Inorg. Chem. **1981**, *20*, 1151–1155

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Synthesis, Characterization, and Electrochemistry of Tertiary Phosphine Complexes of Niobium and Tantalum Halide Clusters[1]

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Received July 22, 1980

Monodentate tertiary phosphines react with the hydrated niobium and tantalum chloride clusters $M_6Cl_{14}\cdot8H_2O$ and $M_6Cl_{15}\cdot7H_2O$ to produce the complexes of stoichiometry $(M_6Cl_{12})Cl_2(PR_3)_4$. Electrochemical measurements, using cyclic voltammetry and coulometry techniques, reveal the presence of three couples, two one-electron oxidations and a single reduction. The monoanions $[(M_6Cl_{12})Cl_2(PR_3)_4]^-$ are formally derivatives of the previously unknown $(M_6Cl_{12})^+$ core. The chemical oxidation of $(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ to $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ occurs when $NOPF_6$ is used as the oxidant. The oxidations of $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ to $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ and $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$ have also been accomplished. When appropriate, the spectral properties (infrared, electronic absorption, X-ray photoelectron, and ESR) of these new complexes have been investigated.

Introduction

The ability of tertiary phosphines to stabilize low oxidation state transition-metal halide complexes which contain metal–metal multiple bonds has permitted the exploration of the redox chemistry of these species. We have recently embarked on a study of the chemical and electrochemical oxidations and reductions of dimeric complexes which have a $(\sigma)^2(\pi)^4(\delta)^a(\delta^*)^b$ electronic configuration ($a = 0$ or 2, $b = 0$–2) associated with the metal M_2^{n+} core[2] and which therefore possess M–M bond orders of between 3 and 4. As a result of our work on the characterization of species such as $Re_2Cl_9^-$, $Re_2Cl_6(PR_3)_2$, $Re_2Cl_5(PR_3)_3$, $Re_2Cl_4(PR_3)_4$, and $Mo_2Cl_4(PR_3)_4$,[3-7] we have been able to define the scope of their redox chemistry. Of particular significance is the discovery that the Re_2^{n+} core may survive up to a four-electron oxidation or reduction without being disrupted, thereby permitting the development of a particularly rich chemistry for such complexes. An interesting aspect of our electrochemical studies on the series of dimers $Re_2Cl_6(PR_3)_2$, $Re_2Cl_5(PR_3)_3$, and $Re_2Cl_4(PR_3)_4$ was our discovery[5,6] of a novel series of coupled electrochemical–chemical reactions.

While metal halide complexes which contain metal–metal multiple bonds might be expected to exhibit a wider range of reversible redox activity than their cluster analogues (e.g., $Mo_2Cl_4(PR_3)_4$ vs. $Mo_6Cl_{12}(PR_3)_2$ and $Re_2Cl_6(PR_3)_2$ vs. $Re_3Cl_9(PR_3)_3$), this aspect of the chemistry of metal halide clusters has generally been neglected. However, we have in recent years identified reduction reactions of Re_3X_9 (X = Cl or Br) in which formation of rhenium(II) species may[8,9] or may not[10] lead to retention of the Re_3 cluster unit and the first ligand-induced reduction of the $[Mo_6Cl_8]^{4+}$ cluster (as present in $[Mo_6Cl_8]Cl_4$ and $[(Mo_6Cl_8)X_6]^{2-}$, where X = Cl, Br, or I) to $[Mo_6Cl_8]^{2+}$.[11] We have now begun to investigate the electrochemistry of metal halide clusters which contain trimeric, tetrameric, and hexameric units and herein describe our results for tertiary phosphine complexes which contain Nb_6 and Ta_6 clusters.

Experimental Section

Starting Materials. The clusters $Nb_6Cl_{14}\cdot8H_2O$,[12] $Nb_6Cl_{15}\cdot7H_2O$,[13] $Nb_6Cl_{14}(Me_2SO)_4$,[14] $Ta_6Cl_{14}\cdot8H_2O$,[12] and $Ta_6Cl_{15}\cdot7H_2O$[13] were prepared according to literature methods. The phosphines used were obtained from Strem Chemicals. Solvents were of the highest purity commercially available and were used without further purification with the exception of acetonitrile which was distilled over CaH_2 and stored under N_2. All reactions were conducted under oxygen-free conditions. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was obtained by reacting tetra-*n*-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo.

Reactions of Niobium and Tantalum Chlorides with Tertiary Phosphines. $Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$. This complex was prepared from $Nb_6Cl_{14}\cdot8H_2O$ according to the procedure reported previously[15] from our laboratory. Anal. Calcd for $C_{36}H_{84}Cl_{14}P_4Nb_6$: C, 25.51; H, 5.00; Cl, 29.28. Found: C, 25.23; H, 4.90; Cl, 29.61; yield 74%.

The reaction of tri-*n*-propylphosphine with $Nb_6Cl_{15}\cdot7H_2O$ brought about reduction of the $Nb_6Cl_{12}^{3+}$ core to $Nb_6Cl_{12}^{2+}$. The reaction conditions are very similar to those used in the previous preparation of $Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$,[15] except that the solution was allowed to reflux for 18 h. Anal. Calcd for $C_{36}H_{84}Cl_{14}P_4Nb_6$: C, 25.51; H, 5.00; Cl, 29.28. Found: C, 25.19; H, 4.85; Cl, 29.23, yield 72%.

$Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ could be prepared in substantially lower yield under room-temperature conditions.

$Nb_6Cl_{14}(PEt_3)_4$. $Nb_6Cl_{14}\cdot8H_2O$ (1.30 g, 1.1 mmol) was dissolved in 45 mL of ethanol. Approximately 3 mL of triethylphosphine was syringed into the solution and the reaction mixture then sealed under N_2 in a 100-mL round-bottom flask. The contents were stirred for 48 h at room temperature and then filtered. The olive green product (1.07 g) was washed thoroughly with ethanol and diethyl ether and then dried in vacuo. Anal. Calcd for $C_{24}H_{60}Cl_{14}P_4Nb_6$: C, 18,89; H, 3.96; Cl, 32.51. Found: C, 18.15; H, 3.99; Cl, 31.85; yield 64%.

Reacting $Nb_6Cl_{14}\cdot8H_2O$ with triethylphosphine under similar conditions to those described above but without stirring produced the complex in the form of black crystals. However, the yield was only 40%, and the reaction required 6 days.

$Nb_6Cl_{14}(PEt_3)_4$ could also be prepared by the reaction of triethylphosphine with either $Nb_6Cl_{14}\cdot8H_2O$ or the dimethyl sulfoxide complex $Nb_6Cl_{14}(Me_2SO)_4$ under refluxing conditions, but in both cases the yields were quite low (8 and 22%, respectively).

$Nb_6Cl_{14}(PEt_2Ph)_4$. With a procedure analogous to that used to prepare $Nb_6Cl_{14}(PEt_3)_4$, the olive green complex $Nb_6Cl_{14}(PEt_2Ph)_4$ could be obtained in high yield. In the workup it was washed well with ethanol and diethyl ether and then dried in vacuo. Anal. Calcd for $C_{40}H_{60}Cl_{14}P_4Nb_6$: C, 27.96; H, 3.52; Cl, 28.88. Found: C, 27.74; H, 3.73; Cl, 28.74; yield: 92%.

As in the case of the synthesis of $Nb_6Cl_{14}(PEt_3)_4$, if the reaction mixture was not stirred, the complex was obtained as black crystals, but again the yield (34%) was lower and reaction times longer.

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Table I. Electronic and Infrared Absorption Spectra of Tertiary Phosphine Complexes Containing the $M_6Cl_{12}^{n+}$ Cores (M = Nb or Ta and *n* = 2–4)

complex	medium	electronic abs max, nm	IR spectra (400–200 cm^{-1})
$(Nb_6Cl_{12})Cl_2(PEt_3)_4$	solid	960, 615 sh, 415	342 vs, 294 s, 274 w, 248 w, 234 m
	CH_2Cl_2	930, ~620, 413, ~328 sh, 250	
$(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$	solid	965, 620, 420	344 vs, 294 s, 274 w, 248 w, 234 m
	CH_2Cl_2	948, ~610, 412, ~330 sh, ~260 sh	
$(Nb_6Cl_{12})Cl_2(PEt_2Ph)_4$	solid	960, 620, 415	344 vs, 293 s, ~280 sh, 250 m, 235 mw
	CH_2Cl_2	920, 620, 412, 325 sh, 266	
$[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$	CH_2Cl_2	1275, 955, 845 sh, 426, ~300 sh, ~255 sh	350 vs, 304 s, ~280 w?, 260 w, 232 mw
$(Ta_6Cl_{12})Cl_2(Me_2SO)_4$			322 vs, 285 w, 244 m, 205 w
$(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$	CH_2Cl_2	808, 681, 480, 408, 338, 273 sh	324 vs, 282 w, 247 m
$[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$	CH_2Cl_2	952, 832, 775, 745, 414, 347, 280 sh	332 vs, 294 m, 256 m
$[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$	CH_2Cl_2	~940 sh, 790, 715 sh, 680, 495 sh, 420 sh, 354, 252	345 vs, 304 w, 268 ms, 234 w

$[Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4]PF_6$. A quantity of $Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ (0.070 g, 0.043 mmol) was added to 15 mL of acetonitrile. Upon addition of an excess of $NOPF_6$ (0.025 g, 1.4 mmol) the suspension of $Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ dissolved immediately to generate a red-brown solution. The volume of solution was reduced by half and diethyl ether added to precipitate the complex. The red-brown precipitate (0.05 g) was collected on a glass frit, washed well with ethanol (to remove unreacted $NOPF_6$) and diethyl ether, and then dried in vacuo. Anal. Calcd for $C_{36}H_{84}Cl_{14}F_6P_5Nb_6$: C, 23.50; H, 4.61; Cl, 26.98; P, 8.42. Found: C, 22.66; H, 4.37; Cl, 26.58; P, 7.59; yield 66%.

$Ta_6Cl_{14}(Me_2SO)_4$. $Ta_6Cl_{14}\cdot 8H_2O$ (0.515 g, 0.298 mmol) was dissolved in 25 mL of dimethyl sulfoxide. The volume of solution was lowered to less than 10 mL by heating the solution under reduced pressure, and the product precipitated by addition of *n*-propyl alcohol. The bright green solid (0.315 g) was filtered off, washed well with diethyl ether, and dried in vacuo. Additional product (0.14 g) could be obtained by adding an equal volume of diethyl ether to the reaction filtrate. Spectroscopic characterization of the two products showed them to be identical. Anal. Calcd for $C_8H_{24}Cl_{14}O_4S_4Ta_6$: C, 5.07; H, 1.28; Cl, 26.20. Found: C, 5.30; H, 1.49; Cl, 25.99; yield 80%.

$Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$. The hydrate $Ta_6Cl_{14}\cdot 8H_2O$ (0.83 g, 0.48 mmol) was dissolved in 30 mL of ethanol. To the stirred solution was added tri-*n*-propylphosphine (2 mL). The reaction mixture was then stirred for 3 days after which time the contents were filtered. The bright green product (0.155 g) was washed well with ethanol and diethyl ether and dried in vacuo. The filtrate was evaporated under reduced pressure and the resulting solid (0.687 g) collected and washed with diethyl ether (to remove residual free phosphine). This was combined with the initial precipitate and dissolved in 200 proof ethanol, and approximately 1 mL of tri-*n*-propylphosphine was added. The mixture was refluxed for 48 h under nitrogen and the insoluble green product (0.528 g) collected, washed with ethanol and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{36}H_{84}Cl_{14}P_4Ta_6$: C, 19.45; H, 3.82; Cl, 22.32. Found: C, 18.70; H, 3.58; Cl, 21.56; yield 49%.

The reaction of $Ta_6Cl_{15}\cdot 7H_2O$ with tri-*n*-propylphosphine in ethanol also afforded $Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ in good yield.

$[Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$. $Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ (0.10 g, 0.050 mmol) was added to 10 mL of acetonitrile in which it is virtually insoluble. Upon addition of $NOPF_6$ (0.031 g, 0.18 mmol) the contents of the reaction vessel immediately changed from green to red-brown and the phosphine complex dissolved. The solvent was stripped off under reduced pressure and the remaining red-brown solid (0.08 g) washed with ethanol and diethyl ether and dried in vacuo. Anal. Calcd for $C_{36}H_{84}Cl_{14}F_6P_6Ta_6$: C, 17.20; H, 3.38; Cl, 19.75; P, 7.39. Found: C, 16.89; H, 3.54; Cl, 19.93; P, 7.10; yield 67%.

$[Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4]PF_6$. $Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ was added to freshly distilled acetonitrile and this mixture treated with a quantity of $NOPF_6$ which was slightly less than that needed to ensure complete oxidation to $[Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4]^+$. The resulting reaction mixture was filtered (the slight excess of $Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$ is insoluble), the filtrate reduced in volume, and an excess of diethyl ether added to precipitate the desired complex. Anal. Calcd for $C_{36}H_{84}Cl_{14}F_6P_5Ta_6$: C, 18.26; H, 3.58; Cl, 20.96; P, 6.54. Found: C, 18.36; H, 3.44; Cl, 21.20; P, 6.41; yield 90%.

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded as Nujol mulls on a Beckman IR-12 spectrophotometer. Far-infrared spectra (500–80 cm^{-1}) were recorded as Nujol mulls between polyethylene plates with use of a Digilab FTS-20B Fourier transform interferometer. Electronic absorption spectra were recorded on CH_2Cl_2 solutions with use of Cary 14 and Cary 17B spectrophotometers and on solid samples with use of a Beckman DU-2 spectrophotometer. X-Band ESR spectra of CH_2Cl_2 glasses were recorded at room temperature and −170 °C with a Varian E-109 spectrometer.

Electrochemical measurements were made on dichloromethane and acetonitrile solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) are referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed with use of a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. Values of *n*, where *n* is the total number of equivalents of electrons transferred in exhaustive electrolysis at constant potentials, were calculated after the total area under the current vs. time curves for the complete reactions was measured. The reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were made at a platinum-bead electrode in solutions deaerated in a stream of dry nitrogen.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Synthesis and Preliminary Characterizations. In an earlier study of the X-ray photoelectron spectra of metal halide clusters[15] we discovered that the tertiary phosphine complex $(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ could be prepared by the direct reaction of tri-*n*-propylphosphine with $(Nb_6Cl_{12})Cl_2\cdot 8H_2O$. Surprisingly, this turned out to be the first example of a *neutral* adduct of the type $(M_6Cl_{12})Cl_2L_4$ (M = Nb or Ta) with other than an oxygen or nitrogen donor. In the present work, we have developed this same synthetic procedure to afford niobium chloride derivatives with triethylphosphine and diethylphenylphosphine, and furthermore we have shown that alternative routes to the green colored complexes $(Nb_6Cl_{12})Cl_2(PR_3)_4$ include the ligand displacement of dimethyl sulfoxide from $(Nb_6Cl_{12})Cl_2(Me_2SO)_4$ and the phosphine-induced reduction of the oxidized cluster $Nb_6Cl_{15}\cdot 7H_2O$ in refluxing ethanol. The extension of these reactions to the tantalum chloride systems is demonstrated by our isolation of green $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ from the room temperature reaction of $Ta_6Cl_{14}\cdot 8H_2O$ with an ethanol solution of tri-*n*-propylphosphine. The possibility of converting $(Ta_6Cl_{12})Cl_2(Me_2SO)_4$ (the latter is a new complex reported here for the first time) to $(Ta_6Cl_{12})Cl_2(PR_3)_4$ species was also explored, but this method afforded products which were contaminated with phosphine oxides, and so this procedure was not pursued in any detail.

The neutral complexes of the type $(M_6Cl_{12})Cl_2(PR_3)_4$ which we isolated are generally insoluble in acetonitrile, ethanol, diethyl ether, and a variety of less polar solvents but exhibit reasonable solubility in acetone and dichloromethane. Electronic absorption spectra (Table I) of the solids (Nb_6Cl_{12})-

Table II. $E_{1/2}$ Values for Tertiary Phosphine Complexes of Niobium and Tantalum Halide Clusters in Dichloromethane[a]

complex	$E_{1/2}(\text{ox})^b$		$E_{1/2}(\text{red})^b$
$(Nb_6Cl_{12})Cl_2(PEt_3)_4$	+1.09	+0.53	−0.99
$(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$	+1.09	+0.53	−1.00
$(Nb_6Cl_{12})Cl_2(PEt_2Ph)_4$	+1.09	+0.53	−0.98
$(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$	+0.77	+0.19	*c*

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. SCE with a Pt-bead working electrode. [c] See text.

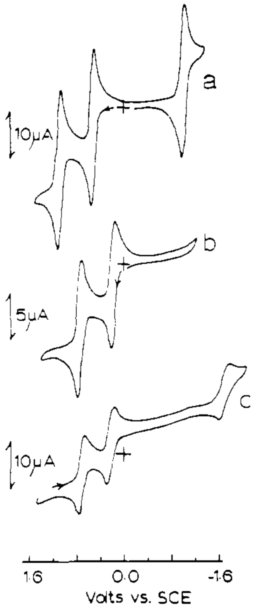

Figure 1. Cyclic voltammograms in 0.2 M TBAH–dichloromethane of (a) $(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ and (b) $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$. The CV of $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$ in 0.2 M TBAH–acetonitrile is shown in trace c.

$Cl_2(PR_3)_4$ (PR_3 = PEt_3, P-*n*-Pr_3, or PEt_2Ph) reveal absorption maxima at approximately 960, 620 (weak), and 415 nm. Dichloromethane solutions of the complexes exhibit these same bands, although the one at lowest energy shifts approximately −25 nm in solution. For a dichloromethane solution of $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$, λ_{max} values were at 808, 681, 480, and 408 nm. These spectral features are characteristic of complexes containing the $Nb_6Cl_{12}{}^{2+}$ and $Ta_6Cl_{12}{}^{2+}$ cores.[14,16-21] Likewise, low-frequency vibrational spectroscopy confirms the identity of these complexes,[22] the absorption bands in the region 400–200 cm^{-1} (Table I) matching closely those reported for other derivatives of these halides.[16,23-26]

Electrochemical and Chemical Redox Properties. One of our principal objectives in preparing the phosphine derivatives $(M_6Cl_{12})Cl_2(PR_3)_4$ was to explore their redox chemistry in a search for new oxidation states which might both be isolable and possess an interesting and significant chemistry. Electrochemical characterizations were carried out with use of the cyclic voltammetry (CV) technique. Voltammetric half-wave potentials vs. SCE for solutions of niobium and tantalum clusters in dichloromethane are presented in Table II. In all instances, the current ratio $i_{p,c}/i_{p,a}$ was equal to unity (or very close to it) for sweep rates (v) between 50 and 400 mV/s and, the ratio $i_p/v^{1/2}$ was constant for sweep rates between 50 and 200 mV/s in accord with diffusion control. In all instances, the values of ΔE_p, the potential separation between the anodic and cathodic peaks, were in the range 60–100 mV and varied with sweep rate, in accord with quasi-reversible electron-transfer processes.[27,28] For example, ΔE_p for the three electrochemical processes of $(Nb_6Cl_{12})Cl_2(PEt_3)_4$ (Table II) varied approximately from 80 to 90 mV for v between 100 and 400 mV/s.

The three couples displayed by each of the niobium complexes (Table II and Figure 1a) correspond to two oxidations and one reduction, whereas for $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ only the two oxidations were observed (Figure 1b), the reduction being at potentials cathodic of the dichloromethane solvent limit (around −1.4 V). The oxidations were shown via coulometry to correspond to one-electron processes (n = 1.0 ± 0.1) (see eq 1). Controlled potential electrolysis experiments

$$(M_6Cl_{12})Cl_2(PR_3)_4 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(M_6Cl_{12})Cl_2(PR_3)_4]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(M_6Cl_{12})Cl_2(PR_3)_4]^{2+} \qquad (1)$$

on the niobium clusters (at +0.6 and +1.2 V) produced solutions of the mono- and dications (golden yellow and orange-brown in color, respectively), which were quite stable under nitrogen and which could be electrochemically reduced back to the parent clusters with little decomposition (as measured by peak currents). Corresponding experiments with $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ converted the green neutral cluster to the golden-yellow monocation and red-orange dication at potentials of +0.4 and +1.0 V, respectively. Measurements on an acetonitrile solution of $(Nb_6Cl_{12})Cl_2(PEt_3)_4$, the only complex to exhibit significant solubility in this solvent, revealed similar electrochemical behavior to that observed in dichloromethane, namely, one-electron oxidations at +0.52 and +1.02 V and a reduction at −0.95 V. Measurements in this solvent were carried out at 200 mV/s and were not pursued further.

With the well-defined electrochemical oxidations which characterize these clusters firmly established, the corresponding chemical oxidations appeared to be feasible. The oxidation of $(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ to the salt $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ was easily accomplished upon stirring of a suspension of the neutral cluster with an acetonitrile solution of $NOPF_6$,[29] the latter reagent being present in an excess. Our attempts to oxidize $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^{n+}$ (n = 0 or 1) to the dication were unsuccessful; neither $NOPF_6$ nor oxidants such as Cl_2/CH_2Cl_2 gave the desired product. In the case of $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$, oxidation to both $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ and $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$ was achieved with use of $NOPF_6$, the only difference being the adjustment of the reaction stoichiometry to control the extent of oxidation. The electron-transfer mechanism in these oxidations is probably outer-sphere and most likely proceeds via the intermediacy of M–Cl···$^+$NO bridges. In all instances the cations displayed CV's which were the same as those of the neutral clusters with the exception that for $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^+$ there was now one oxidation and two reductions, while $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^+$ had one oxidation and one reduction whereas for $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^{2+}$ both processes were reductions.

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Table III. X-ray Photoelectron Spectra of Tri-*n*-propylphosphine Complexes of Niobium and Tantalum Chloride Clusters[a]

complex	Nb $3d_{5/2}$ or Ta $4f_{7/2}$	Cl $2p_{3/2}$		P 2p	
		Cl_b	Cl_t	PF_6^-	P-*n*-Pr_3
$(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$	204.8 (1.3)	199.5 (1.1)	197.7 (1.0)		130.8
$[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$	205.4 (1.4)	200.0 (1.4)	198.0 (1.2)	136.2	130.8
$(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$	23.9 (1.3)	199.8 (1.4)	198.0 (1.2)		131.0
$[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$	24.3 (1.2)	200.1 (1.2)	198.1 (1.2)	136.0	131.1
$[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$	25.0 (1.6)	200.3 (1.4)	198.2 (1.1)	135.6	131.0

[a] Binding energies in eV are referenced to a C 1s energy of 285.0 eV for the carbon atoms of the phosphine ligands; full width at half-maximum values (fwhm) given in parentheses.

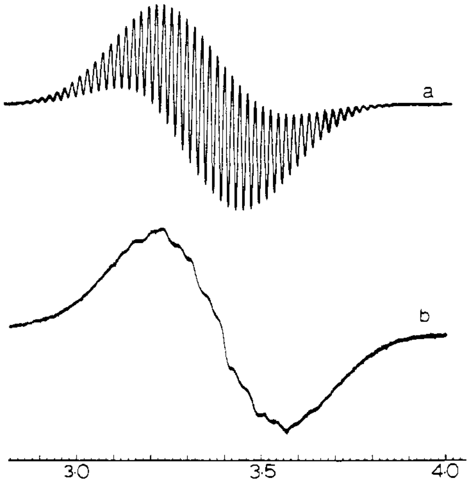

Figure 2. X-Band ESR spectra of dichloromethane solutions of (a) $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ at room temperature and (b) electrochemically generated $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^+$ at -170 °C.

The reduction exhibited by $(Nb_6Cl_{12})Cl_2(PR_3)_4$ at approximately -1.0 V is clearly a one-electron process as demonstrated by the similarity of the peak currents to those of the oxidations (see Figure 1a). However, controlled potential electrolysis at -1.2 V gave *n* values in excess of 1 (for example, $n \approx 1.2$ in the case of $(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ because of partial decomposition of the parent cluster following reduction. This was reflected in the resultant CV by the additional appearance of poorly defined product waves. Our attempts to generate pure solutions containing the monoanions $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^-$ were thereby thwarted even when the electrochemical reductions were carried out at 0 °C under an atmosphere of nitrogen. Similar behavior was exhibited by acetonitrile solutions of this complex. Furthermore, we have not yet been able to prepare salts of this anion using chemical reduction methods.[30]

Since the $E_{1/2}(\text{ox})$ values of the tantalum cluster are, as expected, cathodic of the corresponding oxidations of $(Nb_6Cl_{12})Cl_2(PR_3)_4$ by ~0.3 V,[31] the reduction of $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ to its monoanion may be expected at a potential cathodic of the dichloromethane solvent limit. Acetonitrile is a better electrochemical solvent in terms of its potential limits, but $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ is virtually insoluble in this solvent. Fortunately, the cations $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^{n+}$, where $n = 1$ or 2, are quite soluble, and so their CV's could be recorded. In addition to $E_{1/2}$ values of +0.23 and +0.72 V, there is an additional couple at -1.60 V (vs. SCE) which appears to be the expected reduction to the monoanion (see Figure 1c). However, since (1) the peak currents associated with this process are only 80% of those for the quasi-reversible couples at more positive potentials, (2) the $E_{p,c}-E_{p,a}$ separation of 130–160 mV is 50 mV greater than those of the other couples, and (3) the shapes of the anodic and cathodic components are different, this reduction appears to be irreversible. This was confirmed by controlled potential electrolysis experiments at -1.8 V.

Spectroscopic Characterization of the $[(M_6Cl_{12})Cl_2(PR_3)_4]^{n+}$ Cations. Important features in the electronic absorption spectra and far-infrared spectra of these complexes are given in Table I. Suffice it to say that a comparison of their electronic spectra with those exhibited by other complexes containing the $(M_6Cl_{12})^{n+}$ cores ($n = 3$ or 4), particularly for solvated cationic species,[17,20,21] leaves little doubt as to the identity of these complexes. Furthermore, in addition to the infrared absorption bands of the PF_6^- anions (848–843 and 560 cm^{-1}), the vibrational frequencies which are characteristic of the cluster cores (Table I) shift progressively to higher energies as the charge on the core increases. This is in accord with the trends which have been established with other derivatives.[24-26]

The electron paramagnetic resonance spectra (ESR) of the niobium and tantalum cluster cations $[(M_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^+$ were recorded at room temperature and -170 °C on both the chemically and electrochemically generated species in dichloromethane solutions and the solid phases. The ESR spectra of solid $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$, its dichloromethane solution at -170 °C, and solutions of the electrochemically generated cation (which also contained an excess of tetra-*n*-butylammonium hexafluorophosphate) each showed a single symmetric broad signal with a *g* value of 1.95. A multiline ESR spectrum was obtained only for a dichloromethane solution of $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ at room temperature (Figure 2a). It is in all important respects identical with that reported by Mackay and Schneider[32] for various room-temperature solution spectra of $(Et_4N)_3[(Nb_6Cl_{12})Cl_6]$. Of the 55 lines expected from the coupling of an unpaired electron with six equivalent niobium nuclei ($I = {}^9/_2$) we observe 49. The observed spectrum is in accord with the Hamiltonian $\mathcal{H} = -g\beta HS + (AI)S$, with $g \approx 1.95$ and $A \approx 20.2$ G, the comparable parameters for the $[(Nb_6Cl_{12})Cl_6]^{3-}$ ion being[32] $g = 1.948 \pm 0.003$ and $A = 20.6 \pm 0.5$ G. The striking similarity between the ESR spectra of $[(Nb_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]^+$ and $[(Nb_6Cl_{12})Cl_6]^{3-}$ is in accord with the unpaired electron being in a metal-based orbital singlet with little contribution from the six centrifugal terminally bound ligands.[33]

Under similar experimental conditions to those described above for the paramagnetic niobium complex, we were unable to obtain a significant resolution of the tantalum hyperfine in the ESR spectrum of $[(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4]PF_6$ or its electrochemically generated analogue. However, the appearance of some hyperfine structure (Figure 2b) was apparent in the spectra recorded on dichloromethane glasses (-170 °C).

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(30) Reductants used include lithium, sodium amalgam, and magnesium.

(31) Stability, with respect to oxidation, of low oxidation state transition-metal halides of any group usually decreases with increase in atomic number.

(32) Mackay, R. A.; Schneider, R. F. *Inorg. Chem.* **1967**, *6*, 549.

(33) See: Robbins, D. J.; Thomson, A. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2350 and references therein.

The broad signal at $g = 1.91$ had a peak to peak separation of 340 G.

The X-ray photoelectron spectra (XPS) were recorded on the tri-n-propylphosphine complexes, and the pertinent Nb 3d or Ta 4f, Cl 2p, and P 2p core binding energies are presented in Table III. These data are important for two reasons. First, they further confirm the stoichiometry and gross structure of these complexes, and, second, they provide information as to how variations in the cluster charge are reflected by chemical shifts in the corresponding core electron binding energies. The intensity ratios of the P 2p peaks at 136 and 131 eV, arising from the phosphorus atoms in the PF_6^- and P-n-Pr_3 groups, and the Cl $2p_{3/2}$ peaks at 200 and 198 eV, which are assignable[15] to the chlorine atoms in bridging (Cl_b) and terminal (Cl_t) M–Cl bonds, are both in accord with the presumed structures of these molecules. Deconvolutions of the Cl 2p spectra[15] show that the Cl_b:Cl_t intensity ratios are within 5% of the expected 6:1 stoichiometric ratio. An increase in the oxidation state of the clusters, and therefore in the electronic charge, is paralleled by an appreciable increase in the metal core electron binding energies (approximately 0.6 eV per unit change in charge). This increase is paralleled by a very small but reproducible increase in the Cl 2p binding energies of the Cl_b atoms relative to Cl_t, possibly indicating that the bridging chlorines become more tightly bound as the oxidation state increases. In accord with this interpretation, we observe that the P 2p binding energies of the P-n-Pr_3 ligands are, like the Cl 2p energies of Cl_t, relatively insensitive to the metal oxidation state. Thus these XPS results taken in conjunction with the hyperfine structure associated with the ESR spectra and the observation that the CV's are quite insensitive to changes in the nature of the phosphine ligands point to the HOMO of the $(M_6Cl_{12})^{2+}$ and $(M_6Cl_{12})^{3+}$ ions as being one which is almost exclusively metal based in character.

Comparisons with Other Complexes Containing the $(M_6Cl_{12})^{n+}$ Cores. The redox chemistry of the phosphine derivatives $[(M_6Cl_{12})Cl_2(PR_3)_4]^{n+}$ ($n = 0$–2) in nonaqueous media is generally well behaved, the one exception being our inability to generate pure solutions of the monoanions $[(M_6Cl_{12})Cl_2(PR_3)_4]^-$. Nonetheless, our detection of the latter species is of significance since it demonstrates the existence of a previously unknown oxidation state of these clusters. This state is lower than that previously obtained for the chloride clusters but less than that which can be achieved with the iodide phases $(Nb_6I_8)I_{6/2}$ and $Cs[(Nb_6I_8)I_{6/2}]$.[34]

Attempts to extend our studies to nonaqueous solutions of related complexes were unsuccessful. Thus, dichloromethane solutions of the dimethylsulfoxide complexes $(M_6Cl_{12})Cl_2(Me_2SO)_4$ and acetonitrile solutions of $(Nb_6Cl_{12})Cl_2(Me_2SO)_4$ and of the hydrate $Nb_6Cl_{14}\cdot 8H_2O$ did not exhibit the same well-defined reversible processes which were so characteristic of the CV's of the phosphine systems. In order to study complexes with phosphorus ligands which contained electron-withdrawing substituents and thus to assess their effect upon the oxidation or reduction potentials of these clusters, we prepared the phosphite derivatives $(M_6Cl_{12})Cl_2[P(OR)_3]_4$, where M = Nb or Ta and R = Me or Et.[35] Unfortunately, unlike their phosphine analogues they did not exhibit the desired solubility in such electrochemical solvents as acetonitrile, acetone, dichloromethane, and dimethyl sulfoxide, thereby precluding measurements of their solution properties.

Within the known halide clusters of niobium and tantalum, $(M_6X_{12})^{n+}$, where $n = 2$–4, the only complete series which cover all three oxidation states are the tantalum hydrates $(Ta_6X_{12})X_n(H_2O)_{6-n}\cdot mH_2O$ and the halo anions $[(M_6X_{12})X_6]^{n-}$, where M = Nb or Ta.[24,36,37] Our isolation of $[(Ta_6Cl_{12})Cl_2(PR_3)_4](PF_6)_n$, where $n = 0$–2, represents only the third complete series known and the first to be stabilized by an organic ligand. In fact very few derivatives of the $(M_6X_{12})^{3+}$ and $(M_6X_{12})^{4+}$ clusters which contain organic ligands have previously been obtained. To our knowledge, the only exception is an assortment of dimethyl sulfoxide complexes of $(M_6X_{12})^{3+}$, namely, $(Et_4N)_2[(Nb_6Cl_{12})Cl_5(Me_2SO)]\cdot Me_2SO$, $(Nb_6Cl_{12})Cl_3(Me_2SO)_3\cdot 3Me_2SO$, $(Ta_6Cl_{12})Cl_3(Me_2SO)_3$ and $[(Ta_6Cl_{12})(Me_2SO)_6](ClO_4)_3$, but only the first two were the subject of elemental microanalytical determinations.[26,38]

While several studies have been devoted to the chemical oxidation of the $(M_6X_{12})^{2+}$ cores,[37] few electrochemical investigations have yet been reported. Polarographic measurements on dimethyl sulfoxide solutions of $[(Nb_6Cl_{12})Cl_6]^{n-}$ (n = 2 or 3) and aqueous solutions of $(Nb_6Cl_{12})^{2+}$ have been described,[31,39] but there is only one example, prior to our report, which describes the CV of these clusters. Cooke et al.[40] described the CV's of aqueous solutions of $(Ta_6Cl_{12})^{2+}$ and $(Ta_6Br_{12})^{2+}$ and found values of 0.25 and 0.59 V (vs. SCE) for the two formal electrode potentials[41] of the chloride and 0.35 and 0.65 V for the bromide. In the case of $(Ta_6Cl_{12})^{2+}$(aq), it appears that the second oxidation is more favored than that of $(Ta_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ (Table II), reflecting the greater tendency of phosphines to stabilize the lower oxidation states of these clusters. The stabilizing influence of the phosphine ligands and the favorable solubility properties of the resulting complexes in nonaqueous solvents opens up a solution redox chemistry which is more extensive than that available to the aquated cations.

Acknowledgment. Support from the National Science Foundation through Grant No. CHE79-09233 is gratefully acknowledged. The Digilab FTS-20B and Varian E-109 ESR spectrometers were purchased with grants from the National Science Foundation (Grant Nos. CHE77-08989 and BMS 75-19127).

Registry No. $Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$, 68813-06-9; $Nb_6Cl_{14}(PEt_3)_4$, 76549-94-5; $Nb_6Cl_{14}(PEt_2Ph)_4$, 76549-96-7; $[Nb_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4]PF_6$, 76649-08-6; $Ta_6Cl_{14}(Me_2SO)_4$, 76549-92-3; $Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4$, 76549-95-6; $[Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4](PF_6)_2$, 76649-06-4; $[Ta_6Cl_{14}(P\text{-}n\text{-}Pr_3)_4]PF_6$, 76649-07-5; Nb_6Cl_{14}, 12133-87-8; Ta_6Cl_{14}, 12133-85-6; $(Nb_6Cl_{12})Cl_3(H_2O)_3$, 76549-91-2; $(Ta_6Cl_{12})Cl_3(H_2O)_3$, 12506-81-9; $Nb_6Cl_{14}(Me_2SO)_4$, 70089-07-5.

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(34) Imoto, H.; Corbett, J. D. *Inorg. Chem.* **1980**, *19*, 1241.

(35) The phosphite derivatives were prepared in reasonably good yields upon refluxing of $(M_6Cl_{12})Cl_2(P\text{-}n\text{-}Pr_3)_4$ with methanol or ethanol solutions of $P(OR)_3$ for 18–24 h. Infrared spectroscopy confirmed the replacement of phosphine by phosphite, and carbon and hydrogen microanalyses were in accord with the proposed stoichiometry.

(36) See, for example: Hughes, B. G.; Meyer, J. L.; Fleming, P. B.; McCarley, R. E. *Inorg. Chem.* **1970**, *9*, 1343 and references therein.

(37) Walton, R. A. *Prog. Inorg. Chem.* **1972**, *16*, 1 and references therein.

(38) Converse, J. G.; McCarley, R. E. *Inorg. Chem.* **1970**, *9*, 1361.

(39) McCarley, R. E.; Hughes, B. G.; Cotton, F. A.; Zimmerman, R. *Inorg. Chem.* **1965**, *4*, 1491.

(40) Cooke, N. E.; Kuwana, T.; Espenson, J. *Inorg. Chem.* **1971**, *10*, 1081.

(41) Potentials were measured at 0.852 of the peak current i_p for these reversible i–V waves.[40]