

that the organic moiety of **9A** is basically the same as that for structure **10**.

Conclusion

Results of comparing solution and solid-state NMR spectra suggest that the initial precipitated platinum complexes from Zeise's dimer and hydrocarbons **1**, **3**, and **9** are platinumacyclobutane complexes. These results are in contrast to previous data which had suggested that two of these compounds were endo bidentate complexes. Moreover, the solid-state spectrum of **10** is in excellent agreement with its solution spectrum showing that the phase does not have a significant perturbation on the chemical shift. There are precautionary notes to be made here. We have been careful to speak of these precipitates as initial precipitates. It would be erroneous to *always* consider these as the initially formed complex. Further, it is likely to be erroneous to assume that the initial precipitate and the solubilized complex are always the same. However, MAS/CP NMR spectroscopy has been shown to be a viable tool in investigating this aspect of organometallic chemistry.

Experimental Section

General Data. ^1H , ^{13}C , and ^{196}Pt NMR spectra were obtained by using a Bruker WM-250 spectrometer. MAS/CP spectra were obtained at 37.7 or 50.2 MHz for ^{13}C . Diethyl ether was distilled from CaH_2 prior to use. Pyridine was Baker reagent grade, and CDCl_3 was obtained from Stohler. Zeise's dimer was prepared from K_2PtCl_4 which was purchased from Aldrich. The hydrocarbons **1** and **3** as well as their initially precipitated platinum complexes were prepared as previously described.² Analyses were done by Galbraith Laboratories and were correct for all complexes.

Preparation of 9. *exo*-Tricyclo[3.2.1.0^{2,4}]octane was prepared by the method of Kottwitz⁹ and purified by gas chromatography.

Preparation of 9A. To a suspension of 506 mg (0.86 mmol) $[\text{C}_2\text{H}_4\text{PtCl}_2]_2$ in 10 mL of dry ether was added 360 mg (3.3 mmol) of **9**. This mixture was magnetically stirred at reflux for 5 h during which time the orange solid, Zeise's dimer, was consumed, giving the yellow solid of the platinum complex. This product was filtered and dried by vacuum. Subsequently, it was resuspended in ether by crushing and stirring. Filtration and drying in a vacuum desiccator gave 610 mg of a yellow solid—yield 95%. Shorter reaction times afforded a lower conversion to product.

Preparation of 10. To **9A** (200–600 mg) suspended in 10–15 mL of chloroform was added 3–4 equiv of pyridine with magnetic stirring. After 5 min, the yellow solid dissolved and the volatile components were removed by rotoevaporation at 25 °C to yield a dark yellow oil. Addition of pentane and further rotoevaporation afforded a yellow-white solid. Trituration in more pentane, solvent evaporation, and vacuum desiccation gave the yellow-white pyridine complex in quantitative yield.

Solution Spectra of Pyridine Adducts. Solution spectra for the pyridine derivatives of **2**, **4**, and **10** were obtained by adding 3–4 equiv of pyridine to stirred suspensions of platinum compound in CDCl_3 . Rotoevaporation of these solutions and workup as described for structure **10** yielded solid pyridine derivatives for each of the compounds.

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Registry No. **1**, 3635-94-7; **1A**, 82839-00-7; **2**, 82839-01-8; **3**, 24506-61-4; **3A**, 82839-02-9; **4**, 82839-03-0; **9**, 13377-46-3; **9A**, 82839-04-1; **10**, 82839-05-2; $[(\text{C}_2\text{H}_4)\text{Cl}_2\text{Pt}]_2$, 12073-36-8.

(9) Kottwitz, J.; Vorbruggen, H. *Synthesis* 1975, 636.

Highly Reduced Organometallics. 8.¹ The Synthesis of (Phosphine)pentacarbonylvandate(1–) Anions, $\text{V}(\text{CO})_5\text{PR}_3^-$, by the Thermal Substitution of (Ammine)pentacarbonylvandate(1–), $\text{V}(\text{CO})_5\text{NH}_3^-$

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(Ammine)pentacarbonylvandate(1–) reacts with various phosphines ($\text{L} = \text{Ph}_3\text{P}$, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 0-2$), $(p\text{-ClC}_6\text{H}_4)_3\text{P}$, Me_3P , HPh_2P , F_3P) to provide moderate to high yields of $\text{V}(\text{CO})_5\text{L}^-$. Several of these materials have not been isolated previously and either are unavailable or are not easily prepared by other methods. Interestingly, the reaction of $\text{V}(\text{CO})_5\text{NH}_3^-$ with Ph_4P_2 in liquid ammonia provides high yields (70–75%) of previously unknown $\text{V}(\text{CO})_5\text{Ph}_2\text{PNH}_2^-$, isolated as the Et_4N^+ salt, while the same reaction conducted in THF provides lower yields (35–45%) of $\text{V}(\text{CO})_5\text{Ph}_4\text{P}_2^-$, isolated as the Ph_4P^+ and Ph_4As^+ salts. Proton-decoupled ^{31}P NMR has been used to unambiguously show that $\text{V}(\text{CO})_5\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2^-$ ($n = 0-2$) contain both ligated and unligated diphenylphosphino groups. Infrared and ^1H NMR spectra of the products are also discussed with respect to proposed structures. This "labile ligand method" represents the best method presently available for the synthesis of $\text{V}(\text{CO})_5\text{PR}_3^-$ species.

Introduction

Phosphine-substituted carbonyl anions of vanadium are known to be generally much more reactive than $\text{V}(\text{CO})_6^{-2,3}$

and are potentially useful precursors to new transition-metal clusters containing vanadium, which are presently very uncommon species.⁴ The first reports of a phosphine-substituted carbonylvandate anion appeared in

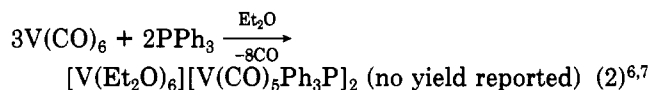
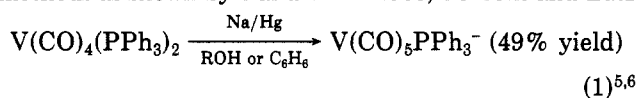
(1) Part 7: Ellis, J. E.; Fjare, K. L. *Organometallics* 1982, 1, 898.

(2) Ellis, J. E.; Faltynek, R. A. *J. Organomet. Chem.* 1975, 93, 205.

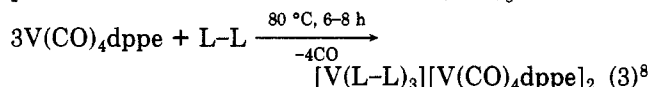
(3) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* 1972, 36, 113.

(4) Ellis, J. E. *J. Am. Chem. Soc.* 1981, 103, 6106.

1961. This substance was made by two independent methods as shown by 1 and 2. In 1968, Behrens and Lutz

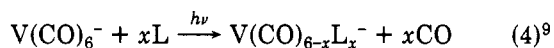


reported that $\text{V}(\text{CO})_4\text{dppe}$ ($\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane) also undergoes disproportionation by bipyridyl or phenanthroline as shown in eq 3. These latter reactions require fairly careful attention to time and temperature or substantial amounts of $\text{V}(\text{L-L})_3$ form.⁸



$\text{L-L} = \text{bpy}$ (89% yield), *o*-phen (66% yield)

In 1971, Davison and Ellis reported the first general route to various $\text{V}(\text{CO})_{6-x}\text{L}_x^-$ ($x = 1, 2$; $\text{L} = \text{PR}_3, \text{P}(\text{OR})_3, \text{AsR}_3, \text{SbR}_3$). This method did not depend upon the availability of a corresponding neutral substituted carbonyl and involved the photopromoted substitution of various π -acceptor ligands into $\text{V}(\text{CO})_6^-$, i.e., eq 4. Later, Rehder and other groups utilized this same general procedure to synthesize many other substituted carbonylvanadate ions.^{2,10}



Recently, we discovered that $\text{V}(\text{CO})_5\text{NH}_3^-$ reacted readily with various phosphines to provide high yields of new $[\text{V}(\text{CO})_5\text{PR}_3]^-$ species which were not readily available by the direct photolysis procedure because $\text{V}(\text{CO})_5\text{L}^-$ and/or L were photosensitive. In this paper are reported the results of this study. Portions of this work have been described previously in a preliminary communication.¹¹

Experimental Section

For general procedures, solvent purification, and the synthesis of $\text{Na}[\text{V}(\text{CO})_5\text{NH}_3]$, $[\text{Ph}_4\text{P}][\text{V}(\text{CO})_5\text{NH}_3]$, and $[\text{Ph}_4\text{As}][\text{V}(\text{CO})_5\text{NH}_3]$ refer to the previous paper in this series.¹ All phosphines were obtained from commercial sources. Unless otherwise noted, approximately 3.9 mmol of $\text{Na}[\text{V}(\text{CO})_5\text{NH}_3]$, generated in situ by the protonation of $\text{Na}_3\text{V}(\text{CO})_5^{12}$ in 75 mL of liquid ammonia, was used in the following reactions.

Tetraethylammonium (Triphenylphosphine)pentacarbonylvanadate(1-), $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{PPh}_3]$ (1). A liquid ammonia solution of $\text{Na}[\text{V}(\text{CO})_5\text{NH}_3]$ was prepared and cooled to -78°C . Solid triphenylphosphine (3.10 g, 11.8 mmol) and tetraethylammonium bromide (3.30 g, 15.7 mmol) were added through a bent tube. Cold THF (40 mL, -60°C) was then introduced. The solution slowly warmed to room temperature, and

subsequently the solvent was removed under vacuum. The residue was triturated with 2×40 mL of isopentane and dried to form a gold powder. THF was added (80 mL), and after filtration the solvent was evaporated. The product was recrystallized from acetone/diethyl ether and was washed with ethanol and diethyl ether and dried in vacuo. Bright yellow crystalline 1 was obtained in 79% yield (1.81 g). The infrared spectrum of this sample was superimposable on that of genuine $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{PPh}_3]$.⁹

Tetraethylammonium (Bis(diphenylphosphino)ethane)pentacarbonylvanadate(1-), $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{dppe}]$ (2). A cold (-78°C) solution of 1,2-bis(diphenylphosphino)ethane (3.13 g, 7.84 mmol) in THF (40 mL) was added to $\text{Na}[\text{V}(\text{CO})_5\text{NH}_3]$ in liquid ammonia. Solid Et_4NBr (1.64 g, 7.8 mmol) was subsequently added all at once. The mixture was protected from light¹³ and allowed to slowly warm to room temperature overnight. After the solvent mixture was evaporated in vacuo, the residue was triturated with isopentane (20 mL). Initially, the solid was quite sticky so the triturations were repeated with an additional 20 mL of isopentane. Then the solid was dried in vacuo. Next, the product was dissolved in THF (80 mL) and filtered to give a clear bright red solution. The insoluble solid was washed with THF (1×20 mL; 1×10 mL) until the washings were colorless. The THF was removed under partial vacuum, and the solid triturated with two 20-mL portions of diethyl ether and dried in vacuo. Recrystallization from acetone/ethanol gave irregular yellow-orange platelike crystals of 2 (2.01 g, 72% yield). A trace amount of another product, $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{dppe}]$,⁹ was also formed as small red cubic crystals.¹⁴ Crystalline 2 is moderately air sensitive and decomposes only after several hours. Solutions of 2 are quite sensitive to both air and light. Crystalline 2 is indefinitely stable at room temperature and melts at 123°C .

This material was originally reported to be formed in low yield as an impure byproduct formed during the photolysis of $\text{V}(\text{CO})_6^-$ and dppe .⁹ Compound 2 is identical with an analytical sample of bona fide $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{dppe}]$ previously isolated in 9% yield from the decomposition of $\text{V}(\text{CO})_5^{9-}$ in liquid ammonia in the presence of dppe .¹⁵ Compound 2 is insoluble in diethyl ether, alkanes, and ethanol, slightly soluble in toluene, and very soluble in acetone, tetrahydrofuran, and acetonitrile.

Synthesis of $\text{Ph}_3\text{SnV}(\text{CO})_4\text{dppe}$ from $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{dppe}]$. Solid 2 (0.50 g, 0.70 mmol) and Ph_3SnCl (0.28 g, 0.71 mmol) were combined and stirred during the addition of CH_2Cl_2 (40 mL) and then H_2O (20 mL). The mixture was stirred vigorously at room temperature for 12 h.

Evaporation of both solvents left a bright yellow flaky solid. This solid was dissolved in CH_2Cl_2 (30 mL). After filtration the clear orange solution was concentrated until yellow solid began to precipitate. Slow addition of diethyl ether to the stirred solution gave a precipitate. This crude solid was filtered, washed with two 15-mL portions of EtOH , and dried in vacuo. Golden yellow, microcrystalline $\text{Ph}_3\text{SnV}(\text{CO})_4\text{dppe}$ was isolated in 82% yield (0.52 g). This compound is identical with the product previously prepared by the reaction of Ph_3SnCl with $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{dppe}]$.³

Tetraphenylarsonium (Bis(diphenylphosphino)ethane)pentacarbonylvanadate(1-), $[\text{Ph}_4\text{As}][\text{V}(\text{CO})_5\text{dppe}]$ (3). Bis(diphenylphosphino)ethane (1.7 g, 4.3 mmol) and $[\text{Ph}_4\text{As}][\text{V}(\text{CO})_5\text{NH}_3]$ (0.83 g, 1.4 mmol) were combined and stirred while 50 mL of THF was introduced.¹³ After 20 min all material had dissolved to form a clear wine-colored solution. Removal of the THF left a bright red sticky solid. The solid was washed and triturated with isopentane (20 mL), then washed with toluene (1×40 mL; 1×20 mL) and isopentane (20 mL) and dried in vacuo. Crystallization from THF/diethyl ether produced 3 as a light orange powder (1.04 g, 76% yield). Anal. Calcd for $\text{C}_{55}\text{H}_{44}\text{AsO}_5\text{P}_2\text{V}$: C, 67.91; H, 4.56; As, 7.70. Found: C, 67.73; H, 4.93; As, 7.76.

Compound 3 is stable in air for several hours but is light sensitive. Although decomposition of the solid is only evident after about 8 h, solutions of 3 decompose within minutes. Compound 3 is stable at room temperature indefinitely under nitrogen

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(7) The unusual reaction shown in eq 2 has been shown recently to involve the disproportionation of neutral $\text{V}(\text{CO})_5\text{Ph}_3\text{P}$, which is formed initially from the reaction of $\text{V}(\text{CO})_6$ and Ph_3P . Ellis, J. E.; Faltynek, R. A.; Rochfort, G. L.; Stevens, R. E.; Zank, G. A. *Inorg. Chem.* 1980, 19, 1082.

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(11) Ellis, J. E.; Fjare, K. L. *J. Organomet. Chem.* 1981, 214, C33.

(12) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* 1981, 103, 6100.

(13) Solutions of 2-4 must be protected from light.

(14) The amount of this product varies with the solvent used in the reaction. If CH_3CN is used rather than THF, the amount of $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{dppe}]$ formed in one reaction was approximately 26%.

(15) Ellis, J. E.; Palazzotto, M. C. *J. Am. Chem. Soc.* 1976, 98, 8264.

and melts with decomposition at about 151 °C.

Tetraethylammonium (Bis(diphenylphosphino)methane)pentacarbonylvanadate(1-), [Et₄N][V(CO)₅dppm] (4). A cold (-78 °C) solution of 1,2-bis(diphenylphosphino)methane (7.5 g dppm, 19.6 mmol) in THF (40 mL) was added by cannula to a stirred liquid ammonia solution of Na[V(CO)₅NH₃] at -78 °C. Solid Et₄NBr (1.64 g, 7.8 mmol) was added all at once. The mixture warmed to room temperature overnight.¹³

The solvents were removed in vacuo, and THF was added (80 mL) to dissolve the product. Filtration provided a bright red solution. After evaporation of the solvent, the crude solid was washed extensively with toluene (1 × 40 mL; 6 × 20 mL) and ethanol (4 × 20 mL) to leave a yellow microcrystalline solid. This was dried in vacuo at room temperature for 12 h. Recrystallization from acetone/ethanol produced large yellow crystals. The yield of pure 4 was 1.99 g (72%). Anal. Calcd for C₃₈H₄₂NO₅P₂V: C, 64.68; H, 6.00; N, 1.98; P, 8.78. Found: C, 64.75; H, 6.52; N, 1.98; P, 8.87.

Solutions of [Et₄N][V(CO)₅dppm] are air sensitive and somewhat light sensitive. An acetonitrile solution in a sealed tube changed from a light yellow to bright red after more than 48-h exposure to light. There is no other visible decomposition and no change in the ¹H NMR spectrum. Crystalline 4 is moderately air sensitive and decomposes to light brown non-carbonyl-containing products. Compound 4 is insoluble in EtOH, MeOH, toluene, Et₂O, and alkanes. It is soluble in THF, CH₃CN, CH₂Cl₂, and acetone.

Tetraethylammonium (Aminodiphenylphosphine)pentacarbonylvanadate(1-), [Et₄N][V(CO)₅PPh₂NH₂] (5). A cold (-78 °C) solution of tetraphenyldiphosphine (4.56 g, 12.3 mmol) in THF (40 mL) was added by cannula to a solution of Na[V(CO)₅NH₃] at -78 °C. Solid Et₄NBr (1.64 g, 7.8 mmol) was subsequently added all at once. When the solution had warmed to room temperature, more THF (40 mL) was added and the solid was triturated. Subsequently, the slurry was filtered. After the solvent was evaporated in vacuo, the residue was washed and triturated with isopentane (40 mL) and dried. Toluene (80 mL) was added, and the slurry was filtered. The bright yellow product was washed with toluene (2 × 20 mL), isopentane (3 × 20 mL), ethanol (5 × 20 mL), and diethyl ether (2 × 20 mL) and dried. It was dissolved in acetone, filtered, and recrystallized from acetone/ethanol to produce bright yellow needles (1.49 g, 73% yield). Slower recrystallization will produce long (6 mm × 1 mm) clear orange needles. Anal. Calcd for C₂₅H₃₂N₂O₅PV: C, 57.46; H, 6.17; N, 5.36; P, 5.93. Found: C, 57.56; H, 6.05; N, 5.50; P, 6.02. Found: C, 57.54; H, 6.22; N, 4.92; P, 6.15.

[Et₄N][V(CO)₅PPh₂NH₂] is quite air sensitive, even large crystals turn brown within minutes. Compound 5 is insoluble in ethanol, diethyl ether, alkanes, and toluene. It is very soluble in THF, acetonitrile, and acetone. Tetrahydrofuran solutions are bright red, while acetonitrile and acetone solutions are yellow-orange. The compound is indefinitely stable at room temperature and melts at 136–138 °C.

Tetraphenylphosphonium (Tetraphenyldiphosphine)pentacarbonylvanadate(1-), [Ph₄P][V(CO)₅P₂Ph₄] (6). Tetraphenyldiphosphine (1.2 g, 3.2 mmol) and [Ph₄P][V(CO)₅NH₃] (1.0 g, 1.8 mmol) were combined in a flask. When THF (80 mL) was added, the solution immediately turned to a reddish hue. Within 15 min the solution became very dark red and all solid had dissolved. A solution spectrum indicated that the reaction had cleanly formed only the desired substitution product 6. Evaporation of the solvent produced an iridescent red foam. After trituration with 40 mL of isopentane the product was dissolved in acetonitrile (60 mL) and filtered. Crystallization from CH₃CN/EtOH gave large red crystals of 6 (0.73 g, 44% yield). Anal. Calcd for C₅₃H₄₀O₅P₃V: C, 70.67; H, 4.48; N, 0.00; P, 10.32. Found: C, 69.85; H, 4.72; N, <0.05; P, 9.34. Compound 6 appears to be stable in air as a solid for several days. Compound 6 is stable indefinitely at room temperature under nitrogen and melts at 141–142 °C. Compound 6 is insoluble in alkanes, diethyl ether, and ethanol. It is very soluble in THF and soluble in CH₃CN and acetone.

Tetraphenylarsonium (Tetraphenyldiphosphine)pentacarbonylvanadate(1-), [Ph₄As][V(CO)₅P₂Ph₄] (7). Solid [Ph₄As][V(CO)₅NH₃] (1.02 g, 1.73 mmol) and Ph₂PPPh₂ (3.13 g, 8.46 mmol) were combined and cooled to 0 °C. Cold THF (50

mL, 0 °C) was added, and the solution was stirred at 0 °C for 1 h. At the end of this time all of the [Ph₄As][V(CO)₅NH₃] had dissolved, and the reaction solution was deep red. The THF was evaporated to give a red solid. The residue was triturated with 2 × 40 mL of isopentane, dried, and dissolved in acetonitrile (80 mL). The resulting slurry was filtered to give a deep red solution. After removal of solvent the red glass was washed with 2 × 20 mL of toluene and dried. Recrystallization from CH₃CN/Et₂O produced red crystals. The supernatant was removed and the crystals were washed with 3 × 20 mL of heptane and dried. The yield of crystals was initially 0.95 g or 58%. Analytically pure 7 was obtained by two more recrystallizations from acetonitrile/EtOH as microcrystalline orange-red material (free of P₂Ph₄) in 35% yield (0.57 g). Anal. Calcd for C₅₃H₄₀O₅P₂AsV: C, 67.38; H, 4.27; P, 6.56. Found: C, 66.83; H, 4.64, P, 6.52.

Solid [Ph₄As][V(CO)₅P₂Ph₄] is stable in air for about 2 days before it becomes darker in color. Solutions of 7 are only slightly air sensitive. The solid is stable at room temperature indefinitely under nitrogen and melts at 145–146 °C. Compound 7 is soluble in THF, CH₃CN, and acetone. It is insoluble in toluene, alkanes, diethyl ether, H₂O, and ethanol.

Tetraethylammonium (Tris(*p*-chlorophenyl)phosphine)pentacarbonylvanadate(1-), [Et₄N][V(CO)₅(*p*-ClC₆H₄)₃P] (8). The same quantities of reactants and procedure for the synthesis of 1 were used except a solution containing tris(*p*-chlorophenyl)phosphine (1.44 g, 3.94 mmol) and tetraethylammonium bromide (3.30 g, 15.7 mmol) in 30 mL of ethanol was added by cannula to the liquid ammonia containing Na[V(CO)₅NH₃]. Slowly the solution warmed to room temperature, and the solvent was removed under vacuum. The residue was triturated with 2 × 40 mL of isopentane and dried. THF was added (80 mL), and the slurry was filtered. Additional THF was added until the washings were colorless. The filtrate was evaporated to dryness. Recrystallization from acetone/diethyl ether gave orange-yellow 8. This was washed with absolute ethanol and diethyl ether and then dried to give 2.28 g (85%) of analytically pure compound. Anal. Calcd for C₃₁H₂₂Cl₃PNO₅V: C, 54.21; H, 4.70; Cl, 15.48. Found: C, 54.11; H, 4.99; Cl, 15.42.

Compound 8 is soluble in acetone, THF, and acetonitrile. It is insoluble in diethyl ether, absolute ethanol, alkanes, and arenes. Compound 8 is moderately air sensitive but is stable under nitrogen at room temperature.

Tetraphenylarsonium (Trifluorophosphine)pentacarbonylvanadate(1-), [Ph₄As][V(CO)₅PF₃] (9). A vessel containing solid [Ph₄As][V(CO)₅NH₃] (0.92 g, 1.56 mmol) was evacuated and refilled with PF₃. Then THF (40 mL) was added while PF₃ was passed over the stirred slurry at room temperature. Within 2 min at room temperature the originally magenta solid dissolved to give a yellow solution and a white solid (containing bands in the ν(N-H) region) possibly due to the reaction of PF₃ and the liberated ammonia. The solution was filtered (medium frit). After all but ca. 5 mL of solvent was removed, heptane (50 mL) was added quickly to yield a yellow solid. This was recrystallized from THF/Et₂O (in which the product is slightly soluble) to provide 0.44 g (43% yield) of the analytical sample. Anal. Calcd for C₂₉H₂₀AsF₃O₅PV: C, 52.59; H, 3.04; P, 4.68. Found: C, 52.94; H, 3.42; P, 4.47.

This substance was made at an early stage of this research, and no attempt was made to optimize the yield. If the reaction were performed at low temperature (e.g., -20 °C) and PF₃ were passed through the solution with a gas dispersion tube, higher yields of the product should be obtainable.

Tetraethylammonium (Trimethylphosphine)pentacarbonylvanadate(1-), [Et₄N][V(CO)₅PMe₃] (10). A solution of Na[V(CO)₅NH₃] was prepared by using the following quantities of reactants and solvent: 6.7 g (12.5 mmol) of [Na(diglyme)V(CO)₅], 2.14 g (37 mmol) of NH₄Cl, 0.90 g (37 mmol) of Na metal, and 250 mL of NH₃. The solution was cooled to -78 °C, and trimethylphosphine (5 mL, ca. 62.5 mmol) was added, followed by addition of cold THF (130 mL, -60 °C). The reaction mixture slowly warmed to room temperature while most the ammonia escaped. The resulting solution was yellow with much solid present. The solvent was removed. After trituration with 40 mL of isopentane a yellow solid was obtained. THF (100 mL) was added, and the slurry was filtered and washed with additional THF (20 mL) until the washings were colorless. Removal of the

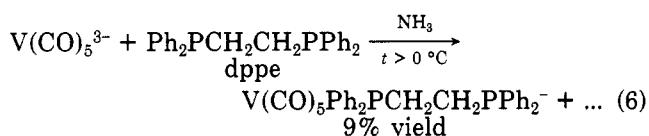
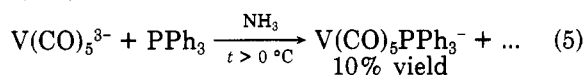
THF left a yellow-orange crystalline material. Recrystallization from acetone/ethanol yielded 3.85 g (74%) of bright yellow crystals. Anal. Calcd for $C_{16}H_{29}NO_5VP$: C, 48.37; H, 7.36; N, 3.53. Found: C, 48.03; H, 7.57; N, 3.57.

Compound 10 is moderately air sensitive as a solid and fairly air sensitive in solution. It is soluble in THF, CH_3CN , and acetone. It is insoluble in alkanes, diethyl ether, and ethanol. The melting point of crystalline 10 is 152–153 °C.

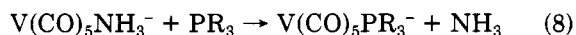
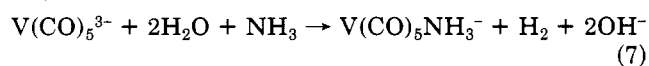
Tetraethylammonium (Diphenylphosphine)pentacarbonylvanadate(1-), [Et₄N][V(CO)₅PPh₂H] (11). A solution of $Na[V(CO)_5NH_3]$ in liquid ammonia was prepared and cooled to -78 °C. Diphenylphosphine (2 mL, approximately 12 mmol) and 20 mL of cold (-60 °C) THF were introduced. The solution was allowed to slowly warm to room temperature. The solvent was removed, and a yellow-brown oil remained. This was triturated with isopentane (2 × 20 mL). The washings were initially clear but became cloudy as they stood in air. The remaining solid was dissolved in 80 mL of THF and filtered. Evaporation of the THF gave yellow platelike crystals. Recrystallization from acetone/ethanol gave large transparent orange crystals in 65% yield (1.29 g). Anal. Calcd for $C_{25}H_{31}NO_5PV$: C, 59.17; H, 6.16; N, 2.76; P, 6.10. Found: C, 59.88; H, 6.47; N, 2.86; P, 6.18. Compound 11 is air sensitive in solution or in the crystalline state. It is soluble in acetone, acetonitrile, and THF and is insoluble in ethanol, alkanes, and diethyl ether. Compound 11 is stable at room temperature under nitrogen and melts at 136–137 °C.

Results and Discussion

During our initial examination of the chemistry of $Na_3V(CO)_5$, it was observed that when the trianion decomposed in the presence of phosphines, low yields of $V(CO)_5PR_3^-$ were obtained,¹⁵ i.e., eq 5 and 6. Although,

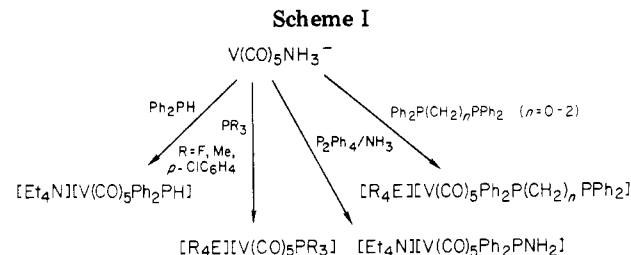


this reaction did not represent a useful route to $V(CO)_5PPh_3^-$, the synthesis of the dppe complex, containing an unligated phosphine, was significant since this material had not been isolated previously as a pure substance (vide infra). It was later observed that when water or NH_4^+ was added to $V(CO)_5^{3-}$ in liquid ammonia in the presence of phosphines, far higher yields of $V(CO)_5PR_3^-$ were obtained. For example, the 79% yield obtained for $[Et_4N][V(CO)_5PPh_3]$ (1) is higher than that previously obtained by the photochemical route (65%).³ Although the mechanism by which $V(CO)_5PR_3^-$ forms in *anhydrous* liquid ammonia during the decomposition of $V(CO)_5^{3-}$ is not yet understood, it is now known that water or any other reasonably acidic Brønsted acid in liquid ammonia efficiently converts $V(CO)_5^{3-}$ to $V(CO)_5NH_3^-$.¹² The amine substituted ion then undergoes rapid substitution at around -20 to 0 °C to give high yields of $V(CO)_5PR_3^-$, i.e., eq 7 and 8.

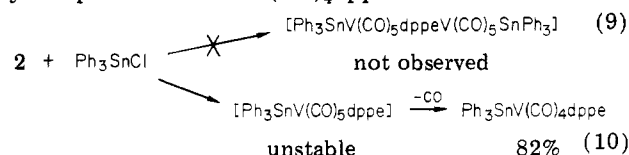


Our initial objective in this study was to determine whether $V(CO)_5NH_3^-$ would serve as a useful precursor to $V(CO)_5PR_3^-$ species which were previously unknown or available only in low or unreported yields by other procedures. This objective has been largely realized. Specific compounds prepared by this "labile ligand" method are summarized in Scheme I and will now be discussed.

$[V(CO)_5Ph_2P(CH_2)_nPPH_2]^-$ ($n = 1, 2$). Both the dppe ($n = 2$)^{10a} (dppe = 1,2-bis(diphenylphosphino)ethane) and



dppe ($n = 1$)^{10b} (dppe = 1,2-bis(diphenylphosphino)methane) monosubstituted anions have been observed by infrared spectroscopy to form during the photolysis of $V(CO)_6^-$ in the presence of these ligands. But these monosubstituted species are quite photosensitive and readily change to $V(CO)_4Ph_2P(CH_2)_nPPH_2^-$. The monosubstituted dppe anion was isolated in impure form and low yield from the photolysis of $V(CO)_6^-$ and dppe but was only characterized by its infrared spectrum and conversion to a triphenyltin derivative.^{10a} As mentioned above, $[Et_4N][V(CO)_5dppe]$ (2) was also prepared in 9% yield as an analytically pure sample by decomposing $Na_3[V(CO)_5]$ in the presence of dppe,¹⁵ but no spectroscopic proof for the presence of the uncoordinated phosphine group was obtained. By our labile ligand method, bona fide 2 was obtained in 72% yield. Chemical proof for the correct formulation was obtained by its reaction with Ph_3SnCl to give an 82% yield of genuine $Ph_3SnV(CO)_4dppe$.³ Presumably, the reaction of 2 with Ph_3SnCl involves the intermediate formation of $Ph_3SnV(CO)_5dppe$ which rapidly loses CO and forms the observed product (eq 9 and 10). Similarly, treatment of 2 with water generates only the hydride $HV(CO)_4dppe$, which has been previously obtained by the protonation of $V(CO)_4dppe^-$.¹⁶



A similar yield (76%) of $[Ph_4As][V(CO)_5dppe]$ (3) was also obtained by reacting preisolated $[Ph_4As][V(CO)_5NH_3]$ with dppe in THF. This material has the same infrared spectrum in the $\nu(CO)$ region (Table I) and rather uninformative ¹H NMR spectrum (Table II) as 2 and was also characterized by ³¹P NMR (Table III) to provide spectroscopic proof for the presence of an unligated PPh_2 group. Rehder and Müller had previously shown ³¹P NMR spectroscopy to be important in establishing that *cis*- $[V(CO)_4\text{triphos}]^-$ ¹⁷ contained both ligated and unligated phosphine groups.¹⁸ The Hamburg group has more recently extended these studies to a variety of related compounds and observe that ³¹P NMR spectra of phosphorus directly bound to ⁵¹V ($I = 7/2$) invariably contain very broad and often difficult to detect signals ($J_{PV} = 110\text{--}660$ Hz),¹⁹ while any uncoordinated phosphorus appears as a normal sharp signal.

The tetraethylammonium salt containing $V(CO)_5dppm^-$ (4) was similarly isolated in 72% yield. Infrared spectra (Table I) and ¹H (Table II) and ³¹P NMR (Figure 1 and Table III) are entirely consistent with the proposed formulation of the anion in 4.

(16) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* 1972, 36, 131.

(17) triphos = $PhP(CH_2CH_2PPh_2)_2$.

(18) Müller, I.; Rehder, D. *J. Organomet. Chem.* 1977, 139, 293.

(19) (a) Rehder, D. *J. Magn. Reson.* 1977, 25, 177. (b) *Ibid.* 1980, 38, 419. (c) Rehder, D.; Dorn, W. L.; Schmidt, J. *Transition Met. Chem. (Weinheim, Ger.)* 1978, 1, 233. (d) Schmidt, H.; Rehder, D. *Ibid.* 1980, 5, 214 and references cited therein.

Table I. Infrared Spectra for $V(CO)_5PR_3^-$

compd	medium	$\nu(CO),^a$ cm^{-1}
(1) $[Et_4N][V(CO)_5PPh_3]$	CH ₃ CN	1968 (m), 1817 (s)
(2) $[Et_4N][V(CO)_5dppe]$	THF	1965 (m), 1860 (sh), 1815 (s)
(3) $[Ph_4As][V(CO)_5dppe]$	THF	1965 (m), 1862 (m), 1815 (s)
(4) $[Et_4N][V(CO)_5dppm]$	CH ₃ CN	1965 (m), 1860 (sh), 1815 (s)
(5) $[Et_4N][V(CO)_5PPh_2NH_2]^b$	CH ₃ CN	1970 (m), 1815 (s)
(6) $[Ph_4P][V(CO)_5P_2Ph_4]$	CH ₃ CN	1963 (m), 1860 (sh), 1817 (s)
(7) $[Ph_4As][V(CO)_5P_2Ph_4]$	CH ₃ CN	1970 (m), 1822 (s)
(8) $[Et_4N][V(CO)_5(p\text{-}ClC_6H_4)_3P]$	CH ₃ CN	1968 (m), 1820 (s)
(9) $[Ph_4As][V(CO)_5PF_3]$	THF	2000 (m), 1890 (sh), 1863 (s)
(10) $[Et_4N][V(CO)_5PMe_3]$	CH ₃ CN	1969 (m), 1859 (sh), 1820 (s)
(11) $[Et_4N][V(CO)_5PPh_2H]^c$	CH ₃ CN	1970 (m), 1823 (s)

^a The weak shoulder or band observed at ca. 1860 cm^{-1} in the spectra of some species may arise from trace amounts of $V(CO)_5^-$ in the products. ^b $\nu(N-H)$: 3460 (vw, sh), 3350 (vw, sharp) cm^{-1} (thick Nujol mull). ^c $\nu(N-H)$: 2280 (w, sharp) cm^{-1} (Nujol mull).

Table II. ¹H NMR Spectral Data (δ , ppm) for $V(CO)_5PR_3^-$, ^{a, b}

compd	δ
1	7.2-7.6 (m, 15 H, C ₆ H ₅)
2	2.03-2.28 (m, 4 H, CH ₂), 7.29-7.77 (m, 20 H, C ₆ H ₅)
3	2.03-2.28 (m, 4 H, CH ₂) ^c
4	7.06-7.24, 7.32-7.60 (m, 20 H, C ₆ H ₅) ^d
5	2.28-2.54 (b, 2 H, NH ₂) ^e , 7.25-7.39, 7.42-7.76 (m, 10 H, C ₆ H ₅)
8	7.3-7.6 (m, 12 H, C ₆ H ₅)
10	ca. 1.3 (br, 9 H, CH ₃) ^f
11	6.65 (d, 1 H, $J_{PH} = 307$ Hz), 7.26-7.77 (m, 10 H, C ₆ H ₅)

^a Solvent = CD₃CN with Me₄Si reference. Spectra were taken on a 80-MHz Varian FT NMR. Tetraethylammonium cations in 1, 2, 4, 5, 8, 10, and 11 have very similar resonance positions: e.g., δ 1.22 (t of t, CH₃), 3.23 (q, CH₂). ^b ¹H NMR spectra are not shown for compounds 6, 7, or 9 as these consist only of uninformative broad overlapped multiplets due to phenyl proton resonance signals. See Table I for identification of salts. ^c The phenyl signals of dppe are overlapped with those of Ph₄As⁺. ^d The methylene resonance signal was obscured by the quartet arising from the methylene group of Et₄N⁺. For $[Ph_4P][V(CO)_5dppm]$, prepared from $[Ph_4P][V(CO)_5NH_3]$ and dppm, the methylene resonance signal was a triplet centered at 3.18 ppm ($J_{PH} = 4.3$ Hz). ^e Broad peak, 13 Hz at half-height. ^f A broad signal due to the methyl hydrogens of PMe₃ was almost entirely superimposed on the lowest field triplet of Et₄N⁺.

Table III. ³¹P {¹H} NMR Spectral Data for Selected $V(CO)_5PR_3^-$, ^{a, b}

compd	$\delta(^{31}P)$	
	coordinated	uncoordinated
1	+58	
3	+56.5	-13.0 (d, $J_{PP} = 37.5$ Hz)
4	+51	-24.9 (d, $J_{PP} = 75.1$ Hz)
5	+86.5	
7	+66	-0.4 (d, $J_{PP} = 233.5$ Hz)

^a rf = 40.5 MHz on a 100-MHz spectrometer. Spectra recorded at room temperature. ^b Solvent = CD₃CN for 1, 3, 4, and 5 and THF for 7. Positive chemical shifts (ppm) are downfield relative to 85% H₃PO₄ at room temperature. All of the coordinated phosphine signals are very broad (1340-1620 Hz). The values reported are the centers of these signals. The ³¹P NMR spectra of both dppe (2 and 3) and P₂Ph₄ (6 and 7) compounds are essentially identical. Spectra of Compounds 8-11 were not examined.

$[V(CO)_5Ph_2PNH_2]^-$ and $[V(CO)_5Ph_2PPPPh_2]^-$. While $V(CO)_5Ph_2P(CH_2)_nPPH_2^-$ ($n = 1, 2$) was synthesized in good yield by the reaction of $Na[V(CO)_5NH_3]$ with the

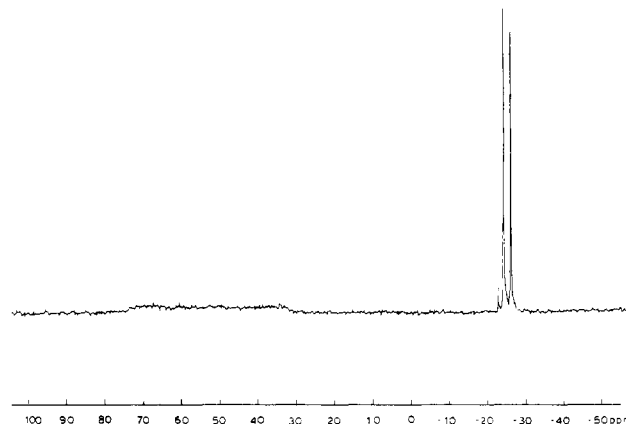


Figure 1. ³¹P{¹H} NMR Spectrum of $[Et_4N][V(CO)_5dppm]$. See Table III for peak positions.

appropriate phosphine in liquid ammonia cosolvent, attempts to obtain the corresponding $V(CO)_5Ph_2PPPPh_2^-$ by this reaction invariably failed. Instead good yields (70-75%) of a novel product (5) containing coordinated aminodiphenylphosphine were obtained. Duplicate elemental analyses on samples of 5 prepared from different reactions gave essentially the same results. The formulation of 5 as $[Et_4N][V(CO)_5PPh_2NH_2]$, containing a P-V bond, is also consistent with its ¹H NMR, ³¹P NMR, and infrared spectra. The NH₂ group 5 is observed in its Nujol mull infrared spectrum as a weak but sharp doublet (3460, 3350 cm^{-1}) and in the ¹H NMR spectrum as a broad and poorly resolved peak centered at 2.41 ppm. Complexes containing this ligand, which is unstable when not coordinated to a metal,²⁰ are quite uncommon but have been prepared by the ammonolysis of coordinated Ph₂PCl groups.²¹ It is not presently known how $V(CO)_5PPh_2NH_2^-$ forms in this reaction, since neither P₂Ph₄ nor $V(CO)_5P_2Ph_4^-$ (vide infra) react with liquid ammonia at -33° or ammonia/THF at room temperature.

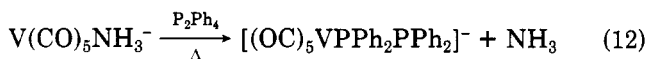
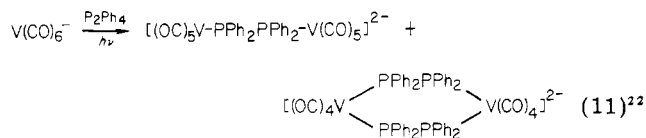
By contrast, bona fide $V(CO)_5P_2Ph_4^-$, containing an unligated PPh₂ group, was obtained from the reaction of preisolated $[Ph_4P][V(CO)_5NH_3]$ or $[Ph_4As][V(CO)_5NH_3]$ with P₂Ph₄ in THF. The deep red $[Ph_4P][V(CO)_5P_2Ph_4]$ (6) an orange-red $[Ph_4As][V(CO)_5P_2Ph_4]$ (7) were difficult to separate from unreacted P₂Ph₄ but were obtained in 44% and 35% yields, respectively, as analytical samples, spectroscopically free of uncoordinated P₂Ph₄. The infrared spectrum of (Table I) and, more importantly, the proton-decoupled ³¹P NMR spectrum (Table III) of

(20) Fluck, E. *Top. Phosphorous Chem.* 1967, 4, 291.

(21) Kraihanzel, C. S.; Bertsch, C. M. *J. Organomet. Chem.* 1972, 43, 343. Gray, G. M.; Kraihanzel, C. S. *Ibid.* 1978, 146, 23.

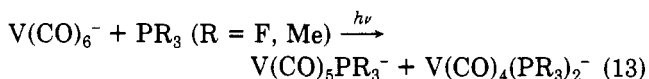
[Ph₄As][V(CO)₅P₂Ph₄] are consistent with the proposed formulation. The latter shows a broad line dowfield of the external H₃PO₄ standard characterization of a phosphorus bound to vanadium and a sharp doublet ($J_{pp} \sim 233.2$ Hz) upfield of the standard due to the unligated PPh₂ group. The infrared and NMR spectra of 6 and 7 are essentially identical.

It is noteworthy that the photolysis of V(CO)₆⁻ in the presence of P₂Ph₄ has yielded only products formulated as the binuclear bridged species, *cis*-[Et₄N]₂[(μ-P₂Ph₄)₂-V(CO)₄]₂⁻ and [Et₄N]₂[(μ-P₂Ph₄)V(CO)₅]₂⁻.²² Thus, this "labile ligand" method has again proven to be useful in the synthesis of materials unavailable by direct photosubstitution (eq 11 and 12).



[V(CO)₅PR₃]⁻ (R = *p*-ClC₆H₄, F, Me) and [V(CO)₅PPh₂H]⁻. Previously, it was reported that attempts to prepare phosphine derivatives of V(CO)₆⁻ using chlorine-substituted phosphine ligands were not successful. Although substitution products could be detected by IR spectroscopy, Rehder and co-workers indicated that rapid decomposition of the reaction mixture occurred upon UV irradiation even when a Duran filter was used.^{19c} Thus, although V(CO)₅P(*p*-FC₆H₄)₃⁻ was prepared by the photolysis of V(CO)₆⁻ in the presence of P(C₆H₄F)₃, the corresponding *p*-chlorophenyl derivative was not. On this basis, it was felt that the synthesis of V(CO)₅P(C₆H₄Cl)₃⁻ from the reaction of V(CO)₅NH₃⁻ and P(*p*-C₆H₄Cl)₃ would further demonstrate the value of this "labile ligand" route to new V(CO)₅L⁻ species. As indicated in the Experimental Section, the reaction provides excellent yields (85%) of [Et₄N][V(CO)₅(*p*-C₆H₄Cl)₃P], which is very similar to the well-established [Et₄N][V(CO)₅Ph₃P].

Rehder had previously reported that when V(CO)₆⁻ was photolyzed in the presence of PF₃ or PMe₃, there were formed both mono- and disubstituted complexes, which were not easily separated (eq 13).^{19a,d} Indeed, completely



substituted V(PF₃)₆⁻ was obtained in the presence of excess PF₃.^{19d} Although [Et₄N][V(CO)₅PF₃] was separated from most unreacted V(CO)₆⁻ and V(CO)₄(PF₃)₂⁻ and isolated as an analytically pure substance, it was mentioned in Rehder's report that ⁵¹V NMR and IR spectra of this material "exhibit admixtures of unsubstituted and multiply substituted complexes".^{19d} No yield was reported for [Et₄N][V(CO)₅PF₃], prepared by the direct photolysis method, so it is not possible to say whether the 43% yield of product obtained from [Ph₄As][V(CO)₅NH₃] represents a substantial improvement in this regard. However, compound 9 prepared by this "labile-ligand" method is entirely free of V(CO)₄(PF₃)₂⁻. The elemental analysis obtained for our product suggests that it could be contaminated by up to 5 mol % of [Ph₄As][V(CO)₆]; however, since the very intense E vibration of V(CO)₅PF₃⁻ at 1863 cm⁻¹ is almost superimposed on the single IR-active ν(CO) band of V(CO)₆⁻, it is not possible on the basis of a qualitative exam-

ination of the product's infrared spectrum to corroborate the presence of V(CO)₆⁻. The IR spectrum of a THF solution of [Ph₄As][V(CO)₅PF₃] shows ν(CO) bands at 2000 (m-sh), 1890 (sh), 1863 (vs) cm⁻¹, which is in good agreement with positions previously reported for these absorptions.^{19d}

A much better yield (74%) of product was obtained in the synthesis of V(CO)₅PMe₃⁻, which was previously only characterized on the basis of a solution infrared spectrum.^{19a} The bright orange-yellow product [Et₄N][V(CO)₅PMe₃] is quite air sensitive. Its infrared spectrum (Table I) agrees well with that previously reported for [V(CO)₅PMe₃]⁻.^{19a}

The final compound of this series [Et₄N][V(CO)₅PPh₂H] has not been reported previously, although the photo-promoted synthesis of the related V(CO)₅PH₃⁻^{19c} and V(CO)₅PPhH₂⁻^{19a} from V(CO)₆⁻ have been briefly described. Good yields (65%) of orange crystalline product were obtained by the substitution of V(CO)₅NH₃⁻ with diphenylphosphine in THF/ammonia. This substance has infrared (ν(PH) 2280 cm⁻¹ (w-sh)) and ¹H NMR spectra that are entirely consistent with the proposed formulation. Although we have not examined any chemical properties of V(CO)₅PPh₂H⁻, it should prove to be a useful precursor to phosphide-bridged bimetallic complexes containing vanadium.

Concluding Remarks. We have shown that V(CO)₅NH₃⁻ is a valuable precursor for the synthesis of a variety of phosphine-substituted carbonyl anions of vanadium. The yields of several previously established V(CO)₅PR₃⁻ species have been dramatically improved. Also, several new compounds of this general formulation have been prepared. The chemistry of most of these reactive anions is unknown. They should prove to be useful precursors to a variety of new organometallic compounds. The availability of the anions bearing unligated phosphine groups may prove to be particularly important in the synthesis of new heterobimetallic and polynuclear phosphine-bridged transition-metal compounds.

Throughout this discussion it has been emphasized that the use of the "labile ligand" method is often superior to the direct photosubstitution process for the generation of V(CO)₅PR₃⁻ species. Recently, we have been informed, however, that several of the compounds mentioned in this paper have been independently prepared by an indirect photolysis method which involves the photogeneration of V(CO)₅(Me₂SO)⁻ (Me₂SO = dimethyl sulfoxide) by the photolysis of V(CO)₆⁻ in the presence of Me₂SO. The Me₂SO complex then reacts thermally with a variety of π-acceptor ligands to generate V(CO)₅L⁻.²³ It is likely that the procedure described in this paper and the "indirect photolysis" method represent complementary strategies for synthesis of M(CO)_xL⁻ species which are not readily available by other methods.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE79-12159) for support of this research. J.E.E. thanks Dr. D. Rehder (Hamburg) for informing us of his studies concerning V(CO)₅(Me₂SO)⁻ before publication.

Registry No. 1, 10170-61-3; 2, 34089-19-5; 3, 82495-28-1; 4, 82495-30-5; 5, 82495-32-7; 6, 82495-34-9; 7, 82495-35-0; 8, 78969-84-3; 9, 82495-36-1; 10, 82510-89-2; 11, 82495-38-3; Na[V(CO)₅NH₃], 81831-31-4; [Ph₄As][V(CO)₅NH₃], 78937-16-3; [Ph₄P][V(CO)₅NH₃], 36580-51-5.