Electron Spin Resonance Studies of Some Aromatic Ketyls complexed with the Tricarbonylchromium Group

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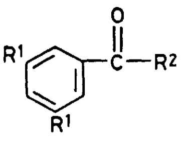
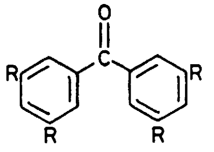
The e.s.r. spectra of some pivalophenone and benzophenone ketyl radicals complexed with the $Cr(CO)_3$ group have been obtained and compared with those of the uncomplexed compounds. The strong decrease of the hyperfine coupling constants of the complexed ring protons is explained in terms of substantial modification of the σ- rather than the π-electron density introduced by the inorganic system. For benzophenone ketyls a model is suggested in which the complexed ring is twisted out of the plane of the carbonyl and the uncomplexed ring. The variation of the coupling constants of the uncomplexed phenyl is explained in terms of the strong electron-withdrawing effect of the $Cr(CO)_3$ group.

SINCE the work of Dessy and his co-workers [1] there have been few papers on the electrochemical reduction of π-arenetricarbonylchromium complexes in non-aqueous media. Benzene derivatives are reduced irreversibly by a two-electron process with rapid follow up chemical kinetics in acetonitrile; on the other hand, the naphthalene system is reduced pseudo-reversibly to form a stable dianion species.[2] The presence of a keto carbonyl group in the ligand changes the reduction from a two-electron irreversible process to a one-electron reversible one.[3,4] However, spectroscopic observation of the complexed radical anion was not possible for acetophenonetricarbonylchromium in acetonitrile, tetrahydrofuran, and dimethyl sulphoxide.[2] In contrast pivalophenone, benzophenone, and fluorenone complexes gave the corresponding ketyl radicals with sufficiently long half-lives when they were reduced in dimethylformamide.[4] In a previous communication [5] we reported that tricarbonylpivalophenonechromium ketyl radical can also be produced chemically by reduction with lithium, sodium, and potassium in dimethoxyethane. Simple, resolved spectra obtained with potassium as reducing agent allowed the hyperfine splitting constants and the isotropic g factor of the $K^+[\text{pivalophenone}\cdot Cr(CO)_3]^{-\cdot}$ ion pair to be measured.



(I)



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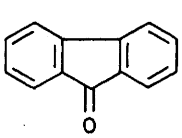

(III)

a; $R^1 = H$ $R^2 = Bu^t$ a; $R = H$
b; $R^1 = R^2 = Bu^t$ b; $R = Bu^t$
c; $R^1 = H$, $R^2 = [^2H_9]\ Bu^t$

In the present paper we report the e.s.r. results of some substituted and deuteriated pivalophenone-, benzophenone-, and fluorenone-tricarbonylchromium complexes: they are also compared with those of the analogous uncomplexed ketones. The spin density distribution and the stereochemistry in solution of these organometallic radicals gives a better understanding of the electronic properties and the mechanism of electron distribution in π-arene complexes. Recent papers on ferrocene [6] and tricarbonylmanganese [7] ketyl complexes have examined the distribution of the spin density in these organometallic substrates.

The deuteriation of the molecules and the substitution of the hydrogen in the *meta*-positions by t-butyl groups greatly simplify the spectra, thus allowing their complete analyses and the assignment of the splittings to the different positions. This would be practically impossible for the unsubstituted compounds.

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[1] R. E. Dessy, F. E. Stary, R. B. King, and H. Waldrop, *J. Amer. Chem. Soc.*, 1966, **88**, 471.

[2] R. D. Rieke, J. S. Arney, W. E. Rich, B. R. Willeford, jun., and B. S. Poliner, *J. Amer. Chem. Soc.*, 1975, **97**, 5951.

[3] V. S. Khandkarova and S. P. Gubin, *J. Organometallic Chem.*, 1970, **22**, 149; S. P. Gubin, *Pure Appl. Chem.*, 1970, **23**, 463.

[4] A. Ceccon, A. M. Romanin, and A. Venzo, *Transition Metal Chem.*, 1975—1976, **1**, 25.

[5] A. Ceccon, C. Corvaja, G. Giacometti, and A. Venzo, *J. Chim. Phys.*, 1975, **72**, 23.

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EXPERIMENTAL

General.—M.p.s are uncorrected. Microanalyses were carried out by Mr. L. Turiaco, Istituto di Chimica Analitica, Università di Padova. I.r. and ^1H n.m.r. analyses were performed using Beckman IR-9 and Bruker HFX-90 spectrometers.

Commercial grade benzophenone (IIa) and fluorenone (III) were carefully crystallized from ethanol before use.

Phenyl t-Butyl Ketone (Ia).—Phenyl t-butyl ketone was prepared according to the procedure of Pearson [8] from phenylmagnesium bromide and t-butyl cyanide, b.p. 97—98° at 16 mmHg.

3,5-*Di-t-butylphenyl t-Butyl Ketone* (Ib).—3,5-Di-t-butylbromobenzene (12 g, 45 mmol), obtained from the 1,3,5-tri-t-butylbenzene following the directions of Bartlett, Roha, and Stiles,[9] was converted into the Grignard reagent with excess of magnesium in diethyl ether under nitrogen. An ethereal solution of t-butyl cyanide (5.35 g, 64 mmol) was then added with stirring and gentle reflux was maintained for 3 h. After acidic hydrolysis and the usual work-up, distillation of the organic residue gave a *fraction* which boiled at 118—122° and 0.5 mmHg and solidified on cooling, yield 2.2 g (18%), m.p. 32°; $\nu_{max.}$ (neat) 3 070, 2 960, 2 945, and 2 850 (C–H) and 1 675 cm^{-1} (C=O); δ 7.54 (3 H, s, ArH), 1.36 (9 H, s, α-Bu^t), 1.32 (18 H, s, other Bu^t) (Found: C, 82.0; H, 12.0. $C_{19}H_{30}O$ requires C, 83.15; H, 11.1%).

Phenyl $[^2H_9]$*t-Butyl Ketone* (Ic).—Deuteriated pivalophenone was synthesized from phenylmagnesium bromide and $[^2H_9]$t-butyl cyanide and it had the same physical characteristics as (Ia). The synthesis of the deuteriated nitrile was achieved by the reaction sequence described herein.

$[^2H_{12}]$Pinacol hexahydrate was obtained from $[^2H_6]$-acetone (99.5 atom %D), magnesium, and mercury(II) chloride, m.p. 41—42°.[10] The compound was then reacted [10] with 25% D_2SO_4 in D_2O to give $[^2H_{12}]$pinacolone in 63% yield, b.p. 105—106°. $[^2H_{12}]$Pinacolone was converted by the halogenoform reaction into $[^2H_9]$pivalic acid which in turn gave the corresponding $[^2H_9]$amide. The amide was purified by sublimation and had m.p. 154—156° Finally, the amide was converted into the $[^2H_9]$t-butyl cyanide with phosphorus pentaoxide.

All the intermediates and ketone (Ic) have physical and spectroscopic characteristics in accord with their structures. The extent of deuteriation of (Ic) determined by n.m.r. was >99 atom %D.

3,3′,5,5′-*Tetra-t-butylbenzophenone* (IIb).—3,5-Di-t-butylbromobenzene [9] (12 g, 45 mmol) and 3,5-di-t-butylbenzaldehyde [11] (8.2 g, 38 mmol) were dissolved in anhydrous tetrahydrofuran (40 ml). The solution was allowed to react with excess of lithium following the procedure of Pearce.[12] The crude bis-(3,5-t-butylphenyl)methanol, $\nu_{max.}$ 3 560 cm^{-1} (O–H), was directly oxidized to the corresponding benzophenone with chromium trioxide in glacial acetic acid at room temperature. The mixture was then poured into ice–water and extracted with ether. Removal of ether gave a semi-solid residue which was purified by chromatography on silica gel (hexane–ethyl ether 4 : 1 as eluant). Crystallization from 85% aqueous ethanol and sublimation of the recrystallized product at 10^{-4} mmHg gave *crystals* (1.34 g), m.p. 118—119°; $\nu_{max.}$(KBr) 3 034, 2 945, 2 894, and 2 859 (C–H) and 1 668 cm^{-1} (C=O); δ 7.67 (6 H, s, ArH) and 1.36 (36 H, s, Bu^t) (Found: C, 85.0; H, 10.85. $C_{29}H_{32}O$ requires C, 85.65; H, 10.4%).

Complexed Ketones.—The tricarbonylchromium complexes of (Ia),[5] (IIa),[13] and (III) [4] were synthesized by literature methods. New complexes were prepared by refluxing *ca.* 2M solutions of the free ketone in anhydrous, oxygen free di-n-butyl ether with 2 mol. equiv. of freshly sublimed $Cr(CO)_6$ under nitrogen for 6—8 h. After removal of the solvent and the excess of $Cr(CO)_6$ the complexes were purified by column chromatography on silica gel (hexane–ethyl ether as eluant) and finally carefully crystallized from ethyl ether–hexane.

Tricarbonyl$[^2H_9]$*pivalophenonechromium* gave red-orange crystals (20%); m.p. 64°; $\nu_{max.}$(KBr) 608, 621, and 651 (C–Cr), 1 675 (C=O), 1 865, 1 905, and 1 965 (C≡O), and 2 230 cm^{-1} (C–^{2}H); δ 6.12 (2 H, d, *J* 6.3 Hz, *o*-H), 5.58 (1 H, tt, *J* 6.3 and 1.2 Hz, *p*-H), and 5.25 (2 H, tt, *J* 6.3 and 1.2 Hz, *m*-H). No signal appeared in the t-butyl proton resonance region as expected. The extent of deuteriation was >99 atom %D at least.

Tricarbonyl(3′,5′-*di-t-butylpivalophenone*)*chromium* gave orange crystals (10%); m.p. 95—97°; $\nu_{max.}$(KBr) 619 and 657 (C–Cr), 1 670 (C=O), and 1 885, 1 950, and 1 960 cm^{-1} (C≡O); δ 1.33 (9 H, s, α-Bu^t), 1.41 (18 H, s, other Bu^t), 5.94 (1 H, t, *J* 1.2 Hz, *p*-H), 6.39 (2 H, d, *J* 1.2 Hz, *o*-H) (Found: C, 64.45; H, 10.8. $C_{22}H_{30}CrO_4$ requires C, 64.6; H, 10.4%).

Tricarbonyl(3,3′,5,5′-*tetra-t-butylbenzophenone*)*chromium* gave orange hygroscopic crystals (10%); m.p. 134—136° (decomp.); $\nu_{max.}$ 618 and 622 (C–Cr), 1 649 and 1 663 cm^{-1} (C=O), 1 874, 1 888, 1 902, 1 908, and 1 965 cm^{-1} (C≡O); δ 7.67 (3 H, m, uncomplexed ring H), 6.40 (3 H, m, complexed ring H), and 1.40 and 1.38 (36 H, 2 × s, Bu^t) (Found: C, 70.9; H, 8.0. $C_{32}H_{42}CrO_4$ requires C, 70.8; H 7.8%).

Preparation of Anions.—The radical anions were produced by reacting *in vacuo* a *ca.* 10^{-3} solution of the ketone with a metal mirror or with small pieces of lithium. With the complexed ketones the reaction was carried out at low temperature (*ca.* −70°). Standard vacuum techniques were used. The solvents, dimethoxymethane (DME) and tetrahydrofuran (THF), were distilled over calcium hydride and stored under vacuum over potassium anthracenide.

The e.s.r. spectra were recorded with a JEOL JES-PE-3X spectrometer equipped with variable temperature accessories. Field calibrations were performed with a Harvey–Wells G 202 gaussmeter whose frequency was measured by a Hewlett–Packard HP 4245 L frequency counter. The isotropic *g* factors were measured by reference to the signal of an aqueous solution of Fremy's salt (*g* 2.005 66).[14]

RESULTS

The uncomplexed ketones reduced by the alkali metals in ether give the expected e.s.r. spectra of the corresponding alkali-metal ketyl ion pairs.[15] The coupling constants

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[8] D. E. Pearson, *J. Amer. Chem. Soc.*, 1950, **72**, 4169.

[9] P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Amer. Chem. Soc.*, 1954, **76**, 2349.

[10] H. Gilman, *Org. Synth.*, 1948, Vol. I, 462.

[11] W. M. Schubert and R. G. Minton, *J. Amer. Chem. Soc.*, 1960, **82**, 6188.

[12] P. J. Pearce, D. H. Richards, and N. F. Scilly, *J.C.S. Perkin I*, 1972, 1655.

[13] J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometallic Chem.* 1965, **4**, 324.

[14] M. Brustolon, C. Corvaja, and L. Pasimeni, *J.C.S. Faraday II*, 1972, 2150.

[15] N. Hirota in ' Radical Ions ', eds. T. Kaiser and L. Kewan, Interscience, New York, 1968.

and the linewidths, obtained by computer simulation, are given in Tables 1, 2, and 3 together with those of the corresponding co-ordinated compounds. In the uncomplexed pivalophenones (Ia—c) the hyperfine coupling for the two *ortho*-protons is different indicating restricted rotation of the phenyl group around the C_{ketyl}–C_{ring} bond. The spectrum of the deuteriated compound (Ic) was simulated with equal *ortho*-coupling constants; probably here the difference is hidden in the larger linewidth. The phenyl ring rotation in the ketyl of the substituted benzophenone (IIb) shows an interesting dependence on the counter ion which will be discussed in a separate paper.

TABLE 1

E.s.r. parameters [a] for the pivalophenone ketyls, free and complexed with $Cr(CO)_3$

Compound	Solvent	Counterion	Ring coupling constant a_2	a_3	a_4	a_5	a_6	$a_H(Bu^t)$	$a_{^{13}C}(C{=}O)$	$a_{^{13}C}(Bu^t)$	Linewidth	$\langle g \rangle$
(Ia)	DME	K [b]	3.92	1.03	6.55	0.72	3.62	0.325			0.10	2.003 7
(Ia)·$Cr(CO)_3$	DME	K [b]	1.78		2.36		1.49	0.287			0.23	1.999 8
(Ib)	DME	K	4.09		5.98		3.78	0.307	9.34	4.14	0.17	
(Ib)·$Cr(CO)_3$	DME	K	1.78		2.36		1.49	0.287			0.20	
(Ic)	DME	K	4.03	1.02	6.51	1.02	4.03		9.3	4.1	0.70	
(Ic)·$Cr(CO)_3$	DME	K	1.76		2.50		1.76				0.50	
	DME	Li	2.00		2.00		2.00			2.9		

[a] Coupling constants and linewidths in gauss. [b] These values differ from those previously [5] published. A more careful examination of the spectrum showed a different hyperfine coupling for the *meta*- and *ortho*-protons.

TABLE 2

E.s.r. parameters [a] for 3,3′,5,5′-tetra-t-butylbenzophenone ketyl, free and complexed with $Cr(CO)_3$

Compound	Solvent	Counterion	Ring coupling constant a_2	a_4	a_6	a_2'	a_4'	a_6'	$\langle g \rangle$	Linewidth
(IIb)	DME	K^+	2.56	3.38	2.56	2.56	3.38	2.56	2.004 0	0.10
			Uncomplexed ring			Complexed ring				
(IIb)·$Cr(CO)_3$	THF	$Bu^n_4N^+$ [b]	2.01	3.33	2.01	1.34	<0.1	1.34		
	THF	Na^+	1.87	4.01	1.87	1.65	<0.1	1.65		
	THF	K^+	1.90	3.76	1.90	1.61	<0.1	1.61	2.000 6	0.14

[a] Coupling constants and linewidths in gauss. [b] Prepared by addition of a large excess of tetra-n-butylammonium perchlorate to the sodium ketyl ion pair solution.

TABLE 3

E.s.r. parameters [a] for fluorenone ketyl, free and complexed with $Cr(CO)_3$

Compound	Solvent	Counterion	Ring coupling constant a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	Linewidth	$\langle g \rangle$
(III)	DME	K^+	2.03	0.10	3.15	0.66	0.66	3.15	0.10	2.03	0.10	2.003 9
			Complexed ring				Uncomplexed ring					
(III)·$Cr(CO)_3$	DME	K^+	1.02		1.35	0.26	0.57	2.72		1.90	0.20	2.002 1

[a] Coupling constants and linewidths in gauss.

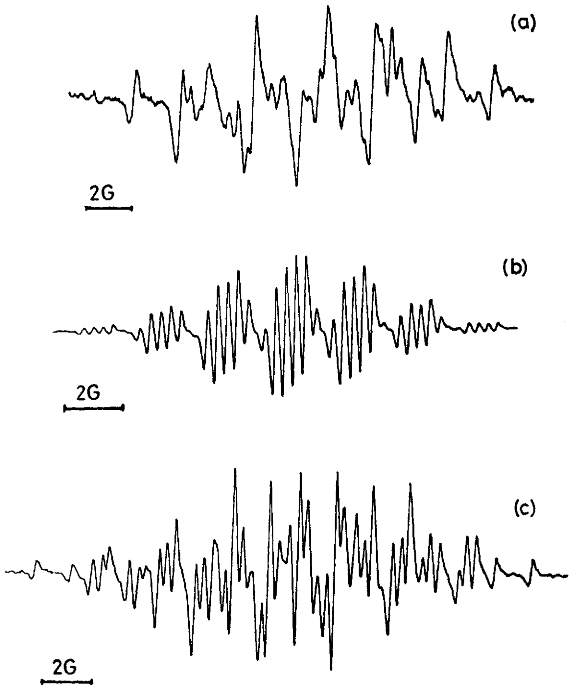
Solutions of complexed pivalophenone, benzophenone, and fluorenone are light orange, red-orange, and dark purple, respectively. When they react with metals a marked darkening occurs and quite strong e.s.r. signals consisting of a complicated hyperfine structure appear. Linewidths of *ca.* 200 mG are usually observed. All the spectra except those of benzophenonetricarbonylchromium could be computer simulated with the sets of hyperfine coupling constants shown in Tables 1, 2, and 3. The assignment of the splittings to the protons in the different positions in the molecule is discussed later.

The e.s.r. spectra change according to the alkali-metal used for reduction because of the hyperfine interaction with the metal, which indicates that the $Cr(CO)_3$-complexed ketyls are present in ether as ion pairs. Changes in the proton coupling constants are also observed by changing the counter ion. The signal intensity decreases remarkably at low temperature probably because of the formation of ion clusters [15] and this prevents a detailed examination of the temperature dependence of the spectra. Prolonged contact with the metal causes decomposition of the complexed ketyls and signals of the corresponding ketyl ligands appear. Further reduction of the solutions of the complexed pivalophenones (Ia and c) gives the spectrum of the radical anion of the biphenyl, while in the case of the complex of (IIb), a very complex, uninterpreted e.s.r. spectrum is produced. No detailed study has been made in order to elucidate these phenomena.

Typical spectra are shown in the Figure.

DISCUSSION

Pivalophenone Ketyls.—Table 1 shows that the ring proton splitting constant *a* of pivalophenone anions are decreased when the ring is bonded to the $Cr(CO)_3$ group. In a preliminary communication [5] we suggested two possible explanations: (a) a distortion of the molecule with the ring twisted out of the plane of the carbonyl group; (b) a distortion of the ring skeleton with new hybridization changing the σ–π interaction parameter through which the proton spin density occurs. Delocalization of the spin density on the $Cr(CO)_3$ group was ruled out [5] by the fact that the g factor of the complexed radical, although lower than that of the uncomplexed one, is distinctly higher than those of chromium complexes with a singly occupied orbital of mainly $3d_{z^2}$ character.[16] Moreover, in the case of substantial delocalization of the unpaired electron in the $Cr(CO)_3$ group we expect a ^{53}Cr splitting which was not observed. If mechanism (a) were operative, delocalization of the unpaired electron in the ring through the σ bonds would occur causing an increase of the *meta*-proton splitting constants relative to those of the *ortho*- and *para*-protons.[17] The observation that the spectra of the complexes of (Ia and b) are practically identical indicates that the protons responsible for the splitting of the e.s.r. lines are the *ortho*- and not the *meta*-ones, the latter having a vanishingly small coupling. Thus, as in the pivalophenone ligand, the complexed phenyl ring lies in the plane of the ketyl group or is little twisted out of this plane and the first possibility is ruled out.



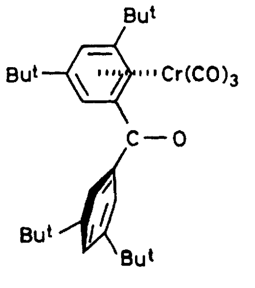
E.s.r. spectra of the tricarbonyl(3,3′,5,5′-tetra-t-butylbenzophenone)chromium ketyl radical in THF: (a) counter ion $Bu^n_4N^+$; (b) K^+; (c) Na^+

With the phenyl ring in the same plane of the keto-group, decreased delocalization of the unpaired electron from the carbonyl into the phenyl group could be the cause of the low hyperfine coupling. A test would be the ^{13}C splitting of the C=O group which in this case should be markedly greater than normal. Unfortunately we did not succeed to detect these ^{13}C satellites even in the complexed radical from (Ic), and the only ^{13}C satellites observed in the spectra of the complexed ketones are due to ^{13}C nuclei of the methyls of the t-butyl group. However, from this splitting we have an indication of the spin density on the carbonyl carbon by using the well known relationship $a_c = B\rho^{\pi}\langle\cos^2\theta\rangle$.[18] Because of the free rotation of the methyls of the t-butyl group, the angular term $\langle\cos^2\theta\rangle$ is averaged to 0.5. Even if the constant B changes with the energy of the molecular orbital occupied by the unpaired electron,[19] the variation is not expected to be large on passing from (Ia) to the complex. What we observe is a decrease of $a_{^{13}C}{}^{Bu^t}$ on complexation which is opposed to decreased delocalization into the phenyl group, unless one invokes an unreasonable unbalance of spin density between carbon and oxygen within the carbonyl group.

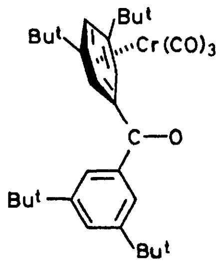
Therefore we conclude that the low values of the ring proton hyperfine couplings can be ascribed to a variation of the $Q_{H\alpha}{}^{CH}$ value which relates the spin density on the carbon π orbital to the proton splitting.[20] This assumption implies a modification of the σ bond skeleton caused by the $Cr(CO)_3$ group.

Benzophenone Ketyls.—The e.s.r. spectrum of the complex of (IIb) shows splittings by two sets of two equivalent (*ortho*) protons and only one splitting by a single (*para*) proton (see Table 2). The measured line-width is 140 mG and this implies that the remaining proton has a coupling constant lower than 100 mG.

As an explanation we suggest a model for the radical anion with one ring out of the plane of the carbonyl group. It is known that in free radicals with twisted phenyl rings the *para*-protons have a very small hyperfine coupling constant.[18] Furthermore, between the two possibilities A and B we indicate B as the more probable on the basis of the following arguments.



A



B

For A the twisted uncomplexed ring cannot exercise its effect of delocalizing the spin density by resonance; therefore, we expect for A an unpaired electron distribution similar to that of the complex of (Ib), the difference being due only to the $-I$ inductive effect of a

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[16] C. Elschenbroich, M. Cais, and F. Stohler, *J. Amer. Chem. Soc.*, 1973, **95**, 6956 and references therein.

[17] K. Schreiner and U. A. Berndt, *Angew. Chem.*, 1974, **86**, 131.

[18] L. Brière, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.

[19] M. Brustolon, C. Corvaja, and G. Giacometti, *Theor. Chim. Acta*, 1971, **22**, 90.

[20] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 632.

phenyl ring with respect to the $+I$ effect of a t-butyl group.

The trend of *ortho*- and *para*-splitting constants on varying X in a series of ketyls C_6H_5–CO–X is shown in Table 4. The *ortho*- and especially the *para*-constants decrease as the electron-attracting power of X increases. With the likely hypothesis that this trend is not altered when the phenyl ring is co-ordinated with $Cr(CO)_3$,* the *para*- and *ortho*-proton constants for the complex of (IIb) should be smaller than the corresponding values for that of (Ib) in the case of structure A. In fact, they are both substantially larger, the *para*-constant for example changing from 2.36 to 3.76 G on passing from $[(Ib)\cdot Cr(CO)_3]^{-\cdot}K^+$ to $[(IIb)\cdot Cr(CO)_3]^{-\cdot}K^+$. This is opposite to the trend shown in Table 4 and makes structure A the less probable.

TABLE 4

Hyperfine coupling constants for C_6H_5–CO–X radical anions

X	α_H^p	α_H^o	$\alpha_H^{o'}$	Ref.
OCH_3	7.64	4.2	4.2	*a*
Bu^t	6.55	3.92	3.62	*b*
CH_3	6.60	4.25	3.71	*c*
CF_3	4.8	3.9	3.3	*d*
$ArCr(CO)_3$	3.33	2.01	2.01	*b*

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Structure B, where the complexed ring is not in the plane of the carbonyl and the uncomplexed phenyl groups, makes the system very suitable for comparison with the ketyls of Table 4. The values of the splitting constants for the *para*- and *ortho*-protons of uncomplexed ring of $(IIb)\cdot Cr(CO)_3$ are very low compared with those of other ketyls and this indicates the exceptionally high electron-withdrawing effect of an arene-$Cr(CO)_3$ group, even greater than that of the trifluoromethyl group. This effect has been studied by several workers [22] for different types of reactions in order to elucidate the mechanism through which it operates. Recent kinetic evidence,[23] for example, has established that, in the stabilization of a negative charge, extra stabilization by resonance is absent when $Cr(CO)_3$ is involved; the strong electron-withdrawing effect was shown to be mostly inductive in nature and its transmission occurs through the ring skeleton mainly involving the σ-framework rather than the π-electron cloud. In a structure like B the twisted arene$Cr(CO)_3$ group can exert its effect only through the σ-skeleton.

Thus, the results agree with the conclusions based on kinetica data concerning the mechanism of stabilization of a negative charge in these complexes. Finally we assign the coupling constant 2.01 G to the *ortho*-protons of the uncomplexed ring and that of 1.34 G to those of the uncomplexed one ($Bu^n{}_4N^+$ counter ion) because a coupling of 1.34 G for the uncomplexed ring protons would be too low compared with the values for other substrates shown in Table 4. At low temperature the central line of the triplet with the large coupling is broader than the external ones. If our assignment is correct, this implies restricted rotation around the uncomplexed ring–carbonyl bond. In contrast, the lines attributed to the hyperfine interaction of the *ortho*-protons of the complexed ring are not broadened in the same temperature range showing that the complexed ring–carbonyl bond does not possess double bond character and free rotation occurs. In this respect it is worth noting that quite a different situation arises when an exocyclic carbon situated between an uncomplexed and a complexed ring has a positive instead of a negative charge. On the basis of n.m.r. data we have shown [24] that the tricarbonylbis-*p*-tolylmethylchromium carbenium ion prefers the conformation with the uncomplexed ring free to rotate while the complexed one cannot rotate because of direct interaction of chromium with the cationic centre. Thus, the tricarbonylchromium group interacts with a charged α-atom through quite different mechanisms according to the sign of the charge and this gives rise to different steric consequences.

Fluorenone Ketyls.—The presence of the *o*–*o'* bond in the fluorenone molecule prevents twisting of the rings thus allowing a delocalization of the unpaired electron on both rings. Here tentative assignment of the splitting constants to the different positions can be made if we assume a marked lowering of the couplings of the complexed ring protons and little modification for the others. If the decrease is the same as that observed on passing from (Ia) to $(Ia)\cdot Cr(CO)_3$ (*ca.* 60%), then the values 0.81, 1.26, and 0.26 G are obtained for the splitting constants of 1-, 3-, and 4-H and an unresolvable splitting for 2-H. These values can be matched by the experimental splittings 1.02, 1.35, and 0.26 G respectively (Table 3).

If our interpretation is correct this indicates that the π-electron distribution is little modified by complexation and that the larger effect is modification of the σ bonds.

Conclusions.—The e.s.r. results indicate that the π-electron spin density distribution in the $Cr(CO)_3$ complexed ketyl radicals is little changed from that of the corresponding uncomplexed ketyls. The marked decrease in the values of the proton hyperfine coupling is caused by a variation of the Q_{CH} value which relates the carbon ρ^{π} spin density to the proton coupling. The lowering of Q_{CH} could arise from bending of the C–H

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* It has been shown by us [4] that for pivalophenone, benzophenone, and fluorenone the effect on the polarographic reduction potential caused by structural variation in forming the radical anion follows the same trend in the complexed as in the uncomplexed series. On the other hand, it is well established that the effect of substituents in the co-ordinated ring manifests similar behaviour to that of the ligand series.[21]

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bond from the ring plane with a consequent introduction of *s*-character into the π-electron orbital.

If we consider that for a planar π-radical $Q_{\mathrm{CH}} = -23$ and for a σ-radical $+137$ G,[25] assuming a linear relationship, a variation of Q_{CH} of *ca.* 60% corresponds to a bending angle of *ca.* 1.6° which is in fairly good agreement with the results of neutron diffraction studies of benzeneCr$(CO)_3$ which showed that the bending angle is 1.7°.[26]

This work was supported by the Italian C.N.R. through its Centro di Studio sugli Stati Molecolari Radicalici ed Eccitati.

[7/777 *Received*, 6*th May*, 1977]

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