J. Am. Chem. Soc. **1983**, *105*, 2303–2307

dence for the formation of $W(CO)_4(NH_3)_2$ in this reaction was obtained.

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Registry No. 1, 67202-46-4; **2**, 67202-63-5; **3**, 67202-62-4; **4**, 84894-06-4; **5**, 23623-69-0; **6**, 84850-66-8; **7**, 51232-76-9; **8**, 84850-68-0; **9**, 84850-69-1; **10**, 84850-71-5; **11**, 84850-72-6; **12**, 84850-74-8; **13**, 84850-76-0; **14**, 84850-78-2; **15**, 84850-80-6; **16**, 84850-82-8; **17**, 84850-84-0; **18**, 84850-85-1; $[Et_4N]_2[W_2(OO)_{10}]$, 15616-71-4; $Li_2[H_2W(CO)_4]$, 84850-86-2; $(TMED)W(CO)_4$, 15024-58-5; $(TMED)Mo(CO)_4$, 14971-45-0; $(TMED)Cr(CO)_4$, 21136-10-7; NH_4Cl, 12125-02-9; CH_3CN, 75-05-8; CO, 630-08-0; K[*sec*-Bu_3BH], 54575-49-4.

Synthesis, Characterization, and Chemistry of Pentacarbonylnitrosylvanadium, $V(CO)_5NO$, a Remarkably Reactive Relative of Hexacarbonylchromium

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Abstract: Thermally unstable, deep red-violet, and remarkably reactive $V(CO)_5NO$ has been prepared in high yields by the reaction of equimolar amounts of $[Et_4N][V(CO)_6]$ and $[NO][BF_4]$ in methylene chloride at −40 °C. Also, $V(CO)_5NO$ has been isolated and characterized for the first time by mass spectra and derivative chemistry. This volatile material undergoes substitution reactions with a large variety of neutral and anionic bases at −30 to 0 °C to provide 42–95% yields of new products. These include $[V(CO)_4NO(Ph_2PCH_2)]_2$, $V(CO)_4(NO)(PMe_3)$, thermally unstable $V(CO)_4(NO)(NMe_3)$, $[Et_4N][V(CO)_4(NO)I]$, $[Ph_4As][(CO)_5MnV(CO)_4NO]$, which contains a Mn–V bond, and $[Et_4N][C_5H_5V(CO)_2NO]$. The last substance is the first example of a carbonylnitrosylcyclopentadienylmetalate ion and the final member of the isoelectronic series $C_5H_5V(NO)_{3-x}(CO)_x^{1-x}$ (x = 0–3) to be prepared. Attempts to synthesize $Ta(CO)_5NO$ and derivatives thereof are also described.

Although pentacarbonylnitrosylvanadium was mentioned in the literature over 20 years ago,[1] until very recently no other information on this mysterious material was available.[2] By comparison, the properties of the only other presently known neutral mononuclear carbonylnitrosylmetal species, $Mn(CO)(NO)_3$, $Mn(CO)_4NO$, $Fe(CO)_2(NO)_2$, and $Co(CO)_3NO$ have been well documented.[3] In view of the isoelectronic nature of $Cr(CO)_6$ and $V(CO)_5NO$ and the important status of the former species in the organometallic chemistry of chromium, it was felt that an unambiguous characterization of $V(CO)_5NO$ and an examination of its reactivity patterns could be of considerable importance in the development of organovanadium chemistry. In this paper are described our initial studies in this area. In addition, evidence for the synthesis of $Ta(CO)_5NO$ will be discussed.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of nitrogen further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred via stainless steel cannulas and syringes; otherwise reactions were generally performed by using standard Schlenck apparatus with a double manifold vacuum line. Reagent grade methylene chloride and acetonitrile were dried with CaH_2, freed of oxygen by nitrogen purge, and distilled immediately before use. Reagent grade tetrahydrofuran, diethyl ether, toluene, and hexane were distilled from alkali metal benzophenone ketyls before use. Deionized water and reagent grade acetone, heptane, and absolute ethanol were freed of oxygen by dispersing nitrogen through the solvents for 1–2 h before use.

The following reagents were purchased from commercial sources and freed of oxygen before use: bis(diphenylphosphino)ethane, nitrosonium tetrafluoroborate, tetraethylammonium bromide, trimethylphosphine, and triphenylphosphine. Tetraethylammonium hexacarbonylvanadate,[4] tetraphenylarsonium hexacarbonylvanadate,[5] tetraphenylarsonium pentacarbonylmanganate,[6] tetraphenylphosphonium hexacarbonyltantalate,[7] and (1,2-dimethoxyethane)sodium cyclopentadienide[8] were prepared by known procedures.

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 of the drybox. Nujol 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 a Varian FT-80 spectrometer. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by Galbraith Laboratories or H. Malissa and G. Reuter Analytische Laboratorien. Low- and high-resolution mass spectra were recorded at 70 eV on an AEI MS-30 spectrometer where the solid probe was cooled to −10 °C (to minimize thermal decomposition of the sample) and allowed to slowly warm to room temperature. UV–visible spectra were recorded on a Cary 17D spectrophotometer.

Pentacarbonylnitrosylvanadium, $V(CO)_5(NO)$ (1). Tetraethylammonium hexacarbonylvanadate (1.0 g, 2.9 mmol) was dissolved in 20 mL of CH_2Cl_2 and cooled to −50 °C. Solid $[NO][BF_4]$ (0.34 g, 2.9 mmol) was placed in another flask and cooled to −50 °C. The $[Et_4N][V(CO)_6]/CH_2Cl_2$ slurry was transferred into the flask containing $[NO][BF_4]$. An additional 20 mL of CH_2Cl_2 was used to transfer all of the $[Et_4N][V(CO)_6]$ into the reaction flask. The reaction mixture rapidly changed from a yellow slurry into a very dark purple solution with purple precipitate on the sides of the flask. The mixture was stirred for 1.5 h at −40 °C. The CH_2Cl_2 was removed in vacuo at −40 °C to leave a dry brown solid. The flask was warmed to −10 °C. Compound (**1**) was extracted with 20 mL of hexane at this temperature and transferred into a Schlenck tube. The solution was cooled to −78 °C and nearly all of

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(2) (a) Schiemann, J.; Weiss, E.; Näumann, F.; Rehder, D. *J. Organomet. Chem.* **1982**, *232*, 219. (b) DPPM = $Ph_2PCH_2PPh_2$; DPPE = $Ph_2P(CH_2)_2PPh_2$; DIARS = *o*-$C_6H_4(AsMe_2)_2$; DPPP = $Ph_2P(CH_2)_3PPh_2$; DPAE = $Ph_2As(CH_2)_2AsPh_2$; PAB = *o*-$C_6H_4(AsPh_2)(PPh_2)$.

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1 precipitated as red-violet crystals. The faint purple hexane supernatant was removed and the crystals dried in vacuo at −78 °C. The amount of **1** obtained in this synthesis was not determined as the crystals readily decompose above 10 °C, but up to 95% isolated yields of derivatives have been obtained from $V(CO)_5NO$ generated by this procedure.

Mass spectrum, *m/e* (rel intensity) 221 (M^+, 17.2), 193 ($M^+ - CO$, 23.3), 165 ($M^+ - 2CO$, 7.7), 137 ($M^+ - 3CO$, 17.5), 135 ($M^+ - 2CO - NO$, 17.5), 109 ($M^+ - 4CO$, 38.7), 107 ($M^+ - 3CO - NO$, 53.7), 51 (V^+, 100); mass spectrum (high resolution), *m/e* 220.9166 (220.9165 calcd for $C_5NO_6{}^{51}V$).

UV-Vis spectrum recorded in CH_2Cl_2: λ 550 nm ($\epsilon = 1200\ M^{-1}\ cm^{-1}$), λ 400 nm ($\epsilon = 335\ M^{-1}\ cm^{-1}$). Note: the extinction coefficients were calculated on the basis that the $V(CO)_5NO$ was quantitatively generated from the reaction of equimolar amounts of $[Et_4N][V(CO)_6]$ and $[NO][BF_4]$. Solution infrared spectra (see Table I) indicate that $V(CO)_5NO$ is the only carbonyl or nitrosyl containing product produced in this reaction.

Compound **1** will slowly evaporate in vacuo at −40 °C, but attempts to sublime it at higher temperatures resulted in extensive decomposition. Compound **1** readily dissolves in solvents such as CH_2Cl_2, arenes, and saturated hydrocarbons to give purple and thermally unstable solutions. In hexane, $V(CO)_5NO$ begins to decompose at around −2 °C and decomposes completely with gas evolution after several minutes at 10 °C. Methylene chloride solutions of $V(CO)_5NO$ are less thermally stable and begin to slowly decompose above −10 °C. Dry, crystalline $V(CO)_5NO$ may be stored for several weeks at −25 °C under nitrogen without significant decomposition. Solid $V(CO)_5NO$ and its solutions decompose thermally to form an insoluble black substance which contains no carbonyl or nitrosyl groups.

In the preparation of compounds **2**–**8**, the reactant ligand was added to a solution of **1** at −40 °C and the stirred mixture was allowed to slowly warm. Substitutions generally occurred rapidly around −5 to 0 °C. During these reactions the deep purple color of the $V(CO)_5NO$ changed to a clear red orange except when the reactant ligand was $C_5H_5^-$ (vide infra).

Tricarbonylnitrosylbis((diphenylphosphino)ethane)vanadium, $V(CO)_3(NO)(DPPE)$ (2). A solution of DPPE (2.28 g, 5.7 mmol) in 15 mL of CH_2Cl_2 at room temperature was transferred into a −40 °C solution of **1**, prepared from 1.0 g (2.9 mmol) of $[Et_4N][V(CO)_6]$ and 0.34 g (2.9 mmol) of $[NO][BF_4]$ in 40 mL of CH_2Cl_2 as indicated above. *Unless otherwise noted, all other reactions described herein were carried out with these quantities of reactants.* An orange solid remained after removal of CH_2Cl_2 at +5 °C. It was dissolved in 60 mL of THF, filtered, and treated with hexane to provide red crystalline $V(CO)_3(NO)DPPE$. The other product, $[V(CO)_4(NO)]_2DPPE$, was soluble in hexane. The solid was transferred to a frit, washed with ethanol (2 × 20 mL) and hexane (20 mL), and dried in vacuo. The yield of **2** was 0.39 g (24%). Clear red crystals of **2** are produced by slow evaporation of an acetonitrile solution.

Anal. Calcd for $C_{29}H_{24}O_4NP_2V$: C, 61.82; H, 4.29; N, 2.49. Found: C, 62.20; H, 4.43; N, 2.65.

Compound **2** is soluble in toluene, Et_2O, THF, acetone, CH_2Cl_2, and CH_3CN. It is insoluble in H_2O and alkanes and slightly soluble in EtOH. Solid **2** is air stable but solutions are slightly air sensitive. Compound **2** is stable at room temperature but decomposes above 130 °C. Compound **2** was recently reported by Rehder and co-workers[2] after this work was completed.

(μ-(Diphenylphosphino)ethane)bis(tetracarbonylnitrosylvanadium), $[V(CO)_4NO]_2DPPE$ (3). A solution of DPPE (0.63 g, 1.6 mmol) in 15 mL of CH_2Cl_2 was added to a cold solution of $V(CO)_5NO$, generated in situ as described above from $[Et_4N][V(CO)_6]$ (1.0 g, 2.9 mmol) and $[NO][BF_4]$ (0.34 g, 2.9 mmol) in 30 mL of CH_2Cl_2, at −30 °C. The CH_2Cl_2 was removed at 0 °C. Most of the brownish-orange solid was dissolved in 40 mL of cold (−40 °C) Et_2O and filtered. An additional 2 × 5 mL of ether at −40 °C was used to dissolve the remainder. The ether solution was evaporated in vacuo, and the residue was recrystallized from hexane to yield 0.47 g (84%) of **3** as an orange powder.

Anal. Calcd for $C_{34}H_{24}N_2O_{10}P_2V_2$: C, 52.06; H, 3.08; N, 3.57; P, 7.90. Found: C, 52.77; H, 3.56; N, 3.24; P, 8.23.

Compound **3** is soluble in alkanes, toluene, CH_2Cl_2, ethers, and acetonitrile. It decomposes slowly in ethers at room temperature to form $V(CO)_3(NO)DPPE$ and reacts quickly with acetonitrile to form a red product which may contain bridging nitrosyls. This acetonitrile product changes to $V(CO)_3(NO)DPPE$ when redissolved in THF. Compound **3** is insoluble in H_2O. It is moderately air sensitive as a solid or in solution. It is stable at room temperature but decomposes above 90 °C.

Tetracarbonylnitrosyl(triphenylphosphine)vanadium, $V(CO)_4(NO)(PPh_3)$ (4). A solution of PPh_3 (1.33 g, 5.08 mmol) at −40 °C was added to the solution of **1**, prepared as indicated for compound **2**. The CH_2Cl_2 was removed at 10 °C to leave a slightly sticky orange solid. The product was extracted with hexane (160 mL was required) and filtered. Removal of the hexane left orange crystals. Recrystallization from CH_2Cl_2/EtOH at −78 °C gave 0.65 g (50%) of bright orange microcrystalline **4**.

Compound **4** has a infrared spectrum identical with that of authentic $V(CO)_4(NO)(PPh_3)$ isolated by Werner from the reaction of $V(CO)_4PPh_3)_2$ with NO.[9] Compound **4** slowly decomposes in solution at room temperature but is fairly stable at temperatures below 0 °C. It is soluble in hexane, toluene, CH_2Cl_2, and THF. It is insoluble in EtOH. Crystalline **4** is stable at room temperature but decomposes quickly above 85 °C.

Tetracarbonylnitrosyl(trimethylphosphine)vanadium, $V(CO)_4(NO)(PMe_3)$ (5). Neat trimethylphosphine (0.6 mL, approximately 6.3 mmol) was added by syringe to a solution of **1** at −45 °C. Evaporation of the CH_2Cl_2 at 0–5 °C left an orange solid. The product was dissolved in toluene and filtered. Recrystallization from toluene/hexane at −78 °C formed orange plates of **5** in 79% yield (0.61 g): mass spectrum, *m/e* (rel intensity) 269 (M^+, 2.3), 241 ($M^+ - CO$, 2.8), 213 ($M^+ - 2CO$, 1.3), 198 ($M^+ - 2CO - CH_3$, 1.6), 185 ($M^+ - 3CO$, 2.8), 183 ($M^+ - 2CO - NO$, 1.5), 170 ($V(CO)(NO)PMe_2{}^+$, 1.0), 157 ($V(NO)PMe_3{}^+$, 3.4), 155 ($V(CO)_2PMe_3{}^+$, 4.1), 142 ($V(NO)PMe_2{}^+$, 8.9), 127 ($VPMe_3{}^+$, 10.7), 76 ($PMe_3{}^+$, 25.0), 61 ($PMe_2{}^+$, 40.6), 28 (CO^+, 100.0); UV-Vis (in CH_2Cl_2) $\lambda = 465$ nm ($\epsilon = 550\ M^{-1}\ cm^{-1}$), $\lambda = 355$ nm ($\epsilon = 252\ M^{-1}\ cm^{-1}$).

Anal. Calcd for $C_7H_9NO_5PV$: C, 31.25; H, 3.37; N, 5.21. Found: C, 31.43; H, 3.07; N, 5.24.

Compound **5** is soluble in toluene, THF, CH_2Cl_2, ether, and acetonitrile and moderately soluble in hexane and ethanol. It is insoluble in H_2O. Compound **5** is slightly air sensitive as a solid and in solution. It is stable at room temperature. Above 95 °C it decomposes rapidly and melts at 105 °C.

Tetracarbonylnitrosyl(trimethylamine)vanadium, $V(CO)_4(NO)(NMe_3)$ (6). Neat trimethylamine (0.4 mL, approximately 5.4 mmol) was added to a solution of **1** at −50 °C. As the reaction mixture warmed to 0 °C it began turning black. A CH_2Cl_2 solution infrared spectrum showed that $V(CO)_4(NO)(NMe_3)$ was present in about the same concentration as the substituted derivatives in the other reactions. Removal of CH_2Cl_2 at 0–5 °C left a black solid. When hexane was added, a yellow orange solution formed initially but became black after 15–20 min at room temperature. The solid was stable at 0 °C overnight but decomposed rapidly at room temperature. Formulation of the product as $V(CO)_4(NO)(NMe_3)$ was based on its infrared spectrum, which was very similar in band positions and intensities to the spectra of the other $V(CO)_4(NO)L$ derivatives.

Tetraethylammonium Iodotetracarbonylnitrosylvanadate(1−) $[Et_4N][V(CO)_4(NO)I]$ (7). Solid $[Et_4N]I$ (3.0 g, 11.7 mmol) was added to a solution of 5.7 mmol of **1** (from 2.0 g (5.7 mmol) of $[Et_4N][V(CO)_6]$ and 0.68 g (5.7 mmol) of $[NO][BF_4]$) at −40 °C. From −20 to −15 °C, the solution turned red-orange. It was cooled to −60 °C and filtered. The insoluble material was washed with CH_2Cl_2 until the washings were clear (approximately 150 mL of CH_2Cl_2 was required). The filtrate was kept cold (−60 °C) and much product precipitated. The filtrate was concentrated in vacuo to about 80 mL and additional orange-yellow solid precipitated. The filtrate was cooled to −78 °C and 100 mL of hexane was added to precipitate more product. The slurry was filtered and the yellow solid washed with 2 × 20 mL of hexane and dried. Recrystallization from cold (−40 °C) acetone and hexane gave 2.46 g (95%) of yellow-orange crystalline **7** which is stable in air for several hours at room temperature.

Anal. Calcd for $C_{12}H_{20}IO_5N_2V$: C, 32.02; H, 4.46; N, 6.22. Found: C, 31.95; H, 4.61; N, 6.15.

Two initial attempts to obtain satisfactory analyses were unsuccessful due to the thermal instabilities of the samples. However, the sample prepared above consisted of larger crystals which did not decompose significantly within a week at room temperature under a nitrogen atmosphere. It is stable indefinitely at 0 °C under an inert atmosphere. Solutions of compound **7** in CH_2Cl_2, acetone, and THF are thermally unstable and decompose rapidly at room temperature but are stable below −10 °C. Compound **7** decomposes rapidly above 80 °C.

Tetraphenylarsonium (Pentacarbonylmanganese)tetracarbonylnitrosylvanadate(1−), $[Ph_4As][(CO)_5MnV(CO)_4NO]$ (8). Compound **1** was prepared as described before from $[Ph_4As][V(CO)_6]$ (0.83 g, 1.4 mmol) and $[NO][BF_4]$ (0.17g 1.4 mmol) in 40 mL of CH_2Cl_2. A solution of $[Ph_4As][Mn(CO)_5]$ (0.86 g, 1.4 mmol) in 30 mL of CH_2Cl_2 at −40 °C was added to the −40 °C solution of **1**. The CH_2Cl_2 was removed at −5 to −4 °C to leave a crystalline orange-yellow solid. The crude solid was dissolved in 30 mL of cold (−30 to −40 °C) CH_2Cl_2 and filtered. An equal volume of heptane was added and the mixture cooled to −78 °C. Filtration separated creamy white crystals of $[Ph_4As][BF_4]$ (0.6 g). An additional 40 mL of heptane was added and an orange-yellow precipitate formed. The solid was transferred onto a frit, filtered, and washed with

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[9] Hieber, W.; Kummer, R. *Z. Naturforsch. B*: **1965**, *20B*, 271.

Table I. Infrared and ^1H NMR Spectra of $V(CO)_5NO$ and Derivatives

compound	IR medium	ν(NO)	ν(CO), cm^{-1}	chemical shift, δ
$V(CO)_5NO$ (**1**)	hexane	1695 m	2100 w, 2050 w, 1990 s	
$V(CO)_3(NO)DPPE$ (**2**)	toluene	1600 m	2000 m, 1920 s	8.03–7.34 (m, 20 H, C_6H_5), 2.46–1.72 (m, 4 H, CH_2)[a]
$[V(CO)_4NO]_2DPPE$ (**3**)	hexane	1660 m	1980 w, 1960 s	7.38–6.87 (m, 20 H, C_6H_5), 2.2 (t, 4 H, $J_{P-H} = 4.0$ Hz)[a]
$V(CO)_4(NO)(PPh_3)$ (**4**)	hexane	1660 m	1980 w, 1963 m	*c*
$V(CO)_4(NO)(PMe_3)$ (**5**)	hexane	1663 m	1960 s	1.5 (br t, PMe_3)[b]
$V(CO)_4(NO)(NMe_3)$ (**6**)	hexane	1650 m	1990 w, 1960 s	*c*
$[Et_4N][V(CO)_4(NO)I]$ (**7**)	Nujol	1597 m	1932 s, 1865 w	*c*
$[Ph_4As][(CO)_4(NO)VMn(CO)_5]$ (**8**)	CH_2Cl_2	1570 m	2060 vw, 2005 w, 1965 s, 1863 w	*c*
$[Et_4N][C_5H_5V(CO)_2(NO)]$ (**9**)	CH_2Cl_2	1482 m	1910 s, 1805 s	4.91 (s, 5 H, C_5H_5)[b,d]

[a] C_6D_6. [b] CD_3CN. [c] ^1H NMR spectra of compounds **4** and **6–8** were not obtained. [d] Et_4N^+ signals: δ 1.34 (t of t, 12 H, CH_3), 3.46 (q, 8 H, CH_2).

heptane. A second crop of **8** was obtained as yellow needles by further concentration of the CH_2Cl_2/heptane filtrate. The total yield of **8** was 0.71 g (74%).

Anal. Calcd for $C_{33}H_{20}AsMnNO_{10}V$: C, 51.39; H, 2.61; N, 1.82; As, 9.71. Found: C, 51.96; H, 2.96; N, 1.41; As, 10.19.

Compound **8** dissolves in CH_2Cl_2 to provide moderately air-sensitive solutions, which are also thermally unstable above 0 °C. It is insoluble in alkanes and is stable as a solid indefinitely at 0 °C under nitrogen but slowly decomposes at room temperature. Above 85 °C it decomposes rapidly.

Tetraethylammonium Cyclopentadienyldicarbonylnitrosylvanadate(1−), $[Et_4N][(\eta^5\text{-}C_5H_5)V(CO)_2(NO)]$ (9). (Dimethoxyethane)sodium cyclopentadienide (0.3 g, 1.7 mmol) was dissolved in 20 mL of THF and cooled to −40 °C. A solution of **1**, prepared from 0.50 g (1.4 mmol) of $[Et_4N][V(CO)_6]$ and 0.17 g (1.4 mmol) of $[NO][BF_4]$ in 30 mL of CH_2Cl_2 at −40 °C was added dropwise in a low-temperature dropping funnel at −78 °C over a 45-min period. The reaction solution bubbled vigorously throughout the addition and turned brown. When the addition of **1** was complete, the solution was allowed to warm to room temperature. A solution of Et_4NBr (0.6 g, 2.8 mmol) in 15 mL of CH_2Cl_2 was added. After 1 h of stirring at room temperature, the CH_2Cl_2 was removed in vacuo. The light tan solid was dissolved in THF (60 mL) and the solution was filtered. The insoluble material was washed with additional THF until the washings were colorless (ca. 4 × 50 mL). Concentration of the THF to 30 mL and addition of 15 mL of hexane precipitated brown crystals. The other reaction product, $[Et_4N][V(CO)_6]$, was soluble in this mixture and was separated by filtration. Compound **9** was recrystallized from acetone/hexane to give 0.20 g (42%) of brown crystals.

Anal. Calcd for $C_{15}H_{25}N_2O_3V$: C, 54.21; H, 7.58; N, 8.43. Found: C, 53.96; H, 7.51; N, 8.28.

Compound **9** is soluble in CH_2Cl_2 and CH_3CN and moderately soluble in THF, giving very air-sensitive solutions. It is insoluble in toluene, alkanes, and diethyl ether. Crystalline **9** is very air sensitive and is stable indefinitely under nitrogen at room temperature but decomposes above 115 °C.

Results and Discussion

Hieber and co-workers reported in 1961 that a thermally unstable violet red vanadium carbonyl nitrosyl species was obtained when NO was passed through a cold solution of $V(CO)_6$ in cyclohexane.[1] On the basis of only an infrared spectrum in cyclohexane, they formulated this species as $V(CO)_5NO$.

$$V(CO)_6 + NO \xrightarrow[0\ ^\circ C]{\text{cyclohexane}} \text{“}V(CO)_5NO\text{”} + CO \qquad (1)$$

No attempts to isolate or characterize this substance by other means were reported. Hieber and Kummer also indicated later that a cyclohexane solution of this nitrosyl complex reacted with tetraphenylbiphosphine to provide $Ph_4P_2[V(CO)_4NO]_2$, but no yield, spectroscopic properties, or other data for this thermally unstable orange-red substance were presented in support of the proposed formulation.[9] Until recently, the only well-characterized derivative of $V(CO)_5NO$ was $V(CO)_4(NO)(Ph_3P)$. This material was obtained by the reaction of $V(CO)_4(Ph_3P)_2$ and NO.[10]

$$V(CO)_4(Ph_3P)_2 + NO \rightarrow V(CO)_4(NO)(Ph_3P) + Ph_3P \qquad (2)$$

Very recently, Rehder and co-workers[2] reported on the synthesis and characterization of a number of neutral compounds with the general formula $V(CO)_{5-n}(NO)L_n$, where n = 1 or 2; L = PR_3, $P(OR)_3$, and AsR_3. These were prepared by a variety of methods which produced low to moderate yields of products. Their results are summarized in eq 3–6 (see ref 2b for ligand abbreviations).

$$V(CO)_6 \xrightarrow[\text{cyclohexane, 0 °C}]{\text{(1) NO}\ \text{(2) L}} V(CO)_4(NO)L \qquad (3)$$

L = $P(OMe)_3$, DPPM; yields, 5–8%

$$[Na(diglyme)_2][V(CO)_6] \xrightarrow[\text{THF, −78 °C}]{\text{(1) NOCl}\ \text{(2) L}} V(CO)_4(NO)L \text{ or } V(CO)_3(NO)L_2 \qquad (4)$$

L = $P(OMe)_3$, PMe_2H; L_2 =DPPE; yields, 3–5%

$$[Et_4N][V(CO)_4L_2] \xrightarrow[\text{−7 to 0 °C}]{\text{NOX}} V(CO)_3(NO)L_2 \qquad (5)$$

X = BF_4 in CH_3CN, Cl in THF;
L_2 = $2PMe_3$, DPPE, DPPM; yields, 12–15%

$$[Et_4N][V(CO)_4L_2] \xrightarrow[\text{−70 °C}\ \text{THF/CH}_3\text{CN}]{[Co(NO)_2Br]_2} V(CO)_3(NO)L_2 \qquad (6)$$

L_2 =
DMPE, DPPE, DIARS, DPAE, PAB, DPPP; yields, 40–54%

Only very low yields of products were obtained from reactions 3 and 4, which were assumed but not proven to involve the intermediacy of a neutral carbonylnitrosyl species. The other methods employed in this study (reactions 5 and 6) are more difficult than our procedure since they all require initial conversion of $V(CO)_6^-$ to $V(CO)_4L_2^-$ by photosubstitution. After isolation, the substituted anions are then treated with a source of NO^+.

In 1981, we had developed a far superior "one-pot" synthesis of vanadium carbonylnitrosyl derivatives. This method involves the initial synthesis of bona fide $V(CO)_5NO$. This remarkably reactive relative of the isoelectronic $Cr(CO)_6$ is not normally isolated, but is reacted in situ with a variety of neutral and anionic Lewis bases at low temperatures (−20 to 0 °C) to generally provide high isolated yields (70–95%) of products which are formally analogous to those obtained from $Cr(CO)_6$ at far higher temperatures (generally ≥100 °C). In this paper the first isolation and unambiguous characterization of $V(CO)_5NO$ will be described, followed by a discussion of its chemical properties. Of particular note is our synthesis of the first anionic derivatives of $V(CO)_5NO$. A preliminary account of this work has previously appeared.[11]

Synthesis, Isolation, and Characterization of $V(CO)_5NO$. The best method we have discovered to prepare $V(CO)_5NO$ is by the reaction of equimolar amounts of $[Et_4N][V(CO)_6]$[4] and $[NO][BF_4]$ in methylene chloride at −40 to −50 °C. Since NO^+ is

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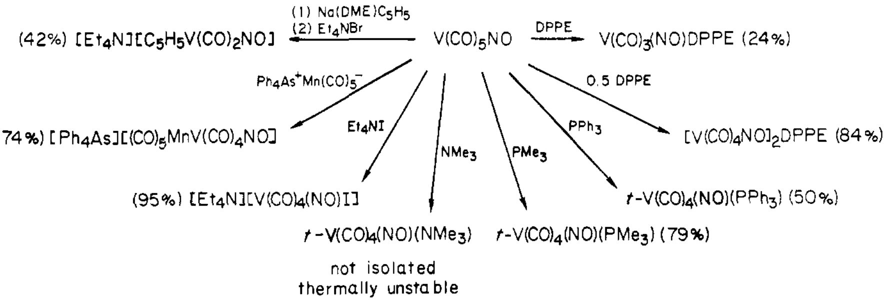
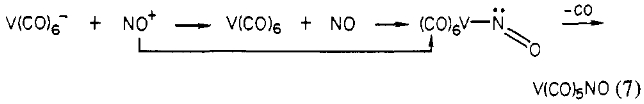
(10) Werner, R. P. M. *Z. Naturforschg. B*: **1961**, *16B*, 478.

(11) Fjare, K. L.; Ellis, J. E. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, KS, September 1982; American Chemical Society: Washington, DC, 1982, INOR 122.

Scheme I



known to be an excellent one-electron oxidizing agent[12] and $V(CO)_6^-$ is readily oxidized to $V(CO)_6$,[13] it is possible that the first step in the reaction of $V(CO)_6^-$ and NO^+ may involve an electron transfer to generate equimolar amounts of $V(CO)_6$ and NO in situ. Alternatively, seven coordinate $V(CO)_6NO$, containing a bent vanadium nitrosyl linkage, could form initially, since it is known that electrophiles such as Ph_3SnCl or Ph_3PAuCl react with $V(CO)_6^-$ to form neutral compounds, $EV(CO)_6$ (E = Ph_3Sn or Ph_3PAu) containing seven coordinate vanadium.[14] These reaction possibilities are summarized in eq 7. In this regard, it



(7)

is important to note that the infrared spectrum of Hieber's product obtained from the reaction of $V(CO)_6$ and NO gas[1] and that of our product obtained from $V(CO)_6^-$ and NO^+ are identical.

Removal of the methylene chloride from the red violet solution at −40 °C provides a deep violet product which can be separated from $[Et_4N][BF_4]$ by extraction with hexane at −10 °C. When the resulting purple hexane solution is cooled to about −78 °C, bona fide $V(CO)_5NO$ precipitates as lovely red-violet crystals, which may be stored under nitrogen at −25 °C for several weeks without apparent decomposition. Crystalline $V(CO)_5NO$ rapidly decomposes at 10–13 °C to form a black solid which contains no CO or NO groups. It seems very likely that the thermal instability of $V(CO)_5NO$ is due to the lability of its carbonyl groups. The presence of the coordinated NO undoubtedly weakens the vanadium–carbonyl bonds by removing substantial electron density from the vanadium. It is well-known that when NO functions as a three-electron donor, it is a substantially better π-acceptor group than CO.[3] This view is consistent with the very high carbonyl stretching frequencies observed for $V(CO)_5NO$ (Table I.) The absorption at 2100 cm^{-1} appears to be the highest energy ν(CO) band observed for any known vanadium carbonyl complex.[15] A complimentary rather low ν(NO) value (1695 cm^{-1}) for a linear nitrosyl group suggests that the following resonance forms are important in describing the electronic ground state of $V(CO)_5NO$:

$$(OC)_5V^-{=}N^+{=}O \rightarrow (OC)_5V{\equiv}N^+{-}O^-$$

Also consistent with this view that the carbonyls are bound more weakly to vanadium than the nitrosyl group are data from the mass spectrum of $V(CO)_5NO$ (see Experimental Section) which show that two CO groups are lost before loss of NO occurs. Due to its thermal instability a conventional elemental analysis could not be obtained. However, a high-resolution mass spectrum (see Experimental Section) was obtained to provide unequivocal proof for the molecular composition of $V(CO)_5NO$.

Reactions of $V(CO)_5NO$ with Lewis Bases. Pentacarbonylnitrosylvanadium undergoes facile reactions with a variety of Lewis bases from −30 to 0 °C. A summary of the reactions reported in this initial paper and the isolated yields of products are shown in Scheme I. below. In all cases, monosubstituted products have trans-$V(CO)_4(NO)L$ geometry. The only compounds in this scheme previously reported are $V(CO)_4(NO)(PPh_3)$[10] and $V(CO)_3(NO)DPPE$.[2] The latter was prepared in 12% yield by the reaction of $[Et_4N][V(CO)_4DPPE]$ with nitrosyl chloride and only in 5% yield from the reaction of $[Na(diglyme)_2][V(CO)_6]$ and NOCl at low temperatures in THF (to generate what Rehder and co-workers referred to as "$V(CO)_5NO$") followed by treatment with DPPE.[2] Since bona fide $V(CO)_5NO$ reacts with THF above −35 °C to provide thermally stable (below 10 °C) yellow solutions of t-$V(CO)_4(NO)(THF)$ (ν(CO, NO), 1955 s, 1610 m cm^{-1}), we believe that the use of the highly reactive and unselective NOCl is responsible for the low yields of derivatives. Our method for generating $V(CO)_5NO$ is essentially quantitative since neither the reactants $[Et_4N][V(CO)_6]$ and $[NO][BF_4]$ nor the solvent are appreciably basic. It is also likely that the use of $[NO][BF_4]$ rather than NOCl as the source of NO^+ may be important because $V(CO)_5NO$ readily reacts with iodide ion and presumably other halide ions at low temperature.[26]

Reactions of $V(CO)_5NO$ with phosphines provide principally monosubstituted products, although with DPPE, 24% yields of the disubstituted $V(CO)_3(NO)DPPE$ could be separated from the principal product, $[V(CO)_4(NO)]_2DPPE$. The latter substance

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[12] Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 329.

[13] Bond, A. M.; Colton, R. *Inorg. Chem.* **1976**, *15*, 2036.

[14] Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113.

[15] Other vanadium carbonyl derivatives with high maximum ν(CO) values are as follows: $H_3SiV(CO)_6$ (2088 cm^{-1}), also thermally unstable at room temperature (Allinson, J. S.; Aylett, B. J.; Colquhoun, H. M. *J. Organomet. Chem.* **1976**, *112*, C7); $C_6H_6V(CO)_4^+$ (2068 cm^{-1}) (Calderazzo, F. *Inorg. Chem.* **1965**, *4*, 223); $Ph_3SnV(CO)_6$ (2067 cm^{-1}) (ref 14).

[16] Fjare, K. L.; Ellis, J. E. *Organometallics* **1982**, *1*, 1373.

[17] Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

[18] Anders, A.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 539. Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1818.

[19] The related anion $C_5H_5CoNO^-$ was reported recently: Weiner, W. P.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3612. This substance has a ν(NO) value in CH_3CN at 1570 cm^{-1}.

[20] Two cyanonitrosylmetalate anions presumably contain linear nitrosyls and have very low ν(NO) values: $K_3[Mn(NO)_2(CN)_2]$, ν(NO) 1455, 1425 cm^{-1} (Behrens, H.; Lindner, E.; Schindler, H. *Z. Anorg. Allg. Chem.* **1969**, *365*, 119) and $K_3[Co(NO)(CN)_3]$, ν(NO) 1485 cm^{-1} (Behrens, H.; Lindner, E.; Schindler, H. *Chem. Ber.* **1966**, *99*, 2399). By contrast the isoelectronic $C_5H_5Cr(NO)(CO)(CN)^-$ has a ν(NO) value of 1612 cm^{-1} (Brünner, H. *Chem. Ber.* **1969**, *102*, 305). Recently, we have prepared $K_2[Mn(CO)_3NO]$ which also has a very low ν(NO) value of 1420 cm^{-1} (Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1689).

[21] Heberhold, M.; Klein, R.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 220.

[22] Fischer, E. O.; Schneider, R. J. J.; Muller, J. *J. Organomet. Chem.* **1968**, *14*, P4. Heberhold, M.; Razavi, A. *Angew. Chem., Int. Ed. Engl.*, **1972**, *11*, 1092.

[23] Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 2205. Fischer, E. O.; Schneider, R. J. J. *Ibid.* **1970**, *103*, 3684.

[24] Ellis, J. E. *J. Organomet. Chem.* **1965**, *86*, 1 and references cited therein.

[25] Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd Ed. Wiley: New York, 1967; pp 571–578. Basolo, F. *Coord. Chem. Rev.* **1982**, *43*, 7.

[26] **Note Added in Proof**: Further studies strongly suggest that $V(CO)_6$ initially forms in the reaction of $V(CO)_6^-$ and NO^+. While $V(CO)_6$ is reasonably stable in CH_2Cl_2, it undergoes facile disproportionation in most ethers, CH_3CN, and similar polar solvents.[24] It is undoubtedly for the latter reason, rather than those suggested in the discussion, that derivatives of $V(CO)_5NO$ cannot be generated in good yields from the reaction of $V(CO)_6^-$ and NOCl in THF.

is formulated on the basis of the spectroscopic and analytical data to contain a μ-DPPE unit, i.e., $[V(CO)_4(NO)PPh_2CH_2]_2$. Consistent with this formulation, it can be prepared free of the mononuclear species in 84% yield by using 0.5 equiv. of DPPE per equivalent of $V(CO)_5NO$. The most thermally stable monosubstituted phosphine derivative we have prepared is $V(CO)_4(NO)(PMe_3)$ (decomposition point ca. 95 °C). This volatile product is isolated in 79% yield from the reaction of $V(CO)_5NO$ with excess PMe_3 in CH_2Cl_2 at −20 to 0 °C. No evidence for the formation of $V(CO)_3NO(PMe_3)_2$ was obtained in this reaction. This latter substance was obtained in 15% yield by the reaction of $[Et_4N][V(CO)_4(PMe_3)_2]$ with $[NO][BF_4]$.[2] The trans configuration assigned to $V(CO)_4(NO)(PMe_3)$ is entirely consistent with its infrared spectrum (Table I) which shows only one sharp and intense ν(CO) band at 1960 cm^{-1} as well as a sharp band of medium intensity at 1663 cm^{-1} due to the coordinated NO. Further characterization of $V(CO)_4(NO)(PMe_3)$ was provided by a satisfactory elemental analysis and a mass spectrum which shows the parent peak and appropriate fragmentation patterns for the compound (see Experimental Section). The ^1H NMR spectrum of $V(CO)_4(NO)(PMe_3)$ shows a curious very broad triplet which probably results from the coupling of the methyl hydrogens with the quadrupolar nuclei ^{14}N ($I = 1$) and ^{51}V ($I = {}^7/_2$) as well as ^{31}P. Interestingly, in the corresponding spectrum of $V(CO)_5PMe_3^-$ a very broad signal was also observed.[16] In contrast to the good thermal stability of $V(CO)_4(NO)(PMe_3)$, the trimethylamine analogue is quite thermally unstable. The very close similarity of the infrared spectrum of the product (Table I) from the reaction of $V(CO)_5NO$ and Me_3N with that of bona fide $V(CO)_4(NO)(PMe_3)$ strongly indicates that this material is correctly formulated as $V(CO)_4(NO)(NMe_3)$.

The first anionic derivatives of $V(CO)_5NO$ were obtained from the reactions of three different types of nucleophilic anions with $V(CO)_5NO$. The reaction of $V(CO)_5NO$ with I^- readily proceeds at quite low temperatures (ca. −20 °C) and provides nearly quantitative yields of $[Et_4N]$[*trans*-$IV(CO)_4NO$]. This compound is isolated as a fairly air-stable yellow crystalline substance. The iodide complex is substantially more thermally and solvolytically stable than $V(CO)_5NO$ and should represent a convenient synthetic equivalent in many applications for $V(CO)_5NO$.

Basic transition-metal species also readily react with $V(CO)_5NO$ at low temperatures to provide new compounds containing metal–vanadium bonds. For example, the reaction of $[Ph_4As][Mn(CO)_5]$ and $V(CO)_5NO$ provides a 74% yield of $[Ph_4As][(CO)_5MnV(CO)_4NO]$, which undoubtedly has the same basic structure as *trans*-$IV(CO)_4NO^-$. Infrared spectra (Table I) of $MnV(CO)_9NO^-$ indicate that no bridging carbonyls are present and are consistent with a structure essentially analogous to that of isoelectronic anionic species $Cr_2(CO)_{10}^{2-}$[17] and $CrMn(CO)_{10}^-$.[18] This general procedure of reacting anionic transition-metal species with $V(CO)_5NO$ promises to be an important route to many new heterometallic di- and polynuclear compounds containing vanadium.

Perhaps the most useful compound prepared thus far from $V(CO)_5NO$ is $C_5H_5V(CO)_2(NO)^-$. This is only the second example of a potentially very large family of anions of the general formula $C_5R_5M(CO)_x(NO)_y^-$ ($y \geq 1$).[19] The properties of the isolated tetraethylammonium salt are entirely consistent with the proposed formulation. The ^1H NMR and IR spectra of this species (Table I) are unexceptional except for the very low ν(NO) value of 1482 cm^{-1}. This is one of the lowest reported nitrosyl stretching frequencies for a complex containing only linear terminal nitrosyl groups.[20] It is interesting to note that $C_5H_5V(CO)_2(NO)^-$ represents the last missing member of the isoelectronic series: $C_5H_5V(NO)_3^+$,[21] $C_5H_5V(CO)(NO)_2$,[22] $C_5H_5V(CO)_2NO^-$, and $C_5H_5V(CO)_3^{2-}$.[23] Also, $C_5H_5V(CO)_2NO^-$ is isoelectronic with $C_5H_5Cr(CO)_3^-$. The latter species, and the analogous molybdenum and tungsten compounds, have been important precursors to many new organometallics, including $[C_5H_5M(CO)_2]_2$, which contain metal–metal triple bonds.[24] We anticipate that the availability of $C_5H_5V(CO)_2NO^-$ will allow similar excursions into organovanadium chemistry.

Attempts to Prepare Ta(CO)₅NO. On the basis of work with $V(CO)_5NO$, it was hoped that the reaction of $Ta(CO)_6^-$ with NO^+ would provide $Ta(CO)_5NO$. This was considered to be a significant "target" since there have been no previous reports of any compounds of the type $M(CO)_x(NO)_y$ containing second- or third-row transition metals. In fact, when various salts containing $Ta(CO)_6^-$ are treated with $[NO][BF_4]$ or $[NO][PF_6]$ in CH_2Cl_2 at low temperature, only extremely low yields of $Ta(CO)_5NO$ derivatives could be obtained. No *direct* evidence for the existence of $Ta(CO)_5NO$ was obtained in any of these reactions. During the reaction of $Ta(CO)_6^-$ and NO^+, the solution turned from orange to an orange-red color, but infrared solution spectra indicated that $Ta(CO)_6^-$ was the only species present in solution. Addition of a large excess of PMe_3 to one of these reactions provided mostly unreacted $Ta(CO)_6^-$, but a small amount of hexane-soluble material was present. This proved to be mostly $Ta(CO)_3(NO)(PMe_3)_2$ and $Ta(CO)_4(NO)(PMe_3)$. Too little of this mixture was present to allow separation of the components. However, a mass spectrum showed parent peaks at m/e values of 447.1 and 399.0 corresponding to $Ta(CO)_3(NO)(PMe_3)_2$ and $Ta(CO)_4(NO)(PMe_3)$, respectively. Also present were peaks due to expected fragments resulting from sequential loss of CO as well as NO and PMe_3. A rather dilute Nujol mull infrared spectrum of this impure mixture showed bands in the ν(CO, NO) region at the following positions: 1993 m, 1980 m, 1935 s, 1635 m, 1595 m cm^{-1}. A comparison of this spectrum with that of vanadium analogues, $V(CO)_4(NO)(PMe_3)$ (this work) and $V(CO)_3(NO)(PMe_3)_2$,[2] indicates that at least one other tantalum carbonyl complex is also present. Attempts to prepare these trimethylphosphine derivatives of an apparently exceedingly unstable $Ta(CO)_5NO$ by other methods are in progress and will hopefully clarify the status of these interesting materials.

Concluding Remarks

We have shown that bona fide $V(CO)_5NO$ is readily available in high yield from the reaction of $[Et_4N][V(CO)_6]$ with $[NO][BF_4]$ in CH_2Cl_2 at low temperatures. This volatile and thermally unstable compound is isoelectronic with $Cr(CO)_6$ but undergoes substitution reactions at much lower temperatures to provide a variety of new and interesting materials. One of our principal objectives in future work will be to examine other possible parallels in the reactivity patterns of $Cr(CO)_6$ and $V(CO)_5NO$. Another important point, however, concerns the mechanism(s) by which $V(CO)_5NO$ undergoes substitution reactions. Will they be second order as they are in the reactions of phosphines and other Lewis bases with other mixed carbonylnitrosyls such as $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$?[25] Alternatively, will the relatively high coordination number of the vanadium in $V(CO)_5NO$ facilitate a first-order process?

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