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Phenylation of cyclic and acyclic pentadienyl carbanions by π-fluorobenzenetricarbonylchromium

Alberto Ceccon, Alessandro Gambaro, Francesca Gottardi *
Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, 35131 Padova (Italy)

Francesco Manoli and Alfonso Venzo
C.N.R., Centro di Studio sugli Stati Molecolari Radicalici ed Eccitati, Via Loredan 2, 35131 Padova (Italy)

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Abstract

Phenylation of cyclopentadienyl, indenyl, fluorenyl, 1,3-pentadienyl, 2,4-dimethyl-1,3-pentadienyl, and 1,1′,5,5′-tetramethyl-1,3-pentadienyl carbanions by π-fluorobenzenetricarbonylchromium in ethereal solvents at 0 °C gives good yields (> 70%) of complexes in which the phenyl-$Cr(CO)_3$ group is σ-bonded to a pentadienyl skeleton. The regio and stereo isomers obtained have been identified by accurate ^1H NMR study. Monotoring of the reaction by IR spectroscopy has shown that the mechanism of substitution of fluorine by the cyclic anions is different from that for substitution by the acyclic anions.

Introduction

As part of our programme on study of the migration of $Cr(CO)_3$ group (TCC) in polycyclic aromatic anions [1] we considered it of interest to prepare TCC-arene complexes in which a TCC-coordinated phenyl ring is linked to a cyclic or acyclic pentadienyl skeleton through a σ-bond. The synthesis of these compounds by direct complexation of the free ligands with $Cr(CO)_3L_3$ ($L = CO$, CH_3CN, NH_3) [2] presents several difficulties. For example, the method does not apply to the preparation of (η^6-phenyl-TCC)cyclopentadiene because of the thermal instability of the ligand [3]. Moreover, the direct complexation of 3-phenylindene and 9-phenylfluorene ligands mainly affords the species in which the inorganic unit is coordi-

* Present address: Montedipe/PM/CER, Stab. to Petrolchimico, Via della Chimica 5, 30175 Porto Marghera (VE) (Italy).

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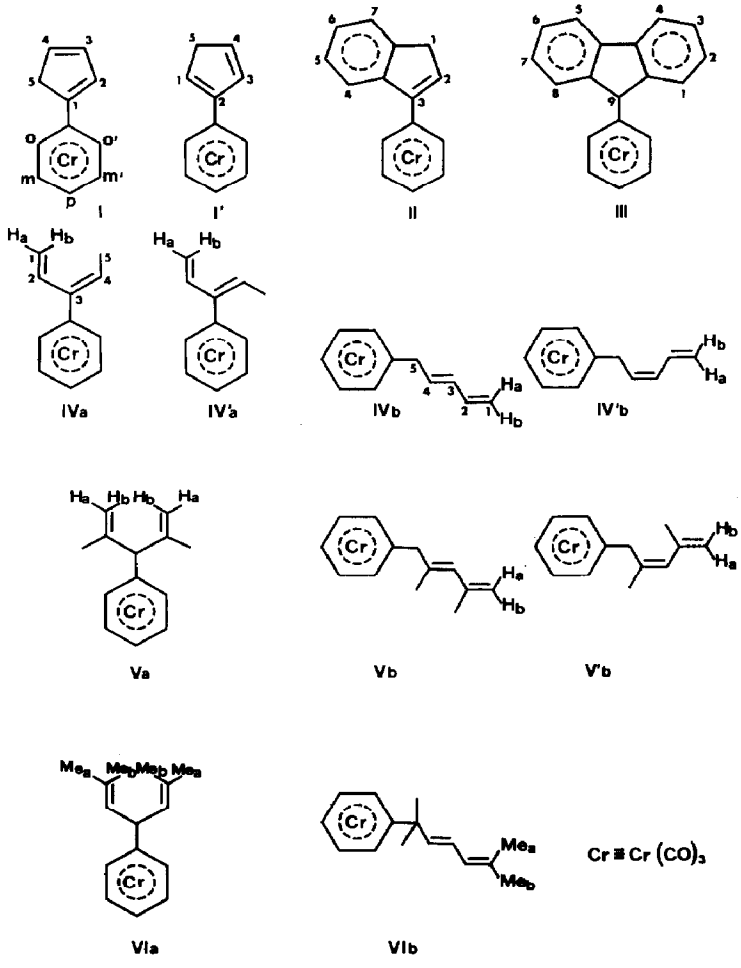


Fig. 1.

nated to the *ortho*-condensed benzo rings (> 95%) [4]. Finally, in the case of systems with acyclic pentadienyl skeletons the purification of the pure ligands is complicated by severe separation problems [5].

We have found that the best procedure for obtaining good yields of compounds containing pentadienyl skeletons σ-bonded to the TCC-phenyl residue involves the reaction between π-fluorobenzene-TCC and pentadienyl anions. It is well known that TCC-complexed halogenoarenes undergo nucleophilic displacement of halogen under mild conditions [6] in a conversion similar to classical nucleophilic aromatic substitution [7]. The powerful electron-withdrawing ability of TCC group enhances the reactivity of the arene ligand towards nucleophiles, and this property has been exploited for preparative purposes [6a].

In this paper we describe the synthesis and ^{1}H NMR characterization of complexes, shown in Fig. 1, obtained by reaction of π-fluorobenzene-TCC with various pentadienyl anions.

IR spectroscopic monitoring of the reaction has shown that cyclic and acyclic pentadienyl anions react by different pathways.

Results and discussion

Reaction of a 2–3 molar excess cyclopentadienyl or pentadienyl anions in ethereal solution with TCC-fluorobenzene at 0 °C under argon takes place with the disappearance of the complexed reagent and formation of the complexed alkylated hydrocarbons within 1.5–2 h. The progress of the reaction was readily monitored by thin layer chromatography (TLC). The products recovered after quenching with oxygen free aqueous NH_4Cl reveal that complete replacement of fluorine atoms by pentadienyl groups had occurred. The results parallel those reported by other authors for the same reaction with carbon [6a,6b], oxygen [6c,6d], and nitrogen [6e] bases.

Slight variations in the detail of the preparation of the various solvent-base systems were necessary: thus dimethoxyethane-K was used to produce potassium cyclopentadienide [8] and THF/KH to give potassiumindenide and fluorenide, whereas the solutions of pentadienyl anion were prepared by the method developed by Yasuda et al. [9] involving treatment of the 1,3- and 1,4-dienes with alkali metals in THF in the presence of tertiary amines.

After hydrolysis the products were extracted with diethyl ether. The residues obtained after evaporation of the extrasts were purified by chromatography on silica column, and yellow complexes were always recovered in high yield (> 70%). Except for the ^1H NMR spectra (see below), physical and spectroscopic data for the complexes are given in the Experimental section.

Cyclic pentadienyls

II and III. Pure products were obtained from indenyl and fluorenyl reaction systems, and their ^1H NMR spectra indicated that the complexes 3-(η^6-phenyl-TCC)indene (II) and 9-(η^6-phenyl-TCC)fluorene (III) had been formed. The spectra were analyzed by computer simulation, and the relevant parameters are listed in Table 1.

For both complexes an AA'BB'C pattern is observed in the δ range typical of TCC-complexed phenyl protons (δ 5.60–6.10 for II and 5.52–5.68 for III). The signals from the indenyl residue in II were analyzed as an $ABCDEF_2$ spin system. The pattern of the phenyl ring protons together with the equivalence of the methylene ones indicates that the two molecular moieties are able to rotate freely from each other. The uncomplexed part of III exhibits an unique ABCD pattern for the benzo rings and a singlet at δ 5.00 for the methyne in position 9. This last resonance is somewhat broadened because of long range coupling constant to phenyl and benzo ring protons (see Table 1).

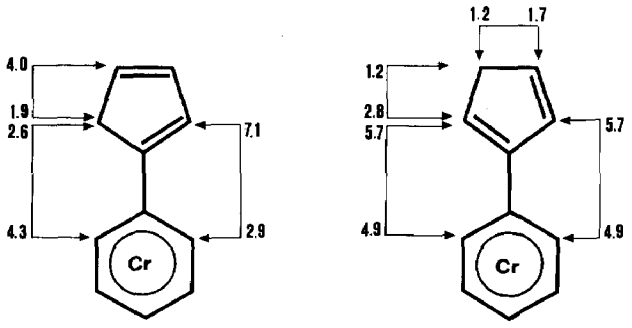
I and I'. Workup of the ether solution in the case of the cyclopentadienyl system required much care: TLC of the reaction solution carried out after hydrolysis showed one yellow spot, whereas three yellow spots were found after evaporation of the solvent in a rotary evaporator. ^1H NMR spectroscopic analysis of the residue indicated the presence of 1-(η^6-phenyl-TCC)cyclopentadiene (I) and 2-(η^6-TCC-phenyl)cyclopentadiene (I') mixed with dimers probably formed by Diels–Alder reactions. It was thus evident that the monomers have a high rate of dimerization in concentrated solution at room temperature and evaporative removal of solvent at low temperature under 10^{-2} torr onto a cold finger at −170 °C left a single, stable, yellow orange solid in quantitative yield. The product was recrystallized from

Table 1

^{1}H NMR parameters for I, I′, II and III

	I [a]	I′ [a]	II [a]	III [a]
H_i	Chemical shifts (ppm) [b]			
$o = o'$	5.976	6.00 [c]	6.021 [c]	5.530
$m = m'$	5.760	5.76 [c]	5.826	5.610
p	5.557	5.61 [c]	5.709	5.679
1	–	6.854	3.565	7.799
2	7.055	–	6.977	7.395
3	6.560	6.846	–	7.470
4	6.531	6.596	7.734	7.923
5	3.362	3.232	7.368	7.923
6	–	–	7.285	7.470
7	–	–	7.554	7.395
8	–	–	–	7.799
9	–	–	–	5.002
i,j	Coupling constants (Hz)			
$o,m = o',m'$	6.72 ± 0.03	6.72 [c]	6.66 ± 0.03	6.56 ± 0.03
$o,p = o',p$	1.03 ± 0.02	1.03 [c]	1.03 ± 0.02	1.06 ± 0.03
$o,m' = o',m$	0.37 ± 0.03	0.37 [c]	0.34 ± 0.03	0.30 ± 0.04
o,o'	1.69 ± 0.04	1.69 [c]	1.75 ± 0.05	1.81 ± 0.05
$m,p = m',p$	6.36 ± 0.02	6.35 [c]	6.37 ± 0.02	6.34 ± 0.03
m,m'	1.38 ± 0.04	1.38 [c]	1.24 ± 0.04	1.17 ± 0.06
o,9	–	–	–	0.3 [c]
m,9	–	–	–	0.1 [c]
p,9	–	–	–	0.0 [c]
1,2	–	–	2.28 ± 0.02	7.67 ± 0.01
1,3	–	1.43 ± 0.07	–	1.08 ± 0.01
1,4	–	1.94 ± 0.07	−0.20 ± 0.04	0.71 ± 0.01
1,5	–	1.74 ± 0.06	0.68 ± 0.01	–
1,6	–	–	−0.20 ± 0.04	–
1,7	–	–	0.78 ± 0.01	–
1,9	–	–	–	0.9 [c]
2,3	2.24 ± 0.04	–	–	7.45 ± 0.01
2,4	1.21 ± 0.04	–	0.15 ± 0.03	1.14 [c]
2,5	−1.28 ± 0.03	–	−0.20 [c]	–
2,6	–	–	0.44 ± 0.02	–
2,7	–	–	0.00 ± 0.01	–
2,9	–	–	–	0.0 [c]
3,4	5.35 ± 0.03	4.84 ± 0.07	–	7.68 ± 0.01
3,5	−1.61 ± 0.04	−1.66 ± 0.06	–	–
3,9	–	–	–	0.7 [c]
4,5	1.61 ± 0.04	1.27 ± 0.05	7.77 ± 0.01	–
4,6	–	–	1.04 ± 0.01	–
4,7	–	–	0.78 ± 0.01	–
4,9	–	–	–	−0.25 [c]
5,6	–	–	7.48 ± 0.01	7.68 ± 0.01
5,7	–	–	1.16 ± 0.01	1.14 ± 0.01
5,8	–	–	–	0.71 ± 0.01
5,9	–	–	–	−0.25 [c]
6,7	–	–	7.52 ± 0.01	7.45 ± 0.01
6,8	–	–	–	1.08 ± 0.01
6,9	–	–	–	0.7 [c]
7,8	–	–	–	7.67 ± 0.01
7,9	–	–	–	0.0 [c]
8,9	–	–	–	0.9 [c]

[a] For proton labelling see Fig. 1; spectrometer frequency 200.13 MHz; solvent acetone-d_6 (10^{-2} M); T 300 K. [b] From internal TMS; least square errors ±0.001. [c] Values not refined by iteration.



I I'

Fig. 2. ^1H-{^1H} NOE enhancements (T 300 K). The numbers at the tip of the arrows indicate the % enhancements upon saturation of the connected nucleus. Cross experiments may give different numerical answers because of different relaxation effects associated with the various nuclei.

pentane at low temperature to give orange needles. Dilute solutions ($\simeq 10^{-2}$ M) of the product in acetone-d_6 are sufficiently stable to allow the recording of a good ^1H NMR spectrum, which shows that only isomers I and I' are present in the ratio 85/15, as indicated by the integrals of the resonances from the methylene protons, which appear as two separated quartets at δ 3.23 and 3.36. The resonances of the protons of the complexed phenyl ring lie in the range δ 5.5–6.1, and the spectra of the two species cannot be satisfactorily resolved; the signals due to the *meta* protons are completely overlapped, and those corresponding to the protons in *ortho* and *para* positions are only partially resolved. However, the spectra of the olefinic moieties, in the range δ 6.5–7.1, are sufficiently resolved to allow a careful analysis. The analysis of the spectrum of both isomers was carried out by computer simulation in the assumption of an A_2BCD spin system for the protons of the cyclopentadienyl residue and an AA'BB'C system for those of the complexed phenyl rings. The spectral data obtained are collected in Table 1.

The proton assignments were confirmed by the NOE data shown in Fig. 2.

Complexes I and I' have very similar physical properties and attempts to separate them by medium pressure chromatography failed. In contrast to the phenylcyclopentadiene ligand isomers [3a], which cannot be kept even at 0 °C, the corresponding TCC complexes are indefinitely stable as solid at room temperature because of their lower rate of dimerization. It was reported previously that electron-withdrawing substituents, such as NO_2 [3a,12], stabilize the cyclopentadienes.

Acyclic pentadienyls

The ^1H NMR spectra of the products obtained from the "open" pentadienyls indicate that mixtures of (η^6-phenyl-TCC)pentadiene isomers in which the phenyl group is linked at carbon 3 or 5 of the olefinic skeleton were formed. Medium pressure chromatography separated the two isomers, the fractions first eluted always being those corresponding to the 3-TCC-phenyl substituted pentadienes. The complexes obtained together with their isomer ratios are listed in Table 2.

3-TCC-phenylpentadienes. The ^1H NMR spectrum of the first chromatographic fraction recovered from the pentadienyl system shows that it is a mixture of the *trans*-3-(η^6-TCC-phenyl)-1,3-pentadiene (IVa), and the *cis*-3-(η^6-TCC-phenyl)-1,3-

Table 2

Phenylation of pentadienyl anions at the C(3) and C(5) carbon atoms with π-fluorobenzene-TCC

Pentadienyl anions	(TCC-phenyl)pentadienes		Isomeric ratio
	3-TCC-Ph	5-TCC-Ph	3-TCC-Ph/5-TCC-Ph
1,3-Pentadienyl [a]	IVa (80%) + IV′a (20%)	IVb (60%) + IV′b (40%)	1/5
2,4-Dimethyl-1,3-pentadienyl [a]	Va	Vb (91%) + V′b (9%)	7/1
1,1′,5,5′-Tetramethyl-1,3-pentadienyl [b]	VIa	VIb	1.3/1

[a] Potassium salt. [b] Lithium salt.

pentadiene (IV′a), in the ratio 5/1. The phenyl ring protons resonate in the range δ 5.5–5.7 and because of the overlap between the signals from the two species it was possible to identify clearly and to analyze by computer simulation only the spectrum of the isomer present in higher percentage, IVa. The signals from the olefinic protons of the two isomers are sufficiently resolved to enable a careful analysis to be carried out, an $ABCDE_3$ spin system being assumed for both isomers.

For methylated pentadiene derivatives only the olefins with unconjugated double bonds 3-(η^6-TCC-phenyl)-2,4-dimethyl-1,4-pentadiene (Va), and 3-(η^6-TCC phenyl)-1,1′,5,5′-tetramethyl-1,4-pentadiene (VIa), were formed. The spectral data for the 3-(TCC-phenyl)pentadienes are listed in Table 3.

The difference in the structures of the olefinic entities in the parent pentadiene, IVa or IV′a, compared with those for the methyl-substituted pentadienes, Va and VIa, suggests that different reaction pathways operate in the two cases (see below).

5-TCC-phenylpentadienes. The second chromatographic fraction corresponding to the 5-phenylated pentadiene is a mixture of *trans*-5-(η^6-TCC-phenyl)-1,3-pentadiene (IVb), and *cis*-5-(η^6-TCC-phenyl)-1,3-pentadiene (IV′b), in the ratio 3/2. The composition was estimated from the integrals of the methylene resonances, which appear as two well resolved doublets at δ 3.25 and 3.40. The spectra of the complexed phenyl moieties are completely overlapped, and it has not been possible to identify the resonances for the single isomers, whereas those corresponding to the olefinic portions are well separated and were analyzed by computer simulation as $ABCDEF_2$ spin systems.

A *trans*/*cis* isomeric mixture in the ratio 10/1 was obtained for the bis-methylated pentadiene, i.e. *trans*-5-(η^6-TCC-phenyl)-2,4-dimethyl-1,3-pentadiene (Vb) and *cis*-5-(η^6-TCC-phenyl)-2,4-dimethyl-1,3-pentadiene (V′b). The ^{1}H NMR spectra of the two species are considerally overlapped, and it was possible to analyze only the spectrum of the predominant isomer Vb. Pure *trans*-5-(η^6-TCC-phenyl)-1,1′,5,5′-tetramethyl-1,3-pentadiene (VIb) was obtained in the case of the tetramethyl compound.

The ^{1}H NMR spectral parameters of the 5-(TCC-phenyl)pentadienes are listed in Table 4.

Examination of the data in the last column of Table 2 shows that the structure of the pentadienyl base markedly influences the regioselectivity of the phenylation. With the parent pentadienyl base the 5-TCC-phenyl-substituted olefin is largely favoured, while the presence of the two electron-donating methyl groups in the positions 2 and 4 of the olefinic skeleton favours the 3-TCC-phenyl-substituted

Table 3

^{1}H NMR parameters for 3-(η^6-TCC-phenyl)pentadienes (IVa, IV'a, Va and VIa)

	IVa [a]	IV'a [a]	Va [a]	VIa [a]
H_i	Chemical shifts (ppm) [b]			
$o = o'$	5.690	[c]	5.630	5.597
$m = m'$	5.628	[c]	5.561	5.544
p	5.657	[c]	5.693	5.594
1a	5.399	5.086	5.110	1.774
1b	5.287	5.397	4.709	1.767
2	5.659	6.415	1.902	5.192
3	–	–	3.843	4.364
4	6.117	6.117	1.902	5.192
5a	1.898	1.953	5.110	1.774
5b	–	–	4.709	1.767
i,j	Coupling constants (Hz)			
$o,m = o',m'$	6.60 ± 0.03	[c]	6.67 ± 0.02	6.65 ± 0.04
$o,p = o',p$	1.03 ± 0.03	[c]	1.04 ± 0.01	1.00 ± 0.03
$o,m' = o',m$	0.34 ± 0.03	[c]	0.32 ± 0.02	0.34 ± 0.04
o,o'	1.73 ± 0.06	[c]	1.62 ± 0.02	1.79 ± 0.05
$m,p = m',p$	6.38 ± 0.03	[c]	6.33 ± 0.01	6.31 ± 0.03
m,m'	1.20 ± 0.06	[c]	1.36 ± 0.02	1.16 ± 0.04
$o,3 = o',3$	–	–	0.47 ± 0.02	0.66 ± 0.04
$m,3 = m',3$	–	–	−0.01 ± 0.02	−0.06 ± 0.03
$p,3$	–	–	–	−0.02 ± 0.04
1a,1b	1.61 ± 0.03	1.31 ± 0.03	1.62 ± 0.01	0.0 [d]
1a,2	11.22 ± 0.03	10.72 ± 0.03	−1.49 ± 0.01	−1.42 [d]
1a,3	–	–	0.00 ± 0.01	0.0 [d]
1a,4	1.24 ± 0.03	1.20 ± 0.05	–	–
1a,5a	0.46 ± 0.03	0.63 ± 0.02	–	–
1a,5b	–	–	–	–
1b,2	17.67 ± 0.03	17.31 ± 0.03	−0.84 ± 0.01	−1.41 [d]
1b,3	–	–	−1.07 ± 0.01	0.0 [d]
1b,4	0.59 ± 0.03	0.56 ± 0.05	–	–
1b,5a	0.47 ± 0.02	0.60 ± 0.02	–	–
1b,5b	–	–	–	–
2,3	–	–	0.3 [d]	9.50 [d]
2,4	0.65 ± 0.03	0.82 ± 0.05	–	–
2,5a	0.57 ± 0.02	0.76 ± 0.02	–	–
2,5b	–	–	–	–
3,4	–	–	0.3 [d]	9.50 [d]
3,5a	–	–	0.00 ± 0.01	0.0 [d]
3,5b	–	–	−1.07 ± 0.01	0.0 [d]
4,5a	7.13 ± 0.02	7.40 ± 0.03	−1.49 ± 0.01	−1.42 [d]
4,5b	–	–	−0.84 ± 0.01	−1.41 [d]
5a,5b	–		1.62 ± 0.01	0.0 [d]

[a] For proton labelling see Fig. 1; spectrometer frequency 400.13 MHz; solvent acetone-d_6 (10^{-2} M); $T = 300$ K. [b] From internal TMS; least square errors ±0.001. [c] The phenyl protons resonances are hidden by those of the predominant isomer IVa. [d] Values were not refined by iteration.

species. The presence of methyl groups at 1 and 5 positions in the tetramethylated pentadienyl base should favour the phenylation at the terminal carbon atoms, but the experimental data indicates that there is no regioselectivity. This can be

Table 4

^{1}H NMR parameters for 5-(η^6-TCC-phenyl)pentadienes (IVb, IV'b, Vb, V'b and VIb)

	IVb [a]	IV'b [a]	Vb [a,b]	VIb [a]
H_i	Chemical shifts (ppm) [c]			
$o = o'$	5.51 [d]	5.51 [d]	5.502	5.755
$m = m'$	5.69 [d]	5.69 [d]	5.700	5.518
p	5.51 [d]	5.51 [d]	5.507	5.693
1a	5.198	5.331	5.003	1.770
1b	5.059	5.218	4.846	1.765
2	6.391	6.821	1.853	5.864
3	6.254	6.229	5.901	6.401
4	5.856	5.602	1.787	5.730
5	3.250	3.406	3.426	1.433
i,j	Coupling constants (Hz)			
$o,m = o',m'$	[d]	[d]	6.45 ± 0.03	6.93 ± 0.04
$o,p = o',p$	[d]	[d]	1.07 ± 0.03	1.01 ± 0.03
$o,m' = o',m$	[d]	[d]	0.39 ± 0.03	0.12 ± 0.04
o,o'	[d]	[d]	1.66 ± 0.04	1.58 ± 0.05
$m,p = m',p$	[d]	[d]	6.40 ± 0.02	6.32 ± 0.04
m,m'	[d]	[d]	1.29 ± 0.03	1.51 ± 0.05
$o,5 = o',5$	[d]	[d]	0.18 ± 0.04	–
$m,5 = m',5$	[d]	[d]	-0.05 ± 0.02	–
$p,5$	[d]	[d]	-0.06 ± 0.03	–
1a,1b	1.78 ± 0.05	2.24 ± 0.04	2.34 ± 0.01	0.73 ± 0.01
1a,2	17.12 ± 0.05	16.59 ± 0.04	-1.53 ± 0.01	-1.29 ± 0.02
1a,3	-0.87 ± 0.05	-1.07 ± 0.04	-0.43 ± 0.01	0.00 ± 0.01
1a,4	0.58 ± 0.05	0.48 ± 0.04	0.00 ± 0.01	0.00 ± 0.01
1a,5	-0.57 ± 0.04	-0.58 ± 0.04	-0.5 [e]	–
1b,2	10.51 ± 0.05	11.19 ± 0.04	-0.96 ± 0.01	-1.11 ± 0.01
1b,3	-0.85 ± 0.05	-1.07 ± 0.04	-1.05 ± 0.01	0.00 ± 0.01
1b,4	0.66 ± 0.05	1.05 ± 0.05	0.00 ± 0.01	0.00 ± 0.01
1b,5	-0.54 ± 0.04	-0.58 ± 0.05	-0.5 [e]	–
2,3	10.12 ± 0.05	10.39 ± 0.04	-0.55 ± 0.01	10.68 ± 0.02
2,4	-0.71 ± 0.06	-1.09 ± 0.04	0.00 ± 0.01	-1.13 ± 0.02
2.5	0.15 ± 0.04	-0.02 ± 0.03	0.0 [e]	–
3,4	14.98 ± 0.05	10.53 ± 0.04	-1.53 ± 0.01	15.22 ± 0.01
3,5	-1.00 ± 0.04	-1.19 ± 0.04	-0.7 [e]	–
4,5	6.98 ± 0.04	7.68 ± 0.04	–	–

[a] For proton labelling see Fig. 1; spectrometer frequency 400.13 MHz; solvent acetone-d_6 (10^{-2} M); T 300 K. [b] *cis*-Isomer (V'b) chemical shifts: $(o) = (o') = 5.55$, $(m) = (m')$ 5.7, (p) 5.5, (1a) 5.0, (1b) 4.80, (2) 1.83, (3) 5.87, (4) 1.8, (5) 3.15 ppm. [c] From internal TMS; least square errors ± 0.001. [d] The phenyl proton spectra of the two isomers IVb and IV'b are completely overlapped. [e] Values not refined by iteration.

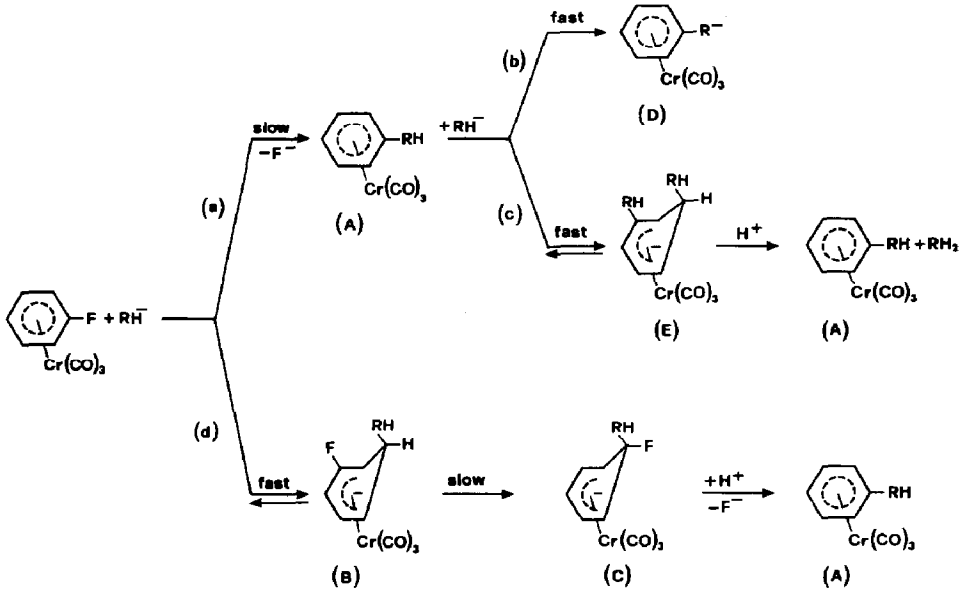
reasonably attributed to steric effects. The pattern of *trans/cis* isomeric ratios found for the set of the 5-TCC-phenylated species (second column of Table 2) is probably attributable to steric factors.

Reaction pathways

As stated above, the disappearance of TCC-fluorobenzene and the formation of the various complexes was monitored by TLC analysis. The progress of the reaction was also monitored by IR spectroscopy, and interesting mechanistic features were observed.

In the case of cyclopentadienyl, indenyl, and fluorenyl anions it was observed that the gradual disappearance of carbonyl stretching absorption bands at 1976 and 1900 cm^{-1} relative to TCC-fluorobenzene was accompanied by the growth of three new bands, at 1941, 1863, and 1839 for cyclopentadienyl, 1939, 1861, and 1837 for indenyl, and 1938, 1861, and 1834 cm^{-1} for fluorenyl systems. The number of bands and the values of their frequency are indicative of the formation of η^6-TCC-arylalkyl carbanions [10]. The behaviour is consistent with a mechanism in which the nucleophilic addition step is rate-determining, and the Meisenheimer-type anion intermediate, which would show a different IR pattern, does not accumulate during the reaction (see below). The complexed hydrocarbon so formed is then deprotonated by the excess of base to give the corresponding η^6-arylalkylcarbanion (cf. path (a)-(b) in Scheme 1).

For "open" pentadienyl bases the IR patterns are quite different. Immediately after the mixing of the reagents the C≡O absorptions due to TCC-fluorobenzene were absent, and bands at 1900, 1807, and 1757 cm^{-1} and at 1903, 1806, and 1728 cm^{-1} for 2,4-dimethylpentadienyl and 1,1′,5,5′-tetramethylpentadienyl systems, respectively, were present and the spectrum showed no further change. The carbonyl stretching patterns of the reaction mixtures are similar to those reported by Cooper and Leong [11] and by Semmelhack et al. [6a] for η^5-TCC-cyclohexadienyl anions, suggesting that, in contrast to those of the "cyclic" bases, the nucleophilic addition to TCC-fluorobenzene is a fast step in which a stable Meisenheimer-type intermediate is formed. Indeed, monitoring of the reaction by TLC on silica gel showed that the disappearance of TCC-fluorobenzene was a slow process and was accompanied by concurrent formation of the products. The discrepancy between the IR and TLC results can be explained by assuming the presence of two intermediates, **B** and **C** (Scheme 1), which have the same IR spectrum, and the interconversion of which must be the slow step of the reaction: hydrolysis on the silica of the TLC plate of



Scheme 1

the firstly formed intermediate **B** regenerates the starting complex, while that of the second one gives the substitution products.

The reaction routes for cyclic and acyclic bases are depicted in Scheme 1.

With the unsubstituted pentadienyl anion there seems to be competition between the pathway a–b, followed by the "cyclic" pentadienyl bases, and pathway d followed by 1,2-dimethyl- and 1,1′,5,5′-tetramethyl-pentadienyl "open" bases. For this system the results of the IR monitoring of the reaction mixture are intriguing: the spectrum (ν(C≡O) 1903, 1806, 1793 cm^{-1}) recorded immediately after the mixing of TCC-fluorobenzene with the nucleophile, indicates the presence of the same η^5-TCC-cyclohexadienyl anion (**B**) as was found in the case of the other "open" pentadienyl anions; however, as the reaction proceeds, three new bands grow up at 1891, 1791, and 1741 cm^{-1}. The frequencies of this set of bands are again characteristic of an η^5-TCC-cyclohexadienyl anion, but its structure must be different from that of the fluorinated species **B** and **C** (cf. Scheme 1). Independent experiments have shown that a set of bands at 1891, 1791, and 1741 cm^{-1} appears when potassium pentadienide and the neutral (η^6-TCC-phenyl)-pentadiene (IVb) are mixed. We believe that the growing species could be the anion **E** formed from **A** through step c. Before the hydrolysis step, formation of **A** is possible only through path a and, as well as rapid nucleophilic addition to give **E**, it can also undergo α-metallation by reaction with the excess of base to form **D**. Evidence of the formation of the anion **D** comes from the presence among the hydrolysis products of the isomers IVa and IV′a, which could not be formed by quenching of Meisenheimer-type anions. The increase in the intensity of absorption bands due to **E** with time corresponds to a slow formation of **A**, which could occur by removal of fluorobenzene-TCC from equilibrium step d.

Experimental

All operations were carried out under purified argon by standard Schlenk techniques. M.p.'s are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, University of Padova. IR and mass spectra were respectively recorded with a Perkin–Elmer 580B and a VG MM 16 spectrometer. The ^1H NMR spectra were recorded with WP-200 SY and AM 400 Bruker spectrometers. The proton spectra were analyzed by computer simulation on a Bruker Aspect-2000 computer by use of the Bruker PANIC program. Commercial grade di-n-butyl ether (Bu_2O) (Carlo Erba) and tetrahydrofuran (THF) (Carlo Erba) were distilled before use from potassium and potassium anthracenide, respectively. HPLC grade acetonitrile (Carlo Erba) was dried over P_2O_5 and distilled before use from anhydrous K_2CO_3. All the solvents used for syntheses with chromium derivatives were carefully deoxygenated by repeated freeze-and-thaw cycles. Fluorene (EGA chemie) was recrystallized from ethanol and sublimed in vacuo. Commercial grade indene (Fluka) and fluorobenzene (EGA Chemie) were distilled in vacuo. Cyclopentadiene was obtained by thermal cracking of the dimer (Fluka) immediate before use. 1,3-Pentadiene and 2,4-dimethyl-1,3-pentadiene were purchased from Aldrich Chemical Co.. 1,1′,5,5′-Tetramethyl-1,4-pentadiene was prepared from 6-methyl-3,5-heptadiene-2-one (ICN Pharmaceuticals, Inc.), and the CH_3Li-LiBr complex (Aldrich) as described by Hall [13].

Preparation of complexes

Potassium (or Lithium) (cyclo)pentadienyl anion was used in 2–3-fold excess with respect to TCC-fluorobenzene. After hydrolysis with NH_4Cl at 0 °C, extraction with ether and removal of solvent, the residue was filtered through a layer of silica gel to remove unchanged starting ligand and small amounts of decomposition products from the tricarbonylchromium complexes. The regio-isomers were separated by chromatography on silica gel column under medium pressure (petroleum ether/ethyl ether as eluent). The yield of TCC complexes was calculated with respect to TCC-fluorobenzene.

(TCC-phenyl)cyclopentadienes (I + I′, nc's).

A mixture of 0.468 g (2.0 mmol) of TCC-fluorobenzene and potassium cyclopentadienide, made from 0.8 g (12.1 mmol) of cyclopentadiene and ca. 0.47 g of K (ca. 12 mmol) in DME (40 ml), was kept for 1.5 h at 0 °C. Yield 0.54 g (97%) Yellow-orange solid. M.p. 92–93 °C (from pentane). (Found: C, 60.7; H, 3.4. $C_{14}H_{10}CrO_3$ calcd.: C, 60.9; H, 3.2%); IR spectrum (THF): $\bar{\nu}$(C≡O) 1962vs, and 1887vs cm^{-1}. Mass spectrum: M^+ 278 (calcd.: 278).

3-(TCC-phenyl)indene (II, nc)

A mixture of 0.840 g (3.6 mmol) of TCC-fluorobenzene and potassium indenide made by treatment of 0.875 g (7.68 mmol) of indene in THF (60 ml) with an excess of KH, was stirred for 2 h at 0 °C. Yield, 1.0 g (85%) Yellow solid. M.p. 135 °C (from THF/hexane). (Found: C, 67.4; H, 3.8. $C_{18}H_{12}CrO_3$ calcd.: C, 65.9; H, 3.7%). IR spectrum (THF): $\bar{\nu}$(C≡O) 1966vs, and 1892vs cm^{-1}. Mass spectrum: M^+ 328 (calcd.: 328).

9-(TCC-phenyl)fluorene (III, nc)

A mixture of 0.906 g (3.9 mmol) of TCC-fluorobenzene and potassium fluorenide, made from 1.2 g of fluorene in THF (60 ml) with an excess of KH, was stirred for 30 min at 0 °C. Yield, 1.03 g (70%) Yellow solid. M.p. 124 °C (from THF/hexane). (Found: C, 71.3; H, 3.6. $C_{22}H_{14}CrO_3$ calcd.: C, 69.9; H, 3.7%); IR spectrum (THF): $\bar{\nu}$(C≡O) 1966vs, and 1889vs cm^{-1}. Mass spectrum: M^+ 378 (calcd.: 378).

3-(TCC-phenyl)-1,3-pentadienes (IVa + IV′a, nc's) *and 5-(TCC-phenyl)-1,3-pentadiene* (IVb + IV′b, nc's)

A mixture of 0.928 g (4.0 mmol) of TCC-fluorobenzene in THF (15 ml) and 19 ml of a 0.43 *M* solution of potassium pentadienide in THF, made from 1,3-pentadiene and potassium in the presence of triethylamine (7 ml), was kept for 3 h at 0 °C. Yield, 0.820 g (73%).

IVa + IV′a (20%). Pale yellow oil. (Found: C, 61.10; H, 4.96. $C_{14}H_{12}CrO_3$ calcd.: C, 60.0; H, 4.32%). IR spectrum (THF): $\bar{\nu}$(C≡O) 1964, 1893, and 1883 cm^{-1}. Mass spectrum: M^+ 280 (calcd.: 280).

IVb + IV′b (80%). Yellow-orange oil. (Found: C, 61.73; H 4.70. $C_{14}H_{12}CrO_3$ calcd.: C, 60.0, H 4.32%). IR spectrum (THF): $\bar{\nu}$(C≡O) 1964, 1893 and 1881 cm^{-1}. Mass spectrum M^+ 280 (calcd.: 280).

3-(TCC-phenyl)2,4-dimethyl-1,4-pentadiene (Va, nc), *and 5-(TCC-phenyl)2,4-dimethyl-1,3-pentadienes* (Vb + V′b, nc's)

A mixture of 0.931 g (4.0 mmol) of TCC-fluorobenzene in 12 ml THF and ca. 10 mmol of potassium 2,4-dimethylpentadienide in 20 ml THF, made from 2,4-di-

methyl-1,3-pentadiene and potassium in the presence of triethyl amine (2 ml), was kept for 2 h at 0 °C. Yield 0.900 g (73%).

Va (85%). Yellow solid. M.p. 64–65 °C (from hexane). (Found: C, 62.0; H, 5.3. $C_{16}H_{16}CrO_3$ calcd.: C, 62.3; H, 5.2%); IR spectrum (THF): $\bar{\nu}$(C≡O) 1963, 1893, and 1880 cm^{-1}. Mass spectrum: M^+ 308 (calcd.: 308).

Vb + V′b (15%). Yellow oil (Found: C, 62.5; H, 5.2. $C_{16}H_{16}CrO_3$ calcd.: C, 62.3; H, 5.2%. IR spectrum (THF): $\bar{\nu}$(C≡O) 1964, 1894 and 1880 cm^{-1}. Mass spectrum: M^+ 308 (calcd.: 308).

3-(TCC-phenyl)-1,1′,5,5′-tetramethyl-1,4-pentadiene (VIa, nc) and *5-(TCC-phenyl)-1,1′,5,5′-tetramethyl-1,3-pentadiene* (VIb)

2,6-Dimethyl-2,5-heptadiene (0.400 g, 3.2 mmol) was added to 2 ml of a 1.6 *M* solution of n-BuLi in hexane containing 0.5 ml of TEMDA. After 1 h stirring at room temperature, 0.400 g (1.7 mmol) of TCC-fluorobenzene in 5 ml THF was added to the brown solution of the base and kept for 1 h at 0 °C. Yield 0.365 g (63%).

VIa (60%). Yellow solid. M.p. 77–78 °C (from hexane). (Found: C, 64.2; H, 60. $C_{18}H_{20}CrCO_3$ calcd.: C, 64.3; H, 6.0%); IR spectrum (THF): $\bar{\nu}$(C≡O) 1962, 1890, and 1881 cm^{-1}. Mass spectrum M^+ 336 (calcd.: 336).

VIb (40%). Pale yellow solid. M.p. 88 °C (from hexane) (Found: C, 64.1; H, 6.1. $C_{18}H_{20}CrCO_3$ calcd.: C, 64.3; H, 6.0%). IR spectrum (THF): $\bar{\nu}$(C≡O) 1962, 1890, and 1881 cm^{-1}. Mass spectrum: M^+ 336 (calcd.: 336).

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References

1 A. Ceccon, A. Gambaro, A. Venzo, V. Lucchini, T.E. Bitterwolf, J. Shade, J. Organomet. Chem., 327 (1987) 55; and previous papers of the series.
2 (a) S. Top, G. Jauen, J. Organomet. Chem., 182 (1979) 381; (b) C.A.L. Mahaffy, P.L. Pauson, Inorg. Synth., 19 (1979) 154.
3 (a) R. Wahren, J. Organomet. Chem., 57 (1973) 415; (b) E.S. Bowmann, G.B. Hughes, J.B. Grutzner, J. Am. Chem. Soc., 98 (1976) 8273.
4 A. Ceccon, A. Gambaro, A. Venzo, unpublished results.
5 C. Prévost, P. Miginiac, L. Miginiac-Groizeleau, Bull. Soc. Chem. Fr., 101 (1964) 2485.
6 (a) M.F. Semmelhack, H.T. Hall, J. Am. Chem. Soc., 96 (1974) 7091, 7092; (b) M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thebtaranonth, W. Wulff, A. Yamashita, Tetrahedron, 37 (1981) 3957; (c) A.C. Knipe, S.J. McGuiness, W.E. Watts, J. Chem. Soc. Chem. Commun., (1979) 842; (d) A.C. Knipe, S.J. McGuiness, W.E. Watts, J. Chem. Soc. Perkin II, (1981), 193; (e) J.F. Bunnett, H. Herrmann, J. Org. Chem., 36 (1971) 4081.
7 B. Nicholls, M.C. Whiting, J. Chem. Soc., (1959) 551.
8 A.P. Hagen, P.J. Russo, Inorg. Syntheses, 17 (1977) 104.
9 H. Yasuda, A. Nakamura, J. Organomet. Chem., 285 (1985) 15, and ref. therein.
10 N.A. Ustynyuk, B.V. Lokshin, Yu.F. Oprunenko, V.A. Roznyatovsky, Yu.N. Luzikov, A. Ustynyuk, J. Organomet. Chem., 202 (1980) 279.
11 V.S. Leong, N.J. Cooper, J. Am. Chem. Soc., 110 (1988) 2644.
12 N.A. Ogorodnikova, A.A. Koridze, S.P. Gubin, J. Organomet. Chem., 215 (1981) 293.
13 J.S. Rayan Zilenovski, S.S. Hall, J. Org. Chem., 44 (1979) 1159.