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THE CHARACTERIZATION OF METHYL, π-ALLYL, MIXED METAL AND CATIONIC DERIVATIVES OF VANADIUM CARBONYL

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Summary

Photosubstitution of $V(CO)_6^-$ by *o*-phenylenebis(dimethylarsine) (DIARS) and 1,2-bis(dimethylphosphino)ethane (DMPE) provide highly reactive carbonylvanadate monoanions which have been protonated to give thermally stable seven coordinate carbonyl hydrides. The DIARS substituted anion, $V(CO)_4DIARS^-$, reacts with methyl iodide, allyl chloride and bromopentacarbonylmanganese to yield $CH_3V(CO)_4DIARS$, h^3-$C_3H_5V(CO)_3DIARS$ and $(OC)_5MnV(CO)_4DIARS$ which represent the first examples of alkyl, h^3-allyl and mixed metal carbonyl derivatives of vanadium carbonyl. The chemical and spectral properties of these and related compounds are described. Controlled oxidation of $V(CO)_4DIARS^-$ provides small yields of a very oxidatively unstable substance that appears to be monomeric $V(CO)_4DIARS$. Reinvestigation of the reaction of vanadium hexacarbonyl and *o*-phenylenebis(dimethylarsine) in heptane has shown that a novel ionic species $[V(CO)_3(DIARS)_2][V(CO)_6]$, the first pnicogen derivative of the unknown $V(CO)_7^+$, is formed instead of the previously formulated neutral dimer $[V(CO)_4DIARS]_2$.

Vanadium is unique among transition metals in its ability to form a large number of monomeric neutral paramagnetic carbonyls which show little or no tendency to dimerize [1-4]. Indeed, only two previously unrefuted reports of dimeric diamagnetic complexes, $[V(CO)_4DIARS]_2$ [5] and $[V(CO)_4(P(C_6H_{11})_3)_2]_2$ [6], have been published. Several monomeric and paramagnetic pnicogen substituted vanadium carbonyls exist, including *trans*-$V(CO)_4(PR_3)_2$ (R = alkyl and phenyl) [6] and *cis*-$V(CO)_4(DPPE)$ [7,8], where DPPE = 1,2 bis(diphenylphosphino)ethane, which show no tendency to dimerize in solution or in the solid state.

Vanadium hexacarbonyl's preference to remain six coordinate also is shared by its anionic derivative, hexacarbonylvanadate(—I) ion, the most important precursor to other vanadium carbonyl species. Undoubtedly, the lack of any reports on alkyl, π-allyl* or mixed transition metal derivatives of these species in the scientific literature is a result of the inertness of $V(CO)_6^-$. Its inability to react with a variety of halides, EX, including CH_3I, CF_3COCl, $C_5H_5Fe(CO)_2I$, Me_3SnCl or Ph_3SnCl in tetrahydrofuran (THF) at room temperature to give species of the type $EV(CO)_6$ [9] dramatically emphasizes the reluctance of vanadium in $V(CO)_6^-$ to become seven coordinate. In contrast, $Co(CO)_4^-$, an extremely weak base and nucleophile compared to most other carbonylmetallate anions [10], reacts rapidly and quantitatively with these electrophilic species under the same conditions [11].

Since phosphine-substituted vanadium carbonyl anions [12] such as $V(CO)_5PPh_3^-$ and $V(CO)_4DPPE^-$ are known to give more thermally, oxidatively and solvolytically stable seven coordinate derivatives than $V(CO)_6^-$ [8,13], it was reasoned that the photosubstitution of even stronger donor ligands such as *o*-phenylenebisdimethylarsine (DIARS) and 1,2-bis(dimethylphosphino)ethane (DMPE) into $V(CO)_6^-$ would form highly reactive carbonylmetallate anions which could serve as precursors to new classes of vanadium carbonyl derivatives. In this paper we describe the results of this inquiry.

Experimental

General methods and materials

All operations were carried out under purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate and molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were performed and worked up by using standard Schlenck technique. Where necessary, solvents were freed of moisture and oxygen by standard methods [14]. Methyl iodide, allyl chloride, benzyl chloride, triphenylstannyl chloride, triethylphosphine, sodium tetraphenylborate and bis(diglyme)sodium hexacarbonylvanadate were obtained from commercial sources and freed of oxygen and moisture; trifluoroacetic anhydride (Aldrich) was distilled under nitrogen before use. Bromopentacarbonylmanganese [15] tetraphenylarsonium hydrogendichloride [16] *o*-phenylenebisdimethylarsine [17], and 1,2-bis(dimethylphosphino)ethane [18] were prepared according to published procedures.

Infrared solution spectra, obtained in air-tight sodium chloride cells, were recorded on a Perkin—Elmer 237B spectrometer. Melting points were determined with a Buchi—Tottoli apparatus on samples sealed in capillary tubes under nitrogen and are uncorrected. NMR spectra were recorded on either a Varian XL-100 or T-60 spectrometer. Elemental analyses and molecular weights, determined by osmometry, were obtained from Spang Microanalytical Laboratory, Ann Arbor, Michigan (see Table 1).

Photolyses were conducted in a borosilicate reaction vessel of about 150 ml capacity, similar to Ace Glass Model 6515. A high pressure Hanovia quartz mercury vapor lamp (450 W, Model 679A-36) inside a cooled quartz photochemical immersion well (Ace Glass Model 6515-25) was the radiation source.

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* While this manuscript was in preparation a preliminary communication on the synthesis and characterization of π-$C_3H_5V(CO)_5$ and related π-allyls appeared [28].

The photosubstitution reactions proceeded in a magnetically stirred solution at room temperature. Their progress was monitored by infrared spectroscopy in the carbonyl stretching frequency region. Removal of carbon monoxide was facilitated by conducting these photolyses under a partial vacuum or by sweeping the solution with a stream of argon.

Tetraethylammonium tetracarbonyl[o-phenylenebisdimethylarsine] vanadate (—I), $[(C_2H_5)_4N][V(CO)_4DIARS]$ (I)

Photolysis of a mixture of 4.0 g (11.5 mmol) of $[Et_4N][V(CO)_6]$ and 3.29 g (11.5 mmol) of DIARS in 150 ml of THF at room temperature after approximately 7 h yielded, after solvent removal, an exceedingly air-sensitive red orange solid which was recrystallized from acetone/heptane to give 4.60 g (70% yield) of bright orange, crystalline and analytically pure I. (See Tables 1 and 2 for analytical and spectral data, respectively.) The salt is soluble in THF, acetone and dichloromethane (with slow decomposition), slightly soluble in benzene, and insoluble in water, diethyl ether and saturated hydrocarbons.

Tetraethylammonium tetracarbonyl[1,2-bis(dimethylphosphino)ethane] vanadate(—I), $[(C_2H_5)_4N][V(CO)_4DMPE]$ (II)

By exactly the same procedure indicated above for I, $[Et_4N][V(CO)_6]$ (4.0 g, 11.5 mmol) and 1,2-bis(dimethylphosphino)ethane (1.83 g, 12.2 mmol) were made to react, and the mixture worked up to give a sticky orange yellow solid. This material was extracted with boiling diethyl ether for 40 h. Recrystallization of the yellow solid remaining in the extraction thimble from acetone/diethyl ether gave 1.0 g (20% yield) of extremely air-sensitive, fluffy, crystalline orange yellow substance which had an infrared spectrum very similar to that observed for I (see Table 2). Attempts to obtain C,H analyses for this extremely oxygen-sensitive compound were unsuccessful. However, the infrared spectrum and chemical behavior of this substance are entirely consistent with the formulation II. Attempts to obtain analytically pure crystals of $[PPN][V(CO)_4DMPE]$, where PPN = bis(triphenylphosphine)iminum ion, were also unsuccessful.

(Triphenylstannyl)tetracarbonyl[1,2-bis(dimethylphosphino)ethane] vanadium, $Ph_3SnV(CO)_4DMPE$ (III)

Pre-cooled methylene chloride (20 ml at 0°C) was added to a vessel containing 1.13 mmol of II and Ph_3SnCl. After stirring the reaction mixture for 30 min the solvent was removed in vacuo. The resulting solid was dissolved in benzene to give a yellow solution which was filtered (to remove Et_4NCl) and dried in vacuo. Four recrystallizations of the solid from dichloromethane/heptane (4/1, V/V) gave yellow, crystalline and analytically pure III.

(Triphenylstannyl)tetracarbonyl[o-phenylenebisdimethylarsine] vanadium, $Ph_3SnV(CO)_4DIARS$ (IV)

Yellow, crystalline analytically pure IV was obtained in 76% yield by the same general procedure described above for III.

Hydridotetracarbonyl[1,2-bis(dimethylphosphino)ethane] vanadium, $HV(CO)_4$-DMPE (V)

Treatment of II with water for 15 min caused essentially complete conversion to V. The product was dissolved in dichloromethane/heptane (4/1,V/V) to give a solution which was filtered through a short column of silica gel at −78°C. Slow removal of solvent in vacuo from the filtrate gave a yellow crystalline V in 88% yield. A second recrystallization from CH_2Cl_2/heptane provided an analytically pure sample of V, which is moderately air-sensitive in the solid state and changes to a brown powder after a few minutes exposure to air. It is indefinitely stable at room temperature under nitrogen.

Hydridotetracarbonyl[o-phenylenebisdimethylarsine] vanadium, $HV(CO)_4$-DIARS (VI)

A slurry of I (0.50 g) and $Ph_4AsHCl_2 \cdot 2H_2O$ [16] (0.44 g) was stirred in 20 ml of benzene at room temperature for 5 h. The resulting pale red solution was filtered and evaporated to dryness. Purification of the residue from CH_2Cl_2/heptane (4/1, V/V) by filtration through a 2 cm column of silica gel and subsequent slow evaporation of the filtrate gave pale yellow, analytically pure crystals of VI. This species is quite soluble and gives very air-sensitive solutions in THF, benzene, toluene and dichloromethane. It is insoluble in saturated hydrocarbons and water and decomposes in chloroform. In the solid state VI retains its yellow color for several minutes in air, while it is stable indefinitely at room temperature under nitrogen. Toluene solutions of VI under argon remain unchanged after several months of storage at 0°C.

Methyltetracarbonyl[o-phenylenebisdimethylarsine] vanadium, $CH_3V(CO)_4$-DIARS (VII)

A solution of 1.00 g (1.72 mmol) of I in 40 ml of THF was cooled to −78°C whereupon CH_3I (0.10 ml, 1.72 mmol) was added via syringe. The solution was allowed to slowly warm with stirring; at ca. −50°C it darkened and became turbid. Filtration of the solution at room temperature and subsequent removal of solvent gave a dark red solid. This material was dissolved in 10 ml of dichloromethane/heptane (4/1, V/V) and passed through a 3 cm column of silica gel (required an additional 30 ml of solvent mixture to completely elute product). The filtrate was slowly concentrated in vacuo whereupon deep violet crystals formed. These were washed with ice cold petroleum ether (2 × 10 ml) and dried, thereby giving 0.28 g (35% yield) of analytically pure VII. The solid can be handled for at least 4 h in air without change. It is very soluble in THF and dichloromethane, moderately soluble in aromatic hydrocarbons, and very slightly soluble in saturated hydrocarbons.

h^3-Allyltricarbonyl[o-phenylenebisdimethylarsine] vanadium, $(h^3\text{-}C_3H_5)V(CO)_3$-DIARS (VIII)

No immediate reaction occurred when allyl chloride (0.18 g, 2.40 mmol) was added to a THF solution (30 ml) of I (0.69 g, 1.19 mmol). After 4.5 h of stirring at room temperature all carbonyl anion was consumed. Filtration of the reaction mixture yielded a clear orange solution which upon concentration gave a highly crystalline orange product. This was recrystallized from dichloromethane/heptane to give 0.33 g (60% yield) of an analytically pure sample of VIII. Like the methyl derivative VII, this substance is stable for several hours in the solid state in air. It also appears to be remarkably stable to oxidation in solution; e.g., heptane solutions of VIII evaporate in air to give unchanged product.

Iodotetracarbonyl[o-phenylenebisdimethylarsine] vanadium, IV(CO)$_4$DIARS (IX)

A slurry of 1.00 g (1.72 mmol) of I in 30 ml of THF was treated with 0.44 g (1.72 mmol) of I_2 in 15 ml of THF at —78°C. The maroon mixture was warmed slowly with stirring to —20°C. Filtration through a jacketed frit maintained at —20°C gave a red-brown solution which was evaporated to dryness at 0°C. The residue was dissolved in 10 ml of benzene to remove ionic impurities, filtered, and dried again. Recrystallization of this material by the same method used for VII yielded 0.42 g (42%) of analytically pure IX. The compound is insoluble in water and aliphatic hydrocarbons, but very soluble in benzene, THF and dichloromethane. Unlike the previously reported $IV(CO)_4[(C_6H_5)_2PCH_2]_2$ [8], this seven coordinate carbonyl iodide is quite thermally stable, remaining unchanged indefinitely at room temperature under nitrogen. It begins to discolor after 30 min of exposure to air.

Pentacarbonylmanganesetetracarbonyl[o-phenylenebisdimethylarsine] vanadium, (OC)$_5$MnV(CO)$_4$DIARS (X)

A solution of 0.80 g (1.38 mmol) of I in 40 ml of THF at —78°C was added via cannula to a stirred slurry of 0.38 g (1.38 mmol) of $BrMn(CO)_5$ in 5 ml of THF at —78°C. The solution remained red-orange on warming to room temperature; however, all bands due to I had disappeared. The residue from this solution was dissolved in benzene. The resulting solution was filtered and evaporated, which left a red-brown oil. Purification of the oil was effected by dissolving it in 40 ml of CH_2Cl_2/heptane (3/1, V/V), passing the resulting solution through a short column of silica gel (2 cm in length) and slow removal of solvent under reduced pressure. A second recrystallization conducted in the same manner as above yielded 0.20 g (23%) of maroon, crystalline X. Finely divided X is pyrophoric on exposure to air. Exposure of THF solutions of X to air cause immediate formation of $Mn_2(CO)_{10}$ as the only identifiable product. X is quite soluble in standard organic solvents including cyclohexane, benzene, methylene chloride, THF and acetone.

Bis(o-phenylenebisdimethylarsine)tricarbonylvanadium(I) hexacarbonylvanadate (—I), [V(CO)$_3$(DIARS)$_2$] [V(CO)$_6$] (XI)

Freshly prepared $V(CO)_6$ [19] (2.20 g, 10 mmol), slurried in 10 ml of heptane, reacted immediately with one equivalent of DIARS to give a quantitive yield (4.60 g) of a slightly air-sensitive, diamagnetic orange yellow solid, which is formulated as XI. Recrystallization of XI from acetone/diethyl ether provided the analytical sample.

Bis(o-phenylenebisdimethylarsine)tricarbonylvanadium(I) tetraphenylborate, [$V(CO)_3(DIARS)_2$]BPh_4 (XII)

Treatment of XI (4.60 g, 4.96 mmol) with $NaBPh_4$ (1.64 g, 5.0 mmol) in the minimum volume of acetone, followed by addition of excess water, provided a light yellow, air-stable BPh_4^- derivative of XI in good yield (3.9 g, 76%). The known compound [Et_4N][$V(CO)_6$] could also be obtained in practically quantitative yield by treating the filtrate from the metathesis step with Et_4NBr.

Results and discussion

Synthesis and properties of $V(CO)_4L_2^-$ (I and II)

The photolysis of $V(CO)_6^-$ in the presence of DIARS and DMPE is a facile route to $V(CO)_4DIARS^-$ (I) and $V(CO)_4DMPE^-$ (II). The DIARS substituted anion as a tetraethylammonium salt is readily recrystallized to provide a thermally stable and analytically pure substance. In contrast, considerable difficulty was experienced with the purification of [Et_4N]$^-$or [$(Ph_3P)_2N$]$^-V(CO)_4$-(DMPE). Invariably, a sticky mass was obtained after attempted recrystallizations which smelled strongly of phosphine. Attempts to remove the phosphine impurity under high vacuum failed. On this basis, the impurity cannot be uncoordinated DMPE; it may be a phosphine oxide derived from the exceedingly oxygen-sensitive DMPE. Extraction of the sticky crude II with diethyl ether for 40 h provided a less sticky material (mullable with difficulty) that could be recrystallized from acetone/diethyl ether to give an extremely air-sensitive sponge-like mass. Attempts to obtain elemental analyses on this substance were unsuccessful due to its high reactivity. Because of the difficulty experienced in handling this substance, and the poor yields obtained (ca. 20%) only two derivatives, the hydride and triphenyltin adducts, were prepared. However, its infrared spectra (Table 2) and derivative chemistry are completely consistent with its proposed formulation. The DMPE anion appears to be more reactive than the DIARS analogue in that the tetraethylammonium salt of the former is quickly hydrolyzed in water, while the same salt of the latter is stable to hydrolysis at room temperature. The infrared spectra of both anions are completely consistent with that expected of a *cis*-$V(CO)_4L_2^-$ species. Virtually identical spectra have been reported for previously known anions of this type including $V(CO)_4[Ph_2PCH_2]_2^-$ [12] and $V(CO)_4[Ph_2AsC_5H_4]_2Fe^-$ [12].

Oxidation of $V(CO)_4DIARS^-$

Our original interest in the DIARS substituted anion concerned a report on the synthesis of the corresponding neutral substance, an unusual binuclear vanadium species [$V(CO)_4DIARS$]$_2$, from DIARS and $V(CO)_6$ [5]. Attempts to obtain this material by oxidation of $V(CO)_4DIARS^-$ with $C_7H_7^+BF_4^-$ or $AgBF_4$ were unsuccessful. Indeed, the oxidation did not proceed cleanly, in contrast to that reported for $V(CO)_4(Ph_2CH_2)_2^-$ [8]. For example, the reaction of an equivalent of $AgBF_4$ with I in benzene at room temperature gave only small yields of a yellow pyrophoric material which had infrared bands at 1990 s, 1900 s, 1876 vs and 1831 s (nujol mull). The relative shapes and intensities of these bands are very similar to those of $V(CO)_4(Ph_2PCH_2)_2$, a paramagnetic monomer [8]. The principal product from the $AgBF_4$ oxidation, a red solid, appears to be ionic in character and has an infrared spectrum which indicates the presence of $V(CO)_3(DIARS)_2^+$ and $V(CO)_6^-$. Indeed, it appears that $V(CO)_4$DIARS may be unstable with respect to disproportionation which is possibly induced by solvent. Other disproportionations of substituted vanadium carbonyl monomers are known and these are base induced. For example, Behrens has shown that $V(CO)_4(Ph_2CH_2)_2$ in the presence of *o*-phenanthroline gives $[V(phen)_3][V(CO)_4(Ph_2CH_2)_2]$ [7]. Davison and Reger also have reported that they were unable to synthesize $V(CO)_3$arene complexes [20]. In view of our observations on the $V(CO)_4$DIARS system it seems possible that $V(CO)_3$ arene is also unstable with respect to disproportionation.

Synthesis and properties of $V(CO)_3(DIARS)_2^+$ (XI and XII)

Our inability to obtain $[V(CO)_4DIARS]_2$ by oxidation of $V(CO)_4DIARS^-$ either with $AgBF_4$ or $[C_7H_7]BF_4$, led to a reexamination of the reaction of $V(CO)_6$ with DIARS in heptane at room temperature [5]. Vanadium hexacarbonyl reacts immediately with DIARS under these conditions to give a slightly air-sensitive diamagnetic, orange-yellow, solid which is formulated as the ionic $[V(CO)_3(DIARS)_2][V(CO)_6]$ on the basis of elemental analysis (Table 1), infrared spectra in the carbonyl stretching frequency region (Table 2), NMR spectra (Table 3) and chemical evidence. All IR active carbonyl stretching fre-

TABLE 1

ANALYTICAL DATA

Complex	Color	Decomposition point (°C)	Yield (%)	Elemental analyses found (calcd.) (%)	
				C	H
$[(C_2H_5)_4N][V(CO)_4DIARS]$ (I)	lt. orange	197	70	45.51 (45.61)	6.01 (6.26)
$(C_6H_5)_3SnV(CO)_4DIARS$ (III)	yellow	154	76	48.02 (48.10)	4.05 (3.91)
$(C_6H_5)_3SnV(CO)_4DMPE$ (IV)	yellow	207	39	51.22 (50.71)	4.89 (4.71)
$HV(CO)_4DIARS$ (V)	pale yellow	94	87	37.16 (37.36)	3.73 (3.81)
$HV(CO)_4DMPE$ (VI)	yellow	123	88	38.12 (38.23)	5.37 (5.46)
$H_3CV(CO)_4DIARS$ (VII)	violet	112	35	38.81 (38.82) mol. wt. found 450 (THF) calcd. 464	4.19 (4.13)
h^3-$C_3H_5V(CO)_3DIARS$ (VIII)	orange	79	60	41.45 (41.58)	4.74 (4.58)
$IV(CO)_4DIARS$ (IX)	red-violet	105	42	29.14 (29.20)	2.98 (2.80)
$(CO)_5MnV(CO)_4DIARS$ (X)	red-brown	175	23	35.22 (35.43) As 23.52 (23.27)	2.94 (2.50)
$[V(CO)_3(DIARS)_2][V(CO)_6]$ (XI)	yellow-orange	115	100	38.04 (37.61) As 32.01 (32.36)	3.53 (3.48)
$[V(CO)_3(DIARS)_2][B(C_6H_5)_4]$ (XII)	yellow-orange	169	76	55.08 (55.00)	5.15 (5.11)

TABLE 2

INFRARED SPECTRA OF DIARS AND DMPE SUBSTITUTED COMPOUNDS IN THE CARBONYL STRETCHING FREQUENCY REGION

Complex	Medium	ν(CO) (cm^{-1})
[Et_4N][$V(CO)_4$DIARS] (I)	THF	1901 s, 1791 vs, 1777(sh), 1743 m
	nujol mull	1892 m, 1771s, 1756 s, 1723 s
[Et_4N][$V(CO)_4$DMPE] (II)	THF	1896 s, 1783 vs, 1766(sh), 1737 s
	nujol mull	1888 s, 1754(sh), 1731 vs(br)
$Ph_3SnV(CO)_4$DIARS (III)	dichloromethane	1964 w, 1884 s, 1867 s, 1852 s
	nujol mull	1975 w, 1882 s, 1875 s, 1843 s
$Ph_3SnV(CO)_4$DMPE (IV)	THF	1969 m 1875 vs(br)
	nujol mull	1967 w, 1886 m, 1863 s, 1852 s
$HV(CO)_4$DIARS (V)	THF	1989 m, 1878 s(br)
	nujol mull	1989 m, 1900 s, 1863 vs, 1830 s
$HV(CO)_4$DMPE (VI)	THF	1981 m, 1865 vs
	nujol mull	1973 wm, 1863 vs, 1842 s
$CH_3V(CO)_4$DIARS (VII)	THF	1941 s, 1860 s, 1832 s
	nujol mull	1926 s, 1843 s, 1819 s
h^3-$C_3H_5V(CO)_3$DIARS (VIII)	heptane	1948 m, 1871 m, 1841 vs
	nujol mull	1945 m, 1846 s, 1832 vs, 1813 s
$IV(CO)_4$DIARS (IX)	THF	2012 m, 1954 s, 1911 s, 1881 m
	nujol mull	2013 s, 1955 s, 1911 vs, 1875 s
$(CO)_5MnV(CO)_4$DIARS (X)	THF	1978 w, 1954 m, 1876(sh), 1863 vs, 1843 w
	cyclohexane	2012 w, 1997 m, 1900 m, 1884 vs, 1865 m, 1843 w
	nujol mull	1957 s, 1878 m, 1859 s, 1824 vs, 1766 m, 1724 m
[$V(CO)_3$(DIARS)$_2$][$V(CO)_6$] (XI)	CH_2Cl_2	2073 vw, 1957 m, 1855 vs(br)[a]
[$V(CO)_3$(DIARS)$_2$][BPh_4] (XII)	CH_2Cl_2	1958 s, 1881 s

[a] Corresponding spectrum of [$V(CO)_4$DIARS]$_2$ in CH_2Cl_2 reported previously [5]: 2085 w, 1970 m, 1890(sh), 1870 s.

quencies of [$V(CO)_3$(DIARS)$_2$][$V(CO)_6$] in methylene chloride are ca. 10 cm^{-1} lower than those reported earlier for [$V(CO)_4$DIARS]$_2$ [5]; otherwise, the spectra are in excellent agreement. We also note that the calculated C and H analyses of [$V(CO)_4$DIARS]$_2$ ($C_{28}H_{32}As_4O_8V_2$ calcd.: C, 37.44; H, 3.60; As, 33.36%) are equally consistent with our ionic formulation. We have repeated the reaction of $V(CO)_6$ with varying amounts of DIARS (0.5, 1.5 or more equivalents) under the same conditions as reported previously [5] and obtain only varying yields of [$V(CO)_3$(DIARS)$_2$][$V(CO)_6$]. This salt is particularly novel since it contains the first reported Group V substituted carbonyl cation derivative of the unknown seven coordinate species $V(CO)_7^+$. The surprising stability of the $V(CO)_3$(DIARS)$_2^+$ system is also evident by its formation under unusual conditions. For example, we have obtained good yields of this cation by treating $IV(CO)_4$DIARS with $AgBF_4$ in THF at low temperatures in the hope of obtaining a presently unknown cation (THF)$V(CO)_4$DIARS$^+$. Also, treatment of $Ph_3SnV(CO)_6$ with DIARS yields $V(CO)_3$(DIARS)$_2^+$ instead of the expected $Ph_3SnV(CO)_4$DIARS, which can be prepared directly from Ph_3SnCl and $V(CO)_4$DIARS$^-$. The former reaction is quite unusual and unprecedented. Although analogous reactions of $V(CO)_6$ with DMPE were not attempted, in view of the similar reactivity patterns of DMPE and DIARS, it seems likely that an analogous cationic species, $V(CO)_3$(DMPE)$_2^+$ would form.

TABLE 3

NMR DATA ON THE VANADIUM METHYL, h^3-ALLYL, HYDRIDES, and CATION[a]

Complex	Solvent	Chemical shift (τ) and (multiplicity)	Assignment	Coupling constants
$HV(CO)_4DIARS$	toluene-d_8	14.48 (1)	V—H proton	
		8.53 (1)	As—CH_3 protons	
$HV(CO)_4DMPE$	toluene-d_8	14.58 (3)	V—H proton	$J(PH) = 23.4$ Hz
$CH_3V(CO)_4DIARS$	benzene-d_6	9.72 (1)	V—CH_3 protons	
		8.93 (1)	As—CH_3 protons	
h^3-$C_3H_5V(CO)_3DIARS$[b]	benzene-d_6	9.39 (1)	As—CH_3 protons	
		8.60 (2)	terminal allylic protons *endo* to V(D)	$J(BD) = 11$ Hz
		7.98 (2)	terminal allylic protons *exo* to V(C)	$J(BC) = 6$ Hz
		5.68 (mult.)	allylic proton on C_2 (B)	
$[V(CO)_3(DIARS)_2][V(CO)_6]$	acetone-d_6	8.27 (1)[c]	As—CH_3 protons	
		2.04 (mult.)	phenylene protons	

[a] Chemical shifts given in τ units; all integrations were satisfactory for the assignments. τ values for phenylene protons on DIARS species and DMPE protons are not listed. [b] See Fig. 1. [c] Room temperature spectrum; NMR varies with temperature indicating a stereochemically nonrigid cation. The limiting spectrum is unattainable. Phenylene multiplet coalesces at −80°C. As—CH_3 proton signal collapses at −40°C, splits into 4-line multiplet at −80°C.

Proof that $[V(CO)_3(DIARS)_2][V(CO)_6]$ is ionic was provided by showing that its metathesis with sodium tetraphenylborate in acetone/H_2O provided a light yellow, air-stable derivative, $[V(CO)_3(DIARS)_2]BPh_4$, in excellent yield. Quantitative yields of $[Et_4N]V(CO)_6$ were also obtained by treating the water-soluble portion of the metathesis reaction with Et_4NBr. The IR spectrum of $[V(CO)_3(DIARS)_2]BPh_4$ is reported in Table 2. The very strong absorption at ca. 1860 cm^{-1} in $[V(CO)_3(DIARS)_2][V(CO)_6]$ is thus largely due to $V(CO)_6^-$.

The seven coordinate nature of the cation was also shown by the equivalence of all methyl groups on the DIARS ligands. (Table 3). If one or more Me_2As groups were uncoordinated, such an equivalence would be less likely. The ^1H NMR of the cation establishes that the molecule is stereochemically nonrigid, as one might expect for a seven coordinate species [21]. However, our inability to observe the slow exchange limit with variable temperature NMR obviated any attempt to characterize the molecular dynamics of the system. The inertness of $V(CO)_3(DIARS)_2^+$ to methyl iodide also provides compelling evidence that all arsenic groups are coordinated to vanadium, which thereby achieves a closed shell configuration [22]. Uncoordinated dimethylarsine groups are quite strong bases which immediately interact with methyl iodide and other electrophilic species [9]. On the basis of these studies we conclude that $[V(CO)_4DIARS]_2$ does not exist. Preliminary evidence also indicates that the reaction of $V(CO)_6$ with $(C_6H_{11})_3P$, previously reported to yield $[V(CO)_4(P(C_6H_{11})_3)_2]_2$, a diamagnetic substance postulated to contain a V—V bond [6], gives instead an ionic product, which is presently incompletely characterized, arising from the disproportionation of $V(CO)_6$ [19]. It thus appears that there is presently only one bonafide example of a vanadium carbonyl species containing a V—V bond, namely $(C_5H_5)_2V_2(CO)_5$ [23]. However, other substances of the general formula $[V(CO)_4PR_2]_2$ [6] may also contain this structural feature.

$Ph_3SnV(CO)_4L_2$, L_2 = DIARS and DMPE (III and IV)

These crystalline, air-stable, substances are the most solvolytically and oxidatively stable derivatives of $V(CO)_4L_2^-$ reported in this paper. The infrared spectra reported for these seven coordinate species are very similar to those of similar $Ph_3SnM(CO)_4$DPPE species (M = V, Nb, Ta) reported previously [13].

$HV(CO)_4L_2$, L_2 = DIARS and DMPE (V and VI)

Before this study began there were only two characterized vanadium carbonyl hydrides. One of these, tricarbonylhydridomesitylenevanadium [2] is described as being thermally unstable at room temperature. The other, 1,2-bis(diphenylphosphino)ethanetetracarbonylhydridovanadium [13] so readily evolves hydrogen and forms the paramagnetic monomer, $V(CO)_4$DPPE, that attempts to observe the ^1H NMR signal for the hydridic proton were unsuccessful. In contrast, the vanadium carbonyl hydrides reported in this study are stable indefinitely under nitrogen at room temperature as crystalline solids or at 0°C in aromatic hydrocarbons. These seven coordinate species are thus the most stable vanadium carbonyl hydrides presently known. Another thermally stable vanadium hydride, $HV(PF_3)_6$, has been reported recently [24].

The presence of a H—V bond in V and VI has been established by chemical and spectral means. For example, the presence of an acidic hydrogen was proven by reacting a yellow solution of 0.30 g of V in THF with 2 ml of a 10% solution of $[(C_4H_9)_4N]OH$ in methanol (Eastman). On mixing these solutions the yellow color of V rapidly gave way to a red color. Infrared spectroscopy showed that complete conversion to the monoanion, $V(CO)_4DIARS^-$, had occurred. Identical results were obtained with VI.

The ^1H NMR of V shows a somewhat broad signal (ca. 20 Hz) in toluene-d_8 at τ14.48 at room temperature. However, in contrast to the temperature dependent signal reported for $HV(CO)_3$ mesitylene [20], no change in the shape of the signal due to the hydride was observed from +20 to —67°C. No attempt was made to observe the ^1H NMR spectrum of $HV(CO)_4$DIARS above room temperature. Similarly, a well resolved triplet [J(PH) = 23.4 Hz] centered at τ14.58 was observed for $HV(CO)_4$DMPE in toluene-d_8 at room temperature (Table 3). Also, no temperature dependence in this signal was observed from +20 to —65°C in toluene-d_8.

$CH_3V(CO)_4$DIARS (VII)

This novel, air-stable, violet compound has been characterized by elemental analysis (Table 1), molecular weight determination (by osmometry in THF, Table 1) and by proton NMR (Table 3). The latter shows two sharp singlets τ8.93 and τ9.72 with relative areas of 12/3 respectively in benzene-d_6. A multiplet centered at τ2.8 due to the phenylene protons (relative area 4) is also observed. The synthesis of this species is particularly noteworthy in that it is the first alkyl derivative of vanadium carbonyl to be reported in the scientific literature. Attempts to obtain the corresponding trifluoromethyl, benzyl, and acetyl compounds from trifluoroacetic anhydride, benzyl chloride and acetyl chloride and the carbonyl anion were unsuccessful.

h^3-C_3H_5 $V(CO)_3$DIARS (VIII)

Although h^3-allyl derivatives of most metal carbonyls have been prepared, none were established for V, Nb and Ta before this study was initiated. A rather thermally unstable trifluorophosphine analogue of tantalum, h^3-C_3H_5-$Ta(PF_3)_5$, which decomposes after several days at 20°C, has been reported, however [25]. By comparison, VIII is a very thermally and oxidatively stable species; e.g., it is stable indefinitely under nitrogen at room temperature and stable to air in the solid state or as heptane solutions for hours. This orange substance has been characterized by elemental analyses (Table 1), infrared spectroscopy (Table 2) and ^1H NMR spectroscopy (Table 3). The ^1H NMR spectrum of VIII (Fig. 1) shows three signals with intensity ratios 1/2/2 at τ 5.68 (*meso*), 7.98 (*syn*) and 8.60 (*anti*), which confirms that the allyl is symmetrically bound to the vanadium. Fluorolube mulls of VIII exhibit C—H stretching frequencies at 3046, 2987 and 2912 cm^{-1} (all weak). Corresponding C—C stretching vibrations appear at 1485 and 1444 cm^{-1} (weak to medium intensity). The positions of these bands correspond closely to those of other h^3-allyl complexes previously reported [26].

$IV(CO)_4$DIARS (IX)

Only two well defined iodocarbonylvanadium species have been reported previously, $IV(CO)_3$mesitylene and $IV(CO)_4$DPPE [8]. Both of these were sufficiently unstable to thermal decomposition that they gave rather unsatisfactory elemental analyses. In contrast, IX, a maroon-red crystalline material, is stable indefinitely at room temperature under nitrogen and gives satisfactory

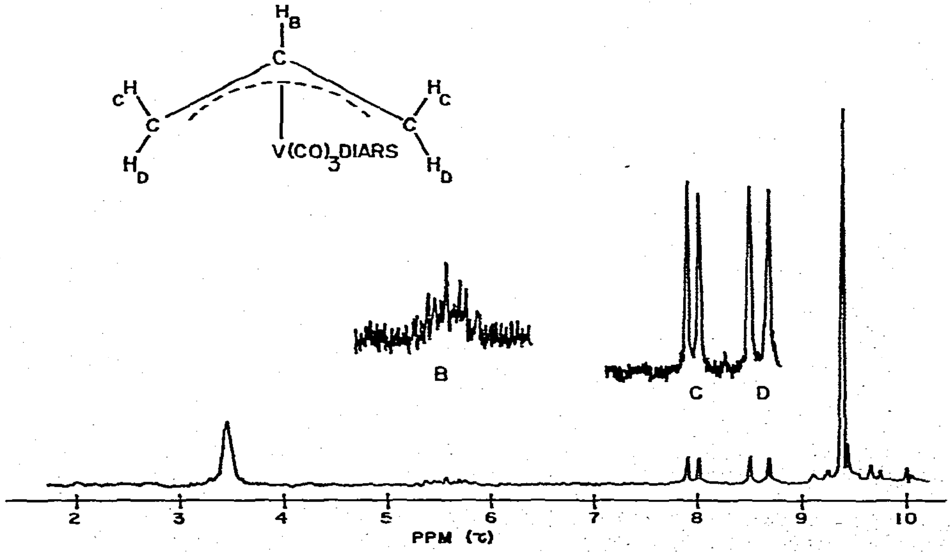

Fig. 1. 60 MHz ^1H NMR spectrum of (h^3-C_3H_5)$V(CO)_3$DIARS in benzene-d_6.

elemental analyses (Table 1). Its infrared spectrum (Table 2) is also very similar to that reported previously for $IV(CO)_4DPPE$ [8].

$(CO)_5MnV(CO)_4DIARS$ (X)

Although mixed transition metal complexes are now very numerous, there has been only one previous report on a compound containing a mixed vanadium to transition metal bond: $(C_5H_5)_2V$—$Cr(CO)_3C_5H_5$, which was prepared by treating vanadocene with $[C_5H_5Cr(CO)_3]_2$ [27]. Previous attempts to obtain carbonylvanadium to other transition metal bonds have been unsuccessful. For example, treatment of $V(CO)_4DPPE^-$ with $BrMn(CO)_5$ gave only $Mn_2(CO)_{10}$ and $V(CO)_4DPPE$ [8]. However, under similar conditions (low temperature at —78°C in THF) with $V(CO)_4DIARS^-$, ca. 20% yields of the red-brown mixed metal species can be obtained. The elemental analyses (Table 1), the infrared spectrum (Table 2) and solubility properties are consistent with this formulation. Curious low energy bands close to those found for $V(CO)_4DIARS^-$ are present in the mull spectrum of $(CO)_5MnV(CO)_4DIARS$; however, these absorptions disappear when the compound is dissolved in THF, dichloromethane or cyclohexane. They reappear on removal of solvent. The formation of bridging carbonyls in the solid state may account for the presence of these low energy carbonyl stretching frequencies. The presence of highly unsymmetrical bridging carbonyls in $(C_5H_5)_2V_2(CO)_5$ has been established recently [23].

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References

1 F. Calderazzo, R. Cini and R. Ercoli, Chem. Ind. (London), (1960) 934.
2 R.P.M. Werner. Z. Naturforsch. B, 16 (1961) 477.
3 W. Hieber, J. Peterhans and E. Winter, Chem. Ber., 94 (1961) 2572.
4 H. Behrens and K. Lutz, Z. Anorg. Allg. Chem., 356 (1968) 225.
5 A.S. Kasenally, R.S. Nyholm, R.J. O'Brien and M.H.B. Stiddard, Nature (London) 204 (1964) 871.
6 W. Hieber and E. Winter, Chem. Ber., 97 (1964) 1037.
7 H. Behrens and K. Lutz, Z. Anorg. Allg. Chem., 356 (1968) 225.
8 A. Davison and J.E. Ellis, J. Organometal. Chem., 36 (1972) 131.
9 J.E. Ellis, unpublished observation.
10 R.E. Dessy, R.L. Pohl and R.B. King, J. Amer. Chem. Soc., 88 (1966) 5121.
11 R.B. King, Advan. Organometal. Chem., 2 (1964) 157.
12 A. Davison and J.E. Ellis, J. Organometal. Chem., 31 (1971) 239.
13 A. Davison and J.E. Ellis, J. Organometal. Chem., 36 (1972) 113.
14 K.B. Wiberg, Laboratory Technique in Organic Chemistry, McGraw—Hill, New York, 1960.
15 R.B. King, Organometallic Syntheses, Academic Press, New York, 1965, p. 174.
16 R.L. Shriver and C.N. Wolf, Org. Syn., 30 (1950) 98.
17 R.D. Feltham and W. Silverthorn, Inorg. Syn., 10 (1967) 159.
18 G.W. Parshall, J. Inorg. Nucl. Chem., 12 (1960), 931.
19 J.E. Ellis and R.A. Faltynek, manuscript in preparation.
20 A. Davison and D.L. Reger, J. Organometal. Chem., 23 (1970) 491.

21 E.L. Muetterties and C.M. Wright, Quart. Rev., 21 (1967) 109.
22 J.E. Ellis, J. Organometal. Chem., 86 (1975) 1.
23 F.A. Cotton, B.A. Frenz and L. Kruczynski, J. Amer. Chem. Soc., 95 (1973) 952.
24 T. Kruck and H.-U. Hempel, Angew. Chem., 86 (1974) 233.
25 T. Kruck and H.-U. Hempel, Angew. Chem., Int. Ed. Engl., 10 (1971) 408.
26 E.O. Fischer and H. Werner, Metal π-Complexes, Vol. 1, Elsevier, Amsterdam, 1966, pp. 177-180.
27 A. Miyake, H. Kondo, and M. Aoyama, Angew. Chem., 81 (1969) 498.
28 M. Schneider and E. Weiss, J. Organometal. Chem., 73 (1974) C7.