Charge Distribution in Bimetallic Organometallic Cations

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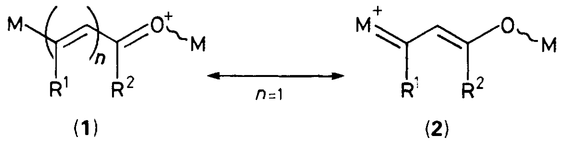
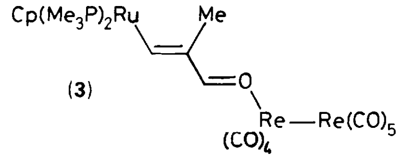
Charge distributions in two monocationic bimetallic organoiron complexes, prepared by transfer of Fp^+ to Fp acyl and vinyl species [Fp = $Fe(CO)_2(C_5H_5)$], have been studied by ^{57}Fe Mössbauer spectroscopy, demonstrating that a considerable degree of polarisation is present in linear organic π-systems interposed between organometallic donor and acceptor groups.

When transition metal centres are combined within the same bonding system, the spread of charge between cationic and neutral positions can be difficult to predict, and yet is important both in determining the size and direction of electric dipoles in the molecules, and in influencing the physical, particularly optical,[1] properties of such compounds. Our work in this area has concerned the preparation of complexes of type (**1**, n = 1), in which a π-system is polarised between two organometallic groups, of which one is a cationic centre. The spread of positive charge within the π-system would be expected to depend on the contribution to bonding of the two structures (**1**) and (**2**). There has been considerable interest in the preparation of structures of this kind,[2] and of bimetallic species in general.[3] A recent report[4] by Bullock *et al.* of an unusual neutral ruthenium, bis-rhenium complex (**3**), which contains a bonding system of this type, and their discussion, based on crystallographic data, of the polarisation of charge within the π-system, prompts us to report our own results with related bis-$Fe(CO)_2(C_5H_5)$ complexes, which in our case are monocations. This communication presents preliminary results of our investigation: the preparation of a new bimetallic enone complex of type (**1**) and the examination by ^{57}Fe Mössbauer spectroscopy of charge distribution in the first two members of the series of bimetallic complexes indicated in Scheme 1, namely (**1**, n = 0, R^2 = Me) and (**1**, n = 1, R^1, R^2 = CH_2–CH_2–CH_2).



(**1**) (**2**)



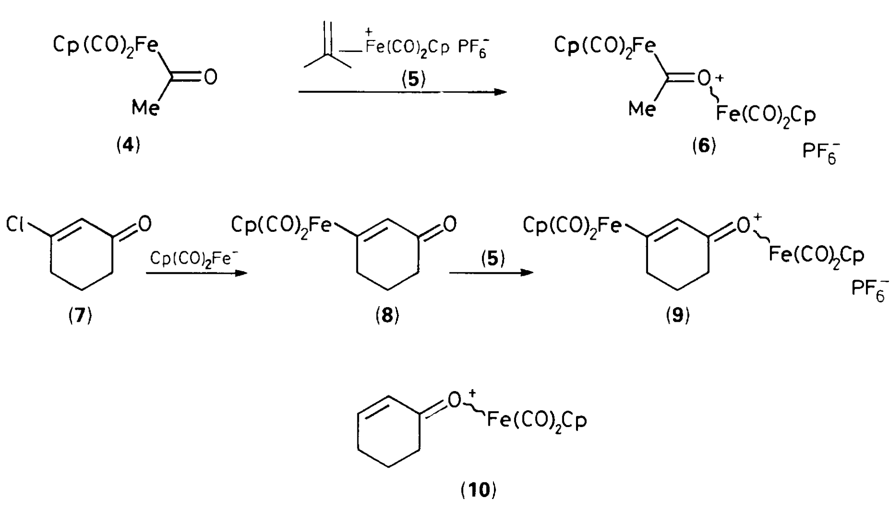
(**3**)

The transfer of Fp^+ [Fp = $Fe(CO)_2(C_5H_5)$] from the isobutene complex (**5**) to a ketone provides convenient access to cationic organoiron derivatives.[5] We have employed this reaction to obtain the bimetallic cationic complexes for this study. First, the readily available bi-metallic cation (**6**)[6] was prepared from the metal acyl complex (**4**) in 72% yield, by ligand transfer from (**5**). A complex extended by an extra alkene group was obtained in a similar manner; the neutral Fp centre was introduced into the vinylogous acid chloride (**7**) by reaction with the Fp^- generated in the normal way from the dimer Fp_2.[7] The product (**8**), formed in 64% yield, was converted by reaction with (**5**) into the bimetallic monocation

Table 1. ^{57}Fe Mössbauer parameters.[a]

Complex	Isomer shift (Rh) δ/mm s^{-1} ±0.02 mm s^{-1}	Quadrupole splitting Δ/mm s^{-1} ±0.02 mm s^{-1}	Line width/mm s^{-1} L ±0.02 mm s^{-1}	Line width/mm s^{-1} R ±0.02 mm s^{-1}	Relative area/% ±5%	Temp./K ±5 K
(**4**)	−0.15	1.68	0.21	0.24		300
(**6**)	−0.07	1.62	0.31	0.31	54	300
	0.00	2.07	0.32	0.32	46	
(**6**)	−0.01	1.64	0.27	0.27	47	80
	0.07	2.09	0.29	0.29	53	
(**8**)	−0.16	1.78	0.20	0.20		300
(**9**)	0.07	1.92	0.24	0.24	33	300
	−0.16	1.82	0.28	0.28	39	
	0.34	0.68	0.38	0.38	28	
(**9**)	0.14	1.92	0.25	0.25	34	80
	−0.09	1.83	0.30	0.30	54	
	0.53	0.90	0.63	0.63	12	
(**10**)	0.09	2.01	0.26	0.21		300

[a] ^{57}Fe Mössbauer spectra were recorded using a constant acceleration spectrometer with a 10 mCi ^{57}Fe in rhodium matrix source at room temperature. Absorbers were cooled to 80 K using a conventional liquid nitrogen cryostat. The spectrometer was calibrated using the magnetic splitting of an enriched ^{57}Fe absorber foil. The data were fitted with Lorentzian functions by a non-linear least-squares fitting programme.



Cp = C_5H_5

Scheme 1

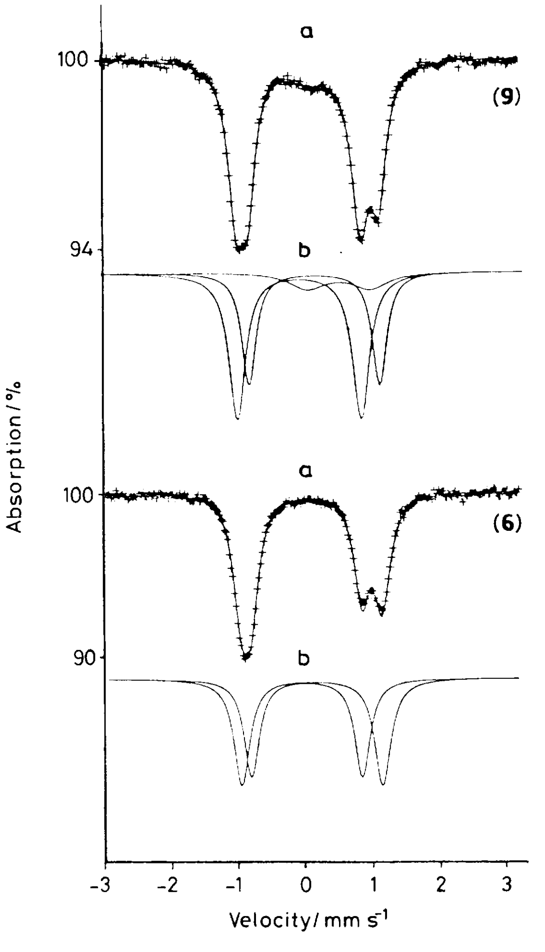


Figure 1. ^{57}Fe Mössbauer spectra of (**9**) and (**6**) at 300 K. (a) Observed data; (b) computer simulation.

(**9**), which was precipitated in 58% yield.† IR spectra of both complexes (**6**) and (**9**) contained two sets of M–CO bands, consistent with the presence of both charged and neutral metal centres.

^{57}Fe Mössbauer spectra obtained from these complexes are shown in Figure 1. Both spectra show two distinct quadrupole splittings, a wide doublet with Δ 2.07 mm s^{-1} for (**6**) and Δ 1.92 mm s^{-1} for (**9**), and a narrow doublet with Δ 1.62 mm s^{-1} for (**6**) and Δ 1.82 mm s^{-1} for (**9**) (see Table 1). Narrow doublets of this second type were observed in the Mössbauer spectra of the neutral starting materials (**4**) and (**8**), which exhibited quadrupole splittings of Δ 1.68 mm s^{-1} and Δ 1.78 mm s^{-1}, respectively. Interpretation of Mössbauer parameters can be complicated by temperature dependence of the spectra,[8] but parameters have recently been successfully employed in studies of the bonding, for example, of di-iron sandwich complexes,[9] biferrocenes,[10] and binuclear ferracycles.[11] In the case of the Fp complexes (**6**) and (**9**), similar Mössbauer parameters were obtained at 80 K (Figure 1) and at 300 K, and so, within this temperature range, inferences concerning charge distribution can be made without the need to consider temperature dependent structural changes. Our results suggest the presence of two distinct metal centres in both the bimetallic complexes, a neutral σ-bound iron centre (Δ 1.6—1.8 mm s^{-1}) and a charged iron centre (Δ 1.9—2.1 mm s^{-1}) which could be bound either as the oxygen adduct in (**1**), or as the cationic carbene centre in (**2**). An intermediate bonding situation in which both (**1**) and (**2**) contribute to the bonding system, such as that proposed for (**3**), seems less applicable to the complexes we have examined, although, for the vinylogous example (**9**), some displacement of Δ for the narrow doublet towards the wider splitting of a charged system was observed. In this case, a greater contribution from (**2**) might be reasonable.

To examine this question further, a model complex resembling the O-bound Fp cation in (**9**) was required. Since it was desirable to retain as many of the other features of (**9**) as possible, in particular the alkene link that distinguishes this situation from that in (**6**), the cyclohexenone complex (**10**)[5] was selected for study. This complex was simply prepared in 84% yield by Fp$^+$ transfer from (**5**) to cyclohexenone by the method of Rosenblum.[5] Examination of (**10**) by Mössbauer spectroscopy revealed a quadrupole splitting Δ 2.01 mm s^{-1}, indicating that the value of Δ in the wider doublet observed in (**9**) was also displaced slightly towards an intermediate position. Mössbauer parameters for (**4**), (**6**), (**8**), (**9**), and (**10**) are listed in Table 1.

The relative areas of the components in the Mössbauer spectra reveal an apparent anomaly. The components for (**6**)

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† Satisfactory microanalysis and spectroscopic characterisation were obtained.

are of equal area within experimental error, as might be expected if the two distinct iron sites had equal recoil-free fractions. However, the situation for (**9**) is more complex due to the presence of an iron(III) impurity (δ 0.34 mm s^{-1}, Δ 0.68 mm s^{-1} at 300 K). At 80 K the relative area of the iron(III) component is much reduced, but the relative areas of the two iron sites are unequal, indicating an apparent transfer of intensity from the iron(III) component to the site in (**9**) with the smaller quadrupole doublet. This could be explained by the different temperature dependence of the recoil-free fractions of the two distinct iron sites and the iron(III) impurity. A full variable temperature study is being undertaken to examine this.

Our findings fit the view that both (**6**) and (**9**) exist in highly polarised forms, rather than in intermediate bonding states, in which a more uniform charge distribution, and hence more similar Δ values for the two metal centres, would be expected. In the case of (**9**), however, the contribution of the carbenoid form may be more significant. If polarisation of charge is maintained with longer polyene spacing groups (Scheme 1, $n > 1$), the preparation of compounds of this type should provide substances with large electric dipoles, and the attendant possibility of unusual non-linear optical properties. The prospect that valuable properties may arise in polarised organometallic systems has been confirmed in studies measuring second order optical properties in ferrocene derivatives,[1] and in channel inclusion complexes of organometallics investigated at du Pont.[12] The preparation of higher members of the series of compounds of type (**1**), and the examination of the control of bonding, and so of charge distribution, by variation of one or both of the metal centres, are currently being undertaken.

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