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COMPLEXES OF METALS WITH AROMATIC SYSTEMS XCIX*. DIPHENYLFULVENECHROMIUM TRICARBONYL AND ITS REDUCTION PRODUCTS

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INTRODUCTION

In view of the continued interest in the reactions of metal carbonyls with 6,6-dialkyl- and 6,6-diphenylfulvenes[2-5], and in view of the recent preparation of bis(diphenylfulvenecobalt) hexafluorophosphate from cobalt(II) chloride[6], we have re-examined the product isolated from the treatment of chromium hexacarbonyl with 6,6-diphenylfulvene. We can now show that in this product the aromatic ligand is bonded to chromium through the five-membered ring and not, as tentatively suggested before[7], through one of the six-membered rings. We have also studied the reduction of this product in proton-active solvents, using sodium borohydride as the reducing agent.

RESULTS AND DISCUSSION

(*a*) *Diphenylfulvenechromium tricarbonyl*

When a 1 : 1 mixture of chromium hexacarbonyl and 6,6-diphenylfulvene were refluxed together in 100–120° petrol the initial rich red colour of the solution darkened to a deep brown within an hour; the mixture was refluxed for two days, by which time a quantity of brown crystals had separated. Purification of these brown crystals is described in the experimental section. Total analysis of the purified product indicates the stoicheiometry $C_{21}H_{14}CrO_3$. The complex melts over the range 203° to 209° with decomposition but can be sublimed at $120°/10^{-3}$ mm to leave only a trace of residue. It dissolves in most of the common organic solvents, the best being acetone, tetrahydrofuran and diethyl ether; the solutions all have an intense brown colour but none can be made very concentrated. As a solid the complex appears to be stable indefinitely in air and its solutions decompose only slowly in air. Cryoscopic measurements on the benzene solution indicate that the complex is monomeric.

Details of the proton magnetic resonance spectrum of the complex in deuteroacetone are given in Table 1. The clearly resolved pair of equally intense triplets at τ 5.23 and 4.28 ppm suggest an A_2B_2 system: the four protons of the five-membered ring of the fulvene bound through this five-membered ring to the metal. Two com-

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plicated peaks, of intensities 3 and 2 relative to each of the above triplets, have their centres at τ 2.63 and 2.32 ppm and may be assigned to the two free phenyl groups of the fulvene.

TABLE 1

PROTON MAGNETIC RESONANCE SPECTRA

Measured in deuteroacetone relative to internal TMS standard.

Complex	*Band pos.* (τ)	*Characteristics*	*Relative intensity*	*Assignment*
$C_5H_4CPh_2Cr(CO)_3$	5.23	Triplet	1	H_α or H_β
	4.28	Triplet	1	H_β or H_α
	2.63 (centre)	Complex	3	Free phenyl groups
	2.32 (centre)	Complex	2	
$Tl[(C_5H_4CHPh_2)Cr(CO)_3]$	5.55	Triplet	2	H_α or H_β
	5.27	Triplet	2	H_β or H_α
	4.70	Singlet	1	Exocyclic proton (of $CHPh_2$)
	2.51	Broad singlet	10	Free phenyl groups

The infrared spectrum of a cyclohexane solution of the complex has strong bands at 2004 and 1927 cm^{-1}, which, together with the analytical results, shows clearly that the complex contains the $Cr(CO)_3$ fragment. Because the cyclohexane solution was so dilute, although intensely coloured, the spectrum over the rest of the 4000 to 660 cm^{-1} range was recorded from a Nujol mull and principal bands appeared at 1600(w), 1495(w), 1360(w), 1310(w), 1075(w), 1060(w), 1027(w), 1000(w), 919(w), 840(m), 824(m), 787(m), 758(s), 748(m), 709(s) and 696(m) cm^{-1}.

The mass spectrum obtained from diphenylfulvenechromium tricarbonyl (with the probe at 80°) shows no peak due to the complex molecule itself; the strongest peak in the spectrum occurs at *m/e* 230 (free diphenylfulvene) and the fragmentation pattern is the same as that of free diphenylfulvene (run separately with the probe at 40°).

From our results we suggest that in this complex a chromium tricarbonyl fragment is bonded to an unchanged 6,6-diphenylfulvene ligand, and that the aromatic ligand is bonded to the metal through the five-membered ring: the PMR spectrum shows clearly that the bonding to the metal cannot be through either of the six-membered rings. The aromatic ligand has not picked up protons from the solvent to form a cyclopentadienyl complex as has been found by Wilkinson[2] and Pauson[4] during the reactions in solution between fulvenes and molybdenum and tungsten hexacarbonyls, but whereas Wilkinson and Pauson used ether solvents we have used petrol. These different reaction conditions could explain the differences, but we need not expect the chemistry of chromium to parallel that of molybdenum and tungsten too closely anyhow.

(b) Reduction of diphenylfulvenechromium tricarbonyl

When finely powdered sodium borohydride was added to a solution of diphenylfulvenechromium tricarbonyl in 1:1 benzene/methanol the opaque brown solution lightened in colour and finally became yellow and transparent (solution A). Hydrogen was, of course, evolved at the same time. The solution A was extremely air-sensitive and turned red in the presence of traces of air. Complete decomposition in air left a murky green mixture. Evaporation of solution A left an oily solid and extraction of this solid with nitrogen-saturated water, followed by filtration, gave a clear pale-yellow aqueous solution which contained an organometallic anion. Addition of aqueous thallium nitrate afforded a flocculent orange precipitate which was filtered off, washed with water and dried. This orange precipitate could be handled briefly in air but its solutions, in benzene, acetone and ethyl acetate, were extremely air-sensitive and again decomposition in solution gave first a red colouration and finally green products. The complex was recrystallised from ethyl acetate.

Total analysis of this thallium precipitate indicates a Cr/Tl ratio of exactly 1:1, and an O/Cr ratio of approximately 3.4:1. The complex decomposes above 150° and attempts to sublime it ended only in decomposition. Because of the air-sensitivity of the solutions we have been unable to determine the molecular weight.

Fulvene complexes of metals may readily be reduced to cyclopentadienyl complexes and the analysis, the reductive preparation and the properties of the orange precipitate suggest that it is the thallium salt of the anion $[(C_5H_4CHPh_2)Cr(CO)_3]^-$. The PMR spectrum of the complex in deuteroacetone is detailed in Table 1 and supports this suggestion. The peaks at τ 5.55 and 5.27 ppm, each of relative intensity 2, can be assigned to the four protons of a monosubstituted cyclopentadienyl ring bound to a metal, and although these peaks are not well resolved they appear to be triplets. The peak of relative intensity 10 at τ 2.51 ppm confirms that the phenyl groups have remained unchanged during the reduction process. It remains, however, to assign the peak of relative intensity 1 which appears at τ 4.7 ppm. It could be assigned to the proton of the exocyclic $CHPh_2$ group; although this proton is formally aliphatic a chemical shift as low as 4.7 ppm is not inconceivable in such surroundings.

The infrared spectrum of the complex was recorded from a potassium bromide disc in the carbonyl stretching region and from a Nujol mull for the rest of the 4000 to 660 cm^{-1} range. Strong CO frequencies are observed at 1923 and 1808 cm^{-1} and the other principal bands are: 1706(s), 1495(w), 1075(w), 1028(w), 824(m), 808(m), 750(m), 741(m), 706(m), 694(m) cm^{-1}. The assignment of the strong band at 1706 cm^{-1} is not clear.

We have tried also a second treatment of the solution A. Formic acid was added till the solution was acidic and the solvent evaporated to give an oily yellow-green solid. Extraction of this solid by benzene or ethyl acetate afforded a yellow-green solution which was filtered and evaporated to an oily yellow-green solid (B). When this oily residue was digested in aqueous alkali addition of aqueous thallium nitrate precipitated the orange product described above. When, however, this oily residue was heated to 80° under vacuum fine green crystals formed and a small volume of gas was evolved. After two hours the conversion of the oil to a mass of radiating clusters of green crystals was complete. A chemical change had obviously taken place and the green crystals were much less soluble in methanol and petrol than had been the oil. The green complex was recrystallised from its very air-sensitive solution in ethyl acetate; the complex may be handled briefly in air but decomposes without melting above 100°. Total analysis of the purified product indicates the stoicheiometry $C_{21}H_{15}CrO_3$. Again we have failed to obtain a molecular weight because the solutions are so air-sensitive. The strongest peak in the mass spectrum of the green complex occurs at *m/e* 232. This peak occurs at *m/e* two units greater than that of diphenylfulvene (*m/e* = 230). There are no ions of higher mass present and the fragmentation pattern is similar to that of free diphenylfulvene except that on the higher mass side of every fragmentation peak of the green complex there are peaks of *m/e* one or two units greater; these extra peaks are not merely isotope peaks. The strong CO peak at *m/e* 28 indicates considerable disruption of the green complex under these conditions (probe at 80°).

The following magnetic measurements show that, as a solid, the green complex is diamagnetic:

$$\chi^{295\,^{\circ}\mathrm{K}} = (-0.47 \pm 0.05) \times 10^{-6}\ \mathrm{cm}^3/\mathrm{g} \quad \chi^{90\,^{\circ}\mathrm{K}} = (-0.33 \pm 0.05) \times 10^{-6}\ \mathrm{cm}^3/\mathrm{g}$$

These give $\chi^{\infty} = (-0.53 \pm 0.09) \times 10^{-6}\ \mathrm{cm}^3/\mathrm{g}$

In the PMR spectrum of a saturated but not very strong solution of the green complex in deuteroacetone we found only one peak, at about τ 3 ppm. The infrared spectrum, obtained from a Nujol mull, has the following principal bands: 1942(s), 1912(s), 1897(m), 1495(w), 1405(w), 1070(w), 1028(w), 900(w), 838(m), 748(m), 723(m), 706(m), 698(m) cm^{-1}.

The similarity between the chemistry of the yellow oil(B) and green crystalline complex described here and the chemistry of the complexes $C_5H_5Cr(CO)_3H$ and $[C_5H_5Cr(CO)_3]_2$ is noteworthy. In the latter system[8] the thermally unstable hydride is easily converted to the green dimer with the evolution of hydrogen. We have failed to isolate any hydride species from the yellow oily solid (B), but with this noteworthy comparison in mind we suggest the following: that reduction of diphenylfulvene-chromium tricarbonyl affords the anion $[(C_5H_4CHPh_2)Cr(CO)_3]^-$, present in solution A and isolated as its orange thallium salt, and that acidification of the solution A affords the hydride $(C_5H_4CHPh_2)Cr(CO)_3H$, present in the oily solid B but not isolated, which is converted by heating *in vacuo* to the green dimer $[(C_5H_4\text{-}CHPh_2)Cr(CO)_3]_2$. The strongest peak in the mass spectrum of the green complex could be due to the loss of the $(C_5H_4CHPh_2)$ ligand from the complex, followed by the radical so formed picking up a proton to give the ion $(C_5H_5CHPh_2)^+$ (*m/e* = 232).

The discordant note in our work has been the failure to find peaks in the PMR spectrum of the green complex assignable to the four protons of the substituted cyclopentadienyl ring, but the signal at τ 3 ppm which we assign to the free phenyl groups was only obtained by computer collection of two hundred scans of the spectrum. Further, King has noted that for the complexes $[C_5H_4C(NMe_2)]M(CO)_3$, where M = Mo or Cr, the PMR signals due to the ring protons are not observed even though the signals due to the protons of the N-methyl groups are[9].

A separation of between τ 0.39 and 0.63 ppm between the signals due to the H_α and H_β protons of substituted cyclopentadienylmanganese tricarbonyl complexes has been noted by Shen, Long and Moreland[10], and so the separation of approximately 0.3 ppm between the symmetrical triplets in the spectrum of the orange thallium salt is consistent with the presence of a mono-substituted cyclopentadienyl ring bound to a metal.

From the sum of our evidence, therefore, we suggest that the reduction of diphenylfulvenechromium tricarbonyl has produced the anion $[(C_5H_4CHPh_2)Cr(CO)_3]^-$ whose subsequent reactions are similar to those of the well known anion $[C_5H_5Cr(CO)_3]^-$, in that acidification produces a hydride species which decomposes on heating to a neutral cyclopentadienylchromium dimer. As mentioned above, Wilkinson[2] and Pauson[4] have found that substituted cyclopentadienylmetal carbonyl complexes are formed spontaneously from the reaction of molybdenum and tungsten hexacarbonyls with fulvenes without the necessity of reducing agents.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of pure, dry nitrogen, using standard techniques. Chromium hexacarbonyl was sublimed before use and 6,6-diphenylfulvene was prepared as reported[11]. Infrared spectra were obtained using a Perkin Elmer model 21 spectrometer and nuclear magnetic resonance spectra using a Varian A60 spectrometer. The mass spectra were obtained using a CH 4 Mass spectrometer with an AN 4 ion source, operating at 50 eV (electron energy) with a direct inlet system and not with the sample directly in the ion source.

Preparation of 6,6-diphenylfulvenechromium tricarbonyl

Chromium hexacarbonyl (3.3 g) and 6,6-diphenylfulvene (3.5 g) were heated together for 44 h in refluxing petrol (70 ml, freed from aromatics by shaking with oleum, dried over sodium and distilled, b.p. ~ 110°). The reaction mixture was cooled to $-10°$ overnight and the brown crystals filtered and washed with pentane. Unreacted chromium hexacarbonyl was removed by sublimation (70°, water pump pressure) and the residue extracted in a Soxhlet apparatus by ether (100 ml). On completion of this extraction the ether was diluted with n-hexane and the mixture evaporated till only n-hexane remained. The crystals thrown down were filtered, washed with pentane and dried *in vacuo* (60°, 1 h). Final purification was by sublimation (120°, 10^{-3} mm). Yield 3.5 g. (Found: C, 68.60; H, 4.00; O, 13.30; Cr, 14.00; mol.wt. cryoscopic in benzene, 367. $C_{21}H_{14}CrO_3$ calcd.: C, 68.85; H, 3.85; O, 13.10; Cr, 14.20%; mol.wt., 366.3.)

Reduction of diphenylfulvenechromium tricarbonyl

(*a*) Finely powdered sodium borohydride was added in small amounts (~2 mg at a time) to a stirred solution of diphenylfulvenechromium tricarbonyl (0.64 g) in 1 : 1 benzene/methanol (total volume 60 ml) until the initial opaque brown solution became light-yellow and transparent (Solution A). The solvent was evaporated and the sticky residue extracted by water (150 ml, scrupulously oxygen free). Filtration through activated charcoal lying on powdered calcium carbonate gave a clear pale-yellow solution. Aqueous thallium nitrate was added and the orange precipitate filtered, washed with water and dried under vacuum (60°, 3 h). The product was recrystallised from ethyl acetate by partial evaporation of the solvent followed by dilution with n-hexane; the mother liquor was decanted and the complex washed with pentane and dried under vacuum (60°, $\frac{1}{2}$ h). Yield 0.39 g. (Found: C, 44.06; H, 2.78; Cr, 8.80; O, 9.20; Tl, 34.70. $C_{21}H_{15}CrTlO_3$ calcd.: C, 44.11; H, 2.64; Cr, 9.10; O, 8.40; Tl, 35.75%.)

(*b*) As in section (*a*) as far as the obtaining of solution A. Then formic acid was added until the solution was definitely acidic; the solvent was evaporated to leave an oily yellow-green residue. This residue was dissolved in the minimum amount of benzene or ethyl acetate (~40 ml). The solution was filtered on a G4 sinter and evaporated to leave a yellow-green oily residue. As this residue was heated in vacuo (80°, 10^{-3} mm) green crystals grew throughout the oil and after two hours this transformation was complete. The green crystals were washed with methanol, recrystallised from ethyl acetate, washed with n-pentane and finally dried under vacuum (60°, $\frac{1}{2}$ h). Yield 0.3 g. (Found: C, 68.69; H, 4.10; O, 13.10; Cr, 13.01. $C_{21}H_{15}CrO_3$ calcd.: C, 68.66; H, 4.12; O, 13.07; Cr, 14.16%.)

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SUMMARY

The preparation and properties of diphenylfulvenechromium tricarbonyl are described. The PMR spectrum indicates that the aromatic ligand is bound to the metal through the five-membered ring. The reduction of diphenylfulvenechromium tricarbonyl affords ring-substituted derivatives of the cyclopentadienylchromium tricarbonyl anion and of the dimeric cyclopentadienylchromium tricarbonyl.

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