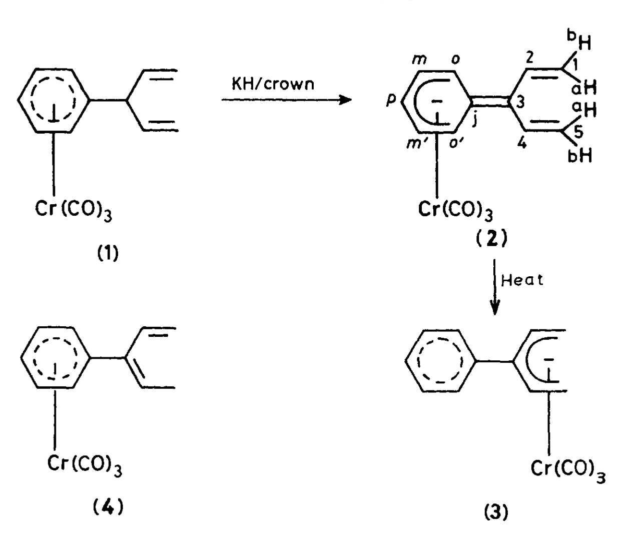
Metal-stabilized Carbanions. The (3-Phenyl-η^5-pentadienyl)tricarbonylchromium Anion

Alberto Ceccon, Alessandro Gambaro, and Alfonso Venzo
Istituto di Chimica-Fisica, Università di Padova, 35131 Padova, Italy

An 'open' pentadienyl anion π-co-ordinated with $Cr(CO)_3$ is obtained by the metal migration occurring in the (pentadien-3-yl-η^6-benzene)tricarbonylchromium anion.

$\eta^6 \rightarrow \eta^5$ haptotropic shifts of the tricarbonylchromium group in condensed systems like fluorenyl,[1] indenyl,[2] and benzocycloheptatrienyl[3] anions are well known. We now report a new example of such a shift involving an open-chain, rather than a condensed, system, namely, the (pentadien-3-yl-η^6-benzene)tricarbonylchromium anion (**2**).

The anion (**2**) was prepared by quantitative metallation of the corresponding neutral species (**1**) with KH–18-crown-6 in anhydrous, oxygen-free tetrahydrofuran (THF) under argon (Scheme 1). Quenching with aqueous THF immediately after ionization produced (**1**) and its isomer (**4**) in the ratio 2:3, as shown by g.l.c. and n.m.r. spectroscopy.



Scheme 1

Table 1. ${}^1H$ n.m.r. parameters (δ values; J in Hz)[a] for the anions (**2**) and (**3**) in [${}^2H_8$]THF, counter-ion K^+–18-crown-6, T 304 K.

	Aryl ring			Pentadienyl		
Anion	$\delta_{o,o'}$	$\delta_{m,m'}$	δ_p	$\delta_{1a,5a}$	$\delta_{1b,5b}$	$\delta_{2,4}$
(**2**)	4.599	5.055	4.463	4.651	4.316	6.346
(**3**)	7.548	7.120	6.988	0.006	2.201	5.127

Coupling constants

(**2**) aryl ring: $J_{o,m} = J_{o',m'} = 7.80$; $J_{o,p} = J_{o',p'} = 0.70$; $J_{o,m'} = J_{o',m} = 0.04$; $J_{o,o'} = 0.93$; $J_{m,p} = J_{m',p} = 5.82$; $J_{m,m'} = 0.42$
pentadienyl: $J_{1a,1b} = J_{5a,5b} = 2.92$; $J_{1a,2} = J_{4,5a} = 17.61$; $J_{1a,4} = J_{2,5a} = 0.02$; $J_{1a,5b}, J_{1a,5a}, J_{1b,4}, J_{1b,5b}, J_{1b,5a}, J_{2b,5b} < 0.01$; $J_{1b,2} = J_{4,5b} = 11.26$; $J_{2,4} = 0.82$

(**3**) aryl ring: $J_{o,m} = J_{o',m'} = 7.81$; $J_{o,p} = J_{o',p'} = 1.27$; $J_{o,m'} = J_{o',m} = 0.57$; $J_{o,o'} = 2.21$; $J_{m,p} = J_{m',p} = 7.42$; $J_{m,m'} = 1.46$
pentadienyl: $J_{1a,1b} = J_{5a,5b} = 1.27$; $J_{1a,2} = J_{4,5a} = 11.29$; $J_{1a,4} = J_{2,5a} = 0.51$; $J_{1a,5b} = J_{1b,5a} = 0.07$; $J_{1a,5a} = -0.07$; $J_{1b,2} = J_{4,5b} = 10.00$; $J_{1b,4} = J_{2,5b} = 0.06$ $J_{1b,5b} = 0$; $J_{2,4} = 1.39$

[a] Chemical shifts from internal Me_4Si; see formulae for numbering. The spectral parameters were obtained by computer simulation on an Aspect 2000 Bruker computer using the Bruker PANIC program.

The ${}^1H$ n.m.r. spectrum of the freshly prepared solution of (**2**) in [${}^2H_8$]THF is shown in Figure 1(A), and the corresponding spectral parameters collected in Table 1.The values and the trend of the chemical shifts and of the J(H,H) values suggests for the aryl–$Cr(CO)_3$ moiety the same planar η^5-benzylidene–$Cr(CO)_3$ structure (bearing a coplanar exocyclic double bond) as that for the $Cr(CO)_3$-complexed di- and tri-phenylmethyl carbanions.[4]

The anion (**2**) is not stable and the $Cr(CO)_3$ unit irreversibly migrates towards the acyclic pentadienyl moiety to form the isomer (**3**). The isomerization process was monitored by ${}^1H$ n.m.r. spectroscopy at various temperatures, and an intermediate situation is shown in Figure 1(B). Use of the first-order kinetic equation for an irreversible process gave satisfactory plots ($r \geqslant 0.997$) up to 90% reaction. From the values for the rate constant, $10^4 k_{\text{isom.}} = 0.71$ (at 304 K), 2.00 (314 K), and 7.87 (324 K) s^{-1}, the activation parameters $\Delta H^\ddagger = 23.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -0.8 \pm 1.0$ cal K^{-1} (at 314 K) were calculated.†

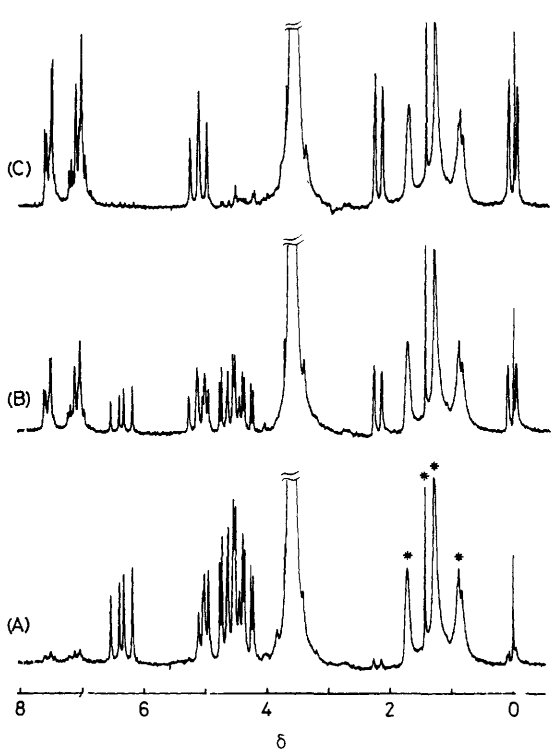


Figure 1. Changes in the ${}^1H$ n.m.r. spectrum of the anion (**2**) in [${}^2H_8$]THF at 324 K, counter-ion K^+, Me_4Si as internal standard. Asterisks indicate impurities (mainly mineral oil). The large peak at δ *ca.* 3.6 is due to the 18-crown-6 ether, (A), initial spectrum; (B), spectrum after *ca.* 15 min; (C), final spectrum.

Unlike (**2**), treatment of the solution of (**3**) with aqueous THF led to complete decomposition of the complex. Morever, attempted isolation of the anions (**2**) and (**3**) as solid salts was unsuccessful.

The spectrum of the final solution is shown in Figure 1(C) and the corresponding spectral parameters are in Table 1. We attribute the final spectrum to the 'open' pentadienyl-complexed anion (**3**) on the basis of the following arguments: (i) the aryl ring resonances in (**3**) are strongly shifted downfield with respect to those in (**2**), indicating loss of co-ordination with $Cr(CO)_3$; in addition, the noticeable difference between the $J_{o,m}$ and $J_{m,p}$ values, which is typical of a quinone-like η^5-$Cr(CO)_3$–benzylidene anionic structure,[4] is lost in (**3**); (ii) the proton resonances of the pentadienyl moiety are strongly shifted upfield with respect to the corresponding signals both in (**2**) and in other unco-ordinated pentadienyl anions.[5] These results have been confirmed by the variations of the ${}^{13}C$ n.m.r. chemical shifts and of the i.r. C≡O stretching frequencies‡ observed on going from (**2**) to (**3**). Moreover, both the ${}^1H$ and the ${}^{13}C$ n.m.r. chemical shifts of

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† 1 cal = 4.184 J.

‡ ${}^{13}C$ N.m.r.: (**2**) (THF–18-crown-6): δ 74.54 (*o*,*o*′), 99.89 (*m*,*m*′), 75.39 (*p*), 135.50 (j), 100.67 (1,5), 135.18 (2,4), 93.65 (3), and 239.94 (C≡O); (**3**) (THF–18-crown-6): δ 129.00 (*o*,*o*′), 127.77 (*m*,*m*′), 125.11 (*p*), 148.36 (j), 53.29 (1,5), 100.80 (2,4), 103.92 (3), and 241.89 (C≡O); $\nu_{max.}$ (C≡O): (**1**) (THF): 1965 and 1889 cm^{-1}; (**2**) (THF–18-crown-6): 1917, 1832, and 1809 cm^{-1}; (**3**) (THF–18-crown-6): 1900, 1812, and 1775 cm^{-1}.

the pentadienyl moiety in (**3**) closely resemble those found for other 'open' metal-co-ordinated pentadienyl anions.[6]

The re-aromatization of the aryl ring on going from (**2**) to (**3**) and the η^5-direct bonding of the electron-withdrawing $Cr(CO)_3$ group to the anionic pentadienyl moiety seem to be the driving force for this novel haptotropic rearrangement occurring between co-ordinative sites separated by a carbon–carbon bond.

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