The Effect of the Iron Tricarbonyl Group on the π-Electron Distribution in Aromatic Ligands

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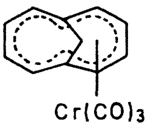
Summary H–H spin–spin coupling constants have been determined for benzocyclobutadiene- and anthracene-iron tricarbonyl and the electronic structure of the ligands is discussed with respect to these data and those for related compounds.



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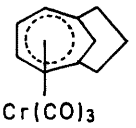

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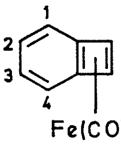

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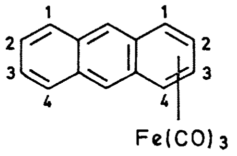

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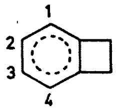

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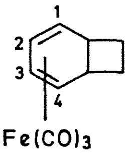

(6)

INDIRECT spin–spin coupling constants between protons provide valuable information about the π-electronic structure of cyclic conjugated systems.[1] The extension of correlations derived for cyclic olefins and aromatic compounds to ligands in metal carbonyl complexes recently established the aromatic and homoaromatic structures of the chromium tricarbonyl complexes (**1**) and (**2**) derived from 1,6-methano[10]annulene[2] and tricyclo[4,3,1,$0^{1,6}$]-deca-2,4-diene,[3] respectively.

In order to test further the effect of metal carbonyl groups on the π-electron distribution in unsaturated ligands, we have analysed the n.m.r. spectra of benzocyclobutadiene- and anthracene-iron tricarbonyl (**3**,**4**),[4,5] and, for comparison, those of benzocyclobutene (**5**)[6] and bicyclo[4,2,0]octa-2,4-dieneiron tricarbonyl (**6**).[7,8] Details of the analyses will be given in the full paper. The results discussed here are shown in the Table.

For (**3**), the observed ratios of the vicinal as well as the

H–H *Coupling constants* (*in Hz*) *for compounds* (**3**)—(**6**), *naphthalene, and anthracene*

	$J_{1,2}=J_{3,4}$	$J_{2,3}$	$J_{1,3}=J_{2,4}$	$J_{1,4}$	Lit.
(**3**)	8·61	6·77	0·68	1·57	This work
(**4**)	6·29[a]	4·21	1·48	*ca.* 0	”
	8·14[b]	6·95	1·26	0·63	”
(**5**)	7·36	7·78	0·98	1·06	”
(**6**)	6·59	4·23	1·62	0·20	,,
Naphthalene	8·28	6·85	1·24	0·74	Ref. 10
Anthracene	8·55	6·59	1·20	0·82	Ref. 10

[a] Co-ordinated ring.
[b] Unco-ordinated ring.

long-range coupling constants indicate bond fixation in the six-membered ring. This becomes especially evident on comparing the data with those found for (**5**) where similar strain effects due to the presence of the four-membered ring should operate.† In (**3**), therefore, the electron demand of the iron tricarbonyl group leads to a reduction of delocalization of π-electrons in the benzene ring.[9]

In contrast, complex formation with the anthracene ligand as in (**4**) results in the fixation of a "butadiene" unit in the ring bonded to the iron tricarbonyl group and enhanced π-delocalization for the residual "naphthalene" unit. The coupling constants in the former part of the molecule are similar to those found for olefinic systems, as for example (**6**). On the other hand, the coupling constants in the uncomplexed outer ring are closer to those in naphthalene than those in anthracene.[10]

The bonding requirements of the iron tricarbonyl group are sufficient to change the nature of the π-electron distribution in the ligand. A possible loss of delocalization energy, therefore, must be overcome by the bonding energy gained in the complex. Preliminary results on the X-ray structure determination of several vinyl-substituted benzenes and naphthalenes and especially the bond length reported for a methoxycarbonyl derivative of (**3**)[11] support our conclusions drawn from the n.m.r. results. The suggestion[11] that unlike the $Fe(CO)_3$ group the $Cr(CO)_3$ group does not lead to appreciable π-bond fixation in the ligand, is also borne out by n.m.r. results for (**1**)[2] and naphthalenechromium tricarbonyl.[12]

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† Since the strain effect tends to increase the magnitude of $J_{2,3}$ and to decrease that of $J_{1,2}$ (ref. 1b), the actual alteration of these constants in (**3**) due to the presence of the iron tricarbonyl group is larger than observed.

[1] (a) H. Günther, *Tetrahedron Letters*, 1967, 2967; (b) J. B. Pawliczek and H. Günther, *Tetrahedron*, 1970, **26**, 1755, and literature cited therein.

[2] H. Günther, R. Wenzl, and W. Grimme, *J. Amer. Chem. Soc.*, 1969, **91**, 3808.

[3] W.-E. Bleck, W. Grimme, H. Günther, and E. Vogel, *Angew Chem.*, 1970, **82**, 292.

[4] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 131.

[5] T. A. Manuel, *Inorg. Chem.*, 1964, **3**, 1794.

[6] M. P. Cava and D. R. Napier, *J. Amer. Chem., Soc.*, 1956, **78**, 500.

[7] T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 336.

[8] H. Günther, lecture given at the meeting of the German Chemical Society, Hamburg, Sept. 15—20, 1969; for a report see H. Günther and R. Wenzl, *Angew. Chem.*, 1969, **81**, 919; *Angew. Chem. Internat. Edn.*, 1969, **8**, 900. In this note, the data for compounds (**3**) and (**4**) given in the table are mistakenly interchanged.

[9] It is interesting to note, however, that a di-derivative of benzocyclobutadiene with a second $Fe(CO)_3$ group in the six-membered ring is not formed (G. F. Emerson, cited by B. J. Nicholson, *J. Amer. Chem. Soc.*, 1966, **88**, 5156, and independent observations in our laboratory).

[10] J. B. Pawliczek and H. Günther, *Z. Naturforsch.*, 1969, **24**b, 1068.

[11] R. E. Davis and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 716.

[12] B. Deubzer, H. P. Fritz, C. G. Kreiter, and K. Öfele, *J. Organometallic Chem.*, 1967, **7**, 289.