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THE CHEMISTRY OF THE GROUP V METAL CARBONYLS
II*. THE PREPARATION OF SOME DERIVATIVES OF TRICARBONYLMESITYLENEVANADIUM(0)

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SUMMARY

Tetracarbonylmesitylenevanadium(I) hexafluorophosphate has been converted into tricarbonyliodomesitylenevanadium(I) by reaction with sodium iodide. Reduction of this species by sodium borohydride has led to the isolation and characterization of tricarbonylhydridomesitylenevanadium(I). This complex shows a variable temperature NMR spectrum for the hydridic proton. Treatment of the hydride with either sodium amalgam or sodium hydroxide generates the carbonylate ion, $[(CH_3)_3C_6H_3V(CO)_3]^-$, which was isolated as a tetrabutylammonium salt.

INTRODUCTION

Apart from the unusual species[1] $[(CH_3)_6C_6Fe(CO)_2]_2$, prepared from hexamethyl-Dewar-benzene and $Fe(CO)_5$, no other binuclear transition-metal arenecarbonyl complexes have been reported, although a number of mononuclear species are well known. The logical systems to be investigated in an effort to prepare such species seemed to be with the metals in Group V and VII. However, it was not certain whether arenevanadiumtricarbonyl complexes would be "well behaved" binuclear and diamagnetic; or monomeric, paramagnetic and isostructural with arenechromiumtricarbonyl compounds.

Previous attempts to prepare arenevanadium carbonyls have led to some interesting chemistry. Treatment of $V(CO)_6$ with arenes[2] leads to disproportionation to give $[(arene)V(CO)_4][V(CO)_6]$ salts. These salts, when reduced[3] with sodium borohydride, gave various (cyclohexadienyl)$V(CO)_4$ complexes. This second result is not surprising in view of the similar reaction[4] of $[(arene)Mn(CO)_3]^+$ cations with sodium borohydride to give the cyclohexadienylmanganese tricarbonyl complexes. It should be noted, however, that the question as to why an aromatic ring π-bonded to a metal carbonyl cation should be reduced, by $NaBH_4$, in preference to expulsion of carbon monoxide and the production of a neutral transition-metal hydride is not fully understood. The reduction[5] of $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ salts with $NaBH_4$ gives

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* For part I see ref. 18.

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(π-C_5H_5)Fe$(CO)_2$H in high yield, whereas [(π-C_5H_5)Fe$(CO)_2$P$(C_6H_5)_3$]$^+$ gives the cyclopentadiene complex (π-C_5H_6)Fe$(CO)_2$P$(C_6H_5)_3$. It had been suggested[6] that (π-C_5H_6)Fe$(CO)_3$ is unstable with respect to (π-C_5H_5)Fe$(CO)_2$H and rapidly rearranges to it. This was proved to be incorrect by the isolation[7] and marked thermal stability of (π-C_5H_6)Fe$(CO)_3$.

It seemed clear that the most logical route into binuclear arenemetalcarbonyl systems would be the reaction of the known Group V and VII arenemetalcarbonyl cations with halide ions to give neutral arenemetalcarbonyl halides and the subsequent reduction of these halides into the corresponding hydrido complexes. Nucleophilic displacement reactions of halide ions on metal carbonyl species such as [(π-C_7H_7)M$(CO)_3$]BF_4 (M=Mo and W), [C_7H_9Fe$(CO)_3$]BF_4, M$(CO)_6$ (M=Cr, Mo, and W) are well known[8-12]. This communication describes our investigations of this route to arene metal-complexes.

EXPERIMENTAL

All solvents were purified and degassed before use. All operations were carried out under an atmosphere of prepurified nitrogen. IR spectra were recorded on a Perkin–Elmer Model 337 spectrometer. Proton NMR spectra were recorded on a Varian A-60 spectrometer, equipped with a variable temperature accessory, or a T-60 spectrometer. Mass spectra were measured, at 70 eV, on a Hitachi Perkin–Elmer RMU-6D mass spectrometer. The polarographic data were obtained using a Heath–Built EUA-19-2 polarograph equipped with three electrodes. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Reagents

The method of Calderazzo[2] was used to prepare tetracarbonylmesitylenevanadium(I) hexafluorophosphate, while a similar procedure to that used by Wilkinson[4] was used to prepare various arenetricarbonylmanganese(I) hexafluorophosphates.

Tricarbonyliodomesitylenevanadium(I)

A mixture of [$(CH_3)_3C_6H_3V(CO)_4$]PF_6 (0.5 g, 1.2 mmol) and NaI (0.38 g, 2.5 mmol) was stirred in 50 ml THF for 1 h at 0°. The original light red solution turned green immediately with evolution of gas. The red crystals of [$(CH_3)_3C_6H_3V(CO)_4$]PF_6 (which were partly soluble in THF) slowly dissolved and reacted during 1 h. The solvent was removed (0°/0.5 mm) leaving a dark green residue. This was extracted with CH_2Cl_2 (4 × 7 ml). The combined extracts were passed through a plug of glass wool and extracted with 20 ml of a saturated aqueous solution of $Na_2S_2O_3$. The deep green CH_2Cl_2 layer was separated and dried briefly with Linde molecular sieves (5A). The solution was filtered and the filtrate treated with 25 ml of hexane. Evaporation (0°/0.5 mm) until the volume of the solution was ca. 15 ml caused the product to separate. It was collected, washed with hexane (2 × 7 ml) and dried *in vacuo*. Pure $(CH_3)_3C_6H_3V(CO)_3I$ (0.24 g, 63%) was obtained as shiny dark green crystals, dec. 90–92° (with formation of I_2). (Found: C, 37.66; H, 3.12; I, 33.24. $C_{12}H_{12}IO_3V$ calcd.: C, 37.72; H, 3.16; I, 33.21%.)

IR. ν(CO) (in THF) 1984s, 1921vs, 1885s; in Nujol mull: 1975s, 1903vs and 1884s cm^{-1}.

NMR. τ(in $CDCl_3$) 3.22(1); 7.73(3).

Mass spectrum. This showed weak peaks corresponding to the ions $[(CH_3)_3C_6H_3V(CO)_nI]^+$ for $n=0$–2 and strong peaks at *m/e* 105 and 120 characteristic of mesitylene[13].

Crystals of $(CH_3)_3C_6H_3V(CO)_3I$ are moderately air stable, but as a fine powder it decomposes immediately in air. It is also unstable in solution, decomposing rapidly in THF and CH_2Cl_2 at room temperature; decomposition is, however, slight for solutions maintained below 0°.

Tricarbonylhydridomesitylenevanadium(I)

A solution of $(CH_3)_3C_6H_3V(CO)_3I$ in THF was prepared as outlined above. To this solution, still at 0°, $NaBH_4$ (0.4 g, 10 mmol) was added in one portion. The solution turned slowly brown with evolution of gas. After 1 h, it was transferred to a separatory funnel containing pentane (20 ml) and water (15 ml). After ca. 1/2 h of intermittent shaking, during which time there was some effervescence, the dark aqueous layer was discarded. The orange organic layer was extracted with water (4 × 15 ml). The pentane layer was filtered and the solvent removed (5°/0.2 mm) to yield $(CH_3)_3C_6H_3V(CO)_3H$ (0.24 g, 67%) as a bright orange powder, dec. 69–72°. (Found: C, 54.98; H, 5.12. $C_{12}H_{13}O_3V$ calcd.: C, 56.25; H, 5.08%.)

IR. ν(CO) (in hexane) 1961vs, 1895s and 1879s cm^{-1}.

NMR. τ(in toluene-d_8) 5.57(3); 8.45(9); 15.8(1).

The peak at $\tau=15.8$ is temperature dependent. It is very broad at −20° but becomes progressively sharper at lower temperatures.

Mass spectrum. This shows strong peaks corresponding to the pairs of ions $[(CH_3)_3C_6H_3V(CO)_nH]^+$ and $[(CH_3)_3C_6H_3V(CO)_n]^+$ for $n=0$–3. Strong peaks, characteristic of mesitylene[13], occurred at *m/e* 105 and 120.

In THF solution $(CH_3)_3C_6H_3V(CO)_3H$ is stable at 25°, in the absence of air, but decomposes slowly at higher temperatures. In other solvents, such as $CHCl_3$ or toluene, it decomposes rapidly at 25° but it is stable at −20° in toluene solution. The solid is air-stable but decomposes slowly at 25°. It can be kept at −20° for relatively long periods without decomposition.

Tetrabutylammoniumtricarbonylvanadium(I)

A. A mixture of $(CH_3)_3C_6H_3V(CO)_3H$ (0.2 g, 0.08 mmol) and NaOH (1 g) was stirred in water (28 ml) at room temperature. The hydride is only sparingly soluble, but the reaction takes place slowly and the solution becomes orange-red. After 12 h most of the hydride had reacted. The solution was filtered and a solution of tetrabutylammonium bromide (0.5 g, 1.5 mmol) in water (10 ml) was added dropwise to the filtrate. This caused the product to separate immediately as a bright orange precipitate. It was collected, washed with water (2 × 4 ml) and dried *in vacuo*. Purification was effected by dissolving the crude material in 30 ml of absolute ethanol and treating the solution with 20 ml of heptane. Reducing the volume to ca. 15 ml by evaporation (25°/0.05 mm) caused small red crystals to separate. These were collected, washed with heptane (2 × 7 ml) and dried *in vacuo* to yield pure $[(C_4H_9)_4N][(CH_3)_3C_6H_3V(CO)_3]$ (0.32 g, 83%), dec. 94–96°. (Found: C, 67.78; H, 10.18. $C_{28}H_{48}NO_3V$ calcd.: C, 67.7; H, 9.76%.)

IR. ν(CO) (in THF) 1838vs, 1753s, 1733 (sh); (in Nujol mull) 1845vs, 1746s and 1725s cm^{-1}.

NMR. τ(in nitromethane-d_3) 3.18(3); 6.77(8); 7.75(9); 8.45(16); 9.03(12).

Polarography. The data (DME *vs.* saturated calomel electrode in acetonitrile) showed a two electron oxidation at −0.915 volts.

B. The anion can also be made by treating a THF solution of the hydride with either excess sodium shot or a 1% sodium amalgam. Monitoring the reaction by IR spectroscopy shows that the reaction is essentially complete in 5–6 days. The THF solution of sodium tricarbonylmesitylenevanadate shows ν(CO) at 1837 vs, 1761s and 1703s cm^{-1}. Removal of the solvent (0°/0.5 mm) and treatment with water enables the water soluble anion to be separated from any unreacted hydride. The anion can be recovered from the aqueous solution by the procedure described in A.

Solutions of $[(C_4H_9)_4N][(CH_3)_3C_6H_3V(CO)_3]$ are extremely air sensitive as is the solid. It is readily soluble in THF and acetonitrile but is decomposed slowly in CH_2Cl_2.

Attempted preparation of arenedicarbonylhalogenomanganese(I) species

Various $[(arene)Mn(CO)_3]PF_6$ salts were treated with alkali metal halides in both acetone and THF. However, rather than the expected $(arene)Mn(CO)_2X$, where X = Br or I, IR and mass spectrometry showed the products[14] to be $Mn_2(CO)_8X_2$.

RESULTS AND DISCUSSION

Treatment of $[(CH_3)_3C_6H_3V(CO)_4]PF_6$ with sodium iodide in THF solution gives the expected $(CH_3)_3C_6H_3V(CO)_3I$. The complex can be isolated as shiny green crystals, which are stable in the absence of air. However, the complex decomposes rapidly in solution at room temperature although decomposition is very slow in solutions kept below 0°.

The reduction of $(CH_3)_3C_6H_3V(CO)_3I$, in THF solution, with $NaBH_4$ proceeds rapidly to give $(CH_3)_3C_6H_3V(CO)_3H$ which can be isolated as a moderately stable orange solid. Its formulation is supported by elemental analysis and IR spectroscopy (ν(CO) at 1961, 1895 and 1879 cm^{-1}). The mass spectrum is typical of that found for transition-metal carbonyl-hydrides and shows a fragmentation scheme corresponding to the pairs of ions $[(CH_3)_3C_6H_3V(CO)_nH]^+$ and $[(CH_3)_3C_6H_3V(CO)_n]^+$ for $n = 0$–3. The NMR spectrum is that expected for an arenemetalhydride $\tau = 5.57(3)$ aromatic, 8.45(9) methyl, 15.8(1) V–H. The latter peak is very broad, *ca.* 51 Hz at −20°, and is found to be temperature dependent; by −52° it is considerably narrower, ca. 19 Hz. The solid decomposes slowly at room temperature but it can be kept at −20° without apparent decomposition. The hydride can also be prepared by treatment of a THF solution of $(CH_3)_3C_6H_3V(CO)_3I$ prepared *in situ* from $[(CH_3)_3C_6H_3V(CO)_4]PF_6$ and NaI by treatment with excess 1% sodium amalgam. The reason for this is probably a reflection of the fact that sodium iodide is extremely difficult to obtain completely anhydrous. Heating solutions of $(CH_3)_3C_6H_3V(CO)_3H$ led to decomposition rather than conversion into the expected arenevanadium tricarbonyl.

The hydride, altough insoluble in water, reacts slowly with aqueous sodium hydroxide to give orange solutions containing the $[(CH_3)_3C_6H_3V(CO)_3]^-$ anion which can be isolated as the tetrabutylammonium salt by precipitation with tetrabutylammonium bromide. The anion can also be produced from the hydride, although very slowly ca. 5–6 days, by treatment of THF solutions with either sodium shot or 1% sodium amalgam.

Attempts to prepare the neutral mesitylenevanadium tricarbonyl have met with failure. Treatment of $[(CH_3)_3C_6H_3V(CO)_3]^-$ salts with $[C_7H_7]BF_4$ led to the production of ditropyl but gave no carbonyl containing vanadium species*. The reaction of $[(CH_3)_3C_6H_3V(CO)_3]^-$ and $(CH_3)_3C_6H_3V(CO)_3I$ in THF gave an immediate brown solution from which no identifiable product could be isolated.

Attempts to extend this approach to the Group VII arene-metal carbonyl systems met with immediate failure. The arenetricarbonylmanganese hexafluorophosphate salts reacted with alkali metal halides in both THF and acetone solution to give the known complexes[14] $Mn_2(CO)_8X_2$, where X = Br, I, instead of the expected (arene)$Mn(CO)_2X$ species.

Although we did not succeed in making any neutral arenemetalcarbonyls, we have managed to synthesize a number of new derivatives of the "arenetricarbonylvanadium" system.

The nucleophilic displacement of carbon monoxide by iodide ion from tetracarbonylmesitylenevanadium(I) salts gave tricarbonyliodomesitylenevanadium(I). The reduction of this halide with sodium borohydride to tricarbonylhydridomesitylenevanadium(I) gave the first characterized carbonylhydride of vanadium. This hydride is isoelectronic with the known $[(CH_3)_3C_6H_3Cr(CO)_3H]^+$ ion produced by protonation[16] of the neutral tricarbonylmesitylenechromium(0) by strong acids. The nature of the temperature-dependent behavior of the high field resonance, which is clearly assignable to the hydrido proton in the vanadium complex, is probably due to vanadium to hydrogen spin-spin coupling. Naturally occurring vanadium has $^{51}V = 99.76\%$, $I = 7/2$. Normally, spin–spin coupling between quadrupolar nuclei and hydrogen is averaged to zero and is not observed because of rapid spin–lattice relaxation of the quadrupolar nucleus. However, Whitesides[17] has found that this type of temperature dependence, which is observed for the protons in $(\pi\text{-}C_7H_7)V(CO)_3$, reflects the variation in the rate of $^{51}V - {}^1H$ spin–lattice relaxation. These studies emphasize that the rate of spin–lattice relaxation will be dependent upon two factors: the nuclear quadrupole coupling constant $(e^2 \cdot q \cdot Q/h)$ and the rotational correlation time.

It is important to recognize that for certain hydrido complexes of metals which have large abundances of quadrupolar nuclei (*e.g.* V, Nb, Ta, Mn, Co, and Re), the magnitude of the nuclear quadrupole coupling constant may be such that the hydride resonance is very markedly broadened at ambient probe temperatures and could easily escape detection.

The hydride can be readily deprotonated to generate the tricarbonylmesitylenevanadate(−I) ion and it can be readily isolated as the tetrabutylammonium salt. The IR spectra of salts of the anion, in THF solution, show three, rather than two bands in the CO stretching region. We attribute this to the reduction of the local C_{3v} symmetry of the anion to C_s symmetry by ion-pair interaction in solution. The isolation of this complex completes the isoelectronic series $[(CH_3)_3C_6H_3Mn(CO)_3]^+$, $(CH_3)_3C_6H_3Cr(CO)_3$ and $[(CH_3)_3C_6H_3V(CO)_3]^-$, and as expected the decreasing

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* Oxidation of $V(CO)_6^-$ to $V(CO)_6$ takes place by treatment with C_7H_7Br[15].

CO stretching frequencies parallel the expected increase in π-bonding with increasing negative oxidation state (Mn–V).

The inability to produce the neutral parent carbonyl by either thermal decomposition of $(CH_3)_3C_6H_3V(CO)_3H$ or oxidation of $[(CH_3)_3C_6H_3V(CO)_3]^-$ with tropylium tetrafluoroborate led us to try a coupling reaction between $(CH_3)_3C_6H_3V(CO)_3I$ and $[N(C_4H_9)_4][(CH_3)_3C_6H_3V(CO)_3]$. However, the fact that even this latter reaction leads to rapid decomposition forces us to conclude that "tricarbonylmesitylenevanadium(0)" is unstable.

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