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METAL-STABILIZED CARBANIONS

VI *. FORMATION OF SOME ARYLMETHYL AND DIBENZOTROPENYL CARBANIONS COMPLEXED WITH TRICARBONYLCHROMIUM. A KINETIC AND A ^{13}C NMR STUDY

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Summary

Rate constants have been measured for the α-metallation of some arylmethanes, of 5*H*-dibenzo[*a*, *d*]cycloheptene and its dihydro derivative, free and complexed with tricarbonylchromium, by potassium hydride in tetrahydrofuran in the presence of 18-crown-6 ether. The stable solutions of the complexed anions have been studied by ^{13}C NMR spectroscopy. With the free ligands the kinetic acidity depends upon the structure to a great extent, but in the corresponding complexes the rates of metallation do not vary appreciably. On the basis of the ^{13}C chemical shift data a close similarity is suggested between the electronic structures of the arylmethyl and dibenzotropenyl anions which would account for their very similar metallation rates.

Introduction

The substantial enhancement of the acidity of the benzylic hydrogens in π-(alkylarene)tricarbonylchromium complexes has been clearly demonstrated in the past ten years. Trahanovsky [1] showed that the mono-tricarbonylchromium (TCC) complex of 1,4-diphenylbutane when exposed to potassium t-butoxide in DMSO underwent exchange of protons only at the position α to the complexed ring; furthermore, the results for the indane complex showed that the exchange is stereoselective, i.e. only the benzylic protons *anti* to the TCC group undergo

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* For part V, see ref. 14. Some of these results were discussed at the Xth International Conference on Organometallic Chemistry, August 1981, Toronto, Canada, Abstract No. 2E79.

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exchange. The protons next to a complexed aromatic ring were found to exhibit fastest exchange in sodium ethoxide-promoted hydrogen-deuterium reaction of several TCC-complexed diarylmethanes but results some exchange also occurred in the complexed ring [2]. Contributions from our laboratory include an account of the rates and products of elimination of some 2-phenylethyl bromides and tosylates complexed with TCC in alcohols with alkoxides [3], the complexation of the aromatic ring increasing the rates of elimination by a factor ranging from 10^2 to 10^3. Direct application of TCC-carbanions in synthesis was reported first by Jaouen [4]; while free $PhCH_2CO_2Me$ is inert toward MeI and NaOH in DMF, the corresponding complex rapidly undergoes double alkylation at the benzylic proton positions under the same conditions.

In spite of considerably body of data on the ease of formation of the TCC-complexed benzylic anions, to our knowledge very few reports are available about the generation of such anions at a concentration suitable for their direct spectroscopic observation. The chemical and spectroscopic properties of the indenyl and fluorenyl anions have been investigated by Nesmeyanov et al. [5] and by our group [6] and a ^{13}C NMR spectroscopic study of some bis(tricarbonylchromium)diphenylmethyl carbanions obtained from the corresponding hydrocarbons with potassium t-butoxide in THF has been published [7]. A likely explanation of this paucity of data may be that when TCC-arylalkyl hydrocarbons have been treated with carbon bases, two concurrent reactions compete successfully with the side-chain metallation: (i) ring metallation [8]; (ii) nucleophilic aromatic addition and substitution, in a two-step mechanism similar to that established for nucleophilic aromatic substitution with formation of an intermediate π-cyclohexadienyl complexed anion [9]. The results for toluene are of interest; when TCC-toluene was treated with n-butyllithium in THF and then with MeI, only 14% of the α-alkylated product was obtained, the rest being a mixture of *o*-, *m*- and *p*-xylenes [8]. Furthermore, results from our laboratory [10] showed that the reaction of the TCC-toluene with n-butyllithium in THF at −78 °C followed by work up the solution afforded 100% of the ring alkylated products, while only unchanged toluene was recovered when the free hydrocarbon was treated with n-BuLi under the same conditions. It becomes clear that the decreased importance of the α-proton abstraction, which should be the thermodynamically favoured process [1], must be ascribed to the powerful electron-withdrawing effect of the metal group which makes the attack at the hydrogens and carbons of the complexed ring kinetically favoured. Thus, n-butyllithium, the reagent commonly used for preparing solutions of α-carbanions for charge distribution studies by spectroscopic techniques, is not the appropriate one for the TCC-complexed substrates.

Some years ago the metallation of a series of free arylmethanes by KH in THF in the presence of 18-crown-6 ether was described [11]. This method provided information on the acidity of the molecular hydrogen as well as that of the alkyl compounds. Recently, by the use of this method, we have obtained stable solutions of TCC-complexed 5*H*-dibenzo[*a*,*d*]cycloheptenyl [12], benzocycloheptenyl [13], and di- and triphenylmethyl [14] carbanions suitable for ^1H NMR studies.

We now report the rates of α-proton abstraction by potassium hydride in THF with 18-crown-6 ether for some TCC-complexed hydrocarbons having benzyl and dibenzotropenyl structures together with the rates for the corresponding free ligands. The products of the reactions of the complexed anions with various electrophiles have been determined. Lastly, information on the negative charge distribution has been obtained by analysis of their ^{13}C NMR spectra.

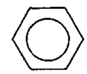
Results and discussion

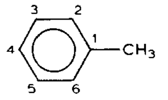
Kinetics

The metallation of a number of free and TCC-complexed hydrocarbons according to

$$R\text{—}H + \overset{+}{K}\,\overset{-}{H} \rightleftharpoons \overset{-}{R}\,\overset{+}{K} + H_2 \qquad (1)$$

RH =


(I)



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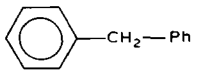

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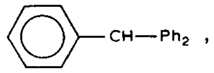

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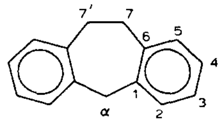
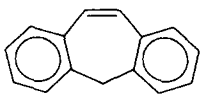
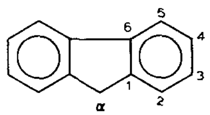


(V)


(VI)



(VII)

in anhydrous THF in the presence of 18-crown-6 ether at 294 ± 0.1 K was monitored by following the evolution of hydrogen. The potassium hydride is very sparingly soluble in the THF/18-crown-6 ether solution and so is present as a suspension. The solvent-base system is not completely inert, and some evolution of hydrogen takes place; consequently, before the addition of the hydrocarbon, the KH/18-crown-6/THF mixture was stirred for several hours and the volumes of hydrogen measured during the ionization of the RH's were corrected for the volumes observed at the corresponding times in the control experiments. The observed rate constants were normally calculated from the first-order expression using the least-squares method up to 70% reaction, but the first-order reversible equation was used for those substrates whose equilibrium did not lie completely over to the right. The reproducibility was satisfactory though the heterogeneity of the system meant that the uncertainty could not be reduced less below 10%. The occurrence of the reaction for the complexed hydrocarbons was readily observable because of the change of the colour of the solution from yellow to red-brown (dark-green in the case of TCC-VI). The percentages of hydrogen and the observed first-order rate constants, for free (k_f) and complexed (k_c) hydrocarbons are listed in Table 1.

Benzene, both free and complexed, is totally inert, since gas evolution was not observed even after prolonged reaction times. Thus, the KH/18-crown-6 ether base-system in THF does not bring about ring metallation of TCC-complexed arenes. In contrast, while free toluene is unreactive, the corresponding complex afforded hydrogen in quantitative yield at appreciable rate. The formation of the TCC-benzyl carbanion was confirmed by the nature of the products obtained after quenching of the solution with electrophiles: (i) treatment with D_2O gave TCC-toluene-α-d, as shown by NMR; (ii) in the reaction with CO_2 only TCC-phenylacetic acid and no TCC-toluic acid were identified; (iii) quenching with MeI gave ethyl- and isopropyl-TCC-benzene in the ratio 85/15, the isopropylbenzene probably being formed through proton abstraction and subsequent metallation of the TCC-ethylbenzene. Thus, in contrast with n-butyllithium (see the Introduction), when TCC-toluene is treated with KH/18-crown-6/THF solvent-base system, ring metallation does not compete at all with α-metallation.

As shown in Table 1, the α-metallation is quantitative for all the complexes, while for the free ligands it ranges from zero to 100% depending on the structure.

The solutions both of the ligands and the complexes were treated with D_2O and MeI immediately after the end of the ionization. The dark coloured solutions of the complexed anions turned yellow immediately on addition of the electrophiles. TLC and NMR analyses of the isolated products indicated that incorporation of deuterium and/or methyl group had occurred exclusively at the benzylic carbon. The addition of the electrophiles was shown to be stereospecific for TCC-V and TCC-VI since the electrophile adds at the *exo* position with respect to the TCC group (see Experimental).

Except for TCC-VII, the metallation rate constants, k_c, have very similar values; in contrast, a much higher sensitivity to structural effects is shown by k_f's. As a consequence, the effect of complexation, as measured by the k_c/k_f ratio, is very strong for the less acidic ligands and weak for the most acidic fluorene, VII (see Table 1, last column). Of particular interest are the results obtained for VI and its 10,11-dihydro analog, V: for the free ligands the lower kinetic acidity of the unsaturated hydrocarbon was attributed to the anti-aromatic character of the anion, a $4n$ π-electron system [15]; in contrast, the two corresponding complexes have about the same kinetic acidity, indicating a similar stability for the two complexed anions. Thus, in the TCC-VI anion the anti-aromatic character of the ligand must be substantially quenched, as we previously demonstrated by ^1H NMR studies [12].

In order to explain the lack of structural effects on k_c both in open (II–IV) and in

TABLE 1

YIELDS AND RATES OF METALLATION OF SOME ARYLMETHYL AND DIBENZOTROPENYL HYDROCARBONS, FREE AND COMPLEXED WITH $Cr(CO)_3$, WITH KH IN THF AT 294.0±0.1 K IN THE PRESENCE OF 18-CROWN-6 ETHER [a]

Compound	H_2 yield [b] (%)		10^4k (s^{-1}) [c]		k_c/k_f
	free RH	TCC-RH	free RH (k_f)	TCC-RH (k_c)	
I	0	0	–	–	–
II	0	100	–	220	very high
III	50	100	0.5	230	460
IV	100	100	1.6	380	240
V	100	100	4.0	350	88
VI	28	100	~ 0.3	250	~ 800
VII [d]	100	100	114	1100	10

[a] [RH] 2×10^{-2} M, [18-crown-6] 5×10^{-2} M. [b] Each figure is the average of two or more determinations. Deviations were within the experimental error (3%). [c] Mean values of two runs. Deviations were within 10%. [d] Data from ref. 6.

cyclic (V and VI) complexed anions, the same electronic structure must be assumed for both types. In this structure the presence of the TCC-phenyl substituent must be of crucial importance in determining the stability of the complexed anions, while the other substituents play a minor role. The prevailance of such a formula for the complexed anion VI must account also for the quenching of its anti-aromatic character. On the other hand, the low value of the k_c/k_f ratio found for fluorene, VII, suggests that the presence of the TCC group is far less important in determining the electronic structure of the anion.

The spectroscopic ^{13}C NMR study confirmed the validity of this hypothesis by providing details of the electronic distribution.

^{13}C NMR results

^{13}C chemical shifts and coupling constants for the free and complexed neutral hydrocarbons are listed in Table 2 and those of the corresponding free and complexed anions are in Table 3. We were not able to obtain a satisfactory NMR spectrum of the ionized TCC-II because of the low stability of its solution (even at $-50\,^\circ$C) when freed from excess KH.

The assignment of the resonances was based on standard ^{13}C correlations, on undecoupled and partially relaxed spectra, and on selective proton decoupling experiments. Furthermore, deuteration at the α-positions allowed direct assignment of the C_α resonances.

The complexation of the neutral arenes with TCC causes the usual strong upfield shift of the complexed ring carbons [16] and a significant increase in the corresponding ^1J(CH) coupling constants [17]. On the other hand, very small complexation effects are shown both by the sp^3 and the sp^2 hybridized carbon atoms not directly involved in the metal coordination [16].

For the anions, the spectroscopic results will be discussed in terms of the ionization effect for each carbon atom, i.e. $\Delta\delta^i = \delta^i_{\text{anion}} - \delta^i_{\text{neutral}}$, which are listed for the ligands ($\Delta\delta^i_L$) and for the complexes ($\Delta\delta^i_C$) in Table 4. For the free ligands, the strong deshielding shown by the C_α resonances upon ionization has been attributed both to the change of hybridization from sp^3 in the reference hydrocarbon to almost sp^2 in the carbanion and to the negative charge effect [18]. For the other carbons in III–VI anions an alternating effect is shown by the C(2), C(3), C(4) and C(5) resonances, i.e. strongly negative $\Delta\delta_L$ values for the C(2) and C(4) and very small for the C(3) and C(5) nuclei. In contrast, the values for VII are negative for all the carbons of the rings. Thus, it appears that the excess charge is located mainly on the positions *ortho* and *para* to the ionization site in the arylmethyl anions III, IV and V, and to some extent also in the anti-aromatic anion VI. For the arylmethyl anions the mechanism of the negative charge delocalization probably involves quinone-like structures with a strong character of double bond between the C(1) and C_α carbon atoms, but contributions from such structures may be important also for the anti-aromatic dibenzotropenyl anion, VI. In contrast, the role of quinone-like structures is of minor importance in the fully aromatic fluorenide where the negative charge resides mainly in the central pentadienyl ring [19]. Some indication of the presence of strong exocyclic double bond character is obtained also from the $\Delta\delta^1_L$ values, which are positive for all the substrates except VII. A downfield shift for the junction carbon resonance is commonly observed in monosubstituted benzenes with electron-donating groups, the largest effect being induced by those substituents

(Continued on p. 217)

TABLE 2

^{13}C CHEMICAL SHIFTS [a] (^1J(C–H) coupling constants in parentheses) FOR SOME FREE AND Cr(CO)$_3$-COMPLEXED ARYLMETHYL, DIBENZOTROPENYL AND FLUORENYL HYDROCARBONS [b]

Compound		C_α	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other carbons	
III		42.1(128)	141.1	128.8(157)	128.3(158)	126.3(161)	128.3(158)	128.8(157)	–	
TCC-III	free ring	40.6(128)	138.3	128.9(161)	128.9(161)	127.2(159)	128.9(161)	128.9(161)	–	
	compl. ring		112.9	93.1(173)	94.3(168)	91.0(174)	94.3(168)	93.1(173)	–	C≡O, 233.6
IV		57.6(125)	144.9	130.1(159)	128.8(159)	126.8(160)	128.8(159)	130.1(159)	–	
TCC-IV	free rings	54.7(129)	141.4	129.4(159)	128.6(161)	127.2(162)	128.6(161)	129.4(159)	–	
	compl. ring		114.8	95.4(173)	91.0(175)	93.1(175)	91.0(175)	95.4(173)	–	C≡O, 232.9
V		41.3(126)	139.9	126.5(159)	129.5(159)	130.0(160)	127.0(159)	139.9	C(7) 33.2(127)	
TCC-V	free ring	39.8(129)	138.7	128.0(160)	129.2(159)	129.9(160)	127.8(162)	139.9	C(7) 32.5(130) [c]	
	compl. ring		111.3	93.9(174)	96.6(172)	96.2(172)	92.2(175)	112.4	C(7) 32.2(130) [c]	C≡O, 234.6
VI		42.1(129)	139.0	126.7(160)	128.5(158)	128.7(158)	129.0(158)	136.2	C(7) 132.1(156)	
TCC-VI	free ring	40.6(131)	137.6	127.2(160)	128.0(157)	128.9(159)	128.3(157)	134.9	C(7) 134.3(157) [c]	
	compl. ring		108.7	90.1(175)	93.5(172)	92.9(174)	92.7(179)	103.8	C(7) 129.1(159) [c]	C≡O, 233.0
VII		37.3(129)	144.0	125.5(162)	127 3(159)	127.3(159)	120.4(159)	142.0		
TCC-VII [d]	free ring	37.5(132)	143.2	127.5(162)	127.3(159)	127.3(159)	120.4(159)	142.0		
	compl. ring		114.3	91.6(175)	93.1(175)	92.0(175)	87.9(176)	112.0		C≡O, 234.3

[a] ^{13}C shifts given in ppm (^1J(C–H) in Hz, ±1 Hz) from internal Me_4Si. [b] Recorded in $CDCl_3$ at 306 K; no significant solvent effect was found in going from $CDCl_3$ to THF. [c] C(7) and C(7′) are the bridge carbons bonded to the uncomplexed and complexed ring, respectively. [d] Data from ref. 6.

TABLE 3

^{13}C CHEMICAL SHIFTS[a] (^{1}J(C–H) coupling constants in parentheses) FOR SOME FREE AND Cr(CO)$_3$-COMPLEXED ARYLMETHYL, DIBENZOTROPENYL AND FLUORENYL ANIONS[b]

Anion		C$_\alpha$	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other carbons	
III		79.0(141)	145.6	116.8(151)	129.2(153)	108.1(143)	129.2(153)	116.8(151)	–	
TCC-III[c]	free ring	86.9(150)	144.7	125.0(156)	128.0(155)	118.7(160)	128.0(155)	125.0(156)	–	
	compl. ring		136.5	76.9[d]	99.4(166)	73.1[d]	100.1(165)	67.3[d]	–	C≡O, 240.7
IV		88.3	148.8	123.7(154)	128.9(154)	114.3(159)	128.9(154)	123.7(154)	–	
TCC-IV	free rings	97.7	147.4	131.3(157)	128.1(157)	122.4(159)	128.1(157)	131.3(157)	–	
	compl. ring		133.5	73.1(170)	99.9(163)	73.5(170)	99.9(163)	73.1(170)	–	C≡O, 241.1
V		84.6(143)	146.0	120.9(150)	128.6(151)	105.6(160)	125.5(152)	128.6	C(7) 40.1(126)	
TCC-V	free ring	90.2(149)	143.3	125.5(155)	126.4(153)	118.2(156)	128.6(152)	138.4	C(7) 39.7(126)[e]	
	compl. ring		136.4	71.8(176)[f]	98.5(164)	77.5(165)[f]	101.6(162)	92.2	C(7′) 39.4(126)[e]	C≡O, 241.2
VI		91.4(144)	164.0	120.4(150)	133.6(151)	111.0(160)	132.4(151)	139.4	C(7) 139.7(148)	
TCC-VI	free ring	94.4(150)	147.7	126.4(164)	128.6(159)	120.8(160)	129.1(154)	146.6	C(7) 136.0(148)[e]	
	compl. ring		137.3	71[d,f,g]	100.4(166)	76.5(174)[f]	101.8(162)	91.0	C(7) 131.1(158)[e]	C≡O, 242.3
VII[h]		82.9(160)	136.5	116.8(154)	120.2(154)	109.5(156)	119.4(150)	121.5	–	
TCC-VII	free ring	83.1(166)	143.3	117.6(154)	122.7(154)	113.0(165)	119.5(153)	126.6	–	
	compl. ring		122.6	85.2(164)	94.5(164)	77.1(171)	93.5(167)	92.7	–	C≡O, 240.3

[a] ^{13}C shifts given in ppm (^{1}J(C–H) in Hz, ±1 Hz) from internal Me$_4$Si. [b] In THF-d_8, T 306 K unless otherwise indicated. [c] T 263 K. [d] ^{1}J(C–H) not detected because of the presence of the large peaks due to the 18-crown-6 ether. [e] See footnote *c* in Table 2. [f] The assignments may be reversed (see text). [g] The resonance is hidden by the peak of the 18-crown-6 ether. [h] Data from ref. 6.

TABLE 4

IONIZATION EFFECTS $\Delta\delta^{\mathrm{i}}_{\mathrm{L}}$ and $\Delta\delta^{\mathrm{i}}_{\mathrm{C}}$ (ppm) ON ^{13}C CHEMICAL SHIFTS OF THE FREE AND COMPLEXED LIGANDS

Compound		C_α	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other carbons	
III		36.9	4.5	−12.0	0.9	−18.2	0.9	−12.0		
TCC-III	free ring	46.3	6.4	−3.9	−0.9	−8.5	−0.9	−3.9		C≡O, 7.1
	compl. ring		23.6	−16.2	5.1	−17.4	6.7	−25.8		
IV		30.7	3.9	−6.4	0.1	−12.5	0.1	−6.4		
TCC-IV	free rings	43.0	6.0	1.9	−0.5	−4.8	−0.5	1.9		C≡O, 8.2
	compl. ring		18.7	−22.3	8.9	−19.6	8.9	−22.3		
V		43.3	6.1	−5.6	−0.9	−24.4	−1.5	−11.3	C(7) 6.9 [a]	
TCC-V	free ring	50.4	4.7	−2.5	−2.8	−11.7	1.6	−1.5	C(7) 7.2 [a]	C≡O, 6.6
	compl. ring		25.1	−22.1	1.9	−18.7	9.4	−20.2	C(7′) 7.1 [a]	
VI		32.7	25.0	−6.3	5.1	−17.7	3.4	3.2	C(7) 7.6 [a]	
TCC-VI	free ring	53.8	10.1	−0.8	0.6	−8.1	0.8	11.7	C(7) 1.7 [a]	C≡O, 9.3
	compl. ring		28.6	≃ −19	6.9	−16.4	9.1	−12.8	C(7′) 2.0 [a]	
VII		45.6	−7.5	−8.7	−7.1	−17.8	−1.0	−20.5		
TCC-VII	free ring	45.6	0.1	−9.9	−5.2	−16.1	−1.4	−13.1		C≡O, 6.0
	compl. ring		8.3	−6.4	1.4	−14.9	5.6	−19.3		

[a] See footnote *c* in Table 2.

which are able to delocalize the electron cloud toward the ring by a resonance effect [20].

For the complexes, the ionization effects will be discussed separately for the various groups of carbon atoms, i.e.: (i) C_α; (ii) the carbons of the uncomplexed ring(s), and (iii) the carbons of the TCC-aryl ring.

The deshielding effect shown by C_α's is greater than that observed for the corresponding ligands, the values ranging from +43.0 ppm for TCC-IV to +53.8 ppm for TCC-VI; only TCC-VII shows the same effect displayed by the free ligand. We believe that the greater downfield shifts observed upon ionization of the complexes must be ascribed to a strong decrease of the negative charge density at C_α, this being the result of the remarkable ability of TCC to accomodate the charge into the TCC-phenyl moiety. However, we cannot exclude the possibility that some re-hybridization of C_α's in the complexes compared with that in the free ligands is at least partly responsible for the effect. (The $^1J(C_\alpha\text{–}H)$ coupling constants do, in fact, increase to some extent, by ca. 6 Hz, on passing from free to complexed anions.) It is striking that the strongest effect is shown by the anti-aromatic anion VI while no effect is observed for the aromatic VII; this correlates well with the effect of complexation, as measured by k_c/k_f, found for the corresponding ionization rate constants.

The comparison of the $\Delta\delta^i_L$ values with the corresponding values for the free ring(s) in the complexes, $\Delta\delta^i_C$, is instructive in evaluating the electron-withdrawing effect of TCC. The chemical shifts of the free ring carbon atoms are in fact little affected by conformational and anisotropic effects of the metal carbonyl group and so for these nuclei the difference $\Delta\delta^i_C - \Delta\delta^i_L$ may be related mainly to the extent of charge polarization due to the long range effect of TCC, a positive value being due to a decreased charge density in the free ring of the complexed anion with respect to that in the ligand anion. The values, as calculated from the data in Table 4, are markedly positive for C(2), C(6) and C(4) carbon atoms and slightly negative for C(3) and C(5). The negative charge density, therefore, must be almost completely siphoned away from the free ring; actually, the carbon atoms of the free ring(s) resonate about at the same frequency as those of the corresponding neutral substrates (cf. Table 2). The alternating trend of the effect favours a mesomeric mechanism.

The chemical shifts of the complexed ring carbon atoms suffer from conformational and other proximity effects induced by the anisotropic TCC group which may contribute to different extents in the neutral and charged species. Electron-donating substituents, for example, favour conformations in which the carbonyls eclipse the C(1), C(3) and C(5) carbon atoms, as suggested for TCC-VII anion [6], and steric effects arising from the interaction of the carbonyls with the substituent may also be important [21]. Thus, the correlation between the ionization effects on the chemical shifts and the distribution of the charge in the complexed ring nuclei is not straightforward. However, some insight into the electronic distribution of the charge density in the aryl-tricarbonylchromium moiety can be obtained from the following analysis:

(a) The chemical shifts of the carbonyls. A downfield shift ranging from +6.0 (η^6-TCC-VII anion) to +9.3 (TCC-VI anion) ppm is shown by the carbonyl resonances upon ionization. These values are comparable in magnitude but opposite in sign to those found for TCC-arylmethyl carbenium ions, in which a substantial

amount of the positive charge is transmitted from the cationic center to the carbonyls [22].

The effects found for the anions suggest that a substantial amount of charge is transferred from the organic into the inorganic moiety. It is worth to note that the ionization effect values of the carbonyls of TCC-VII anion are +6.0 for the η^6-isomer and +11.7 ppm for the η^5-isomer [6], showing that the downfield shift is larger for that isomer in which the TCC directly interacts with the central cyclopentadienyl ring, where the negative charge density is mainly localized.

(b) The non-equivalence of the ortho and meta carbons in the TCC-diphenylmethanide. In the temperature range 243–303 K, the spectrum of TCC-III anion shows the non-equivalence of the *ortho* and *meta* carbon resonances of the complexed ring, while no splitting of the corresponding positions of the uncomplexed ring is observed. The phenomenon can be related to a freezing of free rotation around the bond between the C_α and C(1) (complexed ring) due to an increase of the bond order with the result that the ring carbons experience different magnetic environments, whereas free rotation around the bond between the C_α and C(1) (uncomplexed ring) would be feasible. The same behaviour was observed also in the ^{1}H NMR spectrum [14]. Following the Mislow's terminology [23], the most likely conformation of the TCC-III anion would be the "perpendicular" one where the complexed ring is coplanar with the C_α–H bond and the free ring is perpendicular to this plane. In such a conformation the uncomplexed ring does not contribute substantially to the negative charge delocalization.

(c) The internal complexation effect. Examination of the changes in the ^{13}C chemical shifts of the corresponding positions between the complexed to the uncomplexed rings of the same coordinated substrate, the "internal complexation effects", may be instructive. The values for the anions, Δ_I^-, and for the neutral hydrocarbons, Δ_I, are shown in Table 5. For the neutral complexes, the Δ_I's have about the same value, i.e. -35 ± 3 ppm for the protonated ring carbons and -27 ± 2 ppm for the junction carbons. The Δ_I^- of the C(3) and C(5) nuclei which are *meta* to the ionization site show about the same value in all anions; in contrast, the values of the *para* C(4) and of the *ortho* C(2) and C(6) atoms are much more negative ($\Delta_I^- = -40.7$ to -58.2 ppm) for TCC-III, -IV, -V, and -VI anions, while

TABLE 5

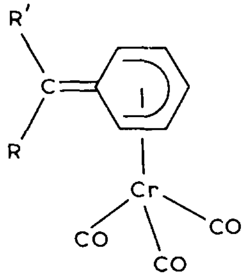
THE INTERNAL COMPLEXATION EFFECT (Δ_I^-) (ppm), FOR THE COMPLEXED ANIONS, WITH THE VALUES FOR THE CORRESPONDING HYDROCARBONS, Δ_I, IN PARENTHESES

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
TCC-III	−8.2	−52.9 ^{a}	−28.3 ^{a}	−45.6	−28.3 ^{a}	−52.9 ^{a}
	(−25.4)	(−35.8)	(−34.6)	(−36.2)	(−34.6)	(−35.8)
TCC–IV	−13.9	−58.2	−28.2	−48.9	−28.2	−58.2
	(−26.6)	(−34.1)	(−37.6)	(−37.6)	(−37.6)	(−34.1)
TCC-V	−7.0	−53.7	−27.9	−40.7	−27.0	−46.2
	(−27.4)	(−34.1)	(−32.6)	(−33.7)	(−34.8)	(−27.5)
TCC-VI	−10.4	−55	−28.2	−44.3	−27.3	−56.7
	(−28.9)	(−37.1)	(−34.5)	(−36.0)	(−35.6)	(−31.1)
η^6-TCC-VII	−20.7	−32.4	−28.2	−35.9	−26.0	−33.9
	(−28.9)	(−35.9)	(−34.8)	(−37.1)	(−33.0)	(−27.7)

^{a} Mean value for the two non-equivalent *ortho* and *meta* positions.

values close to those of neutral hydrocarbons are shown by the same nuclei in η^6-TCC-VII anion. We believe that this behaviour is a clear indication that a mesomeric mechanism for the negative charge transfer operates more effectively in the anions III–VI than in the anion VII. Finally, particularly significant are the $\Delta^-_{C(1)}$ values. For the anions III–VI the $\Delta^-_{C(1)}$'s are anomalously small (−7.0 to −13.9), suggesting that the junction carbon atom of the complexed ring is scarcely involved in the metal coordination; on the other hand, a noticeably higher value is found for η^6-TCC-VII anion. Other evidence for loose coordination of the C(1) bearing an electron-rich group to metals has been discussed recently [24].

The arguments in (a), (b), and (c), above, lead to the suggestion that for the anions III–VI the negative charge is almost completely situated in the phenyltricarbonyl moiety in which the TCC group is bonded to the ring in a pentahapto manner, as shown in the formula:



This planar tricarbonyl(η^5-benzylidene)chromium structure, which was previously suggested for the arylmethyl-TCC anions on the basis of ^{1}H NMR results [14], seems to be by far the most important one in the resonance hybrid of the anions III–VI. This would accounts satisfactorily not only for the ^{13}C NMR results but also for the very similar stabilities shown by the arylmethyl- and dibenzotropenyl-TCC anions and for the quenching of the anti-aromatic character of the anion VI. However, the same structure must have a minor weight in the resonance hybrid of the η^6-TCC-VII anion, for which, on the basis of the relatively high value of $\Delta^-_{C(1)}$, a resonance structure with the TCC group bonded to the phenyl ring in an hexahapto manner seems to be more important. Therefore, it can be inferred that in the complexed fluorenyl anion a large amount of charge still resides in the central pentadienyl ring, in a situation not very different from that of the free anion. This conclusion fits well with the small complexation effect found for the kinetic acidity of VII (see Table 1), and with the previously observed ease of migration of the TCC group from the external phenyl towards the central pentadienyl ring [5,6].

Experimental

All experimental procedures were performed under a static atmosphere of rigorously purified argon. Hexacarbonylchromium (Ventron) was sublimed before use.

Commercial grade THF was distilled from K/anthracene, stored under vacuum over K-anthracenide and transferred to the reaction vessel by standard vacuum techniques. Commercial grade 18-crown-6 (Ega Chemie) was dried in vacuo in the presence of P_2O_5. Toluene, diphenylmethane and triphenylmethane (Fluka) were either distilled or crystallized from ethanol before use. The tricarbonylchromium-complexed toluene, diphenylmethane and triphenylmethane were prepared according by published methods [25,26,10].

The infrared spectra were recorded on a Beckman IR-9 grating spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained using a Bruker WH 90 FT-spectrometer. Chemical shifts (δ) are given in ppm from internal Me_4Si.

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

Synthesis of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene (V) and 5H-dibenzo-[a,d]cycloheptene (VI)

V was made by treating the 10,11-dihydro-dibenzo[a,d]cycloheptene-5-one (Aldrich) with $AlCl_3/LiAlH_4$ in dry diethyl ether (cf. ref. 27) and purified by sublimation at 60 °C/10^{-2} mmHg (yield 84%). M.p. 75–76 °C (ref. 28: 76–77 °C). The 5,5-D_2 analog was obtained similarly by use of $LiAlD_4$. The deuterium content as checked by ^1H NMR was > 99%. ^1H NMR spectra were consistent with the structure of the two compounds. VI and its 5,5-D_2 analog were obtained from 5*H*-dibenzo[*a*,*d*]cycloheptene-5-one (Aldrich) by the procedures used for the 10,11-dihydro analogs. The crude products were purified by crystallization from acetone (yield 65%) and sublimation at 50 °C/10^{-2} mmHg. M.p. 133–134 °C (ref. 27: 133 °C) IR and ^1H NMR spectra were consistent with the structure.

Synthesis of 10,11-dihydro-5H-dibenzo[a,d]cycloheptenetricarbonylchromium (TCC-V, (nc)) and 5H-dibenzo[a,d]cycloheptenetricarbonylchromium (TCC-VI, (nc))

These complexes were obtained by treating the corresponding ligands with $Cr(CO)_6$ in anhydrous diglyme under reflux. The unreacted hydrocarbon and $Cr(CO)_6$ were removed by sublimation under vacuum. The residue was purified by column chromatography (degassed silica; hexane/diethyl ether mixtures as eluent) and crystallized under argon.

TCC-V: Yield 56%. M.p. 114–115 °C (from THF/hexane). (Found: C, 65.25; H, 4.50. $C_{18}H_{14}CrO_3$ calcd.: C, 65.84; H, 4.30%).

TCC-VI: Yield 20%. M.p. 138–139 °C (from CH_2Cl_2/hexane). (Found: C, 66.4; H, 3.68. $C_{18}H_{12}CrO_3$ calcd.: C, 66.24; H, 3.71%). The IR and ^1H NMR spectra of the complexes were as expected.

Preparation, ^{13}C NMR examination and electrophilic quenching of the anions

Solutions of free and complexed anions for ^{13}C NMR measurements were prepared under argon at the appropriate temperature by treating ca. 0.3 *M* solutions of the hydrocarbons in anhydrous, oxygen-free THF containing a slight excess of 18-crown-6 and a ten-fold excess of KH (Fluka, freed from mineral oil by repeated washing with dry cyclohexane). The resulting suspension was allowed to settle and the clear solution was cautiously transferred under argon to the NMR tube maintained at the same temperature. The spectra of the complexes were recorded at room temperature, except in the case of the TCC-III anion which was kept at −10 °C to avoid decomposition. At 0–10 °C, the spectrum of TCC-VI anion exhibits a dynamic process which involves broadening and splitting of the resonance lines. The spectrum reported was recorded at 323 K in order to provide single sharp signals. Details of this phenomenon will be published elsewhere.

For H_2 evolution measurements, 2×10^{-2} M solutions of the substrates in THF containing 5×10^{-2} M 18-crown-6 ether were treated with excess of KH (suspended in THF) under argon at 294 ± 0.1 K.

The quenching of the anions was carried out by treating the freshly prepared solutions, freed from the excess KH, with degassed H_2O, D_2O, or anhydrous MeI in THF under argon with vigorous stirring. The solvent was then removed under vacuum and the residue extracted with peroxide-free diethyl ether. After the solvent was distilled off, the residue was analysed by TLC, HPLC, and NMR techniques, comparisons being made when possible with authentic samples. The *exo*-configuration for the quenching products from the TCC-V and TCC-VI anions was assigned as reported in ref. 5(b).

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