

Highly Reduced Organometallics. 4.¹ Syntheses and Chemistry of Pentacarbonylvanadate(3-) Ion, $V(CO)_5^{3-}$

John E. Ellis,* Kristi Lenz Fjare, and Thomas G. Hayes

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received February 23, 1981. Revised Manuscript Received June 1, 1981

Abstract: Alkali-metal reductions of various salts containing $V(CO)_6^-$ in liquid ammonia provide high yields of the "super-reduced" species $V(CO)_5^{3-}$ which contains vanadium in its lowest known formal oxidation state. Although salts of $V(CO)_5^{3-}$ containing lithium, sodium, and various onium cations rapidly decompose above 0 °C, the trianion has been isolated and characterized as rather thermally stable rubidium and cesium salts, $Rb_3V(CO)_5$ and $Cs_3V(CO)_5$. A treacherously shock sensitive potassium salt, $K_3V(CO)_5$, is also described. Treatment of liquid ammonia solutions of $Na_3V(CO)_5$ with bis(triphenylphosphin)iminium chloride and tetraphenylphosphonium chloride provides thermally unstable, ammonia-insoluble solids believed to contain $V(CO)_5^{3-}$. These decompose on warming to room temperature to provide $V(CO)_5PPh_3^-$. Main-group 4 electrophiles, including R_3EX (R = alkyl, aryl; E = Sn, Pb; X = halide), react with $V(CO)_5^{3-}$ to provide moderate to high yields of the new organometallic derivatives, $(R_3Sn)V(CO)_5^{2-}$ and $(R_3E)_2V(CO)_5^{1-}$. The dianions are the first reported organotin derivatives containing a transition metal in a formally negative oxidation state. Reactions of $V(CO)_5^{3-}$ in liquid ammonia with weak Brønsted acids including water, ammonium cation, and acetonitrile are also described. High yields (85–95%) of $V(CO)_5NH_3^-$ are obtained by the treatment of $V(CO)_5^{3-}$ in liquid ammonia with 2 or more equiv of ammonium chloride. This amine-substituted anion is quite unstable in solution at room temperature but may be isolated as thermally stable Ph_4As^+ or Ph_4P^+ salts.

Substantial interest in the synthesis and chemistry of metal carbonyl anions^{2,3} and other anionic organometallic compounds of the transition elements⁴ has developed in recent years. These useful materials are important as precursors to new organometallic and organic compounds,^{2,3} intermediates in homogeneous catalysis,⁵ photoactive substrates,⁶ and models for the study of ion pairing in solution.^{7,8} Our research group has been particularly interested in these compounds as sources of functional groups ("metalloanalogues") which chemically mimic more familiar electronically equivalent molecular fragments containing only nonmetals.⁹ Several years ago we recognized that there exist sufficiently far reaching parallels in the reactivity patterns of halides and metal carbonyl monoanions (e.g., $Co(CO)_4^-$) and chalconides (especially S^{2-}) and metal carbonyl dianions (especially $Fe(CO)_4^{2-}$) to justify considering these transition-metal monoanions and dianions as pseudohalides and pseudochalconides, respectively.² These ideas also led to the anticipation that previously unknown metal-carbonyl trianions, formally analogous to main-group trianions such as P^{3-} , might be stable entities.^{2,10}

In the past several years we have prepared such species as well as more highly reduced materials ("carbonyl tetraanions") and have termed these species "super-reduced" since they contain transition metals in their lowest known formal oxidation states. Solutions of alkali metals in various solvents and solvent mixtures including liquid ammonia, hexamethylphosphoramide, naphthalene-tetrahydrofuran and benzophenone-dioxane reduce numerous neutral and monoanionic binary carbonyls and metal carbonyl amines to generate high yields of the characterized materials $Na_3M(CO)_4$ (M = Mn, Re),^{11,12} $Na_3M(CO)_3$ (M = Co, Rh, Ir),¹³

and $Na_4M(CO)_4$ (M = Cr, Mo, W).¹ More enigmatic has been the thermally unstable reduction product which was provisionally assigned the composition $Na_3V(CO)_5$ on the basis of a preliminary examination of its chemical properties.¹⁴ In this paper more evidence is presented to show that the reduction of $V(CO)_6^-$ by alkali metals in liquid ammonia does indeed generate $V(CO)_5^{3-}$. Also, the chemical and physical properties of this anion with various cations are discussed and compared with those of related carbonyl anions.

Experimental Section

General Procedures and Starting Materials. All operations were carried out under an atmosphere of purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred via stainless steel cannulae and syringes; otherwise reactions were generally performed by using standard Schlenck apparatus with a double-manifold vacuum line. Liquid ammonia was dried with Na metal and distilled in vacuo directly into the reaction vessel. Reagent grade tetrahydrofuran, diethyl ether, toluene, and heptane were distilled from alkali-metal benzophenone ketyls immediately before use. Acetone was dried over 4A molecular sieves and then subjected to three freeze-thaw cycles under vacuum (or until no effervescence was noted at the melting point).

The following reactants were purchased from commercial sources and degassed before use: bis(diglyme)sodium hexacarbonylvanadate, chlorotriphenylstannane, bromotricyclohexylstannane, chlorotrimethylstannane, chlorotriphenylplumbane, tetraphenylphosphonium bromide, tetraphenylarsonium chloride, and bis(triphenylphosphin)iminium chloride (PPN^+Cl^-).

Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer in 0.1-mm sealed NaCl cells, equipped with Becton-Dickinson steel stopcocks to permit filling outside the drybox. Nujol and Fluorolube mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox under continuously recirculating nitrogen. NMR samples sealed into 5-mm Pyrex tubes were run on either a Varian T60 or FT80 spectrometer. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover unimelt apparatus. Microanalyses were carried out by Galbraith Laboratories, Spang Microanalytical Lab, or H. Malissa and G. Reuter Analytische Laboratorien.

Trisodium Pentacarbonylvanadate(3-), $Na_3V(CO)_5$ (1), and Its Conversion to Tripotassium Pentacarbonylvanadate(3-), $K_3V(CO)_5$ (2). Ammonia (150 mL) was condensed in vacuo into a cold flask (-78 °C) containing $[Na(diglyme)_2][V(CO)_6]$ (2.00 g, 3.92 mmol), sodium metal (0.28 g, 12.2 mmol), and a glass-covered magnetic stir bar. After all ammonia had been transferred, the solution was refluxed for 1–2 h at -33

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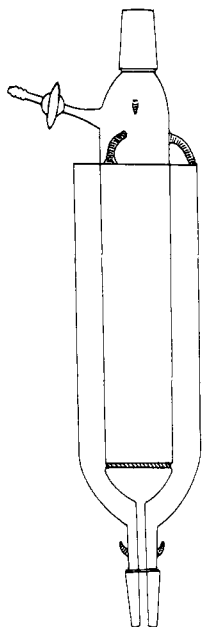


Figure 1. Jacketed low-temperature filtration apparatus for thermally unstable substances.

°C until it changed to the bright cherry red color characteristic of dissolved $\text{Na}_3\text{V}(\text{CO})_5$ (1).¹⁵ The $\text{Na}_3\text{V}(\text{CO})_5$ solution was then cooled to -78 °C and allowed to stand without stirring for about 1 h until most finely divided solid had precipitated. Then, with minimal agitation, the slightly turbid red supernatant was transferred via cannula and filtered at -78 °C with a low-temperature jacketed filtration apparatus with medium-porosity frit of our design (Figure 1).

In this fashion approximately 125 mL of the liquid ammonia solution was filtered rapidly. The remaining 20–25 mL of ammonia was heavily laden with insolubles and filtered more slowly (ca. 0.5 h). The insoluble products (vide infra) include small amounts of NaNH_2 from the excess sodium metal and pyrophoric, shock-sensitive $\text{Na}_2\text{C}_2\text{O}_2$.^{16,17} The filtrate proceeded directly into a stirred solution of excess potassium iodide (previously dried at 180 °C for 24 h in vacuo) (3.91 g, 0.235 mmol) in liquid ammonia (50 mL). Almost immediately a crystalline orange-red solid precipitated from solution leaving a very pale yellow supernatant. The solid was filtered, washed at -78 °C with 2×50 mL liquid ammonia, and slowly warmed to room temperature in vacuo. Washings were lightly colored, indicating the potassium salt is slightly soluble in liquid ammonia. Above -20 °C, it changed to a crystalline dark red-brown solid. Compound 2 was dried further at room temperature for 2.5 h in vacuo. Gas was evolved during this process, undoubtedly ammonia of solvation. During this time the solid became darker brown but remained crystalline.

This procedure provided 1.06 g (88% yield) of shock-sensitive, thermally unstable, pyrophoric 2 whose analysis was consistent with the proposed formulation. Anal. Calcd for $\text{C}_5\text{O}_5\text{K}_3\text{V}$: C, 19.48; K, 38.05; V, 16.50; H, 0.00. Found: C, 19.23; K, 37.85; V, 16.82; H, 0.27. Compound 2 turns jet black on heating above 60 °C after a few minutes. Fast heating caused a violent decomposition at about 120 °C. When the brown crystalline product is held under vacuum for 12 h at room temperature, it also changes to a jet black crystalline solid. The jet black material is especially shock sensitive.

Caution! Care must be exercised when handling this material. Scratching the solid on a glass fritted disk with a metal spatula during removal from the filtration apparatus almost invariably caused rapid deflagration under a nitrogen or argon atmosphere. For this reason it is not recommended that any spatula be used in the transfer of this solid. When these precautions were observed, we experienced no difficulty in manipulating the solid, although we did so with utmost caution. This

(15) If significant product oxidation has occurred during this operation, the solution will have a distinct brownish color.

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(17) The insoluble products are best destroyed by rapid addition of a large volume of water (approximately 100 mL) to the frit as soon as possible after the synthesis is completed. This reaction is accompanied by a yellow flash and a loud pop but no explosion, at least with a preparation on this scale. **Caution!** Drop by drop addition of alcohol or water to the insolubles will often cause an explosion even under a nitrogen atmosphere.

treacherous solid also burns in Fluorolube (vide infra) and explodes on impact, e.g., when grinding or hitting the solid with an agate mortar and pestle in the absence of mulling agent.

Trirubidium Pentacarbonylvandate(3-), $\text{Rb}_3\text{V}(\text{CO})_5$ (3). Ammonia (125 mL) was condensed in vacuo into a cold flask (-78 °C) containing $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ (2.00 g, 3.92 mmol) and sodium metal (0.28 g, 12.2 mmol). Exactly the same procedure was used as described above for filtering the $\text{Na}_3\text{V}(\text{CO})_5$ solution into a vessel containing a stirred solution of excess rubidium iodide (previously dried at 180 °C for 24 h in vacuo) (5.00 g, 0.235 mmol). Precipitation of the insoluble rubidium salt did not commence immediately on addition of filtrate, but within several minutes beautiful red crystals began to deposit. After all of the filtrate was added, the supernatant was very pale yellow, and the red crystalline product was worked up as indicated above for 2. During drying in vacuo at room temperature the red to orange red crystals changed slowly to a brown yellow solid similar to compound 4 in color (vide infra). After 12 h of drying, the compound still had a highly crystalline appearance and an attractive golden brown color.

This procedure supplied 1.54 g (88% yield) of analytically pure 3. Anal. Calcd for $\text{C}_5\text{O}_5\text{Rb}_3\text{V}$: C, 13.42; Rb, 57.31; V, 11.39; H, 0.00. Found: C, 13.52; Rb, 56.86; V, 11.61; H, 0.24. Compound 3 decomposes before melting, slowly above 130 °C. Unlike 2 compound 3 is stable for at least 1 day under an inert atmosphere (N_2 or Ar) at room temperature but does noticeably darken when stored at this temperature for 1 week. Small amounts of the solid do not burn immediately in dry air but it is pyrophoric in larger quantities (ca. 0.10 g) and burns readily in moist air. Although 3 does not appear to be shock sensitive, it will (like 2) deflagrate when scratched with a metal spatula against a fritted glass disk. Compound 3 does not inflame or explode in Fluorolube (unlike 2) and apart from its great reactivity toward air and moisture is rather easily handled.

Tricesium Pentacarbonylvandate(3-), $\text{Cs}_3\text{V}(\text{CO})_5$ (4). **Method 1.** Ammonia (250 mL) was condensed in vacuo into a cold flask (-78 °C) containing $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ (6.0 g, 12.2 mmol) and sodium metal (0.88 g, 38.2 mmol). As indicated for compound 2, the deep red $\text{Na}_3\text{V}(\text{CO})_5$ solution was filtered into a stirred solution containing excess anhydrous cesium iodide (12.63 g, 48.8 mmol) in liquid ammonia (50 mL). A bright orange crystalline precipitate immediately formed on mixing. As before it was filtered and washed with liquid ammonia (3×50 mL). The final two washings were colorless. The dry solid, which we believe contains ammonia of solvation, was bright orange at -40 °C but on warming to room temperature rapidly evolved ammonia and changed to a light brown orange noncrystalline solid.

This material was obtained in high yield (5.84 g, 87%) and proved to be analytically pure 4. Anal. Calcd for $\text{C}_5\text{O}_5\text{Cs}_3\text{V}$: C, 10.18; Cs, 67.61; V, 8.64; H, 0.00. Found: C, 10.07; Cs, 67.28; V, 8.48; H, 0.07. Compound 4 is by far the most thermally stable salt of $\text{V}(\text{CO})_5^{3-}$ and only begins to rapidly decompose above 200 °C. It decomposes completely before melting. However, 4 does darken slightly after 1 week at room temperature under an inert atmosphere. It appears to be indefinitely stable at -10 °C. Like 2 and 3, 4 will usually burn rapidly in air (to give a striking bright white-blue flame) especially if moisture is present. Also, like 2 and 3 it will rapidly deflagrate when scratched with a metal spatula against a fritted glass disk, but unlike 2 one must vigorously scratch before rapid decomposition occurs. Consequently, we routinely handle 4 with metal spatulas with no problem. Because of the ease in handling this material all chemistry of $\text{V}(\text{CO})_5^{3-}$ in the absence of liquid ammonia has been performed with 4, which does not appear to dissolve in any unreactive solvent, including hexamethylphosphoramide and acetonitrile. Compound 4 reacts explosively with protic solvents such as alcohols and water at room temperature.

Method 2 (Not Recommended for Safety Reasons). Exactly the same procedure and quantities of reactants as mentioned previously for the synthesis of 3 were used. The filtrate containing $\text{Na}_3\text{V}(\text{CO})_5$ was added at -78 °C to a slurry of CsClO_4 (dried in vacuo for 24 h at 140 °C) (3.65 g, 15.7 mmol) in ammonia (100 mL). An orange solid formed which looked similar to that obtained by method 1 except this solid was not obviously crystalline. The reaction mixture was refluxed at -33 °C for 0.5 h and then worked up as before to yield 1.96 g (85% yield) of 4 which had an infrared spectrum identical with that of the analytical sample.

Caution! One sample of 4 prepared by method 2 was found to violently explode in the drybox on gentle scratching with a metal spatula. We suspect that slightly soluble CsClO_4 was not removed completely by careful washing. Metatheses of $\text{Na}_3\text{V}(\text{CO})_5$ with perchlorate salts are to be avoided.

Tetraphenylarsonium Amminepentacarbonylvandate(1-), $[\text{Ph}_4\text{As}][\text{V}(\text{CO})_5\text{NH}_3]$ (5). A liquid ammonia solution of 1 was prepared as described in the synthesis of 2 from $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ (2.00 g, 3.92 mmol) and Na metal (0.28 g, 12.2 mmol). After the reflux period, the solution was cooled to -78 °C and solid NH_4Cl (0.63 g, 11.6 mmol) was

Table I. Infrared Active Carbonyl Stretching Frequencies and ¹H NMR Data for E₃V(CO)₅ and Derivatives

compd	medium	ν_{CO} , cm ⁻¹	¹ H NMR (acetone-d ₆) ^a δ (ppm)
K ₃ V(CO) ₅	Nujol	1812 (m), ca. 1600 (b)	
Rb ₃ V(CO) ₅	Fluorolube	1807 (m), 1630 (vs, b), 1580 (vs, b) ^b	
Cs ₃ V(CO) ₅	Fluorolube	1800 (m), 1622 (vs, b), 1562 (vs, b) ^b	
[Ph ₄ As][V(CO) ₅ NH ₃]	Nujol	1958 (m), 1779 (vs), 1747 (vs) ^c	<i>d</i>
[Ph ₄ P][V(CO) ₅ PPh ₃]	THF	1967 (m), 1860 (m), 1824 (vs)	
[Et ₄ N] ₂ [(Ph ₃ Sn)V(CO) ₅]	Nujol	1923 (m), 1819 (m), 1771 (s), 1727 (s)	7.28, 7.60 (m, 15 H, phenyl)
	CH ₃ CN	1927 (m), 1783 s, 1750 (sh)	
[Et ₄ N] ₂ [(Me ₃ Sn)V(CO) ₅]	Nujol	1908 (m), 1745 (s, b)	0.03 (b s, 9 H, Sn-CH ₃)
[Et ₄ N][(Ph ₃ Sn) ₂ V(CO) ₅]	THF	1983 (m), 1878 (s, b)	7.17, 7.58 (m, 30 H, phenyl)
[Et ₄ N][[(C ₆ H ₁₁) ₃ Sn] ₂ V(CO) ₅]	THF	1959 (m), 1864 (s, b)	1.78 (m, 33 H, cyclohex)
[Et ₄ N][(Ph ₃ Pb) ₂ V(CO) ₅]	THF	1988 (m), 1890 (s, b)	7.41, 7.71 (m, 30 H, phenyl)

^a Tetraethylammonium cations in the various compounds have very similar ¹H NMR spectra δ 1.34 (t of t, 12 H, -CH₃), 3.46 (q, 8 H, -CH₂). ^b The positions of these broad bands are ± 5 cm⁻¹. Often Mulls of these salts do not show any bifurcation of the broad band. ^c Mull spectra of less crystalline samples show a very poorly resolved doublet centered at ca 1760 cm⁻¹. ^d Since V(CO)₅NH₃⁻ decomposes rapidly in solvents under ambient conditions, no ¹H NMR spectra were obtained. At low temperature [Ph₄As][V(CO)₅NH₃] is poorly soluble in all solvents.

added all at once to the stirred solution. Within seconds after the addition, the solution turned from the deep red color characteristic of Na₃V(CO)₅ to an orange hue which rapidly changed to deep magenta with simultaneous evolution of gas. After the solution was stirred for 0.5 h at reflux (-33 °C), it was again cooled to -78 °C. Upon rapid addition of a solution of Ph₄AsCl (need not be anhydrous, 2.61 g, 5.98 mmol) in ethanol (40 mL), a deep red crystalline solid immediately formed. The slurry was refluxed for 0.5 h to ensure complete metathesis, cooled to -78 °C, and filtered by using a low-temperature coarse porosity frit (Figure 1). A very pale yellow filtrate was rejected. The filtered solid was triturated with cold (0 °C) 6 N aqueous ammonia (3 × 20 mL) to remove NaCl and then cold (0 °C) absolute ethanol (3 × 20 mL) (in which it is nearly insoluble) and then dried in vacuo at room temperature for 12 h.

A nearly quantitative yield (2.20 g, 95%) of analytically pure crystalline magenta **5** was thereby obtained. Anal. Calcd for C₂₉H₂₃NAsO₅V: C, 58.90; H, 3.92; N, 2.37. Found: C, 58.93; H, 4.04; N, 2.57. This substance is quite thermally stable (decomposes slowly above 110 °C without melting) and may be stored indefinitely under a nitrogen atmosphere at room temperature. Surprisingly, it is fairly resistant to air oxidation and may be handled in air for several minutes without observable deterioration. Compound **5** is insoluble in and does not react with water, diethyl ether, arenes, or alkanes. Solvents which dissolve **5** cause rapid and complete decomposition at room temperature (see Discussion).

Tetraphenylphosphonium (Triphenylphosphine)pentacarbonylvanadate(1-), [Ph₄P][V(CO)₅PPh₃] (**6**). Addition of dry solid [Ph₄P]Br (2.47 g, 5.98 mmol) to a cold (-78 °C) unfiltered liquid ammonia solution (40 mL) of Na₃V(CO)₅, prepared as in synthesis of **5** from [Na(diglyme)₂][V(CO)₆] (1.00 g, 1.96 mmol) and Na metal (0.14 g, 6.1 mmol), caused the precipitation of a dark red thermally unstable solid which we believe is [Ph₄P][V(CO)₅]. After the ammonia evaporated, the residue was dissolved in THF (60 mL), filtered, and reduced to half of the volume. Addition of diethyl ether (200 mL) to the dark red solution provided a bright orange precipitate. Recrystallization of this material from acetone (15 mL)-ether (50 mL) provided 0.72 g (46%) of analytically pure **6**. Anal. Calcd for C₄₇H₅₅P₂O₅V: C, 71.21; H, 4.45. Found: C, 70.76; H, 4.54. This substance decomposes without melting above 150 °C. Higher yield routes are available for the preparation of salts containing V(CO)₅Ph₃P^{-18,44}

Bis(tetraethylammonium) (Triphenylstannyl)pentacarbonylvanadate(2-), [Et₄N]₂[Ph₃SnV(CO)₅] (**7**). A cold (-60 °C) solution of Ph₃SnCl (3.85 g, 10.0 mmol) in THF (50 mL) was added dropwise over a period of 0.5 h to a liquid ammonia solution (120 mL at -60 °C) of **1** (from [Na(diglyme)₂][V(CO)₆] (5.10 g, 10.0 mmol) and Na metal (0.70 g, 30.4 mmol)). Solid excess [Et₄N]Br (12.4 g, 59.0 mmol) was then added directly to the orange solution which caused the precipitation of a flocculent yellow solid. After the ammonia was evaporated, the crude dry product was extracted with hot acetone (150 mL) in a Soxhlet extraction apparatus. The resulting yellow crystalline product was washed with THF until washings were colorless (to remove [Et₄N][V(CO)₆] and [Et₄N][(Ph₃Sn)₂V(CO)₅]) and then carefully triturated with ethanol (3 × 20 mL) to remove [Et₄N]Br. It was dried in vacuo to provide 5.54 g (69%) of analytically pure yellow crystalline **7**. Anal. Calcd for C₃₉H₅₅N₂O₅SnV: C, 58.43; H, 6.87; N, 3.50; Sn, 14.86. Found: C,

58.78; H, 6.86; N, 3.75; Sn, 14.85. Compound **7** is quite thermally stable and melts with decomposition at 224–225 °C. Although solutions of **7** are exceedingly air sensitive, crystalline **7** may be handled in air for at least 30 min before observable deterioration occurs.

Bis(tetraethylammonium) (Trimethylstannyl)pentacarbonylvanadate(2-), [Et₄N]₂[Me₃SnV(CO)₅] (**8**). A cold (-78 °C) slurry of Me₃SnCl (0.53 g, 1.36 mmol) in THF (20 mL) was added rapidly to a cold (-78 °C) slurry of **1** (from [Na(diglyme)₂][V(CO)₆] (1.00 g, 1.96 mmol) and Na metal (0.19 g, 8.26 mmol)). The blue solution of Na₃V(CO)₅ (resulting from an excess of Na metal) almost immediately changed to a deep orange after addition of Me₃SnCl. Solid [Et₄N]Br (1.00 g, 4.76 mmol) was added to the liquid ammonia-THF solution, and solvent was removed. Dissolution of the resulting crude material in excess acetone, followed by filtration (medium porosity frit) and slow concentration, provided a crystalline yellow solid (0.28 g, 23%) which satisfactorily analyzed as **8**. Anal. Calcd for C₂₄H₄₉O₅N₂SnV: C, 46.84; H, 7.96; N, 4.55. Found: C, 47.03; H, 7.24; N, 4.55. Compound **8** was made at an early stage of this research, and no attempt was made to optimize the yield.

Tetraethylammonium Bis(triphenylstannyl)pentacarbonylvanadate(1-), [Et₄N][(Ph₃Sn)₂V(CO)₅] (**9**). A cold (-78 °C) slurry of Ph₃SnCl (5.30 g, 13.7 mmol) in THF (50 mL) was added rapidly to Na₃V(CO)₅ (2.55 mmol, from Na reduction of [Na(diglyme)₂][V(CO)₆] as in preparation **8** in liquid ammonia (75 mL). An immediate precipitation of orange product was noted. Solvent was removed in vacuo, and the resulting deep yellow brown gum was dissolved in EtOH (60 mL), filtered, and treated with [Et₄N]Br (2.9 g, 13.8 mmol). Concentration of the ethanolic solution to 30 mL and addition of 100 mL of water caused an immediate precipitation of product. This was dried, washed with diethyl ether (8 × 20 mL), dissolved in 40 mL of 50:50 (v/v) acetone-ethanol. Concentration of the solution to about 20 mL resulted in the formation of 1.44 g (55% yield) of crystalline yellow **9**. Anal. Calcd for C₄₈H₅₀N₂O₅Sn₂V: C, 57.93; H, 4.94; N, 1.37; Sn, 23.62. Found: C, 57.88; H, 4.78; N, 1.18; Sn, 23.15. **9** is air stable as a solid for several hours at room temperature and quite thermally stable (slowly darkens above 140 °C; melts with decomposition at 196–198 °C). Solutions slowly decompose in air.

Tetraethylammonium Bis(tricyclohexylstannyl)pentacarbonylvanadate(1-), [Et₄N][(C₆H₁₁)₃Sn]₂V(CO)₅ (**10**). A cold (-78 °C) solution of (C₆H₁₁)₃SnBr (0.70 g, 1.6 mmol) in THF (40 mL) was added rapidly to a cold (-78 °C) solution of **1** (from the reduction of [Na(diglyme)₂][V(CO)₆] (0.40 g, 0.78 mmol) by Na metal (0.054 g, 2.3 mmol)) in liquid ammonia (50 mL). After evaporation of the ammonia, the crude sodium salt was dissolved in ethanol (60 mL), filtered, and treated with [Et₄N]Br (0.75 g in 170 mL of H₂O). The precipitated product was dried, washed with diethyl ether, and recrystallized thrice from THF-heptane to yield analytically pure **10** (0.42 g, 44% yield). Anal. Calcd for C₄₉H₈₆O₅N₂Sn₂V: C, 55.63; H, 8.14; N, 1.32. Found: C, 56.52; H, 8.10; N, 0.90 (melting point 132–136 °C). This substance has very similar properties to those of **9**.

Tetraethylammonium Bis(triphenylplumbyl)pentacarbonylvanadate(1-), [Et₄N][(Ph₃Pb)₂V(CO)₅] (**11**). By the same procedure outlined for **9**, the reaction of Ph₃PbCl (2.00 g, 4.22 mmol) with a liquid ammonia solution of Na₃V(CO)₅ (1.96 mmol), followed by metathesis with excess [Et₄N]Br (2.00 g) in 80 mL of H₂O provided an orange flocculent precipitate. This was dissolved in THF (80 mL) and filtered (medium porosity frit). Concentration of the solution in vacuo to a small volume followed by dropwise treatment with heptane provided analytically pure dark orange crystalline **11** in good yield (1.72 g, 73%). Anal. Calcd for C₄₉H₅₀N₂O₅Pb₂V: C, 49.11; H, 4.21; N, 1.17; Pb, 34.58. Found: C,

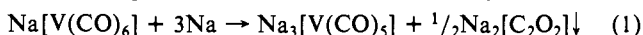
(18) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113. Ellis, J. E.; Faltynek, R. A.; Rochfort, G. A.; Stevens, R. E.; Zank, G. A. *Inorg. Chem.* **1980**, *19*, 1082.

48.71; H, 4.19; N, 1.18; Pb, 34.27. Compound **11** is fairly light sensitive unlike **9** or **10** and is less thermally stable (slow discoloration commences above 50 °C, rapid decomposition without melting above 125 °C).

Results and Discussion

It was previously reported that the reaction of hexacarbonylvanadate(1-) with sodium metal in liquid ammonia yielded a thermally unstable, pyrophoric, deep red substance **1** which had reactivity patterns consistent with those expected for $V(CO)_5^{3-}$.¹⁴ However, at that time we were unable to exclude the possibility that **1** was $HV(CO)_5^{2-}$, $[V(CO)_5]_2^{4-}$, or possibly paramagnetic $V(CO)_5^{2-}$, all of which could react with electrophiles to provide derivatives of $V(CO)_5^{3-}$. For some time the $HV(CO)_5^{2-}$ formulation was favored since the sodium salt was fairly soluble in liquid ammonia like the isoelectronic $Na_2Cr(CO)_5$,^{19,22} but unlike any of the carbonyl trianion salts previously isolated, including $Na_3Mn(CO)_4$,¹² $Na_3Co(CO)_3$,¹³ and $Na_4Cr(CO)_4$.¹ Also the fact that **1** is thermally unstable at room temperature was troubling since none of the other "super-reduced" species exhibited this characteristic. To resolve this issue, it was important to isolate and characterize **1** as stabilized derivatives.

Synthesis and Properties of $Na_3V(CO)_5$ (1**).** Treatment of $[Na(diglyme)_2][V(CO)_6]$ or unsolvated $Na[V(CO)_6]$ ²⁰ with 3 equiv of sodium metal provides the same fairly soluble product,²¹ which may be converted to other very slightly soluble salts of $V(CO)_5^{3-}$ (vide infra). The reaction is believed to proceed according to eq 1. Since the disodium salt of acetylenediolate^{16,23}



is insoluble, low-temperature filtration of the initial reaction mixture provides very pure **1** in liquid ammonia. Essentially, the same procedure has been used to prepare pure $Na_2Cr(CO)_5$ from $Cr(CO)_6$ in liquid ammonia.²² The insoluble product was shown to contain mostly the same material previously identified as " $Na_2C_2O_2$ ".²³⁻²⁵

When liquid ammonia is removed from a filtered solution of **1**, deep red crystals of presumably $[Na(NH_3)_x]_3[V(CO)_5]$ are obtained at -20 to -30 °C. These begin to darken at higher temperatures. Rapid decomposition occurs at about -5 to 0 °C to provide a pyrophoric black noncrystalline solid. The Nujol mull infrared spectrum of this solid shows two very broad bands in the carbonyl stretching frequency region (1840 m, 1720 (s) cm^{-1}). The first band is due to $V(CO)_6^-$ while the second band corresponds to a presently uncharacterized material. Significantly, no IR bands attributable to $NaNH_2$ (or " $Na_2C_2O_2$ ") were observed in concentrated Nujol mulls of this black solid,²⁴ which indicates that deprotonation of ammonia by $V(CO)_5^{3-}$ is not an important decomposition pathway. There is no precedent for the thermal decomposition of mononuclear carbonyl anions under such mild conditions.²⁶ Such unusual behavior suggests that $V(CO)_5^{3-}$ may

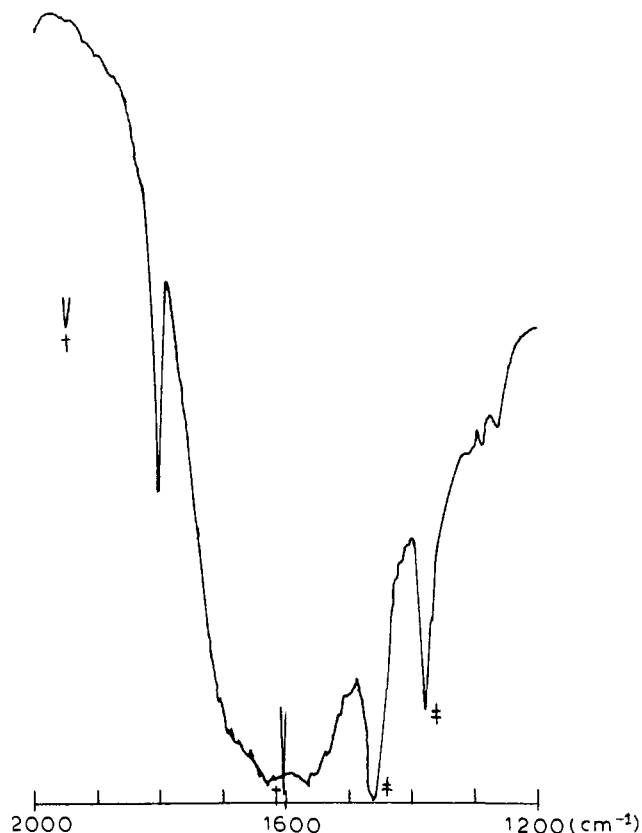


Figure 2. Nujol mull spectrum of $Cs_3V(CO)_5$ in the carbonyl stretching frequency region. Position of bands (ν_{CO}): 1800 (m), 1626 (vs), 1563 (vs) cm^{-1} . The daggers show polystyrene standard bands at 1944 and 1602 cm^{-1} and the double daggers show bands due to Nujol.

not be isostructural with its isoelectronic and trigonal-bipyramidal neighbors $Mn(CO)_5^-$ and $Fe(CO)_5$. Efforts are underway to resolve this issue. Solution or mull infrared spectra of undecomposed **1** have not been obtained. Interestingly, attempts to produce **1** from the reduction of $NaV(CO)_6$ by Na in hexamethylphosphoramide or naphthalene-tetrahydrofuran at room temperature lead only to decomposition. These results also indicate that **1** is unstable in solution at room temperature, unlike $Na_3M(CO)_4$ ¹² ($M = Mn, Re$) or $Na_3M(CO)_3$ ($M = Rh, Ir$).¹³

Isolation and Characterization of $M_3V(CO)_5$ ($M = K, Rb, Cs$). When 3 equiv of potassium, rubidium, or cesium metal in liquid ammonia react with $[Na(diglyme)_2][V(CO)_6]$ or $M[V(CO)_6]$ ($M = K, Rb, Cs$), there result initially orange to deep red solids which cannot be separated from the insoluble byproduct $M_2C_2O_2$.²³ Identical products, free of $M_2C_2O_2$, are obtained by treating filtered solutions of **1** with excess soluble alkali-metal salts.²⁷ This method is similar to that used by Fischer and Vigoureux to isolate $M_2[C_5H_5V(CO)_3]$ ²⁸ ($M = K, Rb, Cs$) except the use of the low-temperature jacketed filtration apparatus depicted in Figure 1 makes the process much more facile and avoids the unnecessarily complex apparatus shown in the aforementioned article. We use this filtration apparatus routinely for all low-temperature filtrations and find it to be superior to commercially available units. An important feature of this apparatus is that the coolant extends down into the lower ground-glass joint.²⁹

Initially orange to red crystalline solids, probably of the composition $[M(NH_3)_x]_3[V(CO)_5]$, precipitate from solution. Removal of ammonia from these materials at 0-23 °C causes the bright colors of the solids to darken. The resulting orange to brown solids have elemental compositions corresponding to the unsolvated

(19) However, ¹H NMR spectra of **1** did not reveal the presence of metal hydrides.

(20) Hieber, W.; Peterhaus, J.; Winter, E. *Chem. Ber.* **1961**, *94*, 2572.

(21) Approximately 2.0 g of **1** dissolves in 100 mL of ammonia at -78 °C.

(22) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79. Lindner, E.; Behrens, H.; Uhlig, D. *Z. Naturforsch.* **1973**, *18B*, 276.

(23) Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 2111.

(24) From the reduction of 6.20 g of $[Na(diglyme)_2][V(CO)_6]$ by sodium metal, 0.86 g of a gray, pyrophoric solid was recovered (0.62 g represents a quantitative yield of " $Na_2C_2O_2$ "). The Nujol mull infrared spectrum of this material, which inflamed in Fluorolube, was nearly superimposable on that of " $Na_2C_2O_2$ " made directly from free carbon monoxide (prominent is a broad band at ca. 2158 cm^{-1} attributable to ν_{C-C}). Weak bands due to $NaV(CO)_6$ and $NaNH_2$ were also present in the impure solid. Nujol mull spectra of $NaNH_2$ show an increase characteristic doublet at 3204 and 3256 cm^{-1} .

(25) Interestingly, " $Na_2C_2O_2$ " prepared by bubbling CO gas through a solution of sodium in liquid ammonia forms a gelatinous white solid which on removal of ammonia turns to a dark gray-black material (Ellis, J. E., unpublished observation, and ref 23). By contrast, the much more thermally stable $K_2C_2O_2$, which has been proved by crystallography to contain $C_2O_2^{2-}$ (Wells, E.; Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 1121), remains white on warming to room temperature.

(26) Certain salts of $M(CO)_4^-$ ($M = Co, Rh$) are reported to decompose at room temperature, but these materials are thermally stable in solution at this temperature, unlike **1**. See: Winzenburg, M. L. Ph.D. Thesis, University of Minnesota, 1979.

(27) Although alkali-metal perchlorates do not oxidize $V(CO)_5^{3-}$ in liquid ammonia, for safety reasons they should not be used in these cation-exchange reactions (see Experimental Section).

(28) Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 2205.

(29) A more detailed drawing of the apparatus is available on request.

compounds $M_3V(CO)_5$ and are obtained in high yields (85–94%) based on $[Na(diglyme)_2][V(CO)_6]$. These materials have the same chemical properties as solutions of **1** in liquid ammonia but since they are insoluble or very slightly soluble ($M = K$), they generally react more slowly. However, unlike **1**, it is possible to carry out reactions of the isolated $M_3V(CO)_5$ in other solvents which often result in much improved yields when the reactant electrophile or the product is ammonia sensitive (e.g., see the $(Ph_3PAu)_3V(CO)_5$ synthesis in the subsequent paper in this series).³⁰

While the cesium and rubidium salts of $V(CO)_5^{3-}$ darken slightly after one week at room temperature under an inert atmosphere, the potassium salt decomposes more rapidly under these conditions, especially under vacuum. Within 48 h at atmospheric pressure, $K_3V(CO)_5$ changes from a crystalline red brown to a crystalline jet black substance. During this transformation the Nujol mull infrared spectrum changes from one nearly superimposable on that of $Cs_3V(CO)_5$ (Figure 2) to one in which the bands from 1820 to 1500 cm^{-1} are more broadened and poorly resolved; also the compound becomes much more shock sensitive and readily explodes on scratching. Clearly $K_3V(CO)_5$ is quite unstable with respect to decomposition at room temperature. We have not yet characterized the decomposition products but note that the sample submitted for analysis analyzed satisfactorily for $K_3V(CO)_5$ (see Experimental Section) and yet was at least partially decomposed since it was reported by the analyst to have a black color.³¹ This result suggests that insignificant formation of gaseous products occurred during slow decomposition at room temperature.³² However, a mass spectroscopic examination of possible volatiles formed during decomposition of $K_3V(CO)_5$ has not yet been done.

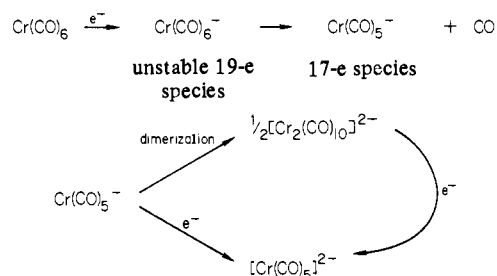
Nujol mull infrared spectra of solid $M_3V(CO)_5$ ($M = K, Rb, Cs$) are extremely similar. They show no absorptions from 4000 to 1820 cm^{-1} , other than those of Nujol, and possess sharp bands of medium intensity at about 1805 cm^{-1} and very broad bifurcated bands at ca. 1620 and 1570 cm^{-1} (Figure 2 for $M = Cs$). These band positions are consistent with those found for other carbonyl trianions^{11–13} but are much lower in energy than those found for carbonyl dianions such as $M_2Cr(CO)_5$ ($M = Na, Cs$).²² In view of probable extensive ion pairing between cation and carbonyl anion which would cause significant perturbation of anion geometry, we believe that it would be premature to conclude anything about anion geometry on the basis of only infrared data.³³

It is not surprising that the least soluble compounds containing $V(CO)_5^{3-}$, namely, $Cs_3V(CO)_5$ and $Rb_3V(CO)_5$ —which appear to be completely insoluble in liquid ammonia at $-33^\circ C$ —are also the most thermally stable. The potassium compound, $K_3V(CO)_5$, is slightly soluble in liquid ammonia and is substantially less thermally stable, while the moderately soluble sodium species $Na_3V(CO)_5$ decomposes rapidly below room temperature. Strong cation–anion interactions accompanied by a substantial crystalline lattice stabilization are likely to be essential for $V(CO)_5^{3-}$ to survive under ambient conditions. The lack of such interactions in the complex cation compounds of $V(CO)_5^{3-}$, to be discussed next, is probably at least partly responsible for their observed poor thermal stabilities.

Attempted Isolation of Other Salts of $V(CO)_5^{3-}$. All liquid ammonia soluble salts of $V(CO)_5^{3-}$ we have examined form thermally unstable solids. Lithium reductions of $[Na(diglyme)_2][V(CO)_6]$ or $LiV(CO)_6$ form a product which is less

soluble than **1**. Partial evaporation of the filtered liquid ammonia solution³⁴ provides beautiful deep red, very air-sensitive crystals which quickly decompose above $0^\circ C$. Complex cations such as tetrabutylammonium and sodium cryptate (2.2.2) complex³⁵ also form soluble and stable salts of $V(CO)_5^{3-}$ in liquid ammonia³⁶ but decompose on attempted isolation. Ammonia insoluble orange to red salts of $V(CO)_5^{3-}$ are formed from solutions of **1** and $[Ba(NH_3)_6][ClO_4]_2$ (Caution! vide supra): $[Me_4N]Br$, $[Ph_4P]Br$, and $[PPN]Cl$ (PPN^+ = bis(triphenylphosphin)iminium cation). But these all decompose on warming. In the case of the Ph_4P^+ and PPN^+ salts, solid-state reactions of $V(CO)_5^{3-}$ with the cations have been shown to yield Ph_4P^+ or PPN^+ salts of $Ph_3PV(CO)_5^-$. The tetraphenylphosphonium salt is reduced to biphenyl and triphenylphosphine in the process. A somewhat similar reaction of $C_5H_5Fe(CO)_2^-$ with $[Ph_4As]Cl$ has been reported previously.³⁷ The fate of the PPN cation in this reduction is unknown. By contrast, the highly nucleophilic $C_5H_5Fe(CO)_2^-$ does not react with PPN cation at room temperature.³⁷ Neither of these reactions represent useful routes to $V(CO)_5Ph_3P^-$ which is best made by other methods.^{18,44} The red orange tetramethylammonium salt, believed to be $[Me_4N]_3[V(CO)_5]^-$,³⁸ decomposes above $0^\circ C$ to yield an impure product which is still under investigation.³⁹ Reactions of tetraalkylammonium cations with strongly nucleophilic carbonyl anions have been reported previously.^{37,39,40} Attempts to metathesize anhydrous lanthanum salts (LaX_3 , $X = Cl, I$) with ammonia solutions of **1** were unsuccessful due to the slight solubility of these halides in liquid ammonia.

Reactions of $V(CO)_6^-$ with Less or More than Three Equivalents of Alkali Metal. It seems likely that the reduction of chromium hexacarbonyl proceeds according to



Thus, depending upon the number of equivalents of alkali metal used, $Cr(CO)_6$ can be reduced either to dimeric $Cr_2(CO)_{10}^{2-}$ or monomeric $Cr(CO)_5^{2-}$.²² Since $V(CO)_6^-$ is isoelectronic with $Cr(CO)_6$, it seems reasonable to propose that essentially the same reduction process occurs. For this reason, it was thought that by adding less than 3 equiv of alkali metal to $V(CO)_6^-$, it might be possible to prepare the intermediate reduction product $[V_2(CO)_{10}]^{4-}$. In practice, all such attempts failed and provided only mixtures of $V(CO)_6^-$ and $V(CO)_5^{3-}$, which do not react with each

(34) Caution! The filtered solid contains "Li₂C₂O₂" which is reported to be a treacherous explosive when dry (see ref 23).

(35) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49. It is possible that sodium ion exchange between cryptated sodium ion and $Na(NH_3)_x^+$ is very facile. In this case, the thermally unstable solid may not be $[Na(cryptate-2.2.2)]_3[V(CO)_5]$, particularly since $V(CO)_5^{3-}$ is likely to have a strong affinity for unsolvated Na^+ .

(36) The non-reactivity of $n-Bu_4N^+$ and $V(CO)_5^{3-}$ in liquid ammonia was shown by near quantitative conversion to $Cs_3V(CO)_5$.

(37) Ellis, J. E. *J. Organomet. Chem.* **1976**, *111*, 331.

(38) A suspension of red-orange $[Me_4N]_3[V(CO)_5]$ in liquid ammonia at $-33^\circ C$ was treated with 2 equiv of Ph_3SnCl which provided on workup a 60% yield of $[Me_4N]_2[(Ph_3Sn)_2V(CO)_5]$. This is about the same yield of $(Ph_3Sn)_2V(CO)_5^-$ as obtained from an identical reaction of **1** with Ph_3SnCl (vide infra).

(39) This incompletely characterized product may be $CH_3V(CO)_5^{2-}$ (or $HV(CO)_5^{2-}$) judging from the similarity of its Nujol mull infrared spectra (1920 (m), 1756 (vs, br), and 1690 (s) cm^{-1}) and that of $Ph_3SnV(CO)_5^{2-}$. HMPA solutions of $Na_2Cr(CO)_5$ and Me_4N^+ have been shown to slowly react to provide bonafide $MeCr(CO)_5^-$ (Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357. Hagen, G. P. PhD Thesis, University of Minnesota, **1978**, p 59).

(40) Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1097.

(30) Ellis, J. E., following paper in this issue.

(31) Poor yields (ca. 25% max.) of $(Ph_3Sn)_2V(CO)_5^-$ have been obtained from this black partially decomposed $K_3V(CO)_5$.

(32) It seems unlikely that the elemental composition of $K_3V(CO)_5$ would remain unchanged on decomposition if gaseous products formed. The observed greater instability of freshly prepared $K_3V(CO)_5$ under vacuum may be the result of slow evolution of small amounts of residual ammonia of solvation. Infrared spectra of thick mulls of freshly prepared $K_3V(CO)_5$ show no significant absorptions in the ν_{N-H} region, however.

(33) For example, major differences are observed in the solid-state mull infrared spectra of $Na_2Fe(CO)_4$ (1.5 dioxane), $K_2Fe(CO)_4$, and $[Na(cryptate)]_2[Fe(CO)_4]$. These differences have been shown from crystallographic determinations to be attributable to large anion distortion by ion pairing (Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434. Teller, R. G.; Finkel, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *Ibid.* **1977**, *99*, 1104).

other in refluxing liquid ammonia.⁴¹ These observations suggest that the presumed intermediate $V(CO)_5^{2-}$ (or $[V(CO)_5]_2^{4-}$) must either be reduced much more rapidly than $V(CO)_6^-$ or undergo rapid disproportionation in liquid ammonia (i.e., $2V(CO)_5^{2-} + NH_3 \rightarrow V(CO)_5NH_3^- + V(CO)_5^{3-}$). Likewise, attempts to prepare $[V_2(CO)_{10}]^{4-}$ from the oxidation of $Na_3V(CO)_5$ by dropwise addition of 1 equiv of $Ag[ClO_4]$ in liquid ammonia provided only $V(CO)_5NH_3^-$ (vide infra) and $V(CO)_5^{3-}$, which do not react with each other in refluxing ammonia. In this case, the intermediate oxidation product, $V(CO)_5^{2-}$ and/or $[V_2(CO)_{10}]^{4-}$, either undergoes disproportionation in liquid ammonia as mentioned before or is oxidized by silver cation much more rapidly than $V(CO)_5^{3-}$. Other possible routes to $[V_2(CO)_{10}]^{4-}$ are under examination.

It was also of interest to determine whether $Na_3V(CO)_5$ is susceptible to further reduction in liquid ammonia. However, **1** appears to be rather inert to excess sodium in liquid ammonia,⁴² like the isoelectronic species $Na_2Cr(CO)_5$.¹

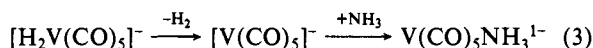
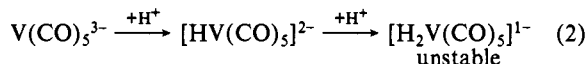
Protonation of $Na_3V(CO)_5$ (1**) in Liquid Ammonia.** Treatment of solutions of **1** with water, alcohols, ammonium salts, certain oxidizing agents (including $Ag[ClO_4]$ (vide supra) and limited amounts of air) provides $V(CO)_5NH_3^{1-}$. Excellent yields of analytically pure $[Ph_4As][V(CO)_5NH_3]$ (85–95%) are most easily obtained by reacting unfiltered liquid ammonia solutions of **1** (contaminated with “ $Na_2C_2O_2$ ”, $NaNH_2$, and other insolubles) with 3 equiv of ammonium chloride followed by metathesis with an ethanolic solution of tetraphenylarsonium chloride. This anion has been isolated previously as the tetraphenylphosphonium salt in lower yield (54%) by a 24-h photolysis of $V(CO)_6^-$ in liquid ammonia at $-60^\circ C$ followed by a rather difficult purification step.⁴³ The chemistry of $V(CO)_5NH_3^{1-}$ will be reported elsewhere. It has proven to be a valuable reagent for high yield nonphotolytic syntheses of new $V(CO)_5L^-$ species (L = phosphines, arsines, isocyanides, etc.).⁴⁴

An interesting property of $V(CO)_5NH_3^-$ is that it immediately decomposes when dissolved in various solvents at room temperature to provide $V(CO)_6^-$ (ca. 70% yield) and other uncharacterized noncarbonyl-containing vanadium species. Also, so far the anion has been shown to be stabilized in the solid state at room temperature by only two cations (Ph_4E^+ ($E = As, P$)). Thus, isolated salts of $V(CO)_5NH_3^-$ are thermally unstable at room temperature (with respect to loss of ammonia) for the following cations: Li^+ , Na^+ , K^+ , Cs^+ , Me_4N^+ , $benzylPh_3P^+$, and even $(Ph_3P)_2N^+$. The PPN salt is a deep purple solid which slowly decomposes at room temperature to provide a black solid containing $V(CO)_6^-$ as the only carbonyl-containing species.

Filtered solutions of **1** react with 2 equiv of ammonium chloride to give almost quantitative yields of $V(CO)_5NH_3^{1-}$.⁴⁵ When this reaction is performed at $-78^\circ C$, a transient red orange intermediate ($H_2V(CO)_5^-$?) forms which rapidly evolves a gas

(probably hydrogen) to yield magenta $V(CO)_5NH_3^-$. Essentially the same process has been postulated to occur when isoelectronic $Cr(CO)_5^{2-}$ is treated with aqueous ammonia. In this case, $H_2Cr(CO)_5$ has been assumed to be the intermediate, which then reductively eliminates molecular hydrogen to provide $Cr(CO)_5NH_3$ as the final product.⁴⁶

When filtered solutions of **1** are treated with 1 equiv of ammonium chloride or excess acetonitrile, a bright yellow tetramethylammonium salt of an incompletely characterized vanadium carbonyl anion can be isolated after metathesis. It has a Nujol mull spectrum ($\nu_{CO} = 1924$ (w), 1754 (vs, b), 1694 (s, br)) similar to that of $[Et_4N]_2[Ph_3SnV(CO)_5]$ and reacts with one more equivalent of ammonium chloride in ammonia to yield only $V(CO)_5NH_3^-$. On this basis we believe the bright yellow solid contains $HV(CO)_5^{2-}$, which is isoelectronic with the recently characterized $HCr(CO)_5^{1-}$.⁴⁷ Work is continuing on the characterization of this key species. In summary, it is likely that the conversion of $Na_3V(CO)_5$ to $V(CO)_5NH_3^-$ occurs by the sequence shown in eq 2 and 3.



Synthesis of $(R_3Sn)V(CO)_5^{2-}$ and $(R_3E)_2V(CO)_5^-$ ($R = \text{alkyl, aryl, } E = Sn, Pb$) from **1.** Treatment of liquid ammonia solutions of **1** with 1 equiv of R_3EX ($R = \text{alkyl, aryl}$; $E = \text{main group 4 elements}$; $X = \text{halide}$) provides isolated and characterized species of the type $(R_3E)V(CO)_5^{2-}$ only for $E = Sn$, presently. Reasonably high yields (60–80%) of $[Et_4N]_2[Ph_3SnV(CO)_5]$ are obtained by this route. Much lower yields (ca. 20%) of $[Et_4N]_2[Me_3SnV(CO)_5]$ have been observed, but no attempts were made to optimize the yield in this reaction. Attempts to make corresponding $Ph_3PbV(CO)_5^{2-}$ by this method failed although it was subsequently prepared by another method not directly involving $V(CO)_5^{3-}$.⁴⁸

These compounds are the first reported organotin derivatives containing a transition metal in a formally negative oxidation state.⁴⁹ They are quite oxygen sensitive in solution and very reactive with a number of electrophiles, unlike the less highly reduced $R_3SnCr(CO)_5^-$ species.¹⁸ A detailed report on some of their chemical reactions will be published elsewhere.⁴⁸ Infrared spectra in the ν_{CO} region and 1H NMR spectra (Table I) of these species are entirely consistent with those expected for dianions of C_{4v} local symmetry. These anions are isoelectronic and presumably isostructural with known $R_3SnCr(CO)_5^-$ and $R_3SnMn(CO)_5^{2-}$.

Treatment of $Ph_3SnV(CO)_5^{2-}$ with an additional equivalent of Ph_3SnCl or direct reaction of **1** with 2 equiv of Ph_3SnCl provides a 50–60% yield of seven-coordinate $(Ph_3Sn)_2V(CO)_5^-$. A recently completed crystal structure determination of $[Et_4N][Ph_3Sn]_2V(CO)_5$ shows the anion to contain two Sn–V bonds (mean bond length = 2.771 Å) with a Sn–V–Sn angle of $137.9(1)^\circ$. The anion structure is approximately a monocapped octahedron.⁴⁸ Solution infrared spectra of $[Et_4N][Ph_3Sn]_2V(CO)_5$ in solvents such as THF or HMPA, in which ion pairing is likely to be unimportant (Table I), are similar to those of mull spectra of the crystalline solid and are not consistent with a molecule of D_{5h} symmetry for which only one infrared active ν_{CO} is expected. It is plausible that a pentagonal-bipyramidal structure with the bulky triphenyltin groups trans to one another may be unfavorable due to the inability of the vanadium dz^2 orbital to interact with the stronger π -acceptor carbonyl groups. In structures of lower symmetry all vanadium d orbitals have the possibility of participating in back bonding to some extent.

(41) For example, treatment of $[Na(\text{diglyme})_2][V(CO)_6]$ (2.00 g, 3.92 mmol) with Na metal (0.18 g, 8.0 mmol) in 125 mL of ammonia provided, after a 1 h reflux at $-33^\circ C$ and filtration into an ammonia solution of cesium iodide (3.06 g, 11.8 mmol), 1.27 g (55% yield) of bonafide $Cs_3V(CO)_5$. From the filtrate there was isolated 0.444 g (32% yield) of $[Et_4N][V(CO)_6]$, identical with an analytical sample.^{18b}

(42) Treatment of $[Na(\text{diglyme})_2][V(CO)_6]$ (2.00 g, 3.92 mmol) with excess Na metal (0.45 g, 19.6 mmol) in 125 mL of liquid ammonia provided a deep blue solution which changed to the deep red color characteristic of $Na_3V(CO)_5$ after a 45-min reflux period. Standard workup of the reaction mixture provided 1.76 g (76% yield) of bonafide $Cs_3V(CO)_5$. A black solid (0.58 g) filtered off before conversion of the product to the cesium salt was shown by its infrared spectrum to contain substantial amounts of $NaNH_2$ (from the reaction of excess Na with ammonia) and “ $Na_2C_2O_2$ ” (see ref 24).

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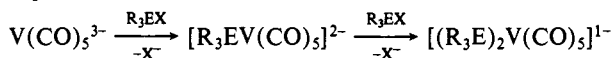
(45) For example, treatment of $[Na(\text{diglyme})_2][V(CO)_6]$ (2.0 g, 3.92 mmol) with Na metal (0.28 g, 12.2 mmol) in 125 mL provided, after a 1 h reflux at $-33^\circ C$ and filtration at $-78^\circ C$ into a flask containing a solution of ammonium chloride (0.420 g, 7.85 mmol) in 25 mL of liquid ammonia at $-78^\circ C$, first a red orange solution which within minutes changed to deep magenta $V(CO)_5NH_3^-$ with gas evolution. Addition of $[Ph_4As]Cl$ (1.70 g, 4.06 mmol) followed by the usual workup provided 2.1 g (91% yield) of microcrystalline $[Ph_4As][V(CO)_5NH_3]$.

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Related $(R_3E)_2V(CO)_5^-$, where $R_3E = (C_6H_{11})_3Sn$ and Ph_3Pb , are similarly prepared in moderate (40–70%) yields by treatment of **1** with 2 equiv of the corresponding R_3EX . Although analogous $R_3EV(CO)_5^{2-}$ have not been isolated from the reaction of 1 equiv of R_3EX with **1**, it is very likely that these are intermediates in the process



Infrared spectra of these bis adducts are very similar to that of $(Ph_3Sn)_2V(CO)_5^-$ which strongly suggests that they also contain seven-coordinate vanadium. These materials are closely related

to previously reported neutral $(R_3P)(R_3Sn)V(CO)_5$ which were assumed but not proven to contain seven-coordinate vanadium. On the basis of our results there is no reason to doubt this assumption.¹⁸

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE-79-12159) for support of this research. Dr. Michael C. Palazzotto is also acknowledged for his preliminary studies on portions of this work. J.E.E. is grateful to Professor Helmut Behrens (Erlangen-Nürnberg), for his helpful comments and interest in this work.

Highly Reduced Organometallics. 5.¹ Synthesis, Properties, and the Molecular Structure of $(Ph_3PAu)_3V(CO)_5$, A Gold–Vanadium Cluster

John E. Ellis

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received February 23, 1981. Revised Manuscript Received June 1, 1981

Abstract: The unusual metal cluster tris((triphenylphosphine)gold)pentacarbonylvandium, $(Ph_3PAu)_3V(CO)_5$ (**1**), has been synthesized by treatment of sodium or cesium salts of the pentacarbonylvandate(3–) ion, $V(CO)_5^{3-}$, with chloro(triphenylphosphine)gold in liquid ammonia (10–15% yields) or in tetrahydrofuran (50–60% yields). An X-ray crystallographic structure determination of this substance shows that **1** is the first neutral derivative of the unknown tetrahedral cluster $(Ph_3PAu)_4$ as well as the only established mixed-metal cluster containing vanadium. In **1** eight-coordinate vanadium is bound to a novel tridentate tris(triphenylphosphine)trigold ligand containing gold–gold bonds. All four metal atoms form a slightly distorted tetrahedral cluster. The $V(CO)_5$ group in **1** is best described as being a pseudooctahedral fragment which is bound to a large trigold unit. Infrared spectra of **1** support this view as they resemble those of the octahedral anions $V(CO)_5L^-$, where $L = PR_3, CNR$, etc. Chemical reactivity studies demonstrate that **1** is a remarkably robust gold–vanadium carbonyl complex. Triphenylphosphine, soluble halide, and acetonitrile which normally cause facile heterolytic cleavage of gold–vanadium bonds at room temperature are found to have no effect on **1**. Crystal data: space group $P\bar{1}$, $a = 12.840$ (6) Å, $b = 19.088$ (6) Å, $c = 12.380$ (4) Å, $\alpha = 93.82$ (3)°, $\beta = 117.26$ (3)°, $\gamma = 92.02$ (3)°, $Z = 2$, $V = 2684$ (4) Å³, and $\rho(\text{calcd}) = 1.941$ g/cm³.

Mixed-metal clusters have attracted wide attention in recent years due to their possible use as homogeneous catalysts and precursors to well-defined bimetallic or multimetallic heterogeneous catalysts.² Although metal clusters containing only gold atoms are now very numerous and have been shown to adopt a variety of unusual geometries,³ only three compounds likely, but not confirmed, to contain mixed-metal clusters of gold and other transition metals have been previously reported. These are $Os_3(CO)_{10}(Ph_3PAu)X$ ($X = H$,⁴ halide⁵) and $Os_3(CO)_{10}S_2-(AuPPh_3)_2$.⁵ Except for an unusual ferrocene derivative, $[(\pi-C_5H_5)Fe(\pi-C_5H_4)Au_2(PPh_3)_2]^+$, which has been shown to contain an open Fe–Au–Au metal chain and a formally four-coordinate central gold atom,⁶ all other mixed gold–transition-metal compounds have been proposed to contain two-coordinate gold. These include AuX_2^- (where $X = CpMo(CO)_3, Mn(CO)_5, CpFe(CO)_2,$

$Co(CO)_4$),⁷ $(Ph_3PAu)_2M(CO)_4$ ($M = Fe$,⁸ Ru ,⁹ Os ¹⁰), and $(Ph_3PAu)_3M'(CO)_4$ ($M' = Mn, Re$).¹¹ In a preliminary report, we implied that $(Ph_3PAu)_3V(CO)_5$ also contained normal two-coordinate gold bound to an unprecedented eight-coordinate vanadium.¹² However, since alternative formulations involving lower coordination numbers for the vanadium (e.g., $(Ph_3PAu)_2V(CO)_4$ ($CO \rightarrow AuPPh_3$)) could not be ruled out and also because this substance was much less reactive and more thermally stable than previously prepared compounds containing gold–vanadium bonds, the molecular structure of $(Ph_3PAu)_3V(CO)_5$ was determined by single-crystal X-ray diffraction techniques. In this paper we present the results of this study and discuss in detail the synthesis and chemical and physical properties of this interesting molecule.

Experimental Section

For general procedures, solvent purification and the synthesis of $Na_3V(CO)_5$ and $Cs_3V(CO)_5$ refer to the previous paper in this series.¹ Chloro(triphenylphosphine)gold was prepared according to a published procedure.¹³

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