

## New PF<sub>3</sub> and Carbonyl Chemistry of Tantalum\*\*

John E. Ellis,\* Garry F. Warnock, Mikhail V. Barybin, and Marie K. Pomije

Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday

**Abstract:** Reduction of [TaCl<sub>5</sub>] by six equivalents of alkali metal naphthalenide in 1,2-dimethoxyethane at -60 °C followed by treatment with gaseous PF<sub>3</sub> provides the first homoleptic phosphane complex containing tantalum in the -1 oxidation state, [Ta(PF<sub>3</sub>)<sub>6</sub>]<sup>-</sup>. This can be protonated by concentrated sulfuric acid to yield the previously unknown highly

acidic and volatile hydride [HTa(PF<sub>3</sub>)<sub>6</sub>]. An improved normal-pressure synthesis

of [Ta(CO)<sub>6</sub>]<sup>-</sup> is described. Reduction of the latter species by sodium in liquid ammonia gives the carbonyl trianion [Ta(CO)<sub>5</sub>]<sup>3-</sup> which undergoes monoprotonation and stannylation to form [HTa(CO)<sub>5</sub>]<sup>2-</sup> and [Ph<sub>3</sub>SnTa(CO)<sub>5</sub>]<sup>2-</sup>, respectively. The hydride is a useful precursor to [(Ph<sub>3</sub>PAu)<sub>3</sub>Ta(CO)<sub>5</sub>], the only known gold cluster of tantalum.

### Keywords

carbonyl ligands · organometallic compounds · phosphorus ligands · tantalum compounds

### Introduction

Since [Ta(CO)<sub>6</sub>]<sup>-</sup> is the only known homoleptic complex containing tantalum in the -1 oxidation state,<sup>[1]</sup> and the naphthalenide-facilitated reductive carbonylation of [TaCl<sub>5</sub>] has been shown to be an effective route to this anionic tantalum species,<sup>[2]</sup> corresponding reductions in the presence of other potential ligands have recently been examined to determine whether analogous new compounds of the general formula [TaL<sub>6</sub>]<sup>-</sup> are accessible by this route. We now report on the synthesis of the trifluorophosphane complex [Ta(PF<sub>3</sub>)<sub>6</sub>]<sup>-</sup> by this procedure and its conversion to the long-sought hydride [HTa(PF<sub>3</sub>)<sub>6</sub>]. Attempts to prepare the latter species have been noted by Kruck and co-workers in connection with the synthesis of [(η<sup>3</sup>-allyl)Ta(PF<sub>3</sub>)<sub>5</sub>],<sup>[3]</sup> which to our knowledge is the only previously established Ta-PF<sub>3</sub> complex. In this paper we also report an improved atmospheric-pressure synthesis of [Ta(CO)<sub>6</sub>]<sup>-</sup> and present the first full account of the synthesis and chemical properties of the superreduced species [Ta(CO)<sub>5</sub>]<sup>3-</sup>.<sup>[4]</sup> It is hoped that the procedures and methods reported herein will facilitate future studies on these and related low-valent homoleptic tantalum complexes.

### Experimental Procedure

**General:** All operations were performed under an atmosphere of 99.9% argon or 99.5% carbon monoxide further purified by passage through columns of activated BASF catalyst and molecular sieves. The CO was also passed through a column of Ascarite, which is a self-indicating sodium hydroxide nonfibrous silicate formula-

tion for the quantitative absorption of CO<sub>2</sub>. Similar products used by microanalysts should also provide satisfactory results. Despite this purification procedure, when CO of 98% or lower initial purity was used, reduced yields of [Ta(CO)<sub>6</sub>]<sup>-</sup> often resulted. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air [5]. Solutions were transferred through stainless steel double-ended needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double-manifold vacuum line [5-8]. Commercial grade PF<sub>3</sub> (Pennwalt Ozark Mahoning) was purified by passage through two -78 °C traps and two columns of 4 Å molecular sieves, and subsequent isolation at -196 °C in a 1 or 2 L gas storage flask. The PF<sub>3</sub> was then subjected to two freeze-pump-thaw cycles to remove O<sub>2</sub> and other noncondensable gases. Liquid ammonia was purified by distillation from sodium metal. Other solvents were freed of impurities by standard procedures and stored under argon. Unless otherwise stated, other reagents were obtained from commercial sources and freed of oxygen and moisture before use. Since commercial grades of "resublimed" [TaCl<sub>5</sub>] often gave erratic results, only freshly sublimed [TaCl<sub>5</sub>] was used in the synthesis of [TaL<sub>6</sub>]<sup>-</sup> (L = CO or PF<sub>3</sub>). Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer or a Mattson Galaxy 6021 FTIR spectrometer with samples sealed in 0.1 mm NaCl or CaF<sub>2</sub> cells. Nujol (mineral oil) mulls of air-sensitive compounds were prepared in a drybox (Vacuum Atmospheres) filled with nitrogen. NMR samples were sealed into 5 mm tubes and were run on Nicolet NT-300 WB, IBM NR-200 AF or NR-300 AF spectrometers. <sup>13</sup>C NMR spectra were acquired with a 45° pulse and a 4 s delay between pulses to aid in the detection of carbonyl <sup>13</sup>C resonances. Melting points are uncorrected, and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by H. Malissa and G. Reuter Analytische Laboratorien, Engelskirchen, West Germany.

**Electrochemical Measurements:** All electrochemical experiments were performed with a BAS 100 electrochemical analyzer. Cyclic voltammetry (CV) and chronocoulometry (CC) experiments were performed at ambient temperature (23 °C) with a normal three-electrode configuration consisting of a highly polished glassy carbon-disk working electrode (*A* = 0.07 cm<sup>2</sup>), and a Ag/AgCl reference electrode containing 1.0 M KCl. Scan rates of 50-500 mVsec<sup>-1</sup> were employed in the CV studies. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte. Tetrabutylammonium hexafluorophosphate was used without further purification. Tetrabutylammonium tetrafluoroborate was dried in vacuo overnight at 110 °C. All of the supporting electrolytes were purchased from Southwestern Analytical Chemicals. In most cases, the electrolyte and solvent were passed down an alumina column prior to the electrochemical experiments. In all cases, working solutions were prepared by recording background cyclic voltammograms of the electrolyte solution before addition of the complex. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution. Potentials are reported versus aqueous Ag/AgCl and are not corrected for the junction potential. A standard

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electrochemical current convention is used (anodic currents are negative). For future corrections and for the correlation of these data with those of other workers, the  $E^\circ$  for the ferrocenium/ferrocene couple under conditions identical to those used for the compounds under study was + 0.44 V. No  $iR$  compensation was used.

**[Et<sub>4</sub>N][Ta(CO)<sub>6</sub>]<sub>2</sub> (1):** A solution of K<sub>2</sub>C<sub>10</sub>H<sub>8</sub> was prepared by vigorous stirring of potassium metal (1.58 g, 40.5 mmol) with naphthalene (5.2 g, 41 mmol) in 1,2-dimethoxyethane (DME, 100 mL) at room temperature for 4 h with a glass-covered magnetic stir bar in a standard 500 mL round-bottom flask. This solution was then cooled to -60 °C while being stirred, and a cold (-60 °C) solution of [TaCl<sub>5</sub>] was added by cannula. The latter clear and colorless solution was prepared by addition of solid [TaCl<sub>5</sub>] microcrystals (2.40 g, 6.7 mmol) over a period of about 20 min to 100 mL of vigorously stirred, cold (-60 °C) DME. (If solid [TaCl<sub>5</sub>] is added too rapidly it will decompose and give yellow to yellow-brown solutions. Also, partially hydrolyzed [TaCl<sub>5</sub>] will cause turbidity at this stage. Reduced yields of 1 or [Ta(CO)<sub>6</sub>]<sup>-</sup> (vide infra) will result in any case.) Usually within 15–30 min a homogeneous deep red-brown solution formed, unless excess K<sub>2</sub>C<sub>10</sub>H<sub>8</sub> was present. The solution was stirred for 1 h at -60 °C and then the reaction vessel was evacuated until evolution of dissolved argon gas nearly ceased. Phosphorus trifluoride (ca. 3.6 g, 42 mmol) was then introduced from a 1 L gas storage flask. Within a few minutes, the pressure of the system decreased to about 30 torr, and the storage flask was isolated from the reaction mixture. The reaction mixture was allowed to warm slowly to room temperature over a period of about 16 h while being stirred vigorously and connected to a mercury bubbler/manometer. Subsequently, the mixture was filtered into a flask containing an excess of powdered Et<sub>4</sub>NBr (4.2 g, 20 mmol). The pale red-brown filtrate—Et<sub>4</sub>NBr slurry was stirred for 8 h. Solvent was then removed in vacuo. The resulting tan solid was vigorously triturated with pentane (3 × 50 mL) to remove naphthalene, and then dried in vacuo. This solid was partially dissolved in THF (50 mL) and then H<sub>2</sub>O (200 mL) was added with vigorous stirring. Initially an oily solid formed, but this solidified completely on removal of most of the THF in vacuo. After removal of the supernatant the solid was triturated with water (2 × 50 mL) and dried in vacuo to give a free-flowing brown solid. This was dissolved in a mixture of acetone (30 mL), toluene (15 mL), and 1-butanol (5 mL) and filtered to provide a red-brown solution. On slow removal of about 40 mL of the solvent in vacuo, a tan crystalline mass formed. An uncharacterized intensely brown impurity remained in the toluene/butanol-rich supernatant. The product was separated by filtration, washed with toluene (2 × 20 mL) and pentane (2 × 20 mL), and then dried in vacuo. An additional slow recrystallization of the solid from acetone/toluene/1-butanol provided 1.28 g (23%) of nearly colorless microcrystalline 1 of satisfactory purity. Anal. calcd for C<sub>8</sub>H<sub>10</sub>F<sub>18</sub>NP<sub>6</sub>Ta (%): C, 11.45; H, 2.40; F, 40.76. Found: C, 11.30; H, 2.03; F, 40.63. IR (mineral oil mull):  $\tilde{\nu}$  = 831 vs, 774  $\text{cm}^{-1}$  (P-F region); (CH<sub>2</sub>Cl<sub>2</sub>) 842 vs, 784  $\text{cm}^{-1}$ . <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C, CFC<sub>3</sub> external std):  $\delta$  = 11.5 (d, <sup>1</sup>J<sub>PF</sub> = 1240 Hz), <sup>31</sup>P NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C, H<sub>3</sub>PO<sub>4</sub> external std):  $\delta$  ≈ +150 (very broad,  $W_{1/2}$  ≈ 10000 Hz, unresolved Ta-P and F-P coupling). Compound 1 slowly darkens above 200 °C and rapidly decomposes at 292–296 °C. It is essentially insoluble in alkanes, toluene, and diethyl ether, and soluble without decomposition in CH<sub>2</sub>Cl<sub>2</sub>, THF, DME, and acetone. It is poorly soluble in ethanol and insoluble in water. Although 1 is stable to dry air for extended periods, it does react slowly with water to form HF and uncharacterized species.

**[HTa(PF<sub>3</sub>)<sub>6</sub>] (2):** Excess concentrated H<sub>2</sub>SO<sub>4</sub> (2.0 mL, 38 mmol) was added to solid 1 (0.37 g, 0.44 mmol). A volatile yellow solid formed immediately. Sublimation at 25 °C/0.05 torr onto a dry ice/acetone-cooled probe gave deep yellow crystals of spectroscopically pure 2 (0.24 g, 77% yield); decomp. without melting begins at approx. 114 °C, solid turns black at approx. 140 °C. MS (70 eV), *m/e* (rel intensity, selected peaks): 709.8 (*M*<sup>+</sup>, 5.8), 708.8 (*M*<sup>+</sup>-H, 0.6), 621.9 (*M*<sup>+</sup>-PF<sub>3</sub>, 8.7), 620.9 (*M*<sup>+</sup>-H-PF<sub>3</sub>, 2.5), 602.9 (*M*<sup>+</sup>-H-F-PF<sub>3</sub>, 4.9), 533.9 (*M*<sup>+</sup>-2PF<sub>3</sub>, 5.3), 270.0 (*M*<sup>+</sup>-5PF<sub>3</sub>, 15), 269.0 (*M*<sup>+</sup>-H-5PF<sub>3</sub>, 20), 88.0 (PF<sub>3</sub>, 69), 69.0 (PF<sub>2</sub>, 100); high resolution MS: *m/e* = 709.7696 (calcd) *m/e* = 709.7646 (observed). IR (mineral oil mull):  $\tilde{\nu}$  = 891 sh, 870 sbr, 842 sbr (P-F region); (CCl<sub>4</sub>) 900 vs, 843  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (500 MHz, 1:1 CD<sub>2</sub>Cl<sub>2</sub>: 1,1,2-C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>, 0 °C):  $\delta$  = -8.7 (sept, <sup>2</sup>J<sub>PH</sub> = 57 Hz, <sup>3</sup>J<sub>PH</sub> = 5 Hz). <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C, CFC<sub>3</sub> external std):  $\delta$  = 3.2 (d, <sup>1</sup>J<sub>PF</sub> = 1280 Hz, coord PF<sub>3</sub>), -32.0 (d, <sup>1</sup>J<sub>PF</sub> = 1402 Hz, free PF<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C, H<sub>3</sub>PO<sub>4</sub> external std):  $\delta$  = 153 (q, <sup>1</sup>J<sub>PF</sub> = 1290 Hz, coord. PF<sub>3</sub>), 110 (q, <sup>1</sup>J<sub>PF</sub> = 1400 Hz, free PF<sub>3</sub>).

**Reduction of 2 by Na/Hg to form 1:** A solution of [HTa(PF<sub>3</sub>)<sub>6</sub>] (1.84 g, 2.59 mmol) in diethyl ether (125 mL) was treated with 0.75% sodium amalgam (2.6 mL = 11 mmol Na) while being stirred. Slow gas evolution commenced almost immediately, and after 3 h the reaction mixture was nearly colorless. The ether was removed in vacuo and the residue was taken up in THF (125 mL) and stirred for 0.5 h. The resulting pale yellow solution was filtered through a plug of diatomaceous earth (Kieselguhr) and stirred for 12 h at room temperature with excess finely divided Et<sub>4</sub>NBr (1.09 g, 5.2 mmol). After filtration, solvent was removed in vacuo and the residue was recrystallized from THF/Et<sub>2</sub>O to give 1.64 g (75%) of colorless crystalline 1.

**[Et<sub>4</sub>N][Ta(CO)<sub>6</sub>] (3):** We prepared a solution of NaC<sub>10</sub>H<sub>8</sub> by stirring sodium metal (3.88 g, 0.17 mol) cut into small pieces (ca. 2–4 mm on an edge) and sublimed naphthalene (21.8 g, 0.17 mol) in DME (300 mL) for 5 h at room temperature with a large glass-covered magnetic stir bar (ca. 45 × 8 mm) in a standard 1 L round-bot-

tom flask. Sublimed [TaCl<sub>5</sub>] (10.0 g, 28 mmol) was placed in an angled or bent Schlenk tube and slowly tapped over a period of about 10 min into cold (-60 °C) magnetically stirred DME (100 mL). At the end of the addition the solution was clear and colorless. The cold [TaCl<sub>5</sub>] solution was then rapidly transferred by cannula (ca. 1.3 mm inside diameter) to the cold (ca. -40 °C) and vigorously stirred solution/slurry of NaC<sub>10</sub>H<sub>8</sub>. Within 15 min the deep green color of C<sub>10</sub>H<sub>8</sub><sup>-</sup> changed to the rich red-brown color of the intermediate. The solution was stirred for 1.5 h at -40 °C and then cooled to -60 °C, after which argon was removed by evacuation and replaced by CO at approximately atmospheric pressure. The reaction mixture was stirred for 12 h at -60 °C under CO and then slowly warmed to room temperature over a period of about 3 h. After evacuation of the CO and addition of argon, the reaction mixture was filtered through a 20–30 mm deep plug of diatomaceous earth to provide an intense yellow-orange solution. All but about 20 mL of solvent was then evaporated under reduced pressure and oxygen-free H<sub>2</sub>O (200 mL) was added to precipitate the naphthalene while the mixture was stirred vigorously. The resulting slurry was filtered into a flask containing an excess of Et<sub>4</sub>NBr (8.8 g, 42 mmol) dissolved in H<sub>2</sub>O (20 mL). (The wet naphthalene was washed with additional water until it was colorless.) A precipitate of 3 formed immediately on mixing. This was isolated by filtration, washed extensively with H<sub>2</sub>O (3 × 50 mL), and dried in vacuo at room temperature. It was then recrystallized from THF/diethyl ether to provide microcrystalline and free-flowing orange-yellow 3 (5.93 g, 45% based on [TaCl<sub>5</sub>]), which was identical to the previously described bona fide [Et<sub>4</sub>N][Ta(CO)<sub>6</sub>] [2].

**[Na(diglyme)<sub>2</sub>][Ta(CO)<sub>6</sub>] (4):** The synthesis of 4 was carried out by essentially the same procedure used for the synthesis of 3 except that the carbonylation was conducted in a 1 L Morton flask equipped with a mechanical stirrer/glass paddle assembly that permitted more effective mixing. A cold (-60 °C) solution of [TaCl<sub>5</sub>] (9.0 g, 25 mmol) in DME (100 mL) was added by cannula to a cold (-60 °C) solution of NaC<sub>10</sub>H<sub>8</sub> (0.15 mol) prepared by the interaction of Na metal (3.50 g, 0.15 mol) and naphthalene (25.7 g, 0.20 mol) in DME (300 mL) as described above. After carbonylation (as described for 3), the stirring was stopped to permit the solids to settle. The reaction mixture was filtered under an atmosphere of argon gas and then treated with excess diethyleneglycoldimethyl ether (diglyme, 20 mL, 0.14 mol). After removal of all but 50 mL of solvent, pentane (500 mL) was added to precipitate the product. The supernatant was decanted and additional pentane (500 mL) was employed to remove excess diglyme. The solid was transferred to a medium-porosity filtration apparatus, thoroughly washed with pentane (5 × 50 mL), and dried in vacuo at room temperature to provide 8.4 g (52% based on [TaCl<sub>5</sub>]) of slightly sticky yellow-orange 4, which was of satisfactory purity and spectroscopically identical to the previously described compound [2]. In other syntheses of [Ta(CO)<sub>6</sub>]<sup>-</sup>, it was found that use of a mechanical stirrer often did not provide significantly better yields of product compared with that obtained with glass-covered magnetic stir bars.

**[Na(diglyme)<sub>2</sub>][Ta(<sup>13</sup>CO)<sub>6</sub>] (5):** This product was prepared with the apparatus shown in Figure 1. Powdered [TaCl<sub>5</sub>] (2.0 g, 5.6 mmol) was slowly added to a cold (-60 °C) solution of NaC<sub>10</sub>H<sub>8</sub> (33.6 mmol) in DME (150 mL) through a bent Schlenk tube. The cold reaction mixture was then transferred by cannula to the 250 mL reaction flask shown in Figure 1. The solution was stirred for about 15 min and then the inert gas was removed by evacuation. The 99% enriched <sup>13</sup>CO contained in a 1 L bulb (ca. 42 mmol) at about atmospheric pressure was then admitted into the reaction flask, and the mixture was stirred at -60 °C for 4 h and then slowly warmed to room temperature. Argon was introduced to restore atmospheric pressure, the solution filtered, and diglyme

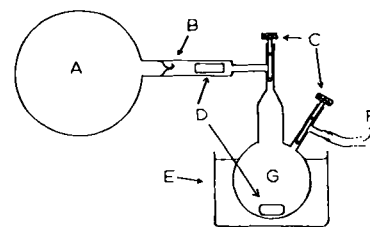


Fig. 1. Apparatus used for the synthesis of 99% <sup>13</sup>CO-enriched [Ta(CO)<sub>6</sub>]<sup>-</sup>. A = 1 L bulb of 99% <sup>13</sup>CO-labeled carbon monoxide; B = break seal; C = Teflon high-vacuum valves; D = glass-covered magnetic stir bar; E = solid CO<sub>2</sub>/acetone slush bath; F = tubing to inert atmosphere manifold; G = 250 mL reaction vessel.

(4.0 mL, 28 mmol) added with stirring. Subsequent removal of the DME and trituration of the residue with pentane (2 × 20 mL) provided 1.06 g (30% based on [TaCl<sub>5</sub>]) of bright yellow and free-flowing [Na(diglyme)<sub>2</sub>][Ta(<sup>13</sup>CO)<sub>6</sub>], which was spectroscopically pure and used without further treatment. IR (DME):  $\tilde{\nu}$  = 1818  $\text{cm}^{-1}$  (CO). <sup>13</sup>C NMR (75.4 MHz, NH<sub>3</sub>, -50 °C):  $\delta$  = 211 (brs,  $W_{1/2}$  = 820 Hz).

**Cs<sub>3</sub>[Ta(CO)<sub>6</sub>] (6) from Na<sub>3</sub>[Ta(CO)<sub>6</sub>]:** A cold (-70 °C) solution of sodium metal (0.22 g, 9.4 mmol) in liquid ammonia (50 mL) was added by cannula to a magnetically stirred and cold (-70 °C) solution of 4 (2.00 g, 3.1 mmol) in liquid ammonia (50 mL). Within seconds at -70 °C the yellow-orange Na[Ta(CO)<sub>6</sub>] changed to the deep red of Na<sub>3</sub>[Ta(CO)<sub>6</sub>]. The solution was stirred for 30 min at -70 °C and then transferred through a cannula to a jacketed low-temperature medium-porosity filtration unit [9], which was cooled with isopropyl alcohol/CO<sub>2</sub> to about -70 °C. (Caution: The filter cake contains pyrophoric Na<sub>2</sub>C<sub>2</sub>O<sub>2</sub> [10], which can be safely destroyed by addition of 100 mL of water under a protective blanket of argon or

nitrogen gas). The filtrate was added to a cold stirred solution of excess anhydrous cesium iodide (3.25 g, 12.5 mmol) in ammonia (25 mL). A bright orange crystalline precipitate formed immediately on mixing. The cesium salt was separated by filtration at  $-60^{\circ}\text{C}$  with the jacketed low-temperature filtration apparatus, washed thoroughly with liquid ammonia ( $4 \times 25\text{ mL}$ ), and dried in vacuo while slowly warmed to room temperature. The initial orange microcrystalline product is undoubtedly an ammonia solvate, since above  $-40^{\circ}\text{C}$  it crumbled to a powder in vacuo and became much darker in color. A deep brown-red very shock-sensitive (CAUTION!) solid was thereby obtained (0.90 g, 40% based on 4), which provided satisfactory analyses for unsolvated **6**. Anal. calcd for  $\text{C}_5\text{O}_3\text{Cs}_3\text{Ta}$ : C, 8.34; Cs, 55.40; Ta, 25.14; H, 0.00. Found: C, 8.23; Cs, 55.68; Ta, 25.03; H, 0.12. IR (mineral oil mull):  $\tilde{\nu} = 1813\text{ w}$  (sharp),  $1560\text{ vs}$  (very broad)  $\text{cm}^{-1}$  (CO region).  $^{13}\text{C}$  NMR (99% enriched  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  prepared from **5**) (75.4 MHz,  $\text{NH}_3$ ,  $-50^{\circ}\text{C}$ ):  $\delta = 293\text{ s}$ ,  $W_{1/2} = 10\text{ Hz}$ .

**[Et<sub>4</sub>N][HTa(CO)<sub>5</sub>]** (**7**) from  $\text{Na}_3[\text{HTa}(\text{CO})_5]$ : A solution of  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  in liquid ammonia was prepared by the reaction of **4** (2.04 g, 3.2 mmol) with sodium metal (0.22 g, 9.6 mmol) as described above. One equivalent of ethanol (0.15 g, 3.2 mmol) in cold ( $-70^{\circ}\text{C}$ ) THF (50 mL) was transferred by cannula into the cold ( $-70^{\circ}\text{C}$ ) solution of the trianion. Almost immediately the deep red of the trianion changed to the orange-red of  $\text{Na}_3[\text{HTa}(\text{CO})_5]$ , which is unstable as a solid at room temperature. After brief stirring, the flask's contents were allowed to settle for 3 h at  $-70^{\circ}\text{C}$ . The solution was then filtered with a jacketed low-temperature filtration apparatus, as described above, into a cold ( $-78^{\circ}\text{C}$ ) liquid ammonia solution of  $[\text{Et}_4\text{N}][\text{BH}_4]$  (0.93 g, 6.4 mmol). Immediate precipitation of beautiful microcrystalline orange-red product occurred. The product was separated by filtration, washed thoroughly with liquid ammonia ( $4 \times 25\text{ mL}$ ) and dried in vacuo at room temperature. By this procedure 1.30 g (70% yield based on **4**) of satisfactorily pure **7** was obtained. Anal. calcd for  $\text{C}_2\text{H}_4\text{N}_2\text{O}_5\text{Ta}$ : C, 43.30; H, 7.09; N, 4.81; Found: C, 43.26; H, 6.69; N, 4.77. IR (mineral oil mull):  $\tilde{\nu} = 1922\text{ w}$ ,  $1750\text{ s}$ ,  $1710\text{ sh cm}^{-1}$  (CO region).  $^1\text{H}$  NMR (300 MHz,  $\text{NH}_3$ ,  $-50^{\circ}\text{C}$ ):  $\delta = -2.23\text{ (s)}$  for  $\text{Na}_3[\text{HTa}(\text{CO})_5]$ .

**[Et<sub>4</sub>N][Ph<sub>3</sub>SnTa(CO)<sub>5</sub>]** (**8**): Liquid ammonia (100 mL) was transferred to **3** (3.00 g, 6.26 mmol) and the resulting slurry was refluxed for 0.5 h to help solubilize the poorly soluble **3** in this medium. The magnetically stirred slurry was then cooled to  $-60^{\circ}\text{C}$  and to this was transferred a solution of sodium metal (0.432 g, 18.8 mmol) in ammonia (75 mL) at  $-60^{\circ}\text{C}$ . Almost immediately the deep red color characteristic of  $[\text{Ta}(\text{CO})_5]^{3-}$  was obtained. After 1 h, a cold ( $-78^{\circ}\text{C}$ ) solution of  $\text{Ph}_3\text{SnCl}$  (2.41 g, 6.26 mmol) in THF (50 mL) was added dropwise with efficient stirring. Near the end of the addition the solution/slurry had changed to a bright orange color. Solid  $\text{Et}_4\text{NBr}$  (2.63 g, 12.5 mmol) was then introduced and the reaction mixture was refluxed for about 0.5 h. After most of the ammonia had evaporated, the resulting solid was thoroughly washed with THF ( $3 \times 25\text{ mL}$ ) and absolute ethanol (25 mL), and then dried in vacuo. The solid was taken up in acetonitrile (60 mL) and filtered to give an orange-red solution. On removal of all but about 10 mL of solvent in vacuo, orange-red crystals of product formed. The remaining product was crystallized by dropwise addition of 30 mL of ethanol. The resulting orange crystals were washed with ethanol ( $2 \times 20\text{ mL}$ ) and then diethyl ether ( $2 \times 30\text{ mL}$ ), and dried in vacuo to provide 4.15 g (71% based on **3**) of satisfactorily pure **8**. Anal. calcd for  $\text{C}_{39}\text{H}_{53}\text{N}_2\text{O}_5\text{SnTa}$ : C, 50.29; H, 5.95; N, 3.01. Found: C, 49.75; H, 5.83; N, 3.03. IR (mineral oil mull):  $\tilde{\nu} = 1936\text{ m}$ ,  $1774\text{ vs}$ ,  $1732\text{ s}$ ,  $\text{sh}$ ; ( $\text{CH}_3\text{CN}$ ):  $1942\text{ m}$ ,  $1785\text{ vs}$ ,  $1755\text{ m}$ ,  $\text{sh cm}^{-1}$  (CO region).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = 7.0\text{--}7.7\text{ (m)}$ ,  $15\text{H}$ ,  $\text{Ph}_3\text{Sn}$ ),  $3.11\text{ (q)}$ ,  $16\text{H}$ ,  $\text{CH}_2$  of  $\text{Et}_4\text{N}^+$ ),  $1.18\text{ (tt)}$ ,  $24\text{H}$ ,  $\text{CH}_3$  of  $\text{Et}_4\text{N}^+$ ). M.p.  $222^{\circ}\text{C}$  with decomp.

**[Ph<sub>3</sub>PAu]<sub>3</sub>Ta(CO)<sub>5</sub>** (**9**): Cold THF (60 mL,  $-70^{\circ}\text{C}$ ) was added by cannula to a stirred, finely ground mixture of solid  $[\text{Ph}_3\text{PAuCl}]$  (1.00 g, 2.0 mmol) and **7** (0.393 g, 0.68 mmol). Within 2 h the originally light orange slurry had become dark red. After 4 h, when the reaction mixture was a very dark brown-red, it was warmed to room temperature. After filtration, all but about 5 mL of solvent was removed in vacuo. Diethyl ether (200 mL) was slowly added with rapid stirring to produce a dark brown-red solid. Crystallization from  $\text{CH}_2\text{Cl}_2$ /heptane gave 0.42 g (54% yield based on **7**) of homogeneous orange-red and satisfactorily pure **9**. M.p.  $120^{\circ}\text{C}$  with decomp. Anal. calcd for  $\text{C}_{59}\text{H}_{45}\text{Au}_3\text{O}_5\text{P}_3\text{Ta}$ : C, 41.72; H, 2.67. Found: C, 41.59; H, 2.80. IR (Nujol mull):  $\tilde{\nu} = 1970\text{ s}$ ,  $1900\text{ m}$ ,  $1840\text{ s}$ ,  $1825\text{ s cm}^{-1}$  (CO); (THF or  $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu} = 1976\text{ s}$ ,  $1892\text{ w}$  (sh),  $1855\text{ s cm}^{-1}$  (CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^{\circ}\text{C}$ ):  $\delta = 56.5\text{ (s)}$ .

## Results and Discussion

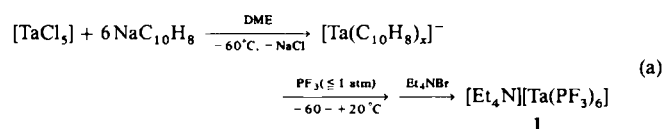
**Synthesis of  $[\text{Ta}(\text{PF}_3)_6]^-$  and  $[\text{HTa}(\text{PF}_3)_6]$  by the Naphthalenide Route:** Reduction of  $[\text{TaCl}_5]$  by six equivalents of alkali metal naphthalenide in 1,2-dimethoxyethane provides a deep red-brown solution that contains one or more species that function as synthetic equivalents of "naked"  $\text{Ta}(1-)$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of products from these reactions resemble those recently reported for  $[\text{Zr}(\eta^4\text{-C}_{10}\text{H}_8)_3]^{2-}$ .<sup>[12]</sup> On this basis they are provisionally formulated as  $[\text{Ta}(\text{C}_{10}\text{H}_8)_x]^-$ , where  $x = 2$  and/or  $3$ , but

coordination of solvent may also be important in their stabilization. Unlike the aforementioned zirconium complex, these substances are quite unstable in solution. Several attempts to isolate tractable pure products from these reactions with a variety of cations have been largely unsuccessful to date, but efforts continue in this area.<sup>[13,14]</sup> They are extremely useful precursors to  $[\text{Ta}(\text{PF}_3)_6]^-$ ,  $[\text{Ta}(\text{CO})_6]^-$ , and possibly other classes of homoleptic  $\text{Ta}(1-)$  complexes. Since  $[\text{Ta}(\text{PF}_3)_6]^-$  and  $[\text{HTa}(\text{PF}_3)_6]$  are new substances, they will be described first along with related information from previous studies on  $\text{PF}_3$  chemistry of the Group 5 metals.

Although the  $\text{PF}_3$  chemistry of most transition metals has been extensively explored, particularly through the pioneering efforts of T. Kruck and co-workers,<sup>[15,16]</sup> relatively few studies have involved the Group 5 metals. In 1974 Kruck and Hempel reported that UV irradiation of solutions of  $[\text{V}(\text{CO})_6]^-$  in the presence of excess  $\text{PF}_3$  gave almost quantitative yields of  $[\text{V}(\text{PF}_3)_6]^-$ .<sup>[17]</sup> Protonation of the latter anion was shown to yield the remarkably stable  $[\text{HV}(\text{PF}_3)_6]$ ;  $^1\text{H}$  NMR spectroscopy established that this species contains a  $\text{H-V}$  bond.<sup>[17]</sup> The species may be considered as a model for the exceedingly unstable corresponding carbonyl hydrogen complex, which has been postulated to be  $[\text{HV}(\text{CO})_6]^{[18]}$  or  $[\text{V}(\text{CO})_5\text{COH}]$ .<sup>[19]</sup> More recently, Collong and Kruck isolated the neutral  $[\text{V}(\text{PF}_3)_6]$  by oxidation of the corresponding anion with phenyldiazonium ion.<sup>[20]</sup> The only other  $\text{V-PF}_3$  complexes, without  $\eta^5$ -dienyl units,<sup>[16]</sup> appear to be mixed  $\text{CO-PF}_3$  complexes of the general formula  $[\text{V}(\text{CO})_6-n(\text{PF}_3)_n]^-$ .<sup>[21,22]</sup>

Rehr and co-workers have obtained similar Nb- $\text{PF}_3$  complexes, that is, *fac*- $[\text{Nb}(\text{CO})_3(\text{PF}_3)_3]^-$  and  $[\text{Nb}(\text{PF}_3)_6]^-$ ,<sup>[21a,23]</sup> by the Kruck-inspired photolysis route using  $[\text{Nb}(\text{CO})_6]^-$ , but to our knowledge extensions of this procedure to tantalum have not been reported. Since Kruck and Hempel had mentioned attempts to prepare the unknown  $[\text{HTa}(\text{PF}_3)_6]$  in their report on  $[(\eta^3\text{-allyl})\text{Ta}(\text{PF}_3)_5]$ ,<sup>[13]</sup> we felt that this hydride and its conjugate base  $[\text{Ta}(\text{PF}_3)_6]^-$  would be significant targets for initial tests of the generality of our naphthalenide route to low valent  $[\text{TaL}_6]^-$  complexes.

Slightly more than 6 equivalents of gaseous  $\text{PF}_3$  were introduced into an evacuated flask containing  $[\text{Ta}(\text{C}_{10}\text{H}_8)_x]^-$  at  $-60^{\circ}\text{C}$  in DME with stirring. On being warmed to room temperature with efficient magnetic stirring, the reaction mixture was a pale red-brown. After filtration, cation exchange and two careful fractional crystallizations, satisfactorily pure ivory-colored samples of the new substance  $[\text{Et}_4\text{N}][\text{Ta}(\text{PF}_3)_6]$  (**1**) were obtained in 15–25% yields [Eq. (a)]. Addition of excess  $\text{PF}_3$  did not result in a significant increase in the yield of **1**, so alternative procedures to this compound are being investigated. However, since 1–3 g of **1** is easily obtained from inexpensive precursors in this "one-pot reaction", these relatively modest yields should present no problem in future explorations of the

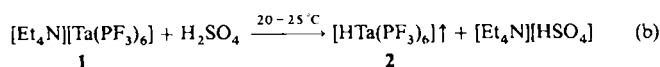


chemical properties of this new substance. As in the case of  $[\text{V}(\text{PF}_3)_6]^-$ , the  $\text{Et}_4\text{N}^+$  salt of the tantalum analogue is extremely stable thermally, only beginning to darken at temperatures above  $200^{\circ}\text{C}$  under an inert atmosphere and rapidly decomposing above  $290^{\circ}\text{C}$ . By contrast,  $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_6]$  (vide infra) darkens above  $142^{\circ}\text{C}$  and rapidly decomposes above  $190^{\circ}\text{C}$ , nearly  $100^{\circ}$  lower than the  $\text{PF}_3$  complex!

Spectroscopic properties of **1** are entirely consistent with the presence of the octahedral anion  $[\text{Ta}(\text{PF}_3)_6]^-$  and share many features with those previously observed for  $[\text{V}(\text{PF}_3)_6]^-$ .<sup>[14, 17, 23]</sup> For example, in  $\text{CH}_2\text{Cl}_2$ , **1** exhibits  $\tilde{\nu}(\text{P-F})$  absorptions at 842 (vs) and 784 (s)  $\text{cm}^{-1}$ , while for the vanadium analogue in  $\text{CH}_2\text{Cl}_2$  the corresponding values are 847 (vs) and 786 (s)  $\text{cm}^{-1}$ .<sup>[14]</sup> As expected, these values are shifted to substantially lower energies than the corresponding absorptions of  $[\text{W}(\text{PF}_3)_6]$ , which occur at 914 (vs) and 852 (s)  $\text{cm}^{-1}$ .<sup>[24]</sup> Also,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra of **1** have  $\delta_{\text{F}}$ ,  $\delta_{\text{P}}$ , and  $^1J_{\text{PF}}$  values ( $\delta(^{19}\text{F}) = +11.5$  (d,  $^1J_{\text{PF}} = 1240$  Hz),  $\delta(^{31}\text{P}) \approx +150$  (very br,  $W_{1/2} \approx 10000$  Hz because of unresolved Ta-P and F-P coupling)) that are very similar to those previously reported for the vanadium and niobium analogues.<sup>[23]</sup> On the basis of these data the synthesis and isolation of  $[\text{Ta}(\text{PF}_3)_6]^-$  have been established and all members of the homoleptic trifluorophosphine-metalates(1-) of the vanadium group are now known.

Although we have not systematically explored the chemical properties of **1**, like  $[\text{V}(\text{PF}_3)_6]^-$  it is stable towards oxidation in dry air, and only slowly undergoes hydrolysis. Indeed, we have used aqueous workups of **1**, analogous to those discussed later for  $[\text{Ta}(\text{CO})_6]^-$ , with only slight reductions in yield. However,  $[\text{Ta}(\text{PF}_3)_6]^-$  does suffer extensive decomposition when exposed to moisture for several days at room temperature. Reactions of **1** with  $[\text{NO}][\text{BF}_4]$  and  $[\text{Ph}_3\text{C}][\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  to room temperature were carried out in the hope of generating the unknown neutral  $[\text{Ta}(\text{PF}_3)_6]$ , but these led to rapid decomposition and failed to provide any tractable substances. Electrochemical oxidations of **1** were studied by cyclic voltammetry in a 0.1 M solution of  $[\text{Bu}_4\text{N}][\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$  and showed a quasi-reversible one-electron oxidation<sup>[25]</sup> at  $E^{\text{ox}} = +0.85$  V vs. Ag/AgCl at ambient temperature. Corresponding oxidations of  $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_6]$  showed an irreversible two-electron oxidation at  $-0.01$  V.<sup>[26]</sup> Thus,  $[\text{Ta}(\text{PF}_3)_6]^-$  was found to be nearly 0.9 V more difficult to oxidize than  $[\text{Ta}(\text{CO})_6]^-$ . Very similar results have been obtained with other supporting electrolytes  $[\text{nBu}_4\text{N}][\text{X}]$ , where X =  $\text{BF}_4$  or  $\text{SbF}_6$ . Oxidation of **1** at room temperature in a previously described flow-through thin-layer infrared spectroelectrochemical cell<sup>[27]</sup> in 0.1 M  $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{CH}_2\text{Cl}_2$  at  $E_{\text{app}} = +1.20$  V resulted in a decrease in the intensities of the  $\tilde{\nu}(\text{P-F})$  bands due to **1** at 842 and 784  $\text{cm}^{-1}$ , while peaks due to an uncharacterized oxidation product grew in at 875 and approximately 839  $\text{cm}^{-1}$ . The latter species is *unlikely* to be neutral  $[\text{Ta}(\text{PF}_3)_6]$  since attempts to reduce it back to  $[\text{Ta}(\text{PF}_3)_6]^-$  electrochemically were unsuccessful. Similar results were obtained at  $-70^\circ\text{C}$  in the same medium. Possible alternative approaches to the neutral  $[\text{Ta}(\text{PF}_3)_6]$  are under investigation.

Addition of concentrated sulfuric acid to **1** at room temperature caused immediate formation of a yellow, volatile and quite malodorous substance, which proved to be the hydride  $[\text{HTa}(\text{PF}_3)_6]$  (**2**). The latter was easily isolated from  $\text{H}_2\text{SO}_4$  by sublimation at  $30^\circ\text{C}$  under a moderate vacuum (ca. 0.1 torr). High yields of **2** (70–80% based on **1**) have been routinely obtained by this procedure [Eq. (b)]. Although **2** readily volatilized at room temperature to form large and beautiful



golden polyhedra, none of these proved to be suitable for a single-crystal X-ray structural determination. However, the spectroscopic properties of **2** are entirely consistent with the presence of a seven-coordinate tantalum hydride bound to six  $\text{PF}_3$  groups. In this respect and others (vide infra) it closely

resembles the vanadium analogue  $[\text{HV}(\text{PF}_3)_6]$  previously reported by Kruck and co-workers.<sup>[17]</sup> Its mass spectrum (70 eV) displays the molecular ion and fragments derived mainly from successive losses of  $\text{PF}_3$  from the ions  $[\text{HTa}(\text{PF}_3)_5]^+$  ( $m/e$  621.9) and  $[\text{HTa}(\text{PF}_3)_4\text{PF}_2]^+$  ( $m/e$  602.9). Much less intense peaks due to  $[\text{Ta}(\text{PF}_3)_6]^+$  and derived fragments were also observed. Also noteworthy were relatively intense peaks at  $m/e$  values of 257.0, 238.0, and 219.0, which are undoubtedly due to the ions  $[\text{TaF}_4]^+$ ,  $[\text{TaF}_3]^+$ , and  $[\text{TaF}_2]^+$ , respectively. The high resolution mass spectrum was obtained to provide unequivocal proof for the molecular composition of  $[\text{HTa}(\text{PF}_3)_6]$ . Infrared spectra (mineral oil mull) showed three intense peaks in the P-F region at  $\tilde{\nu} = 891$ , 870, and 842  $\text{cm}^{-1}$ . Solution infrared spectra could only be obtained in relatively nonbasic solvents such as saturated hydrocarbons,  $\text{CCl}_4$ , and  $\text{CH}_2\text{Cl}_2$ , owing to the high acidity of **2** (vide infra). Freshly prepared solutions in dry  $\text{CCl}_4$  showed two peaks at  $\tilde{\nu} = 900$  (vs), 843 (m)  $\text{cm}^{-1}$  that are very similar in appearance to those of **1** except that they are shifted approximately 60  $\text{cm}^{-1}$  to higher energies. After several minutes at room temperature in NaCl infrared cells, solutions of **2** in  $\text{CCl}_4$  or heptane generated appreciable amounts of  $[\text{Ta}(\text{PF}_3)_6]^-$  because of the reaction of **2** with NaCl. Within 30 min nearly all of **2** had decayed to the anion under these conditions. The relative shapes and intensities of the P-F stretching modes of **2** are quite similar to those previously reported for  $[\text{HV}(\text{PF}_3)_6]$  in the gas phase (at  $\tilde{\nu} = 911$  (vs), 846 (s)  $\text{cm}^{-1}$ )<sup>[17]</sup> and for  $[\text{W}(\text{PF}_3)_6]$ .<sup>[24]</sup> Attempts to observe the  $\nu(\text{Ta-H})$  absorption in **2** were unsuccessful. For example, the infrared spectrum of  $[\text{DTa}(\text{PF}_3)_6]$ , obtained from the reaction of **1** with  $\text{D}_2\text{SO}_4$ , was essentially identical to that of **2** from 400–625  $\text{cm}^{-1}$ , so no corresponding  $\nu(\text{Ta-D})$  absorption was apparent.

Initial attempts to obtain NMR spectra of **2** were unsuccessful owing to either its poor solubility (e.g., in saturated hydrocarbons,  $\text{CHCl}_3$ , or  $\text{CH}_2\text{Cl}_2$ ) or its high Brønsted acidity (e.g., it immediately protonates polar solvents such as THF, MeCN, and  $\text{Me}_2\text{SO}$ ). In this respect **2** is very similar to  $[\text{HV}(\text{PF}_3)_6]$ . Kruck employed the poorly basic  $[\text{Ni}(\text{PF}_3)_4]$  as a solvent to obtain the  $^1\text{H}$  NMR spectrum of  $[\text{HV}(\text{PF}_3)_6]$ .<sup>[17]</sup> Since **2** has solubility properties similar to solid perfluorocarbons, we explored the use of liquid perfluorocarbons and chlorofluorocarbons as possible NMR solvents and found that **2** was reasonably soluble and stable (at  $0^\circ\text{C}$ ) in a 1:1 mixture of  $\text{CD}_2\text{Cl}_2$ :1,1,2-trichlorotrifluoroethane.  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectra confirmed the presence of **2** in these solutions. In particular, the  $^1\text{H}$  NMR spectrum (Fig. 2) showed a well-resolved binomial septet of multiplets centered at about  $\delta = -8.7$  due to a hydrogen directly bound to tantalum. This value is very similar to that previously reported for  $[\text{HV}(\text{PF}_3)_6]$  ( $\delta_{\text{H}} = -8.4$ ).<sup>[17]</sup>

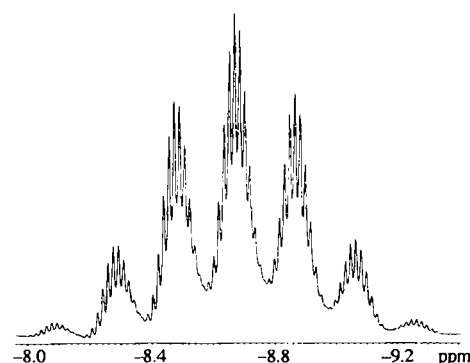
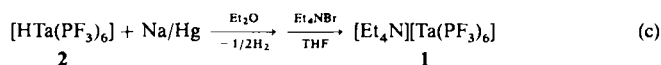


Fig. 2. 500 MHz  $^1\text{H}$  NMR spectrum of  $[\text{HTa}(\text{PF}_3)_6]$  in 1:1  $\text{CD}_2\text{Cl}_2$ /1,1,2- $\text{C}_2\text{F}_3\text{Cl}_3$ ,  $\delta = -8.7$ ;  $^2J_{\text{PH}} = 57$  Hz,  $^3J_{\text{FH}} = 5$  Hz.

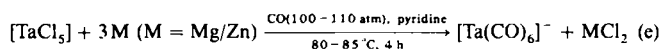
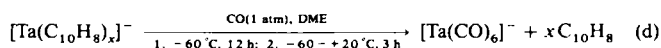
The spectrum is consistent with the presence of a fluxional seven-coordinate hydride, where six equivalent PF<sub>3</sub> groups are coupled to the hydrogen. The <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra, the details of which are shown in the experimental section, also corroborate the existence of [HTa(PF<sub>3</sub>)<sub>6</sub>] in solution. The relatively well-resolved <sup>31</sup>P resonances of **2** (*W*<sub>1/2</sub> ≈ 360 Hz) compared to the extremely broad one observed for **1** (*W*<sub>1/2</sub> ≈ 10 000 Hz) suggests that [HTa(PF<sub>3</sub>)<sub>6</sub>] may not have the high octahedral symmetry of [Ta(PF<sub>3</sub>)<sub>6</sub>]<sup>−</sup> or the isoelectronic [W(PF<sub>3</sub>)<sub>6</sub>].<sup>[24]</sup> Interesting also is the observation of free PF<sub>3</sub> in the <sup>19</sup>F and <sup>31</sup>P NMR spectra of **2**, which undoubtedly arose from some decomposition of the hydride. All of these data leave no doubt about the existence of [HTa(PF<sub>3</sub>)<sub>6</sub>].

Few reactions of **2** have been examined to date. However, it does function as a strong Brønsted acid in the presence of relatively weak Lewis bases such as THF. On this basis, a determination of its gas-phase acidity and that of [HV(PF<sub>3</sub>)<sub>6</sub>] would appear to be of interest, particularly since [HCo(PF<sub>3</sub>)<sub>4</sub>] and [HIr(PF<sub>3</sub>)<sub>4</sub>] have been claimed to be exceedingly strong gas-phase acids, for example, substantially stronger, than HI and similar to CF<sub>3</sub>SO<sub>3</sub>H.<sup>[28]</sup> As expected on the basis of the high solution acidity of **2**, it readily reacts with alkali metal amalgams in diethyl ether [Eq. (c)], as Kruck and co-workers had previously observed for [HCo(PF<sub>3</sub>)<sub>4</sub>].<sup>[29]</sup> After appropriate cation



exchange and workup, high yields (70–80%) of pure and colorless **1** were isolated. Pure **2** was also obtained by the addition of concentrated H<sub>2</sub>SO<sub>4</sub> to the crude (but naphthalene-free) reaction mixture containing **1**, followed by sublimation. Since **2** could then be readily converted to pure **1** by the procedure mentioned above, this modified route to **1** directly from [TaCl<sub>5</sub>] is now the method of choice. Although this modified procedure provided **1** in about the same yield as the original route, it is much easier to carry out because no difficult fractional crystallization steps are involved in the purification.

**Facile Syntheses of [Ta(CO)<sub>6</sub>]<sup>−</sup> and [Ta(<sup>13</sup>CO)<sub>6</sub>]<sup>−</sup> by the Naphthalenide Route:** Two low-pressure routes to [Ta(CO)<sub>6</sub>]<sup>−</sup> from [TaCl<sub>5</sub>] were reported in 1983 and involved either the carbonylation of the presumed naphthalenetantalate species [Ta(C<sub>10</sub>H<sub>8</sub>)<sub>x</sub>]<sup>−</sup> at atmospheric pressure from −60 °C to +20 °C<sup>[21]</sup> [Eq. (d)] or the reductive carbonylation of [TaCl<sub>5</sub>] with a magnesium/zinc/pyridine mixture<sup>[14]</sup> [Eq. (e)]. The former naphthalenide procedure has provided [Ta(CO)<sub>6</sub>]<sup>−</sup> in



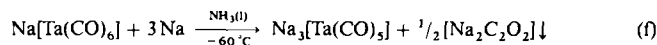
yields as high as 53% (based on [TaCl<sub>5</sub>]),<sup>[21]</sup> while the latter Mg/Zn/pyridine route gave [Ta(CO)<sub>6</sub>]<sup>−</sup> in yields varying from 6% (at 17 °C, 1 atm CO, 24 h) to 28–35% (at 80–85 °C, 110 atm CO, 4 h).<sup>[14]</sup> Even with the availability of these procedures, however, Calderazzo and Pampaloni recently stated that “the preparation of [Ta(CO)<sub>6</sub>]<sup>−</sup> is still not completely satisfactory”<sup>[13]</sup> and Rehder and co-workers reported obtaining only a 15% yield of this product from our original normal-pressure synthesis (using LiC<sub>10</sub>H<sub>8</sub>).<sup>[30]</sup> On the basis of these concerns,

and since [Ta(CO)<sub>6</sub>]<sup>−</sup> is a key precursor for the study of carbonyl and related low-valent tantalum chemistry, we felt it was important to report on a simplified procedure, developed from experience we have gained over the past 10 years in the preparation of numerous Group 4 carbonyls by the naphthalenide route.<sup>[31, 32]</sup> Reproducible and satisfactory (40–45%) yields of [Ta(CO)<sub>6</sub>]<sup>−</sup> were obtained by substitution of a standard round-bottom flask/magnetic stir bar assembly for the originally specified Morton (or “creased”) flask/mechanical stirrer unit<sup>[21]</sup> in the carbonylation step. Only slightly lower yields of the tantalate were obtained with magnetic stirring, for example, a 45% yield for [Et<sub>4</sub>N][Ta(CO)<sub>6</sub>] (**3**) compared to a 52% yield for [Na(diglyme)<sub>2</sub>][Ta(CO)<sub>6</sub>] (**4**) obtained with mechanical stirring. Also, it was found to be unnecessary to disperse CO through the solution. Equally good results were obtained simply by maintenance of a CO blanket (at about 1 atm) over the rapidly stirred reaction mixture during the carbonylation stage. In the synthesis of **3**, an aqueous extraction of the precursor Na[Ta(CO)<sub>6</sub>] proved to be an especially convenient method for complete separation of the naphthalene from the carbonyltantalate(1−). The latter was then quickly and quantitatively precipitated as **3** with aqueous tetraethylammonium bromide. At room temperature, Na[Ta(CO)<sub>6</sub>] proved to be sufficiently stable in oxygen-free water (pH ≥ 7) that no significant loss occurred during this step. Crystalline **3** is probably the least air-sensitive and most easily handled and purified of any commonly available salt of [Ta(CO)<sub>6</sub>]<sup>−</sup>, so we have generally obtained the anion in this form rather than **4**. If a sodium salt is necessary, one may easily be prepared by treatment of **3** with NaBPh<sub>4</sub> in methanol. After filtration and solvent removal, high yields of unsolvated Na[Ta(CO)<sub>6</sub>] have been obtained.<sup>[21]</sup> Since several students, including undergraduates, have successfully carried out the synthesis of **3** in this laboratory, we believe the synthesis described herein qualifies as the first satisfactory route to [Ta(CO)<sub>6</sub>]<sup>−</sup>.

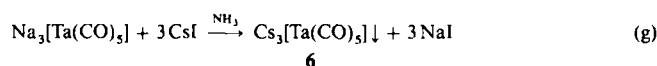
Finally, to emphasize the particular utility of our low-pressure route to [Ta(CO)<sub>6</sub>]<sup>−</sup>, this method was used to synthesize the 99% <sup>13</sup>C-labeled [Ta(<sup>13</sup>CO)<sub>6</sub>]<sup>−</sup>, which to our knowledge has not been previously described in the literature. Since <sup>13</sup>CO is expensive and not easily recovered without special equipment,<sup>[33]</sup> only a slight excess of <sup>13</sup>CO (contained in a 1 L gas storage bulb at about atmospheric pressure) was used in this synthesis. The reaction was carried out at subambient pressure in the apparatus described in the Experimental Section. Even under these less than ideal conditions, a 30% yield of pure [Na(diglyme)<sub>2</sub>][Ta(<sup>13</sup>CO)<sub>6</sub>] (**5**) was isolated from this reaction. The previously unreported <sup>13</sup>C NMR spectrum of [Ta(CO)<sub>6</sub>]<sup>−</sup> showed a resonance centered at δ<sub>C</sub> = +211, extremely broad (*W*<sub>1/2</sub> ≈ 820 Hz) because of unresolved <sup>181</sup>Ta–<sup>13</sup>C coupling. Thus, the <sup>13</sup>C chemical shifts for [V(CO)<sub>6</sub>]<sup>−</sup>, [Nb(CO)<sub>6</sub>]<sup>−</sup>, and [Ta(CO)<sub>6</sub>]<sup>−</sup> are 224,<sup>[34, 35]</sup> 217,<sup>[36]</sup> and 211, respectively, which follow the same trend as corresponding values previously reported for [Cr(CO)<sub>6</sub>], [Mo(CO)<sub>6</sub>], and [W(CO)<sub>6</sub>], of 212, 204, and 192, respectively.<sup>[37]</sup> Compound **5** was used in the synthesis of <sup>13</sup>C-enriched [Ta(CO)<sub>5</sub>]<sup>3−</sup> and [HTa(CO)<sub>5</sub>]<sup>2−</sup>, which will now be described.

**Synthesis and Properties of [Ta(CO)<sub>5</sub>]<sup>3−</sup>:** More than 40 years ago, Helmut Behrens showed that alkali metal–ammonia solutions were unusually effective in reducing a variety of neutral metal carbonyls to corresponding carbonylmetalate mono- and dianions.<sup>[38]</sup> To determine whether carbonylmetalates could be reduced further in liquid ammonia, we first examined the reaction of [Na(diglyme)<sub>2</sub>][V(CO)<sub>6</sub>] with sodium metal in this medium. This reaction provided high yields (>90%) of the first Group 5 carbonyl trianion salt Na<sub>3</sub>[V(CO)<sub>5</sub>].<sup>[39]</sup> Several previ-

ously unknown classes of vanadium carbonyls including  $[\text{HV}(\text{CO})_5]^{2-}$ ,<sup>[40]</sup>  $[\text{V}(\text{CO})_5(\text{CNR})]^-$ ,<sup>[41]</sup>  $[(\text{Ph}_3\text{Pb})_2\text{V}(\text{CO})_5]^-$ ,<sup>[42]</sup> and  $[(\text{Ph}_3\text{PAu})_3\text{V}(\text{CO})_5]^{[43]}$  were subsequently obtained from this useful precursor. Corresponding reductions of  $[\text{Na}(\text{diglyme})][\text{Ta}(\text{CO})_6]$  (**4**) proceeded cleanly to give beautiful deep red solutions of thermally unstable  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  along with insoluble disodium acetylenediolate [Eq. (f)].<sup>[44, 45]</sup> Although IR spectra of  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  could not be obtained owing to its instability,  $^{13}\text{C}$  NMR spectra of the 99%  $^{13}\text{C}$ -enriched  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  in liquid ammonia at  $-50^\circ\text{C}$ , prepared from **5**, showed a single sharp ( $W_{1/2} = 10$  Hz) resonance in the metal carbonyl region at  $\delta_{\text{C}} = +293$ , which is slightly downfield of the corresponding value previously established for  $[\text{V}(\text{CO})_5]^{3-}$  ( $\delta_{\text{C}} = +290$ ).<sup>[40]</sup> After filtration and cation exchange, deep red-brown (and



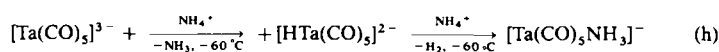
dangerously shock-sensitive)  $\text{Cs}_3[\text{Ta}(\text{CO})_5]$  (**6**) was isolated in 40% yield [Eq. (g)] as a satisfactorily pure substance. The rather poor yield of **6** resulted from its appreciable solubility in



liquid ammonia, unlike  $\text{Cs}_3[\text{V}(\text{CO})_5]$ , which is nearly insoluble in this medium.<sup>[11]</sup> The IR spectrum of solid **6** as a mineral oil mull (Fig. 3) closely matched that of the vanadium analogue,<sup>[11]</sup> which indicated that both compounds contain

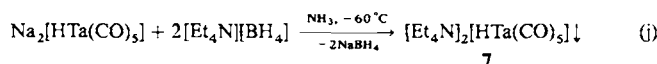
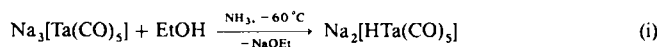
$[\text{M}(\text{CO})_5]^{3-}$  units in similar environments. The general shape and position of the IR spectral signature of **6** in the  $\nu(\text{CO})$  region was also quite similar to that previously reported for another carbonyl trianion salt,  $\text{Na}_3[\text{Mn}(\text{CO})_4]$ .<sup>[45]</sup> Since dry samples of **6** were difficult and dangerous to isolate and handle, nearly all reactions of  $[\text{Ta}(\text{CO})_5]^{3-}$  examined to date have been conducted with the trianion generated in situ in liquid ammonia.

**Protonation and Stannylation of  $[\text{Ta}(\text{CO})_5]^{3-}$ —Synthesis and Characterization of  $[\text{HTa}(\text{CO})_5]^{2-}$  and  $[\text{Ph}_3\text{SnTa}(\text{CO})_5]^{2-}$ :** Addition of one equivalent of ethanol or ammonium chloride to liquid ammonia solutions of  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  caused the deep red trianion salt to change immediately to a red-orange product. Attempts to isolate the latter species as the sodium salt were unsuccessful, but a  $^1\text{H}$  NMR spectrum of the product in liquid ammonia (at  $-50^\circ\text{C}$ ) showed a fairly sharp ( $W_{1/2} = 30$  Hz) singlet at  $-2.23$ . Corresponding spectra of freshly prepared liquid ammonia solutions of  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  showed no absorptions in the metal hydride region. Addition of more ethanol or  $\text{NH}_4\text{Cl}$  caused the red-orange product immediately to decompose with gas evolution to give a purple substance, which has been identified as the ammine complex  $[\text{Ta}(\text{CO})_5\text{NH}_3]^-$ .<sup>[4]</sup> These reactions are summarized in [Eq. (h)].



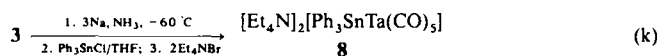
No evidence for a possible dihydride  $[\text{H}_2\text{Ta}(\text{CO})_5]^-$  was observed in any of these protonation reactions in liquid ammonia. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the corresponding 99%  $^{13}\text{C}$ -enriched product (from  $\text{Na}_3[\text{Ta}(\text{CO})_5]$ ) in liquid ammonia at  $-50^\circ\text{C}$  showed a rather broad resonance at  $\delta_{\text{C}} = +232$ , which is about 11 ppm downfield of the  $\delta_{\text{C}}$  value for  $[\text{Ta}(\text{CO})_6]^-$  (vide supra). The large line width ( $W_{1/2} = 126$  Hz) of the  $^{13}\text{C}$  resonance of  $[\text{HTa}(\text{CO})_5]^{2-}$  precluded possible resolution of *cis*- and *trans*- carbonyl groups. These have been observed for the isoelectronic  $[\text{HW}(\text{CO})_5]^-$  at  $\delta_{\text{C}} = 205$  and  $210$ ,<sup>[46]</sup> 13 and 18 ppm downfield of the  $\delta_{\text{C}}$  value of  $+192$  for  $[\text{W}(\text{CO})_6]$ .<sup>[47]</sup> The corresponding  $^1\text{H}$  NMR spectrum of  $[\text{HTa}(\text{CO})_5]^{2-}$  showed a broad and poorly resolved multiplet centered at  $-2.22$ .

Treatment of the ammoniacal solution of  $\text{Na}[\text{HTa}(\text{CO})_5]$  with two equivalents of  $[\text{Et}_4\text{N}][\text{BH}_4]$  resulted in rapid precipitation of air-sensitive orange-red microcrystals of  $[\text{Et}_4\text{N}]_2[\text{HTa}(\text{CO})_5]$  (**7**) in 70% yield [Eqs. (i) and (j)]. Preliminary studies showed that both  $[\text{Et}_4\text{N}][\text{BH}_4]$  and  $\text{NaBH}_4$  were readily



soluble in liquid ammonia, so thorough washing of **7** with liquid ammonia followed by drying provided a satisfactorily pure sample without further treatment.

The reaction of  $[\text{Ta}(\text{CO})_5]^{3-}$  with  $\text{Ph}_3\text{SnCl}$  in liquid ammonia was examined to obtain an additional monosubstituted derivative,  $[\text{Ph}_3\text{SnTa}(\text{CO})_5]^{2-}$ . In this synthesis, it was established that the poorly ammonia-soluble but very easily prepared  $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_6]$  (**3**) could also be used successfully as a direct precursor to  $[\text{Ta}(\text{CO})_5]^{3-}$ . After cation exchange and purification a 71% yield of orange-red crystalline  $[\text{Et}_4\text{N}]_2[\text{Ph}_3\text{SnTa}(\text{CO})_5]$  (**8**) was isolated [Eq. (k)]. The success of this reaction



shows that  $\text{Et}_4\text{N}^+$  and  $[\text{Ta}(\text{CO})_5]^{3-}$  do not readily react in liquid ammonia at  $-60^\circ\text{C}$ . Earlier we reported that  $[\text{nBu}_4\text{N}]^+$  was stable (for hours) in the presence of  $[\text{V}(\text{CO})_5]^{3-}$  in liquid ammonia.<sup>[11]</sup>

Infrared spectra of **7** and **8** as mineral oil mulls were extremely similar in the  $\nu(\text{CO})$  region and exhibited three band patterns characteristic of  $[\text{XM}(\text{CO})_5]$  molecules of  $\text{C}_{4v}$  symmetry.<sup>[48]</sup> As expected, the  $\tilde{\nu}(\text{CO})$  positions of the hydride (1922 (w), 1750 (vs), and 1710 (sh)  $\text{cm}^{-1}$ ), were at somewhat lower energy than corresponding bands for the triphenylstannyl product (1936 (m), 1774 (vs), and 1732 (sh)  $\text{cm}^{-1}$ ). Vanadium analogues of **7** and **8** have been prepared by the same procedures from  $[\text{V}(\text{CO})_5]^{3-}$  and have extremely similar IR spectral properties in the carbonyl region.<sup>[4, 40]</sup> While the  $\text{Ph}_3\text{Sn}$  derivative **8** formed stable but quite air-sensitive solutions in aprotic polar solvents such as acetonitrile, from which it was easily recrystallized, the hydride salt **7** rapidly decomposed in acetonitrile, dimethylsulfoxide, and hexamethylphosphoramide at room temperature. No  $\nu(\text{Ta-H})$  absorption could be identified in the infrared spectrum of **7**.

Like the isoelectronic  $[\text{HW}(\text{CO})_5]^-$ ,<sup>[49, 50]</sup> **7** is a strong hydride donor, as was demonstrated by the immediate reaction of a suspension of **7** in THF at  $-50^\circ\text{C}$  with  $\text{Fe}(\text{CO})_5$  to generate

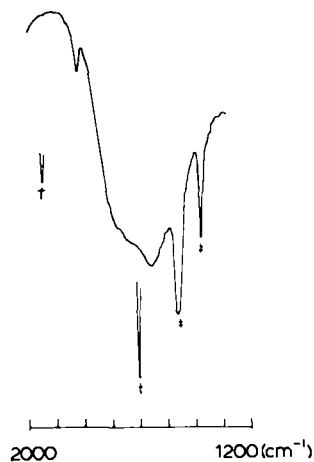


Fig. 3. IR spectrum of  $\text{Cs}_3[\text{Ta}(\text{CO})_5]$  (mineral oil mull) in the carbonyl stretching frequency region: 1813 w, 1560 vs br  $\text{cm}^{-1}$ . Absorptions marked with daggers and double daggers are polystyrene reference peaks (at 1944 and 1602  $\text{cm}^{-1}$ ) and mineral oil peaks, respectively.

caused the deep red trianion salt to change immediately to a red-orange product. Attempts to isolate the latter species as the sodium salt were unsuccessful, but a  $^1\text{H}$  NMR spectrum of the product in liquid ammonia (at  $-50^\circ\text{C}$ ) showed a fairly sharp ( $W_{1/2} = 30$  Hz) singlet at  $-2.23$ . Corresponding spectra of freshly prepared liquid ammonia solutions of  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  showed no absorptions in the metal hydride region. Addition of more ethanol or  $\text{NH}_4\text{Cl}$  caused the red-orange product immediately to decompose with gas evolution to give a purple substance, which has been identified as the ammine complex  $[\text{Ta}(\text{CO})_5\text{NH}_3]^-$ .<sup>[4]</sup> These reactions are summarized in [Eq. (h)].

$[\text{Fe}(\text{CO})_4(\text{CHO})]^-$  and  $[\text{HFe}(\text{CO})_4]^-$  as well as the labile  $[\text{Ta}(\text{CO})_5(\text{THF})]^-$ . The former were identified by their characteristic  $^1\text{H}$  NMR chemical shifts at  $\delta = +14.8$ <sup>[51]</sup> and  $-8.8$ <sup>[52]</sup> respectively. NMR integration showed the formyl:hydride ratio to be about 2:1 at  $-50^\circ\text{C}$  in THF. The latter thermally unstable and deep purple  $[\text{Ta}(\text{CO})_5(\text{THF})]^-$  was independently prepared by the photolysis of  $[\text{Ta}(\text{CO})_6]^-$  in THF at  $-78^\circ\text{C}$ , a method previously used to generate  $[\text{V}(\text{CO})_5(\text{THF})]^-$ <sup>[53]</sup>. The  $[\text{Ta}(\text{CO})_5(\text{THF})]^-$  produced by these two different routes reacted quantitatively with  $\text{PPh}_3$  within 2 h at  $-60^\circ\text{C}$  to provide the known  $[\text{Ta}(\text{CO})_5(\text{PPh}_3)]^-$ <sup>[54]</sup>.

**Synthesis of  $[(\text{Ph}_3\text{PAu})_3\text{Ta}(\text{CO})_5]$ , a Gold–Tantalum Cluster, from  $[\text{HTa}(\text{CO})_5]^{2-}$  and  $[\text{Ph}_3\text{PAuCl}]$ :** Attempts to prepare the tantalum analogue of  $[(\text{Ph}_3\text{PAu})_3\text{V}(\text{CO})_5]$ <sup>[43]</sup> by the interaction of  $[\text{Ph}_3\text{PAuCl}]$  with  $\text{Na}_3[\text{Ta}(\text{CO})_5]$  in liquid ammonia or with a suspension of  $\text{Cs}_3[\text{Ta}(\text{CO})_5]$  in THF were totally unsuccessful. For this reason, we examined the reaction of **7** with three equivalents of  $[\text{Ph}_3\text{PAuCl}]$  in THF and were able to isolate orange-red  $[(\text{Ph}_3\text{PAu})_3\text{Ta}(\text{CO})_5]$  (**9**) in 54% yield as a satisfactorily pure substance. The infrared spectrum of this substance in the  $\nu(\text{CO})$  region is nearly superimposable on that of the structurally characterized  $[(\text{Ph}_3\text{PAu})_3\text{V}(\text{CO})_5]$ , so there is no uncertainty concerning the nature of **9**. To our knowledge, the only other mixed metal cluster formally containing Ta(0) is the silver species  $[\{\text{AgTa}(\text{CO})_4(\text{dmpe})\}_3]$ , where  $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ <sup>[55]</sup>. Although the fate of the hydrogen in  $[\text{HTa}(\text{CO})_5]^{2-}$  remains unknown in this reaction, it would appear that **7** may prove to be a generally useful precursor to tantalum carbonyls that cannot be prepared directly from  $[\text{Ta}(\text{CO})_5]^{3-}$  or  $[\text{Ta}(\text{CO})_6]^-$ . We continue to examine the basic reactivity patterns of these and related carbonylmetalates of the Group 5 metals.

### Concluding Remarks

We have established that treatment of a naphthalene-stabilized low-valent tantalum species with  $\text{PF}_3$  provides a facile route to  $[\text{Ta}(\text{PF}_3)_6]^-$ , the first homoleptic phosphantantalate(1–) species, in 15–25% yields. Use of this same general procedure for the synthesis of related  $[\text{TaL}_6]^-$  species, where L = isonitriles, organophosphines, phosphites, and related acceptor ligands, will be an important extension of this work, since presently molecules of this type are known only for L =  $\text{PF}_3$  and CO. An improved normal-pressure synthesis of  $[\text{Ta}(\text{CO})_6]^-$  based on our naphthalenide route was also presented, as well as the first full account of the synthesis and chemistry of  $[\text{Ta}(\text{CO})_5]^{3-}$ , the only known complex containing tantalum in a formal oxidation state of  $-3$ .

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