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PROTON- AND CARBONYL-MEDIATED ELECTRON TRANSFER PROCESSES FROM THE HEXACARBONYLVANADATE(– I) ANION *

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Summary

Hexacarbonylvanadate(– I) derivatives of several heterocyclic nitrogen bases, $BH^+[V(CO)_6]^-$, have been synthesized. The deep red volatile pyridinium derivative $[C_5H_5NH]^+[V(CO)_6]^-$, was studied by X-ray diffraction methods and found to be tetragonal, space group $I4_1/amd$, with a 10.384(3), c 12.373(3) Å and $Z = 4$. Solution of the structure by the heavy-atom method followed by full-matrix least-squares refinement gave the final residuals ($R = 0.0450$ and $R_w = 0.0442$) for 180 unique observed reflections. Coordination about the vanadium atom, which lies at a site of local $\bar{4}2m$ symmetry, is octahedral due to two independent carbonyl groups. The pyridine moiety is disordered. The major feature of the molecular structure is the interaction of the nitrogen proton with the carbonyl oxygens of $[V(CO)_6]^-$ in the equatorial plane of the octahedron. The structural features are regarded as evidence in favour of the carbyne-type of structure for the C_6HO_6V precursor of $V(CO)_6$ ($C_6HO_6V \rightarrow 1/2\ H_2 + V(CO)_6$). Several substitution and redox processes involving the protonated nitrogen base derivatives have been observed, namely: (a) nitrogen base exchange; (b) dihydrogen evolution upon treatment with sodium metal; (c) electron-transfer from $[V(CO)_6]^-$ to the nitrogen-bonded proton, with dihydrogen evolution; (d) electron-transfer from $[V(CO)_6]^-$ to the cation with carbon–carbon coupling in the case of the acridinium derivative. All the compounds reported are deeply coloured (the quinolinium derivative is black), suggesting the existence of a multicentre CO-mediated charge transfer from vanadium to the nitrogen base.

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contribution to Organometallic Chemistry.

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Introduction

Thermal and chemical [1] or photochemical [2] cleavage of metal–hydrogen bonds are well established for compounds of general formula $MH(CO)_n$ [3] containing a transition metal–hydrogen bonded ground state. For vanadium, experimental evidence [4] excludes that the V–H bond containing species is a reasonable representation of the ground state situation, while a more reasonable formulation for the hydrogen-containing precursor of $V(CO)_6$, see equation 1, is the carbyne structure $(OC)_5V{\equiv}COH$, corresponding to protonation of the carbonyl oxygen of the hexacarbonylvanadate(−I) anion [5]. A recent paper pointed out that the carbyne structure $(OC)_3Co{\equiv}COH$ should be about 7 kcal more stable than the formyl species $(OC)_3CoC(O)H$ [6], the ground-state structure in this case, being, of course, $CoH(CO)_4$, as shown by electron-diffraction studies [7].

$$\text{“}C_6HO_6V\text{”} \rightarrow 1/2H_2 + V(CO)_6 \qquad (1)$$

We now present some new observations about electron-transfer processes from $[V(CO)_6]^-$, which may throw some light into the mechanism of reaction 1 and focus attention on the general problem of the relationship between the ground-state properties and the reactivity of $MH(CO)_n$ complexes.

Experimental

Unless otherwise stated all of the preparations described in this paper were carried out under prepurified nitrogen in anhydrous solvents, the latter being dried by conventional methods. The IR spectra were measured with a Perkin–Elmer Mod. 283 instrument equipped with grating. Sodium hexacarbonylvanadate(−I) was prepared as previously described [8].

Preparation and properties of hexacarbonylvanadates(−I) of protonated nitrogen bases

As previously reported [9] for the preparation of $[C_5H_5NH]^+[V(CO)_6]^-$, the derivatives of Table 1 were synthesized by treating an aqueous solution of $NaV(CO)_6$ with the appropriate nitrogen base under slightly acidic conditions (pH 4–5).

Method A. The methyl-quinolinium complex VIIB was prepared from preformed $[C_9H_7NMe]^+\ I^-$ and $NaV(CO)_6$ in water. The compounds prepared in aqueous solution were generally collected by filtration, and after drying over P_4O_{10} under reduced pressure (except when stated otherwise, vide infra), they were found to be analytically pure. The preparation of compound I by Method B (see Table 1) is described in detail.

Sodium hexacarbonylvanadate(−I), $NaV(CO)_6$, (0.584 g; 2.41 mmol) suspended in n-pentane (50 cm^3) was treated at dry-ice temperature with 2.49 mmol of dry HCl. The suspension was stirred for 1 h and then treated with 2.4 mmol of dry pyridine. No reaction apparently took place until the temperature was raised to about −10°C. The brick-red suspension was evaporated to dryness under reduced pressure and the solid residue sublimed at 60°C/ca. 10^{-2} mmHg to give 0.58 g (81% yield) of I.

A solution of compound I (0.114 g; 0.63 mmol) in tetrahydrofuran (10 cm^3) was treated with sodium sand (0.040 g; 1.7 mmol) at room temperature. The colour of the solution turned gradually from red to yellow during about 10 min, and evolution of gas (H_2 by gas chromatography) was detected. The IR spectrum of the solution showed absorptions at 1880sh and 1851vs cm^{-1} due to $[V(CO)_6]^-$. Similar results were obtained with the quinolinium derivative VIIA.

The acridinium derivative VIII was converted into the pyridinium complex with pyridine when a suspension of 0.280 g (0.7 mmol), in n-heptane (30 cm^3), was treated with pyridine (0.08 cm^3; 1.0 mmol). The green colour of the suspension gradually changed to orange-brown. After 4 h stirring at room temperature the mixture was filtered and the solid was dried under reduced pressure to give, after sublimation at 60°C/ca. 10^{-2} mmHg, 0.150 g (72% yield) of compound I. Evaporation of the solvent from the filtrate gave 0.070 g of acridine (identified from its IR spectrum (Nujol), vide infra).

The 2-bromopyridinium derivative VI was obtained from aqueous solution and was dried in vacuo after collection by filtration. The compound was unstable with respect to formation of $V(CO)_6$; when a sample (0.137 g; 0.36 mmol) was suspended in toluene (5 cm^3), evolution of gas (H_2 by gas chromatography) occurred immediately upon contact of the solid with the liquid. The IR spectrum of the resulting solution showed the $V(CO)_6$ band at 1971 cm^{-1}. Gas-volumetric monitoring of the reaction at 24.5°C showed that 0.68 mmol of VI gave 0.4 mmol of H_2, corresponding to a H_2/V molar ratio of 0.59. The excess is believed to come from the parasitic reaction [10] of $V(CO)_6$ with toluene to give $[V(CO)_4\text{toluene}][V(CO)_6]$.

The acridinium derivative VIII was found to be rather unstable, thermally and chemically. During preparation of the compound, the drying time had to be reduced in order to minimize the decomposition. The compound (0.122 g; 0.306 mmol) was introduced in a Schlenk tube and kept at 30.2°C under reduced pressure (ca. 10^{-2} mmHg) for 18 h, with a cold trap inserted in between the pump and the Schlenk tube. The green colour of the solid gradually changed to grey and $V(CO)_6$ (0.054 g, $\bar{\nu}(CO)$, n-hexane, 1973 cm^{-1}) was found in the cold trap. The residual solid (0.06 g) was identified as 9,9′-biacridan (or 9,10,9′,10′-tetrahydrobiacridyl), from the IR spectrum in Nujol, which was superimposable on that of an authentic sample prepared from acridine by photoreduction in ethanol [11a,b].

The instability of the acridinium derivative VIII towards oxygen Lewis bases is exemplified by the reaction with tetrahydrofuran. When VIII (0.892 g; 2.23 mmol) was dissolved in tetrahydrofuran (100 cm^3) the green colour rapidly changed to yellow with evolution of CO (no dihydrogen was detected) and a white solid separated. The IR spectrum of the solution showed the typical carbonyl stretching vibration of $[V(CO)_6]^-$. The mixture was filtered and the white solid washed with tetrahydrofuran and dried in vacuo to give 0.286 g (71.2%) of 9,9′-biacridan, identified from its IR spectrum in Nujol, m.p. 261–263°C dec. (lit. [11], 263°C dec.) and elemental analysis (Found: C, 85.7; H, 5.6; N, 7.4. $C_{26}H_{20}N_2$ calcd.: C, 86.6; H, 5.6; N, 7.8%). Gas-volumetric monitoring of the reaction showed that 0.253 mmol of compound VIII, when treated with THF (10 cm^3) gave 0.466 mmol of CO (corresponding to a CO/V molar ratio of 1.84 arising from disproportionation [9] of $V(CO)_6$ with tetrahydrofuran to give $[V(thf)_n][V(CO)_6]_2$.

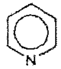
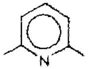
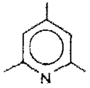
Collection and reduction of X-ray data of $[C_5H_5NH][V(CO)_6$ (I)

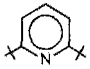
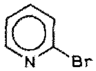
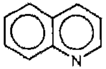
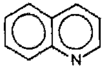
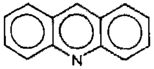
Crystals of this compound were grown by slow diffusion of an aqueous solution of pyridine and hydrochloric acid in approximately equimolar amounts into an aqueous solution of $NaV(CO)_6$. A crystal of approximate dimensions 0.28 × 0.29 × 0.33 mm^3 was sealed in a glass capillary under argon and mounted on a three-circle

(Continued on p. 6)

TABLE 1

HEXACARBONYLVANADATE(−I) DERIVATIVES OF HETEROCYCLIC NITROGEN BASES, $BX^+[V(CO)_6]^-$

B		X	pK_a	Metal complex. Formula	Method of preparation [a]	Yield (%)	Colour	Analysis [b]	
								CO	V
	, C_5H_5N	H	5.20 [c]	I, $C_{11}H_6NO_6V$	A B	34 81	Brick-red	56.0 (56.2)	16.7 (17.0)
	, C_5H_4MeN	H	6.03 [c]	II, $C_{12}H_8NO_6V$	A	49	Orange-red	53.5 (53.7)	n.d.
	, $C_5H_3Me_2N$	H	6.69 [c]	III, $C_{13}H_{10}NO_6V$	A	44	Orange-red	51.8 (51.4)	15.4 (15.6)
	, $C_5H_2Me_3N$	H	7.43 [c]	IV, $C_{14}H_{12}NO_6V$	A	59	Brick-red	49.7 (49.3)	14.9 (14.9)

 , C_5H_3-t-Bu_2N	H	3.53 [d] 4.2 [e]	V, $C_{19}H_{22}NO_6V$	A	93	Yellow-orange	40.1 (40.9)	12.1 (12.4)
 , C_5H_4NBr	H	0.90 [f]	VI, $C_{11}H_5BrNO_6V$	A	67	Brown	44.1 (44.5)	13.1 (13.5)
 , C_9H_7N	H	4.94 [g]	VIIA, $C_{15}H_8NO_6V$	A B	84 29	Black	47.7 (48.1)	14.4 (14.6)
 , C_9H_7N	Me		VIIB, $C_{16}H_{10}NO_6V$	A	73	Blue-black	45.9 (46.3)	13.9 (14.0)
 , $C_{13}H_9N$	H	5.60 [g]	VIII, $C_{19}H_{10}NO_6V$	A B	63 26	Green	42.4 (42.1)	12.6 (12.8)

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[a] Method A, in aqueous solution. Method B, in saturated hydrocarbon suspension with dry HCl from $NaV(CO)_6$. Purification by sublimation for I and VIIIA, with some decomposition for the latter, and by washing with H_2O and short drying under reduced pressure over P_4O_{10} for VIII. [b] Calculated value (%) in parentheses. [c] From: Rodd's Chemistry of Carbon Compounds, S. Coffey (Ed.), 2nd edit., Vol. 4, Part F, Elsevier, Amsterdam, 1976, p. 158. [d] In 42% alcohol/water. From: R.F. Evans and H.C. Brown, J. Org. Chem., 27 (1962) 3127. See also: H.C. Brown and B. Kanner, J. Am. Chem. Soc., 88 (1966) 986. [e] W.J. le Noble and T. Asano, J. Org. Chem., 40 (1975) 1179. [f] The same as *c*, p. 164. [g] From: A. Albert, R. Goldacre and J. Phillips, J. Chem. Soc., (1948) 2240.

Siemens AED computer-controlled automatic diffractometer. Attenuation filters were automatically inserted into the diffracted beam to prevent the counting rate from exceeding 9000 cps. The intensity of the reflections was obtained from a profile measurement by the method of Lehmann and Larsen [12] with a programme written by Belletti et al. [13]. 975 reflections having $6.0° < 2\theta < 116.0°$ were measured, of these, 472 were systematically extinct and 173 were considered unobserved, having $I < 2\sigma(I)$. The remaining 330 reflections, of which 180 were unique, were retained and used for the structural analysis. The intensity of a standard reflection, measured every 50 reflections, did not deviate from the mean value by more than would be predicted by counting statistics. Data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied. An automatic searching routine located and centered 24 reflections with 2ϑ comprised between 31.0 and 62.5° and a tetragonal unit cell was deduced from an indexing routine. Systematic absences (hkl, $h + k + l = 2n + 1$; $hk0$, h, $k = 2n + 1$, and $0kl$, $k + l = 2n + 1$) indicated the unambiguous space group $I4_1/amd$. The intensity data were collected at room temperature using nickel-filtered Cu-K_α radiation. All computations were performed on the CDC Cyber 76 computer of CINECA (Casalecchio, Bologna).

Crystal Data. $M = 299.11$, tetragonal, space group $I4_1/amd$ (No. 141), a 10.384(3); c 12.373(3) Å; U 1334.1(6) Å^3; Cu-K_α (λ 1.54178 Å); $Z = 4$; $D_c = 1.489$ g cm^{-3}. $F(000) = 600$. The structure was solved by the heavy-atom method. The number of molecules in the unit cell indicated that they must be situated on crystallographic symmetry elements. The vanadium atom was shown by the Patterson function to occupy a special position of $\bar{4}2m$ symmetry, while the two independent carbonyl groups at C(1) and C(2) have crystallographically imposed mm and 2 symmetry, respectively.

Extensive disorder of the pyridine ring was found to exist about the crystallographic $\bar{4}$ axis. After isotropic refinement of the anion, inspection of a difference Fourier synthesis showed two peaks with electron densities corresponding each to a carbon atom. One, C(3), lies on a mirror at a special position of the space group, while the other, C(4), occupies a general position, so that the disorder can be described in terms of two different orientations of the molecule about the $\bar{4}$ axis. A satisfactory model was achieved by introducing these two atoms with occupancy factors of 0.5 and by imposing geometric constraints on their z coordinate (fixed at 7/8). The positional and thermal (anisotropic for all atoms except C(3) and C(4)) parameters were refined by a full-matrix least-squares procedure converging to a conventional R index of 0.0560. At this stage, the exceptionally large thermal parameters of C(2) and O(2) indicated that further disorder involving a carbonyl group had to be considered. These atoms do not lie exactly on the twofold axis, but are disordered in two positions, thus having a site occupancy factor of 0.5 at general positions. The refinement of this model was successfully completed with final residuals of $R = 0.0450$ and $R_w = 0.0442$. The function $\Sigma w(|F_0| - |F_c|)^2$, with a weighting scheme $w = [\sigma^2(F_0) + 0.005(F_0)^2]^{-1}$ was minimized. A final difference Fourier map was devoid of any significant feature. The scattering factors and anomalous dispersion corrections used for oxygen and carbon were those incorporated in the SHELX-76 program set [14]; for vanadium, the values were taken from the literature [15]. The final atomic coordinates are given in Table 2. Tables of thermal parameters and structure factors may be obtained from the authors.

Results and discussion

Because of their low solubility in water, the protonated nitrogen base derivatives of the $[V(CO)_6]^-$ anion, (I–VIII), can be obtained from a reaction in aqueous solution, according to the stoichiometry shown in eq. 2.

$$BH^+ + [V(CO)_6]^- \rightarrow BH^+[V(CO)_6]^- \qquad (2)$$

The sublimable pyridinium complex had been described earlier [9], together with the methylpyridinium compound $[C_5H_5NMe]^+[V(CO)_6]^-$, both being red microcrystalline substances. The new observations reported in this paper clarify the nature of the electronic interactions between the $[V(CO)_6]^-$ anion and the protonated nitrogen base. Moreover, the X-ray diffracton study of compound I has revealed structural details which account for its volatility. The pyridinium derivative is an ionic compound, with the NH group interacting preferentially with four of the carbonyl groups of the $[V(CO)_6]^-$ anion. Figure 1A is a perspective view of the anion, showing the distribution of the C(2)O(2) carbonyl group in two positions related by the twofold axis. Coordination around vanadium is approximately octahedral and involves the carbon atoms of the independent carbonyl groups. Bond distances and angles in the anion are given in Table 3. The two V–C bond distances are not significantly different (V–C(1), 1.934(9); V–C(2), 1.926(14) Å). These values agree well with those found in other hexacarbonylvanadate(−I) anions (i.e., 1.931(9) Å in $[(PPh_3)_2N][V(CO)_6]$ [16]; 1.88(2)–1.95(3) Å in $[V(CO)_4(1,2,4,5\text{-}C_6H_2Me_4)][V(CO)_6]$ [10] and 1.868(17)–1.922(18) Å in $[V(CN\text{-}t\text{-}Bu)_6][V(CO)_6]$ [17], but are somewhat shorter than those found in neutral $V(CO)_6$ (1.993(5)–2.006(4) Å) [18]. The vanadium atom lies in the mean least-squares plane formed by the four-symmetry related C(2) atoms, which show a slight, but significant tetrahedral distortion, as indicated by their deviations, ±0.118 Å, from the plane.

The disorder in the pyridine ring is illustrated in Fig. 1B, which shows the superposition of two orientations tilted by about 28° around the fourfold axis. Under the influence of the symmetry elements there are four and eight symmetry-related positions for C(3) and C(4), respectively. The only two independent bond distances in the ring are: C(3)–C(4), 1.37(1) and C(4)–C(4′), 1.35(1) Å.

The O(2)...C(4) contact is 2.99 Å, which is short for an O...HC(aromatic) contact [19] and is at the upper limit of experimentally observed N...O contacts in hydrogen-bonded pyridinium derivatives with oxygen containing anions (e.g., the values found are 2.565(8) [24], 2.69 [25], 2.76(1) [26], 2.80 [27], 2.80(2) and 2.89(2)

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) RELATIVE TO $C_5H_5NH^+[V(CO)_6]^-$

Atom	x/a	y/b	z/c
V	0	2500	3750
O(1)	0	2500	6232(5)
C(1)	0	2500	5313(7)
O(2)	1900(16)	234(14)	3535(10)
C(2)	1113(15)	1021(13)	3655(13)
C(3)	0	3828(16)	8750
C(4),N	1135(9)	3149(10)	8750

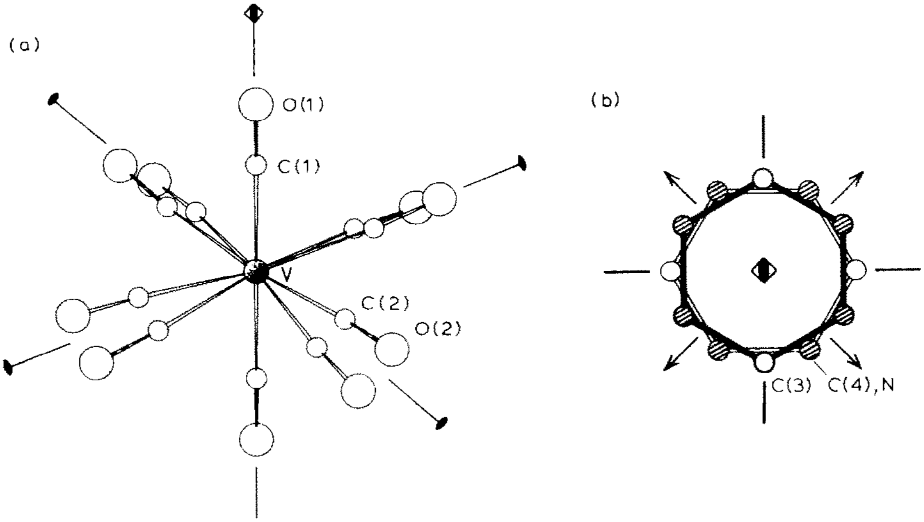


Fig. 1. (A) A perspective view of the $[V(CO)_6]^-$ anion, showing the C(2)O(2) disorder. (B) Projection of the pyridine along [001], showing the two disordered distributions. The dashed atoms are those involved in the hydrogen bond to the carbonyl groups.

[28] Å. Since the sum of the N and O Van der Waals radii is [20] 2.9 Å and C(3) is never involved in short interactions to the carbonyl oxygen, it may be concluded that the C(4) site is occupied for three quarters by a carbon atom and for one quarter by a nitrogen atom. Hydrogen-bonding between the pyridinium hydrogen and the carbonyl oxygen on the equatorial plane of the $[V(CO)_6]^-$ anion is therefore strongly implied by the observed distances. Moreover, it is possible to correlate the two different orientations of the anion with those of the aromatic ring. As it can be seen from Fig. 2, which shows the anion environment for one of the two related distributions, the O(2) atom interacts with the ring through hydrogen-bond forming layers normal to [001] and lying at $z = 3/8$ and $5/8$. The layers are linked by O(1)...ring centroid interactions at 3.12 Å, between the O(1) atoms and the π-electron density of the pyridine. If the thickness of the pyridine ring is assumed to be the same as that of an aromatic ring (1.70 Å [20]), it may be concluded that the interactions between layers are essentially of the Van der Waals type. Figure 3 shows that each pyridine, which is associated with six $[V(CO)_6]^-$ anions, interacts with two

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°) IN THE $[V(CO)_6]^-$ ANION OF $[C_5H_5NH]^+[V(CO)_6]^-$

V–C(1)	1.934(9)	C(1)–O(1)	1.137(11)
V–C(2)	1.926(14)	C(2)–O(2)	1.165(21)
C(1)–V–C(1) [a]	180	V–C(1)–O(1)	180
C(1)–V–C(2)	93.5(5)	V–C(2)–O(2)	171(1)
C(2)–V–C(2) [b]	90.2(6)		
C(2)–V–C(2) [c]	173.0(7)		

[a] $\frac{1}{4} - y, \frac{1}{4} - x, \frac{3}{4} - z$. [b] $\frac{1}{4} - y, \frac{1}{4} + x, \frac{3}{4} - z$. [c] $\bar{x}, \frac{1}{2} - y, z$.

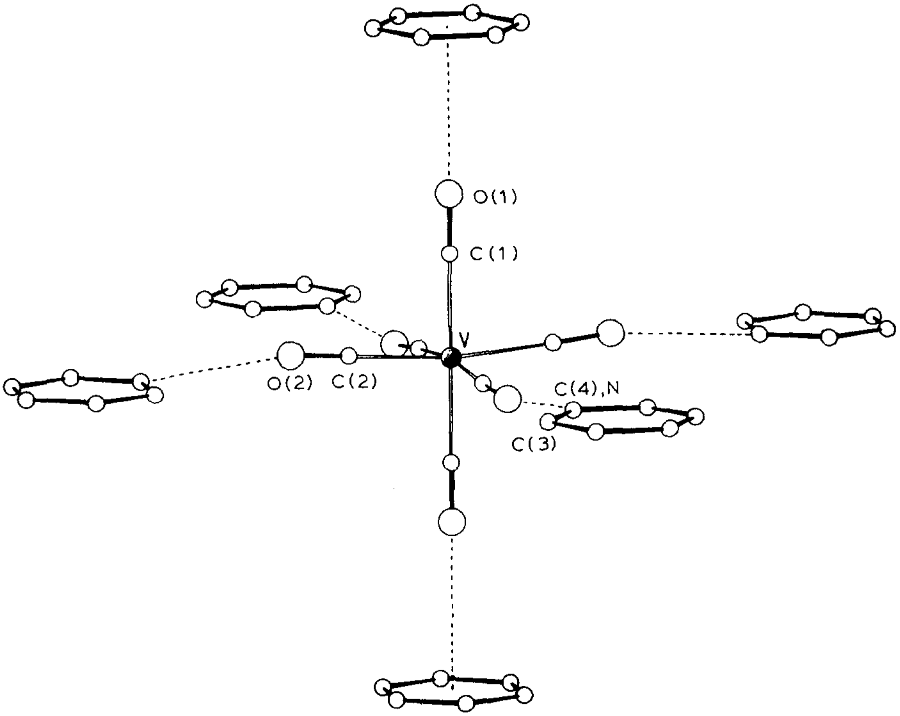


Fig. 2. A perspective view of the structure showing the $[V(CO)_6]^-$ anion–pyridine interaction.

axial and with four equatorial carbonyl groups. The equatorial interaction is shown in Fig. 3.

The relatively high volatility of the pyridinium derivative can now be understood, when account is taken of the facts that we are probably dealing with a small lattice energy because of the small charge density of the ions and that the cation–anion

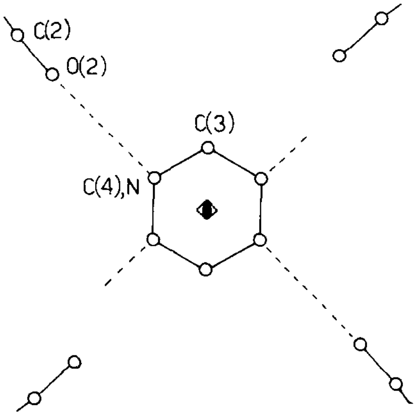


Fig. 3. The equatorial environment of the pyridinium cation.

TABLE 4

IR CARBONYL STRETCHING VIBRATIONS OF BX^+ $[V(CO)_6]^-$ DERIVATIVES [a]

Compound	$\nu(CO)$ (cm^{-1})		
	Et_2O	THF	Acetone
I	1903m	1893m	1857vs
	1862vs	1856vs	
	1850sh		
II	1900m	1891m	1854vs
	1857vs	1854vs	
	1849sh		
III	1899m	1890m	1862vs
	1860vs	1860vs	
	1850sh		
IV	1896m	1892m	1858vs
	1857vs	1856vs	
	1845sh		
V	1903m	1889m	1858vs
	1863vs	1858vs	
	1851sh		
VIIA	1902m	1892m	1859vs
	1858vs	1856vs	
	1843sh		
VIIB	1902m	1893m	1860vs
	1859vs	1857vs	
	1844sh		

[a] Compounds VI and VIII react with the solvent, see Experimental Section.

interactions are mainly of the hydrogen-bond type, to form an infinite two-dimensional array of $C_5H_5NH^+ \ldots [V(CO)_6]^-$ pairs in the direction parallel to the equatorial plane of the distorted $[V(CO)_6]^-$ octahedron.

The interaction of these compounds with solvents, as indicated by the IR data in the carbonyl stretching region (Table 4) is of interest. The polarity of diethyl ether or THF is insufficient to overcome the ionic interactions within the pairs, and the hydrogen-bonding persists along with the distortion of the vanadium octahedron, as suggested by the fact that more than one IR-active carbonyl stretching vibration is observed. (This is a well established phenomenon for alkali cations interacting with carbonylmetalate anions [29] and interaction of Lewis acids other than alkali cations with metal-coordinated terminal carbonyl groups has also been reported [30].) In solvents of relatively high dielectric constant, such as acetone, on the other hand, the preferred hydrogen-bonding is presumably to the solvent, so that the octahedral symmetry of the $[V(CO)_6]^-$ anion is restored and only one IR-active CO stretching vibration is observed.

The solid-state study carried on compound I offers indirect evidence in favour of the carbyne type of structure for the precursor $V(CO)_6$. Although of no practical preparative importance, it is of interest to note that the pyridinium derivative can be prepared in hydrocarbon solution, showing that pre-ionization of the "C_6HO_6V" precursor in water is not necessary. The interaction of the precursor with pyridine to give I may be visualized as a competition for the proton between the pyridine nitrogen and the carbonyl oxygen of the $[V(CO)_6]^-$ anion. Protonation of doubly-

[31] and triply-bridging [32] carbonyl groups has been reported in the literature, but there is no example of protonation of terminal carbonyl groups to our knowledge. Although a complete reorganization of the precursor upon contact with pyridine cannot be excluded, it is reasonable to assume that the pyridinium derivative I represents an energy minimum along the way from $(OC)_5V{\equiv}COH$ to the completely solvent-separated ions. An example of the interception of an intermediate was described earlier [33] for $NR_3H^+ [Co(CO)_4]^-$, where the nitrogen-bonded proton interacts with the $Co(CO)_3$ moiety of the anion which maintains the C_{3v} symmetry of $CoH(CO)_4$ itself [7].

The pyridinium, quinolinium and acridinium salts have versatile chemistry and several types of reaction have been observed; viz: (a) evolution of dihydrogen on treatment with sodium in tetrahydrofuran, (b) nitrogen base exchange, (c) electron-transfer from $[V(CO)_6]^-$ to proton with formation of dihydrogen; (d) electron-transfer to the cation, with subsequent carbon–carbon coupling; these are indicated in equations 3–6, respectively.

It is of interest that the chemical behaviour of the protonated nitrogen bases can be related to some extent with the pK_a values of the nitrogen bases (Table 1). For example, the derivative of the weak base 2-bromopyridine is readily transformed into $V(CO)_6$, free base, and dihydrogen, according to equation 5. This is believed to be due to a particularly weak N–H bond and its rather facile cleavage. Of particular interest is the reductive carbon–carbon coupling which the acridinium derivative

$$BH^+ \left[V(CO)_6\right]^- + Na \xrightarrow{THF} {}^1\!/_2 H_2 + \left[V(CO)_6\right]^- + Na^+ + B \qquad (3)$$

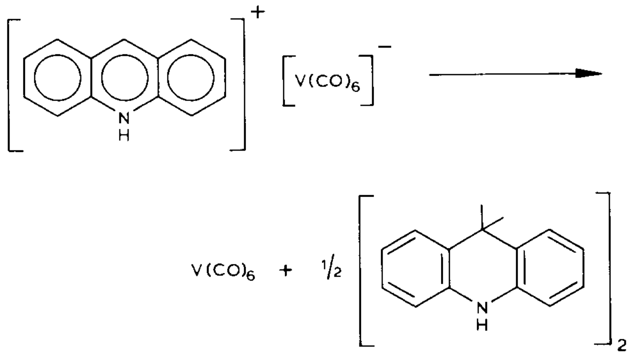
(B = pyridine , quinoline)

$$BH^+ \left[V(CO)_6\right]^- + B' \longrightarrow B'H^+ \left[V(CO)_6\right]^- + B \qquad (4)$$

(B = acridine , B' = pyridine)

$$BH^+ \left[V(CO)_6\right]^- \longrightarrow {}^1\!/_2 H_2 + V(CO)_6 + B \qquad (5)$$

(B = 2-bromopyridine)



(6)

undergoes either thermally or in the presence of oxygen Lewis bases, leading to $V(CO)_6$ and 9,9′-biacridan. In this case the hydrogen is retained by the organic substrate after the electron-transfer from $[V(CO)_6]^-$ has occurred, and the organic radical so obtained undergoes coupling at the 9 position of the ring. Interestingly, acridine was reported [34] to be reduced catalytically to 9,10-dihydroacridine by dihydrogen in the presence of ruthenium or under water-gas-shift conditions in the presence of cobalt. The product of reductive carbon–carbon coupling, 9,9′-biacridan, can be prepared by UV irradiation of acridine in alcohol solution [11a,b] or by chemical reduction [11c,35]. The monoelectronic reduction of organic substrates by $[V(CO)_6]^-$, followed by C–C coupling has precedents in the case of the 1,3-dithiolium- [36] and tropilium [37] hexacarbonylvanadates.

The colours of the compounds reported in this paper deserve some comment. The deep colour probably arises from a charge-transfer band from $[V(CO)_6]^-$ to the nitrogen base. The carbonyl groups are believed to be involved in the charge-transfer process, which may occur either directly or through the proton. The fact that both the quinolinium (VIIA) and the methylquinolinium (VIIB) derivatives are deeply coloured suggests that the interaction is direct from the axial carbonyl groups to the nitrogen base. As shown in Fig. 2, the axial carbonyl groups point directly to the π-system of the nitrogen base. Relevant to this point is the recent interpretation of the black colour of $V(CO)_6$ as being due to a solid-state excitation process ($V(CO)_6 \rightarrow [V(CO)_6]^+[V(CO)_6]^-$) [38].

Dihydrogen is formed from the "C_6HO_6V" precursor or from wet ethereal solution containing H_3O^+ $[V(CO)_6]^-$. In both cases an electron-transfer process from $[V(CO)_6]^-$ to proton is to be envisaged, through the carbonyl groups. The role of the highly unsaturated carbonyl groups as electron transmitters has recently been revealed by the outer-sphere oxidation [39] of carbonyl metalates by $V(CO)_6$ which occurs in hydrocarbon solvents.

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References and Notes

1 H.D. Kaesz and R.B. Saillant, Chem. Rev., 72 (1972) 231.
2 (a) G.L. Geoffroy, M.G. Bradley and R. Pierantozzi, Am. Chem. Soc., Adv. Chem. Ser., 167 (1978) 181; (b) G.M. Geoffroy, Progr. Inorg. Chem., 27 (1980) 123.
3 F. Calderazzo, Ann. N.Y. Acad. Sci., 415 (1983) 37.
4 F. Calderazzo, G. Pampaloni and D. Vitali, Gazz. Chim. Ital., 111 (1981) 455.
5 Typical experimental conditions for reaction 1 are: a suspension of $NaV(CO)_6$ under Ar was treated at dry-ice temperature with dry HCl in saturated hydrocarbon, and the mixture was then allowed to warm to about −30°C.
6 K.M. Nicholas, Organometallics, 1 (1982) 1713.
7 E.A. McNeil and F.R. Scholer, J. Am. Chem. Soc., 99 (1977) 6243.
8 F. Calderazzo and G. Pampaloni, J. Organomet. Chem., 250 (1983) C35.
9 F. Calderazzo and R. Ercoli, Chim. Ind. (Milano), 44 (1962) 990.
10 F. Calderazzo, G. Pampaloni, D. Vitali and P.F. Zanazzi, J. Chem. Soc., Dalton Trans., (1982) 1993.

11 (a) F. Mader and V. Zanker, Chem. Ber., 97 (1964) 2418; (b) H. Göth, P. Cerutti and H. Schmid, Helv. Chim. Acta, 48 (1965) 1395); (c) H. Inoue, I. Sonoda, N. Inoguchi and E. Imoto, Bull. Chem. Soc. Japan, 51 (1978) 3097.

12 M.S. Lehmann and F.K. Larsen, Acta Cryst., A, 30 (1974) 580.

13 D. Belletti, F. Ugozzoli, A. Cantoni and G. Pasquinelli, Gestione on-line di diffrattometro a cristallo singolo Siemens AED con sistema General Automation Jumbo 220, Centro Studio Strutturistica Diffrattometrica, C.N.R., Istituto Chimica Generale, Università di Parma, Internal Reports No. 1,2 and 3, 1979.

14 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.

15 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4.

16 R.D. Wilson and R. Bau, J. Am. Chem. Soc., 96 (1974) 7601.

17 L.D. Silverman, P.W.R. Crofield and S.J. Lippard, Inorg. Chem., 20 (1981) 3106.

18 S. Bellard, K.A. Rubinson and G.M. Sheldrick, Acta Cryst., B, 35 (1979) 271.

19 An acceptable value for the C(aromatic)...O contact would be 3.5 Å, resulting from the sum of 1.4 and 1.14 Å (Van der Waals radii of oxygen and hydrogen, respectively [20]), with addition of 1.0 Å for the C–H bond distance. Experimentally determined values are, for example: 3.084(7) and 3.116(4) [21], 3.11(1) [22] and 3.28 Å [23].

20 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 3rd edit., 1960.

21 A. Mangia, M. Nardelli, C. Pelizzi and G. Pelizzi, Acta Cryst., B, 30 (1974) 17.

22 C. Pelizzi, G. Pelizzi and P. Tarasconi, J. Organomet. Chem., 124 (1977) 151.

23 V. Cody and P.A. Lehmann, Cryst. Struct. Commun., 11 (1982) 1671.

24 T. Glowiak and M. Sabat, J. Cryst. Mol. Struct., 5 (1975) 247.

25 J. Bernstein, H. Regev and F.H. Herbstein, Acta Cryst., B, 36 (1980) 1170.

26 A.J. Serewicz, B.K. Robertson and E.A. Meyers, J. Phys. Chem., 69 (1965) 1915.

27 J.M. Le Carpentier, A. Mitschler and R. Weiss, Acta Cryst., B, 28 (1972) 1288.

28 C. Belin and J. Rozière, Acta Cryst., B, 36 (1980) 467.

29 (a) W.F. Edgell, M.T. Yang and N. Koizumi, J. Am. Chem. Soc., 87 (1965) 2563; (b) W.F. Edgell and J. Lyfor, ibid., 93 (1971) 6407; (c) M. Darensbourg and C. Borman, Inorg. Chem., 15 (1976) 3121; (d) M.Y. Darensbourg, D.J. Darensbourg and D.A. Drew, J. Am. Chem. Soc., 98 (1976) 3127; (e) W.F. Edgell, S. Hedge and A. Barbetta, ibid., 100 (1978) 1406; (f) M.Y. Darensbourg and J.M. Hanckel, J. Organomet. Chem., 217 (1981) C9; (g) F. Calderazzo, G. Pampaloni and G. Pelizzi, 233 (1982) C41.

30 (a) D.F. Shriver and S.A. Alich, Coord. Chem. Rev., 8 (1972) 15; (b) D.F. Shriver, J. Organomet. Chem., 94 (1975) 259; (c) S.B. Butts, E.M. Holt, S.H. Strauss, N.W. Alcock, R.E. Stimson and D.F. Shriver, J. Am. Chem. Soc., 101 (1979) 5864.

31 K.H. Whitmire and D.F. Shriver, J. Am. Chem. Soc., 103 (1981) 6754.

32 G. Fachinetti, Chem. Commun., (1979) 397.

33 F. Calderazzo, G. Fachinetti, F. Marchetti and P.F. Zanazzi, Chem. Commun., (1981) 181.

34 R.H. Fish, A.D. Thormodsen and G.A. Cremer, J. Am. Chem. Soc., 104 (1982) 5234.

35 H. Inoue and K. Higashiura, Chem. Commun., (1980) 549.

36 A.R. Siedle and R.B. Johannesen, J. Org. Chem., 40 (1975) 2002.

37 R.P.M. Werner and S.A. Manastyrskyj, J. Am. Chem. Soc., 83 (1961) 2023.

38 G.F. Holland, M.C. Manning, D.E. Ellis and W.C. Trogler, J. Am. Chem. Soc., 105 (1983) 2308.

39 F. Calderazzo and G. Pampaloni, Chem. Commun., (1984) 1249.