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Monomeric Pentacoordinated $TaBr_3(PPhMe_2)_2$. Synthesis, Crystal Structure, and Aliphatic C–H Activation in Solution

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Reduction of $TaBr_5$ by magnesium turnings activated by diethyl ether in CH_2Cl_2 in the presence of phenyldimethylphosphine offers the paramagnetic compound $TaBr_3(PhPMe_2)_2$, which is the first monomeric Ta(III) adduct to be structurally characterized. It crystallizes in the monoclinic system ($P2_1/c$) with unit cell dimensions a = 8.46 (1) Å, b = 20.80 (2) Å, c = 8.836 (8) Å, β = 98.77 (5)°, and Z = 4. $TaBr_3(PhPMe_2)_2$ consists of square-pyramidal molecules, with one bromine in two possible apical positions. The phosphorus ligands occupy cis positions in a flat square-pyramidal polyhedron (basal angle ≃ 173°). The apical tantalum–bromine bond (2.382 (2) Å average) is significantly shorter than the basal one (2.524 (2) Å average). The solution behavior of this unsaturated d^2 compound is puzzling. Dynamic equilibrium between diamagnetic species and paramagnetic $TaBr_3(PhPMe_2)_2$ stabilized by aromatic agostic C–H interactions is observed in CH_2Cl_2 solutions. Spontaneous intra- and intermolecular oxidative C–H additions involving the methyl groups occur in acetonitrile with formation of Ta(V) species having η^2-CHPMePh or bridging η^2-CH_2PMePh moieties.

Introduction

The molecular chemistry of niobium(III) or tantalum(III) halide derivatives appears dominated so far by their tendency to form dinuclear, diamagnetic adducts such as $M_2X_6L_3$ (M = Nb, Ta; X = Cl, Br; L = C_4H_8S (THT);[1,2] X = Cl, L = SMe_2,[3,4] PCy_3[5]) and $M_2Cl_6L_4$ (M = Nb, Ta; L = PMe_3,[6] $PhPMe_2$;[7] M = Ta, L = py,[8] γ-pic[9]) with monodentate ligands. The monomeric adducts have been restricted to the paramagnetic $NbCl_3L_3$ (L = py, γ-pic, 3,5-Me_2py[8]) and $TaX_3(PMe_3)_3$ (X = Cl, Br,[10] I[11]) compounds. The tantalum(III) chloro derivative rapidly decomposes in solution to give $Ta_2Cl_6(PMe_3)_4$.[10]

We wish now to report the synthesis and X-ray structure determination of $TaBr_3(PhPMe_2)_2$. It represents the first monomeric Nb(III) or Ta(III) halogen adduct for which X-ray data are available, as well as the first example of the unprecedented MX_3L_2 (M = Nb, Ta) stoichiometry. This pentacoordinated species crystallizes as square-pyramidal molecules, with an apical bromine atom occupying either vacant site of the basal square plane. In acetonitrile solutions, $TaBr_3(PhPMe_2)_2$ undergoes spontaneous C–H activation reactions to Ta(V) species involving the Me groups.

Experimental Section

All manipulations (including handling of the monocrystals) were routinely performed under argon by using Schlenk-tube and vacuum-line techniques. Solvents were purified by standard methods; tantalum(V) bromide (Alfa Inorganics) and phenyldimethylphosphine (Fluka) were used as received. The IR and ESR spectra were recorded on Perkin-Elmer 577 and Bruker ER-200D spectrometers, respectively. All NMR samples were prepared on the vacuum line to preclude side reactions that could be induced by moisture. The elemental analyses were performed by the Centre de Microanalyses du CNRS.

Preparation of $TaBr_3(PhPMe_2)_2$. A solution of phenyldimethylphosphine (1.35 g, 9.8 mmol) in 16 mL of CH_2Cl_2 was added dropwise to a suspension of $TaBr_5$ (1.64 g, 2.82 mmol) and Mg turnings (0.50 g) in 35 mL of CH_2Cl_2. The yellow suspension turned orange-red, and freshly distilled diethyl ether (0.2 mL, 1.9 mmol) was then added to the reaction mixture, which was stirred in the dark for 3 days. A green suspension was obtained. The magnesium derivatives were separated by filtration and washed twice with CH_2Cl_2. The filtrate was concentrated to about one-eighth of its initial volume, giving a dark green, slightly oily solution, in which green microcrystals appeared after 1 or 2 days at room temperature. Freshly distilled pentane (≃3 mL) was carefully added. After several days at room temperature, precipitation of dark red crystals was observed. Separation of the green mother liquor and high-vacuum drying yielded $TaBr_3(PhPMe_2)_2$ as red, highly air-sensitive crystals, soluble in common organic solvents (1.4 g, 75%).

Table I. Summary of Crystal Data and Intensity Collection of $TaBr_3(PhPMe_2)_2$

formula	$TaBr_3C_{16}H_{22}P_2$
formula weight	699.98
space group	$P2_1/c$ (monoclinic)
a, Å	8.46 (1)
b, Å	29.80 (2)
c, Å	8.836 (8)
β, deg	98.77 (5)
V, Å^3	2200.3
Z	4
d(calcd), g cm^{-3}	2.11
cryst dimens, mm	0.65 × 0.55 × 0.48
temp, °C	20
radiation	Mo Kα (graphite monochromatized) (λ = 0.71073 Å)
μ, cm^{-1}	104.7
scan mode	ω–2θ
scan range, deg	1.00 + 0.45 tan θ
detector aperture, mm	2.50 + 0.50 tan θ
2θ limits, deg	2–50
octants colled	$\pm h,k,l$
no. of total measmts	3865
R_{int} (equiv reflcns)	0.028
no. of unique data used ($I > \sigma(I)$)	1974
final R	0.0555
final R_ω	0.0613
goodness of fit	2.06
largest shift/esd for final cycle	0.40

All solutions and products are extremely sensitive to oxygen and/or moisture; formation of blue, oily deposits was immediately observed. Anal. Calcd for $C_{16}H_{22}Br_3P_2Ta$: C, 27.57; H, 3.18; P, 8.89 Found: C, 27.58; H, 3.34; P, 8.72. IR (Nujol), cm^{-1}: 1580, 1560 w ($\nu_{C=C}$); 1295 s, 1280 s, 1330 m, 1300 m, 1030 w, 1000 w, 945 vs, 920 vs, 910 vs, 875 m, 840 m, 740 vs, 710 s, 690 s, 450 m, 420 w, 340 vs, 330 vs, 300 s, 290 sh, 235 w, 205 vs (ν_{Ta-Br}). $^{13}C\{^1H\}$ NMR (CD_3CN, 0.12 M), ppm: 3 (d) (J_{P-C} = 56 Hz), 3.5 (d) (J_{P-C} = 58 Hz), 5 (d) (J_{P-C} = 50 Hz), 5.2 (d)

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Table II. Positional and Equivalent Isotropic Thermal Parameters[a] of $TaBr_3(PhPMe_2)_2$ (Estimated Standard Deviations in Parentheses)

atom	x	y	z	B, Å^2
Ta	0.00237 (8)	0.12388 (2)	0.24219 (8)	2.96 (1)
Br1	0.2597 (2)	0.16491 (8)	0.3363 (3)	6.70 (5)
Br2	0.0292 (3)	0.07979 (8)	0.4887 (2)	6.79 (6)
Br3	0.1269 (4)	0.0727 (1)	0.0903 (5)	3.96 (7)
Br4	−0.1849 (4)	0.1760 (1)	0.3175 (4)	4.11 (7)
P1	−0.2474 (5)	0.0722 (1)	0.1551 (5)	3.18 (9)
P2	−0.0178 (5)	0.1785 (1)	0.0066 (5)	3.27 (9)
C1	−0.406 (2)	0.0824 (7)	0.259 (2)	5.6 (5)
C2	−0.205 (2)	0.0128 (5)	0.200 (2)	5.7 (5)
C3	−0.339 (2)	0.0706 (5)	−0.042 (2)	3.2 (3)
C4	−0.488 (2)	0.0903 (5)	−0.090 (2)	4.4 (4)
C5	−0.557 (2)	0.0844 (6)	−0.241 (2)	5.1 (4)
C6	−0.484 (3)	0.0597 (6)	−0.343 (2)	5.8 (5)
C7	−0.337 (2)	0.0410 (7)	−0.294 (2)	5.3 (5)
C8	−0.265 (2)	0.0471 (6)	−0.151 (2)	4.7 (4)
C9	0.041 (2)	0.2353 (6)	0.071 (2)	5.8 (5)
C10	0.117 (2)	0.1647 (8)	−0.135 (3)	6.5 (5)
C11	−0.208 (2)	0.1871 (5)	−0.115 (2)	3.3 (3)
C12	−0.245 (2)	0.1691 (6)	−0.260 (2)	4.3 (4)
C13	−0.393 (2)	0.1767 (7)	−0.351 (2)	5.0 (5)
C14	−0.504 (2)	0.2050 (7)	−0.286 (2)	5.4 (5)
C15	−0.478 (2)	0.2228 (6)	−0.147 (2)	4.7 (4)
C16	−0.322 (2)	0.2162 (5)	−0.057 (2)	4.3 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

(J_{P-C} = 49 Hz), 7 (m), 9.5 (d) (J_{P-C} = 55 Hz), 12.5 (br), 61.5 (d) (J_{P-C} = 58 Hz), 128–137 (phenyl). ^{31}P NMR (CH_2Cl_2), ppm: 21.8 (70% of the relative area), 28.5, 34, 49.

X-ray Crystallography

Space Group Determination and Data Collection. Crystals suitable for X-ray diffraction were grown slowly in the reaction mixture by the above procedure, after covering the solution with a layer of pentane.

Monocrystals of $TaBr_3(PhPMe_2)_2$ are air-unstable, red parallelepipeds of various shapes and sizes. One of them, introduced into a sealed Lindeman capillary under nitrogen, was mounted onto an Enraf Nonius CAD-4 automatic diffractometer. The crystal parameters and basic information about data collection and structure refinement are given in Table I. Corrections for Lorentz and polarization effects were applied, but corrections for absorption were not because of the irregular shape of the crystal used. Reflections with $I > \sigma(I)$ were considered to be observed.

Solution and Refinement of the Structure. The structure was solved on a PDP 11/60 computer using the Enraf-Nonius SDP package.[12] The atomic position of the Ta atom was found by Patterson techniques, and the other non-hydrogen atoms were found by subsequent difference-Fourier synthesis. One Br atom was found to be located on two independent positions (Br3 and Br4); best refinement was obtained with occupancy factors of 0.5 for each of them. These two positions are nearly symmetrical with respect to a plane formed by the other two Br atoms and the two P atoms, giving a nearly pseudooctahedral geometry to the Ta atom. Furthermore, the Br3, Br4, and Ta atoms define a pseudomirror plane for the whole molecule midway between and parallel to the phenyl rings.

Refinement of coordinates and thermal parameters, first isotropic and then anistropic, of the 23 independent non-hydrogen atoms of the asymmetric unit, with introduction of a secondary extinction parameter, led to final values of 0.0555 for $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and of 0.0613 for $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2|^{1/2}$. Owing to the low parameter-to-data ratio, hydrogen atoms were not introduced into the refinement.

The final atomic coordinates and equivalent isotropic thermal parameters are listed in Table II, with estimated standard deviations in parentheses. The numeration is shown in Figure 1, which represents an ORTEP view of the molecule. Intramolecular distances and angles are selected in Table III. Least-squares planes (Table IV), anisotropic thermal parameters (β values) (Table V), and calculated and observed structure factors are available as supplementary material.

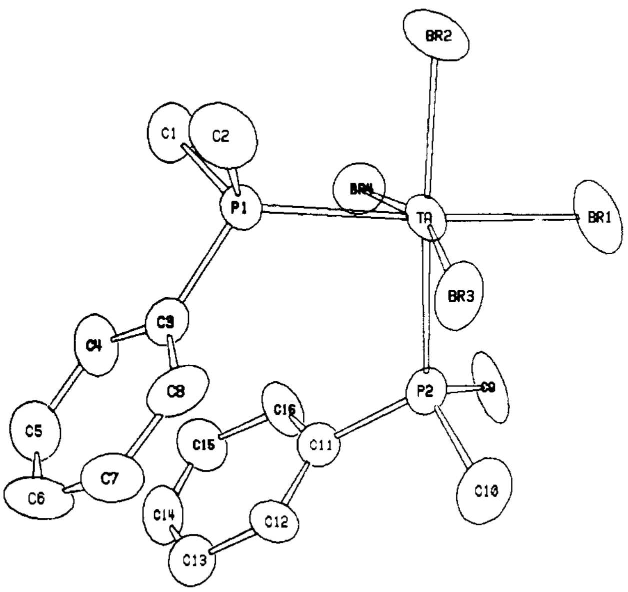

Figure 1. ORTEP drawing of the $TaBr_3(PhPMe_2)_2$ molecule, showing the non-hydrogen atoms. The bromine atoms Br3 and Br4 have an occupancy of 50% and correspond to the apex of the distorted square-pyramidal polyhedron.

Table III. Selected Bond Lengths (Å) and Angles (deg) in $TaBr_3(PhPMe_2)_2$ (Standard Deviations in Parentheses)

	Coordination Polyhedron		
	Distances		
Ta-Br1	2.524 (2)	Ta-P1	2.632 (3)
Ta-Br2	2.524 (2)	Ta-P2	2.627 (3)
Ta-Br3	2.380 (2)		
Ta-Br4	2.385 (2)		
	Angles		
Br1-Ta-Br2	90.47 (6)	Br2-Ta-P1	84.87 (8)
Br1-Ta-Br3	93.60 (7)	Br2-Ta-P2	173.02 (8)
Br1-Ta-Br4	99.69 (8)	Br3-Ta-P1	82.24 (9)
Br1-Ta-P1	173.14 (8)	Br3-Ta-P2	86.0 (1)
Br1-Ta-P2	84.81 (8)	Br4-Ta-P1	85.70 (9)
Br2-Ta-Br3	99.43 (9)	Br4-Ta-P2	81.5 (1)
Br2-Ta-Br4	94.28 (8)	P1-Ta-P2	100.27 (9)
	Ligand Parameters		
	Distances		
P1-C1	1.765 (13)	P2-C9	1.829 (12)
P1-C2	1.838 (12)	P2-C10	1.86 (2)
P1-C3	1.796 (12)	P2-C11	1.812 (11)
	Angles		
C1-P1-C2	101.1 (7)	C9-P2-C10	104.4 (7)
C1-P1-C3	104.9 (6)	C9-P2-C11	103.1 (5)
C2-P1-C3	103.1 (6)	C10-P2-C11	102.3 (6)

Results and Discussion

Synthesis and Crystal Structure. Tantalum pentabromide is reduced smoothly by magnesium turnings in CH_2Cl_2 under argon and in the presence of phenyldimethylphosphine (molar ratio $PhPMe_2/TaBr_5$ = 3.5) and diethyl ether (less than 1 equiv/mol of metal) to give bright red crystals of $TaBr_3(PhPMe_2)_2$ in 50–75% yield. The compound is paramagnetic in the solid state (μ_{eff} = 1.19 μ_B at room temperature), and its ESR spectra could easily be measured at room temperature (g_{av} = 1.55; ΔG = 1500 G). These magnetic properties suggest stabilization of tantalum(III) bromide as a mononuclear species, which was further confirmed by a single-crystal structure determination.

The crystal structure of $TaBr_3(PhPMe_2)_2$ consists of monomeric discrete molecules, the closest intermolecular Ta–Ta distance being 8.457 Å. All intermolecular contacts appear to be normal. The coordination polyhedron of the pentacoordinated tantalum(III) adduct is square pyramidal, with an apical bromine occupying either vacant site (Br3 *or* Br4) of the square plane formed by the

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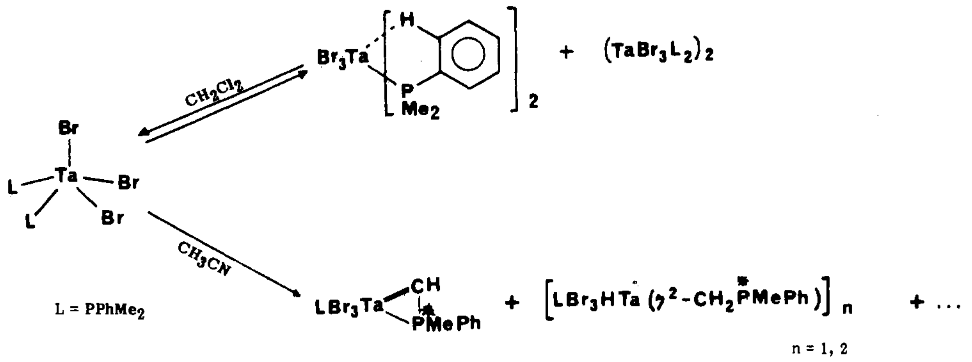
Scheme I



two phosphines and the two other bromines. The molecular configuration is depicted in Figure 1, with labeling of the atoms. Selected bond distances and angles are collected in Table III.

The pentacoordinated polyhedron of the metal is a flat square pyramid (basal P–Ta–Br angles of ≃173°) with the apical bromine Br3 and Br4 bent toward the phosphorus ligands. The latter are in a cis arrangement, with nearly parallel phenyl rings (angle between the planes of the rings 8.6°). The apical tantalum–bromine bond lengths are significantly shorter (2.382 (2) Å average) than the sum of the covalent radii (2.52 Å) or the basal Ta–Br1 and Ta–Br2 bonds (2.524 (2) Å). However, the fact that the apical Br atoms have occupancy factors of 0.5 prevents any worthwhile comparison of these values. The basal tantalum–bromine distances compare well with the values of the terminal Ta–Br bonds of $Ta_2Br_6(THT)_3$. The Ta–P (2.632 (3) or 2.627 (3) Å) bonds and the structural parameters of the phosphines are in agreement with the data reported in the literature for Ta(II) or Ta(III) derivatives. No intramolecular short contacts are observed. Although the carbons of the methyl groups are slightly closer to the metal than those of the phenyl groups, the distances between Ta and methyl carbon atoms C1, C2, C9, and C10 (range 3.684–3.808 Å) remain largely superior to those observed normally for agostic C—H interactions.[14]

$TaBr_3(PhPMe_2)_2$ appears to the best of our knowledge to be the first example of a monomeric pentacoordinated tantalum(III) halogen compound, although five-coordinated derivatives with square-pyramidal geometries, $Nb(NMe_2)_5$,[15] or more frequently with trigonal-bipyramidal geometries, $Ta(CHCMe_3)_2(2,4,6\text{-}Me_3C_6H_2)(PMe_3)_2$ or $Ta(OAr)_2Me_3$ (OAr = 2,6-di-*tert*-butylphenoxide),[16] are known for the d^0 configuration. Calculations have shown for electronic configurations d^0–d^4 that this latter geometry is slightly favored.[17]

The existence of the unsaturated d^2 compound $TaBr_3(PhPMe_2)_2$ as a monomeric entity is surprising in view of the strong tendency of tantalum to favor coordination numbers higher than 5 and metal–metal bonds in its lower oxidation states. $TaCl_3(PMe_3)_3$ decomposes readily in solution to the dimer $Ta_2Cl_4(PMe_3)_4(\mu\text{-}Cl)_2$, but no indications of the tendency toward dimerization of the bromo analogue are available in the literature. Previously, attempts to gain molecular tantalum tribromide–phenyldimethylphosphine adducts offered $[TaBr_3(PhPMe_2)]_n$ or $[TaBr_3(PhPMe_2)_2]_n$ as yellow-green, essentially diamagnetic solids, depending on the isolation procedure.[7] The addition of a small amount of diethyl ether during the reduction allows the isolation of monomeric $TaBr_3(PhPMe_2)_2$, although the reaction mixture appears to contain the same molecular species, but in different ratios from those found in the absence of ether (^{31}P NMR). Diethyl ether has been recognized to favor the formation of the mononuclear $MCl_3(PMe_3)_3$ intermediate, as compared to toluene,[6] and its behavior may be comparable here, although more puzzling phenomena may occur during the precipitation of the red $TaBr_3(PhPMe_2)_2$ compound from the dark green reaction medium.

Structural data of low-valent tantalum bromo adducts are so far restricted to $Ta_2Br_4(THT)_2(\mu\text{-}Br)_2(\mu\text{-}THT)$[1] while those of tantalum phosphine adducts concern the $Ta_2Cl_4(PMe_3)_4(\mu\text{-}Cl)_2$[6] dimer and its hydride derivatives. The coordination sphere of $Ta_2Cl_6(PMe_3)_4$ (Ta–Ta = 2.721 (1) Å) appears relatively crowded and therefore distorted, with the PMe_3 groups in axial and equatorial positions and nonbonding interactions between the axial ligands. The increase in the bulkiness of the phosphine from PMe_3 to $PPhMe_2$ is small; comparable structures may be expected and are observed for instance with $Nb_2Cl_4(PR_3)_4(\mu\text{-}Cl)_4$.[19] Destabilization of a dimeric structure may therefore more probably result from interactions involving the bromine atoms, although octahedral bromo-bridged structures are known for tantalum or tungsten and may be formed in solution. The lower stability of a dimer with all phosphines in equatorial positions[6] could be an additional factor for the formation of the monomer. Finally, another way to escape the steric problems of the dimers is by aggregation into larger polyhedrons, which is illustrated by the isolation of $[TaBr_3(PhPMe_2)]_n$ or $[TaBr_3(PhPMe_2)_2]_n$ and the puzzling behavior of the tantalum bromide phosphine adducts in solution.

Solution Behavior. As often observed for early-transition-metal derivatives, although well-defined in the solid state, the pentacoordinated $TaBr_3(PhPMe_2)_2$ exhibits complex and puzzling behavior in solution. This phenomenon was found to be dilution, temperature, and solvent dependent: drastically different behaviors were observed in CH_2Cl_2 and in MeCN, but free ligand or phosphonium salts[7] were never detected for perfectly dry solutions.

The red crystals of $TaBr_3(PhPMe_2)_2$ dissolve in CH_2Cl_2 to give yellow-green solutions. Their ESR spectra display a broad resonance ($g = 1.83$) that at −170 °C shows the eight lines ($g = 1.81$, $A \simeq 200$ G) characteristic of coupling to a tantalum nucleus ($I = {}^7/_2$, 100%). The magnetic susceptibility data obtained by the Evans method[20] ($\mu_{eff} = 0.37\ \mu_B$ at 298 K, for a 0.035 M solution) confirm the paramagnetism, although the magnetic moments are significantly lower than in the solid state. Magnetic measurements at various concentrations establish the existence of an equilibrium ($K = 3.5$ at 298 K) between magnetically different species ($S = 0$, $S = 1$). Equilibria between para- and diamagnetic Ta(III) species or between Ta(III) species and those resulting from a possible oxidation by CH_2Cl_2 may be considered. The absence of aging effect, as well as the similitude of the $^{31}P\{^1H\}$ spectra

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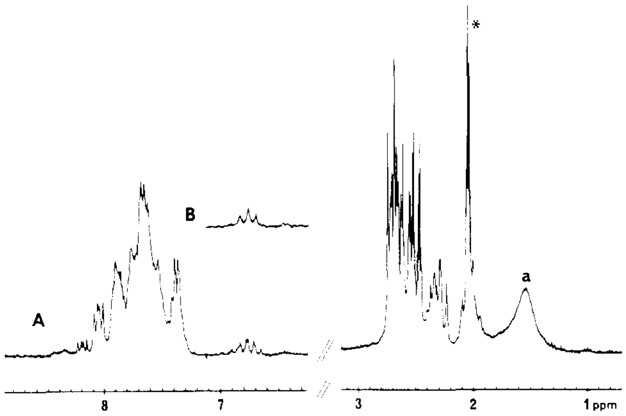


Figure 2. ^1H NMR spectra (250 MHz) of a 0.12 M solution of $TaBr_3(PhPMe_2)_2$ in CD_3CN at room temperature (the solvent peak is denoted by an asterisk): A, ^1H spectrum; B, $^1H\{^{31}P\}$ spectrum.

obtained on the reaction medium and upon redissolution of $TaBr_3(PhPMe_2)_2$ in CD_2Cl_2 (several molecular species with equivalent phosphorus ligands), argues against extensive reoxidation.

The main features of the broad ^1H NMR spectra of the large isotropic shifts (from ≃5.2 to 9.80 ppm), with Curie-law behavior observed in the aromatic region, suggesting delocalization of π spin density.[21] Splitting at −80 °C of the signals of the ortho and meta protons may probably be attributed to agostic C–H⇀M interactions involving the aromatic hydrogens, which appear as an alternative to stabilize the unsaturated monomeric $TaBr_3(PhPMe_2)_2$ adduct. The complexity of this region (peak overlapping, magnetic broadening, and exchange phenomena) however precluded complete analysis.

The above experimental data may be rationalized on the basis of a dynamic equilibrium between monomeric paramagnetic $TaBr_3(PhPMe_2)_2$ isomers and diamagnetic species, probably $Ta_2Br_6(PhPMe_2)_4$, which are favored by the concentration (exclusively diamagnetic behavior is found for a 0.18 M solution) (Scheme I). Addition of excess phenyldimethylphosphine to a CD_2Cl_2 solution of $TaBr_3(PhPMe_2)_2$ leads to further coordination (^{31}P NMR new peak at 18 ppm; ESR $g = 1.79$, $A = 200$ G) with a strong increase of the paramagnetism ($\mu = 2.04\ \mu_B$ at 298 K). Formation of $TaBr_3(PhPMe_2)_3$, whose dimerization would be hindered in the presence of excess ligand, is the most likely.

In contrast with the CH_2Cl_2 solutions, the acetonitrile solutions of $TaBr_3(PhPMe_2)_2$ are diamagnetic over the dilution (0.35–0.08 M) and temperature (+80 to −45 °C) ranges explored. This diamagnetism may result from an almost complete dimerization of the Ta(III) adduct and/or from oxidative-addition processes involing the phosphine and/or the solvent. Attempts to recover the initial Ta(III) compound from these solutions failed, and oxidative reactions appear to be the main processes. The formation of linear[22] or heterocyclic[23] diimine complexes by reductive coupling of acetonitrile is known, but stepwise addition of MeCN to a solution of $TaBr_3(PhPMe_2)_2$ in CD_2Cl_2 gave no evidence for such reactions.

The highly complex NMR spectra (^1H, ^{31}P, and ^{13}C) indicate dynamic equilibrium between several molecular species, most of them displaying nonequivalent phosphorus ligands.

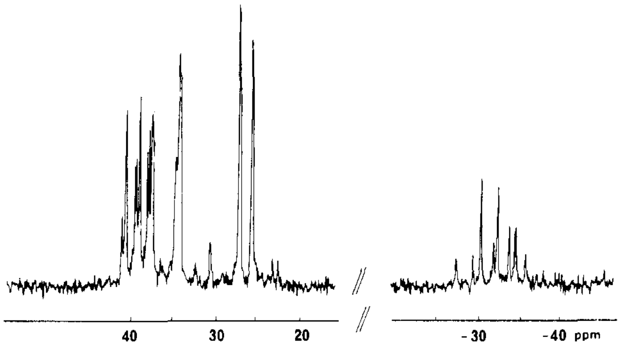
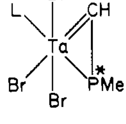


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of a 0.12 M solution of $TaBr_3(PhPMe_2)_2$ in CD_3CN at −40 °C.

The ^1H spectra show a complex pattern for the aliphatic protons (numerous multiplets between ca. 1.95 and 2.68 ppm), while those of the phenyl groups appear as usual around 7.70 ppm. Characteristic of these spectra (Figure 2) is the broad signal a at high field (δ 1.40), whose area corresponds to ≃20% of the aliphatic protons. Its sharpening as the temperature is decreased accounts for protons in interaction with the metal through either "agostic" or metalated C–H bonds. The presence of several multiplets around −32 ppm in the $^{31}P\{^1H\}$ spectra (Figure 3)—at high field with respect to the usual coordination shifts—may be unambiguously attributed to metalated phosphines of three-membered metallocycles.[24,25] Further information was gained from the ^{13}C NMR with the unexpected observation of a methine-type carbon signal at 61.5 ppm (dd) ($^1J_{P–C} = 58$ Hz; $^1J_{C–H} = 140$ Hz) together with a broad peak at 12.5 ppm. Modified spin-echo sequences[26] (used to determine the parity of the carbon peaks) allowed the assignment of the latter resonance to a methylene carbon.

Quantitative analysis of the ^{31}P and ^{13}C spectra suggest that the predominant three-membered metallocycle is stabilized by a tantalum–carbon double bond (quadrupolar relaxation effects or peak overlapping may account for the nonobservation of the corresponding CH proton). A distorted octahedral polyhedron such as **1** and/or its isomers fit the spectroscopic data (AB spectrum in the ^{31}P NMR: δ(A) −28.1, δ(B) −32.2; $J_{P_A–P_B} = 105$ Hz).



1, L = $PPhMe_2$

Three-membered metallocycles, $\overline{\text{M—C—P}}$, which are relatively common for electron-rich centers,[24,25] seem rare for the early transition metals.[7] $\overline{\text{M═CH—P}}$ metallocycles are to date restricted to tantalum. They have been formed from lower oxidation states[28a] or in more complicated synthetic procedures.[28b] The spontaneous obtention of a $Ta(\eta^2\text{-CHPMePh})$ moiety (20% of the molecular species for a 0.12 M solution) from a d^2 compound illustrates the effectiveness of tantalum for the stabilization of metal–carbon double bonds.

Molecular weight data obtained by the Signer method[29] indicate a significant increase in the molecular complexity ($M_{r_{\text{exptl}}} = 960 \pm 100$, $M_{r_{\text{calcd}}} = 697$) and therefore suggest that both intra- and intermolecular C–H activation processes are involved.[30]

The CH_2 groups (peaks at 1.40 and 12.5 ppm in the ^1H and ^{13}C spectra, respectively) may therefore belong to species having

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terminal η^1- or η^2-CH_2PMePh ligands or to dinuclear species with bridging $-PMe(Ph)CH_2-$groups and a six-membered (alternating Ta, C, P) ring. Oxidative addition to Ta(V) is likely for all metalated species. The ^1H spectra show a broad multiplet at 6.80 ppm, which appears as a triplet in the $^1H\{^{31}P\}$ spectra (J_{H-H} = 16 Hz) (Figure 2) and is attributed to the hydrido ligands (from -3 to $+10$ ppm[7,31] are reported for terminal Ta–H). Attempts to trap hydrobromic acid (which could be eliminated in the C–H activation process) failed. No further coordination by addition of phenyldimethylphosphine was observed. This, as well as the absence of ionic species,[7] supports coordinatively saturated molecular tantalum(V) species (Scheme I).

The C–H bond activation in the tantalum complex showed no evidence of fast (NMR time scale) reversal up to temperatures as high as 80 °C.

Reactions between $TaBr_3(PhPMe_2)_2$ and H_2, C_1 molecules, alkenes, and alkynes are in progress.

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Registry No. $TaBr_3(PhPMe_2)_2$, 99211-55-9; $TaBr_3(PhPMe_2)$, 99128-45-7; $[(PhPMe_2)Br_3HTa(\eta^2\text{-}CH_2PMePh)]_n$, 99128-46-8; PMe_2Ph, 672-66-2; $TaBr_5$, 13842-76-7.

Supplementary Material Available: Tables IV and V, containing anisotropic thermal parameters (β's) and least-square planes, and listings of observed and calculated structure factors and nonessential bond lengths and angles for $TaBr_3(PhPMe_2)_2$ (15 pages). Ordering information is given on any current masthead page.

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Synthesis, X-ray Structure, and Chemical Reactivity of the Tetranuclear Cluster $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$. X-ray Structure of the Binuclear Compound $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$

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The preparation of a mixed-metal atom cluster compound, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**), containing Pt–Ag and Ag–Ag bonds is described. The molecular structure of this compound has been determined by a single-crystal X-ray diffraction study. The crystals are found to be triclinic, space group $P\bar{1}$, with a = 12.438 (9) Å, b = 13.160 (7) Å, c = 11.128 (7) Å, α = 103.53 (5)°, β = 101.27 (6)°, γ = 74.75 (5)°, and Z = 1. The structure was refined to R = 0.079 and R_w = 0.096 with use of 1615 unique reflections with $F^2 \geq 3\sigma(F^2)$. The anion resides on a center of symmetry and shows interesting distances: Pt–Ag′ = 2.772 (3) Å, Pt–Ag = 3.063 (3) Å, Ag–Ag′ = 2.994 (6) Å, F···Ag = 2.60 (1) Å, and F···Ag = 2.69 (1) Å. The chemical reactivity of this unusual cluster toward different kinds of neutral ligands has been studied. The reaction of **1** with PPh_3 gives a new anionic organometallic compound, $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (**2**), that crystallizes in space group $P\bar{1}$ with a = 12.710 (3) Å, b = 18.865 (5) Å, c = 12.129 (5) Å, α = 103.10 (3)°, β = 114.44 (2)°, γ = 77.07 (2)°, and Z = 2. The structure was refined to R = 0.066 and R_w = 0.076 using 3291 unique reflections with $F^2 \geq 2\sigma(F^2)$. Compound **2** retains the Pt–Ag bond (Pt–Ag = 2.796 (2) Å) of the starting cluster, but there are no weak contacts between F and Ag, probably as a consequence of the coordination of the PPh_3 to the Ag. $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ reacts with L = $AsPh_3$ or $SbPh_3$ with precipitation of silver chloride and formation of $[trans\text{-}Pt(C_6F_5)_2L_2]$ and $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ and with CO to give AgCl and the new anionic carbonyl (NBu_4)-$[trans\text{-}PtCl(C_6F_5)_2(CO)]$, which is air- and temperature-stable (ν(CO) at 2084 cm^{-1}).

Introduction

Silver salts, AgA, of weakly coordinating anions (A = BF_4, PF_6, NO_3, $^1/_2$ SO_4 or ClO_4) have frequently been used as halide abstractors from halo complexes of transition metals, since the insolubility of silver halides leads to precipitation of AgX and to the replacement of X by the less nucleophilic anion A. The anion A can, in turn, be easily displaced by other ligands, neutral or anionic, thus making this method a very powerful one for the synthesis of a variety of cationic or neutral complexes.[2,3]

In a number of recently reported cases, the interaction of a silver salt with an anionic or neutral complex has led to polynuclear complexes containing metal–silver bonds.[4-8] In most of the reported processes the precursor has been a halide-free complex, but in one case an iodine-containing complex $\{[WI(CO)_3(\eta^5\text{-}C_5H_5)]_4Ag\}BF_4$, with Ag–I bonds and without any W–Ag bond has been described.[9] Here we wish to report an example of the halide-containing precursor[10] $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ that can react with $AgNO_3$ or $AgClO_4$ without AgCl precipitation to give the new type of anionic Pt–Ag cluster $(NBu_4)_2[trans\text{-}Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**), with platinum–silver as well as silver–silver bonds.

Reaction of **1** with $AsPh_3$ or $SbPh_3$ causes AgCl precipitation and formation of a mixture of $[trans\text{-}Pt(C_6F_5)_2L_2]$ and $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$, whereas with PPh_3 the intermediate $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (**2**) can be isolated. On the other hand, complex **1** reacts with CO at normal pressure to give the

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