present structure that this compound will turn out to be $[Co(AA)_2]_3H_2O$, derived from $[Co(AA)_2]_4$ by removal of one of the terminal $Co(AA)_2$ groups and insertion of the water molecule into the position thus opened on one of the cobalt atoms.

The persistence of the central part of the $[Co(AA)_2]_4$ molecule in which two octahedra share only an edge, while the shared faces are lost, is not necessarily surprising. Although in a kinetic sense a species with three bridging groups might be in general more stable than one with only two, in a thermodynamic sense, the effects of ring distortions and repulsions may tend to cancel the advantage of additional bonding. Moreover, the coplanar arrangement of the metal atoms and the two chelate rings to which the bridging oxygen atoms belong may permit a significant degree of π bonding to occur, thus increasing the stability of this portion of the $[Co(AA)_2]_4$ molecule.

Acknowledgment.—We wish to thank Mrs. S. M. Morehouse, who measured a large portion of the data on the XRD-5, and Professors D. P. Shoemaker and A. Davison for some helpful discussions. Computation necessary to determine the crystal structure was performed on the MIT Computation Center IBM 7090 and 7094 machines.

TABLE VII
"BEST PLANES" OF LIGANDS

Direction cosines		Distances to origin	
$L = 0.567$	$M = 0.552$	$N = 0.611$	$D = 5.34$
Distances of atoms from plane			
R_1O_1	−0.011		
R_1O_2	0.011	Co_1	0.258
R_1C_2	0.022	R_1C_1	0.139
R_1C_3	0.013	R_1C_5	−0.221
R_1C_4	−0.036		
$L = -0.383$	$M = 0.493$	$N = 0.781$	$D = -3.76$
R_4O_1	0.006		
R_2O_2	−0.011	Co_1	0.162
R_2C_2	−0.006	R_2C_1	−0.076
R_2C_3	−0.026	R_2C_5	0.030
R_2C_4	0.038		
$L = -0.242$	$M = 0.445$	$N = 0.862$	$D = 8.87$
R_3O_1	0.003		
R_3O_2	0.001	Co_2	−0.141
R_3C_2	−0.019	R_3C_1	0.119
R_3C_3	0.025	R_3C_5	0.138
R_3C_4	−0.012		
$L = 0.796$	$M = 0.602$	$N = 0.052$	$D = 6.71$
R_4O_1	−0.009		
R_4C_2	0.009	Co_2	0.235
R_4C_2	0.022	R_4C_1	−0.058
R_4C_3	0.005	R_4C_5	−0.096
R_4C_4	−0.028		

CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

The Reaction of Hexacarbonylvanadium with Aromatic Compounds. III. Reduction of the $[V(CO)_4arene]^+$ Cations to Tetracarbonyl-π-cyclohexadienylvanadium Derivatives[1]

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The hexacarbonylvanadate of the $[V(CO)_4C_6H_6]^+$ cation reacts with sodium tetrahydridoborate to give the red crystalline volatile $V(CO)_4C_6H_7$ in about 60% yield. On the basis of infrared and nmr data this is shown to be tetracarbonyl-π-cyclohexadienylvanadium. Methyl-substituted cyclohexadienyl compounds $V(CO)_4C_6H_{7-n}(CH_3)_n$ are also described, being obtained by reduction of the methyl-substituted arene vanadium compounds $[V(CO)_4C_6H_{6-n}(CH_3)_n]^+$. Similar reactions with $NaBD_4$ yielded the corresponding deuterated compounds. The nmr spectra suggest that the addition of hydrogen occurs preferentially at unsubstituted positions of the aromatic ring in $[V(CO)_4C_6H_{6-n}(CH_3)_n]^+$. The type of bonding between the metal and the cyclohexadienyl system and the conformation of the cyclohexadienyl ligand are briefly discussed.

Introduction

The reactions of hexacarbonylvanadium with aromatic compounds to give the tetracarbonylarenevanadium(I) hexacarbonylvanadate(−I), $[V(CO)_4arene][V(CO)_6]$, have been described previously.[2,3]

It was conceivable that the still unknown $V(CO)_3$-arene compounds could be obtained by reduction of the $[V(CO)_4arene]^+$ cations. However, some attempts to synthesize them by sodium metal or lithium tetrahydridoaluminate reductions were unsuccessful. In the course of similar experiments with $NaBH_4$ it was found instead that the vanadium cations were reduced to a new class of complexes, namely the tetracarbonyl-π-cyclohexadienylvanadium derivatives. The properties of these new compounds are described in the present paper.

Experimental Section

All the operations were carried out in an atmosphere of prepurified nitrogen.

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[1] Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug. 30–Sept. 3, 1965.

[2] Part II: F. Calderazzo, *Inorg. Chem.*, **4**, 233 (1965).

[3] F. Calderazzo, *ibid.*, **3**, 1207 (1964).

Table I

Properties[a] and Analytical Data of $V(CO)_4C_6H_7$ and Its Methyl Derivatives

Compound	Mp, °C	% C		% H		% V	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$V(CO)_4C_6H_7$ (I)	66 dec	49.61	49.68	2.91	2.88	21.04	21.04
$V(CO)_4(CH_3)_2C_6H_5$ (II)[b]	63–68 dec	53.35	53.14	4.10	4.20	18.86	19.08
$V(CO)_4(CH_3)_2C_6H_5$ (III)[c]	n.d.	53.35	52.73	4.10	4.18	18.86	19.29
$V(CO)_4(CH_3)_3C_6H_4$ (IV)[d]	92–94 dec	54.94	55.30	4.61	4.34	17.92	18.05
$V(CO)_4(CH_3)_3C_6H_4$ (V)[e]	70–73 dec	54.94	55.24	4.61	5.03	17.92	17.83
$V(CO)_4(CH_3)_3C_6H_4$ (VI)[f,g]	. . .						
$V(CO)_4(CH_3)_4C_6H_3$ (VII)[h]	73–74	56.39	56.35	5.07	5.49	17.08	16.90
$V(CO)_4(CH_3)_4C_6H_3$ (VIII)[i]	73–75	56.39	56.22	5.07	5.32	17.08	17.33
$V(CO)_4(CH_3)_6C_6H$ (IX)[g]	. . .						

[a] All compounds are brown-red. [b] Prepared by reduction of the 1,2-dimethylbenzenevanadium cation. [c] Prepared by reduction of the 1,4-dimethylbenzene derivative. Molecular weight (cryoscopy in cyclohexane) calcd 270, found 290. [d] Prepared from the 1,3,5-trimethylbenzene derivative. [e] Prepared from the 1,2,3-trimethylbenzene derivative. [f] Prepared from the 1,2,4-trimethylbenzene derivative. [g] Identified by infrared spectrum only. [h] Prepared from the 1,2,4,5-tetramethylbenzene derivative. [i] Prepared from the 1,2,3,4-tetramethylbenzene derivative.

Diethyl ether and tetrahydrofuran were refluxed over sodium, distilled over lithium tetrahydridoaluminate, and used shortly after distillation.

The $[V(CO)_4arene]^+$ were prepared as hexacarbonylvanadates according to the procedure previously described.[2,3]

The infrared spectra were recorded on Perkin-Elmer Model 221 and 521 instruments equipped with grating. The spectra in the C–O stretching region were measured on an expanded abscissa scale (5 cm^{-1}/cm or 10 cm^{-1}/cm) and calibrated with CO.

The nmr spectra were measured on a Varian DP60 A spectrometer using tetramethylsilane as internal standard. The solutions for nmr were prepared in the usual glass tubes which were then sealed under nitrogen. The melting points (uncorrected) were determined in sealed capillaries under nitrogen.

Microanalyses are by Dr. K. Eder, Ecole de Chimie, Geneva, Switzerland.

(1) **Preparation of $V(CO)_4C_6H_7$.**—The reduction of the benzene cation $[V(CO)_4C_6H_6]^+$ is here described in detail, the operations being substantially identical for the preparation of all the other cyclohexadienyl complexes. The yields are in the range 30–60%, except for the compounds derived from the hexamethylbenzene and the 1,2,4-trimethylbenzene cations, which were identified only by infrared spectrum (see Table I) because of the low yields.

Sodium tetrahydridoborate (0.052 g, 1.37 mmoles) in 10 ml of tetrahydrofuran was allowed to react with tetracarbonylbenzenevanadium(I) hexacarbonylvanadate(−I) (0.21 g, 0.46 mmole) for 15 min at room temperature. The solvent was evaporated at reduced pressure and *n*-pentane added to the solid residue. By filtration a yellow crystalline residue of $NaV(CO)_6$ was separated from the clear red-brown solution of the cyclohexadienyl complex. By evaporation of the solvent and sublimation of the brown crystalline solid at 45° (~10^{-2} mm), 0.07 g of pure $V(CO)_4C_6H_7$ was obtained (63% yield).

Sodium hexacarbonylvanadate formed in the reaction was dissolved in water and the $[V(CO)_6]^-$ anion characterized by precipitation with $[Ni(o\text{-phenanthroline})_3]^{2+}$.

Infrared data for some of the compounds prepared are as follows (KBr disks). The bands in the C–H and C–O stretching regions are not reported (for them, see Tables II and III).

$V(CO)_4C_6H_7$ (I).—1520 m, 1480 w, 1460 m, 1440 m, 1410 s, 1330 mw, 1310 m, 1260 w, 1190 w, 1160 wm, 1148 m, 1096 w, 1050 m, 995 m (sh), 980 ms, 968 m, 918 m, 885 w, 865 s, 835 w (sh), 770 ms, 680 m, 652 m, 620 vs, 610 vs, 590 vs, 570 s, 560 s, 500 vs, 485 vs, 444 s, 428 s, 370 wm, 325 w cm^{-1}.

$V(CO)_4(CH_3)_2C_6H_5$ (III).—1540 w, 1520 m, 1500 mw, 1460 m, 1455 m, 1443 m, 1430 mw, 1383 s, 1350 w, 1310 ms, 1220 w, 1210 w, 1195 w, 1185 w, 1165 w, 1120 w, 1105 w, 1055 w, 1035 s, 1025 m, 1000 sh, 985 s, 950 m, 910 m, 860 ms, 800 s, 700 m, 640 s, 615 vs, 590 vs, 570 s, 500 s, 475 vs, 450 s, 435 ms, 390 m, 370 m, 345 mw cm^{-1}.

$V(CO)_4(CH_3)_2C_6H_4D$ (IIID).—1535 w, 1500 m, 1465 w, 1450 m, 1440 m, 1430 mw, 1380 s, 1350 w, 1330 ms, 1310 w, 1290 ms, 1260 vw, 1200 w, 1165 w, 1120 w, 1070 w, 1030 s, 1010 sh, 1000 m, 985 sh, 950 m, 920 w, 895 m, 860 s, 840 m, 820 w, 795 w, 775 w, 725 w, 700 w, 633 s, 610 vs, 590 vs, 565 s, 505 s, 475 vs, 450 s, 432 ms, 385 w, 370 m, 350 mw, 340 mw cm^{-1}.

$V(CO)_4(CH_3)_3C_6H_4$ (IV).—1455 m, 1440 m, 1390 s, 1385 s, 1365 w, 1330 wm, 1275 wm, 1265 w, 1145 w, 1050 s, 1014 m, 1010 m, 975 ms, 930 w, 895 m, 860 mw, 838 w, 800 w, 688 w, 630 s, 620 s, 600 vs, 594 vs, 564 m, 515 ms, 485 ms, 475 ms, 460 ms, 445 ms, 430 ms, 400 m, 380 wm, 340 wm cm^{-1}.

$V(CO)_4(CH_3)_3C_6H_3D$ (IVD).—1452 m, 1442 m, 1390 s, 1384 s, 1364 w, 1330 wm, 1320 wm, 1265 wm, 1143 w, 1048 ms, 1042 s, 1020 w, 1010 wm, 1004 m, 964 m, 900 w, 893 m, 853 w, 835 w, 810 m, 685 w, 625 s, 615 s, 595 vs, 564 m, 515 ms, 485 ms, 475 ms, 455 ms, 445 ms, 430 ms, 385 m, 380 wm (sh), 335 wm cm^{-1}.

$V(CO)_4(CH_3)_4C_6H_3$ (VII).—1510 m, 1460 ms, 1445 m, 1435 m (sh), 1390 s, 1325 m, 1265 w, 1210 w, 1190 w, 1165 w, 1095 w, 1045 ms, 1030 ms, 1020 m, 1005 mw, 990 w, 960 m, 935 w, 870 m, 800 mw, 720 w, 660 w, 640 ms, 610 s, 590 vs, 550 ms, 510 s, 485 s, 470 m, 445 ms, 380 m, 365 m cm^{-1}.

Results

The hexacarbonylvanadate $[V(CO)_4C_6H_6][V(CO)_6]$ is reduced in a few minutes at room temperature in tetrahydrofuran solution according to the reaction

$$[V(CO)_4C_6H_6][V(CO)_6] + NaBH_4 \longrightarrow V(CO)_4C_6H_7 + NaV(CO)_6 + {}^1/_2B_2H_6 \quad (1)$$

Sodium hexacarbonylvanadate was shown to be present in the reaction mixture. The separation of the cyclohexadienyl complex is very easy because of its volatility and its solubility in nonpolar solvents. After evaporation of the solvent, the cyclohexadienyl vanadium complex is dissolved in pentane and finally sublimed. Reaction 1 is of general applicability to all $[V(CO)_4\text{-}arene]^+$ cations. By essentially the same experimental procedure the methyl-substituted cyclohexadienyl compounds $V(CO)_4C_6H_{7-n}(CH_3)_n$ were obtained in reasonable yields. By carrying out reaction 1 with $NaBD_4$ the corresponding deuterated compounds $V(CO)_4C_6H_6D$ and $V(CO)_4C_6H_{6-n}(CH_3)_nD$ were similarly prepared. The new complexes are all brown-red solids, moderately stable in air in the solid state, but rapidly oxidized in solution. They are soluble in nonpolar and polar organic solvents, giving deep red solutions. In polar solvents such as tetrahydrofuran

TABLE II

INFRARED SPECTRA OF $V(CO)_4C_6H_7$ AND METHYL-SUBSTITUTED AND DEUTERATED DERIVATIVES IN THE C–O STRETCHING REGION[a]

$V(CO)_4$ compound	ν_{C-O}, cm^{-1}					
C_6H_7 (I)	2021 m	~1974 vw (sh)	1963 mw	1935 m	1920 s	~1890 vw
C_6H_6D (ID)	2021 m	~1974 vw (sh)	1963 mw	1935 m	1920 s	~1890 vw
$(CH_3)_2C_6H_5$ (II)	2014 m	~1970 vw (sh)	1955 mw	1928 m	1909 s	~1886 vw
$(CH_3)_2C_6H_5$ (III)	2014 m	~1964 vw (sh)	1954 mw	1926 m	1909 s	~1883 vw
$(CH_3)_2C_6H_4D$ (IIID)	2014 m	~1964 vw (sh)	1954 mw	1926 m	1909 s	~1883 vw
$(CH_3)_3C_6H_4$ (IV)	2009 m	~1961 vw	1949 mw	1925 m	1907 s	~1880 vw
$(CH_3)_3C_6H_3D$ (IVD)	2008 m	~1960 vw	1948 mw	1924 m	1906 s	~1878 vw
$(CH_3)_3C_6H_4$ (V)	2012 m	...	1954 mw	1923 m	1909 s	~1883 vw
$(CH_3)_3C_6H_4$ (VI)	2011 m	~1963 vw	1948 mw	1925 m	1904 s	~1881 vw
$(CH_3)_4C_6H_3$ (VII)	2007 m	~1958 vw	1947 mw	1920 m	1901 s	~1875 vw
$(CH_3)_4C_6H_3$ (VIII)	2002 m	...	1941 mw	~1908 m (sh)	1891 s	...
$(CH_3)_6C_6H$ (IX)	2002 m	...	1941 mw	1916 m	1901 s	~1870 vw

[a] Heptane solutions. The limit of accuracy is ±1.0 cm^{-1}, except for the two bands labeled vw. Throughout this paper D next to a Roman numeral signifies that the compound is a deuterated one. So, for example, IV and IVD are both obtained by reduction of the same cation, namely $[V(CO)_4(1,3,5\text{-}(CH_3)_3C_6H_3)]^+$, by $NaBH_4$ and $NaBD_4$, respectively.

and acetone fading of the color is observed, suggesting a slow replacement of the ligands by the solvent. The same is true for benzene solutions. Heptane solutions are, on the contrary, stable under an inert atmosphere. Instantaneous decomposition was observed with CCl_4 and CS_2. The vanadium cyclohexadienyl complexes are monomeric in cyclohexane as shown by direct cryoscopic molecular weight determinations on the dimethyl derivative (III), obtained from the *p*-xylene cation. The monomeric nature of these complexes is also evidenced by their high volatility. By analogy with the diamagnetic cyclopentadienyl derivative[4] $C_5H_5V(CO)_4$, no unpaired electrons are expected for the complexes described in this paper. The sharpness of some of the nmr peaks (*vide infra*) indicates that this prediction is probably correct. In addition to that, esr measurements were carried out on compounds VII and VIII and no signals were observed either in solution or in the solid state. Magnetic susceptibility measurements will be carried out on these compounds and on the previously described[2,3] $[V(CO)_4\text{arene}]^+$ cations and the results reported later.

A schematic representation of the molecule $V(CO)_4C_6H_7$ is shown in Figure 1. The same configuration obviously holds also for the methyl-substituted derivatives, the only difference being that some of the positions in the ring are occupied by methyl groups. However, slight conformational changes of the hydrocarbon ligand are here possible because of conjugation and steric effects of the methyl groups. The two hydrogens of the methylene group are not equivalent because of their different orientation with respect either to the metal or to the remaining five carbon atoms of the cyclohexadienyl system. H_α is the hydrogen in the *endo* position with respect to the metal.

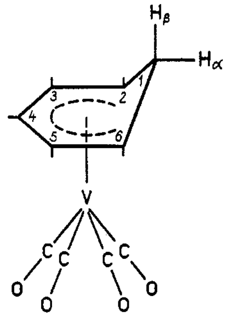

Figure 1.—A schematic molecular configuration of $V(CO)_4C_6H_7$.

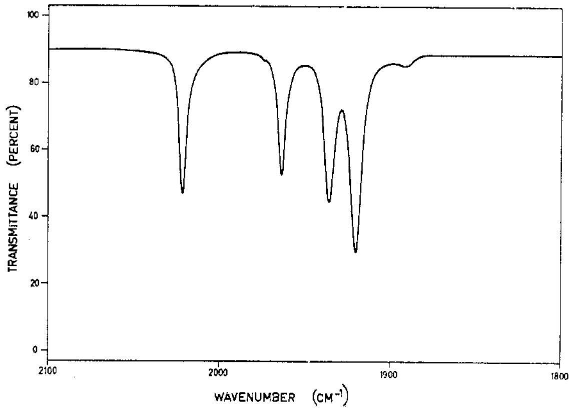

Figure 2.—The infrared spectrum of $V(CO)_4C_6H_7$ in the CO stretching region; heptane solution.

Infrared Spectra.—The infrared spectra of tetracarbonyl-π-cyclohexadienylvanadium and its methyl-substituted analogs in the C–O stretching region are presented in Table II. The spectrum of $V(CO)_4C_6H_7$ in the C–O stretching region is represented in Figure 2. Before discussing further the infrared data, it is important to show that all the bands reported in Table II are due to C–O stretching vibrations. Since the products described in this paper are obtained by reduction of $[V(CO)_4\text{arene}]^+$ with $NaBH_4$, the presence in the molecule of a BH_4 group not easily detected by analysis had to be considered as a real possibility.

Examples of transition metal tetrahydroborates are the recently described titanium[5] and zirconium[6] bis(cyclopentadienyl) complexes, $Ti(C_5H_5)_2BH_4$ and $Zr(C_5H_5)_2(BH_4)_2$, respectively. In these compounds vibrations due to the BH_4 group are found in the 2000 cm^{-1} region. In our case they would therefore interfere with the C–O stretching vibrations. That the bands reported in Table II are due exclusively to C–O

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(6) R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, **3**, 1798 (1964).

TABLE III

INFRARED SPECTRA OF TETRACARBONYL-π-CYCLOHEXADIENYLVANADIUM COMPOUNDS IN THE REGION 3100–2700 CM^{-1}

V(CO)$_4$ compound	ν, cm^{-1}											Medium
C_6H_7 (I)	3048 w	3033 w	2970 mw	2945 m		2895 mw				2795 ss	2730 w	C_6D_6
C_6H_7 (I)	3090 m	3060 w	3030 w	2945 w		2895 w				2822 vs	2800 (sh)	KBr
C_6H_6D (ID)[a]	3090 mw	3060 wm	3025 w	2950 w		2920 w				. . .	. . .	KBr
$(CH_3)_3C_6H_4$ (IV)[b]		3024 w	2972 m	2940 m (sh)	2930 s	2900 m	2880 m	2855 mw	2810 w	2790 vs	2730 w	KBr
$(CH_3)_3C_6H_3D$ (IVD)[b]		3025 w	2970 m	2940 m	2915 s	2900 sh	2880 sh	2855 mw	2810 w	. . .	2730 w	KBr
$(CH_3)_4C_6H_3$ (VII)			2982 mw	2927 s		2900 mw (sh)		2855 m		2770 s	2750 w (sh)	CD_3COCD_3
			2975 mw	2920 m		2890 m		2845 mw		2800 s		KBr

[a] The band at 2822 cm^{-1} (KBr) of the nondeuterated compound is shifted to 2070 cm^{-1} on deuteration; ν_{obsd}/ν_{obsd} = 1.36 (calcd 1.41). [b] In the deuterated compound two new bands at 2090 and 2070 cm^{-1} are present.

stretching vibrations is shown by the fact that the deuterated compounds have an infrared spectrum in this region superimposable on that of the corresponding nondeuterated compounds.

The two very weak bands in the C–O stretching region reported in Table II are almost certainly attributable to ^{13}C–O stretching vibrations of the two more intense vibration modes. Although in some of the methyl-substituted complexes isomers are possible and nmr evidence of their existence is available, we do not believe that the observed weak bands in the C–O stretching region represent a further evidence of isomeric products since a very similar infrared pattern is found in all cases, in particular with the unsubstituted $V(CO)_4C_6H_7$. The compounds described have therefore four main C–O stretching vibrations.

For a C_{4v} symmetry of the $V(CO)_4$ group, only two C–O stretching vibrations were to be expected in case of negligible coupling of these vibrations with the rest of the molecule. It is hard to decide whether the appearance of a larger number of bands is due to the nonvalidity of the "local symmetry" rule[7] in this particular case or rather to a distortion of the $V(CO)_4$ moiety. However, the latter explanation appears more likely. In support of this view is that the X-ray structure[8] of the closely related compound $Mo(CO)_3$-C_7H_8 has shown that the $Mo(CO)_3$ moiety does not possess C_{3v} symmetry due to the C–Mo–C (of the CO groups) angles being considerably different one from the other.

It will be noticed that the infrared spectra in the C–O stretching region show a regular shift of all the bands to lower wavenumbers by increasing methyl substitution on the ring. A similar shift has been already observed[2,3,9,10] in $Cr(CO)_3$arene and $[V(CO)_4$arene$]^+$ complexes and can be explained by an increased degree of d_π–p_π bonding from the metal to the CO ligands by the inductive effect of the methyl groups. The transmission of these electronic effects has been previously discussed[3] for the case of the $[V(CO)_4$arene$]^+$ complexes.

Another interesting region of the infrared spectrum of the tetracarbonyl-π-cyclohexadienylvanadium complexes is that around 3000 cm^{-1}. The infrared data concerning this region are reported in Table III. The main feature here is the presence of a *relatively* strong band at 2820–2770 cm^{-1}. This is clearly due to a stretching vibration involving the $>CH_2$ group of the cyclohexadienyl ring since this band shifts on deuteration. This confirms further that the compounds reported in this paper do not contain any B–H bond and that the hydrogen originating from $NaBH_4$ forms a C–H bond. These results are in agreement with those reported by Winkhaus, Pratt, and Wilkinson[11] for the cyclohexadienyl complex of manganese, $Mn(CO)_3C_6H_7$.

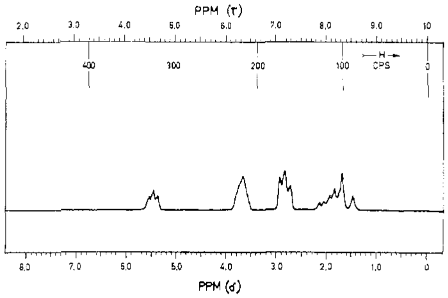

Figure 3.—Nuclear magnetic resonance spectrum (60 Mc/sec) of $V(CO)_4C_6H_7$ in deuteriobenzene.

Nuclear Magnetic Resonance Spectra.—The nuclear magnetic resonance data are reported in Table IV and the spectrum of $V(CO)_4C_6H_7$ is in Figure 3. Some of the data have been obtained both on the deuterated and the nondeuterated compounds. The quality of the spectra was not excellent, broadening of the lines being often observed, in particular for the unsubstituted compound. The cause of this could be, of course, a slow process of decomposition by the solvent to some paramagnetic species. It seems, however, reasonable to take also into consideration a relaxation phenomenon associated with the electric quadrupole moment of the vanadium nucleus as a possible cause of line broadening. Although multiplicity of peaks and coupling constants remained sometimes undetermined, the position, the number, and the relative intensities of the peaks corresponded in each case to the proposed structures, which are therefore completely justified.

The spectrum of $V(CO)_4C_6H_7$ shows a remarkable solvent dependence, all the lines being shifted to lower fields by substituting C_6D_6 with CD_3COCD_3. Apart from this shift, the spectra of $V(CO)_4C_6H_7$ in deuterioacetone and deuteriobenzene are very similar. The high-field lines can be directly assigned to the protons of the methylene group on the basis of the results obtained on the deuterated compounds. The nonequivalent methylene protons give rise to a rather complex

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(10) D. A. Brown and H. Sloan, *J. Chem. Soc.*, 3849 (1962).

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TABLE IV

NUCLEAR MAGNETIC RESONANCE SPECTRA OF TETRACARBONYL-π-CYCLOHEXADIENYLVANADIUM COMPOUNDS[a]

$V(CO)_4C_6H_7$ (I) in C_6H_6		
4.55	(1) Poorly resolved triplet	$H_{(4)}$
~6.35	(2) Broad band with a basic triplet structure	$H_{(3)} + H_{(5)}$
7.17	(2) Triplet	$H_{(2)} + H_{(6)}$
7.83–8.53	(2) Complex band (seven main components)	$H_\alpha + H_\beta$
$V(CO)_4C_6H_7$ (I) in CD_3COCD_3		
3.58	(1) Poorly resolved triplet	$H_{(4)}$
~5.38	(2) Broad band with a basic triplet structure	$H_{(3)} + H_{(5)}$
6.33	(2) Triplet	$H_{(2)} + H_{(6)}$
7.25–7.63	(1) Complex band (five main components)	$H_\alpha + H_\beta$
7.82–7.9	(1) AB doublet	
$V(CO)_4C_6H_6D$ (ID) in CD_3COCD_3		
3.52	(1) Poorly resolved triplet	$H_{(4)}$
~5.32	(2) Broad band with a basic triplet structure	$H_{(3)} + H_{(5)}$
6.30	(2) Triplet	$H_{(2)} + H_{(6)}$
7.43	(1) Broad band	H_β (or H_α)
$V(CO)_4C_6H_4(CH_3)_3$ (IV) in C_6D_6		
6.31	(2) Singlet	$H_{(3)} + H_{(5)}$
7.85	(3) Singlet	$CH_{3(4)}$
8.03	(2) Singlet	$H_\alpha + H_\beta$
8.57	(6) Singlet	$CH_{3(2)} + CH_{3(6)}$
$V(CO)_4C_6H_4(CH_3)_3$ (IV) in CD_3COCD_3		
5.48	(2) Singlet	$H_{(3)} + H_{(5)}$
7.39	(3) Singlet	$CH_{3(4)}$
7.58	(2) Singlet	$H_\alpha + H_\beta$
8.26	(6) Singlet	$CH_{3(2)} + CH_{3(6)}$
$V(CO)_4C_6H_3D(CH_3)_3$ (IVD) in CD_3COCD_3		
5.48	(2) Singlet	$H_{(3)} + H_{(5)}$
7.40	(3) Singlet	$CH_{3(4)}$
7.61	(1) Broad band	H_β (or H_α)
8.26	(6) Singlet	$CH_{3(2)} + CH_{3(6)}$
$V(CO)_4C_6H_3(CH_3)_4$ (VII) in CD_3COCD_3		
3.88	(1) Broad singlet	$H_{(4)}$
7.46	(2) Singlet[b]	$H_\alpha + H_\beta$
8.27	(12) Singlet[c]	CH_3 groups
$V(CO)_4C_6H_2D(CH_3)_4$ (VIID) in CD_3COCD_3		
3.89	(1) Broad band	$H_{(4)}$
7.52	(1) Broad band[b]	H_β or H_α
8.27	(12) Singlet[c]	CH_3 groups

[a] The data given in the columns from the left to the right are: chemical shift in ppm from tetramethylsilane as internal standard ($\tau = 10 - \delta$), relative integrated intensity, multiplicity, assignment. [b] A peak of low intensity is present on the low-field side of the main line, probably due to small amounts of the $>CHCH_3$ product. [c] A shoulder is present at the high-field side of the peak, probably due to isomeric products, containing the $>CHCH_3$ group.

pattern in C_6D_6 which is resolved into two separate sets of bands (each of relative intensity 1) in deuterioacetone (see Table IV). Deuterioacetone appears therefore to have, if any, a beneficial effect on line separation as far as the methylene protons of $V(CO)_4C_6H_7$ are concerned. It appears, therefore, remarkable to note that the methylene group of the methyl-substituted compounds gives only a singlet of relative intensity 2, reduced to 1 on deuteration. In the case of the compound obtained from the *sym*-trimethylbenzene cation, the three methyl groups are, as expected, not equivalent and give rise to two distinct peaks, of which the one of intensity 6 at τ 8.25 clearly arises from the two methyl groups adjacent to the $>CH_2$ group. From this comes the general conclusion that protons adjacent to the methylene group are at higher fields. On this basis the peaks at τ 7.17 (C_6D_6) and 6.33 (CD_3COCD_3) of the unsubstituted product are assigned to the $H_{(2)}$ and $H_{(6)}$ protons.

In all the compounds examined, except the trimethyl derivative, a band of intensity 1 is observed in the region τ 3.5–3.9 in deuterioacetone. The assignment of this band to the proton in position 4 is straightforward. The addition of hydrogen to the aromatic ring of the methyl-substituted cations $[V(CO)_4C_6H_{6-n}(CH_3)_n]^+$ can obviously occur either at an unsubstituted or at a substituted position of the ring. The products obtained from the symmetrically substituted trimethylbenzene cation are particularly indicated to elucidate this point since only the substitution on a position already occupied by a methyl group would give rise to a proton resonance in the τ 4 region. In the nmr spectrum of the trimethylbenzene derivative a peak at τ 4.17 is just noticeable. This brings us to the general conclusion that hydrogen addition to methyl-substituted arenecarbonylvanadium cations occurs predominantly at an unsubstituted position of the aromatic ring; the products with the alternative arrangement are probably also present but their relative amount is very small.

That the above-mentioned τ 4.17 peak is significant is indicated by the fact that a cyclohexadienyl derivative could be obtained, although in low yields, from the hexamethylbenzene cationic complex.

Additional complications could arise from the hydrogen addition taking place at nonequivalent *ortho*, *meta*, and *para* positions of the aromatic ring of $[V(CO)_4C_6H_{6-n}(CH_3)_n]^+$. The cyclohexadienyl complex from the toluene cation would be very useful to elucidate this point by nmr measurements. The nmr data of Table IV were obtained on compounds for which only one positional isomer of this type was to be expected.

Discussion

The reduction of the $[V(CO)_4arene]^+$ cations by $NaBH_4$ was found to be a clean and smooth reaction, the only products observed being the tetracarbonylcyclohexadienylvanadium complexes and $NaV(CO)_6$. The identification of diborane in the course of the reaction was not tried. The fact that the maximum yield obtained is about 60% should be attributed to partial decomposition of the cyclohexadienyl complexes in the solvent used for the reaction rather than to the formation of by-products.

The cyclohexadienyl complexes of manganese[11] are similarly obtained by reduction of the $[Mn(CO)_3arene]^+$ cations with $NaBH_4$. However, it was later recognized[12] that the cyclohexadiene complex $MnH(CO)_3C_6H_8$ was also a product of the reaction. On the basis of chemical and spectral data it is possible to conclude that the system $[V(CO)_4arene]^+$–$NaBH_4$–tetrahydrofuran does not yield at least in noticeable amounts (a) the still unknown complexes $V(CO)_3arene$, (b) com-

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(12) G. Winkhaus, *Z. Anorg. Allgem. Chem.*, **319**, 404 (1963).

pounds containing metal–hydrogen bonds, or (c) compounds containing the metal–B–H grouping. As to point (b), products of this type were sought repeatedly either by nmr measurements at very high fields or by chemical methods.

The mechanism of formation of the compounds described in this paper is worth discussing since it is strictly related to the problem of the conformation of the cyclohexadienyl ligand. The formation of the cyclohexadienyl compounds from the $[V(CO)_4C_6H_6]^+$ cation can occur either by a direct attack of H^- on a carbon atom of the benzene ring or by the preliminary formation of a labile metal–hydrogen bond followed by a concerted electron transfer to the metal and formation of the $>CH_2$ group. The second mechanism represents a nucleophilic attack on the vanadium cation and appears to be the most likely. By the first mechanism hydrogen can be introduced either in the *exo* or in the *endo* position, whereas the second mechanism can most probably only lead to the addition of hydrogen in the *endo* position (with respect to the metal). From a mechanistic viewpoint the hydrogen from the BH_4^- should therefore be in the *endo* position. Winkhaus, Pratt, and Wilkinson[11] reached the same conclusion from spectroscopic considerations on $Mn(CO)_3C_6H_7$.

Whether the methylene group is pointing away from or toward the metal atom is an additional question. The unusual intensity of the band at about 2800 cm^{-1} was explained by those authors[11] as due to an interaction between one of the hydrogens of the methylene group and the metal atom. The methylene group was therefore preferably considered as pointing toward the metal, in order to have the maximum possible interaction between the *endo* hydrogen and the metal. However, by analogy with the known X-ray structure[8] of the cycloheptatriene compound $Mo(CO)_3C_7H_8$, in our manganese cyclohexadienyl compounds one would prefer to consider the methylene group as bent away from the metal. Any interaction with the metal would therefore become unlikely. In our opinion both the position and the intensity of the band at about 2800 cm^{-1} are not very unusual for a $>CH_2$ group in a ring of the cyclohexadienyl type and no further interaction with the metal is probably necessary to account for them. The explanation for the rather high intensity of the band at about 2800 cm^{-1} *relative* to the other bands in the C–H stretching region could be that the latter are of low intensity because of the formation of the bond to the metal, whereas the $>CH_2$ group would be much less or not affected at all by bond formation. It is in fact known[13] that in the series of $Cr(CO)_3$arene complexes the C–H stretching vibrations are considerably lowered in intensity relative to the corresponding uncomplexed aromatic hydrocarbons. The position of the band under discussion is also not surprisingly unusual for a methylene group in a cyclic unsaturated system, since frequency shifts of the C–H stretching bands are observed for methylene groups in cyclic systems, depending on the ring strain. The symmetric stretching vibration associated with the $>CH_2$ group in cycloheptatriene[14] is at 2849 cm^{-1}. All this should be confirmed by intensity measurements in the C–H stretching region on a cyclohexadienyl–metal compound and using C_7H_8 and $Cr(CO)_3C_7H_8$ as the reference system. It is, on the other hand, already significant that $Mo(CO)_3C_7H_8$ shows[15] its strongest band in the C–H stretching region at about 2820 cm^{-1}.

In conclusion, although it appears reasonable from a mechanistic viewpoint to consider the addition of hydrogen to the aromatic ligand to occur in such a way as to become *endo* with respect to the metal, it does not appear justified to infer a metal–hydrogen interaction from the available infrared data. These latter are not in contradiction with a bent away conformation of the methylene group with respect to the metal.

Two possibilities can be discussed in connection with the type of bonding existing between the cyclohexadienyl group and the vanadium atom. The metal can be in fact symmetrically arranged with respect to five carbon atoms, namely carbon atoms from 2 to 6 in Figure 1, which then constitute a delocalized system. Churchill and Mason[16] have recently shown by X-ray work the possibility of existence of a localized type of bonding between cobalt and a phenyl-substituted cyclopentadiene system in the compound $(C_5H_5)Co(C_5H_5C_6H_5)$. Mason and Wilkinson[17] have later mentioned that such a type of bonding could also exist in some of the known cyclohexadienyl systems. If this is the case, the C_6H_7 group and the vanadium atom should be held together by two σ bonds to carbon atoms 2 and 6, with the three remaining carbon atoms (in positions 3, 4, and 5) constituting a π-allyl type system. It is interesting to note in this connection that the two equivalent protons in positions 2 and 6 have a chemical shift roughly corresponding to the expected one for protons bonded to saturated carbon atoms.

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