The Reaction of Hexacarbonylvanadium with Aromatic Compounds. Part 4.[1] Properties of Tetracarbonylvanadium Arene Cations and the Crystal and Molecular Structure of Tetracarbonyl(1,2,4,5-tetramethylbenzene)vanadium(I) Hexacarbonylvanadate(1—) *

Fausto Calderazzo, Guido Pampaloni, and Dario Vitali
Istituto di Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy
Pier Francesco Zanazzi,
Istituto di Mineralogia, University of Perugia, Piazza Università, 06100 Perugia, Italy

---

Improved syntheses of the cationic arene complexes of vanadium(I), $[V(CO)_4(C_6H_{6-n}Me_n)]^+$, are reported together with their ^1H n.m.r. spectra. An *X*-ray crystal and molecular structure determination of the title compound has been carried out. Crystals are monoclinic, space group $P2_1/a$, $a = 18.135(5)$, $b = 12.746(4)$, $c = 10.025(4)$ Å, $\beta = 93.03(2)°$, and $Z = 4$. $R = 0.072$ for 1 007 observed reflections (Mo-K_α radiation). In the cation the vanadium atom is half-sandwiched between the arene ligand and the four carbonyl groups, the latter being oriented in such a way as to become eclipsed with respect to two of the methyl groups. The $[V(CO)_6]^-$ anion is a nearly regular octahedron with a mean V–C distance of 1.93 Å and two sets of C–V–C angles, thus leading to a slight trigonal elongation of the octahedron.

A few examples of half-sandwich complexes of vanadium with aromatic hydrocarbons as ligands are known, *e.g.* the cation[2] $[V(CO)_4(C_6H_{6-n}Me_n)]^+$, the anion $[V(CO)_3(C_6H_3Me_3\text{-}1,3,5)]^-$,[3a] and the neutral complex $[V(CO)_3(C_6Ph_6)]$,[3b] which displays the expected paramagnetic behaviour for a 17-electron species. The structure of the $[V(CO)_4(C_6H_{6-n}Me_n)]^+$ cation was assumed[2] to contain the $V(CO)_4$ moiety of C_{4v} symmetry according to i.r. measurements in the carbonyl-stretching region.

We now report some new observations concerning the preparation of the $[V(CO)_4(C_6H_{6-n}Me_n)]^+$ cations, their ^1H n.m.r. data, and the crystal and molecular structure of one of them as the hexacarbonylvanadate(1−) derivative $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+[V(CO)_6]^-$.

Experimental

All manipulations and reactions of the metal complexes were carried out under an atmosphere of prepurified argon, unless otherwise stated. I.r. spectra were measured with a Perkin-Elmer 283 instrument equipped with grating and each spectrum was calibrated with CO and water vapour. Proton n.m.r. spectra were measured with a Varian DP-60A instrument, lowt-emperature spectra with a JEOL PS 100 at 100 MHz. Hexacarbonylvanadium was prepared as described elsewhere.[4] Solvents and reagents were purified according to conventional methods.

Preparation of $[V(CO)_4(C_6H_{6-n}Me_n)]^+[V(CO)_6]^-$.—Hexacarbonylvanadium (2.57 g, 11.7 mmol) in heptane (75 cm^3) was stirred with 1,2,4,5-tetramethylbenzene (16 g, 0.12 mol) under an initial argon atmosphere at 35 °C for 48 h, the internal pressure being kept constant by letting the evolved gas escape from the reaction vessel through a no-return valve. The reaction mixture was finally filtered and the solid was dried *in vacuo* and then washed with distilled water, dried again *in vacuo* and dissolved in tetrahydrofuran (thf). The complex was reprecipitated from the thf solution by addition of diethyl ether, filtered off, and dried *in vacuo* (yield 58.85%).

By using similar procedures the toluene and the mesitylene complexes were prepared in yields of 22 and 67%, respectively.

The reaction of $C_6H_3Me_3\text{-}1,3,5$ with $[V(CO)_6]$ was monitored by measuring the amount of CO evolved with time. Assuming that the stoicheiometry of the reaction is as in equation (1)

$$2[V(CO)_6] + C_6H_{6-n}Me_n \longrightarrow [V(CO)_4(C_6H_{6-n}Me_n)]^+[V(CO)_6]^- + 2\,CO \quad (1)$$

the number of moles of CO evolved corresponds to that of $[V(CO)_6]$ which has reacted. The reaction was carried out at 32.8 °C, in neat $C_6H_3Me_3\text{-}1,3,5$ previously saturated with CO under a total pressure ($p_{C_6H_3Me_3\text{-}1,3,5} + p_{CO}$) equal to the atmospheric pressure, *i.e.* under conditions of substantially constant arene concentration and CO partial pressure.

Despite the numerous attempts made, no simple kinetic expression was found to fit the experimental data, suggesting that a secondary reaction liberating carbon monoxide was interfering with the main reaction. The CO evolved was slightly over the expected amount, and yet unreacted $[V(CO)_6]$ was still found at the end.

Reaction of $[V(CO)_4(C_6H_3Me_3\text{-}1,3,5)]^+[V(CO)_6]^-$ *with Tetrahydrofuran.*— A solution of the mesitylene complex (3.9×10^{-2} mol dm^{-3}) in thf initially prepared under an atmosphere of argon was stirred at 19.9 ± 0.1 °C and the reaction was monitored by measuring the CO evolved. After about 24 h, the gas evolved corresponded to a CO : complex molar ratio of 0.4 : 1. The i.r. spectrum of the resulting solution showed the presence of unreacted starting material and an intense band at about 1 860 cm^{-1}, typical of $[V(CO)_6]^-$. On the basis of the expected stoicheiometry for reaction (2), it was calculated that the reaction had proceeded to the extent of about 20%.

$$3\,[V(CO)_4(C_6H_{6-n}Me_n)][V(CO)_6] \xrightarrow{\text{thf}} 2\,[V(thf)_m][V(CO)_6]_2 + 6\,CO + 3\,C_6H_{6-n}Me_n \quad (2)$$

A similar experiment carried out under a total constant pressure of carbon monoxide and solvent of 1 atm (≈10^5 N m^{-2}) gave substantially the same results, even in terms of gas evolved with time. After about a week the observed CO : complex molar ratio was 1.44 : 1.

Crystallographic Data Collection and Molecular Structure Refinement.—Crystals of the $C_6H_2Me_4\text{-}1,2,4,5$ complex were

---

* *Supplementary data available* (No. SUP 23358; 8 pp.): observed and calculated structure factors, thermal parameters.

Table 1. Crystal data and summary of intensity data and structure refinement for $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5]^+[V(CO)_6]^-$

Formula	$C_{20}H_{14}O_{10}V_2$
M	515.8
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	18.135(5)
b/Å	12.746(4)
c/Å	10.025(4)
β/°	93.03(2)
U/Å^3	2 314.0
Z	4
D_c/g cm^{-3}	1.480
Measured reflections	2 288
Refined reflections	1 007
R	0.072
R'	0.077

Table 2. Fractional atomic co-ordinates for non-hydrogen atoms in $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+[V(CO)_6]^-$, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
V(1)	0.069 9(2)	0.243 6(3)	0.204 5(4)
V(2)	0.321 2(2)	0.220 3(2)	0.708 7(3)
O(1)	0.115 7(9)	0.139 6(14)	0.473 7(17)
O(2)	0.183 3(9)	0.418 8(11)	0.275 9(17)
O(3)	0.027 9(10)	0.343 5(21)	−0.071 9(19)
O(4)	−0.041 8(10)	0.061 2(14)	0.131 8(19)
O(5)	0.194 4(10)	0.118 6(12)	0.091 4(18)
O(6)	−0.052 7(10)	0.372 4(13)	0.326 6(20)
O(7)	0.462 4(8)	0.091 2(12)	0.656 0(16)
O(8)	0.359 3(8)	0.100 6(12)	0.972 6(14)
O(9)	0.179 9(8)	0.099 8(10)	0.764 9(14)
O(10)	0.282 1(8)	0.102 6(12)	0.442 9(14)
C(1)	0.098 3(13)	0.179 9(18)	0.372 7(24)
C(2)	0.141 5(11)	0.353 4(15)	0.248 8(19)
C(3)	0.043 5(13)	0.308 0(20)	0.033 8(26)
C(4)	−0.000 7(14)	0.132 3(19)	0.156 5(24)
C(5)	0.145 5(13)	0.165 1(17)	0.131 0(24)
C(6)	−0.008 3(12)	0.324 2(16)	0.277 9(21)
C(7)	0.409 6(12)	0.138 2(15)	0.677 1(21)
C(8)	0.344 4(11)	0.146 1(14)	0.872 8(22)
C(9)	0.232 6(11)	0.142 9(14)	0.738 2(19)
C(10)	0.295 3(10)	0.142 8(14)	0.543 9(21)
C(11)	0.397 8(6)	0.365 2(9)	0.685 9(13)
C(12)	0.345 8(6)	0.365 8(9)	0.578 2(13)
C(13)	0.270 6(6)	0.367 7(9)	0.600 9(13)
C(14)	0.247 3(6)	0.369 0(9)	0.731 3(13)
C(15)	0.299 3(6)	0.368 4(9)	0.839 0(13)
C(16)	0.374 5(6)	0.366 5(9)	0.816 3(13)
C(17)	0.482 7(13)	0.370 8(17)	0.671 1(24)
C(18)	0.364 9(11)	0.367 5(15)	0.432 1(20)
C(19)	0.162 7(13)	0.380 9(19)	0.744 8(23)
C(20)	0.282 4(13)	0.368 7(18)	0.988 6(25)

Table 3. Interatomic distances (Å) and angles (°) in $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+[V(CO)_6]^-$

(*a*) Distances

V(1)-C(1)	1.92(3)	V(2)-C(10)	1.96(2)
V(1)-C(2)	1.94(2)	V(2)-C(11)	2.33(2)
V(1)-C(3)	1.94(3)	V(2)-C(12)	2.33(2)
V(1)-C(4)	1.95(3)	V(2)-C(13)	2.33(2)
V(1)-C(5)	1.88(2)	V(2)-C(14)	2.34(2)
V(1)-C(6)	1.93(2)	V(2)-C(15)	2.34(2)
		V(2)-C(16)	2.34(2)
C(1)-O(1)	1.16(2)		
C(2)-O(2)	1.15(2)	C(7)-O(7)	1.16(2)
C(3)-O(3)	1.17(3)	C(8)-O(8)	1.18(2)
C(4)-O(4)	1.19(2)	C(9)-O(9)	1.15(2)
C(5)-O(5)	1.15(2)	C(10)-O(10)	1.15(2)
C(6)-O(6)	1.14(2)		
		C(11)-C(17)	1.56(2)
		C(12)-C(18)	1.52(2)
V(2)-C(7)	1.95(2)	C(14)-C(19)	1.56(2)
V(2)-C(8)	1.92(2)	C(15)-C(20)	1.53(3)
V(2)-C(9)	1.92(2)		

(*b*) Angles

C(1)-V(1)-C(2)	87.7(9)	C(7)-V(2)-C(9)	116.7(7)
C(1)-V(1)-C(3)	178.8(11)	C(7)-V(2)-C(10)	75.9(8)
C(1)-V(1)-C(4)	92.9(10)	C(8)-V(2)-C(9)	76.3(8)
C(1)-V(1)-C(5)	87.3(10)	C(8)-V(2)-C(10)	120.3(7)
C(1)-V(1)-C(6)	93.4(9)	C(9)-V(2)-C(10)	72.9(8)
C(2)-V(1)-C(3)	91.6(9)	V(1)-C(1)-O(1)	179(2)
C(2)-V(1)-C(4)	178.7(10)	V(1)-C(2)-O(2)	179(2)
C(2)-V(1)-C(5)	88.9(9)	V(1)-C(3)-O(3)	177(3)
C(2)-V(1)-C(6)	91.4(8)	V(1)-C(4)-O(4)	177(2)
C(3)-V(1)-C(4)	87.8(10)	V(1)-C(5)-O(5)	176(2)
C(3)-V(1)-C(5)	91.8(10)	V(1)-C(6)-O(6)	177(2)
C(3)-V(1)-C(6)	87.6(10)	V(2)-C(7)-O(7)	178(2)
C(4)-V(1)-C(5)	89.9(10)	V(2)-C(8)-O(8)	179(2)
C(4)-V(1)-C(6)	89.7(9)	V(2)-C(9)-O(9)	175(2)
C(5)-V(1)-C(6)	179.3(11)	V(2)-C(10)-O(10)	176(2)
C(7)-V(2)-C(8)	74.4(9)		

recrystallized by dissolution in thf and slow diffusion of a layer of diethyl ether. A prismatic crystal of $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+[V(CO)_6]^-$ of dimensions 0.40 × 0.35 × 0.20 mm was sealed in a Lindemann capillary and mounted on a Philips PW1100 four-circle diffractometer equipped with graphite monochromator and using Mo-K_α radiation. Crystals of the complex are monoclinic, space group $P2_1/a$ (from systematic absences). The unit-cell dimensions were measured from the angular settings of 25 reflections. Data are in Table 1.

Intensity data were collected by the $\omega/2\theta$ method, using a scan speed of 0.05° s^{-1}, a scan width of 1.4ω°, and a 5 s background count at the scan extremities; $\theta_{max.} = 20°$. Lorentz-polarisation corrections were applied; $\sigma(F)$ values were calculated from counting statistics. No absorption correction was applied [μ(Mo-K_α) = 9.6 cm^{-1}]. Of 2 288 reflections measured, 1 007 with $I \geqslant 3\sigma(I)$ were used in the refinement.

The structure was determined in straightforward fashion by Patterson methods and refined using anisotropic temperature factors for V and O atoms. The phenyl ring of the tetramethylbenzene ligand was constrained to a perfect hexagon, with C–C distances of 1.395 Å. The minimized quantity was $\Sigma w|F_o^2 - F_c^2|/\Sigma F_o^2$; the weighting factor used in the final refinement stages was $w = 1/[\sigma^2(F) + 0.0009\ F^2]$. The SHELX 76 [5] computing package were used for all calculations. The atomic scattering factors were taken from ref. 6 for vanadium, and from ref. 5 for O and C. The final R factor was 0.072 (R' = 0.077) for 178 parameters. Positional parameters of atoms are listed in Table 2 and bond distances and angles are in Table 3.

Results and Discussion

Higher yields of the arene complexes of vanadium(I) as hexacarbonylvanadate derivatives have been obtained; the improvement derives from not allowing the partial pressure of carbon monoxide to become too low during the displacement of carbon monoxide from $[V(CO)_6]$ by the arene.

In an earlier paper [2] it was suggested that the formation of the arene complexes was occurring *via* displacement of the coordinated CO of $[V(CO)_6]$ by the arene acting initially as an

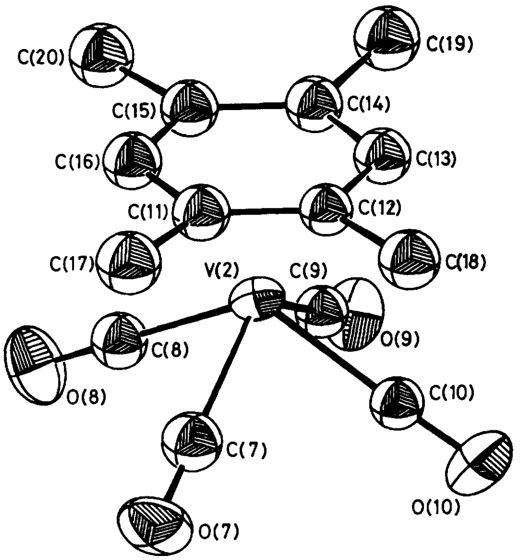


Figure 1. View of cation in $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+[V(CO)_6]^-$

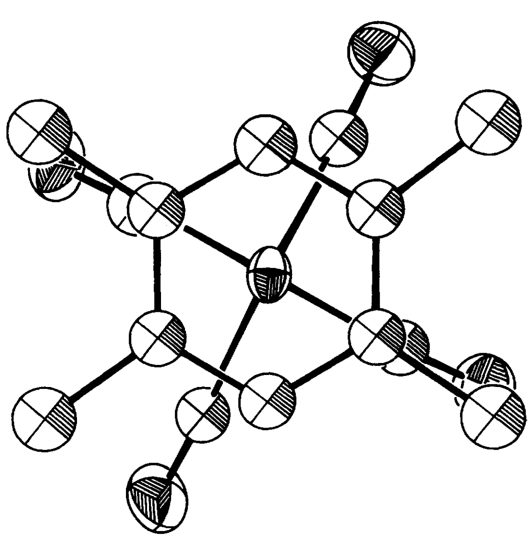


Figure 2. View of the $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+$ cation along the four-fold symmetry axis of the $V(CO)_4$ group

η^2 unidentate ligand, followed by electron transfer and further CO displacement. Despite our attempts to carry out a kinetic study of the complex formation, no further insight into this problem could be obtained.

As already noted earlier [1,2] the thermal and chemical stability of these complexes increased with methyl substitution on the ring. We have specifically investigated the chemical stability of the mesitylene complex with respect to substitution by thf. By operating at different partial pressures of carbon monoxide it was found that the CO evolved with time was substantially constant and the i.r. spectrum of the resulting solution was consistent with the presence of unreacted starting material and $[V(CO)_6]^-$ only. This suggests that the substitution [see equation (2) of the Experimental section] of the arene and carbon monoxide ligands by thf leads to the so-called disproportionation product [7] of $[V(CO)_6]$ with thf. The fact that the rate of the displacement reaction is not substantially affected by carbon monoxide suggests that the rate-determining step in the reaction sequence is the substitution of the arene ligand by thf.

The *X*-ray diffractometric study of $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+[V(CO)_6]^-$ has definitely established the molecular structure of the complex cation and, moreover, serves to elucidate further the molecular structure of the $[V(CO)_6]^-$ anion.[8] The complex cation and the $[V(CO)_6]^-$ anion exist as discrete units in the crystal.

In the $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+$ cation, the four-fold axis of symmetry for the $V(CO)_4$ moiety passes through the centre of the six-membered ring, see Figure 2. This axis is nearly parallel to the crystallographic *b* axis. The vanadium atom is almost equidistant from the six carbon atoms of the six-membered ring, the mean V–C distance being 2.33 Å in the range 2.33—2.34 Å. The perpendicular distance of the vanadium atom from the ring plane is 1.87 Å.

The tetracarbonylvanadium fragment which possesses approximately C_{4v} symmetry has C–V–C angles averaging 74.9°, in the range 72.9—76.3°. The mean bond distances in the tetracarbonylvanadium moiety are V–C 1.94 Å, C–O 1.16 Å. The angles between the vanadium–carbonyl bonds and the axis passing through the centre of the six-membered ring are in the range 119.3—121.6° (mean value 120.7°). The mean V–C distance within the carbonyl groups of the cationic moiety is identical within experimental error to the corresponding distance in another vanadium(I) tetracarbonyl derivative, $[V(CO)_4(\eta^3\text{-}C_3H_5)(PPh_3)]$.[9] The mean V–C distance within the carbonyl groups of $[V(CO)_4(\eta^5\text{-}C_5H_5)]$ [10] is 1.91 ± 0.03 Å. The carbonyl groups are substantially linear in all these cases, including the present complex.

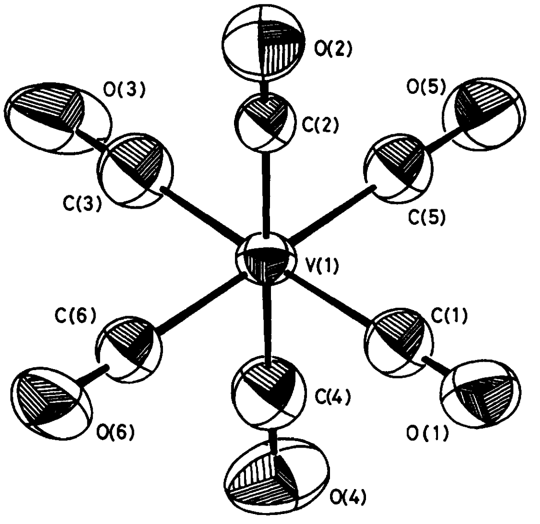
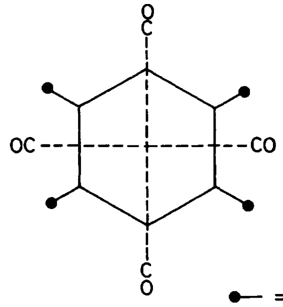


Figure 3. View of the $[V(CO)_6]^-$ anion

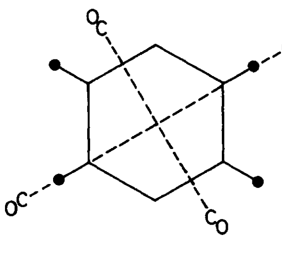
Planarity of the arene ligand was imposed, an assumption which seems reasonable in view of earlier reports [11] on bis-arene and arene–carbonyl complexes of chromium. Slight deviations, if any, from planarity have been detected only with accurate measurements at liquid-nitrogen temperature [12] or they have been assumed [13] to be due to packing effects.

The C–C bond distances to the methyl groups of the arene ligand, see Table 3, are all the same within experimental error. It can be clearly seen from Figure 2 that two of the carbonyl groups of the $V(CO)_4$ moiety are almost eclipsed with respect to two of the methyl groups of the arene ligand, whereas the best plane containing the remaining two carbonyl groups forms a dihedral angle of about 30° with the plane containing the other two methyl groups of the η^6-arene ligand. It is interesting to note that the carbonyl groups are not staggered with respect to the methyl groups, as in (I), but they rather assume the eclipsed orientation roughly shown in (II). Orientation (I) might have been expected to be more favourable on the basis of purely steric arguments. While the problem of carbonyl group orientation in tricarbonylchromium arene complexes has been treated extensively,[14–16] there is no instance in the literature of a four-fold relationship to a cyclic six-membered ligand, as in the present vanadium complexes.

The non-bonding distances within the $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+$ moiety are O(9) ··· C(19) 3.602(2), C(9) ··· O(14) 2.895(2), and C(7) ··· C(11) 2.903(2) Å. These values themselves do not appear to suggest any specific van der Waals interaction between carbonyl and methyl groups. To a reasonable approximation, the $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+$ cation may be regarded as a complex of seven-co-ordinate d^4 vanadium(I), the idealized molecular geometry being that of a capped trigonal prism (III) where the positions 'A' are occupied by the four carbonyl groups. The orientation of the six-membered ring with respect to the four carbonyl groups is presumably dictated, *in the solid state*, by packing effects or by the preferred use of metal *d* orbitals for bonding. Concerning the latter hypothesis, it is noted that orientation (I), which involves overlap between the carbonyl groups and the ring carbon atoms possessing the maximum electron density due to the *ortho*-directing effect of the methyl groups, is not the preferred one. The effect of *ortho*- and *para*-directing ring substituents with respect to *meta*-directing groups on the geometry of tricarbonylchromium arene complexes has been examined previously by Sim and co-workers.[14–16] As discussed below, the ¹H n.m.r. data suggest that orientation (II) does not persist in solution.

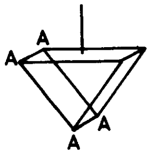


(I)



●— = CH_3

(II)



(III)

The hexacarbonylvanadate anion (Figure 3) exhibits a nearly perfect octahedral structure with V–C distances in the range 1.88—1.95 Å (mean 1.93 Å). The C–O distances average 1.16 Å and the mean V–O non-bonding distance is 3.09 Å. The $[V(CO)_6]^-$ anion has a three-fold axis roughly aligned with the crystallographic *b* axis. It is worth noting that the C–V–C angles within the ' octahedron ' are divided into two sets of relatively large [mean value 92.6(10)°] and small [mean value 87.9(9)°] values, thus suggesting that the anion is in fact elongated along a trigonal axis, the molecular symmetry thus tending to become D_{3d}. Previous results of the *X*-ray diffractometric study [7a] of $[N(PPh_3)_2]^+[V(CO)_6]^-$ can be taken to suggest that a similar elongation, although much smaller than in the present case, is operating within the anion. Further studies, both in solution and in the solid state are, however, necessary in order to generalize this observation.

Table 4. Proton n.m.r. data of $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+$ cations as hexacarbonylvanadates(1−) [a]

Arene	Chemical shift (p.p.m.)	Δ/p.p.m.[b]
C_6H_6	+7.23 (s, 6 H)	0.0
C_6H_5Me	+7.2—7.26 (m, 5 H)	*c*
	+2.54 (s, 3 H)	+0.31
$C_6H_4Me_2$-*p*	+7.16 (s, 4 H)	+0.19
	+2.47 (s, 6 H)	+0.27
$C_6H_3Me_3$-1,3,5	+7.05 (s, 3 H)	+0.40
	+2.55 (s, 9 H)	+0.40
$C_6H_2Me_4$-1,2,4,5	+7.33 (s, 2 H)	+0.50
	+2.47 (s, 12 H)	+0.35
C_6Me_6	+2.60 (s, 18 H)	+0.47

[a] In [²H₆]acetone for freshly prepared solutions at room temperature; positive downfield shifts relative to $SiMe_4$ as internal standard. [b] Δ = δ (complexed arene) − δ (uncomplexed arene), both measured in the same solvent under the same conditions. [c] Proton n.m.r. spectrum of toluene in [²H₆]acetone: +7.1—7.18 (m, 5 H), +2.23 (s, 3 H). Proton n.m.r. spectrum of $[Cr(CO)_3(C_6H_5Me)]$ in [²H₆]acetone: +5.37—5.77 (m, 5 H), +2.18 (s, 3 H).

The shortest intermolecular non-bonding distances (O ··· O 3.03, O ··· C 3.17, and C ··· C 3.75 Å) are greater than the sum of the van der Waals radii, indicating no unusually close approaches between neighbours, and a fairly loose packing.

Table 4 reports the ¹H n.m.r. spectra of some $[V(CO)_4(C_6H_{6-n}Me_n)]^+$ cations as hexacarbonylvanadates, in comparison with the corresponding resonances of the uncomplexed aromatic hydrocarbon in the same solvent. (The ¹H n.m.r. spectra of tricarbonylchromium arene complexes have been studied extensively.[17]) The present ¹H n.m.r. data show the phenyl and methyl resonances for the symmetrical vanadium-bonded arenes as singlets, thus in agreement with either the presence of conformer (I) in solution or with a rapid (on the n.m.r. time-scale) rotation about the vanadium–arene bond giving a time-averaged spectrum. Single resonances for both the ring and methyl protons were observed for the $[V(CO)_4(C_6H_2Me_4\text{-}1,2,4,5)]^+$ cation down to −80 °C, which was the lowest temperature we could reach in [²H₈]thf as solvent. The chemical shifts of the ring protons in our compounds do not compare with those observed for tricarbonylchromium arene complexes.[17] In fact, while the ring protons of the chromium(0) complexes are shifted by about 1.5 p.p.m. *upfield* with respect to the corresponding uncomplexed aromatic compound, the ring protons of the vanadium(I) complexes are shifted by about 0.1—0.5 p.p.m. *downfield* with respect to the uncomplexed aromatic hydrocarbon. It appears that the dominating factor in determining the proton chemical shifts in the present case is the electron transfer to the central metal atom and the positive charge on the cation which both co-operate effectively to deshield the protons. It is interesting to note that in other cationic bis(η^6-arene) complexes, *e.g.* of iridium(I),[18] the ring protons of the arene ligand are still shifted *upfield* by 0.1—0.5 p.p.m. on complexation. Another interesting aspect of these measurements is that the effect of complexation to vanadium on the methyl protons is comparable to that on the ring protons and in the same direction, *i.e. downfield.* The largest effect was observed for the hexamethylbenzene complex, despite the fact that the effect is now distributed among six methyl groups. By taking the chromium(0) complexes as a reference, the effect of complexation on the chemical shift of the methyl protons is smaller than in the present case and much smaller than the similar effect on the ring protons.

Acknowledgements

The authors wish to thank the National Research Council (C.N.R., Rome) for financial support, and the Scuola Normale Superiore of Pisa for a postdoctoral fellowship (to G. P.).

References

1 Part 3, F. Calderazzo, *Inorg. Chem.*, 1966, **5**, 429.
2 F. Calderazzo, *Inorg. Chem.*, 1964, **3**, 1207.
3 (*a*) A. Davison and D. L. Reger, *J. Organomet. Chem.*, 1970, **23**, 491; (*b*) M. Schneider and E. Weiss, *J. Organomet. Chem.*, 1976, **114**, C43.
4 F. Calderazzo, G. Pampaloni, and D. Vitali, *Gazz. Chim. Ital.*, 1981, **111**, 455.
5 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
6 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101.
7 (*a*) W. Hieber, E. Winter, and E. Schubert, *Chem. Ber.*, 1962, **95**, 3070; (*b*) F. Calderazzo and R. Ercoli, *Chim. Ind. (Milan)*, 1962, **44**, 990.
8 R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1974, **96**, 7601; M. Schneider and E. Weiss, *J. Organomet. Chem.*, 1976, **121**, 365; L. D. Silverman, P. W. R. Corfield, and S. J. Lippard, *Inorg. Chem.*, 1981, **20**, 3106.
9 M. Schneider and E. Weiss, *J. Organomet. Chem.*, 1976, **121**, 189.
10 J. B. Wilford, A. Whitla, and H. M. Powell, *J. Organomet. Chem.*, 1967, **8**, 495.
11 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314; E. Keulen and F. Jellinek, *J. Organomet. Chem.*, 1966, **5**, 490; E. Förster, G. Albrecht, W. Dürselen, and E. Kurras, *J. Organomet. Chem.*, 1969, **19**, 215; L. H. Ngai, F. E. Stafford, and L. Schäfer, *J. Am. Chem. Soc.*, 1969, **91**, 48; L. Schäfer, J. F. Southern, S. J. Cyvin, and J. Brunvoll, *J. Organomet. Chem.*, 1970, **24**, C13.
12 B. Rees and P. Coppens, *J. Organomet. Chem.*, 1972, **42**, C102.
13 F. G. N. Cloke, K. P. Cox, M. L. H. Green, J. Bashkin, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 1981, 117.
14 O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1966, 822.
15 O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1967, 228, 1619.
16 M. A. Busch, T. A. Dullforce, and G. A. Sim, *Chem. Commun.*, 1969, 1491.
17 W. McFarlane and S. O. Grim, *J. Organomet. Chem.*, 1960, **5**, 147; H. P. Fritz and C. G. Kreiter, *J. Organomet. Chem.*, 1967, **7**, 427; B. Deubzer, H. P. Fritz, C. G. Kreiter, and K. Öfele, *J. Organomet. Chem.*, 1967, **7**, 289.
18 A. C. Sievert and E. L. Muetterties, *Inorg. Chem.*, 1981, **20**, 289.

Received 17th February 1982; Paper 2/294