mole^{-1}. This is in very good agreement with the value of -1.08 obtained for the optically pure sample with an initial specific rotation of $-1458°$. The close agreement of the two values for ΔV^* is experimental proof that the value of ΔV^* does not depend upon the initial rotation of the sample.[2]

The relationship

$$\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}{}_{p=0} = \ln k_{p=0} + \ln t \qquad (2)$$

has been used to obtain a value for the specific rate constant for the disappearance of d or l ion at zero pressure, $k_{p=0}$, for a sample under pressure for time t.[2] The value for $\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}{}_{p=0}$ is a value obtained from a linear extrapolation of the $\ln \ln ([\alpha]_{D_0}/[\alpha]_D)^{1/2}$ vs. p data to zero pressure. Equation 2 is valid only if the value of ΔV^* is constant over the entire pressure range. The rate constant for racemization (change in optical activity), k', is double the rate constant for the disappearance of d or l ions, k. The rate constants for racemization, k', obtained from our data are $3.10 \pm 0.65 \times 10^{-3}$ hr.$^{-1}$ for $[Fe(phen)_3](ClO_4)_2$ and $9.70 \pm 1.70 \times 10^{-4}$ and $6.82 \pm 2.13 \times 10^{-4}$ hr.$^{-1}$ for $[Ni(phen)_3](ClO_4)_2$. These correspond to half-lives of race-

mization of 9.3 ± 2.0 days, 29.8 ± 5.2 days, and 42.3 ± 13.2 days, respectively. An inspection of the half-lives calculated from the rate constants shows that the compounds, especially the iron complex, should racemize very rapidly at 1 atm. pressure in the solid state. In fact, the iron complex used in the pressure studies was used for a period of 4 months with no noticeable change in the $[\alpha]_D$ of the control samples, although the calculated half-life for racemization is approximately 10 days. One explanation for this discrepancy would be that the volume of activation changes rapidly toward more negative values as the pressure approaches atmospheric pressure. This would produce a smaller value for the racemization rate constant and a corresponding increase in the half-life. A rapid increase in the value of ΔV^* as the applied pressure approaches atmospheric pressure has been observed in solution.[13]

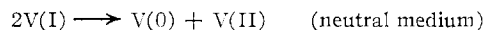(13) C. C. McCune, F. W. Cagle, Jr., and S. S. Kistler, *J. Phys. Chem.*, **64**, 1773 (1960).

Contribution from Cyanamid European Research Institute,
Cologny, Geneva, Switzerland

The Dimesitylenevanadium(I) Cation

By FAUSTO CALDERAZZO

Hexacarbonylvanadium oxidizes dimesitylenevanadium(0) to the $[V(C_6H_3(CH_3)_3)_2]^+$ cation, the compound $[V(C_6H_3(CH_3)_3)_2][V(CO)_6]$ (I) being formed. The corresponding iodide $[V(C_6H_3(CH_3)_3)_2]I$ (II) can be prepared by a metathetical reaction of I with LiI in tetrahydrofuran. Dimesitylenevanadium(0), characterized here for the first time, was obtained by the reaction of VCl_3 with mesitylene and aluminum in the presence of aluminum halides, followed by treatment with aqueous alkali. A reinvestigation of this reaction has shown that in the first stage, the aluminum reduces $V(III)$ to the dimesitylenevanadium(I) cation; the iodide (II) was in fact isolated from the first stage products by the metathetical reaction mentioned above. The dimesitylenevanadium(I) iodide in the presence of water yields dimesitylenevanadium(0) predominantly by the disproportionation reactions below.

$$2V(I) \longrightarrow V(0) + V(II) \qquad \text{(neutral medium)}$$

$$3V(I) \longrightarrow 2V(0) + V(III) \qquad \text{(alkaline medium)}$$

Introduction

Diarene–metal complexes of formula $M(arene)_2$ ($M = V$, Cr, Mo, W) can be synthesized by a two-stage reaction, the first stage of which consists of treating the anhydrous metal halide with aluminum and aluminum chloride in the presence of aromatic hydrocarbons.[1,2]

Fischer and co-workers postulated the formation of the cations $[M(arene)_2]^+$ during this stage, the zerovalent complexes being formed in a second stage car-

ried out in the presence of water. Dibenzenechromium[3] was obtained by using an alkaline solution of dithionite, whereas a simple treatment with an aqueous alkaline solution gave dibenzenevanadium,[4] dibenzenemolybdenum, and dibenzenetungsten.[5] In the latter three cases disproportionation reactions with simultaneous formation of the zerovalent complex and of the uncomplexed metal in its highest oxidation state were reported.

However, the presence of the cations $[Cr(arene)_2]^+$ and $[V(arene)_2]^+$ in the pre-"hydrolytic" mixtures of the reactions on $CrCl_3$ and VCl_4 was later questioned

(1) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 56 (1959).

(2) H. Zeiss, "Arene Complexes of the Transition Metals" in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Co., New York, N. Y., 1960.

(3) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955); *Z. anorg. allgem. Chem.*, **286**, 146 (1956).

(4) E. O. Fischer and H. P. Kögler, *Ber.*, **90**, 250 (1957).

(5) E. O. Fischer, F. Scherer, and H. O. Stahl, *ibid.*, **93**, 2065 (1960).

by Zeiss.[6] This author appears to prefer as an alternative interpretation of the first stage of the reaction the presence of the zerovalent complex bonded to AlCl₃ in some sort of a donor–acceptor adduct, *viz.*, M(arene)₂·AlCl₃.

In the case of the synthesis of dibenzenechromium the presence of an adduct between AlCl₃ and the complex with the metal already in its zerovalent state has been recently ruled out independently by Hein[7] and Fischer[8] and their co-workers.

It is also known[9] that the $[Cr(C_6H_5-C_6H_5)_2]^+$ cation disproportionates extremely slowly in water or methanol solution to $Cr(C_6H_5-C_6H_5)_2$ and Cr^{2+}.

$$2[Cr(arene)_2]^+ \longrightarrow Cr^0(arene)_2 + Cr^{2+} + 2\ arene \quad (1)$$
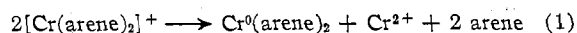
In the presence of OH⁻ ions or acetate ions, the Cr^{2+} formed in reaction 1 behaves as a reducing agent toward still unreacted $[Cr(arene)_2]^+$, according to the over-all equation

$$3[Cr(arene)_2]^+ \longrightarrow 2Cr^0(arene)_2 + Cr^{3+} + 2\ arene \quad (2)$$
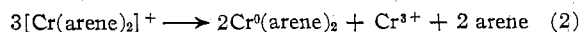
In the case of the synthesis of dibenzenevanadium some questions still remained unanswered. It has been briefly stated[4] that, on the basis of experiments performed on $[V(C_6H_3(CH_3)_3)_2][AlCl_4]$, the corresponding diarenevanadium(0) complex was obtained according to a disproportionation reaction of the type

$$5V^I(arene)_2 \xrightarrow{H_2O} 4V^0(arene)_2 + V(V) + 2\ arene \quad (3)$$
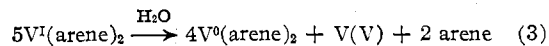
Unfortunately, the experimental details concerning eq. 3 and the isolation of the tetrachloroaluminate of the dimesitylenevanadium(I) cation have not yet been published. The questions about the vanadium system, therefore, are the following: First, is the $[V(arene)_2]^+$ cation formed from the system VCl₃–AlCl₃–Al–arene or is the vanadium in the zero oxidation state forming an addition compound with AlCl₃, for example V(arene)₂·AlCl₃? Second, is eq. 3 proposed by Fischer and Kögler, satisfactory? An additional question is: If eq. 3 is correct, why is the behavior of chromium so different, a reducing agent (dithionite) being required during the preparation of $Cr(C_6H_6)_2$? The only way of interpreting eq. 3 is to think in terms of a chain of oxidation–reduction reactions initiated by a disproportionation of the type

$$2[V(arene)_2]^+ \longrightarrow V^0(arene)_2 + V^{2+} + 2\ arene \quad (4)$$
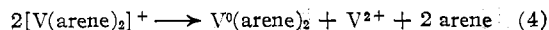
While, by analogy with the chromium case (eq. 1), the occurrence of disproportionation (4) seemed quite reasonable, the following steps appeared very difficult to explain. The formation of $V^0(arene)_2$ according to eq. 3 would in fact imply that three other $[V(arene)_2]^+$ cations have to be reduced in three distinct and subsequent steps by V(II), V(III), and V(IV). More intriguing was perhaps the fact that the latter reductions have to be considered relatively faster than disproportionation (4) in order to avoid deviations from the

stoichiometry of eq. 3. However, from an inspection of the standard oxidation potentials[10] of vanadium in acid solution and from studies[11,12] of the reactions of V(III) with some oxidizing agents, it was concluded that V(III) is a slow and rather weak reducing agent.

Since these observations seemed to exclude the formation of V(0) complexes by the disproportionation reaction (3), it was felt worthwhile to investigate its validity. Preliminary to that was the study of the products formed in the system vanadium halide–Al–AlCl₃–mesitylene. Since this system, as mentioned before, had been questioned as a source of $[V(arene)_2]^+$ cations, it was considered necessary to provide an independent and reliable method of preparing the dimesitylenevanadium(I) cation.

It has been shown[13] that hexacarbonylvanadium reacts with $V(C_5H_5)_2$ in an atmosphere of carbon monoxide to give the $[V(C_5H_5)_2(CO)_2]^+$ cation as the hexacarbonylvanadate.

$$V^{II}(C_5H_5)_2 + V^0(CO)_6 + 2CO \longrightarrow$$
$$[V^{III}(C_5H_5)_2(CO)_2][V^{I-}(CO)_6] \quad (5)$$
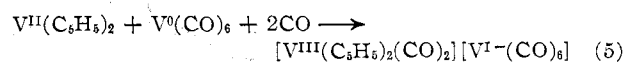
It therefore was decided to investigate whether a similar oxidation reaction of $V(C_6H_3(CH_3)_{3,2}$ by $V(CO)_6$ could occur, thus making the cation $[V(C_6H_3(CH_3)_3)_2]^+$ straightforwardly available.

Results

Dimesitylenevanadium, although not yet characterized, has been briefly mentioned[1,14] in some review articles. Dimesitylenevanadium is now obtained in 10–20% yields from the reaction of VCl₃ with AlCl₃ (or AlBr₃), aluminum, and mesitylene, followed by treatment of the resulting reaction mixture with aqueous alkaline solutions. No attempts were made to find the most suitable operative conditions. Before the treatment with aqueous alkaline solutions, the reaction system VCl₃–AlCl₃–Al–mesitylene usually consisted of two liquid layers, from which the excess aluminum could be easily separated by filtration. By treating this two-phase mesitylene solution with anhydrous LiI, a product having the composition $C_{18}H_{24}IV$ was precipitated in good yields.

Heptane solutions of hexacarbonylvanadium and dimesitylenevanadium immediately formed a brown precipitate of $[V(C_6H_3(CH_3)_3)_2][V(CO)_6]$. Its formation can be straightforwardly interpreted in terms of an electron transfer from dimesitylenevanadium(0) to hexacarbonylvanadium(0).

$$V^0(C_6H_3(CH_3)_3)_2 + V^0(CO)_6 \longrightarrow$$
$$[V^I(C_6H_3(CH_3)_3)_2][V^{I-}(CO)_6] \quad (6)$$
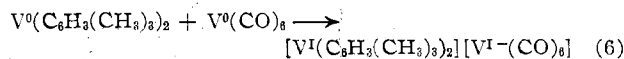
The presence of the $[V(CO)_6]^-$ anion in this compound was evidenced by two infrared bands at 1859 (vs) and 1894 (vw) cm.⁻¹ in the carbonyl stretching region.

(6) Reference 2, pp. 397 and 405.

(7) F. Hein and K. Kartte, *Z. anorg. allgem. Chem.*, **307**, 52 (1960).

(8) E. O. Fischer and J. Seeholzer, *ibid.*, **312**, 244 (1961).

(9) F. Hein and H. Scheel, *ibid.*, **312**, 264 (1961).

(10) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall Inc., New York, N. Y., 1952.

(11) J. B. Ramsey and M. J. Heldman, *J. Am. Chem. Soc.*, **58**, 1153 (1936); T. F. Rutter, *Z. anorg. allgem. Chem.*, **52**, 368 (1907).

(12) I. P. Alimarin, E. R. Nikolaeva, V. I. Tikhonova, and L. V. Bobrova, *Zh. Neorgan. Khim.*, **7**, 298 (1962).

(13) F. Calderazzo and S. Bacciarelli, *Inorg. Chem.*, **2**, 721 (1963).

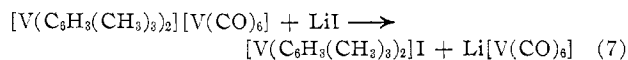(14) E. O. Fischer and H. P. Fritz, *Angew. Chem.*, **73**, 353 (1961).

Although the reason for the weak band at 1894 cm.$^{-1}$ is not yet clear, this is the characteristic infrared pattern of many hexacarbonylvanadates.[15] Moreover, the $[V(CO)_6]^-$ could be replaced by other anions, such as I$^-$, by a metathetical reaction in tetrahydrofuran

$$[V(C_6H_3(CH_3)_3)_2][V(CO)_6] + LiI \longrightarrow$$
$$[V(C_6H_3(CH_3)_3)_2]I + Li[V(CO)_6] \quad (7)$$

The iodide obtained from reaction 7 was found to be identical with the product precipitated with LiI from the system VCl_3–$AlCl_3$–Al–mesitylene. This latter was, therefore, undoubtedly identified as the iodide of dimesitylenevanadium(I), $[V(C_6H_3(CH_3)_3)_2]I$.

By thermal treatment under high vacuum, $[V(C_6H_3(CH_3)_3)_2]I$ gave dimesitylenevanadium and 1,3,5-trimethylbenzene. Two important considerations arise from this experiment. First, aluminum halide used for the synthesis of dimesitylenevanadium does not cause any appreciable rearrangement of the aromatic hydrocarbon to isomeric trimethylbenzenes. Second, since iodine was not found in the volatile products, the formation of dimesitylenevanadium can be explained by the following intermolecular reaction similar to (4)

$$2[V(C_6H_3(CH_3)_3)_2]I \longrightarrow V(C_6H_3(CH_3)_3)_2 +$$
$$VI_2 + 2C_6H_3(CH_3)_3 \quad (8)$$
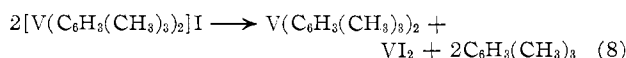
The iodide is poorly soluble in water, but the solution is unstable, giving the zerovalent complex $V(C_6H_3(CH_3)_3)_2$, extractable with heptane. A quantitative investigation of these aqueous solutions was, therefore, undertaken (Table I).

TABLE I
TREATMENT OF $[V(mes)_2]I$ WITH WATER; mes = $C_6H_3(CH_3)_3$

Expt.	Medium	V introduced as $[V(mes)_2]I$, g.	V found as V^{n+}, g.	V found as $V^0(mes)_2$, g.	V found/V introduced, %	$V(0)/V^{n+}$
1	Neutral	0.111	0.056	0.051	96.4	0.91
2	Neutral	0.148	0.075	0.072	99.3	0.96
3	Alkaline	0.095	0.032	0.062	98.9	1.94
4	Alkaline	0.169	N.d.	0.106	...	1.68[a]
5	Alkaline	0.182	0.066	0.117	100.3	1.77

[a] This figure is probably low, V^{n+} being calculated as the difference between the vanadium introduced and that recovered as $V^0(mes)_2$.

The formation of the zerovalent complex is accompanied by the appearance of cationic vanadium in oxidation states ≥ 2, the ratio of the amounts of vanadium present in the two forms being dependent on the pH of the reaction medium. In a neutral medium a violet aqueous solution of V(II) is formed; the presence of bivalent vanadium in this solution is confirmed by its absorption spectra.[16,17] The amounts of V(II) present in the aqueous layer and $V(C_6H_3(CH_3)_3)_2$ in the heptane layer are in good agreement with a disproportionation reaction of the type shown in eq. 4.

(15) F. Calderazzo and R. Ercoli, *Chim. Ind.* (Milan), **44**, 990 (1962).
(16) C. K. Jørgensen, *Acta Chem. Scand.*, **12**, 1537 (1958).
(17) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

Having shown that dimesitylenevanadium dissolved in heptane was not appreciably affected by aqueous alkali, the behavior of $[V(C_6H_3(CH_3)_3)_2]I$ in an alkaline medium was studied. The cationic vanadium formed in this medium is largely precipitated as a green-brown solid (probably $V(OH)_3$) soluble in dilute HCl. The absorption spectra of these blue-green solutions did not give any conclusive information about the oxidation states of the vanadium. Band maxima at 16,400 and 24,400 cm.$^{-1}$ were present and they could be tentatively assigned[17,18] to V(III), while the absence of strong absorptions around 13,000 cm.$^{-1}$ indicated that no considerable amounts of VO^{2+} were present. V(V), being a d^0 system, does not show inner 3d transitions and therefore is not easily detectable by this method. However, the analytical data (ratios of zerovalent complex to cationic vanadium in the range 1.7–2.0) showed conclusively that V(III) is predominantly formed in alkaline medium.

Experimental

Unless otherwise stated, all the reactions and operations here described were carried out under an atmosphere of pure nitrogen.

The infrared spectra were recorded with a Perkin-Elmer Model 221 instrument equipped with a grating prism unit. Visible absorption spectra were recorded with a Cary Model 11 spectrophotometer.

Tetrahydrofuran was dried over sodium and over lithium tetrahydroaluminate and employed shortly after distillation.

Mesitylene was Fluka pure grade product dried over sodium and distilled. LiI·$\sim$2H$_2$O was dried at 100–120° for several hours *in vacuo*.

Vanadium was determined by reduction with sulfur dioxide and titration with potassium permanganate.[19] The CO content of $[V(C_6H_3(CH_3)_3)_2][V(CO)_6]$ was determined by decomposition with iodine in pyridine.

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

(1) **Preparation of $V(C_6H_3(CH_3)_3)_2$.**—Anhydrous VCl$_3$ (5.0 g., 0.0318 mole), 0.8 g. of aluminum powder (0.0296 g.-atom), 8.2 g. of anhydrous AlBr$_3$ (0.0307 mole), and 50 ml. of dry 1,3,5-trimethylbenzene were introduced in a 250-ml. flask equipped with a stirrer, a reflux condenser, and a thermometer. The mixture was vigorously stirred and gradually heated. At about 60° the appearance of an orange-red color indicated that the reaction had started. The mixture was then heated at 130° for 2 hr. After cooling, the excess of aluminum was filtered off giving a filtrate consisting of two layers, the upper one being orange and the lower red-brown. Mesitylene was evaporated from this two-layered solution at room temperature *in vacuo* and the resulting brown oil crystallized to a red-brown solid by addition of heptane. The final solid was treated carefully at 0° with 200 ml. of 1 N NaOH and 200 ml. of pentane and the mixture stirred at room temperature for 3–4 hr. The organic layer was separated and evaporated, and the crystalline residue sublimed at 60–80° ($\sim$5 × 10^{-2} mm.). The sublimate was then crystallized from heptane giving 1.3 g. of dimesitylenevanadium (14% yield) as a deep red crystalline solid (m.p. 126–127° uncor.) soluble in hydrocarbons and other organic solvents. The compound reacts with CCl$_4$.

Dimesitylenevanadium is very easily oxidized by air even in the solid state, but is thermally very stable. It can be heated in a sealed tube to 250° without decomposition. The vapors are red-brown. The infrared spectra were recorded on Nujol

(18) E. L. Martin and K. E. Bentley, *Anal. Chem.*, **34**, 354 (1962).
(19) A. I. Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, Green and Co., Ltd., London, 1960.

and Fluorolube mulls and in heptane solution. The compound shows bands at 3020, 2960, 2925, 2870, 1610, 1525, 1480, 1280, 1255, 1035, 995, 910, 895, 875, 845, and 816 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{24}V$: C, 74.21; H, 8.30; V, 17.48. Found: C, 73.96; H, 8.42; V, 17.8.

(2) **Reaction between $V(C_6H_3(CH_3)_3)_2$ and $V(CO)_6$.**—A solution of $V(CO)_6$ (0.35 g., 1.60 mmoles) in heptane (45 ml.) was added slowly at room temperature to a stirred solution of $V(C_6H_3-(CH_3)_3)_2$ (0.62 g., 2.13 mmoles) in heptane (20 ml.). The brown precipitate immediately formed was filtered, washed with heptane, and dried *in vacuo* (0.735 g., 90% yield based on $V(CO)_6$).

$[V(C_6H_3(CH_3)_3)_2][V(CO)_6]$ could not be sublimed. It is insoluble in hydrocarbons and moderately soluble in tetrahydrofuran giving an orange-brown solution (solubility about 2.5% w./v.) and acetone. It is readily oxidized by air and decomposes without melting at 160–165°.

The infrared spectra were recorded on tetrahydrofuran solutions (1859 (ss) and 1894 (vw) cm.$^{-1}$), and on Fluorolube and Nujol mulls (1620 (wm), 1310 (w), 1170 (w), 1042 (s), 1000 (m), 920 (w), 895 (w), 870 (m), and 840 (w) cm.$^{-1}$).

Anal. Calcd. for $C_{24}H_{24}O_6V_2$: CO, 32.93; V, 19.96. Found: CO, 32.5, 32.9; V, 20.50, 20.20.

(3) **Preparation of $[V(C_6H_3(CH_3)_3)_2]I$.** (a) **From $[V(C_6H_3-(CH_3)_3)_2][V(CO)_6]$.**—A solution of 0.6630 g. (1.30 mmoles) of the hexacarbonylvanadate in tetrahydrofuran (27 ml.) was introduced into a tetrahydrofuran solution of anhydrous LiI (0.5 g. in 10 ml.). The orange precipitate immediately formed was filtered, washed with tetrahydrofuran, and dried *in vacuo* (0.38 g., 69.9% yield). The filtrate showed the infrared absorption bands at 1859 (vs) and 1894 (vw) cm.$^{-1}$ of the $[V(CO)_6]^-$ anion. The iodide is insoluble in hydrocarbons and tetrahydrofuran and only slightly soluble in acetone and water. The aqueous solution is, however, unstable and becomes cloudy after a few minutes. The product decomposes at 160° and mesitylene is condensed in the colder region of the capillary. On exposure to air the iodide burns immediately with evolution of iodine. The infrared spectrum of the iodide was recorded on Nujol and fluorolube mulls. The compound has infrared absorption bands at 1620 (wm), 1460 (w), 1395 (w), 1310 (w), 1170 (w), 1080 (w), 1043 (s), 997 (m), 915 (w), 895 (w), 880 (w), and 842 (w) cm.$^{-1}$. No infrared bands were observed in the carbonyl stretching region.

Anal. Calcd. for $C_{18}H_{24}IV$: C, 51.69; H, 5.78; I, 30.34; V, 12.18. Found: C, 50.91; H, 5.60; I, 30.68; V, 12.30.

(b) **From the Reaction Mixture of VCl_3 with $AlCl_3$, Aluminum, and Mesitylene.**—VCl_3 (9.8 g., 0.062 mole), $AlCl_3$ (16.6 g., 0.1245 mole), Al (1.68 g., 0.062 g.-atom), and mesitylene (80 ml.) were allowed to react as in (1) for 1 hr. at 100°.

The final reaction mixture, after filtration of the aluminum, consisted of two liquid layers. The lower brown layer was added to a stirred ice-cold solution of anhydrous LiI (14.4 g.) in tetrahydrofuran (250 ml.) over a period of 1 hr. The orange precipitate formed was finally filtered, washed several times with tetrahydrofuran (colorless washings), and dried *in vacuo* (13.7 g., 52.8% yield based on the VCl_3 employed). The aspect, the chemical properties, and the infrared spectra of the solid obtained here corresponded to those of the iodide described in (3a).

Anal. Calcd. for $C_{18}H_{24}IV$: C, 51.69; H, 5.78; I, 30.34; V, 12.18. Found: C, 51.22; H, 5.71; I, 30.08; V, 12.39.

(4) **Thermal Treatment of $[V(C_6H_3(CH_3)_3)_2]I$.**—The iodide obtained as in (3b) was heated *in vacuo* in a Schlenk tube equipped with a water-cooled finger. A trap cooled with Dry Ice–acetone was inserted between the vacuum and the Schlenk tube. At 95–120° small amonts of a deep red sublimate identified as dimesitylenevanadium (m.p. 125–127°) collected on the cold finger. A colorless liquid having an infrared spectrum identical with that of the mesitylene used in (3b) was collected in the trap.

(5) **Treatment of $V(C_6H_3(CH_3)_3)_2$ with Aqueous Alkali.**—Dimesitylenevanadium (0.2683 g.) corresponding to 0.0469 g. of vanadium was shaken with 30 ml. of 1.33 N KOH and 40 ml. of heptane for 1 hr. at 45° and 12 hr. at room temperature. After

filtration the two layers were separated. No vanadium was detectable by the analytical method employed in the colorless aqueous layer, which remained colorless on acidification with dilute HCl. The heptane layer, evaporated to dryness, gave a deep red crystalline residue of 0.2680 g. This was decomposed with dilute HNO_3, and 0.0473 g. of vanadium was found (101% of that introduced).

(6) **Treatment of $[V(C_6H_3(CH_3)_3)_2]I$ with Water.**—The iodide used for the experiments was analyzed with the following results. *Anal.* Calcd.: V, 12.18; I, 30.34. Found: V, 12.65; I, 30.37.

(a) **In Neutral Solution. Expt. 2 in Table I.**—$[V(C_6H_3-(CH_3)_3)_2]I$ (1.1708 g.) corresponding to 0.148 g. of vanadium was added to a 250-ml. flask together with 50 ml. of H_2O and 70 ml. of heptane. The mixture was shaken at room temperature for 24 hr.[20] and then transferred through a G3 filter into a separatory funnel. The two layers were separated, and there was no solid reaction residue. The clear violet aqueous layer, which showed three absorption band maxima at 17,900, 27,700, and 23,250 cm.$^{-1}$ (the latter one probably being due[21] to some V(III)), contained 0.075 g. of vanadium (calcd. for stoichiometry (4) 0.074 g.). The heptane layer was transferred into a weighed 100-ml. flask and evaporated to dryness *in vacuo* at room temperature, giving a deep red crystalline residue (0.4346 g., calcd. 0.4232 g.). The dimesitylenevanadium was then decomposed with dilute HNO_3 and the vanadium determined (0.072 g., calcd. 0.074 g.). The vanadium in the heptane layer and that found in the aqueous layer accounted for 99.3% of the vanadium introduced; V(0)/V^{n+} = 0.96 (calcd. 1).

(b) **In Alkaline Solution. Expt. 5 in Table I.**—$[V(C_6H_3-(CH_3)_3)_2]I$ (1.4416 g.), corresponding to 0.1824 g. of vanadium, was treated as in (a) at room temperature with 50 ml. of 1.33 N KOH and 70 ml. of heptane.[22] The reaction mixture was filtered through a G3 filter and the green-brown solid obtained was washed several times with water and heptane. The two liquid layers were separately collected. The red-brown heptane layer was evaporated to dryness giving 0.6894 g. (calcd. for stoichiometry (10) 0.695 g.) of a deep red crystalline residue. After decomposition of dimesitylenevanadium with dilute HNO_3, the vanadium was determined (0.117 g., 0.1216 g. calcd.).

The almost colorless aqueous layer became blue-green on acidification with dilute HCl. To this, the solution of the green-brown solid (in dilute HCl) was added. The blue-green solution so obtained showed absorption band maxima at 16,400, 24,400, and 27,500 cm.$^{-1}$. It contained 0.066 g. of vanadium (calcd. 0.0608 g.). The vanadium in the heptane layer together with that found in the aqueous layer accounted for 100.3% of the vanadium introduced; V(0)/V^{n+} = 1.77 (calcd. 2).

Conclusion

The three questions in the Introduction now can be answered reasonably well.

The isolation of the iodide $[V(C_6H_3(CH_3)_3)_2]I$ from the system VCl_3–Al–$AlCl_3$–mesitylene, in the absence of water or any other proton-active (potentially oxidizing) reagent, shows directly and conclusively that vanadium is present in that system as $[V(C_6H_3-(CH_3)_3)_2]^+$. Similar proton-free metathetical reactions on the systems MX_n–Al–$AlCl_3$–benzene (M =

(20) Experiment 1 in Table I was carried out in a similar manner, except that the mixture was shaken initially at 45° for 1 hr. and then at room temperature for about 11 hr. The reaction was almost complete after the first hour.

(21) The small quantities of vanadium there present as V(III) should be attributed to accidental oxidation during the operations and to spontaneous oxidation of V^{2+} by H^+.

(22) Experiments 3 and 4 in Table I were carried out similarly except that the mixture was treated in the first 45 min. at 45° and then 11 hr. at room temperature. The reaction was almost complete after the first 45 min.

V, Cr, Mo, W) have not been described before. Derivatives of the cationic species [M(arene)$_2$]$^+$ have always been prepared from aqueous solutions, or indirectly. For example, the iodide, the reineckate, and the picrate of the cation [Cr(C$_6$H$_6$)$_2$]$^+$ are isolated from its aqueous solutions.[3] [Mo(C$_6$H$_6$)$_2$]I and [W(C$_6$H$_6$)$_2$]I are obtained[5] by oxidation of the zerovalent complex with iodine.

No confirmation could be obtained that V^0(arene)$_2$ complexes can be formed by a disproportionation reaction of the type shown in eq. 3 involving the formation of V(V). The behavior of [V(C$_6$H$_3$(CH$_3$)$_3$)$_2$]$^+$ with water is best represented by a disproportionation of the type shown in eq. 4 followed by

$$V^{2+} + [V(\text{arene})_2]^+ \longrightarrow V^{3+} + V^0(\text{arene})_2 \quad (9)$$
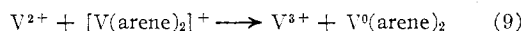
Reaction 9 becomes important only in alkaline medium, as a consequence of the enhanced reducing properties of V(II) in alkaline solutions.[10] In alkaline medium the over-all reaction can, therefore, be best represented as

$$3[V(C_6H_3(CH_3)_3)_2]^+ \longrightarrow 2V(C_6H_3(CH_3)_3)_2 + V^{3+} + 2C_6H_3(CH_3)_3 \quad (10)$$
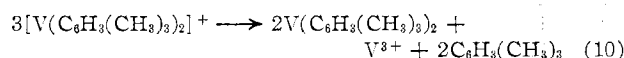
with, perhaps, to a small extent, a further reduction by V^{3+}.

$$[V(C_6H_3(CH_3)_3)_2]^+ + V^{3+} + H_2O \longrightarrow V(C_6H_3(CH_3)_3)_2 + VO^{2+} + 2H^+ \quad (11)$$
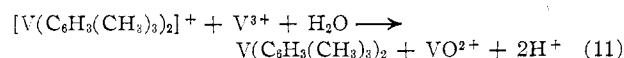
The fact that the ratios V(0)/V^{n+} in alkaline medium are lower than the theoretical value of 2 for eq. 10 can be explained by the competititive oxidation of the intermediate V(OH)$_2$ by H$^+$.

From the present study it appears that the chromium and vanadium systems are actually closely related, the only difference being that reaction 4 is much faster than (1). This explains the use of dithionite ions in the case of the synthesis of diarenechromium(0) complexes. The excellent yields reported[8] (as high as 98%) are to be attributed to the fact that reaction 1 is kinetically unfavored, enabling the reduction to be carried out exclusively by the dithionite. The dithionite, although used in a more recent preparation[23] of V(C$_6$H$_6$)$_2$, is probably not effective in this particular case because of the relatively high rate of reaction 4. The highest yields of dibenzenevanadium actually reported[23] are 46%. From the present study, it is seen that only two-thirds of the vanadium employed can be converted into V^0(arene)$_2$, corresponding to a maximum yield of 67%. Slightly higher yields could be obtained if conditions were found which suppress the spontaneous oxidation of V(OH)$_2$ by H$^+$ and if some advantage could be taken of the reduction by V(III) (eq. 11). There is no evidence, however, from the present study that reaction 11, although favored in principle by an alkaline medium, plays an important role.

The formation of uncomplexed metal ions in their highest oxidation states in the presence of the corresponding zerovalent complexes seems to be limited now to the case of molybdenum and tungsten, where M(C$_6$H$_6$)$_2$ and MO$_4$$^{2-}$ in a molar ratio 5:1 were found[5] to be formed.

(23) E. O. Fischer and A. Reckziegel, *Ber.*, **94**, 2204 (1961).

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Further Examples of Complexes Related by Electron-Transfer Reactions: Complexes Derived from Bis(trifluoromethyl)-1,2-dithietene

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A new series of four-coordinate bis chelate complexes of the general type [MS$_4$C$_4$(CF$_3$)$_4$]^z has been prepared. This series is closely related to that previously described[1,2] containing [MS$_4$C$_4$(CN)$_4$]^z complexes ($z = -1, -2$) in that its members undergo facile one-electron transfer reactions and those with $z = -1, -2$ are believed to have a planar structure. Complexes with $z = -2$, M = Pd, Pt, Co; $z = -1$, M = Pd, Pt, Co, Fe; and $z = 0$, M = Pt, Co, have been synthesized and supplement the nickel complexes with $z = 0, -1, -2$ obtained in earlier work.[1,2] The syntheses of all complexes are presented in detail. Chemical stabilities are discussed in terms of polarographic half-wave potentials. The results of magnetic susceptibility, electron spin resonance, nuclear magnetic resonance, and infrared spectral studies are presented and discussed in terms of probable electronic structures and chemical bonding in the complexes.

Introduction

Recent work in these laboratories[1,2] has demonstrated

(1) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).
(2) A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

that complexes of the general type **1** undergo reversible and unusually facile electron-transfer reactions which have permitted the synthesis of a wide variety of complexes with total charge $z = 0, -1, -2$. The principal portion of the previous work has dealt with