Journal of Organometallic Chemistry, 195 (1980) C5—C8

Preliminary communication

A CARBON-13 NMR SPECTROSCOPIC STUDY OF A $Cr(CO)_3$-STABILISED BENZYL ANION

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(Received May 2nd, 1980)

Summary

^{13}C and ^1H NMR chemical shift and coupling constant data indicate that the bis(tricarbonylchromium)diphenylmethyl carbanion is stabilised by delocalisation of negative charge onto the carbonyl moieties. In contrast to the analogous cation, there does not appear to be a direct interaction between the chromium and the α-carbon atom.

In recent years the synthetic potential of (arene)$Cr(CO)_3$ complexes has been amply demonstrated, and many hitherto difficult functional group transformations have been facilitated [1,2]. One of the most original characteristics of this series is the hermaphroditic ability to enhance the kinetic generation and the stabilization of either carbocations or carbanions in the benzylic position [3]. Recently, several such π-complexed carbocations have been isolated and analyzed spectroscopically thus permitting a greater understanding of the stabilizing factors [4]. In contrast, although the chemistry of the analogous carbanions has begun to be explored, we are not aware of any direct observations on the intermediates themselves, except for η^6-fluorenetricarbonylchromium in which the $Cr(CO)_3$ moiety migrates to the 5-membered ring [5]. We now report the synthesis and properties of the bis(tricarbonylchromium)diphenylmethyl carbanion (I).

Bis(tricarbonylchromium)diphenylmethane (II) [6] was treated with an excess of t-BuOK in dry THF for 5 min at room temperature under an argon atmosphere. Very dry hexane was then added to the carefully filtered and concentrated solution; the anion I precipitated as small orange crystals of its K^+ salt (70% yield). These crystals were reasonably stable at room temperature under argon for almost two days. The spectroscopic characteristics of complexes I and II are presented in Table 1.

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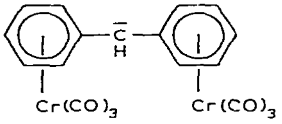
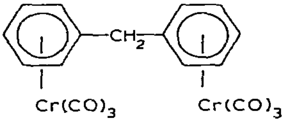
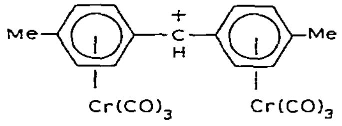
TABLE 1

SPECTRAL CHARACTERISTICS OF BENZYL ANIONIC, NEUTRAL AND CATIONIC $Cr(CO)_3$ COMPLEXES

				
C(1)^{a,b}	135.4	(t, ^2J(CH) 6.4)	112.1	117.1
C(2)	99.9	(dd, ^1J(CH) 169.4 ^2J(CH) 7.3)	95.1	97.8
C(3)	82.2	(ddd, ^1J(CH) 167.4, ^2J(CH) $\sim$ 12, ^2J(CH) $\sim$ 6)	94.9	96.4
C(4)	79.4	(dt, ^1J(CH) 174.9, ^2J(CH) 6.6)	93.4	—
C_α	77.4	(d, ^1J(CH) 153)	38.6	141.4
CO	238.7		233.8	230.8
H(2)	4.76	(d, ^3J(HH) 6)	5.41	—
H(3)	5.25	(t, ^3J(HH) 6)	5.41	—
H(4)	4.47	(d, ^3J(HH) 6)	5.41	—
H_α	3.68	(s)	3.37	—
ν(CO)^{c,d}	1941, 1858 cm^{-1}		1975, 1901 cm^{-1}	2030, 1980 cm^{-1}

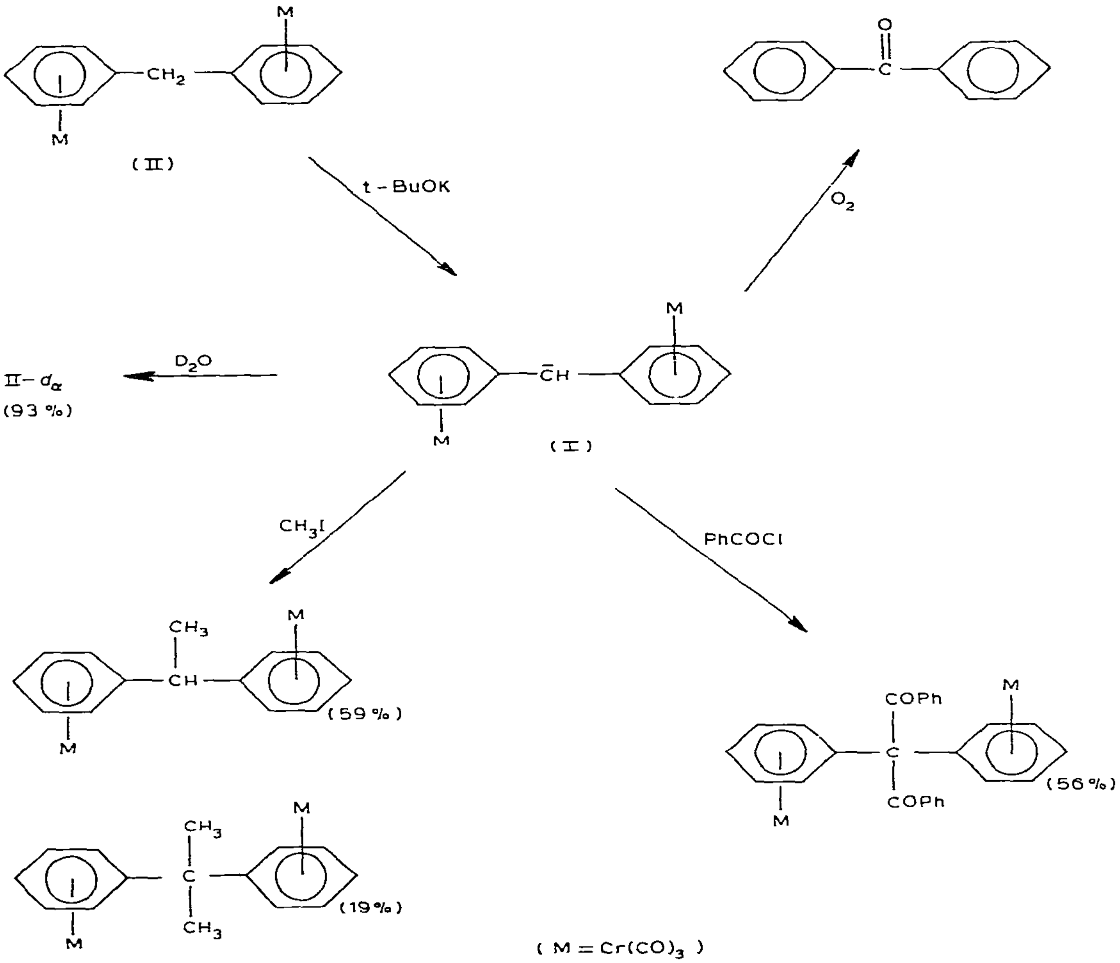
[a] ^{13}C NMR spectra were recorded in THF-d_8 on a Bruker WH-80 spectrometer. [b] Shifts in δ units, J in Hz, dd is doublet of doublets, etc. [c] A_1 and E modes respectively, solvent THF. [d] Data for the cations taken from refs. [4a] and [4d].

The $^{13}C_\alpha$ chemical shift found for the salt I (77.4 ppm) is downfield from that of the sp^3-hybridized precursor II (38.6 ppm). Interestingly, the same tendency has also been reported for the related $Cr(CO)_3$-stabilized carbenium ions ($^{13}C_\alpha$; 141.4 ppm) as well as for the lithium salt of the free ligand [7]. In the absence of rehybridization the ^{13}C chemical shift in aromatic molecules is proportional to the local charge density [8]. However, ^{13}C chemical shifts depend not only on the charge density at the carbon atom but also on hybridization and on anisotropic, diamagnetic and paramagnetic effects [9]; so, a direct correlation between ^{13}C shieldings and charge distribution may not obtain. In the case of diphenylmethyllithium, the downfield shift of the $^{13}C_\alpha$ resonance has been interpreted as direct evidence for the sp^2 hybridization of the α-carbon atom [7].

It is noticeable that, for the benzylic nuclei, the spectral changes observed in going from the diphenylmethane to the anion are very similar for the free and complexed molecules. Thus, ΔC_{free} is 43 ppm while ΔC_{cmplx} is 39 ppm; ΔH_{free} is 0.33 ppm while ΔH_{cmplx} is 0.31 ppm. These data suggest that there is no direct interaction between the chromium and the benzylic carbon atom such as has been postulated for the analogous carbocation [4b,c]; of course, in the present case there is no vacant orbital available to accept electron density from a suitably oriented chromium d orbital.

The ^{13}C—H spin—spin coupling constants are generally of the order of 160—200 Hz for sp^2 carbons and it is believed that ^1J(C—H) is decreased by a negative charge [7]. The value for $^1J(C_\alpha$—H) of 153 Hz in I suggests a less localized negative charge than in $(C_6H_5)_2$CHLi for which $^1J(C_\alpha$—H) is 142 Hz. Olah et al. [7] have rationalized this increased value of ${}^1J(C_\alpha—H)$ upon formation of the anion* by involving sp^2 hybridization. Such a planar structure would facilitate resonance delocalisation of the negative charge onto the aromatic ring, and indeed a marked shielding of the *ortho* and *para* protons (ΔH(2) 0.65 ppm, ΔH(4) 0.94 ppm) is observed in the π-complexed anion. Arguments based solely on the ring-current contribution to the α-proton shift are, however, somewhat ambiguous as local anisotropic contributions to protons in close proximity to free or π-complexed arenes are known to be important factors [10].

What then is the role of the tricarbonylchromium moiety? Clearly, the excess electron density is siphoned off via the metal onto the carbonyl ligands which then exhibit low ν(CO) values and a deshielding of the ^{13}CO resonance relative to the neutral precursor. The changes in carbonyl chemical shifts and infrared stretching frequencies of Seyferth's closely analogous cation [4a], relative to $(C_6H_5)_2CH_2[Cr(CO)_3]_2$, are similar but of opposite sign to those for the anion discussed here.



SCHEME 1

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*The increase in ${}^1J$(CH) is 16 Hz in the free anion and 19 Hz in the Cr(CO)$_3$ complex.

The species I with only a fractional negative charge at C_α does not show abnormally lowered reactivity in contrast to the analogous cation whose reactivity is considerably modified [4a]. Thus, the electron-withdrawing $Cr(CO)_3$ unit increases the kinetic acidity of the α-proton [3], assists the delocalisation of the incipient negative charge but does not inhibit the chemistry of the anions, as exemplified in Scheme 1.

ACKNOWLEDGEMENT

We thank D.G.R.S.T. for financial support.

References

1 G. Jaouen in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Academic Press, New York, N.Y., Vol. 2, Chapter 2, 1978.
2 M.F. Semmelhack, Ann. N.Y. Acad. Sci., 295 (1977) 36.
3 G. Jaouen, Ann. N.Y. Acad. Sci., 295 (1977) 59.
4 (a) D. Seyferth, J.S. Merola and C.S. Eschbach, J. Amer. Chem. Soc., 100 (1978) 4124; (b) M. Acampora, A. Ceccon, M. Dal Farra, G. Giacometti and G. Rigatti, J. Chem. Soc. Perkin II, (1977) 483; (c) A. Ceccon, A. Bobbo and A. Venzo, J. Organometal. Chem., 162 (1978) 311; (d) M. Acampora, A. Ceccon, M. Dal Farra and G. Giacometti, J. Chem. Soc. Chem. Commun., (1975) 871.
5 (a) K.M. Nicholas, R.C. Kerber and E.I. Stiefel, Inorg. Chem., 10 (1971) 1519; (b) A.N. Nesmeyanov, N.A. Ustynuk, L.G. Makarova, S. Andre, Yu.A. Ustynuk, L.N. Novikova and Yu.N. Luzikov, J. Organometal. Chem., 154 (1978) 45.
6 G. Jaouen and S. Top, J. Organometal. Chem., 182 (1979) 381.
7 R. Waack, M.A. Doran, E.B. Baker and G.A. Olah, J. Amer. Chem. Soc., 88 (1966) 1272.
8 H. Spiesecke and W.G. Schneider, Tetrahedron Lett., (1961) 468.
9 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, N.Y., Chapter 6, 1972.
10 A. Agarwal, J.A. Barnes, J.L. Fletcher, M.J. McGlinchey and B.G. Sayer, Can. J. Chem., 55 (1977) 2575; M.M. Maricq, J.S. Waugh, J.L. Fletcher and M.J. McGlinchey, J. Amer. Chem. Soc., 100 (1978) 6902.