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The Reactions of Hexacarbonylvanadium with Aromatic Compounds. II. Reactions with Polymethyl Substituted Hydrocarbons, Naphthalene, and Anisole[1,2]

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By reaction of $V(CO)_6$ with aromatic compounds at 35° some new complex cations $[V(CO)_4C_6H_{6-n}R_n]^+$ have been prepared as the hexacarbonylvanadates. With highly substituted methylbenzenes the yields are 20–53%. The complex cation is characterized by two main infrared CO stretching bands, whose position depends on the nature and the number of the substituents R_n. In this series of compounds a correlation has been found to exist between the shift from the benzene derivative of the cationic CO stretching vibrations and $\Delta\mu_{R_n}$, the group contribution to the dipole moment, calculated from the literature data for $Cr(CO)_3$arene complexes.

Introduction

It has been previously reported[1] that hexacarbonylvanadium reacts with aromatic hydrocarbons giving the ionic hexacarbonylvanadates $[V(CO)_4\text{arene}]^+[V(CO)_6]^-$ (I), with arene = benzene, toluene, *p*-xylene, 1,3,5-trimethylbenzene. The reaction is accompanied by the formation of water-soluble hexacarbonylvanadates, $V[V(CO)_6]$ and $V[V(CO)_6]_2$, whose formation arises from the thermal elimination of the ligands from the cation of I. A further oxidation step of $V[V(CO)_6]$ by $V(CO)_6$ should explain the presence of $V[V(CO)_6]_2$. It was shown that this elimination, which is the major event in the case of benzene, becomes progressively less favored as the degree of methyl substitution increases from toluene to 1,3,5-trimethylbenzene.

It was decided, therefore, to extend the reaction to other methyl-substituted benzenes, since better yields appeared possible, thus facilitating the study of the properties of this new class of compounds. A further point of interest was the preparation of compounds I containing arene ligands with a functional group attached to them.

Experimental

All the operations were carried out in an atmosphere of pure nitrogen. The aromatic hydrocarbons liquid at room temperature and anisole were the Fluka pure grade products dried over sodium and fractionated. 1,2,4,5-Tetramethylbenzene and naphthalene were the Fluka pure grade products and were used without further purification. Hexamethylbenzene was purchased from Eastman Kodak and used without further purification. Tetrahydrofuran and diethyl ether were dried over sodium, distilled over lithium tetrahydroaluminate, and stored under nitrogen. The hexacarbonylvanadates of Table I were obtained by dissolving in tetrahydrofuran and immediately precipitating with diethyl ether after elimination of the reaction by-products as described below. They are all red crystalline compounds, moderately stable in air in the dry state, sensitive in solution. They are soluble in tetrahydrofuran and acetone, insoluble in all the other common organic solvents. The hexafluorophosphate derivatives of Table I were prepared from the corresponding hexacarbonylvanadates in almost quantitative yields by the metathetical reaction with NH_4PF_6 already described in the previous paper. They are crystalline solids, stable in air in the dry state for at least 10 min., practically insoluble in tetrahydrofuran and all the other common organic solvents, and soluble in acetone.

Microanalyses are by Dr. K. Eder, Ecole de Chimie, Geneva, Switzerland. The infrared spectra were recorded on a Perkin-Elmer Model 221 instrument equipped with a grating prism unit. The CO stretching region was recorded on an expanded abscissa scale (5 cm.$^{-1}$/cm.). Each spectrum was calibrated with CO. The limit of accuracy of the measurements on the solution spectra was therefore ±0.5 cm.$^{-1}$.

(1) **Reaction between $V(CO)_6$ and Aromatic Hydrocarbons.**—The compounds $[V(CO)_4\text{arene}][V(CO)_6]$ were prepared and separated from the reaction mixtures by the operative procedure previously described.[1] However, the run with hexamethylbenzene is described in detail to show how the data of Table II were obtained.

Hexacarbonylvanadium (1.91 g., 8.7 mmoles) was introduced into a 100-ml. flask protected against light and containing 7.0 g. of hexamethylbenzene and heptane (30 ml.). A pressure of about 15 mm. was briefly applied and the flask closed. The mixture was magnetically stirred for 48 hr. at 35 ± 2°. During this time the carbon monoxide evolved was evacuated three times. The orange-brown solid formed in the reaction was filtered and washed thoroughly with heptane to remove unreacted hexamethylbenzene and $V(CO)_6$. The solid was then dried *in vacuo*, treated with water, dried again, and crystallized from tetrahydrofuran–diethyl ether (0.97 g., 41% yield). The aqueous washings contained 0.098 g. of vanadium (22% based on the $V(CO)_6$ employed).

In the reactions with 1,2,4,5-tetramethylbenzene and naphthalene, heptane was also used as solvent. In all the other cases the pure aromatic hydrocarbon was employed.

$[V(CO)_4C_{10}H_8][V(CO)_6]$ was actually isolated by the usual procedure as a red crystalline substance, decomposing at 86–90°, but in quantities insufficient for analysis.

(2) **Reaction with Anisole.**—Hexacarbonylvanadium (1.75 g., 8.0 mmoles) and anisole (2.6 g., 24.0 mmoles) in 60 ml. of heptane were allowed to react for 48 hr. at 35 ± 2° as described in (1). The yellow-green precipitate formed during the reaction was filtered and washed with heptane (solution A), then dried *in vacuo*. The solid was practically completely soluble in water; the aqueous solution contained 39.5% of the starting vanadium. The solid left from the treatment with water was dried and then treated with tetrahydrofuran. A red solution was obtained, whose infrared spectrum showed the bands reported in Table III. This solution was unstable. The above-mentioned solution A, still containing unreacted $V(CO)_6$, was kept at room temperature for 3 days; the yellow-green precipitate formed was filtered, washed with heptane, and dried under high vacuum. It is very unstable and burns immediately on contact with

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[1] Part I: F. Calderazzo, *Inorg. Chem.*, **3**, 1207 (1964).

[2] Presented in part at the VIII International Conference on Coordination Chemistry, Vienna, Sept. 7–11, 1964.

TABLE I

PROPERTIES[a] AND ANALYTICAL DATA OF $[V(CO)_4arene]X$; $X = [V(CO)_6]^-$, PF_6^-

Compound	Dec. point, °C.	C, %		H, %		V, %		F, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[V(CO)_4(1,2\text{-}(CH_3)_2C_6H_4)][V(CO)_6]$	100–104	44.29	44.26	2.06	2.15	20.87	20.77	...	...
$[V(CO)_4(1,2,3\text{-}(CH_3)_3C_6H_3)][V(CO)_6]$	88–92	45.44	45.73	2.41	2.57	20.29	20.50	...	...
$[V(CO)_4(1,2,4\text{-}(CH_3)_3C_6H_3)][V(CO)_6]$	85–88	45.44	45.36	2.41	2.50	20.29	20.26	...	...
$[V(CO)_4(1,2,4,5\text{-}(CH_3)_4C_6H_2)][V(CO)_6]$	106–108	46.53	46.00	2.73	2.88	19.74	20.03	...	...
$[V(CO)_4((CH_3)_6C_6)][V(CO)_6]$	120–121	48.55	48.55	3.33	3.39	18.72	18.56	...	...
$[V(CO)_4(CH_3OC_6H_5)][V(CO)_6]$[b]	N.d.								
$[V(CO)_4(C_{10}H_8)][V(CO)_6]$[b]	86–90								
$[V(CO)_4(1,2,3\text{-}(CH_3)_3C_6H_3)]PF_6$	160–166	36.47	36.76	2.82	2.95			26.63	26.17
$[V(CO)_4((CH_3)_6C_6)]PF_6$	160–170	40.87	41.01	3.86	4.11			24.24	24.23

[a] All compounds are red except $[V(CO)_4(1,2,3\text{-}(CH_3)_3C_6H_3)]PF_6$ (red-orange). The anisole derivative gives a red solution in tetrahydrofuran. [b] Characterized by infrared spectrum.

air. A sample (0.1641 g.) of the solid was treated with water; only a minimum amount of a red-brown solid was insoluble (*ca.* 0.002 g.). After filtration, the aqueous solution was shown to contain the anion $[V(CO)_6]^-$, which was extracted with diethyl ether after treatment with KOH, and cationic vanadium as a green-brown flocculate precipitate (probably $V(OH)_3$). The total vanadium amounts to 0.0296 g. (18.3% of the original solid actually dissolved in water). This result suggests that the yellow-green solid was not simply $V[V(CO)_6]$ and $V[V(CO)_6]_2$ (V% calcd. 37.7 and 31.2, respectively) but most probably a mixture of these with $[V(C_6H_5OCH_3)_6][V(CO)_6]_2$ (V% calcd. 13.4), the latter arising from the disproportionation (1).

Results

The new compounds prepared are listed in Table I. As can be seen from the data of Table II, 20–53% yields were obtained with the five polymethylbenzenes used. These are to be compared with 8–15% yields previously reported with benzene, toluene, and *p*-xylene in approximately the same reaction conditions. The previous suggestion that the higher yields with increasing number of methyl groups on the aromatic ring can be attributed to the increased resistance of the newly formed $[V(CO)_4\text{-}arene]^+$ against ligand elimination rather than to kinetic factors is confirmed by the present data. The total conversions of vanadium (into $[V(CO)_4arene]$-$[V(CO)_6]$ and water-soluble hexacarbonylvanadates) in Table II are only of qualitative significance since the initial concentration of $V(CO)_6$ is not the same in all the runs and heptane had to be used as solvent in the case of aromatic hydrocarbons solid at room temperature. The total conversion data do, however, show that there are no overriding kinetic peculiarities associated with any one of the five polymethylbenzenes used. The figures of the $V_{H_2O}/V_{complex}$ ratio in Table II represent, on the other hand, a direct measure of the resistance of the complex cation against ligand elimination. In fact, since the compounds I are insoluble in the reaction medium, the elimination is a heterogeneous process and the above ratio is therefore independent of the reaction conditions, at constant temperature. From the data of Table II it is also possible to conclude that both the number of methyl substituents and their position in the ring are important in determining the course of the reaction. It will be noted that an asymmetric arrangement of the methyl groups within the ring has a favorable effect, the $V_{H_2O}/V_{complex}$ ratio with 1,2,3-trimethylbenzene being the lowest of the series and that with *o*-xylene being lower than with *p*-xylene (1.2 against 2.4,[1] respectively). While the stabilizing effect caused by the number of methyl (electron-releasing) groups can be generally attributed to an increase of the metal–ring and metal–CO bond orders by an inductive effect, the reason for the thermal stability being also related to the position of the substituents on the ring is not clearly understood and requires further investigation. The infrared data (*vide infra*) show that the C–O bond orders (and therefore also the metal–CO bond orders) are approximately the same for the two xylene complexes and for the three trimethylbenzene complexes. It appears, therefore, that the position of the substituents within the ring affects some variables other than the metal–ring and the metal–CO bond orders.

TABLE II

REACTIONS OF HEXACARBONYLVANADIUM WITH AROMATIC COMPOUNDS

Reaction time 48 hr.; temperature 35 ± 2°

Aromatic compd.	Vanadium, % found,[a] as $[V(CO)_4arene]$-$[V(CO)_6]$	Water-soluble hexacarbonyl vanadates	$\frac{V_{H_2O}}{V_{complex}}$[b]
$1,2\text{-}(CH_3)_2C_6H_4$	29.8	35.2	1.18
$1,2,4\text{-}(CH_3)_3C_6H_3$	32.1	31.4	0.98
$1,2,3\text{-}(CH_3)_3C_6H_3$	53.4	5.2	0.10
$1,2,4,5\text{-}(CH_3)_4C_6H_2$	20.3	19.7	0.97
$(CH_3)_6C_6$	40.9	22.0	0.54
$C_6H_5OCH_3$	≤ 1	39.5	...
$C_{10}H_8$	≤ 1	19.7	...

[a] Based on $V(CO)_6$ employed. [b] Ratio V (as water-soluble hexacarbonylvanadates)/V (as $[V(CO)_4arene][V(CO)_6]$).

In the case of anisole and naphthalene runs no conclusion can be drawn because of secondary reactions. In the preparation of compounds I containing a functional group ($-COOCH_3$, $-NH_2$, $-OCH_3$) attached to the aromatic ring, anisole was used initially since the methoxy group is electron-releasing and its basicity is low compared with that of amino groups. The second point appears to be very important since in the presence of Lewis bases $V(CO)_6$ disproportionates very rapidly according to the equation[3]

$$3V(CO)_6 + nB \longrightarrow [VB_n][V(CO)_6]_2 + 6CO \qquad (1)$$

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(3) F. Calderazzo and R. Ercoli, *Chim. Ind.* (Milan), **44**, 990 (1962); W. Hieber, J. Peterhans, and E. Winter, *Chem. Ber.*, **94**, 2572 (1961).

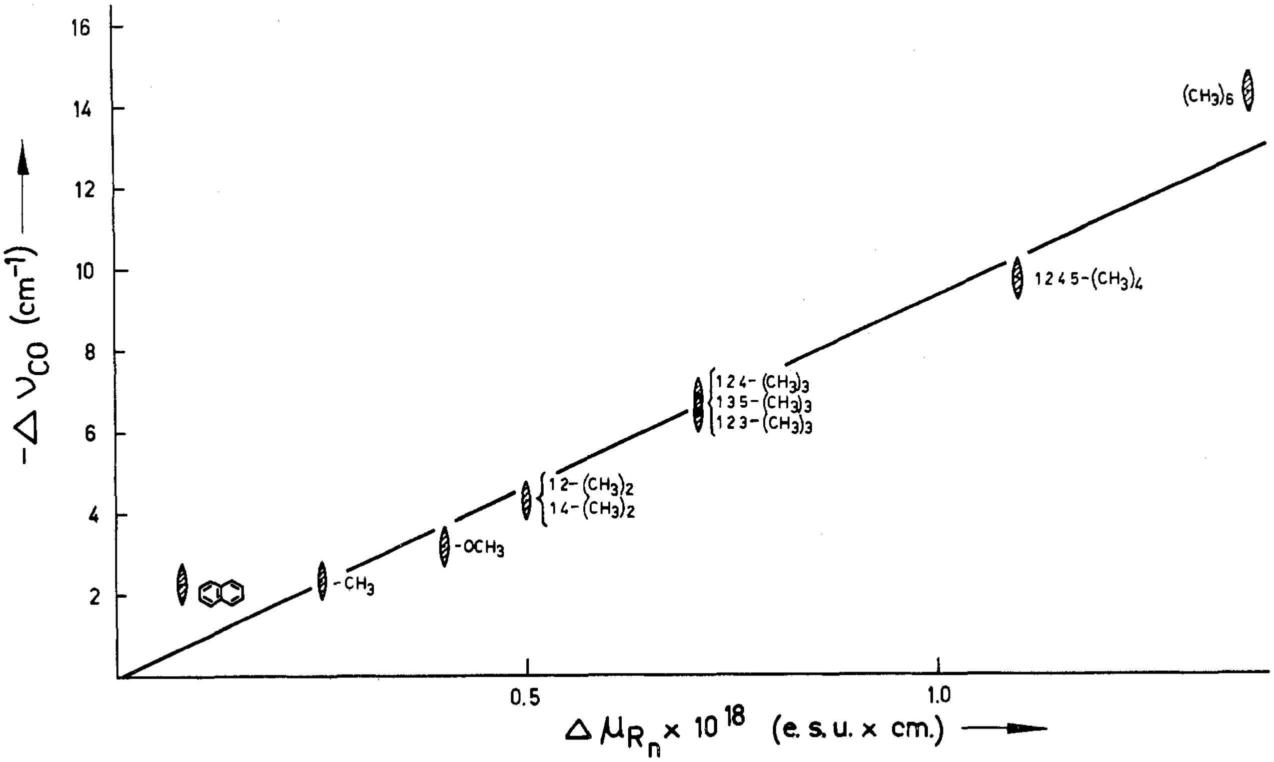

Figure 1.—A_1 vibration mode. Plot of the CO stretching frequency shifts from $[V(CO)_4C_6H_6]^+$ *vs.* group moments.

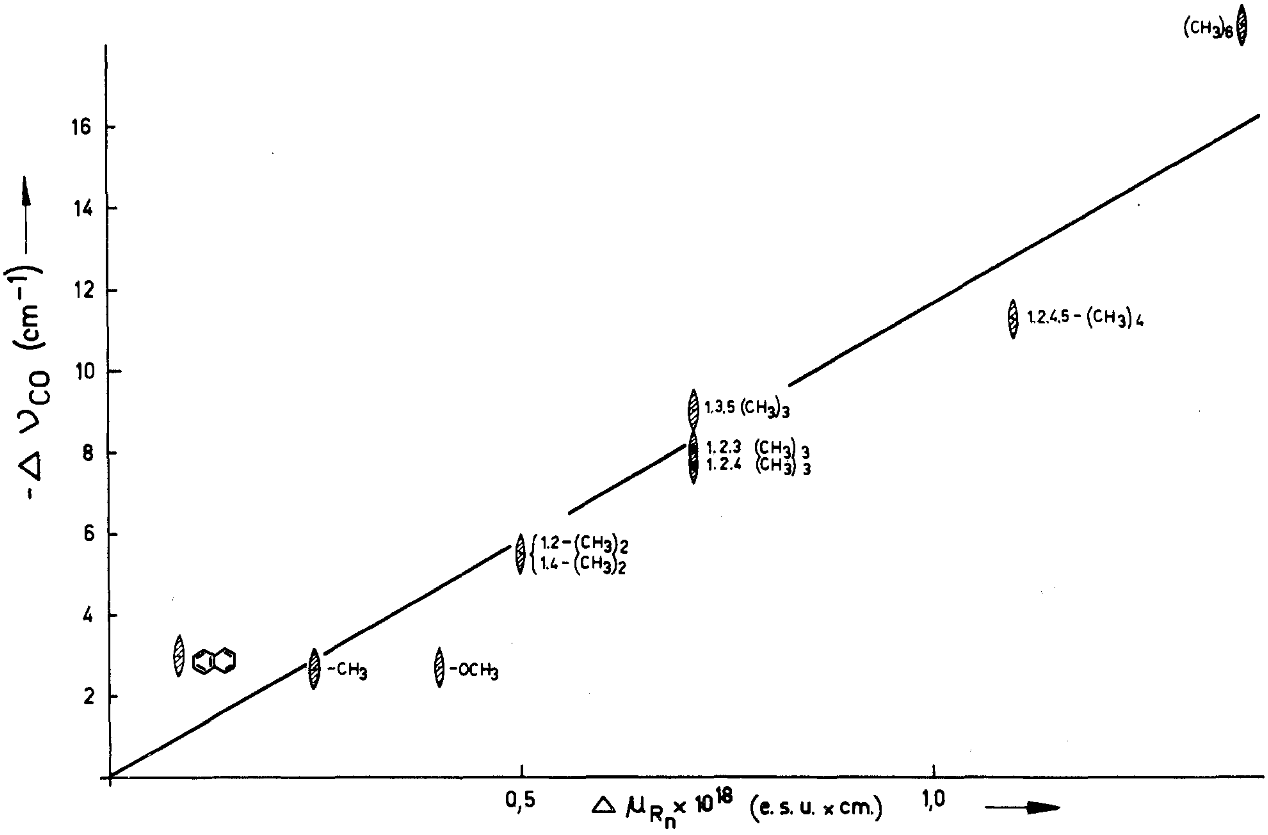

Figure 2.—E vibration mode. Plot of CO stretching frequency shifts from $[V(CO)_4C_6H_6]^+$ *vs.* group moments.

with $n = 6$ in most of the cases. Since this reaction would compete strongly with the π-arene complex formation, the experiment with anisole was carried out with small anisole/$V(CO)_6$ molar ratios and in heptane as reaction medium. Nevertheless, the π-arene complex $[V(CO)_4C_6H_5OCH_3][V(CO)_6]$ could only be prepared in very poor yields, and it was identified solely by its infrared spectrum.

In the reaction with naphthalene considerable amounts of decomposition products were formed and the

π-complex could be isolated in trace amounts insufficient for analysis. However, the infrared CO stretching bands are perfectly comparable in relative intensity and number with those of all the other compounds of this class. This leaves no doubt about the existence of $[V(CO)_4C_{10}H_8][V(CO)_6]$.

Infrared Spectra.—The carbonyl stretching frequencies of the cations $[V(CO)_4\text{arene}]^+$ are reported in Table III. It has been previously[1] suggested that the structure of the $[V(CO)_4\text{arene}]^+$ cation is a tetragonal pyramid (C_{4v} local symmetry) for which two infrared CO stretching bands are expected ($A_1 + E$). The weak band at 2018 cm.$^{-1}$ is probably attributable to a slight distortion of the molecule, which causes the asymmetric nondegenerate vibration to be also infrared active. In agreement with the known assignments of bands in octahedral complexes,[4,5] the higher frequency band should be assigned to the A_1 mode. From the data of Table III it will be noted that both bands are influenced in their position by the number and the nature of the substituents on the aromatic ring. It has been already suggested[1] that the shift to lower wave numbers induced by electron-releasing groups is probably due to an increased degree of d_π–p_π bonding from the metal to the CO ligand. With the data made available by the present research, this view is substantiated. Fischer has already mentioned[6] the fact that in the series of tricarbonylarenechromium complexes the shift of the carbonyl stretching vibrations can be related to the electric dipole moment of the whole molecule. On the basis of the present data it is possible to show that a correlation of this type exists also for the related vanadium compounds. By using the known[7–9] dipole moment values for the complexes $Cr(CO)_3$arene, from the relationship

Table III

Infrared Spectra in the Carbonyl Region[a] of $[V(CO)_4\text{arene}][V(CO)_6]$

Arene	ν_{CO}, cm.$^{-1}$ A_1	E
C_6H_6[b]	2068.0	1986.0
C_7H_8[b]	2065.7	1983.3
$C_{10}H_8$	2065.7	1983.0
$C_6H_5OCH_3$	2064.8	1983.3
1,2-$(CH_3)_2C_6H_4$	2063.7	1980.5
1,4-$(CH_3)_2C_6H_4$[b]	2063.8	1980.5
1,2,3-$(CH_3)_3C_6H_3$	2061.5	1978.0
1,2,4-$(CH_3)_3C_6H_3$	2061.2	1978.3
1,3,5-$(CH_3)_3C_6H_3$[b]	2061.2	1977.0
1,2,4,5-$(CH_3)_4C_6H_2$	2058.3	1974.8
$(CH_3)_6C_6$	2053.7	1967.6

[a] Tetrahydrofuran solutions. The bands at 1894–1895 and 1859 cm.$^{-1}$ due to the anion $[V(CO)_6]^-$ are not reported. The weak cationic band at 2018 cm.$^{-1}$ is not reported. Wave numbers for the A_1 and E modes ±0.5 cm.$^{-1}$. The relative intensities of the three bands of the cation are m, w, s, respectively, in all cases. [b] Already reported previously.[1]

$$\mu_{Cr(CO)_3C_6H_{6-n}R_n} - \mu_{Cr(CO)_3C_6H_6} = \Delta\mu_{R_n} \qquad (2)$$

the contribution of the ring substituents to the dipole moment are evaluated taking the dipole moment of $Cr(CO)_3C_6H_6$ as conventional reference. $\Delta\mu_{R_n}$ will be positive for electron-releasing groups, as shown in Table IV.

From the data of Table III, the CO stretching frequency shifts

$$\nu_{[V(CO)_4C_6H_{6-n}R_n]^+} - \nu_{[V(CO)_4C_6H_6]^+} = \Delta\nu_{R_n} \qquad (3)$$

from $[V(CO)_4C_6H_6]^+$ in cm.$^{-1}$ are evaluated. According to (3), the $\Delta\nu_{R_n}$ will all be negative because the vanadium compounds described in this paper and in the previous one contain electron-releasing groups on the ring, which tend to shift the CO stretching vibrations to lower wave numbers.

From the graphs of Figures 1 and 2, it is seen that the infrared shifts from $[V(CO)_4C_6H_6]^+$ are approximately on a straight line when plotted against the group moments both for the A_1 and E modes. Although the experimental uncertainties are high for the dipole moments, there is no doubt that the correlation is a genuine one. However, only a qualitative explanation of this empirical correlation can be offered here. In the idealized model of Figure 3 a species such as $[V(CO)_4C_6H_6]^+$ can be thought of as having a ring–CO dipole AB ($+\delta$ $-\delta$) lying on the z axis since this is, although of a different order, a rotational axis both for the benzene ring and for the CO groups. The recently published X-ray structures of $Mn(CO)_3C_5H_5$[10] and $Cr(CO)_3C_6H_6$[11] justify this view. For the sake of simplification the center of the full charge 1+ of the cation is considered to be exactly on the vanadium atom. The separation of the two δ charges arises from the fact that the formation of the metal–ring bond will cause a transfer of negative charge from the ring to the metal[12] and from the latter to the CO groups. The exact position of the center of the negative charge $-\delta$ is not known but,

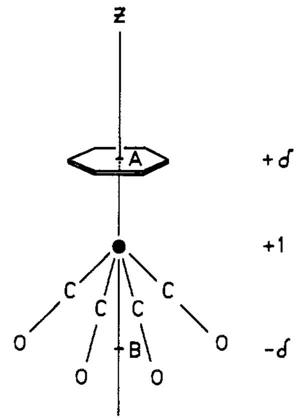

Figure 3.—Separation of partial charges in $[V(CO)_4C_6H_6]^+$.

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(4) L. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(5) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(6) R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960).

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(8) E. W. Randall and L. E. Sutton, *Proc. Chem. Soc.*, 94 (1959).

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TABLE IV

DIPOLE MOMENTS OF $Cr(CO)_3$arene IN BENZENE SOLUTION. EVALUATION OF GROUP MOMENTS[a]

Arene	$\mu \times 10^{18}$, e.s.u. cm.	Accepted value	$\Delta\mu_{R_n} \times 10^{18}$, e.s.u. cm.
Benzene	4.81 (7); 5.08 (8); 4.92 (9)	4.94	0.00
Toluene	5.12 (7); 5.26 (8); 5.20 (9)	5.19	0.25
p-Xylene	5.41 (7); 5.52 (8); 5.39 (9)	5.44	0.50
m-Xylene	... ; ... ; 5.37 (9)	5.44	0.50
o-Xylene	... ; ... ; 5.41 (9)	5.44	0.50
1,3,5-Trimethylbenzene	5.59 (7); 5.81 (8); 5.56 (9)	5.65	0.71
1,2,3-Trimethylbenzene	... ; ... ; ...	5.65	0.71
1,2,4-Trimethylbenzene	... ; ... ; ...	5.65	0.71
1,2,4,5-Tetramethylbenzene	... ; 6.04 (8); ...	6.04	1.10
Hexamethylbenzene	6.27 (7); 6.48 (8); 6.22 (9)	6.32	1.38
Naphthalene	5.02 (7); ... ; 6.33 (9)	5.02	0.08
Anisole	... ; 5.43 (8); 5.26 (9)	5.34	0.40

[a] Literature data in parentheses.

as discussed[13] by Bigorgne and Messier for the case of some carbonyl nickel derivatives with phosphorus-containing ligands, it should be somewhere between the carbon and the oxygen atoms of the CO groups. The assumption is made now that the charge 1+ on the vanadium remains constant, or approximately so, by varying the R on the arene ligand. As a consequence of that, when electron-releasing groups are present, additional negative charge will be transferred from the π-orbitals of the aromatic ring along the z axis to the metal and from this to the CO groups. The net effect will be an increase of the absolute value of the charge δ and therefore of the ring–CO dipole moment. The last step in the transmission of these electronic effects is an increase of the d_π–p_π bonding from the metal to the CO ligands, which is exactly what is measured in the infrared spectrum. The experimentally found $\Delta\nu_{CO}$ values show that the preceding assumption is correct. It is then seen that, as long as the charge on the vanadium remains approximately constant by varying R, the preceding arguments are valid, no matter which is the effective charge on the metal.

All the above brings us to the conclusion that the $\Delta\mu_{R_n}$ should be approximately the same for $Cr(CO)_3$arene and for $[V(CO)_4arene]^+$. The $\Delta\nu_{CO}$ values are, however, larger for $Cr(CO)_3$arene than for $[V(CO)_4arene]^+$, which is in agreement with the different number of CO groups present in the two types of molecules.

From the data in Table III it will be noted that the CO stretching frequencies of di- and trisubstituted benzene complexes of vanadium depend, within the experimental error, essentially on the number of methyl substituents and not on their relative position within the ring. This, combined with the fact that the three tricarbonylxylenechromium compounds show substantially the same dipole moment, indicates that it is the total inductive effect of the methyl groups which counts, no matter how the dipoles on the ring are oriented.

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(13) M. Bigorgne and C. Messier, *J. Organometal. Chem.*, **2**, 79 (1964).