, 28.5, 47.9 ppm, respectively, the last being largely predominant. The instability of the bromo derivatives in CH_2Cl_2, as well as the observation of different chemical shifts for the $PhPMe_2$ complexes after isolation from CH_2Cl_2 media, suggests that an important structural change, probably in the molecular complexity, occurs by isolation.

The ^1H and ^{31}P spectra of the isolated bromo derivatives show the presence of several species. For instance, the ^{31}P spectra of CH_2Cl_2 or CH_3CN solutions of $[TaBr_3(PhPMe_2)]_n$ exhibit a sharp doublet ($\delta = -1.5$ ppm; $^1J_{P-H} = 528$ Hz, confirmed by ^1H decoupling) as the major resonance (70% of the total peak area) accompanied by several smaller peaks located around 69 ppm. No free ligand was detected. The ^1H NMR spectrum measured on freshly prepared solutions confirms the immediate formation of a phosphonium salt ($\delta = 8.38$ ppm; J = 528 Hz). Similar behavior was observed for solutions of $[TaBr_3(PhPMe_2)_2]_n$, as shown by the presence of the same phosphonium ion as the main phosphorus species (75% of total peak area), but the other ^{31}P signals were found at different fields (20.6 and 19.6 ppm). The observation of ^1H and ^{31}P spectra of high resolution means that the reduction of the metal produces species remaining diamagnetic. Unfortunately, the fast electron transfer reactions between the metal and the phosphorus ligand suggested by the NMR data could not be investigated cleanly by electrochemical techniques. Conductivity measurements confirm the formation of ionic species in solution; for instance, $\Lambda = 15\Omega^{-1}$ $cm^2 \cdot mol^{-1}$ for $[TaBr_3(PhPMe_2)_2]_n$ 0.5 10^{-3} molar in CH_2Cl_2 [17].

We are presently investigating the reactivity of $Ta_2Cl_6(PhPMe_2)_4$ and $Cp_2Ta_2Cl_4$ $(PhPMe_2)_2$, especially towards small molecules and unsaturated species.

Experimental

All the manipulations were conducted under dry de-oxygenated argon, using Schlenk tubes and vacuum-line techniques. All solvents were carefully distilled over the standard drying reagents and deoxygenated. Trimethylcyclopentadienyltin was prepared as described in the literature [18]. Phenyldimethylphosphane (Strem), tantalum pentachloride (Fluka) and tantalum pentabromide (Alfa Inorganics) were used without further purification. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 577 spectrometer. NMR spectra were obtained on a WH-90 Bruker spectrometer operating in the Fourier transform mode (^{31}P chemical shifts are given positively towards low fields relatively to 85% H_3PO_4 as external reference). Molecular weight data were obtained on a Knauer vapor pressure osmometer. The RPE spectra were registered on an ER-200 Bruker machine. Conductivity measurements were performed with a Tacussel CD 6 NG apparatus on dichloromethane solution. Mass spectra (VG Micromass 70-70F spectrometer) and microanalysis data were effected by the Service Central de Microanalyses du C.N.R.S.

Synthesis of $Ta_2Cl_6(PhPMe_2)_4$

Phenyldimethylphosphane (3.6 ml, 25.1 mmol) was added to a suspension of Ta_2Cl_{10} (3 g, 4.05 mmol) and magnesium turnings (0.230 g) in 37 ml of CH_2Cl_2 at room temperature. Reduction by magnesium started after 60 mn; and after 48 h stirring, the dark green reaction mixture was filtered, leaving the magnesium derivatives and a green filtrate.

The filtrate was evaporated to dryness, giving an oily residue, which was redissolved in a small volume (≃ 3 ml) of CH_2Cl_2. Addition of toluene (≃ 5 ml) induced crystallization after about 2 days at room temperature. A large amount of freshly distilled diethylether (≃ 15 ml) was then added and an oily phase separated out. This oil was converted to crystals after maintaining it at room temperature for 1 week. The mother liquor was separated out using a syringe and the crystals were washed with pentane, dried in high vacuum, and recrystallized in CH_2Cl_2-Et_2O to yield 2.96 g (65%) of highly air-sensitive, olive-green crystals of $Ta_2Cl_6(PhPMe_2)_4$ soluble in CH_2Cl_2 and CH_3CN. *Anal.* Calcd for $C_{32}H_{44}P_4Cl_6Ta_2$: C, 34.07; H, 2.86; Cl, 18.90; P, 11.00. Found: C, 32.63; H, 2.72; Cl, 17.10; P, 10.52%. *IR*: (cm^{-1}): 1590 m, 1300s, 1260m, 1135vs, 1115vs, 1075sh, 1025m, 1000w, 950vs, 925vs, 875vs, 850s, 790s, 750vs, 690vs, 495m, 480m, 440m; 390sh, 365m, 310sh, 290s, 280s.

Synthesis of [$TaBr_3(PhPMe_2)_2$]$_n$

A solution of $PhPMe_2$ (1.20 ml, 8.40 mmol) in 15 ml CH_2Cl_2 was added to a stirred suspension of Ta_2Br_{10} (1.72 g, 1.48 mmol) and magnesium turnings (0.22 g, 9.0 mmol) in 45 ml of the same solvent at room temperature. The color changed rapidly from yellow to orange–red and then to green-yellow while the attack of magnesium started. Stirring was maintained for 36 to 48 h, giving a dark green suspension. The precipitate of magnesium by-products was eliminated by filtration and carefully washed with CH_2Cl_2. The filtrate was evaporated and the oily residue was extracted with a minimum of CH_2Cl_2. The solution was concentrated to half of its volume and the same volume of hexane was carefully added to give two layers. Slow diffusion of hexane at room temperature in the CH_2Cl_2 induced crystallization. After two days, the crystallization was improved by adding more hexane. After about 5 weeks, the mother liquor was separated out with a syringe, the precipitate was washed with hexane and dried in high vacuum giving 1.9 g (92%) of green-yellow crystals of [$TaBr_3(PhPMe_2)_2$]$_n$. The compound is highly air-sensitive, insoluble in hexane, toluene, diethylether, and slightly soluble in acetonitrile and dichloromethane. *Anal.* Calcd. for $C_{16}H_{22}P_2Br_3Ta$: C, 27.55; H, 3.18; Br, 34.40; P, 8.89. Found: C, 26.83; H, 3.28; Br, 34.32; P, 8.19. *IR*: (cm^{-1}): 1590w, 1300m, 1290m, 1260m, 1130m, 1115w, 1035s, 1025vs, 945m, 915w, 870w, 735s, 680m, 525m, 425s; 390s, 350sh, 320sh, 290s, 275s, 200w.

Synthesis of [$TaBr_3(PhPMe_2)$]$_n$

The same procedure was followed to reduce the tantalum pentabromide (1.7 g, 1.47 mmol) to its oxidation state 3. After separation of the excess of magnesium and its derivatives, the CH_2Cl_2 filtrate was concentrated at -20 °C and some crystals formed just before the obtaining of the oily residue. The mixture was left at -30 °C for about two weeks, the mother liquor was then separated out with a syringe, the precipitate washed with hexane and dried in high vacuum. Finally 1.57 g (96%) of light green crystals of $TaBr_3(PhPMe_2)$, slightly soluble in CH_2Cl_2, insoluble in C_6H_6, MeCN and CH_3NO_2, were collected. *Anal.* Calcd for $C_8H_{11}PBr_3Ta$: C, 17.18; H, 1.98; Br, 42.90; P, 5.55. Found: C, 18.71; H, 2.06; Br, 41.25; P, 5.95%. *IR* (cm^{-1}): 1590w, 1305s, 1295s, 1160w, 1130vs, 1120sh, 1045vs, 1025vs, 995m, 975sh, 945s, 922m, 912m, 870s, 790sh, 760vs, 740vs, 735sh, 675s, 490m, 482m, 455w, 430m; 380s, 360s, 290s, 280sh, 225vs, 215vs.

Synthesis of [$CpTaCl_2(PhPMe_2)$]$_2$

$PhPMe_2$ (2.0 ml, 14.0 mmol) was added to a stirred suspension of Ta_2Cl_{10} (2.43 g, 3.37 mmol) and magnesium turnings (0.53 g, 21.8 mmol) in 35 ml CH_2Cl_2 at room temperature. The color of the suspension changed from white to orange and then to olive green. Stirring was maintained for 48 h. The dark green reaction mixture was filtered and the precipitate washed with CH_2Cl_2, leaving magnesium and magnesium chloride. To the filtrate (≃ 40 ml) (assumed to be a solution of $Ta_2Cl_6(PhPMe_2)_4$ in a 90% yield) a solution of Me_3SnCp (2.20 ml, 13.24 mmol) in 5 ml CH_2Cl_2 was added at room temperature, and the coloration went progressively from dark green to dark reddish. Stirring was maintained for 3 days. The grey–brown reaction mixture was then evaporated to dryness, leaving a dark oily residue, which was washed several times with pentane to remove the stannic derivatives. Extraction with toluene (≃ 30 ml) gave a green solution, which was evaporated to dryness; then the traces of solvent were removed under high vacuum. 2.34 g (76%) of [$CpTaCl_2\cdot PhPMe_2$]$_2$ were obtained as a dark green powder, soluble in toluene, dichloromethane, chloroform and acetonitrile, but only slightly soluble in THF (with decomposition). *Anal.* Calcd for $C_{26}H_{32}Cl_4P_2Ta_2$: C, 34.28; H, 3.54; Cl, 15.60; P, 6.81. Found: C, 33.59; H, 3.49; Cl, 16.34; P, 6.89%. *IR*: (cm^{-1}): 3105w; 1590w, 1418m, 1300m, 1283m, 1105w, 1025m, 952s, 912s, 864s, 754s, 720w, 700w, 422m; 410sh, 340sh, 330s, 310s, 290sh, 280vs, 265sh, 255sh. *Mass spectrometry* (110 °C, 70 eV): $CpTaCl_2(C_6H_3)(PhPMe_2)$ 15%, $CpTaCl_2(PhPMe_2)$ 2%, $CpTaCl(C_3H_6P)$ 18%, $CpTaCl(C_3H_5)$ 15%, CpTaCl 14%, $PhPMe_2$ 100%. *NMR*: ($CDCl_3$): ^{1}H δ = 6.75s (Cp), 2.15d (10 Hz) (PMe_2); ^{13}C{^{1}H}: 124.3 (Cp); 13.25 (29.4 Hz) (PMe_2); 131.7 (5.9 Hz), 129.9 (2.9 Hz), 127.8 (8.8 Hz) (C_6H_5).

Synthesis of $Ta_2Cl_6(PhPMe_2)_4H_2$

Molecular hydrogen was bubbled for about 5 mn into a reaction vessel containing a dark green suspension of $Ta_2Cl_6(PhPMe_2)_4$ (568 mg, 0.50 mmol) in 10 ml toluene at room temperature. Stirring was maintained under an atmosphere of hydrogen for an hour, and the reaction mixture became dark blue, with precipitation of a dark blue product. After concentration, the solid was removed by filtration, and dried in high vacuum. Finally 545 mg (≃ 96%) of dark blue crystals of $Ta_2Cl_6(PhPMe_2)_4H_2$ (m.p. 55°, 160 °C dec.), insoluble in toluene, THF slightly soluble in CH_2Cl_2, soluble in CH_3CN (with decomposition), were obtained. *Anal.* Calcd for $C_{32}H_{46}P_4Cl_6Ta_2$: C, 34.01; H, 4.11; Cl, 18.86; P, 10.98. Found: C, 33.15; H, 3.97; Cl, 19.66; P, 9.86%. *IR*: 1730w (νTa–H); 1585w, 1575w, 1305m, 1295m, 1260m, 1130s, 1120s, 1100s, 1085s, 1070s, 1050s, 1020s, 980w, 955m, 945m, 920m, 875m, 815vs, 740vs, 690s, 495m; 395w, 300vs, 285sh, 255sh.

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