

[Fe₂(CO)₆I(N:CR¹R²)] Complexes with Bridging Atoms of Widely Differing Sizes and Bridging Characteristics

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Summary Syntheses and spectroscopic data are reported for the complexes [Fe₂(CO)₆I(N:CR¹R²)] (R¹ = R² = Ph or *p*-MeC₆H₄; R¹ = Ph, R² = Bu^t) which contain bridging atoms of widely different sizes and bridging characteristics.

BRIDGING groups in metal carbonyl complexes are well established and may involve a range of elements including H, C, O, N, halogens, P, As, and S.¹ The complexes may involve bridging by one atom {e.g. [(OC)₅Cr(H)Cr(CO)₅]}² or by two or more identical or different atoms {e.g. [Fe₂(CO)₆(NH₂)₂]³ and [Fe₂(CO)₈H]⁻ (ref. 4), which may be

both iodine and nitrogen groups are acting as three-electron donors, possibly in bridging positions, the complexes provide for the first time a system for studying the competing effects of two groups with widely differing bridging characteristics.

Treatment of [Fe(CO)₄I₂] with [R¹R²C:NLi] (R¹ = R² = Ph or *p*-MeC₆H₄; R¹ = Ph, R² = Bu^t) in ether at ambient temperature yielded a mixture of the symmetrically bridged complexes [Fe(CO)₃N:CR¹R²]₂ and [Fe₂(CO)₆I(N:CR¹R²)], which were separated by chromatography on silica gel. The latter complexes were obtained as deep-red crystals (R¹ = R² = Ph) or deep-red oils (R¹ = R² = *p*-MeC₆H₄; R¹ = Ph, R² = Bu^t).[†] Molecular weight and

TABLE

Spectroscopic data for [Fe₂(CO)₆I(N:CR¹R²)] complexes

	R ¹ =R ² =Ph	R ¹ =R ² = <i>p</i> -MeC ₆ H ₄	R ¹ =Ph, R ² =Bu ^t
I.r. (cm ⁻¹ ; cyclohexane)	2083s, 2050s, 2016s, 2006s, 1982vw	2084s, 2053s, 2018s, 2008s, 1980vw	2081s, 2044s, 2009s, 1987s, 1980s, 1963vw
¹ H n m r. (τ)	2.68	2.87(4), 7.63(3)	2.70(5), 8.78(9)
Mössbauer (mm s ⁻¹)	δ = 0.16 Δ = 1.70		
Mass (<i>m/e</i> parent)	587	615	600

unsymmetrically placed between the metals as in [(π-C₅H₅)₂-Ti(EPh)₂Mo(CO)₄] (E = O, S, Se)⁵ and [(π-C₅H₅)Ti(NMe₂)₃-Mo(CO)₃].⁶ In addition the bridging unit may be strengthened by a metal-metal bond as for [Fe₂(CO)₆(SEt)₂].⁷

We report the synthesis of the complexes [Fe₂(CO)₆I(N:CR¹R²)] (R¹ = R² = Ph, *p*-MeC₆H₄; R¹ = Ph, R² = Bu^t) which incorporate a small (2nd Period) and a large (5th Period) bridging atom. The diamagnetism of the complexes and the noble-gas rule required the presence of a metal-metal bond. Since their formulations indicate that

spectroscopic data (Table) confirm the dinuclear formulations with bridging iodine and nitrogen, but on the basis of the i.r. spectra it is not possible to assign planar or puckered Fe₂NI bridging units. Compared with the symmetrically-bridged methyleneamino-complexes (I), the presence of the bridging iodine causes an additional ν(CO) band to appear and the ν(CO) frequencies to increase, in keeping with the lowering of the symmetry and the presence of a poorer three-electron donor.

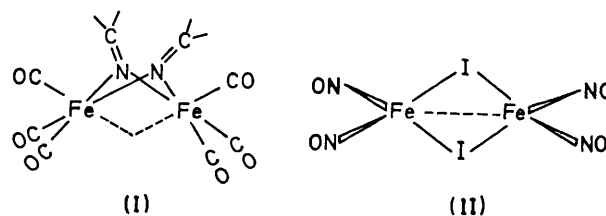
The nature of a [M₂X₂] bridging unit is dependent on the

[†] Satisfactory C, H, N, and I analyses were obtained for each complex.

co-ordination of the metal, the size of the bridging atoms (X) and their repulsions across the ring, and the presence or absence of a metal-metal bond.⁸ For 5- and 7-co-ordination, distorted planar bridging systems are found having small MXM angles, *e.g.* $[\text{Fe}(\text{NO})_2\text{I}]_2$ (II) 73° and $\alpha\text{-}[\text{NbI}_4]$ 74° ,⁸ whereas for 6-co-ordination a bending deformation of the $[\text{M}_2\text{X}_2]$ unit about a line through the two bridging groups achieves a shorter metal-metal bond distance, *e.g.* $[\text{Fe}_2(\text{CO})_6(\text{SEt})_2]$ 2.54 \AA ⁷ compared with $[\text{Fe}(\text{NO})_2\text{SEt}]_2$ 2.72 \AA .⁸ The larger the bridging atom the larger the metal-metal distance, *e.g.* $[\text{Fe}(\text{NO})_2\text{I}]_2$ (II) 3.05 \AA ⁸ compared with distances given above. In this complex the non-bonding I-I distance across the planar $[\text{Fe}_2\text{I}_2]$ ring is 4.15 \AA compared with the van der Waals distance of 4.3 \AA .⁸ Iodine is thus not expected to partake in a non-planar bridging unit which will tend to decrease this separation, whereas the smaller nitrogen atom commonly occurs in such environments in iron carbonyl complexes. The structures of the latter complexes are characterised by short metal-metal bonds ($\sim 2.4 \text{ \AA}$) and small MNM, NMN, and dihedral angles.⁹ Thus the bridging characteristics of iodine and nitrogen are apparently widely different.

The decrease in σ -donation from the bridging atom when nitrogen is replaced by iodine, and the decreased π -bonding to the metal compared with the methyleneamino-bridging group are consistent with the larger Mössbauer isomer shift value for $[\text{Fe}_2(\text{CO})_6\text{I}(\text{N}:\text{CPh}_2)]$ (0.16 mm s^{-1}) compared

with the value for $[\text{Fe}_2(\text{CO})_6(\text{N}:\text{CPh}_2)_2]$ (0.03 mm s^{-1}). The difference in their quadrupole splittings (1.70 and 0.87 mm s^{-1} respectively) reflect the expected significant distortion of the structure of the homo-bridged complex [(I) see ref. 10] to an extent much larger than would be expected in the direct replacement of one bridging methyleneamino-group by iodine. The quadrupole splitting of 1.70 mm s^{-1} may reflect a tendency towards five-co-ordination which could occur through a lengthening of the metal-metal distance and a tendency towards planarity of the Fe_2IN ring.



$[\text{Fe}(\text{CO})_6\text{I}(\text{N}:\text{CPh}_2)]$ reacts with $[\text{Ph}_2\text{C}:\text{NLi}]$ in ether at ambient temperature to form the bis-methyleneamino-bridged complex $[\text{Fe}(\text{CO})_6(\text{N}:\text{CPh}_2)_2]$ obtained as orange-yellow crystals, m.p. $136\text{--}138^\circ$.

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