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Syntheses and Properties of Homoleptic Carbonyl and Trifluorophosphane Niobates: $[Nb(CO)_6]^-$, $[Nb(PF_3)_6]^-$ and $[Nb(CO)_5]^{3-}$ [†,1]

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Reductive carbonylations of $NbCl_4(THF)_2$, THF = tetrahydrofuran, mediated by sodium naphthalene in 1,2-dimethoxyethane, DME, or sodium anthracene in THF, provide $[Nb(CO)_6]^-$ as the tetraethylammonium salt in 60% or 70% isolated yields, respectively, the highest known for atmospheric pressure syntheses of this metal carbonyl. Corresponding reductions involving PF_3 give about 40% yields of $[Et_4N][Nb(PF_3)_6]$, which in the past was only accessible by a photochemical route. Electrochemical data for $[Nb(CO)_6]^-$ and $[Nb(PF_3)_6]^-$ are compared and show that the PF_3 complex is almost 1 V more difficult to oxidize than the CO analogue. Protonation of $[Nb(PF_3)_6]^-$ by concentrated sulfuric acid yields a volatile, thermally unstable species, which has been shown by ^1H NMR and mass spectral studies to be the new niobium hydride, $Nb(PF_3)_6H$. Previously unpublished ^{93}Nb and ^{13}C NMR studies corroborate prior claims that the sodium metal reduction of $[Nb(CO)_6]^-$ in liquid ammonia affords $[Nb(CO)_5]^{3-}$, the only known Nb(III−) species. The first details of this synthesis and those of $[Nb(CO)_5H]^{2-}$, $[Nb(CO)_5SnPh_3]^{2-}$, $[Nb(CO)_5NH_3]^-$, and $[Nb(CO)_5(CNtBu)]^-$ are presented.

Introduction

Hexacarbonylniobate(1−) has been a key precursor in the study of niobium carbonyls and associated low-valent niobium chemistry, particularly since neutral homoleptic niobium carbonyls are unknown.[2] Although $[Nb(CO)_6]^-$ was first reported in 1961,[3] the original high-pressure route and subsequent modifications[4] employed in its synthesis were difficult and dangerous. Consequently, progress in niobium carbonyl chemistry was slow until the discovery of facile atmospheric pressure syntheses of this substance. Especially important in this regard was the magnesium−zinc−pyridine mediated reductive carbonylation procedure developed by Calderazzo, Pampaloni, and coworkers, which gave nearly 50% yields of $[Nb(CO)_6]^-$ salts, based on $NbCl_5$ (eq 1).[5] Somewhat lower yields of this anion

$$2NbCl_5 + 6M\ (M = Mg/Zn) \xrightarrow[16-18\ ^\circ C]{CO\ (1\ atm),\ pyridine} M[Nb(CO)_6]_2 + 5MCl_2 \quad (1)$$

were generally obtained by corresponding alkali metal−naphthalene−1,2-dimethoxyethane (DME) reductions, discovered in our laboratory,

$$NbCl_5 + 6AC_{10}H_8 \xrightarrow[-60\ ^\circ C]{DME} \xrightarrow[-60\ to\ +20\ ^\circ C]{CO\ (1\ atm)} A[Nb(CO)_6] + 5ACl + 6C_{10}H_8 \quad (2)$$

where A = alkali metal.[6] However, one group reported on their failure to obtain hexacarbonylniobate(1−) by the naphthalene anion route.[7] Since the precursor, $NbCl_5$, undergoes facile hydrolysis and is not compatible with many ether solvents at normal temperatures, we recently examined the use of the readily available $NbCl_4(THF)_2$,[8] which is much less reactive in this regard than $NbCl_5$.[2] We were surprised to discover that reductive carbonylations of $NbCl_4(THF)_2$, mediated by the radical anions of naphthalene or anthracene, consistently gave about 60% or 70% isolated yields, respectively, of $[Nb(CO)_6]^-$, the highest reported for syntheses of this complex carried out at atmospheric pressure. In this article we describe these modified reduction procedures and also show that they are effective in the preparation of $[Nb(PF_3)_6]^-$, which previously was available only by a photochemical route.[9] In this report, the first details of the synthesis, characterization, and chemical properties of the highly reduced carbonylmetalate, $[Nb(CO)_5]^{3-}$,[10] are also presented. It is hoped that the information reported herein will help to facilitate future studies on these and related low-valent niobium complexes.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of 99.5% argon or 99.5% carbon monoxide, further purified by passage through columns of activated BASF catalyst and molecular sieves. Also, the CO was passed through a column of Ascarite, which is a trademark for a self-indicating sodium hydroxide nonfibrous silicate formulation, for the quantitative absorption of CO_2. Similar products used by microanalysts should provide satisfactory results. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to

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[†] Dedicated to Professor Alan Davison of MIT, who many years ago introduced one of us to the wonders of group 5 metal carbonyl chemistry.

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air. Solutions were transferred via stainless steel double-ended needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double-manifold vacuum line.[11,12] Commercial grade PF_3 (Pennwalt Ozark Mahoning) was purified by passage through two −78 °C traps, two columns of 4 Å molecular sieves, and subsequent isolation at − 196 °C in a 1 or 2 L gas storage flask. The PF_3 was then subjected to two freeze−pump−thaw cycles to remove O_2 and other noncondensable gases. Naphthalene was sublimed in vacuo before use. A literature procedure was used to prepare $NbCl_4(THF)_2$ from $NbCl_5$.[8] Partially hydrolyzed or otherwise impure $NbCl_5$ gave diminished yields of $NbCl_4(THF)_2$, but the product was of satisfactory purity for the syntheses herein. 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. Solution infrared spectra were recorded on a Mattson Galaxy 6021 FTIR spectrometer with samples sealed in 0.1 mm NaCl or CaF_2 cells. Nujol (mineral oil) mulls of air-sensitive compounds for IR spectra were prepared in a Vacuum Atmospheres Corp. drybox. NMR samples were sealed into 5 mm tubes and were run on a Varian Unity 300 or 500 spectrometer or a Nicolet NT-300 WB instrument for the liquid ammonia studies. Melting points are uncorrected and were obtained for samples in sealed capillary tubes with a Thomas-Hoover Uni-Melt model 6427-H10. Microanalyses were carried out by H. Malissa and G. Reuter Analytische Laboratorien, Lindlar, 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^2) and a Ag/AgCl reference electrode containing 1.0 M KCl. Scan rates of 50−500 mV/s 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, Inc. In most cases, the electrolyte and solvent were passed down a column of dry alumina 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 help remove O_2 from the solution. Potentials are reported versus aqueous Ag/AgCl and are not corrected for the junction potential. A standard electrochemical current convention is used (anodic currents are negative). To allow future corrections and the correlation of these data with other workers, the $E^{\circ\prime}$ 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_4N][$Nb(CO)_6$] (1). A. Sodium Naphthalene in 1,2-Dimethoxyethane (DME). Sodium naphthalene was prepared by adding 300 mL of DME at room temperature to a mixture of naphthalene (21.00 g, 163.8 mmol) and sodium metal (3.08 g, 134 mmol), cut into about 30 small pieces, in a standard 1 L round-bottom flask, equipped with a large glass-covered magnetic stir bar. The resulting deep green solution was stirred at room temperature for 5 h under an atmosphere of argon and was then cooled to −50 °C with continued stirring. A yellow slurry of $NbCl_4(THF)_2$ (10.00 g, 26.4 mmol) in 150 mL of cold (−50 °C) DME was then added to the cold solution of $NaC_{10}H_8$ via cannula. The mixture turned deep red-brown after the addition had been completed and was stirred at −50 °C for 15 h under argon. The reaction flask was evacuated until the evolution of argon nearly ceased and then was filled with carbon monoxide. The mixture turned dark brown with a yellow hue, was stirred under the CO atmosphere for 20 h at −50 °C, and then was warmed to room temperature over a period of 3 h. Argon was exchanged for CO, and the brown solution was filtered through a medium-porosity frit, containing a 2.5 cm plug of diatomaceous earth, to give a deep yellow-orange filtrate and a brown filter cake. The filter cake was washed with an additional 75 mL of DME. All but ca. 20 mL of DME was removed from the filtrate in vacuo, and 200 mL of O_2-free water (pH: 8−8.5) was added to it. The obtained yellow slurry was filtered through a 2.5 cm plug of diatomaceous earth into a flask containing 13 g (61.9 mmol) of Et_4NBr dissolved in 70 mL of H_2O. The filter cake was washed with additional water (ca. 120 mL) until the naphthalene became colorless. The filtrate mixture was vigorously stirred, and a bright yellow precipitate formed in the receiving flask. It was separated by filtration, washed with water (2 × 70 mL), and dried in vacuo (10^{-2} Torr) for 9 h. Recrystallization of the resulting solid from THF/Et_2O afforded 6.25 g, 61% yield based on $NbCl_4(THF)_2$, of pure, free-flowing microcrystalline yellow **1**, which was identical to the previously described substance.[6]

1. B. Sodium Naphthalene in Tetrahydrofuran (THF). When THF was employed in the above-described reaction, on exactly the same scale and using an identical procedure, there resulted 1.75 g (17% yield) of pure **1**.

1. C. Sodium Anthracene in THF. A solution of sodium anthracene was prepared by stirring sodium metal (0.700 g, 30.3 mmol), cut into approximately 25 small pieces, and anthracene (6.41 g, 36.0 mmol) in 250 mL of THF for 4.5 h at room temperature with a large glass-covered magnetic stir bar in a standard 1 L round-bottom flask. The resulting deep blue solution was then cooled to −40 °C, and a cold (−40 °C) solution/slurry of $NbCl_4(THF)_2$ was added to it via cannula. The latter yellow solution/slurry was obtained by adding 100 mL of THF to $NbCl_4(THF)_2$ (2.27 g, 6.0 mmol), followed by stirring at room temperature for 15 min and then at −40 °C for 10 min. A purple-brown solution formed in about 5 min after the addition had been completed. This solution was stirred for 5 h at −40 °C. Then argon was exchanged for carbon monoxide. The mixture changed from the purple-brown to an orange-brown within a few seconds. It was stirred under the CO atmosphere for 15 h while slowly warming to room temperature. All but 20 mL of the THF was removed in vacuo, and 200 mL of O_2-free water was added to the reaction flask with rapid stirring. As much THF as possible was removed in vacuo, and the yellow slurry was filtered into a 500 mL flask, containing a solution of Et_4NBr (2.5 g, 12 mmol) in 50 mL of H_2O, using approximately 2.5 cm of diatomaceous earth to facilitate filtration. A very finely divided yellow solid, formed in the receiving flask, was stirred for 1 h, then all H_2O was removed in vacuo, and then 150 mL of THF was added to the resulting yellow solid. The obtained bright yellow solution was filtered, and all of the THF was removed in vacuo to give a bright yellow solid. It was recrystallized from THF/Et_2O to provide 1.63 g (70%) of pure **1**.

[Et_4N][$Nb(PF_3)_6$] (2). A. Sodium Naphthalene in DME. Sodium naphthalene was prepared by adding a solution of naphthalene (10.15 g, 79.2 mmol) in 100 mL of DME to sodium metal (1.53 g, 67 mmol, cut into about 20 pieces) suspended in 75 mL of DME, followed by stirring for 4 h at room temperature. The deep green solution was then transferred to a 1 L Morton (creased) flask outfitted with an overhead stirrer and cooled to −60 °C. A cold (−60 °C) slurry consisting of 5.00 g (13.2 mmol) of $NbCl_4(THF)_2$ in 150 mL of DME was added to the Morton flask with stirring. Within seconds after this addition, the reaction mixture assumed the deep red brown color of the intermediate. It was stirred at −60 °C for 18 h in the Morton flask and then transferred to a standard 1 L round-bottom flask outfitted with a three-way stopcock attached to a 2 L (ca. 7.2 g, 84 mmol) bulb of PF_3. Argon was removed by evacuation of the flask, and the PF_3 was introduced. The brown mixture was slowly warmed over 15 h while being stirred under the PF_3 atmosphere. (Since PF_3 is quite soluble in organic solvents at low temperature, the reaction was carried out under a partial vacuum during this stage.) Argon was admitted, and the reaction mixture was filtered through a medium-porosity frit into a receiver flask containing 5.55 g (26.4 mmol) of dry, finely ground Et_4NBr. Since this cation exchange reaction often does not proceed effectively in DME, i.e., precipitation of KBr from this medium is slow, the latter was removed in vacuo and 300 mL of THF was added. The slurry was stirred for 15 h and filtered

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through a medium-porosity frit, and THF was removed in vacuo. The light tan solid was washed with pentane (2 × 100 mL). Low-temperature (−78 °C) recrystallization from THF/diethyl ether resulted in 3.76 g (5.01 mmol) of ivory-colored **2** in 38% yield. Mp: 171 °C dec. Anal. Calcd for $C_8H_{20}F_{18}NNbP_6$: C, 12.80; H, 2.68; N, 1.87. Found: C, 12.92; H, 2.61; N, 1.89. IR: ν(P−F) region (mineral oil mull) 836 s, 773 m, cm^{-1}; (THF) 838 s, 784 m, cm^{-1}; (CH_2Cl_2) 842 s, 785 m, cm^{-1}. ^{19}F NMR (282 MHz, CD_2Cl_2, 20 °C, $CFCl_3$ external standard): $\delta = 9.50$ (d of d, $^1J_{PF} = 1250$ Hz, $^2J_{NbF} = 55$ Hz) ppm. ^{31}P NMR (121 MHz, CD_2Cl_2, 20 °C, H_3PO_4 external standard): $\delta = 167$ (m) ppm.

2. B. Sodium Anthracene in THF. Sodium anthracene was prepared by stirring sodium metal (1.53 g, 67 mmol, cut into about 20 pieces) with anthracene (14.1 g, 79 mmol) in 280 mL of THF with a large magnetic stir bar in a standard 1 L round-bottom flask for 5 h at room temperature. The flask was outfitted with a three-way stopcock connected to the vacuum/argon manifold and a 2 L bulb of PF_3. The deep blue solution of $NaC_{14}H_{10}$ was then cooled to −40 °C, and a cold (−40 °C) solution/slurry of $NbCl_4(THF)_2$ (5.00 g, 13.2 mmol) in 120 mL of THF was added to it via cannula. A purple-brown solution formed in about 5 min after the addition had been completed. This solution was stirred for 12 h at −40 °C. Next the reaction flask was cooled to −55 °C, and argon was removed in vacuo. The PF_3 in the 2 L bulb was then introduced to the reaction mixture. The mixture changed from a purple-brown to an orange color within a few seconds. It was stirred under the PF_3 atmosphere for 15 h at −55 °C and then was allowed to slowly warm to room temperature. During this period, the reaction mixture changed from the orange to a deep brown color. The brown mixture was filtered through a medium-porosity frit into a flask containing finely ground Et_4NBr (5.55 g, 26.4 mmol). The brown slurry was stirred at room temperature for 15 h, and then all of the THF was removed in vacuo. The deep brown solid was dissolved in 150 mL of THF, cooled to −78 °C, and filtered through a medium-porosity jacketed frit at −78 °C. The anthracene-containing filter cake was washed with 2 × 40 mL of cold (−78 °C) THF, which was also added to the filtrate. THF was removed in vacuo from the filtrate to give a brown solid. The solid was stirred in 100 mL of warm (40 °C) heptane for 20 min and allowed to settle, and then the heptane was removed by cannula. This washing process was repeated one more time to remove any remaining anthracene. The brown solid was then dissolved in 30 mL of THF and filtered slowly to remove brown impurity. A light tan solid was precipitated by adding 150 mL of pentane to the filtrate. Recrystallization from THF/heptane resulted in 4.13 g (5.50 mmol) of ivory-colored pure **2** in 42% yield. This substance was identical in all respects to the product obtained by the sodium naphthalene route.

$Nb(PF_3)_6H$ (3). Deaerated concentrated H_2SO_4 (0.50 mL, 9.4 mmol) was slowly added to magnetically stirred, finely divided solid $[Et_4N][Nb(PF_3)_6]$ (0.12 g, 0.16 mmol) at 20 °C under a partial vacuum (0.05 Torr) in a 100 mL flask equipped with a side tube cooled to −78 °C. During this addition, a yellow solid rapidly formed and immediately began to sublime onto the walls of the cold tube. Sublimation continued over a 4 h period. The resulting yellow microcrystalline solid melted with decomposition at 0 °C, so the quantity of **3** obtained in this synthesis was not determined. IR: ν(P−F) region (mineral oil mull) 879 s, 834 s, cm^{-1}. MS (ion spray, 1:1 CH_2Cl_2/1,1,2-trichlorotrifluoroethane solution, negative ion) *m*/*e* = 620.6 $[Nb(PF_3)_6]^-$. ^{1}H NMR (300 MHz, 1:1 $CH_2Cl_2/C_2Cl_3F_3$, −60 °C): $\delta = -8.4$ (m, $^2J_{HP} = 60$ Hz) ppm.

$Cs_3[Nb(CO)_5]$ (4) from $Na_3[Nb(CO)_5]$. A deep blue solution of sodium (0.25 g, 11 mmol) in 20 mL of liquid ammonia was transferred via cannula at −70 °C to a cold (−70 °C) bright yellow orange solution of $[Na(diglyme)_2][Nb(CO)_6]$[6] (2.00 g, 3.62 mmol) in 30 mL of liquid ammonia. A deep red solution of $Na_3[Nb(CO)_5]$ formed rapidly. This was filtered at −78 °C into a well-stirred cold (−70 °C) solution of CsI (2.82 g, 10.9 mmol) in 25 mL of ammonia. Immediate precipitation of a brightly colored orange solid occurred on mixing. This was separated by filtration at −70 °C, washed thoroughly with ammonia (3 × 50 mL), and dried in vacuo. Above about −40 °C in vacuo the initial beautiful orange microcrystalline product changed to a deep brown-red *very shock sensitive* powder (**CAUTION!**). The latter was isolated in moderate yield (1.03 g, 50%) and gave analyses consistent with unsolvated **4**. Anal. Calcd for $C_5Cs_3NbO_5$: C, 9.61; Cs, 63.12; H, 0.00. Found: C, 9.47; Cs, 63.35; H, 0.07. IR: ν(CO) region (mineral oil mull) 1810 w, sh, 1566 vs, br, cm^{-1}. Due to the explosive nature of solid **4**, all reactions of $[Nb(CO)_5]^{3-}$ examined to date have been carried out with $Na_3[Nb(CO)_5]$ generated in situ in liquid ammonia. Although the latter solutions are extremely air sensitive, they are thermally stable for many hours at −40 °C and in all other respects are no more difficult or hazardous to handle than any other ammoniacal solutions of carbonylmetalates.

$[Et_4N]_2[Nb(CO)_5H]$ (5) from $Na_2[Nb(CO)_5H]$. A solution of $Na_3[Nb(CO)_5]$ was prepared by the reaction of $[Na(diglyme)_2][Nb(CO)_6]$ (2.66 g, 4.82 mmol) with sodium metal (0.337 g, 14.6 mmol) in 70 mL of liquid ammonia, as described above. Addition of absolute ethanol (0.22 g, 4.8 mmol) in 50 mL of cold THF (−70 °C) caused the reaction mixture to instantly change from a deep red to an orange red hue, characteristic of $Na_2[Nb(CO)_5H]$. Filtration through a medium-porosity frit at −70 °C into a cold (−70 °C) ammoniacal solution of $[Et_4N][BH_4]$ (1.42 g, 9.2 mmol in 50 mL of NH_3) caused an immediate precipitation of product. This was separated by filtration, washed thoroughly with liquid ammonia (4 × 25 mL), and dried in vacuo at room temperature to give 1.59 g (66%) of satisfactorily pure microcrystalline bright orange **5**. Mp 122−125 °C dec. Anal. Calcd for $C_{21}H_{41}N_2NbO_5$: C, 51.01; H, 8.36; N, 5.66. Found: C, 51.33; 8.21; N, 5.56. IR: ν(CO) region (mineral oil mull), 1923 w, 1720 s, br, cm^{-1}. ^{1}H NMR spectra were obtained for the thermally unstable sodium salt, $Na_2[Nb(CO)_5H]$, in liquid ammonia at −50 °C. $^1H\{^{93}Nb\}$ NMR (300 MHz, NH_3, −50 °C). $\delta = -1.89$ (s) ppm. ^{93}Nb NMR (73.3 MHz, NH_3, −50 °C; $NbCl_6^-$ in CH_3CN at 20 °C external std): $\delta = -2122$ (br d, $^1J(^{93}Nb-^1H) \approx 80$ Hz) ppm.

$[Et_4N]_2[Nb(CO)_5SnPh_3]$ (6). A solution of $Na_3[Nb(CO)_5]$ was prepared by the reaction of $[Na(diglyme)_2][Nb(CO)_6]$ (2.50 g, 4.53 mmol) in liquid ammonia (50 mL) with sodium metal (0.313 g, 13.6 mmol) in liquid ammonia (100 mL) at −70 °C. An immediate formation of the deep-red $Na_3[Nb(CO)_5]$ was noted, and the solution was stirred for 1 h. A solution of Ph_3SnCl (1.74 g, 4.51 mmol) in THF (60 mL) was cooled to −70 °C and then slowly added via an 18 gauge cannula to the solution of trianion over a period of 20 min. A deep orange solution formed rapidly after 1 h of stirring, and an excess of solid Et_4NBr (2.00 g, 9.52 mmol) was added quickly via a bent Schlenk tube. The ammonia was allowed to evaporate as the flask warmed to room temperature. The solvent mixture was removed in vacuo. The dry solid was dissolved in acetonitrile (100 mL) at room temperature and then filtered through a medium-porosity frit to yield a clear orange solution. After concentration to approximately 10 mL, ethanol (200 mL) was slowly added and bright yellow-orange microcrystals formed. The product was filtered, washed with ethanol (3 × 40 mL), washed with diethyl ether (3 × 40 mL), and dried in vacuo to give 2.90 g (76% yield) of satisfactorily pure unsolvated **6**. The orange crystals darken from 205 to 211 °C and melt at 216 °C with decomposition. Anal. Calcd. for $C_{39}H_{55}N_2NbO_5Sn$: 55.54; H, 6.57; N, 3.32. Found: C, 55.42; H, 6.48; N, 3.45. IR: ν(CO) region (CH_3CN, 20 °C) 1948 m, 1790 vs, 1750 m, sh, cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 7.0-7.7$ (m, 15 H, $Sn(C_6H_5)_3$), 3.11 (q, 16 H, CH_2 of Et_4N^+), 1.18 (tt, 24 H, CH_3 of Et_4N^+) ppm.

$[Ph_4As][Nb(CO)_5NH_3]$ (7) from $Na[Nb(CO)_5NH_3]$. A solution of $Na_3[Nb(CO)_5]$ in liquid ammonia was prepared as described above from $[Na(diglyme)_2][Nb(CO)_6]$ (2.00 g, 3.62 mmol), except that no initial filtration was carried out. To the cold (−70 °C), stirred solution was added solid NH_4Cl (0.580 g, 10.9 mmol) all at once. Within seconds the solution turned from the deep red color characteristic of $Na_3[Nb(CO)_5]$ to an orange hue that rapidly changed to red-violet with simultaneous evolution of gas. After the solution was stirred for 0.5 h at reflux (−33 °C), it was again cooled to −70 °C. Upon addition of a solution of Ph_4AsCl (need not be anhydrous, 2.41 g, 5.52 mmol) in ethanol (40 mL), a deep red-violet crystalline solid immediately formed. The slurry was cooled to −70 °C and filtered, using a low-temperature coarse-porosity frit. The filtered solid was triturated with cold (0 °C) absolute ethanol (3 × 25 mL) and then dried in vacuo at room temperature for 12 h to give 0.92 g (40% yield) of pure **7**. Anal. Calcd for $C_{29}H_{23}O_5AsNNb$: C, 55.26; H, 3.20; N. 2.22. Found: C, 55.13; H, 3.26; N, 2.34. IR: ν(CO) region (mineral oil mull) 1963 m, 1781 vs, br, 1759 vs, br, cm^{-1}.

$[Et_4N][Nb(CO)_5(CNtBu)]$ (8) from $Na[Nb(CO)_5NH_3]$. An ammoniacal solution of $Na_3[Nb(CO)_5]$ in 50 mL was prepared by the reaction of $[Na(diglyme)_2][Nb(CO)_6]$ (1.00 g, 1.81 mmol) and sodium metal (0.125 g, 5.5 mmol), as described above. To this magnetically stirred solution at − 70 °C was added 3 equiv of solid NH_4Cl (0.29 g, 5.4 mmol). Immediately the reaction mixture turned orange and bubbled vigorously. As the gas evolution ceased, the mixture turned to the red-violet color characteristic of $Na[Nb(CO)_5NH_3]$. A cold (−70 °C) THF solution of excess *t*-BuNC (1.00 mL, 2.3 mmol) was added by cannula, followed by solid Et_4NBr (0.76 g, 3.6 mmol), to the stirred reaction mixture. The ammonia evaporated as the mixture warmed slowly to room temperature. A rapid color change from red violet to orange was observed to occur at about 0 °C. All of the solvent was removed in vacuo. The residue was dissolved in THF (60 mL), and filtration produced a bright orange solution. The volume of solvent was reduced to about 5 mL, and excess ether (150 mL) was added slowly with stirring. The crystalline product formed was washed with diethyl ether (3 × 25 mL). An additional crystallization from acetone/ether gave 0.51 g (63% yield) of orange microcrystalline **8** of the correct composition. Mp: 108 °C dec. Anal. Calcd for $C_{18}H_{29}N_2NbO_5$: C, 48.44; H, 6.55; N, 6.28. Found: C, 48.21; H, 6.75; N, 6.23. IR (CH_3CN): ν(CN), 2090 w; ν(CO), 1966 m, 1830 s, cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 3.11$ (q, 8 H, CH_2 of Et_4N^+), 1.46 (s, 9 H, tBuNC), 1.18 (tt, 12 H, CH_3 of Et_4N^+) ppm.

Results and Discussion

Improved Normal Pressure Synthesis of $[Nb(CO)_6]^-$ via Reductive Carbonylations of $NbCl_4(THF)_2$ Mediated by Sodium Naphthalene and Sodium Anthracene. Prior methods for the laboratory synthesis of $[Nb(CO)_6]^-$ on reasonable scales, i.e., yielding at least gram quantities of the anion, directly from $NbCl_5$, include the above-mentioned magnesium−zinc−pyridine route of Calderazzo and Pampaloni (eq 1)[5] and the alkali metal−naphthalene−DME mediated reduction (eq 2),[6] both of which employ normal pressures of carbon monoxide and conventional laboratory procedures/apparatus. A higher pressure (1700−1900 psi) version of the Calderazzo−Pampaloni route has been recently reported by Bitterwolf to afford 60−72% isolated yields of $[Nb(CO)_6]^-$.[13] Smaller scale normal pressure syntheses of $[Nb(CO)_6]^-$ from $NbCl_5$ have involved sonochemical (eq 3, where))) represents sonication)[14] and sodium−1,3,5,7-cyclooctatetraene (COT) mediated reductive carbonylations (eq 4),[15] respectively. Formation of various salts containing $[Nb(CO)_6]^-$

$$\underset{(1\ \text{mmol})}{NbCl_5} + \text{excess Na} \xrightarrow[\substack{10\ °\text{C, THF} \\ -5\text{NaCl}}]{\text{))), CO (1 atm)}} \underset{23\%}{Na[Nb(CO)_6]} \quad (3)$$

$$NbCl_5 + 6Na + 6CO \xrightarrow[\substack{40\ °\text{C, 60 h} \\ -5\text{NaCl}}]{\text{COT}} \underset{46\%}{Na[Nb(CO)_6]} \quad (4)$$

has also been observed in atmospheric pressure carbonylations of bis(mesitylene)niobate(1−) (eq 5)[16] and bis(mesitylene)niobium(0), (eqs 6 and 7).[17]

$$K[Nb(mes)_2] + 6CO \xrightarrow[20\ °\text{C, 2 h}]{\text{DME}} K[Nb(CO)_6] + 2mes \quad (5)$$

$$2Nb(mes)_2 + 7CO \xrightarrow[20\ °\text{C, 48 h}]{\text{heptane}} [Nb(mes)_2CO][Nb(CO)_6] \quad (6)$$

$$Nb(mes)_2 + 6CO + CoCp_2{}^* \xrightarrow[20\ °\text{C, 7 days}]{\text{toluene}} [CoCp_2{}^*][Nb(CO)_6] + 2mes \quad (7)$$

Finally, under rather forcing conditions (50 atm, 110 °C), potassium tris(cyclooctatetraene)niobate underwent carbonylation to give good yields of $K[Nb(CO)_6]$ (eq 8).[18]

$$K[Nb(C_8H_8)_3] + 6CO \xrightarrow[50\ \text{atm, 110 °C}]{\text{THF}} K[Nb(CO)_6] + 3C_8H_8 \quad (8)$$

A significant problem associated with the naphthalene anion mediated reductive carbonylation of $NbCl_5$ is the tendency for the latter to decompose in DME and especially THF to give solvolysis products,[19] which do not undergo facile reductive carbonylations. For example, poor or zero yields of $[Nb(CO)_6]^-$ often resulted when solid $NbCl_5$ was added too quickly to cold DME. Attempts to substitute DME by more compatible solvents or employ less reactive solvates of $NbCl_5$[19] in this synthesis did not result in significantly improved yields.[20] Since we have had substantial success with reductive carbonylations of $ZrCl_4(THF)_2$ in DME,[21a] corresponding reactions of the related niobium species $NbCl_4(THF)_2$ were investigated. These were found to be far more reproducible and gave better yields of product than analogous ones using $NbCl_5$.

Addition of a cold yellow slurry of $NbCl_4(THF)_2$ in DME to a rapidly stirred cold (−50 to −60 °C), deep green solution/slurry of $NaC_{10}H_8$ (5.0 equiv) in DME under argon resulted in the formation of a deep red-brown, thermally unstable and presently uncharacterized intermediate, which functions as a convenient source of “naked” atomic Nb(I−) in chemical reactions.[21b] Removal of the argon in vacuo from the reaction mixture, followed by introduction of carbon monoxide at atmospheric pressure, resulted in slow uptake of CO at −50 °C and formation of dark brown insolubles and a deep orange-yellow solution of $Na[Nb(CO)_6]$. To ensure completion of the carbonylation process, the reaction mixture was then slowly warmed to room temperature with efficient magnetic stirring under an atmosphere of carbon monoxide. The product was subsequently isolated as $[Et_4N][Nb(CO)_6]$ (**1**), which is considerably more robust and easily handled than the corresponding sodium salt. Indeed, dry microcrystalline samples of **1** survived for many hours in air at room temperature, unlike the quite air

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(21) (a) Jang, M.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1973. (b) In our original study involving alkali metal naphthalene reductions of $NbCl_5$,[6] the yields of $[Nb(CO)_6]^-$ were largely independent of whether the initial (reduction) reactions were carried out under an atmosphere of argon or dinitrogen. However, in the present study only argon was used in corresponding reactions so the possible effect of dinitrogen on these syntheses is unknown. A commercial bath cooler was generally used to maintain the low temperature used in the synthesis, but standard insulated CO_2/acetone baths were also effective. Carrying out the initial $C_{10}H_8{}^-$ reduction or carbonylation steps at temperatures higher than −50 (±5) °C resulted in reduced yields of $[Nb(CO)_6]^-$, but no attempts to optimize the time required for this synthesis have been carried out to date.

sensitive alkali metal salts of $[Nb(CO)_6]^-$. Pure **1** was thereby obtained in amounts varying from 0.98 g (2.5 mmol) to 6.25 g (16.0 mmol) in 60−63% yields based on $NbCl_4(THF)_2$. Provided that efficient mixing is employed, there should be no problem in performing this synthesis on a substantially larger scale.

When the same reaction was conducted in THF, under otherwise identical conditions, only 17−20% yields of **1** were obtained. These reproducibly poor results in THF must involve the formation and/or reactivity of the presumed anionic intermediate(s) in this solvent, since the precursors, $NbCl_4(THF)_2$ and $NaC_{10}H_8$, and the final product, $[Nb(CO)_6]^-$, are stable in THF under the reaction conditions. Also, the intermediate reduction products produced in THF may be substantially different from those obtained in DME. Until these species can be isolated, characterized, and carefully examined, the origin of the solvent dependence in this reductive carbonylation synthesis (eq 9) will remain obscure.

$$NbCl_4(THF)_2 + 5[C_{10}H_8]^- \xrightarrow[\substack{-50\text{ to }-60\ ^\circ C\\ -4Cl^-}]{\text{DME or THF}} \xrightarrow[-60\text{ to }+20\ ^\circ C]{\text{CO (1 atm)}} \underset{\substack{60-63\%\ (DME)\\ 17-20\%\ (THF)}}{[Nb(CO)_6]^-} + 5C_{10}H_8 \quad (9)$$

Because of our recent success in obtaining high yields of $[V(CO)_6]^-$ via *anthracene* radical anion mediated reductive carbonylations of $VCl_3(THF)_3$ at atmospheric pressure,[22] corresponding reactions with $NbCl_4(THF)_2$ were examined. In contrast to analogous sodium naphthalene reactions, which had to be carried out in DME to obtain decent yields of $[Nb(CO)_6]^-$, vide supra, we found that relatively small scale sodium anthracene reductions, vide infra, worked fine in THF and provided up to 70% yields of **1**, eq 10. A purple-brown intermediate initially formed under an argon atmosphere. This species appeared to be substantially more stable in solution than that obtained from related naphthalene reactions. Attempts to characterize this substance are in progress. At −40 °C in THF, it quickly reacted with CO at normal pressures to provide $[Nb(CO)_6]^-$ and smaller amounts of decomposition products than obtained from the naphthalene reactions. However, formation of the intermediate in the anthracene reaction proved to be relatively slow in THF at −40 °C, due to the poor solubilities of both $NaC_{14}H_{10}$ and $NbCl_4(THF)_2$. As a result we have had little success in doing this synthesis with more than about 15 mmol of $NbCl_4(THF)_2$, without employing inordinately large volumes of solvent. Use of other alkali metals/solvent combinations in this reaction have not been examined to date. However, attempts to carry out the reaction at 0 °C, which works well for vanadium,[22] led to much reduced yields of $[Nb(CO)_6]^-$. For these reasons, relatively large scale $[Nb(CO)_6]^-$ preparations are best carried out by the $NbCl_4(THF)_2/NaC_{10}H_8/DME$ method.

$$NbCl_4(THF)_2 + 5[C_{14}H_{10}]^- \xrightarrow[\substack{-40\ ^\circ C\\ -4Cl^-}]{\text{THF, Ar}} \xrightarrow[-40\text{ to }+20\ ^\circ C]{\text{CO (1 atm)}} \underset{70\%}{[Nb(CO)_6]^-} + 5C_{14}H_{10} \quad (10)$$

Synthesis and Isolation of $[Nb(PF_3)_6]^-$; Identification of the Thermally Unstable Hydride, $Nb(PF_3)_6H$. Several years ago, Rehder and co-workers reported that prolonged UV irradiation of $[Nb(CO)_6]^-$ in THF with excess PF_3 provided "light yellow" solutions of $[Nb(PF_3)_6]^-$.[9] To the best of our knowledge, this substance has not been isolated previously as a pure substance and was only characterized on the basis of its NMR spectra.[23] Since sodium naphthalene mediated reductions of $TaCl_5$ provided a route to the previously unknown tantalum analogue, $[Ta(PF_3)_6]^-$,[24] similar reactions involving $NbCl_4(THF)_2$ were examined. These were carried out in exactly the same manner as analogous carbonylation reactions, except that only a slight excess (6.4 equiv) of gaseous PF_3 was introduced into the evacuated reaction vessel. Since PF_3, unlike CO, is very soluble in organic solvents at the temperatures of −50 to −60 °C employed in these reactions, the pressure in the reaction apparatus was well below atmospheric throughout the reaction period, until at the end when argon gas was admitted. Multigram quantities of pure ivory colored and microcrystalline $[Et_4N][Nb(PF_3)_6]$ (2) were easily isolated in 38% and 42% yields, respectively, from the corresponding naphthalene−DME and anthracene−THF reactions (eq 11). No attempts to perform these reactions in the presence of a larger excess of PF_3 have been carried out to date. We had hoped that the anthracene-mediated synthesis of $[Nb(PF_3)_6]^-$ would proceed in substantially higher yield than the corresponding naphthalene reaction, in view of the dramatic differences observed in analogous syntheses of $[V(PF_3)_6]^-$.[22] However, no significant difference in yields was observed in the two niobium reactions. Since the naphthalene−DME reaction (eq 11) is quicker and easier to carry out, this particular synthesis of **2** is the recommended one.

$$NbCl_4(THF)_2 + 5[\text{arene}]^- \xrightarrow[\text{or THF }(-40\ ^\circ C)]{\text{DME }(-55\ ^\circ C)^*} \xrightarrow[\text{2. }Et_4NBr,\ 20\ ^\circ C]{\text{1. }PF_3,\ -55\ ^\circ C} [Et_4N][Nb(PF_3)_6] + 5\text{arene} \quad (11)$$

$$^*\text{arene} = C_{10}H_8 \text{ or } C_{14}H_{10};\ \text{solvent} = \text{DME or THF};$$

$$\text{yield} = 38\% \text{ or } 42\%\ \mathbf{2},\ \text{respectively}$$

Pure **2** melted with decomposition at 171 °C, about 30 °C higher than the decomposition point previously reported for **1**.[6] Also **2** is less thermally stable than the other analogous group 5 compounds, $[Et_4N][M(PF_3)_6]$ for M = V (mp 269 °C dec)[22] and Ta (dec ≥200 °C),[24] respectively. Compound **2** can be easily dissolved in THF, acetone, CH_2Cl_2, and many other polar organic solvents to provide *colorless* stable solutions that were substantially less O_2 sensitive than the corresponding ones of **1**. However, those of **2** and especially $Na[Nb(PF_3)_6]$ quickly decomposed in the presence of moisture, unlike $[Nb(CO)_6]^-$, $[V(PF_3)_6]^-$,[22] and $[Ta(PF_3)_6]^-$,[24] which are far more resistant to hydrolysis. Thus, the convenient aqueous workup described in the Experimental Section for **1**, or that previously employed for $[Et_4N][V(PF_3)_6]$,[22] totally failed for **2**. When THF solutions of **2** were stirred under a CO atmosphere for days, no reaction was observed. Also **2** did not undergo thermal reactions with isocyanides or phosphines. These results indicate that $[Nb(PF_3)_6]^-$ is inert toward thermal substitution reactions under normal conditions, as is the case for $[Nb(CO)_6]^-$.

Infrared spectral properties of **2** were entirely consistent with the presence of octahedral $[Nb(PF_3)_6]^-$ units and were very similar to those previously reported for $[Ta(PF_3)_6]^-$. For example, the infrared spectrum of **2** in CH_2Cl_2 in the $\nu(P-F)$ region showed two absorptions at 842 and 785 cm^{-1}, which

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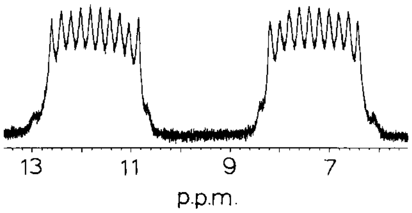

Figure 1. ^{19}F NMR spectrum (282 MHz) of $[Et_4N][Nb(PF_3)_6]$ in CD_2Cl_2 at 23 °C, $\delta = 9.50$ (doublet of decets, $^1J_{P-F} = 1250$ Hz, $^2J_{Nb-F} = 55$ Hz) ppm.

were nearly identical in shape, position, and relative intensity to those previously reported for $[Et_4N][Ta(PF_3)_6]$ in CH_2Cl_2, 842 (vs), 784 (s) cm^{-1}.[24] Essentially identical IR spectral features in the ν(P−F) region were also found for $[PPN][Ta(PF_3)_6]$. A single-crystal X-ray structural characterization has been carried out for the latter salt and confirmed the octahedral nature of the tantalum in the anion.[25a] On this basis, there is no doubt concerning the nature of the anion in **2**. NMR spectra of **2** were in good agreement with those reported many years ago by Rehder et al.[23] However, by using a higher field instrument, well-resolved coupling between ^{19}F and ^{93}Nb ($I = {}^9/_2$, 100% abundant) was observed for the first time in the ^{19}F NMR spectrum of **2**, which is shown in Figure 1.

Since treatment of $[Et_4N][Ta(PF_3)_6]$ with concentrated H_2SO_4 generated a thermally stable, though very acidic, "hydride", $Ta(PF_3)_6H$,[24] the corresponding reaction of **2** was examined. Compound **2** reacted with excess cold (0 °C) concentrated H_2SO_4 to rapidly generate an analogous yellow volatile solid. However, the latter quickly decomposed at about 0 °C, so a pure sample of the product could not be isolated at ambient temperatures. Compound **2** did not react with concentrated or anhydrous H_3PO_4, so it is assumed that sulfuric acid functioned as a monoprotonating agent in this reaction (eq 12). Despite its

$$[Et_4N][Nb(PF_3)_6] + H_2SO_4 \xrightarrow{0\ ^\circ C} \underset{\text{dec, } \sim 0\ ^\circ\text{C}}{Nb(PF_3)_6H\uparrow} + [Et_4N][HSO_4] \qquad (12)$$

thermal instability, the hydride, $Nb(PF_3)_6H$ (**3**), was characterized by infrared, ^1H NMR, and ion spray mass spectral data. Its infrared spectrum was obtained as a quickly mulled solid in mineral oil. In the ν(P−F) region, two peaks at 879 and 834 cm^{-1} were observed in addition to a band at 891 cm^{-1}, due to free PF_3, which was present immediately and increased in intensity with time, while those at lower wavenumber decayed.[25b] Similar absorptions at 870 and 842 cm^{-1} were previously reported for the significantly more stable $Ta(PF_3)_6H$ (dec ~114 °C).[24] As in the case of the tantalum complex, no ν(M−H) absorption could be identified in the IR spectra. As expected, protonation of **2** to form **3** caused the IR-active ν(P−F) bands of the coordinated PF_3 groups to shift to significantly higher energies. Exactly the same trend was observed for the corresponding tantalum system and was discussed in some detail previously.[24] Both the ^1H NMR and ion spray mass spectral data were collected for **3** in a cold (−60 °C) 1:1 CD_2Cl_2 (or CH_2Cl_2)/1,1,2-trichloro-trifluoroethane solvent system. The ^1H NMR spectrum was acquired over a 4 h period and exhibited five peaks of the predicted septet, $^2J_{PH} = 60$ Hz, expected of a fluxional seven-coordinate hydride of this composition. The multiplet was centered at −8.4 ppm, which is very similar to the corresponding value of $\delta = -8.7$, septet, $^2J(PH) = 57$ Hz, reported for $Ta(PF_3)_6H$ in the same solvent mixture.[24] Decomposition prohibited further NMR data collection. The only peak present in the ion spray mass spectrum of **3** was in the negative ion scan at $m/e = 620.6$, corresponding to $[Nb(PF_3)_6]^-$. Repeated attempts to observe peaks in a positive ion scan were unsuccessful. No successful reactions of this quite thermally unstable substance have been carried out to date.

Table 1. Electrochemical Data for $[Et_4N][NbL_6]$, L = Co (**1**), PF_3 (**2**)[a]

complex	*E*° (*V*)[b]	*D (cm²/s)*[c]
1	−0.04	6.0×10^{-6} ($n = 2$)
2	+0.92	5.9×10^{-5} ($n = 1$)

[a] **1** in CH_2Cl_2 with 0.1 M $[Bu_4N][BF_4]$; **2** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$. [b] Irreversible processes. Potentials represent E_{anode} and were measured versus Ag/AgCl in 1.0 M KCl. [c] Determined by chronocoulometry.[25]

Electrochemical Studies of $[Et_4N][Nb(CO)_6]$ (1) and $[Et_4N][Nb(PF_3)_6]$ (2). Cyclic voltammetry studies of **1** and **2** were carried out to shed some light on the remarkable oxidative stability of **2** compared to **1**.[25] The results are shown in Table 1 and indicate that **2** is nearly 1 V more difficult to oxidize than **1** under very similar conditions. Also, electrochemical oxidations of **1** and **2** were irreversible, where **1** underwent a two-electron oxidation process, while **2** was oxidized by one electron. Thus, for the carbonyl complex in CH_2Cl_2 with supporting electrolyte, the second oxidation wave apparently was located at a more negative potential than the first one. These electrochemical results for **1** were consistent with prior studies on the reactions of $[Nb(CO)_6]^-$ with chemical "one-electron" oxidants.[26] Invariably the latter have involved two-electron oxidations and the formation of Nb(I) carbonyls.[27] Thus, available chemical and electrochemical data strongly suggest that the unknown neutral 17-electron radical $Nb(CO)_6$ is unstable toward disproportionation at least in polar solvents. Essentially the same electrochemical behavior was exhibited by $[Et_4N][Ta(CO)_6]$ in CH_2Cl_2,[24] whereas $[Et_4N][V(CO)_6]$ has been known for many years to undergo reversible one-electron oxidations in the same solvent to provide the 17-electron $V(CO)_6$.[26−28] These electrochemical results suggested that the 17-electron $Nb(PF_3)_6$ should be about as strongly oxidizing as elemental bromine and stable toward disproportionation in CH_2Cl_2, but all attempts to observe this elusive species, or the tantalum analogue[24] of the known $V(PF_3)_6$,[29] have been unsuccessful to date.

Synthesis and Characterization of $Na_3[Nb(CO)_5]$ and $Cs_3[Nb(CO)_5]$. Treatment of $[Nb(CO)_6]^-$ with sodium in liquid ammonia at about −70 °C rapidly provided a deep red and extremely air sensitive solution of a highly reduced carbonylmetalate. The properties of this substance, vide infra, were very similar to those previously reported for $Na_3[V(CO)_5]$[30] and $Na_3[Ta(CO)_5]$.[24] Insoluble, pyrophoric disodium acetylenediolate, $Na_2C_2O_2$, the major CO reduction product of sodium in liquid ammonia,[31] also formed during this reaction. Although reductive

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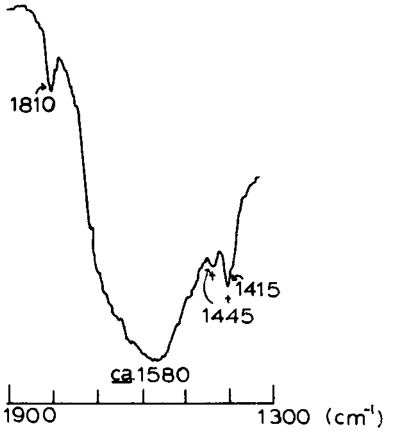

Figure 2. Silicone fluid mull infrared spectrum of $Cs_3[Nb(CO)_5]$ in the ν(CO) region: 1810 w, ~1580 vs, br, cm^{-1}. Absorptions marked with daggers at 1445 and 1415 cm^{-1} are due to silicone fluid.

coupling of coordinated carbon monoxide is now a well-established reactivity pattern for low-valent group 5 metal carbonyls,[32] it is not known whether the production of the $Na_2C_2O_2$ was mediated by niobium in this reaction. The latter required 3 equiv of sodium to go to completion. Attempts to isolate the sodium salt of the carbonylniobate product led to decomposition, but treatment of the filtered deep red ammoniacal solution with 3 equiv of cesium iodide resulted in rapid precipitation of lovely orange microcrystals at −70 °C. These were isolated by filtration, carefully washed with liquid ammonia (in which the product was slightly soluble), and dried in vacuo. Above about −40 °C, the crystalline product crumbled to a deep brown-red powder (**4**), which proved to be *quite shock sensitive* (**CAUTION!**), like the analogous tantalum compound.[24] Satisfactory elemental analyses were obtained for unsolvated $Cs_3[Nb(CO)_5]$, which was isolated in about 50% yield based on $[Nb(CO)_6]^-$ (eq 13).

$$\mathrm{Na[Nb(CO)_6]} + 3\mathrm{Na} \xrightarrow[-\frac{1}{2}\mathrm{Na_2C_2O_2}]{\mathrm{NH_3}\ (-70\ ^\circ\mathrm{C})} \xrightarrow[-3\mathrm{NaI}]{3\mathrm{CsI/NH_3}\ (-70\ ^\circ\mathrm{C})} \underset{\mathbf{4},\ \text{ca. } 50\%}{\mathrm{Cs_3[Nb(CO)_5]}\downarrow} \qquad (13)$$

Infrared spectra of **4** as mineral or silicone fluid mulls (**4** *quickly inflamed in fluorolube*!) in the ν(CO) region (Figure 2) were very similar to that previously reported for pure $Cs_3[Ta(CO)_5]$.[24] Since solid **4** was dangerous to manipulate and much was unavoidably lost during the workup due to its significant solubility in liquid ammonia, all chemical reactions of $[Nb(CO)_5]^{3-}$ have been carried out with the sodium salt, generated in situ in liquid ammonia.

Table 2. $^{93}Nb\{^1H\}$ NMR Spectral Data for Selected Niobium Carbonyls[a]

compound	δ *ppm*
$Na_3[Nb(CO)_5]$	-2138, $w_{1/2} \approx 1100$ Hz[b]
$Na[Nb(CO)_6]$	-2136, $J_{Nb-C} = 236$ Hz
$Na_2[Nb(CO)_5H]$	-2122, $J_{Nb-H} \approx 80$ Hz, $w_{1/2} \approx 270$ Hz[c]
$Na_2[Nb(^{13}CO)_5H]$	-2123, $J_{Nb-C} = 235$ Hz[d]
$Na[Nb(CO)_5NH_3]$	-1880, $w_{1/2} \approx 2000$ Hz

[a] 73.3 MHz, liquid ammonia, −50 °C ($NbCl_6^-$ in CH_3CN, 20 °C, external reference). [b] Spectrum was identical in proton-coupled mode; for 99% ^{13}C enriched $Na_3[Nb(^{13}CO)_5]$, $\delta_{Nb} = -2140$, $w_{1/2} \approx 1900$ Hz, ppm. [c] Broad doublet observed in proton-coupled ^{93}Nb NMR spectrum; for $^{93}Nb\{^1H\}$ NMR, same chemical shift for broad singlet, $w_{1/2} \approx 200$ Hz. [d] Binomial sextet; no Nb−H coupling could be resolved in proton-coupled ^{93}Nb NMR spectrum.

Although IR spectra of $Na_3[Nb(CO)_5]$ could not be obtained owing to its instability, ^{13}C NMR spectra of the 99% ^{13}C-enriched $Na_3[Nb(^{13}CO)_5]$ in liquid ammonia at −50 °C provided good evidence for its formation. The latter was prepared by an analogous reduction of $[Na(diglyme)_2][Nb(^{13}CO)_6]$[33] with sodium in liquid ammonia and showed an intense but poorly resolved decet at $\delta_C = 296$ ($^1J(^{93}Nb-^{13}C) \approx 250$ Hz) ppm, due to the coupling of ^{93}Nb with the equivalent carbonyl groups. This quite downfield δ_C value,[34] which has an uncertainty of about ±2 ppm due to poor resolution of the broad resonance, is in good agreement with corresponding ^{13}CO resonance positions previously reported for $Na_3[Ta(CO)_5]$, $\delta_C = 293$,[24] and $Na_3[V(^{13}CO)_5]$, $\delta_C = 290$ ppm,[35] in liquid ammonia at −50 °C. The presence of pentacarbonylvanadium units in $Na_3[V(^{13}CO)_5]$ in liquid ammonia was previously confirmed by its ^{51}V NMR spectrum, which exhibited a well-resolved binomial sextet.[35] In contrast, the ^{93}Nb NMR spectrum of $Na_3[Nb(^{13}CO)_5]$ (NH_3, −50 °C) consisted of an intense, very broad ($w_{1/2} \approx 1900$ Hz), unresolved multiplet centered at about −2140 ppm ($NbCl_6^-$ in CH_3CN at 20 °C, $\delta_{Nb} = 0$ ppm, external reference). The approximately 2 ppm upfield shift in the ^{93}Nb resonance of $Na_3[Nb(^{13}CO)_5]$ compared to that of $Na_3[Nb(^{12}CO)_5]$ is due to isotopic replacement of ^{12}C by ^{13}C. A very similar isotope effect has been observed and discussed in some detail for $[Nb(CO)_6]^-$.[36,37] The relatively large nuclear electric quadrupole moment of ^{93}Nb, compared to that of ^{51}V, and the likely high electric field gradient at the niobium nucleus, arising from the asymmetric nature of this carbonylniobate, undoubtedly led to the severe line broadening, which prevented any resolution of $^{93}Nb-^{13}C$ coupling.[36] By comparison, under the same conditions, the ^{93}Nb NMR spectrum of the octahedral precursor $[Nb(^{13}CO)_6]^-$ consisted of a well-resolved binomial septet,[33] in good agreement with prior studies on this species.[37]

^{93}Nb and ^{13}C spectral data for $[Nb(CO)_5]^{3-}$ and its protonation products have been collected in Tables 2 and 3. As expected in terms of the low formal oxidation states of the niobium complexes, the ^{93}Nb resonances are shifted strongly upfield and are located in the region previously found for niobium carbonyls.[36a] However, in view of the highly reduced nature of $Na_3[Nb(CO)_5]$, we were surprised to find that its ^{93}Nb resonance position was only about 2 ppm upfield of $Na[Nb(CO)_6]$. Even more surprising, at first glance, were the relatively downfield ^{93}Nb resonances of $Na_2[Nb(CO)_5H]$ and $Na[Nb(CO)_5NH_3]$ compared to that of the presumably less electron rich niobium center in $Na[Nb(CO)_6]$. Although the shielding and deshielding

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(32) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90 and references therein.

(33) This substance was prepared by the original $NaC_{10}H_8$-mediated reductive carbonylation of $NbCl_5$ in DME[6] using 99% ^{13}CO in a previously described apparatus.[24] IR (THF): $\nu(^{13}C^{16}O)$ 1820 cm^{-1}. $^{13}C\{^1H\}$ NMR (75.5 MHz, NH_3, −50 °C): δ(CO) +215.4 (decet, $^1J(^{93}Nb-^{13}C) = 236$ Hz) ppm. ^{93}Nb NMR (73.3 MHz, NH_3, −50 °C, $NbCl_6^-$ in CH_3CN at 20 °C external std): δ −2138 (septet, $^1J(^{93}Nb-^{13}C) = 236$ Hz) ppm. The latter value agrees well with that previously reported for $[Et_4N][Nb(^{12}CO)_6]$ in THF at −50 °C: Bechthold, H. C.; Rehder, D. *J. Organomet. Chem.* **1982**, *233*, 215.

(34) The origins of the remarkably downfield ^{13}CO resonances exhibited by certain carbonylmetalates of the early transition metals have been recently discussed: Kaupp, M. *Chem.*—*Eur. J.* **1996**, *2*, 348.

(35) Warnock, G. F.; Philson, S. B.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 893.

(36) (a) Rehder, D. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, NY, 1987; pp 488−492. (b) Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, NY, 1987; pp 51−88.

(37) Jameson, C. J.; Rehder, D.; Hoch, M. *Inorg. Chem.* **1988**, *27*, 3490 and references therein.

Table 3. $^{13}C\{^1H\}$ NMR Chemical Shifts of Selected 99% ^{13}CO Enriched Carbonylmetalates[a]

compound	*δ ppm*	ref
$Na_3[V(^{13}CO)_5]$	290, $J_{V-C} = 139$ Hz	35
$Na_3[Nb(^{13}CO)_5]$	296, $J_{Nb-C} \approx 250$ Hz[b]	this work
$Na_3[Ta(^{13}CO)_5]$	293, $w_{1/2} = 10$ Hz	24
$Na[V(^{13}(CO)_6]$	224, $J_{V-C} = 116$ Hz	35
$Na\ [Nb(^{13}CO)_6]$	215, $J_{Nb-C} = 236$ Hz[c]	this work
$Na[Ta(^{13}CO)_6]$	211, $w_{1/2} \approx 820$ Hz[d]	24
$Na_2[V(^{13}CO)_5H]$	250, $J_{V-C} = 124$ Hz	35
$Na_2[Nb(^{13}CO)_5H]$	235, $J_{\ Nb-C} \approx 235$ Hz[e]	this work
$Na_2[Ta(^{13}CO)_5H]$	232, $w_{1/2} = 126$ Hz[f]	24

[a] 75.5 MHz, liquid ammonia, −50 °C (TMS, 20 °C, external reference); ^{13}CO contained approximately 90% ^{16}O, 10% ^{18}O. [b] Poorly resolved decet δ 296 ± 2 ppm. [c] Sharp decet. [d] Broad due to unresolved $^{181}Ta-^{13}C$ coupling. [e] Poorly resolved decet. [f] Broad unresolved multiplet.

factors that help to determine the chemical shifts of quadrupolar nuclei, including ^{93}Nb, are well understood and include an important paramagnetic contribution,[36] to our knowledge, no detailed study on ^{93}Nb chemical shifts for niobium carbonyls has been carried out. Presently we have no explanation for the unexpected relative positions of these resonances. However, corresponding ^{51}V chemical shifts for $Na_3[V(CO)_5]$, $Na[V(CO)_6]$, $Na_2[V(CO)_5H]$, and $Na[V(CO)_5NH_3]$ are even more unusual in terms of their relative positions, $\delta_V = -1965, -1981, -1988$, and -1605 ppm, respectively, in liquid ammonia at −50 °C.[35] Since the ^{13}C NMR data for the niobium carbonyls shown in Table 3 have not been previously reported, corresponding values for the vanadium and tantalum analogues were included for comparison. The carbonyl resonances observed for the niobium carbonyls in Table 3 follow the generally observed, though counterintuitive, trend for metal carbonyls; i.e., as a given metal center becomes more electron rich and corresponding IR ν(CO) bands move to lower energy, the carbonyl ^{13}C NMR resonances shift downfield.[38,39] Also, usually carbonyl ^{13}C resonance positions steadily become less positive (i.e., shift upfield) as the atomic number of the metal increases in a triad for a given type of binary or substituted metal carbonyl.[40] This is the trend observed for $Na[M(CO)_6]$ and $Na_2[M(CO)_5H]$, M = V, Nb, Ta, in Table 3. However, for $Na_3[M(CO_5]$, the carbonyl ^{13}C resonance is most downfield for niobium. This is the same unusual trend previously observed for the half-sandwich group 4 carbonyls, $[(C_5R_5)M(CO)_4]^-$ (R = H, Me; M = Ti, Zr, Hf), for which zirconium has the most downfield δ(CO) values.[41]

Protonation of $[Nb(CO)_5]^{3-}$. Isolation and Characterization of $[Nb(CO)_5H]^{2-}$. Dropwise addition of 1 equiv of ethanol or ammonium chloride in liquid ammonia to ammoniacal solutions of $Na_3[Nb(CO)_5]$ at −70 °C rapidly caused the deep red color of the trisodium salt to change to a lighter orange-red hue. Attempts to isolate the sodium salt were thwarted by facile decomposition. However, treatment of the filtered solutions with 2 equiv of $[Et_4N][BH_4]$, which has good solubility in liquid ammonia, rapidly gave insoluble bright orange microcrystals of $[Et_4N]_2[Nb(CO)_5H]$ (**5**). These were collected, thoroughly washed with liquid ammonia, which quantitatively removed the soluble byproduct $NaBH_4$, and dried in vacuo to provide analytically pure **5** in 66% yield (eqs 14 and 15). Nujol mull

$$Na_3[Nb(CO)_5] + EtOH \xrightarrow[\text{-NaOEt}]{NH_3\ -70\ °C} Na_2[Nb(CO)_5H] \quad (14)$$

$$Na_2[Nb(CO)_5H] + 2[Et_4N][BH_4] \xrightarrow[-2NaBH_4]{NH_3\ -70\ °C} \underset{66\%}{[Et_4N]_2[Nb(CO)_5H]\downarrow} \quad (15)$$

infrared spectra of **5** in the ν(CO) region showed bands at 1923 w, 1720 s, br, which is nearly the same pattern observed for the tantalum analogue, except that the very broad and poorly resolved peak at 1720 cm^{-1} in **5** was sharper and bifurcated in $[Ta(CO)_5H]^{2-}$, with bands at 1922 w, 1750 s, 1710 m, sh, cm^{-1}.[24] Compound **5** was insoluble in THF and other ether solvents, and attempts to dissolve it in aprotic polar solvents such as acetonitrile, dimethyl sulfoxide, and hexamethylphosphoramide resulted in rapid decomposition. Consequently, all solution NMR studies had to be obtained with liquid ammonia solutions of the precursor, $Na_2[Nb(CO)_5H]$, vide infra.

Freshly and *carefully* prepared solutions of $Na_3[Nb(CO)_5]$ in liquid ammonia invariably showed a very weak sharp singlet at $\delta_{Nb} = -2136$ ppm, due to traces of $[Nb(CO)_6]^-$,[37] superimposed on an intense, very broad ($w_{1/2} \approx 1100$ Hz) resonance at $\delta_{Nb} = -2138$ ppm, due to $Na_3[Nb(CO)_5]$, vide supra. Also, generally a much weaker, broad ($w_{1/2} \approx 200$ Hz) resonance at $\delta_{Nb} = -2122$ ppm was present in varying amounts. Addition of 0.5 equiv of ethanol caused the absorption at −2122 ppm to dramatically increase in intensity while the intensity of the very broad peak at −2138 ppm decreased markedly. During this and subsequent additions of ethanol, the intensity of the sharp resonance at −2136 ppm, due to $[Nb(CO)_6]^-$, remained essentially unchanged. Examination of the proton-coupled ^{93}Nb NMR spectrum of the above solution showed no change in the very broad resonance at −2138 ppm, but the peak at −2122 ppm changed to a somewhat broader doublet ($w_{1/2} \approx 270$ Hz), with $^1J(^{93}Nb-^1H) \approx 80$ Hz. This experiment gave good evidence for the production of a niobium monohydride in this reaction and also strongly suggested that the species at −2138 ppm was nonhydridic in character. Addition of another 0.5 equiv of ethanol to the solution caused all of the resonance at −2138 ppm, attributed to $Na_3[Nb(CO)_5]$, to disappear, while that at −2122 ppm became the major species present.

Initial attempts to observe the 300 MHz ^1H NMR spectrum of the niobium monohydride were unsuccessful, but the ^{93}Nb-decoupled ^1H NMR spectrum showed a sharp singlet at $\delta = -1.89$ ppm, a value similar to that previously reported for $[Ta(CO)_5H]^{2-}$, $\delta_H = -2.23$ ppm.[24] Niobium hydrides are often difficult to observe by usual ^1H NMR spectroscopy due to the considerable line broadening caused by unresolved niobium−hydrogen coupling.[42] The same protonation study was carried out with 99% ^{13}C enriched $Na_3[Nb(^{13}CO)_5]$ and followed by $^{93}Nb\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. The ^{93}Nb NMR spectrum was particularly informative since it consisted of a well-resolved binomial sextet at −2123 ppm with $^1J(^{93}Nb-^{13}C) = 235$ Hz and thereby confirmed that *the niobium monohydride was a*

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(39) However, it has been pointed out that sometimes, particularly with half-sandwich carbonyl complexes of the early transition metals, there is no correlation between IR ν(CO) values and corresponding NMR $\delta(^{13}CO)$ values: Ellis, J. E.; Stein, B. K.; Frerichs, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 4066.

(40) Mann, B. E.; Taylor, B. E. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

(41) (a) Frerichs, S. R.; Ellis, J. E. *J. Organomet. Chem.* **1989**, *359*, C41. (b) See ref 34 for a calculational study on these half-sandwich carbonylmetalates.

(42) See: Labinger, J. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, NY, 1982; Vol. 3, p 707.

pentacarbonyl, i.e., $Na_2[Nb(^{13}CO)_5H]$. The coupling of ^{93}Nb to five equivalent ^{13}CO units indicated that this species was fluxional in liquid ammonia at −50 °C, as was the vanadium analogue, $[V(CO)_5H]^{2-}$.[35] This result, inter alia, also provided important additional support for the formulation of the precursor as a pentacarbonyl species, i.e., $Na_3[Nb(CO)_5]$. Corresponding $^{13}C\{^1H\}$ NMR spectra showed that when ethanol was added to $Na_3[Nb(^{13}CO)_5]$, the previously mentioned decet at $\delta_C = +296$ ppm, attributed to pentacarbonylniobate(3−), decreased in intensity and a new decet, also poorly resolved, grew in at $\delta_C = +235$ ($^1J(^{93}Nb-^{13}C) \approx 235$ Hz) ppm. This carbon resonance position is in good agreement with that previously observed for $Na_3[Ta(^{13}CO)_5H]$, $\delta_C = +232$ ppm,[24] and the niobium−carbon coupling constant is consistent with the value obtained from ^{93}Nb NMR spectra.

Stannylation of $[Nb(CO)_5]^{3-}$. Isolation and Characterization of $[Nb(CO)_5SnPh_3]^{2-}$. Derivatization of carbonylmetalates by their reaction with electrophilic triphenyltin reagents was first examined by Hein more than 40 years ago.[43] The resulting mixed-metal derivatives are generally isolated in high yields and are often much easier to handle and crystallize and more thermally stable than their respective precursors or hydride derivatives thereof. For these reasons, the preparation of triphenyltin derivatives has been recognized for many years to be one of the best methods for obtaining evidence for the existence of highly reactive and thermally unstable mononuclear carbonylmetalates,[44] *provided* one has unambiguously established that the latter are not present in their protonated forms.[45] Cooper and co-workers have employed this same strategy to provide important additional evidence for the existence of other classes of highly reactive metalates in several elegant studies, including those involving homoleptic alkyne[46] and isocyanide[47] metalates.

Addition of 1 equiv of Ph_3SnCl to ammoniacal solutions of $Na_3[Nb(CO)_5]$ resulted in an almost instantaneous formation of a bright orange reaction mixture. Following cation exchange, isolation, and recrystallization from acetonitrile/ethanol, sparkling orange and free-flowing crystalline $[Et_4N]_2[Nb(CO)_5SnPh_3]$ (**6**) was procured in 76% yield, based on $[Nb(CO)_6]^-$ (eq 16). Compound **6** easily dissolved in aprotic polar solvents,

$$Na_3[Nb(CO)_5] + Ph_3SnCl \xrightarrow[-NaCl]{NH_3,\ -70\ ^\circ C} \xrightarrow[NH_3]{2Et_4NBr} \underset{76\%}{[Et_4N]_2[Nb(CO)_5SnPh_3]} \quad (16)$$

such as acetonitrile, to provide deep orange, thermally stable but very air sensitive solutions. Infrared spectra of **6** in acetonitrile in the ν(CO) region exhibited the three-band pattern often observed for monosubstituted pentacarbonylmetal species of C_{4v} local symmetry, i.e., 1948 m, 1790 vs, 1750 m sh, cm^{-1}. These values are very similar to those reported for $[Et_4N]_2[Ta(CO)_5SnPh_3]$, 1942 m, 1785 v, 1755 m sh, cm^{-1},[24] and are shifted about 100 cm^{-1} to lower energy of the corresponding bands at 2034 m, 1904 vs, 1879 m, cm^{-1}, reported for $[PPN][W(CO)_5SnPh_3]$, which has been structurally characterized.[48]

Synthesis of $[Nb(CO)_5L]^-$, L = NH_3 and CNtBu, via the Protonation of $[Nb(CO)_5H]^{2-}$ in Liquid Ammonia. Addition of 1 equiv of ethanol or ammonium chloride to ammoniacal orange-red solutions of $Na_2[Nb(CO)_5H]$ initially gave a lighter orange solution, but within seconds, gas evolution occurred and the reaction mixture changed dramatically to a dark purple hue. Attempts to isolate the purple compound as the sodium salt were prevented by facile decomposition, so this reaction was followed by ^{93}Nb NMR spectroscopy in liquid ammonia. Following addition of ethanol to $Na_2[Nb(CO)_5H]$, the resonance at $\delta_{Nb} = -2122$ ppm, due to the niobium monohydride, vide supra, disappeared and was replaced by a much broader ($w_{1/2} \approx 2000$ Hz) absorption at −1880 ppm. The sharp weak resonance at $\delta_{Nb} = -2136$ ppm, due to small amounts of $[Nb(CO)_6]^-$, remained unchanged in intensity during the reaction. A corresponding study carried out with 99% ^{13}C labeled $Na_2[Nb(^{13}CO)_5H]$ showed the same results, except that the ^{93}Nb resonance due to the purple product at ca. −1880 ppm was even broader ($w_{1/2} \approx 2500$ Hz) due to unresolved $^{93}Nb-^{13}C$ coupling. A $^{13}C\{^1H\}$ NMR spectrum of this purple solution showed an unresolved multiplet centered at about $\delta_C = +220$ ppm, a value similar to those reported for $[V(CO)_5NH_3]^-$, $\delta_C = +225$,[35] and $[Ta(CO)_5NH_3]^-$, $\delta_C = +220$ ppm, where the latter is the weighted average of ^{13}C resonances observed for the *trans*-CO (+225 ppm) and *cis*-CO (+219 ppm) groups in the tantalum complex.[49] The latter complexes are also intensely colored red-violet (M = V) or violet (M = Ta) compounds. Although these NMR studies could not establish the composition of the purple niobium product, the isolation of this species as a stable tetraphenylarsonium salt, vide infra, has provided good evidence for its formulation in liquid ammonia (eq 17). Attempts to observe the transient orange intermediate were unsuccessful. The latter is believed to be $[Nb(CO)_5H_2]^-$, which may be a labile η^2-H_2 complex analogous to the known $Cr(CO)_5(\eta^2\text{-}H_2)$.[50]

$$Na_2[Nb(CO)_5H] \xrightarrow[-70\ ^\circ C]{EtOH\ or\ NH_4Cl} \begin{matrix}\text{unstable}\\ \text{orange}\\ \text{intermed}\end{matrix} \xrightarrow[+NH_3]{-H_2} Na[Nb(CO)_5NH_3] \quad (17)$$

Treatment of the above filtered purple solution with 1 equiv of tetraphenylarsonium chloride resulted in rapid deposition of beautiful deep red-violet microcrystals. These were appreciably soluble in liquid ammonia, so the purification procedure (see Experimental Section) ultimately gave only a 40% isolated yield of satisfactorily pure $[Ph_4As][Nb(CO)_5NH_3]$ (**7**), eq 18. Compound **7** quickly decomposed in polar organic solvents, due to the lability of the coordinated ammine group, vide infra. However, its IR mineral oil mull spectrum in the ν(CO) region showed a three-band pattern at 1963 m, 1781 vs, br, and 1759 vs, br, cm^{-1}, which is consistent with the presence of

$$Na[Nb(CO)_5NH_3] + Ph_4AsCl \xrightarrow[-NaCl]{NH_3,\ -70\ ^\circ C} \underset{40\%\ \text{isolated}}{[Ph_4As][Nb(CO)_5NH_3]\downarrow} \quad (18)$$

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(43) Hein, F.; Kleinert, P.; Jehn, W. *Naturwissenschaften* **1957**, *44*, 34.

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$[Nb(CO)_5NH_3]^-$ units of C_{4v} local symmetry about niobium. As expected, the band positions of this ion were shifted to somewhat lower energy than corresponding ones of the previously known $[Nb(CO)_5PPh_3]^-$, i.e., ν(CO) in THF: 1971, 1863, 1830 cm^{-1},[51] since NH_3 is a better donor than PPh_3. Also, weak broad absorptions were observed at about 3380 and 3310 cm^{-1}, presumably due to the coordinated ammine group in **7**.

Compounds of the general formula $[M(CO)_{6-x}L_x]^-$, where M = V, Nb, Ta and L = PR_3, $P(OR)_3$ and so on, are valuable reagents for the general exploration of group 5 carbonylmetalate(1−) chemistry since they are usually more reactive and often form more stable products with electrophiles than the unsubstituted hexacarbonylmetalates(1−).[52] Compounds of this type have been prepared generally by UV-photopromoted ligand substitutions of $[M(CO)_6]^-$, a reaction first discovered by Davison.[51] However, attempts to substitute one or more CO groups by isocyanides in these photolysis reactions invariably failed due to destruction of the ligand and/or product by UV radiation. Earlier we had shown that $[V(CO)_5NH_3]^-$ [53] and $[Ta(CO)_5NH_3]^-$ [49] were useful reagents for conventional syntheses of the corresponding $[M(CO)_5(CNR)]^-$, which were previously unknown species. The reactions proceeded under very mild conditions due to the substantial lability of the coordinated NH_3 group. The combination of a relatively strong pure donor ligand (NH_3) coordinated to a very electron rich anionic metal center undoubtedly caused the ammonia to be a very good leaving group in these reactions. Thus, these vanadium and tantalum complexes functioned as useful synthons for respective 16-electron $[M(CO)_5]^-$ groups in many of their reactions.[49,53] On this basis, we have examined corresponding reactions of the niobium analogue, $[Nb(CO)_5NH_3]^-$, and report on the one involving *tert*-butylisocyanide.

Addition of a slight excess of *tert*-butylisocyanide (1.3 equiv) in THF to the deep purple liquid ammonia solution of $Na[Nb(CO)_5NH_3]$ at −70 °C, to which tetraethylammonium bromide had been added, caused no immediate color change. However, on warming to about 0 °C, after much of the ammonia had evolved, the reaction mixture quickly changed to the orange color of the product. Following an unexceptional workup and recrystallization from acetone/ether, a 63% yield of satisfactorily pure free-flowing $[Et_4N][Nb(CO)_5(CNtBu)]$ (**8**) was obtained. The spectroscopic properties of **8** were in good agreement with those of the vanadium[53] and tantalum[49] analogues. All of the data for **8** are fully consistent with the proposed formulation of this species, the synthesis of which is summarized in eq 19.

$$Na[Nb(CO)_5NH_3] + t\text{-BuNC} + Et_4NBr \xrightarrow[\substack{-70\text{ to }+20\ ^\circ C\\ -NaBr,\ NH_3}]{NH_3/THF} \underset{63\%}{[Et_4N][Nb(CO)_5(CNtBu)]} \qquad (19)$$

Concluding Remarks

We have established that $NbCl_4(THF)_2$ is an extremely useful precursor in alkali metal naphthalene and anthracene mediated reductive carbonylation reactions, which gave $[Nb(CO)_6]^-$ in 60−70% yields, the highest reported for syntheses conducted at atmospheric pressure. Analogous reactions with PF_3 afforded about 40% isolated yields of $[Nb(PF_3)_6]^-$, which was previously unknown as a pure substance. Use of this same general procedure for the synthesis of related $[NbL_6]^-$, where L = isonitriles, phosphites, and related acceptor ligands, will be of interest since molecules of this type are now only known for L = CO and PF_3. Details of the synthesis and chemistry of $[Nb(CO)_5]^{3-}$ were reported, including previously unpublished ^{93}Nb and ^{13}C NMR studies, which provided the first good spectroscopic evidence for the existence of $[Nb(CO)_5]^{3-}$ in solution. The trianion is the only compound containing niobium in its lowest known formal oxidation state of −3. Also of interest is the monoprotonated product of the trianion, $[Nb(CO)_5H]^{2-}$. It is the sole example of a hydride containing niobium in a formally negative oxidation state, i.e., Nb(I−), and the only known simple unsubstituted carbonyl hydride of niobium. In this sense, $[Nb(CO)_5H]^{2-}$ may be thought of as a formal reduction product of the unknown $Nb(CO)_6H$, for which only substituted derivatives have been reported; e.g., $Nb(CO)_2(dmpe)_2H$,[54] dmpe = 1,2-bis(dimethylphosphino)ethane, $[C_5H_5Nb(CO)_3H]^-$,[55,56] $Nb(CO)_4(dppe)H$,[7] dppe = 1,2-bis(diphenylphosphino)ethane, and $Nb(PF_3)_6H$ (this work).

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