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Preliminary communication

anti-7,8-Benzotricyclo[4.2.0.$0^{2,5}$]deca-3,7,9-triene complexes of iron, molybdenum and chromium

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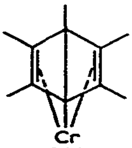
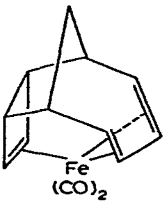
In the variegated field of oligoolefin transition metal-π complexes, there are very few cases in which the metal is simultaneously coordinated to two or more double bonds which are neither conjugated nor belong to the same ring in a polycyclic molecule. To the best of our knowledge the only complexes reported to possess this rare π-coordination feature, are the hexamethyl-Dewar-benzene complex (I)[1,2], the irradiation product of cyclobutadiene · $Fe(CO)_3$ and cycloheptatriene (II)[3], and the molybdenum complex of 7,8-dimethyltricyclo[4.2.0.$0^{2,5}$]deca-3,9-diene (III) reported by Nenitzescu *et al.*[4] (who characterized the complex only by elemental analysis).



(I)



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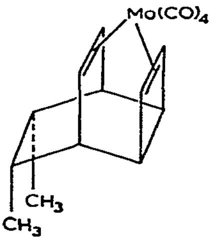


(III)

The elegant synthesis of *anti*-7, 8-benzotricyclo[4.2.0.$0^{2,5}$]deca-3, 7, 9-triene (IV) has been reported by Paquette[5], and we now describe the preparation and characterization of some transition-metal-π-complexes of this ligand. On refluxing (IV) with $M(CO)_6$ (M = Mo,Cr) in n-Bu_2O, complexes of benzotricyclodecatriene·$M(CO)_4$ (Va,b) are obtained as yellow air stable needles in 50 and 40% yield respectively★. The preparation of the corresponding iron complex (Vc) involved reaction of (IV) with $Fe_2(CO)_9$ in hexane/benzene at 55° to give yellow-orange crystals in 60% yield★. Under similar conditions, the *cis*-dichloro precursor of (IV)(VI) did not react at all with $Fe_2(CO)_9$.

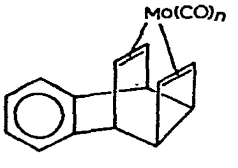
★All new compounds gave satisfactory C, H and M analysis and/or mass spectra.

TABLE 1

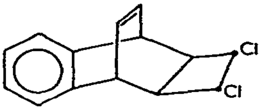
PROPERTIES OF THE BENZOTRICYCLODECATRIENE COMPLEXES

Compound	m.p. (C°)	$\nu(CO)_{max}$ (cm^{-1})	$\tau^{a,c}$						
			Aryl	Vinyl	Δδ	Cyclobutene vinyl	Δδ	Methine	Cyclobutene methine
IV	–	–	2.9 (m,4H)	3.82 (t,2H)	–	3.98 (s,2H)	–	6.3 (m,2H)	7.38 (t,2H)
Va	174-176(d)	2040, 1970, 1915[b]	2.92 (s,4H)	5.2 (t,2H)	1.42	4.92 (t,2H)	0.94	5.98 (m,2H)	7.38 (m,2H)
Vb	200(d)	2040, 1955, 1920[b]	2.92 (s,4H)	5.61 (t,2H)	1.79	5.26 (t,2H)	1.28	5.90 (m,2H)	7.52 (m,2H)
Vc	124-126(d)	2035, 1975, 1963[b]	2.99 (s,4H)	6.00 (m,2H)	2.18	5.49 (t,2H)	1.51	5.84 (m,2H)	7.52 (m,2H)

[a] All NMR spectra were taken in $CDCl_3$/TMS at 100 MHz. [b] Hexane. [c] Double irradiation of Va, Vb and Vc made possible unequivocal assignment of cyclobutene–vinyl, the bridge-vinyl and methine protons.



(Va: M=Mo, n=4;
Vb: M=Cr, n=4;
Vc: M=Fe, n=3)



(VI)

The IR and PMR data were in good agreement with the proposed structures (Table 1). Complexes produced by rearrangement of the skeleton could not be detected in any of the reaction mixtures. Furthermore, on heating at 160° in decalin for 12 h, Va was recovered unchanged, as was also Vc after irradiation at 254 nm for 12 h.

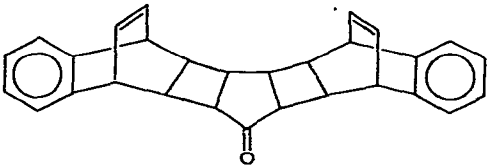
The PMR spectra of the three complexes Va-Vc, exhibit two main features:

(a) The protons of both the bridge and cyclobutene double bonds exhibit medium upfield shifts[6][★]. The bridge vinyl protons absorb at higher field than those of the cyclobutene double bond.

(b) There is definite spin-spin interaction between the junction and vinyl cyclobutene protons in contrast to the situation with the uncomplexed molecule (IV) and related compounds[7]. This might be rationalized by the decrease in bond order of the cyclobutene double bond *i.e.* increase of the sp^3 character of the corresponding carbon atoms (*cf.* however ref. 8).

The mass spectra show common fragmentation patterns for the three complexes: each displays a strong molecular ion and prominent fragments corresponding to successive losses of CO groups followed by consecutive loss of two acetylene fragments and the metal to yield the most abundant ion, m/e 128, which corresponds to naphthalene; *cf.* for example the mass spectrum of Va: m/e 384 (M), 356, 328, 300, 272, 246, 220, 128.

Treatment of IV with $Fe(CO)_5$ at reflux yielded small quantities of Vc and the white crystalline non-complexed dimeric ketone, VII, as indicated by IR, NMR, and mass spectra data[★★].



(VII)

A similar dimerization of olefinic ligand with carbonyl insertion has been previously reported[10–12] in the study of the reaction of norbornadiene with $Fe(CO)_5$.

[★] Green *et al.* reported the butadiene·$Fe(CO)_3$ and norbornadiene·$Fe(CO)_3$ to exhibit similar, albeit upheld shift of the vinylic protons.

[★★] m.p. 260°; IR ν(C=O) 1710 cm^{-1} corresponding to five membered cyclic ketone fused symmetrically to two substituted cyclobutane rings[9]. $\tau_{\text{TMS}}^{(\text{CDCl}_3)}$ (100 MHz) : 2.97 (A_2B_2,4H, aryl protons), 3.42 (t,2H, bridge vinyl protons), 5.88 (m,2H, methine protons), 7.51 (4 line pattern, 1 H, proton α to keto group), 7.91 (m,3H, cyclobutane protons).

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