

THE EFFECT OF TRICARBONYLCHROMIUM ON THE THERMODYNAMIC STABILITY OF STABLE CARBOCATIONS

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Summary

The pK_{R^+} 's for the ionization equilibria between a number of p,p' -substituted diphenylmethanols mono- and bis-complexed with the $Cr(CO)_3$ group and the corresponding carbocations in aqueous sulfuric acid were determined by spectrophotometric methods. The same pK_{R^+} 's were measured for two ferrocenyltricarboxylchromiumarylmethanols in aqueous trifluoroacetic acid. The introduction of the $Cr(CO)_3$ group can make the complexed cation either more or less stable than the corresponding free ion, depending upon the structure. The effect of the complexation is explained in terms of electronic and conformational effects.

Introduction

The high degree of stabilization of carbonium ions α to an organometallic substituent has been recognized for some time. Several methods have been used to obtain quantitative measures of the unusual stability of these ions. For example, kinetic studies have shown that solvolysis of ferrocenylmethyl acetates is faster than that of triphenylmethyl acetates [1], and solvolysis of benzyl and diphenylmethyl chlorides complexed with tricarbonylchromium is 10^5 and 10^3 times as fast as that of the corresponding free substrates [2]. Moreover, the thermal isomerization of tricarbonylchromiumbenzyl thiocyanate to isothiocyanate occurs at moderate temperatures whereas that of benzyl thiocyanate does not [3].

1H and ^{13}C NMR techniques have been widely used to demonstrate the stability of α -ferrocenylmethyl [4], π -arenetricarbonylchromium [5], α -cymantrenyl [6], cyclobutadienetricarbonyliron [7] and α -(ethynyl)hexacarbonyldicobalt [8] carbonium ions, but chemical shifts do not give reliable quan-

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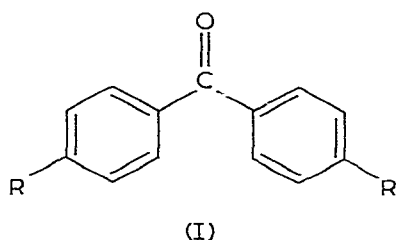
tative information on the thermodynamic stability of the ions.

pK_{R^+} values of ionization of metallocenylmethyl alcohols give useful information on the relative stabilities of this class of carbocations, and a considerable body of data is available for the ferrocenyl system [9]. In contrast very few results are available for arylalkyl ions complexed with the tricarbonylchromium group. The only data are the pK_{R^+} 's of the *para*-substituted benzyl cations in H_2SO_4 [10]. It appears that the primary benzyl cation complexed with tricarbonylchromium is about as stable as the diphenylmethyl cation, and over 5.5 pK_{R^+} units more stable than the uncomplexed benzyl cation. In fact only a lower limit for the difference of the pK_{R^+} 's between free and complexed ions can be given because the pK_{R^+} 's for the uncomplexed benzyl cations are not available (except for the mesityl cation [11]).

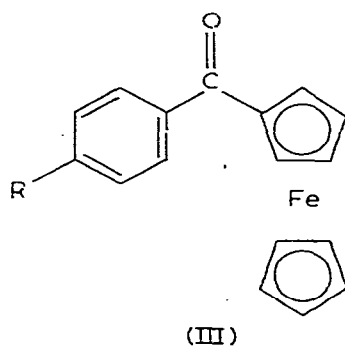
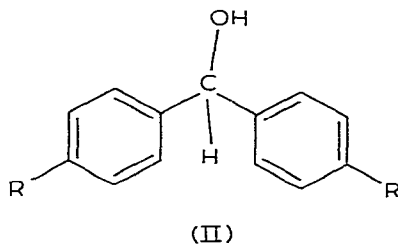
It seemed desirable to measure the pK_{R^+} 's of a series of complexed carbocations the free ligands of which have measurable pK_{R^+} 's. Thus we have measured the pK_{R^+} 's of diphenylmethyl cations with one or both phenyl rings complexed with tricarbonylchromium. The effect of this group on the stability of the ferrocenylphenylmethyl cation, a much more stable species, was also investigated.

Results

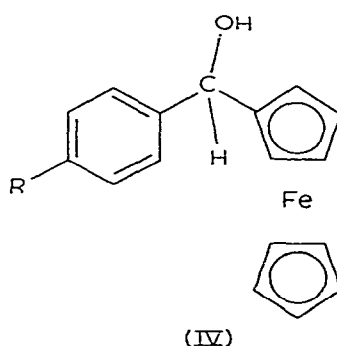
Mono- and bis-tricarbonylchromium diphenylmethanols, $II \cdot Cr(CO)_3$ and $II \cdot Cr_2(CO)_6$, have been obtained by reduction of the corresponding benzophenones, $I \cdot Cr(CO)_3$ and $I \cdot Cr_2(CO)_6$, which in turn were obtained by treating



(a, R = H ;
b, R = CH₃ ;
c, R = OCH₃)



(a, R = H ;
b, R = CH₃)



the free ligands with $\text{Cr}(\text{CO})_6$ (see Experimental). The complexed ferrocenylarylketones, $\text{III} \cdot \text{Cr}(\text{CO})_3$, and the corresponding carbinols, $\text{IV} \cdot \text{Cr}(\text{CO})_3$, were synthesized analogously. Physical and spectroscopic properties of the complexes are reported in the Experimental.

Reproducible UV spectra of the diphenylmethanols, mono- and bis-complexed with $\text{Cr}(\text{CO})_3$ were obtained with solutions in anhydrous oxygen-free methanol or diglyme; in contrast the complexed ferrocenyl alcohols were stable only in freshly distilled oxygen-free tetrahydrofuran if the solutions were kept in the dark at -20°C . UV data for the alcohols in inert and ionizing solvents are listed in Table 1.

Mono- and bis-complexed diphenylmethanols show a new well-defined absorption band in the 400–500 nm region in concentrated sulfuric acid, the position of the λ_{max} changing with the nature of the substituent. Corresponding complexed and free cations show absorption maxima at ca. the same wavelength, but the spectral changes occurring in the complexed series are attributed to the formation of the complexed and not the free diphenylmethyl cations on the basis of the following arguments: (a) the formation of the species responsible for the

TABLE 1

UV DATA OF ALCOHOLS IN DIFFERENT SOLVENTS AND pK_{R^+} VALUES FOR THE HYDRATION OF CATIONS COMPLEXES WITH $\text{Cr}(\text{CO})_3$ AT 25°C

Compound	$\lambda_{\text{max}}(\text{nm}) (10^{-4} \epsilon (M^{-1} \text{ l cm}^{-1}))$			% acid at half-ionization ($\pm 0.1\%$)	pK_{R^+} (± 0.05)		
	MeOH	H_2SO_4 96%	CF_3COOH 70%				
IIa		442 (4.36) ^a		77.8	-13.3 ^a		
IIb		472 (7.41) ^a		66.4	-10.4 ^a		
IIc		507 (11.0) ^a		44.0	-5.7 ^a		
IIa · $\text{Cr}(\text{CO})_3$	3.16 (0.95)	441 (1.20)		66.3	-10.4		
IIb · $\text{Cr}(\text{CO})_3$	3.17 (0.93)	468 (3.37)		64.5	-9.4		
IIc · $\text{Cr}(\text{CO})_3$	3.17 (0.82)	503 (6.80)		42.8	-5.4		
IIa · $\text{Cr}_2(\text{CO})_6$	3.18 (1.82)	443 (0.53)		64.7	-9.5		
IIb · $\text{Cr}_2(\text{CO})_6$	3.19 (1.79)	468 (1.36)		60.0	-8.9		
IIc · $\text{Cr}_2(\text{CO})_6$	3.19 (1.70)	503 (4.55)		40.5	-4.9		
IVa	440; (0.011)	258 (0.37) ^b	407; (0.33);	328; (1.25);	256 (0.97)	3.7	+0.35
IVb	440; (0.012)	231; (1.47) ^b	410; (0.39)	343; (1.12)	285 (0.63)	2.1	+0.65
IVa · $\text{Cr}(\text{CO})_3$	318 (0.70) ^b		565 (0.93)			25.8	-1.0
IVb · $\text{Cr}(\text{CO})_3$	317 (1.09) ^b		580 (1.01)			19.7	-0.6

^a From ref. 11. ^b In tetrahydrofuran.

spectral changes can be reversed simply by diluting the concentrated sulfuric acid solutions and the complexed alcohols recovered by extraction with ether; (b) a large variation of the molar absorptivities is observed on passing from free to mono- and bis-complexed carbinols; (c) the ^1H and ^{13}C NMR spectra of $\text{IIb} \cdot \text{Cr}(\text{CO})_3$ in fluorosulfonic acid are characteristic of a complexed cation [5].

In contrast to the diphenylmethyl ions, the ferrocenyl ions produced in 70% trifluoroacetic acid show a strong shift to longer wavelength upon complexation. The assignment of the new band to complexed ferrocenyl cations is based on the same arguments reported for the diphenylmethyl system. It is noteworthy that the tetrafluoroborate of ionized $\text{IVb} \cdot \text{Cr}(\text{CO})_3$ was recently isolated as a stable salt, and its solution in methylene chloride shows a UV spectrum practically identical to that given by the alcohol in 70% aqueous trifluoroacetic acid [12].

The $\text{p}K_{\text{R}^+}$ values for the ionization equilibria of free, mono- and bis-complexed diphenylmethanols in sulfuric acid and of free and complexed ferrocenylarylmethanols in trifluoroacetic acid at 25°C are shown in the last column of Table 1. For the complexed diphenylmethanols the $\text{p}K_{\text{R}^+}$ values were determined by the method of Deno [11]. The slopes of the plots $\log Q$ vs. J_0 were equal to unity for all compounds investigated. The quantity $d(\log Q) / d(\% \text{H}_2\text{SO}_4)$ was nearly constant in the range of acid concentrations used for the $\text{p}K_{\text{R}^+}$ measurements.

For the ferrocenylarylmethanols, trifluoroacetic acid/water mixtures were used instead of sulfuric acid/water mixtures since the ionization of the complexed alcohols take place at concentrations H_2SO_4 too low to ensure adequate solubility of the non-ionized species. For the determination of $\text{p}K_{\text{R}^+}$ we have used the H_{R} -acidity function of the trifluoroacetic acid/water system [13]. It is striking that the $\text{p}K_{\text{R}^+}$ value found for IVa in CF_3COOH (+0.35) is very close to that found for the same substrate in H_2SO_4 (+0.40 [9b]). When Deno's method was applied to the values obtained for the complexed ferrocenyl alcohols, the slopes of the plots H_{R} vs. $\log Q$ were found not to be unity. The $\text{p}K_{\text{R}^+}$ values were then calculated by using the Bunnett-Olsen equation [14], in which the H_0 function was replaced by H_{R} . Least-square analysis of the plots $\log Q + H_{\text{R}}$ vs. $H_{\text{R}} + \log c_{\text{H}^+}$ gave linear relationships with good correlation coefficients (0.98 to 0.99).

Discussion

The effect of tricarbonylchromium on the thermodynamic stability of a positive charge situated in the α -position of a side-chain strongly depends upon the structure of the carbonium ion.

We first consider the diphenylmethyl system. The introduction of the first $\text{Cr}(\text{CO})_3$ unit in the parent compound IIa causes a stabilization of the cation of 2.9 $\text{p}K_{\text{R}^+}$ units, and this agrees with the results of the solvolysis of the diphenylmethyl chlorides [2]. The stabilization is noticeably lower than that shown by benzyl cations (7.7 $\text{p}K_{\text{R}^+}$ units for the mesityl system [10]). The introduction of a second tricarbonylchromium group makes the cation even more stable, but the effect is equivalent to only 0.9 $\text{p}K_{\text{R}^+}$ units.

It may be of interest to compare the effect of a tricarbonylchromium group with that of a ferrocenyl group. The replacement of a phenyl by a ferrocenyl

group in the diphenylmethyl cation causes a stabilization of 13.65 pK_{R^+} units (see Table 1), while a second ferrocenyl group further stabilizes the ion by 4.0 pK_{R^+} units [9d]. (Contrary to the trend observed for the ferrocenylmethyl ions based on pK_{R^+} data, a calorimetric study of the heats of formation of the same ferrocenyl cations in 96% H_2SO_4 showed that in the diphenylmethyl system the replacement of a phenyl by a ferrocenyl group causes a stabilization of ca. 9 kcal/mol, but the second ferrocenyl group stabilizes the system by 22 kcal/mol [15]).

The above data clearly indicate that the cation-stabilizing ability of the tricarbonylchromium is much lower than that of the ferrocenyl group, and that in both series the second organometallic unit stabilizes the ion to a much smaller extent than the first. It is generally accepted that the mechanism of stabilization of α -positive charge by both ferrocenyl [16] and phenyltricarbonylchromium groups [5] involves direct overlapping of the filled d -orbitals of the metal with the empty p -orbital of the α -carbon. However, the $Cr(CO)_3$ group can also exert a very strong electron-withdrawing effect through the σ -skeleton of the phenyl ring [17–19]. This may account for the much lower efficiency of this organometallic entity in stabilizing positive charges.

On the basis of the preceding results one would expect that the complexation with $Cr(CO)_3$ of a ferrocenyl carbinol would cause only a further small stabilization of the corresponding cation. Actually, ferrocenyltricarbonylchromium cations are less stable than the corresponding uncomplexed carbinols, the difference being 1.35 and 1.25 pK_{R^+} units for IVa and IVb, respectively. Thus, the tricarbonylchromium group does not stabilize these ions and, on the contrary, behaves as an electron-withdrawing group. This ambivalent behaviour has been already observed in various reactions, e.g. in the bimolecular substitution of benzyl chlorides and 2-phenylethyl bromides with $NaSCN$ in acetone [20] and in ionization to give α -hydroxybenzyl cations in H_2SO_4 [10] in which some complexed cations are less stable than the free ions.

Further insight into the varying electronic effect shown by tricarbonylchromium on variation of the structure of the free cation has been obtained by studying the effect of the substituents in diphenylmethanols. Trahanovsky [10] found that for the complexed benzyl cations the plot of pK_{R^+} vs. Hammett σ gives a $\rho = -5.1 \pm 0.5$, a value much lower than that one would expect for the uncomplexed series for which a value of $\rho -10$ may be estimated [21]. Different behaviour is shown by the complexed diphenylmethyl ions; for the uncomplexed cations correlate well with σ^+ , the plot for the complexed analogs deviates markedly from linearity, as shown in Fig. 1. A poor relationship is found also with Hammett σ constants. The stabilizing effect of the $Cr(CO)_3$ group decreases rapidly with the introduction of electron-donating substituents and the same behaviour is shown by the bis-complexed substrates, too. Thus, the nature of the effect of complexation depends upon the intrinsic stability of the uncomplexed ion. We suggest a blend of electronic and conformational effects in order to account for these results.

Let us consider the conformations which the complexed cations can assume in solution. In this respect, 1H and ^{13}C NMR results on IIb- $Cr(CO)_3$ in fluorosulfonic acid are informative [5]. From the variable temperature experiments it was suggested that the most probable conformation of the ion is that in

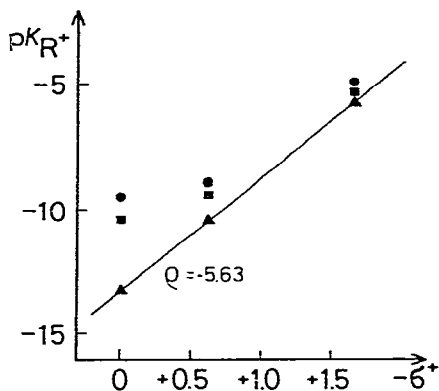


Fig. 1. Plot of pK_{R^+} of diphenylmethanols vs. σ^+ . (\blacktriangle), free ligands; (\blacksquare), mono-complexed carbinols; (\bullet), bis-complexed carbinols.

which the complexed ring lies on the same plane of the $H-C_{exo}-C(1)$ atoms ($C(1)$ being the junction carbon of the complexed ring), while the uncomplexed ring is free to rotate. A different situation exists for the uncomplexed ion, in which the aryl rings can delocalize the charge by resonance through significant contribution of structures having $C(1)-C_{exo}$ double bond character, with a greater retention of rotation. Therefore, in $[IIb \cdot Cr(CO)_3]^+$ the uncomplexed ring will contribute only to a small extent to the stabilization of the ion by resonance; the need for stabilization increases, and so the tricarbonylchromium group will contribute substantially to the delocalization of the charge, and a ΔpK_{R^+} 1.0 is observed. If we extend these considerations to the parent cation, $[IIa]^+$, which is ca. 10^3 times less stable than the $[IIb]^+$ cation, we would expect a greater stabilization by the $Cr(CO)_3$ unit. The observed value (ΔpK_{R^+} 2.9) confirms our hypothesis. On the other hand, in the uncomplexed p,p' -dimethoxydiphenylmethyl cation, $[IIc]^+$, the presence of the two substituents makes the ion 7.6 pK_{R^+} units more stable than the unsubstituted cation, $[IIa]^+$. This very large effect is attributed to the great importance of para-quinonoid-type structures in the resonance hybrid. It is very likely that in the $[IIc \cdot Cr(CO)_3]^+$ ion, in addition to the complexed ring the uncomplexed ring is also locked in the plane of the sp^2 -hybridized carbon, so that the positive charge is delocalized over the whole molecule. The need for additional stabilization is thus small, as shown by the small value of ΔpK_{R^+} , viz. 0.3 units.

In conclusion, the extent of the direct participation by the tricarbonylchromium group changes appreciably along the series of substrates; the effect of the metal competes with that of the substituents, and this accounts satisfactorily for the deviations from the Hammett $\sigma-\rho$ relationship. Different factors operate in the complexed primary benzyl cations in which conformational effects are unlikely to be mixed in with the electronic effects of substituents; thus the contribution by the chromium atom is very important and constant throughout the series; the contribution of the substituents simply adds to that of the metal, and the Hammett relationship is obeyed.

We believe that the unusual electron-withdrawing effect shown by the $Cr(CO)_3$ group in the ferrocenylarylmethyl cations $[IV]^+$ is connected with the

existence of a conformation different from that proposed for the diphenylmethyl cations. It is noteworthy that in the negatively charged complexed ketyl radical anions, $[\text{ArCOAr} \cdot \text{Cr}(\text{CO})_3]^-$, the organometallic group acts as a strong electron-withdrawing group [18,19]. An ESR study [22] of these anions suggested a conformation in which the uncomplexed ring lies preferably on the plane of the carbonyl group while the complexed ring is twisted out of this plane. A very similar conformation is probable for the ferrocenyl cations. Thus in these very stable cations the *d*-orbital overlap by the iron is so effective to exclude an analogous interaction by the chromium atom and the phenyltricarboxylchromium ring becomes free to rotate and to exert only its electron-withdrawing effect.

Experimental

Melting points are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, Padova, Italy.

IR spectra were recorded as KBr disk on a Beckman IR-9 spectrophotometer. NMR spectra were recorded on a Bruker HFX-90 and WH-90 spectrometers; chemical shifts (δ) are given in ppm taking tetramethylsilylane (TMS) as internal standard. UV spectra were recorded on a Cary-14 double beam spectrophotometer equipped with variable temperature accessories.

Commercial grade di-*n*-butyl ether, diethylglycoldimethyl ether (diglyme) and tetrahydrofuran were dried over Na/K alloy and distilled under nitrogen just before use. Benzophenone, *p,p'*-dimethoxybenzophenone, ferrocene and $\text{Cr}(\text{CO})_6$ were commercial samples. *p,p'*-Dimethylbenzophenone was prepared by a Friedel-Crafts reaction between toluene and carbon tetrachloride [23]. Phenyl- and *p*-tolyl-ferrocenyl ketones were prepared by Friedel-Crafts reaction of the appropriate benzoyl chloride with ferrocene in methylene chloride [24]. The crude products were purified by column chromatography over silica gel (ethyl ether/hexane mixtures as eluents) and finally crystallized from methanol.

The ketones were converted into the corresponding alcohols by treatment with excess NaBH_4 in methanol. Physical and spectroscopic properties were as expected.

Complexed ketones

The complexes were prepared by refluxing under nitrogen for 24–30 h (4–6 h for the ferrocenyl ketones) ca. 2 *M* solutions of the ketones in anhydrous oxygen-free di-*n*-butyl ether with a more-than-twice molar ratio of freshly sublimed $\text{Cr}(\text{CO})_6$. After cooling, the solutions were diluted with anhydrous acetone and filtered under nitrogen through a 2-inch layer of deactivated, neutral alumina. The solvents and unreacted $\text{Cr}(\text{CO})_6$ were then removed under vacuum and the residue chromatographed through a 4-foot column of silica gel. Successive elutions with hexane/ethyl ether mixtures gave first the unreacted ketones followed by the mono-complexed species, which were crystallized under nitrogen from ethyl ether/hexane. Finally, an elution with pure ethyl ether gave, in the case of benzophenones, small amounts of bis-complexed compounds, which were also crystallized from ethyl ether/hexane. Yields, physical

TABLE 2
¹H NMR CHEMICAL SHIFTS (δ, ppm) OF ALCOHOLS COMPLEXES WITH Cr(CO)₃

Compound	Uncomplexed ring resonances				Complexed ring resonances				C—H methine	O—H
	H _O	H _β	H _γ	H _δ	H _O	H _β	H _γ	H _δ		
IIa · Cr(CO) ₃ ^a	7.27	7.14	—	—	5.44	5.22	—	—	5.63	2.50
IIb · Cr(CO) ₃ ^a	—	—	—	2.32	5.30	5.03	—	2.12	5.32	2.47
IIc · Cr(CO) ₃ ^a	7.30	6.87	—	3.79	5.69	5.11	—	—	—	—
IIa · Cr ₂ (CO) ₆ ^b	—	—	—	—	5.21	4.97	—	—	5.31	2.25
IIb · Cr ₂ (CO) ₆ ^b	—	—	—	—	5.46	5.06	—	—	—	—
IIc · Cr ₂ (CO) ₆ ^b	—	—	—	—	5.90	5.29	—	—	5.24	2.48
					5.68	5.16	—	2.18	5.01	2.46
					5.51	5.08	—	—	—	—
					5.64	5.05	—	—	4.86	2.33
								3.70		
Ferrocene ring resonances ^c										
	H _α	H _β	H _γ							
IVa · Cr(CO) ₃ ^d	—	—	—	—	—	—	—	—	—	—
IVb · Cr(CO) ₃ ^b	4.16–4.48	—	4.23	—	5.88	5.52	2.17	—	5.20	2.52
					5.69	5.37				

^a For CDCl₃ solutions with Me₄Si as internal reference. ^b For CD₃COCD₃ solutions with Me₄Si as internal reference. ^c H_α and H_β refers to the substituted cyclopentadienyl ring, H_γ to the unsubstituted cyclopentadienyl ring protons. ^d No spectra could be recorded (see Results).

and spectroscopic characteristics of these complexes are given below.

Benzophenone-Cr(CO)₃ [2]. Red crystals. Yield, 20%; m.p. 86–87° C. IR: $\nu(\text{C}\equiv\text{O})$ 1906, 1925, 1977 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1663 cm^{-1} . NMR data agree with literature reports [25].

Benzophenone-Cr₂(CO)₆ [26]. Dark red crystals. Yield, 1.3%; m.p. 165° C (dec.). IR: $\nu(\text{C}\equiv\text{O})$ 1884, 1890, 1960, 1981 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1661 cm^{-1} . NMR (CD_3COCD_3): δ 6.34 (d, 4H, J 6.6 Hz, *ortho*-protons), 6.01 (t, 2H, J 6.5 Hz, *para*-proton), 5.74 ppm (t, 4H, J 6.5 Hz, *meta*-protons).

p,p'-Dimethylbenzophenone-Cr(CO)₃ [5]. Orange crystals. Yield, 29%. IR: $\nu(\text{C}\equiv\text{O})$ 1901, 1913, 1962, 1983 cm^{-1} ; $\nu(\text{C}=\text{O})$: 1658 cm^{-1} . NMR (CDCl_3): (a) uncomplexed ring: δ 7.69 (d, 2H, J = 7.8 Hz; *ortho*-protons), 7.22 (d, 2H, J 7.8 Hz, *meta*-protons), 2.43 (s, 3H, *p*-methyl protons); (b) complexed ring: 6.05 (d, 2H, J 7 Hz, *ortho*-protons), 5.11 (d, 2H, J 7 Hz, *meta*-protons), 2.31 ppm (s, 3H, *p*-methyl protons).

p,p'-Dimethylbenzophenone-Cr₂(CO)₆ (nc). Red crystals. Yield, 1%. M.p. 161–162° C. Found: C, 50.89; H, 3.09; $\text{C}_{21}\text{H}_{14}\text{Cr}_2\text{O}_7$ calcd.: C, 52.29; H, 2.90%. IR: $\nu(\text{C}\equiv\text{O})$ 1885, 1893, 1925, 1961, 1972 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1647 cm^{-1} . NMR (CD_3COCD_3): δ 6.13 (d, 4H, J 7.1 Hz, *ortho* protons), 5.16 (d, 4H, J 7.1 Hz, *meta* protons), 2.29 ppm (s, 6H, *p*-methyl protons).

p,p'-Dimethoxybenzophenone-Cr(CO)₃ (nc). Orange crystals. Yield, 26%. M.P. 135–135.5° C. Found: C, 56.65; H, 3.90. $\text{C}_{18}\text{H}_{14}\text{CrO}_6$ calcd.: C, 57.28; H, 3.73%. IR: $\nu(\text{C}\equiv\text{O})$ 1892, 1910, 1968 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1656 cm^{-1} . NMR (CDCl_3): (a) uncomplexed ring: δ 7.79 (d, 2H, J 9 Hz, *ortho*-protons), 6.96 (d, 2H, J 9 Hz, *meta*-protons) 3.86 (s, 3H, *p*-methoxy protons); (b) complexed ring: 6.18 (d, 2H, J 7 Hz, *ortho*-protons), 5.16 (d, 2H, J 7 Hz, *meta*-protons), 3.74 ppm (s, 3H, *p*-methoxy protons).

p,p'-Dimethoxybenzophenone-Cr₂(CO)₆ (nc). Red crystals. Yield, 1.1%, M.p. 172.5–173.5° C. Found: C, 49.43; H, 3.00; $\text{C}_{21}\text{H}_{14}\text{CrO}_6$ calcd.: C, 49.03; H, 2.74%. IR: $\nu(\text{C}=\text{O})$ 1885, 1908, 1961, 1985 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1641 cm^{-1} . NMR (CD_3COCD_3): δ 6.46 (d, 4H, J 7 Hz, *ortho*-protons), 5.54 (d, 4H, J 7 Hz, *meta*-protons), 3.85 ppm (s, 6H, *p*-methoxy protons).

Ferrocenylphenyl ketone-Cr(CO)₃ [27]. Red crystals. Yield, 50%. M.p. 165° C (dec.). Found: C, 56.41; H, 3.59. $\text{C}_{20}\text{H}_{14}\text{CrFeO}_4$ calcd.: C, 56.36; H, 3.31%. IR: $\nu(\text{C}\equiv\text{O})$ 1875, 1896, 1902, 1967, 1980 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1633 cm^{-1} . NMR (CDCl_3): δ 6.21 (d, 2H, J 7.1 Hz, *ortho*-protons), 5.61 (t, 1H; J 7.2 Hz, *para*-proton), 5.30 (t, 2H, J 7.1 Hz, *meta*-protons), 4.95 (m, 2H, H_α -protons *), 4.60 (m, 2H, H_β -protons), 4.30 ppm (s, 5H, H_γ -protons).

Ferrocenyl-p-tolyl ketone-Cr(CO)₃ (nc). Red-orange crystals. Yield, 55%. M.p. 164° C (dec.). Found: C, 57.06; H, 3.78; $\text{C}_{21}\text{H}_{16}\text{CrFeO}$ calcd.: C, 57.30; H, 3.66%. IR: $\nu(\text{C}\equiv\text{O})$ 1874, 1880, 1893, 1902, 1975, 1982 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1625 cm^{-1} . NMR (CDCl_3): δ 6.46 (d, 2H, J 6.8 Hz, *ortho*-protons), 5.53 (d, 2H, J 6.8 Hz, *meta*-protons), 4.95 (m, 2H, H_α -protons *), 4.64 (m, 2H, H_β -protons), 4.31 (s, 5H, H_γ -protons), 2.26 ppm (s, 3H, *p*-methyl protons).

Reduction of the ketones to alcohols

The complexed benzophenones were reduced to the corresponding second-

* See footnote c in Table 2.

ary alcohols by treatment at room temperature under nitrogen with excess NaBH_4 in anhydrous methanol [2]. For the complexed ferrocenyl ketones, the reduction was carried out in a 1/1 mixture of methanol and peroxyde-free tetrahydrofuran. Yields, physical characteristics and IR data of the alcohols are given below. NMR data are reported in Table 2.

Diphenylmethanol-Cr(CO)₃ [2]. Yellow crystals. Yield 87%. M.p. 99–100° C. IR: $\nu(\text{O-H})$: 3577 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1851, 1870, 1892, 1907, 1966. 1984 cm^{-1} .

Diphenylmethanol-Cr₂(CO)₆ [26]. Yellow crystals. Yield, 50%. M.p. 148–149° C. IR: $\nu(\text{O-H})$ 3510 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1971, 1960, 1895, 1870, 1855 cm^{-1} .

p,p'-Dimethyldiphenylmethanol-*Cr(CO)₃*. Yield 70%. Analytical and spectroscopic data have been reported previously [5].

p,p'-Dimethyldiphenylmethanol-*Cr₂(CO)₆* (nc). Yellow crystals. Yield, 50%. M.p. 135° C. Found: C, 51.71; H, 2.90. $\text{C}_{21}\text{H}_{16}\text{Cr}_2\text{O}_7$ calcd.: C 52.03; H, 3.30%. IR: $\nu(\text{O-H})$ 3560 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1885, 1900, 1960, 1981 cm^{-1} .

p,p'-Dimethoxydiphenylmethanol-*Cr(CO)₃* (nc). Yellow crystals. Yield 84%. M.p. 88.5–89° C. Found: C, 58.24; H, 4.95; $\text{C}_{18}\text{H}_{16}\text{CrO}_6$ calcd.: C, 56.30; H, 4.24%. IR: $\nu(\text{O-H})$ 3512 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1853, 1864, 1875, 1954 cm^{-1} .

p,p'-Dimethoxydiphenylmethanol-*Cr₂(CO)₆* (nc). Yellow crystals. Yield, 74%. M.p. 139–139.5° C. Found: C, 49.5; H, 2.89. $\text{C}_{21}\text{H}_{16}\text{Cr}_2\text{O}_9$ calcd.: C, 48.8; H, 3.09%. IR: $\nu(\text{O-H})$ 3560 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1885, 1900, 1960, 1981 cm^{-1} .

Ferrocenylphenylmethanol-Cr(CO)₃ [27]. Golden-yellow crystals. Yield, 80%. M.p. 160° C(dec.). IR: $\nu(\text{OH})$ 3570 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1875, 1962, 1980 cm^{-1} . NMR spectrum could not be recorded owing to the high instability of this compound in the solvents generally used for spectroscopy.

Ferrocenyl-p-methyl-phenylmethanol-Cr(CO)₃ (nc). Golden-yellow crystals. Yield, 92%. M.p. 136–138° C. Found: C, 57.12; H, 4.28. $\text{C}_{21}\text{H}_{18}\text{CrFeO}_4$ calcd.: C, 57.03; H, 4.10%. IR: $\nu(\text{O-H})$ 3538 cm^{-1} ; $\nu(\text{C}\equiv\text{O})$ 1869, 1878, 1957 cm^{-1} .

Formation of the ions

The H_2SO_4 solutions of the complexed diphenylmethanols, prepared by adding small aliquots (0.1 ml usually) of freshly prepared stock solutions in oxygen-free methanol or diglyme, were highly unstable and the absorbance attributed to the cation must be extrapolated to zero time.

To obtain reproducible data (no more than $\pm 5\%$ deviation in almost three entries for each acid concentration), the following experimental conditions must be observed: (a) the acid medium must be thoroughly purged with nitrogen before the use; (b) the heat of formation of the ions must be dispersed by means of a thermostatted jacket while the solution is efficiently stirred; (c) no more than 10^{-5} molar concentration of the ions are required to satisfy the Lambert-Beer law.

The decay of the absorbance of the cations follows first-order kinetics contrary to the benzyltricarboxylchromium cations which decompose by a higher than first-order process [10]. The first-order rate constants calculated (k , sec^{-1}) for the mono-complexed series in 96% sulfuric acid are the following: parent, 1.5×10^{-3} ; *p*-methyl, 8×10^{-4} ; *p*-methoxy, 1.6×10^{-4} ; thus, the reactivity of these ions is correlated with their thermodynamic stability, the less stable ion being the most

reactive. Similar behaviour was found in the bis-complexed cations, which are less reactive than the corresponding mono-complexed analogs.

The solutions of the ferrocenyl alcohols, free and complexed, in trifluoroacetic acid/water mixtures were sufficiently stable to record reproducible UV spectra and no zero-time extrapolation was necessary.

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