localized nature. Clearly more structural work on these types of complexes is needed before more definite ideas of bonding can be systematized.

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CONTRIBUTION FROM ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO, MILANO, ITALY

The Cation Dicyclopentadienyldicarbonylvanadium(III)

BY FAUSTO CALDERAZZO AND SERGIO BACCIARELLI

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Vanadium hexacarbonyl behaves as an oxidizing agent in non-polar solvents. The reaction at 15° of $V(CO)_6$ with dicyclopentadienylvanadium(II) and CO at atmospheric pressure gives the hexacarbonylvanadate of the new cationic species $[V(C_5H_5)_2(CO)_2]^+$. Yields of the diamagnetic solid are almost quantitative. The cation is isoelectronic with the neutral compound $Ti(C_5H_5)_2(CO)_2$.

Introduction

Calderazzo and Calvi[1] recently have isolated the hexacarbonylvanadate of the cation vanadium(0) π-tropylium-π-cycloheptatriene, $[V(C_7H_7)(C_7H_8)]$-$[V(CO)_6]$ in the course of the reaction between $V(CO)_6$ and C_7H_8. It was suggested also that the compound could be formed by a mechanism of intermolecular hydride elimination involving a molecule of $V(CO)_6$ from an intermediate $V(C_7H_8)(CO)_3$, followed by further substitution of carbon monoxide.

This suggestion has led us to study the reaction of vanadium hexacarbonyl with dicyclopentadienylvanadium in an attempt to prove that vanadium hexacarbonyl can act, in some cases, as an oxidizing agent in non-polar solvents. Such a reaction would provide additional evidence relative to the proposed mechanism of reaction.

Results

Preliminary experiments had shown that equimolecular quantities of $V(CO)_6$ and $V(C_5H_5)_2$ dissolved in heptane or toluene reacted readily at room temperature *under a nitrogen atmosphere*, with formation of nonvolatile brown-red compounds. However, the infrared spectra and analyses of reaction products clearly showed that a mixture of at least two different compounds was formed.

Further and similar experiments, carried out at 15° *under an atmosphere of carbon monoxide* in a gasvolumetric apparatus, led to a very brisk uptake of two moles of CO per mole of $V(C_5H_5)_2$ employed. An orange precipitate of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ (I) was formed in a high yield according to the scheme

$$V^{II}(C_5H_5)_2 + V^0(CO)_6 + 2CO \longrightarrow [V^{III}(C_5H_5)_2(CO)_2][V^{I-}(CO)_6]$$

The hexacarbonylvanadate of the new cationic species $[V(C_5H_5)_2(CO)_2]^+$ is moderately stable in air in the dry state, whereas its solutions in tetrahydrofuran or acetone must be handled under nitrogen. It is not sublimable, it is insoluble in H_2O and aliphatic and aromatic solvents, and sparingly soluble in CS_2. It is diamagnetic either in solution (sharpness of the peaks in the n.m.r. spectrum) or in the solid state (magnetic susceptibility measurements).

The infrared spectra of I showed three bands in the carbonyl stretching region at about 2050 (s), 2010 (s), and 1860 (ss) cm.$^{-1}$, the latter one being attributed[2-4] to the anion $[V(CO)_6]^-$.

A single C–H stretching frequency was found at about 3120 cm.$^{-1}$, while other infrared absorptions due to π-bonded cyclopentadienyl rings were located in the region between 7 and 12 μ as outlined in the Experimental section. The n.m.r. spectrum of I in acetone (10% solution by weight) showed only one sharp proton resonance peak centered at 1.48 ± 0.02 p.p.m. from benzene to high fields. π-Bonded cyclopentadienyl rings in diamagnetic dicyclopentadienyl metals and cyclopentadienyl metal carbonyls dissolved in toluene[5] or tetrahydrofuran[6] have a single proton resonance peak between 2.5 and 3.2 p.p.m. relative to benzene. The lower shift found in our case does not seem to be due only to a solvent effect; a decreased electron density in the rings therefore probably is responsible for the unusually low value of the chemical shift.

The salt-like character of I was demonstrated by preparing from it some derivatives of the cationic component.

By treatment of I with iodine in toluene the anionic carbon monoxide was quantitatively displaced at room temperature, whereas pyridine as a solvent, higher temperatures, very long reaction times, and a strong

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excess of I_2 were required for the displacement of the cationic carbon monoxide.

By decomposition of I with an aqueous solution of I_2–KI at 15°, six moles of CO were given off according to the stoichiometry

$$[V(C_5H_5)_2][V(CO)_6] + 2I_2 \longrightarrow [V(C_5H_5)_2(CO)_2]^+ + V^{3+} + 4I^- + 6CO \quad (1)$$

In the presence of an excess of I_2, the triiodide $[V(C_5H_5)_2(CO)_2]I_3$ (II) was precipitated; it could be brought back into solution as $[V(C_5H_5)_2(CO)_2]^+$ by reduction with SO_2. The aqueous solution of the cation dicyclopentadienyldicarbonylvanadium(III) so obtained was perfectly stable for several days under a nitrogen atmosphere; by addition of an aqueous solution of $NaV(CO)_6$ the hexacarbonylvanadate of the cation was precipitated and was shown to be identical with the starting compound I by comparing the infrared spectra.

On the other hand, from an acetone solution of I treated with $NaB(C_6H_5)_4$ the yellow-orange tetraphenylborate $[V(C_5H_5)_2(CO)_2][B(C_6H_5)_4]$ (III) could be separated.

The infrared spectra of II and III were recorded; the band at about 1860 $cm.^{-1}$ had disappeared and only the cationic CO stretching frequencies at about 2040 and 2000 $cm.^{-1}$ were present.

Experimental

The infrared absorption spectra were obtained on Nujol and hexachlorobutadiene mulls with a Perkin-Elmer Model 221 instrument and a sodium chloride prism. N.m.r. spectra were obtained on a Varian V-4300B spectrometer operating at 40 Mc.

$V(C_5H_5)_2$ was prepared from anhydrous VCl_3 and NaC_5H_5 in tetrahydrofuran according to the method described by Fischer and Hafner[7] and slightly modified by us.

Preparation of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$.—The reaction was carried out in the gas-volumetric apparatus described elsewhere.[8]

$V(CO)_6$ (0.69 g., 3.15 mmoles) and 0.57 g. of $V(C_5H_5)_2$ (3.15 mmoles) were introduced under N_2 in a two-necked flask.

After the flask was cooled in a Dry Ice–acetone bath, nitrogen was evacuated from it and replaced with pure carbon monoxide. The flask then was connected with a gas-volumetric buret and the whole system thermostated at 15°. Toluene (32 ml.), previously saturated with CO, then was introduced into the flask: a very rapid absorption of gas took place immediately and in the time of its completion (5–10 min.) a flaky orange precipitate was formed; 6.07 mmoles of CO was absorbed, ratio $CO/V(C_5H_5)_2 = 1.93:1$.

After filtration under nitrogen, the precipitate was washed with pentane and dried (1.25 g., 87% yield). The compound was purified by dissolution under nitrogen in acetone and reprecipitation with pentane. It is insoluble in non-polar solvents and H_2O and very slightly soluble in CS_2.

Anal. Calcd. for $C_{18}H_{10}O_8V_2$: C, 47.39; H, 2.21; V, 22.3. Found: C, 46.63, 46.50; H, 2.29, 2.36; V, 22.2, 22.0.

When heated under nitrogen in a sealed capillary, the compound decomposed without melting at about 140°.

The infrared spectra showed three bands in the carbonyl stretching region at about 2050 (s), 2010 (s), and 1860 (ss) $cm.^{-1}$. Other absorption bands due to the cyclopentadienyl rings were located at about 1445 (m), 1430 (m-w), 1165 (w), 1120 (w), 1075 (w-m), 1023 (m-w), 1010 (w), 888 (vw), 855 (m), and 843 (w) $cm.^{-1}$.

Magnetic susceptibility measurements at room temperature obtained with the Faraday method on two different preparations showed that the compound was diamagnetic. Attempts were not made to measure exactly the small diamagnetic susceptibility.

Reaction of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ with Iodine. Preparation of $[V(C_5H_5)_2(CO)_2]I_3$.—In the gas-volumetric apparatus mentioned above, 0.3175 g. (0.696 mmole) of $[V(C_5H_5)_2(CO_2)[V(CO)_6]$ was suspended in 15 ml. of toluene and treated in a CO atmosphere with 0.84 g. of I_2 (3.3 mg.-atoms) dissolved in 10 ml. of toluene. Carbon monoxide was readily evolved, the evolution being apparently complete in a few minutes: 92.3 ml. of CO (S.T.P. conditions) was measured, corresponding to 36.3% (36.8% calcd. for the evolution of six moles of CO per mole of $[V(C_5H_5)_2(CO)_2[V(CO)_6]$).

In another experiment performed under similar conditions, 0.3746 g. (0.821 mmole) of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ suspended in 10 ml. of H_2O was treated in small portions with a standardized aqueous solution of I_2–KI (see Table I). The evolution of CO, initially very rapid, progressively slowed down because of the preliminary and transitory precipitation of the triiodide. When all the anion $[V(CO)_6]^-$ had been decomposed (4.84 mmoles of CO, 36.2%), a stable deep orange precipitate of the triiodide was formed. No further evolution of CO was observed even in the presence of a strong excess of iodine and over very long reaction times.

TABLE I

DECOMPOSITION OF $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ WITH AQUEOUS I_2–KI

I_2, mg.-atoms added	CO, mmoles evolved	CO/I_2[a]
0.81	2.30	2.84
1.05	3.03	2.88
1.34	3.80	2.84
1.60	4.44	2.78
1.73	4.72	2.72
4.0	4.84	. . .

[a] Stoichiometry (1) requires $CO/I_2 = 3$.

The triiodide was recovered by filtration under nitrogen, washed with aqueous KI, then with H_2O, and dried *in vacuo*. The triiodide, soluble in polar organic solvents such as acetone and tetrahydrofuran, was purified by dissolution in pure acetone and further precipitation with pentane.

Anal. Calcd. for $C_{12}H_{10}I_3O_2V$: C, 23.33; H, 1.63; I, 61.62. Found: C, 23.20, 23.44; H, 1.70, 1.60; I, 62.34.

The infrared spectrum of the triiodide $[V(C_5H_5)_2(CO)_2]I_3$ as well as that of the tetraphenylborate $[V(C_5H_5)_2(CO)_2][B(C_6H_5)_4]$ described below showed only two strong absorption bands in the carbonyl stretching region at about 2040 and 2000 $cm.^{-1}$.

In a third experiment, after decomposition with aqueous I_2–KI of the anionic portion of compound I, SO_2 was passed through the reaction flask, yielding a stable solution of $[V(C_5H_5)_2(CO)_2]^+$, to which an aqueous solution of $NaV(CO)_6$ was added. The yellow-orange precipitate which immediately formed was collected by filtration under a nitrogen atmosphere, washed with H_2O, and dried *in vacuo*. Its infrared spectrum was superimposable on that of the starting compound I.

Preparation of $[V(C_5H_5)_2(CO_2)][B(C_6H_5)_4]$.—Operating in a nitrogen atmosphere, 0.67 g. of I was dissolved in acetone (15 ml.) and treated with 1.2 g. of $NaB(C_6H_5)_4$ dissolved in 15 ml. of methanol.

A yellow-orange precipitate was formed immediately; after addition of 50 ml. of H_2O, the precipitate was filtered, washed with H_2O and methanol, and finally dried *in vacuo* (0.75 g., yield 91%). The filtrate contained 0.071 g. of vanadium (calcd. 0.075 g.).

The compound was stable in air, soluble in acetone and tetrahydrofuran, very slightly soluble in methanol, and insoluble in aliphatic and aromatic solvents.

Anal. Calcd. for $C_{36}H_{30}BO_2V$: C, 77.71; H, 5.43; B, 1.94; V, 9.15. Found: C, 77.45, 77.57; H, 5.68, 5.73; B, 2.06; V, 8.95.

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Discussion

The reaction between $V(CO)_6$, $V(C_5H_5)_2$, and CO can be interpreted straightforwardly in terms of an electron transfer from $V(C_5H_5)_2$ to $V(CO)_6$. This fact allowed us to look more deeply into the details of the above mentioned mechanism of formation of $[V(C_7H_7)(C_7H_8)][V(CO)_6]$ from $V(CO)_6$ and C_7H_8. In that case the postulated hydride elimination from an intermediate $V(C_7H_8)(CO)_3$ could be conceived as a two-step process involving a hydrogen elimination and an electron abstraction; the first step being either a hydrogen transfer to $V(CO)_6$ to form the unstable[3] vanadium hexacarbonyl hydride $HV(CO)_6$ or an electron transfer to $V(CO)_6$.

The successful reaction between $V(CO)_6$ and $V(C_5H_5)_2$ seems to suggest that the intermediate formation of the unstable $HV(CO)_6$ is not necessarily required during the reaction of $V(CO)_6$ with C_7H_8.

The cation $[V(C_5H_5)_2(CO)_2]^+$ has not been described so far, whereas the uncharged $V(C_5H_5)(CO)_4$ and the anion $[V(C_5H_5)(CO)_3]^{2-}$ have been reported.[7,9]

The diamagnetic $[V(C_5H_5)_2(CO)_2]^+$ is isoelectronic with $Ti(C_5H_5)_2(CO)_2$ described some years ago by Murray.[10] The latter compound was reported to have two infrared carbonyl stretching bands at about 1965 and 1885 cm.$^{-1}$, to be compared with the bands at about 2050 and 2010 cm.$^{-1}$ for the related vanadium complex. In the latter case, the shift of the carbonyl stretching bands toward higher frequencies must be attributed to the increased positive charge on the metal.

At least one other case of oxidation–reduction reaction involving a metal carbonyl and a metal π-complex is known in the literature. As a matter of fact, Hein and Reinert,[11] in an attempt to prepare $Cr(CO)_6$, treated iron pentacarbonyl with bis-(diphenyl)-chromium(0) at 90–95° for 3–4 hr., the end product of the reaction being $[Cr(C_6H_5{-}C_6H_5)_2]_2[Fe_4(CO)_{13}]$. The mild conditions of formation of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ from $V(C_5H_5)_2$, $V(CO)_6$, and CO at atmospheric pressure and 15° clearly show the strong tendency of vanadium hexacarbonyl to act as an electron acceptor. Vanadium hexacarbonyl seems, therefore, to offer new and wider possibilities of straightforward preparation of cationic metal carbonyl species. Several complex cations have been reported recently such as $[C_5H_5Fe(CO)_3]^+$, $[C_5H_5Mo(CO)_4]^+$, $[C_5H_5W(CO)_4]^+$, $[C_5H_5Cr(CO)_4]^+$, and $[Mn(CO)_6]^+$. These cations were obtained in the presence of CO under pressure by the action of Friedel–Crafts halogen acceptors on metal carbonyl halides or cyclopentadienyl metal carbonyl halides,[12,13] or by the action[14] of $BF_3{-}O(CH_3)_2$ on the hydride $C_5H_5Cr(CO)_3H$, or, finally, by the action[15] of $NaB(C_6H_5)_4$ on $C_5H_5Fe(CO)_2Cl$. Other reactions of $V(CO)_6$ with metal complexes containing π-bonded aromatic ring systems will be investigated.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

Infrared Spectroscopic Study of Derivatives of Cobalt Tricarbonyl Nitrosyl

BY W. D. HORROCKS, JR., AND R. CRAIG TAYLOR

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Infrared spectra of mono- and disubstituted derivatives of $Co(CO)_3NO$ in which CO is replaced by PCl_3, $PCl_2C_6H_5$, $PCl(C_6H_5)_2$, $P(C_6H_5)_3$, *p*-tolyl isonitrile, *t*-butyl isonitrile, and *o*-phenanthroline are recorded. The π-electron accepting abilities of coördinated CO and NO are compared and a "spectrochemical series" for π-bonding ligands is proposed.

Introduction

Considerable interest has been shown recently in the infrared spectra of transition metal carbonyl compounds and their derivatives in the C–O stretching region. Several studies have dealt with the effect on the observed C–O frequencies of replacing some of the CO groups by other ligands.[1–8] In the present work we have studied the N–O frequencies as well as the C–O frequencies in mono- and disubstituted derivatives of cobalt tricarbonyl nitrosyl. A number of investigations have been made concerning the infrared absorp-

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