Organometallics 1982, 1, 898–903

Highly Reduced Organometallics. 7.[1] The Synthesis of Alkyl and Phenyl Isocyanide and Related Monosubstituted Vanadium Carbonyl Anions, $V(CO)_5L^-$, by the Thermal Substitution of (Amine)pentacarbonylvanadate(1–), $V(CO)_5NH_3^-$

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Received March 29, 1982

(Amine)pentacarbonylvanadate(1–) reacts with various isocyanides, RNC (R = Me, c-Hx, *t*-Bu, Ph) to form $[V(CO)_5CNR]^-$ in high yields (60–85%). These anions have been characterized by elemental analysis and infrared and ^1H NMR spectra and are the first examples of (isocyanide)pentacarbonylvanadate ions. Treatment of $Na[V(CO)_5NH_3]$ with NaCN in liquid ammonia provides, after cation exchange, up to 56% yields of $[Et_4N]_2[V(CO)_5CN]$. The reactions of $[V(CO)_5NH_3]^-$ with *n*-BuNC and acetonitrile also provide $V(CO)_5L^-$ species. On the basis of infrared spectra, these materials are formulated as $[V(CO)_5CN\text{-}n\text{-}Bu]^-$ and $V(CO)_5(CH_3CN)^-$, respectively. The latter product was isolated in 30% yield as a thermally unstable Ph_4As^+ salt.

Introduction

For many years an important method for the synthesis of a wide variety of substituted neutral and cationic carbonyls and related organometallics has involved ligand substitution reactions of complexes bearing easily displaced ligands. These labile ligands are generally non or weak π acceptors such as ethers, amines, halides, nitriles, olefins, etc. Five representative examples of such reactions are shown in eq 1–5.

$$\mathrm{Mn(CO)_3(arene)^+ + dien \xrightarrow{-arene} Mn(CO)_3(dien)^+} \qquad (1)$$ [2]

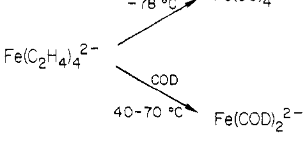
$$\mathrm{W(CO)_3(CH_3CN)_3 + cycloheptatriene \xrightarrow{-3CH_3CN} W(CO)_3(\eta\text{-}C_7H_8)} \qquad (2)$$ [3]

$$\mathrm{W(CO)_3(diglyme) + COT \xrightarrow{-diglyme} W(CO)_3(C_8H_8)} \qquad (3)$$ [4]

$$\mathrm{W(CO)_5Br^- + CH_3Li \xrightarrow[-Br^-]{THF} LiW(CO)_5CH_3} \qquad (4)$$ [5]

$$\mathrm{C_5H_5Re(CO)_2THF + N_2 \xrightarrow[-THF]{toluene} C_5H_5Re(CO)_2N_2} \qquad (5)$$ [6]

Only recently has this "labile ligand" procedure been extended to metal complexes containing transition metals in formally negative oxidation states. Undoubtedly the most spectacular results in this area have been obtained by K. Jonas and co-workers.[7] They have shown that $Fe(C_2H_4)_4^{2-}$ readily sheds all coordinated ethylene in the presence of CO or COD as shown in eq 6. We have observed more recently that phosphines in $Fe(CO)_3PR_3^{2-}$ are quite labile.[7] It appears that the coordinated phosphine is strongly repelled by the negative charge on the $Fe(CO)_3^{2-}$ unit. By contrast, the ligands in $Fe(CO)_4^{2-}$ are inert to thermal displacement at normal temperatures, as they are in $Co(CO)_4^-$, $Mn(CO)_5^-$, and $V(CO)_6^-$.[8]



(6)

Recently, we discovered that the reaction of $V(CO)_5^{3-}$ with ammonium chloride in liquid ammonia provided nearly quantitative yields of $V(CO)_5NH_3^-$. The observed thermal instability of this amine complex suggested that the coordinated ammonia might be quite labile. In the presence of a variety of potential π-acceptor ligands, L, it was possible to obtain high yields of $V(CO)_5L^-$ which were not readily accessible by photosubstitution methods. In this paper the synthesis and characterization of several new $V(CO)_5L^-$ complexes are discussed in detail, including the first examples of isocyanide-substituted carbonyl anions of vanadium, $V(CO)_5CNR^-$. A preliminary account of portions of this work has appeared previously.[9]

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 cannulae and syringes; otherwise reactions were generally performed by using standard Schlenck apparatus with a double manifold vacuum line. Ammonia was dried with Na metal and distilled in vacuo directly into the reaction vessel. Reagent grade acetonitrile was dried with CaH_2, freed of oxygen by a nitrogen purge, and distilled immediately before use. Reagent grade tetrahydrofuran and diethyl ether were distilled from alkali-metal benzophenone ketyls before use. Reagent grade acetone, heptane, absolute ethanol, and isopentane were freed of oxygen by bubbling nitrogen through the solvents for 1–2 h before use.

The following reagents were purchased from commercial sources and freed of oxygen before use: ammonium chloride, benzyltriphenylphosphonium chloride, bis(diglyme)sodium hexacarbonylvanadate, bis(triphenylphosphin)iminium chloride, cyclohexyl isocyanide, sodium cyanide, *tert*-butyl isocyanide, *n*-butyl isocyanide, tetraethylammonium bromide, and tetraphenylphosphonium bromide. Phenyl isocyanide,[17d] methyl isocyanide,[17d]

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and tetraethylammonium hexacarbonylvanadate[8c] 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 Corporation drybox under continuously recirculating nitrogen. NMR samples sealed into 5-mm Pyrex tubes were run on a Varian FT-80 or XL-100 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 Labortorien.

Sodium (Amine)pentacarbonylvanadate(1−), Na[V(CO)$_5$NH$_3$] (1). Liquid ammonia (75 mL) was distilled into a cold flask (−78 °C) containing $[Na(diglyme)_2][V(CO)_6]$ (2.0 g, 3.9 mmol), Na metal (0.27 g, 11.7 mmol), and a glass-covered stir bar. The mixture was refluxed at −33 °C for approximately 1 h, until the color of the solution turned from dark blue to red. After the solution was cooled to −78 °C, solid NH_4Cl (0.63 g, 11.7 mmol) was added all at once. Immediately the solution turned orange and bubbled vigorously. As the gas evolution ceased, the solution turned red-purple, the color of $Na[V(CO)_5NH_3]$ in solution. To ensure complete conversion to 1 the reaction mixture was refluxed at −33 °C for 45 min. The solution of 1 was always cooled to −78 °C for the substitution and cation metathesis reactions. Unless otherwise noted, all of the following syntheses were conducted with the following quantities of reactants and solvent: 2.0 g of $[Na(diglyme)_2][V(CO)_6]$, 0.27 g of Na, and 0.63 g of NH_4Cl in 75 mL of liquid ammonia.

Tetraphenylarsonium (Amine)pentacarbonylvanadate(1−), [Ph$_4$As][V(CO)$_5$NH$_3$] (2). The preparation of 2 from 1 has already been described in an earlier paper.[19]

Tetraphenylphosphonium (Amine)pentacarbonylvanadate(1−), [Ph$_4$P][V(CO)$_5$NH$_3$] (3). A cold (−78 °C) solution of Ph_4PBr in EtOH (1.97 g of Ph_4PBr, 4.7 mmol in 40 mL of EtOH) was added by cannula to a stirred solution of 1, also at −78 °C. A dark purple solid formed. The mixture was refluxed at −33 °C for 30 min to ensure a complete metathesis. Next it was cooled to −78 °C and then transferred by cannula into a jacketed low-temperature frit[19] (−78 °C) and filtered. The filtrate was pinkish yellow. Dark purple 3 remained on the frit. It was washed with three 20-mL portions of 6 M NH_4OH at 0 °C to remove NaBr, three 20-mL portions EtOH to remove unmetathesized Ph_4PBr, 10-mL of acetone to remove $[Ph_4P][V(CO)_6]$ and dried in vacuo for 12 h. Dark purple crystalline 3 was obtained (1.68 g, 78% yield). Compound 3 is moderately air sensitive, gradually turning black after several hours. It is indefinitely stable at room temperature under nitrogen but decomposes rapidly above 130 °C. It is insoluble in diethyl ether, alkanes, EtOH, and aqueous ammonia. It is slightly soluble in liquid ammonia and acetone and is very soluble with complete decomposition in CH_3CN and THF. Compound 3 reacts more quickly than 2 in substitution reactions in these solvents. This substance was previously synthesized in substantially lower yields by the photolysis of $V(CO)_6^-$ in liquid ammonia.[10]

Bis(triphenylphosphin)iminium (Amine)pentacarbonylvanadate(1−), [PNP][V(CO)$_5$NH$_3$] (4). Bis(triphenylphosphin)iminium chloride (2.8 g of [PNP]Cl, 4.9 mmol) in a cold (−78 °C) ethanol solution (20 mL) was added by cannula to a stirred solution of 1 at −78 °C. Immediately the solution became bright red and a bright red solid formed. After 15 min the solid had darkened considerably as the crystal size increased. The mixture was stirred for 30 min to ensure complete metathesis and then was transferred onto a low-temperature frit (see Figure 1 of ref 19). A light orange filtrate was elluted, and the solid product 4 was very dark purple. Compound 4 was washed with three 20-mL portions of 6 M NH_4OH, at 0 °C, three 20-mL portions of EtOH at −40 °C, three 20-mL portions of diethyl ether at −40 °C and dried in vacuo for 30 min. Dark purple crystalline 4 was obtained as 2.75 g (91% yield). Unfortunately 4 is unstable at room temperature temperature and decomposes completely within a few hours to a black solid which contains $[PNP][V(CO)_6]$. Compound 4 appears to be stable below 0 °C but is very air sensitive, and it immediately oxidizes in air with liberation of heat to form greenish products, including $[PNP][V(CO)_6]$.

Benzyltriphenylphosphonium (Amine)pentacarbonylvanadate(1−), [PhCH$_2$Ph$_3$P][V(CO)$_5$NH$_3$] (5). A cold solution (−78 °C) of benzyltriphenylphosphonium chloride (1.84 g, 4.9 mmol) in 40 mL of ethanol was transferred to a stirred, cold solution (−78 °C) of 1. The solution changed from dark purple to salmon pink and NaCl precipitated. Unfortunately, 5 was soluble in the liquid ammonia–ethanol mixture and colud not be isolated in the same manner as 2–4. After much of the ammonia had evaporated at temperatures above −33 °C, beautiful large red but thermally unstable crystals formed. However, attempts to isolate the product by rapid addition of cold (0 °C) 6 M NH_4OH (80 mL) gave $[PhCH_2Ph_3P][V(CO)_6]$ (1.31 g, 56%) as the only characterized product.

Tetraethylammonium (Cyclohexyl isocyanide)pentacarbonylvanadate(1−), [Et$_4$N][V(CO)$_5$CNC$_6$H$_{11}$] (6). A cold (−40 °C) acetonitrile solution of cyclohexyl isocyanide (40 mL of CH_3CN, 1.5 mL (approximately 12 mmol) of cyclohexyl isocyanide) was transferred to a cold solution of 1 at −78 °C. Solid Et_4NBr (1.64 g, 7.8 mmol) was added all at once. The mixture was then slowly warmed to room temperature overnight. The remaining solvent was removed. The residue was dissolved in THF to give a turbid solution which was filtered (medium porosity frit). Evaporation of solvent from the filtrate eventually caused the formation of feathery bright yellow crystals. The solid was triturated with 70 mL of diethyl ether. Another 40 mL of Et_2O was added, and the slurry was transferred onto a frit. This process was repeated with an additional 40 mL of diethyl ether. The light yellow 6 was recrystallized from an acetone–ether mixture and washed with ethanol 3 × 20 mL) and Et_2O (2 × 20 mL) before drying in vacuo. Bright shiny yellow plates of $[Et_4N][V(CO)_5CNC_6H_{11}]$ were obtained in 70% yield (1.2 g). Anal. Calcd for $C_{20}H_{31}N_2O_5V$: C, 55.81; H, 7.26; N, 6.51. Found: C, 55.84; H, 7.24; N, 6.50.

Crystalline 6 is moderately air sensitive and decomposes to a white material after 15–20 min. Solutions or wet crystals decompose rapidly. Compound 6 is insoluble in diethyl ether, ethanol, and alkanes. It is quite soluble in tetrahydrofuran, acetone, and acetonitrile. The solid is indefinitely stable at room temperature and melts at 109–110 °C.

Tetraethylammonium (Methyl isocyanide)pentacarbonylvanadate(1−), [Et$_4$N][V(CO)$_5$CNCH$_3$] (7). A solution of 1 was prepared as described previously with the following quantities of materials: $[Na(diglyme)_2][V(CO)_6]$ (5.0 g, 9.8 mmol), Na (0.68 g, 30 mmol), NH_4Cl (1.59 g, 30 mmol), and liquid ammonia (200 mL). Subsequently, cold acetonitrile (60 mL at −40 °C), Et_4NBr (12.6 g, 60 mmol, and then methyl isocyanide (1.5 mL, ca. 29 mmol) were added.

After the solution was slowly warmed to room temperature, the solvent was removed in vacuo. The residue was triturated with 40 mL of isopentane, dried, and subsequently dissolved in 140 mL of THF. The resulting orange solution was then filtered. The insoluble material was washed with THF until the washings were colorless. Evaporation of the solvent left a bright yellow solid 7. The solid was scraped off the walls of the flask and washed with 40 mL of diethyl ether. Recrystallization from acetone–diethyl ether formed light yellow plates of 7. The crystals were washed with ethanol (20 mL) and ether (2 × 10 mL) and then were dried. Compound 7 was obtained in 68% yield (2.35 g). Anal. Calcd for $C_{15}H_{23}N_2O_5V$: C, 49.73; H, 6.40; N, 7.73. Found: C, 50.03; H, 6.01; N, 7.63.

Crystalline 7 is moderately air sensitive and oxidizes rapidly in solution to non-carbonyl-containing materials. Compound 7 is insoluble in alkanes and ether. It is moderately soluble in ethanol and is soluble in acetone, acetonitrile, and tetrahydrofuran. Although 7 is indefinitely stable at room temperature, it begins decomposing slowly above 120 °C and is totally decomposed without melting at 190 °C.

Tetraphenylarsonium (Methyl isocyanide)pentacarbonylvanadate(1−), [Ph$_4$As][V(CO)$_5$CNCH$_3$] (8). Solid $[Ph_4As][V(CO)_5NH_3]$ (1.00 g, 1.70 mmol) was added to a cold (0 °C) stirred solution of methyl isocyanide (0.6 mL, ca. 12 mmol) in 50 mL of THF. After 45 min all of the purple crystals of 2 had dissolved. Evaporation of the THF left a free-flowing red

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solid. The solid was dissolved in 40 mL of acetone and filtered. Concentration of the acetone and slow dropwise addition of diethyl ether produced golden red needles of **8**. The crystals were washed with 20 mL of diethyl ether and 5 mL of absolute ethanol and dried in vacuo for 12 h. Analytically pure **8** was isolated in good yield (0.86 g, 83%). Anal. Calcd for $C_{31}H_{23}AsNO_5V$: C, 60.50; H, 3.77; N, 2.28. Found: C, 60.05; H, 3.87; N, 2.35.

Crystalline $[Ph_4As][V(CO)_5CNCH_3]$ is stable in air for several hours. Solutions of **8** are more air sensitive and show decomposition within a few minutes. Compound **8** is soluble in acetone, acetonitrile, and THF and slightly soluble in ethanol. It is insoluble in alkanes and diethyl ether. Compound **8** is stable at room temperature under nitrogen and melts with decomposition (it bubbles and turns black) at 128 °C.

Tetraethylammonium (*tert*-Butyl isocyanide)pentacarbonylvanadate(1−), $[Et_4N][V(CO)_5CN\text{-}t\text{-}Bu]$ (9). To a stirred solution of **1** at −78 °C was added 1.0 mL of *t*-BuNC (ca. 2.3 mmol), followed by 2.5 g of $Et_4N^+Br^-$ (11.9 mmol). The solution was allowed to warm gradually to room temperature over a period of 12 h. All solvent was removed from the resulting orange slurry. The residue was dissolved in 60 mL of THF. After being filtered (medium porosity fritted disk), the volume of the deep orange solution was reduced to about 10 mL and excess ether (~150 mL) was added slowly with stirring. By this procedure crystalline product readily formed. This was washed with ether (2 × 50 mL). The brown-yellow supernatant was rejected. An additional crystallization from THF–ether gave the analytical sample in 76% yield (1.20 g). Due to the slight solubility of the product in this mixed solvent system, each crystallization results in a diminished yield. Anal. Calcd for $C_{18}H_{29}N_2O_5V$: C, 53.46; H, 7.23; N, 6.93. Found: C, 53.65; H, 7.40; N, 7.10.

The product forms slightly oxygen-sensitive crystals which decompose after several minutes exposure at room temperature. Solutions of **9** are much more air sensitive and rapidly decolorized to give a pale flocculent solid which contains no bands in the ν(CO) region. The solubility properties of this material are very similar to those of compound **7**. Compound **9** darkens above 100 °C and melts with decomposition at 102–105 °C.

Tetraethylammonium (*n*-Butyl isocyanide)pentacarbonylvanadate(1−), $[Et_4N][V(CO)_5CN\text{-}n\text{-}Bu]$ (10). All reaction conditions are identical with those described for compound **9**, except 0.85 mL of *n*-BuNC was added. After all solvent was removed, a yellow gum was obtained. This was triturated with heptane (4 × 20 mL) to remove free *n*-BuNC. Dissolution of the product in THF gave a yellow-orange solution. A yellow oil formed on addition of excess ether to the concentrated THF solution. It did not solidify on addition of pentane. On standing at −20 °C the compound did crystallize but remelted above 0 °C. The species may be a low melting solid. No attempts to obtain elemental analyses for the oil were made, so the purity of compound **10** is unknown. Infrared solution spectra of **10**, however, show $[V(CO)_5CN\text{-}n\text{-}Bu]^-$ to be the only carbonyl-containing species present after several attempts at crystallizations. The substance is moderately soluble in ether and is thereby easily separated from any $[Et_4N][V(CO)_6]$ formed in this reaction, since the latter species is almost completely insoluble in diethyl ether.

Tetraethylammonium Cyanopentacarbonylvanadate(2−), $[Et_4N]_2[V(CO)_5CN]$ (11). A solution of **1** was prepared and cooled to −78 °C. Solid NaCN (2.00 g, 39.2 mmol) and tetraethylammonium bromide (4.19 g, 19.6 mmol) were added with a bent Schlenck tube, along with cold acetonitrile (40 mL, −40 °C). The reaction mixture was allowed to warm to room temperature, and the ammonia was evaporated.

Removal of the solvent in vacuo left a dry yellow gold solid. THF was added to the slurry which was triturated and then filtered. The insoluble solid was washed with THF until the filtrate was colorless to remove $[Et_4N][V(CO)_6]$. (Approximately 120 mL of THF was required.) The solid was dried in vacuo and subsequently extracted with acetonitrile (5 × 20 mL). The orange filtrate was concentrated, and then diethyl ether was added to precipitate a yellow solid. The slurry was poured onto a frit and filtered. The solid was washed with 3 × 20 mL of EtOH to remove Et_4NBr and 20 mL of Et_2O and then dried in vacuo. Bright yellow microcrystalline **11** was obtained in 56% yield. Compound **11** is soluble in acetonitrile. It is insoluble in THF, diethyl ether, alkanes, and absolute ethanol. $[Et_4N]_2[V(CO)_5CN]$ is quite air sensitive but is stable when stored under nitrogen at room temperature. At temperatures above 95 °C, compound **11** decomposes gradually to form a black solid. Anal. Calcd for $C_{22}H_{40}N_3O_5V$: C, 55.34; H, 8.44; N, 8.80. Found: C, 54.84; H, 8.57; N, 9.23.

The infrared solution spectrum of **11** is identical with that previously reported[10] for $[Ph_4P]_2[V(CO)_5CN]$. Interestingly, this material was described as a black solid which dissolved in CH_3CN to give a deep red solution.

Tetraphenylarsonium (Acetonitrile)pentacarbonylvanadate(1−), $[P_4As][V(CO)_5CH_3CN]$ (12). Compound **2** (0.50 g, 0.85 mmol) was cooled in a vessel to −40 °C, and cold CH_3CN was added (8 × 5 mL) until all of **2** had dissolved. The solution was slowly concentrated in vacuo at −40 °C. Cold (−40 °C) toluene (150 mL) and hexane (300 mL) were added, and a red-brown solid precipitated out. The solid was filtered at low temperature (−40 °C) and washed with isopentane (1 × 10 mL and 1 × 20 mL) and pumped on until dry and free flowing (ca. 15 min). Within several minutes at room temperature, the compound began to decompose, changing from a brick-red to a dark brown solid. Among the decomposition products is $[Ph_4As][V(CO)_6]$. The isolated yield of **12** was 0.16 g (30% yield). Unfortunately, **12** is only stable for a short time at room temperature. However, it appears to suffer no change below 15 °C under an inert atmosphere.

Tetraethylammonium (Phenyl isocyanide)pentacarbonylvanadate(1−), $[Et_4N][V(CO)_5CNC_6H_5]$ (13). Phenyl isocyanide (1.5 mL, approximately 12 mmol) in cold CH_3CN (40 mL, −40 °C) was transferred into a stirred solution of **1** at −78 °C. Solid Et_4NBr (1.64 g, 7.8 mmol) was added all at once. The reaction mixture slowly warmed to room temperature overnight.

After the solvent was removed in vacuo, the residue was triturated with isopentane (40 mL). Then the product was dissolved in 60 mL of THF to form a cherry red solution and filtered. Concentration of the solution and slow addition of diethyl ether produced orange crystals of **13**. The crystals were filtered, washed with diethyl ether, and dried in vacuo. Analytically pure **13** was obtained in 70% yield (1.17 g). Anal. Calcd for $C_{20}H_{25}N_2O_5V$: C, 56.51; H, 5.94; N, 6.60. Found: C, 56.64; H, 5.87; N, 6.75.

$[Et_4N][V(CO)_5CNPh]$ is quite air sensitive in solution and as a crystalline solid. It is indefinitely stable at room temperature but decomposes slowly above 65 °C. It is insoluble in diethyl ether, alkanes, and alcohol. It is very soluble in acetone, THF, and CH_3CN.

Results and Discussion

Photosubstitution of phosphines and related ligands into $V(CO)_6^-$ has been the standard method for the synthesis of $[V(CO)_{6-x}L_x]^-$ (x = 1–3; L = PR_3, AsR_3, etc.).[10,11]

$$V(CO)_6^- + xL \xrightarrow{h\nu} [V(CO)_{6-x}L_x]^- + xCO \qquad (7)$$

Other less important methods include the reduction of either an appropriate neutral $V(CO)_{6-x}L_x$ or $Ph_3SnV(CO)_{6-x}L_x$. Specific examples are

$$V(CO)_5PPh_3 \xrightarrow{Na/Hg} V(CO)_5PPh_3^- \qquad (8)^{8c}$$

$$Ph_3SnV(CO)_4dppe \xrightarrow{Na/Hg} V(CO)_4dppe^- + 0.5(Ph_6Sn_2) \qquad (9)^{12}$$

The use of neutral $V(CO)_{6-x}L_x$ in the preparation of corresponding monoanions is severely limited since the neutral complexes must often be prepared from the desired monoanion. Because $V(CO)_6$ is very susceptible to base induced disproportionation reactions, neutral $V(CO)_{6-x}L_x$ are often unknown and not available from the reaction of $V(CO)_6$ and L, particularly if L is very basic. For example, *o*-phenylenebis(dimethylarsine) (diars) and ammonia

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Table I. Infrared and ^{1}H NMR Spectra for $V(CO)_5L^-$

compd	medium	ν(CN), cm^{-1}	ν(CO),[b] cm^{-1}	chem shift,[a] ppm
$[Ph_4As][V(CO)_5NH_3]$ (**2**)	Nujol		1965 w, 1780 s (b), 1750 s (b)	*b*
$[Ph_4P][V(CO)_5NH_3]$ (**3**)	Nujol		1956 w, 1780 s (b), 1750 s (b)	*b*
$[PNP][V(CO)_5NH_3]$ (**4**)	Nujol		1960 w, 1780 s (b), 1740 s (b)	*b, d*
$[Et_4N][V(CO)_5CNC_6H_{11}]$ (**6**)	CH_3CN	2080 w	1955 m, 1825 s	1.35–1.82 (m, 11 H)[h]
$[Et_4N][V(CO)_5CNCH_3]$ (**7**)	CH_3CN	2120 w	1965 m, 1860 sh, 1830 s	*c*
$[Ph_4As][V(CO)_5CNCH_3]$ (**8**)	CH_3CN	2120 w	1970 m, 1830 s	3.18 (b s, 3 H)
$[Et_4N][V(CO)_5CN\text{-}t\text{-}Bu]$ (**9**)	CH_3CN	2090 w, 2060 sh	1965 m, 1862 sh, 1830 s	1.39 (s, 9 H)
$[Et_4N][V(CO)_5CN\text{-}n\text{-}Bu]$ (**10**)	CH_3CN	2090 w	1968 m, 1861 sh, 1828 s	*d*
$[Et_4N]_2[V(CO)_5CN]$ (**11**)	CH_3CN	2060 w	1960 m, 1795 s, 1750 m	*e*
$[Ph_4As][V(CO)_5CH_3CN]$ (**12**)	CH_3CN	*g*	1970 w, 1820 s, 1770 sh	*b, d*
$[Et_4N][V(CO)_5CNPh]$ (**13**)	CH_3CN	2050 w	1940 m, 1842 s, 1595 m	7.05–7.46 (5 H)
	THF	2040 w	1930 m, 1845 s, 1595 m	

[a] Solvent = CD_3CN; Me_4Si reference; resonance positions of cation signals are not shown. Multiplicity in parentheses. [b] ^{1}H NMR spectra of $V(CO)_5NH_3^-$ and $V(CO)_5CH_3CN^-$ were not obtained since they decompose rapidly in solvents under ambient conditions. [c] Methyl resonance position of CH_3NC in **7** is obscured by overlap of the methylene resonance signal of Et_4N^+. [d] This compound was not isolated as an analytically pure substance. [e] Tetraethylammonium cations in the various compounds have very similar ^{1}H NMR spectra: δ 1.34 (t of t, 12 H, CH_3), 3.46 (q, 8 H, CH_2). [f] A weak shoulder at ca. 1860 cm^{-1} was observed in some spectra. This may arise from trace amounts of $V(CO)_6^-$ in the products.[20] [g] The ν(CN) of coordinated CH_3CN was not observed in CH_3CN solution spectra of **12**. [h] Part of this broad multiplet overlaps the methyl peak of Et_4N^+.

readily disproportionate $V(CO)_6$ according to eq 10 and 11.[13] Similarly, compounds of the type $Ph_3SnV(CO)_{6-x}L_x$

$$2V(CO)_6 + 2\text{diars} \xrightarrow{\text{hexane}} [V(CO)_3(\text{diars})_2{}^+][V(CO)_6{}^-] + 3CO \quad (10)^{11c}$$

$$3V(CO)_6 + 6NH_3 \rightarrow [V(NH_3)_6][V(CO)_6]_2 + 6CO \quad (11)^{14}$$

are generally prepared by the reaction of Ph_3SnCl and $V(CO)_{6-x}L_x{}^-$.[15] In some cases these tin derivatives can also be prepared in moderate yields by the thermal substitution of $Ph_3SnV(CO)_6$ by L,[15] but if L is a good base, heterolytic cleavage of the Sn–V bond occurs preferentially. For example

$$Ph_3SnV(CO)_6 + n\text{THF} \rightarrow Ph_3Sn(\text{THF})_n{}^+ + V(CO)_6{}^- \quad (12)^{15}$$

$$Ph_3SnV(CO)_6 + \text{dmpe} \rightarrow Ph_3Sn(\text{dmpe})^+ + V(CO)_6{}^- \quad (13)^{12}$$

Attempts to extend the photosubstitution method represented by eq 1 to the synthesis of $V(CO)_5CNR^-$ have been unsuccessful.[16] However, recently we discovered that $V(CO)_5NH_3^-$ readily undergoes thermal substitution by various isocyanides in acetonitrile–ammonia, THF–ammonia, or neat THF from −20 to 0 °C to give high isolated yields of $V(CO)_5CNR^{1-}$; i.e.

$$V(CO)_5NH_3^- + CNR \rightarrow V(CO)_5CNR^- + NH_3 \quad (14)$$

The only previously reported isocyanide-substituted carbonyl monoanions are $Mn(CO)_{5-x}(CNCH_3)_x{}^-$, $x = 1$–3,[17a] and various $C_5H_5M(CO)_{3-x}(CNR)_x{}^-$ (M = Mo, R = Me, x = 1, 2; M = Mo, R = Ph, x = 1; M = W, R = CH_3, x = 1).[17b,c] These were all prepared by sodium amalgam reduction of the corresponding substituted neutral halometal carbonyls. Recently, various $Co(CO)_3CNR^-$ (R = C_6H_{11}, *tert*-butyl, etc.) have been prepared in this laboratory.[18] This paper also includes discussions on the syntheses and properties of $V(CO)_5NH_3^-$, $V(CO)_5(CH_3CN)^-$, and $V(CO)_5CN^{2-}$, the only substituted carbonyl dianion prepared by this procedure, presently.

(Amine)pentacarbonylvanadate(1−) Ion. Treatment of a liquid ammonia solution of $Na_3V(CO)_5$[19] with 2 or more equiv of NH_4Cl gives high yields of magenta $Na[V(CO)_5NH_3]$ (**1**); i.e.

$$V(CO)_5{}^{3-} + 2NH_4{}^+ \xrightarrow{NH_3(l)} V(CO)_5NH_3{}^- + NH_3 + H_2\uparrow \quad (15)$$

In this reaction, the $V(CO)_5{}^{3-}$ is undoubtedly protonated twice to give the very unstable putative intermediate $H_2V(CO)_5{}^-$ which reductively eliminates hydrogen to provide **1**. Although **1** appears to be indefinitely stable in liquid ammonia from −78 to −33 °C, it rapidly decomposes upon removal of the ammonia to give a yellowish brown solid in which $V(CO)_6^-$ is the only metal carbonyl product. Other alkali metals including Li^+, K^+, Rb^+, and Cs^+ also form thermally unstable and ammonia-soluble salts of $V(CO)_5NH_3^-$. The complex cations Me_4N^+ and Et_4N^+ give thermally unstable and ammonia-soluble salts of $V(CO)_5NH_3^-$, while the larger cations PNP^+, Ph_4P^+, and Ph_4As^+ provide insoluble salts. Of the latter salts only $[Ph_4As][V(CO)_5NH_3]$ (**2**) and $[Ph_4P][V(CO)_5NH_3]$ (**3**) are indefinitely stable at room temperature under a nitrogen atmosphere. The PNP salt **4** is stable for periods of up to 30 min at room temperature but decomposes almost completely within 24 h to a black solid in which $[PNP][V(CO)_6]$ is the only carbonyl-containing product. Undoubtedly, the relative stability of the crystalline lattice of **2** and **3** plays an important role in stabilizing the $V(CO)_5NH_3^-$ anion. It is rather surprising that $PhCH_2Ph_3P^+$ and Ph_4P^+ behave so differently in this regard since these two cations often considered to be interchangable in the preparation of inorganic and organometallic anions. For example, compound **5** containing $PhCH_2Ph_3P^+$, is quite soluble in ammonia and very thermally unstable (above 0 °C) as a solid, while compound **3**, containing Ph_4P^+, is only slightly soluble in ammonia and is thermally stable

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(13) A survey of the reactions of $V(CO)_6$ appears in: Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

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

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

(16) Another group also has had no success in the synthesis of $V(CO)_5CNR^-$ by the direct photosubstitution method: Rehder, D., private communication.

(17) (a) Adams, R. D. *Inorg. Chem.* **1976**, *15*, 174. (b) Adams, R. D. *Ibid.* **1976**, *15*, 169. (c) Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544. (d) Casanova, J.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.

(18) These have been made in up to 70% yield by the procedure

$$Na_3Co(CO)_3 \xrightarrow[NH_3]{2NH_4{}^+} \xrightarrow[-78\ ^\circ C]{RNC} H_2 + 2Na^+ + Na[Co(CO)_3CNR]$$

Ellis, J. E.; Warnock, G., unpublished results.

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

at room temperature as a solid. The relative solubilities of the Ph_4As^+ (**2**). Ph_4P^+ (**3**) and PNP^+ (**4**) salts in THF and other solvents are $4 > 3 \gg 2$ and parallel their relative susceptibility toward aerial oxidation as crystalline solids. Crystalline **2** is practically insoluble in THF at room temperature and may be handled for several minutes in air without observable change. By contrast, **3** and **4** oxidize rapidly in air. As was mentioned in the Experimental Section, compound **3** was first prepared in 54% yield by the photolysis of $V(CO)_6^-$ in liquid ammonia for 24 h.[10] Our synthesis of **3** and other salts by the protonation of $V(CO)_5^{3-}$ in the liquid ammonia represents a significantly easier and higher yield route to this useful anion.

Infrared spectra of crystalline **2**–**4** in the $\nu(CO)$ region (see Table I) are very similar and characteristically show a sharp band of medium intensity (at ca. 1960 cm^{-1}) and a broad band of strong intensity at much lower energy (ca. 1755 cm^{-1}) which is often bifurcated in pure crystalline samples. The relative intensities and positions of these bands are reasonable in terms of previously reported spectra of $V(CO)_5L^-$ complexes.[20] Also, weak bands are observed at ca. 1580 cm^{-1} which are attributable to $\nu(C{=}C)$ of the phenyl groups of the cations. Concentrated Nujol mull spectra of **2** show very weak bands at 3475 (sh), 3390 (b), and 3320 (sh) cm^{-1} which are probably due to $\nu(N{-}H)$ of coordinated NH_3. The only other significant absorptions present in the 4000–3000-cm^{-1} region in mull spectra of **2** occur at 3085 (sh) and 3060 (w) cm^{-1} and are due to $\nu(C{-}H)$ of Ph_4As^+.

Substitution Reactions of $V(CO)_5NH_3^-$. The easiest way to synthesize $V(CO)_5L^-$ species from $V(CO)_5NH_3^-$, where L is a π-acceptor group, is to add the appropriate ligand in a THF or acetonitrile solution to a liquid ammonia solution of **1** prepared in situ at −33 °C to −78 °C. The resulting mixture is then allowed to slowly warm to room temperature while most of the ammonia escapes. At −20 to 0 °C the substitution process is rapid. Interestingly, $V(CO)_5NH_3^-$ does not appear to undergo any facile thermally promoted substitution reactions in liquid ammonia from −78 to −33 °C.[21] This is presumably because the concentration of the 16-electron species $[V(CO)_5]^-$ in this medium is extremely small unless its formation is photopromoted.[21] Although we do not have any evidence to indicate that the substitution reactions of $V(CO)_5NH_3^-$ are actually unimolecular, such a pathway seems credible in view of the recent report that the related $V(CO)_5PR_3^-$ do undergo phosphine exchange reactions by a dissociative mechanism, presumably involving the intermediate $[V(CO)_5]^-$.[20b]

$$V(CO)_5L^- \xrightarrow{-L} V(CO)_5^- \xrightarrow{+L'} V(CO)_5L'^- \qquad (16)$$

Another important method for preparing $V(CO)_5L^-$, especially when L or $V(CO)_5L^-$ is somewhat ammonia sensitive, is to add the ligand to preisolated **2** or **3** in an ether solvent at −20 to 0 °C. In this fashion exposure of L to ammonia is minimized. This second method will be discussed in more detail in the following paper in this series.[22]

(Alkyl isocyanide)- and (Phenyl isocyanide)pentacarbonylvanadate(1−) Ions, $V(CO)_5CNR^{1-}$. Treatment of $[Et_4N][V(CO)_5NH_3]$, prepared by adding $[Et_4N]Br$ to an ammoniacal solution of **1** with 3–5 equiv of RNC leads to the formation of 60–85% isolated yields of $V(CO)_5(CNR)^-$.

$$V(CO)_5NH_3^- + RNC \xrightarrow[\substack{\text{or } NH_3\text{–}CH_3CN \\ -20 \text{ to } 0\ ^\circ C}]{NH_3\text{–THF}} V(CO)_5CNR^- + NH_3 \qquad (17)$$

This reaction has been done with R = phenyl, methyl, *n*-butyl, *tert*-butyl, and cyclohexyl and thus appears to be a general procedure for the synthesis of any $V(CO)_5CNR^-$. The chemical properties of these materials have not been explored, but they are oxygen sensitive like the related $V(CO)_5PR_3^-$. Only in the case of R = *n*-butyl (compound **10**) was a crystalline product not isolated at room temperature. The spectroscopic properties of **10** are so similar to those of other $V(CO)_5CNR^-$ (R = alkyl), however, that we have no doubt about the correctness of its formulation.

Infrared solution spectra (Table I) of **6** through **11** show the characteristic pattern in the $\nu(CO)$ region of a $V(CO)_5L^-$ species. An excellent analysis of the infrared spectra of $V(CO)_5CNMe^-$ as the Na^+, Et_4N^+, and Ph_4As^+ salts in various media has been presented recently by Darensbourg and Hanckel.[20] Except for the presence of a weak $\nu(CN)$ absorption at ca. 2100 cm^{-1}, the infrared spectra of $V(CO)_5PPh_3^-$ and $V(CO)_5CNMe^-$ are nearly superimposable, which indicates that in this environment PPh_3 and CNMe have very similar electronic effects.[20] The ^1H NMR spectra of the $V(CO)_5CNR^-$ salts which were isolated as analytically pure substances appear in Table I. These spectra are entirely consistent with the proposed formulations. Since the methyl proton signals of the coordinated CNMe group in compound **7** are obscured by the methylene proton signals in Et_4N^+, $V(CO)_5(CNMe)^-$ was also isolated as the Ph_4As^+ salt **8** to avoid this problem. The methyl resonance in **8** is fairly broad (10 Hz at half-height), probably due to coupling to ^{14}N and ^{51}V, both quadrupolar nuclei. The methyl resonance in $C_5H_5V(CO)_3CH_3^-$ is similarly broadened (4 Hz at half-height).[23]

Although there is nothing exceptional about the ^1H NMR spectrum of the phenyl isocyanide complex **13** (Table I), the infrared spectrum of this substance appears to be unusual. Phenyl isocyanide is generally considered to be a better π-acceptor ligand than alkyl isocyanide groups.[24] Accordingly, the $\nu(NC)$ stretch of **13** is approximately 90 cm^{-1} lower than that of free PhNC,[24] while the corresponding $\nu(NC)$ stretches of the alkyl isocyanide complexes are only 30–50 cm^{-1} lower than those of the corresponding free alkyl isocyanides.[25] Surprisingly, however, the A_1^2 $\nu(CO)$ vibrational mode for **13** is significantly *lower* in energy (1940 cm^{-1}) than the corresponding bands in the alkyl isocyanide complexes, which occur from 1955 to 1970 cm^{-1}. Finally, there is a band of medium intensity at 1595 cm^{-1} which is more intense than one usually observes for $\nu(C{=}C)$ modes associated with phenyl rings. Bands in this region are also observed for $\nu(CN)$ modes in η^1- or η^2-iminoacyl complexes. The latter have been prepared from isocyanide-substituted metal carbonyl anions.[17c] For these reasons, we believe that it would be premature to state that **13** definitely contains an anion entirely analogous to the alkyl isocyanide complexes discussed previously—despite that fact that the ^1H NMR and elemental analyses are entirely consistent with the formulation $[Et_4N][V(CO)_5CNC_6H_5]$. Hopefully, a single-

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[20] (a) Darensbourg, M. Y.; Hanckel, J. M.*J. Organomet. Chem.* **1981**, *217*, C9. (b) *Organometallics* **1982**, *1*, 82.

[21] However, $V(CO)_5NH_3^-$ appears to undergo photopromoted substitution by CN^- in liquid ammonia to provide ca. 35% yields of $V(CO)_5CN^{2-}$.[10]

[22] Fjare, K. L.; Ellis, J. E. *Organometallics*, in press.

[23] Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. M. Chem. Soc.* **1978**, *100*, 7902.

[24] Cotton, F. A.; Zingales, F. *J. Am. Chem. Soc.* **1961**, *83*, 351.

[25] Malatesta, L.; Bonati, F. "Isocyanide Complexes of Metals"; Wiley: Interscience: New York, 1969.

crystal X-ray study will resolve this issue.

Cyanopentacarbonylvanadate(2−) Ion, $V(CO)_5CN^{2-}$. Addition of excess solid sodium cyanide (10 equiv) and tetraethylammonium bromide to ammoniacal solutions of 1 provides, after an unexceptional workup, 50–60% yields of $[Et_4N]_2[V(CO)_5CN]$. This is the only carbonyl dianion prepared thus far from $V(CO)_5NH_3^-$. If 20 equiv of NaCN are used, the yield of the product remains essentially unchanged, but when 5 equiv of NaCN are used, the yield of 12 goes down to approximately 35%, so large excesses of CN^- are required to ensure the formation of reasonable yields of product. In principle, other $V(CO)_5X^{2-}$ species could be prepared by this general route, provided that X^- is not so basic that it deprotonates the coordinated or free ammonia.

$$V(CO)_5NH_3^- + X^- \rightarrow V(CO)_5X^{2-} + NH_3 \qquad (18)$$

Attempts to prepare the unknown $[(OC)_5MnV(CO)_5]^{2-}$ by this procedure were unsuccessful. It appeared that $Mn(CO)_5^-$ has no tendency to combine with the $V(CO)_5^-$ fragment in THF.[26] We have also noted that other weakly basic, poor, or non π-acceptor ligands such as Ph_2S and arenes do not combine with $V(CO)_5NH_3^-$ to give isolable compounds at room temperature. The only other known substituted pentacarbonylvanadate dianions are $Ph_3SnV(CO)_5^{2-}$, $Ph_3PbV(CO)_5^{2-}$,[27] and an incompletely characterized species thought to be $HV(CO)_5^{2-}$.[19]

Infrared solution spectra of $V(CO)_5CN^{2-}$ in acetonitrile (Table I) are consistent with those expected for a pentacarbonylmetal fragment of C_{4v} symmetry. Even though compound 12 is a dianion the CO stretching frequencies occur in approximately the same positions as corresponding bands for $V(CO)_5NH_3^-$, indicating the cyanide group in $V(CO)_5CN^{2-}$ is an effective π acceptor. Consistent with this view is the low ν(CN) value (2060 cm^{-1}) for 12 compared to the ν(CN) value for uncoordinated CN^- (2086 cm^{-1}).[28] An essentially identical infrared spectrum was reported for the previously reported $[Ph_4P]_2[V(CO)_5CN]$, prepared in 35% yield by the photolysis of $V(CO)_6^-$ in liquid ammonia in the presence of excess (ca. 8 equiv) of NaCN. Interestingly, the tetraphenylphosphonium salt was reported to be a *black* crystalline solid,[10] while $[Et_4N]_2[V(CO)_5CN]$ is bright yellow. Both dissolve in CH_3CN to give red solutions.

(Acetonitrile)pentacarbonylvanadate(1−), $V(CO)_5(CH_3CN)^-$. When purple $[Ph_4As][V(CO)_5NH_3]$ is dissolved in acetonitrile at room temperature, an immediate reaction occurs. An orange-yellow solution is formed containing a thermally unstable substance which is formulated as $V(CO)_5(CH_3CN)^-$ on the basis of its infrared spectrum. Over a period of several minutes at room temperature the ν(CO) bands due to $V(CO)_5(CH_3CN)^-$ (Table I) decay as a band at ca. 1855 cm^{-1} due to $V(CO)_6^-$ grows. The infrared solution spectrum of this substance is entirely consistent with that expected for a $V(CO)_5L^-$ species of C_{4v} symmetry. Wrighton and co-workers have previously reported the preparation of $V(CO)_5(CH_3CN)^-$ by photolyzing $V(CO)_6^-$ in neat acetonitrile.[11b] The infrared spectrum of $V(CO)_5(CH_3CN)^-$ they observe (ν(CO) in CH_3CN 1956 (m), 1851 (s), 1811 (m) cm^{-1}) is similar to ours except for the strong absorption at 1851 cm^{-1} which is very likely due to $V(CO)_6^-$.[11b] The latter forms when $V(CO)_5(CH_3CN)^-$ decomposes.

As indicated in the Experimental Section, brick-red $[Ph_4As][V(CO)_5(CH_3CN)]$ was isolated in low yield (30%) at −40 °C from the reaction of 2 with neat acetonitrile, but the solid rapidly decomposed above 15 °C to give a chocolate substance which contained $[Ph_4As][V(CO)_6]$ as the only metal carbonyl product.

Concluding Remarks. In general, it seems likely that any anionic complex containing a metal in a formally negative oxidation state and poor or non π-acceptor ligands will be sufficiently labile to permit thermal-promoted ligand-exchange reactions. This process has obvious advantages over direct photopromoted substitutions when the ligand or the product is photosensitive. Also, in contrast to the photolysis reactions there is generally no need to monitor the course of these thermal reactions to minimize the presence of undesired products, e.g., in the present study, species such as $V(CO)_6^-$ or $V(CO)_4L_2^-$.

Acknowledgment. We thank the donors of the petroluem Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE79-12159) for support of this research.

Registry No. 1, 81831-31-4; 2, 78937-16-3; 3, 36580-51-5; 4, 81831-32-5; 5, 81831-33-6; 6, 78954-04-8; 7, 78953-99-8; 8, 78954-00-4; 9, 78954-02-6; 10, 81831-35-8; 11, 81831-36-9; 12, 81831-38-1; 13, 78969-86-5.

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[26] Several attempts to prepare $VM(CO)_{10}^{2-}$ from the reaction of $V(CO)_5^{3-}$ and $M(CO)_5Br$ (M = Mn, Re) also failed (Stevens, R. E., unpublished observations).

[27] Ellis, J. E.; Hayes, T. G.; Stevens, R. E. *J. Organomet. Chem.* 1981, *216*, 191.

[28] Value from a Nujol mull infrared spectrum of NaCN.

1,3-Dithiol-2-ylidene Derivatives of (Arene)chromium Carbonyl Complexes

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Received October 15, 1981

The syntheses of (1,3-dithiol-2-ylidene)chromium complexes ($Cr(\eta^6\text{-arene})(CO)_2CS_2C_2RR'$; R, R′ = COOMe, COOMe; COH, Ph; COOEt, H) by reaction of $Cr(\eta^6\text{-arene})(\eta^2\text{-}CS_2)(CO)_2$ complexes with activated acetylenes are reported. Phosphite/phosphonite substitution of CO in the product complexes may be effected by irradiation of the compounds in the presence of excess phosphite/phosphonite ligand. The metal–carbene unit, in contrast, is stable to irradiation in the presence of phosphite/phosphonite or carbon monoxide.

Introduction

Reaction of η^2-carbon disulfide complexes with activated acetylenes has been shown to result in the formation of 1,3-dithiol-2-ylidene derivatives for iron and manganese complexes and heterocyclic five-membered metallorings for rhodium compounds.[1] We have found that the ad-

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