An Infrared Spectroscopic Study of the Tautomeric Equilibria in Solutions of Tricarbonylbis(η-dienyl)isocyanidedi-iron Complexes

By **John Bellerby, Michael J. Boylan, Mary Ennis,** and **A. R. Manning,*** Department of Chemistry, University College, Belfield, Dublin 4, Ireland

Infrared spectra of solutions of $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ derivatives (dienyl = C_5H_5, C_5H_4Me, or C_9H_7; R = alkyl or benzyl) show that four isomers are present. They have structures based on *cis*- and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2]$. In two isomers the isocyanide ligand has replaced a μ-CO group, whilst in others it has replaced a terminal (t) ligand. The equilibria shift towards this latter pair when (*a*) R = Me < Et < Bu^n < Bu^i < Bu^s < cyclo-C_6H_{11} < Bu^t, (*b*) R = $CH_2C_6H_4X$-*p* as X is varied along the series Cl < H < Me < OMe, and (*c*) for dienyl = C_5H_5 ~ C_5H_4Me < C_9H_7. The destabilization of the μ-RNC isomers is attributed in (*a*) partly to increasing steric interactions between R and the $Fe(\eta\text{-dienyl})(CO)_t$ moieties, and in both (*a*) and (*b*) to the decreasing overall electron-withdrawing ability of R. Changes in solvent and temperature also affect the equilibria.

IN solution, organoisocyanide complexes $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ [1] exist as mixtures of isomers which interconvert rapidly at room temperature.[2] Here, we describe the preparation of a number of related complexes of the general type $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ (dienyl = C_5H_5, C_5H_4Me, or C_9H_7; R = alkyl or benzyl), and report their i.r. spectra. The various tautomers have been identified, and the factors affecting their relative concentrations have been investigated. A preliminary report of this work has been published.[3]

EXPERIMENTAL

Literature methods were used to prepare the organoisocyanides [4,5] and $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ (dienyl = C_5H_5,[6] C_5H_4Me,[6] or C_9H_7 [7]). Other chemicals were purchased. All the reactions were carried out under an atmosphere of nitrogen in purified solvents, and were monitored by i.r. spectroscopy.

Solutions of $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ (*ca.* 1 g) and RNC (mol ratio 2 : 3) in benzene (*ca.* 50 cm³) were stirred at room temperature or 40 °C. The reactions were more rapid for dienyl = C_5H_5 or C_5H_4Me than with C_9H_7. When they were complete, the solvents were removed at reduced pressures. The residues were either chromatographed (alumina–benzene) and recrystallized, or directly recrystallized from hexane or toluene–hexane mixtures. Yields of the desired products were usually *ca.* 60%. Their melting points and analyses are given in Table 1.

Infrared spectra were run on a Perkin-Elmer 337 spectrophotometer and a Perkin-Elmer 56 readout recorder using Beckmann-RIIC type F-05 i.r. cells with potassium bromide plates. The cell path lengths were 1 mm (with heptane, carbon disulphide, or acetonitrile as solvent) or 0.1 mm (xylene, tetrahydrofuran, or acetonitrile) using solutions having concentrations of *ca.* 3×10^{-4} and 3×10^{-3} mol dm^{-3} respectively. Since the nature of the spectra was independent of solute concentration, the latter was adjusted so that the most intense absorption band had an absorbance of *ca.* 0.7 (*ca.* 20% transmittance). Where the range of relative peak heights prevented them from being measured on the same spectrum, a number of spectra was obtained by varying solution concentrations or, preferably, cell path lengths. A slit program of 4 was used except for heptane where it was 2. The variable-temperature spectra were obtained using a RIIC VLT 2 variable-temperature cell. The spectra were calibrated using CO, DCl, and water vapour.[8] They are summarized in Tables 2 and 3 where relative peak heights are a measure of the relative absorbances (or optical densities) of each absorption band above the base line of the spectrum.

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TABLE 1

Melting points and analyses for some [$Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)$] complexes

R	M.p. (θ_c/°C) *	Analysis (%)					
		Found			Calc.		
(*a*) Dienyl = C_5H_5		C	H	N	C	H	N
Me	166—168 (d)	49.0	3.5	3.7	49.1	3.6	3.8
Et	139—140	50.2	3.7	5.6	50.4	4.0	3.7
Pr^i	140—142 (d)	52.2	4.3	3.5	51.7	4.3	3.5
Bu^n	142—144	52.8	4.7	3.3	52.9	4.7	3.4
Bu^i	114—115	52.4	4.5	3.3	52.9	4.7	3.4
Bu^s	141—143	53.1	4.7	3.4	52.9	4.7	3.4
Bu^t	146—148	53.0	4.5	3.5	52.9	4.7	3.4
C_6H_{11}	136—138 (d)	55.0	5.0	3.2	55.2	4.9	3.2
CH_2Ph	144—146	56.6	4.1	3.1	56.9	3.9	3.2
$CH_2C_6H_4Me$-*p* + $0.5C_6H_6$	128—129	60.4	4.5	3.0	60.4	4.6	2.8
$CH_2C_6H_4OMe$-*p*		55.9	3.9	3.0	55.9	4.0	3.0
$CH_2C_6H_4Cl$-*p*	138—140	52.4	3.2	2.8	52.8	3.4	2.9
CH(Me)Ph	129—130 (d)	56.6	4.5	3.2	57.7	4.2	3.1
(*b*) Dienyl = C_5H_4Me							
Me	88—90	51.9	4.4	3.4	51.7	4.3	3.6
Bu^t	92—94	55.2	5.1	3.3	55.0	5.3	3.2
C_6H_{11}	decomp. 71	56.8	5.1	3.1	57.0	5.4	3.0
CH_2Ph	60—61	58.4	4.8	2.9	58.6	4.5	3.0
(*c*) Dienyl = C_9H_7							
Me	194—196 (d)	59.5	3.9	2.8	59.1	3.7	3.0
Bu^n	103—105	60.6	4.5	2.6	61.4	4.5	2.8
Bu^t	150—152	61.1	4.5	2.5	61.4	4.5	2.8
C_6H_{11}	decomp. 118	62.6	4.8	2.5	62.8	4.7	2.6
CH_2Ph	126—127	65.3	4.6	2.5	64.2	3.9	2.5

* Determined in sealed tubes. d = Melts with decomposition, decomp. = decomposes without melting.

RESULTS

The [$Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)$] derivatives listed in Table 1 are purple to brown solids soluble in organic solvents. They are somewhat less stable than their [$Fe_2(\eta\text{-dienyl})_2(CO_4)$] precursors especially when dissolved in chlorinated solvents.

The i.r. spectra of the complexes (Tables 2 and 3) show seven absorption bands, A—G, having wavenumbers between 1 600 and 2 200 cm^{-1}. Band A is very broad and asymmetric, and its shape changes markedly for [$Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_3(CNCH_2Ph)$] in carbon disulphide solution on decreasing the temperature. Both bands B and C have

TABLE 2

Infrared spectra (1 700—2 100 cm^{-1}) of [$Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)$] derivatives in hexane solution unless stated otherwise

R	Absorption band [a]							
	A	B	C	D		E	F	G
(*a*) Dienyl = C_5H_5								
Me	1 734 (8.6)	1 772 (10)	1 801 (5.0)	1 953 (16.1)	1 957	1 997 (11.1)	2 116	2 138 (2.6)
Et	1 737 (1.5)	1 772 (10)	1 801 (3.2)	1 952 (12.1)	1 957	1 997 (7.7)	2 109	2 127 (1.7)
Pr^i	1 733 (1.2)	1 772 (10)	1 801 (2.2)	1 953 (9.4)	1 957	1 997 (4.3)	2 106	2 113 (1.4)
Bu^n	1 731 (1.7)	1 772 (10)	1 802 (2.7)	1 954 (10.1)	1 958	1 998 (5.9)	2 115	2 126 (2.0)
Bu^i	1 730 (1.4)	1 772 (10)	1 801 (2.2)	1 952 (9.6)	1 956	1 997 (4.8)	2 113	2 125 (2.4)
Bu^s	1 732 (0.9)	1 772 (10)	1 801 (1.4)	1 953 (7.6)	1 955	1 997 (3.3)	2 119	2 117 (1.7)
Bu^t		1 773 (10)	1 795	1 953 (6.3)	1 959		2 076 (0.8)	2 112 (1.4)
C_6H_{11}	1 726 (0.4)	1 773 (10)	1 800 (1.1)	1 953 (7.2)	1 956	1 997 (1.9)	2 101	2 116 (1.8)
$CH_2C_6H_4OMe$-*p*	1 722 (10.9)	1 772 (10)	1 801 (16.7)	1 954 (34.3)	1 957	1 998 (33.3)		2 116 (0.4)
$CH_2C_6H_4Me$-*p*	1 719 (10.0)	1 770 (10)	1 803 (19.0)	1 954 (34.2)	1 958	1 998 (35.3)		2 116 (0.5)
CH_2Ph	1 718 (15.0)	1 771 (10)	1 803 (27.5)	1 955 (45.0)	1 960	1 999 (53.8)		2 114 (<0.3)
$CH_2C_6H_4Cl$-*p*	1 712 (34.3)	1 769 (10)	1 804 (75.6)	1 955 (104)	1 959	1 998 (136)		2 120 (<0.3)
CH(Me)Ph	1 708 (7.3)	1 771 (10)	1 803 (11.2)	1 953 (21.2)	1 957	1 997 (21.9)		2 102 (1.0)
(*b*) Dienyl = C_5H_4Me								
Me	1 734 (6.7)	1 768 (10)	1 798 (5.6)	1 947 (16.)1		1 992 (13.4)	2 116	2 134 (1.9)
Bu^t		1 766 (10)	1 792	1 947 (5.2)			2 071 (0.9)	2 107 (1.1)
C_6H_{11}	1 726	1 765 (10)	1 792 (0.9)	1 946 (6.2)		1 993 (1.7)	2 105	2 113 (1.6)
CH_2Ph	1 717 (18.1)	1 766 (10)	1 799 (20.2)	1 951 (42.8)		1 992 (46.6)	2 088	1 113 (1.3)
(*c*) Dienyl = C_9H_7								
Me [b]	1 728	1 766 (10, br)	1 802	1 949 (10.8)	1 959	1 990 (2.6)	2 125	2 139 (8.3)
Bu^n	1 735	1 774 (9.8), 1 783 (10)	1 806 (1.3)	1 949 (13.2)	1 953	1 991 (2.6)	2 103	2 123 (4.5)
Bu^t		1 774 (11.7), 1 779 (10)	1 800	1 941 (14.5)		1 988 (1.1) [c]	2 081	2 117 (5.2)
C_6H_{11}	1 736	1 774 (10.7), 1 781 (10)	1 808 (0.7)	1 950 (13.9)		1 989 (3.3)	2 076	2 116 (5.2)
CH_2Ph [b]	1 711 (2.7)	1 766 (10, br)	1 796 (2.7)	1 946 (11.8)		1 992 (10)	2 103	2 121 (5.9)

[a] Peak positions with relative peak heights in parentheses. If no relative peak height is given the absorption band is a shoulder. br = Broad. A is due to $\nu(CN_\mu)$, B and C to $\nu(CO_\mu)$, D and E to $\nu(CO_t)$, and E and F to $\nu(CN_t)$. [b] In CCl_4 solution. [c] Probably due to an impurity.

two components. Those of B are always obvious for the η-C_9H_7 derivatives and are resolved in hexane solutions. One of those of C is very weak. It appears as a high-frequency shoulder to B when the other is absent or nearly so. Bands D and E are asymmetric with a well defined shoulder to D for the benzyl isocyanide complexes in hexane solution. Bands F and G are very broad. They normally coalesce to give an asymmetric band, but they are well resolved, or nearly so, for the derivatives of t-butyl isocyanide. G is more intense than F.

TABLE 3

Effect of solvent and temperature on the i.r. spectra (1 600—2 200 cm^{-1}) of some $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ derivatives

R	Solvent [a]	Absorption band [b]						
		A	B	C	D	E	F	G
(*a*) Dienyl = C_5H_5								
C_6H_{11}	CS_2	1 721 (sh)	1 757 (10)	1 785 (0.5)	1 948 (6.0)	1 987 (0.6)	*c*	*c*
	CS_2 (−78 °C)	1 721 (sh)	1 751 (10)	1 785 (0.5)	1 947 (6.0)	1 987 (0.4)	*c*	*c*
	Xylene	1 734 (sh)	1 761 (10)	1 792 (0.5)	1 945 (4.8)	1 988 (0.7)	2 100 (sh)	2 126 (2.2)
	thf	1 732 (sh)	1 761 (10)	1 789 (sh)	1 943 (4.2)	1 983 (1.0)	2 100 (sh)	2 124 (1.9)
Bu^t	Xylene		1 761 (10)	1 787 (sh)	1 945 (4.6)		2 073 (0.7)	2 114 (1.7)
	thf		1 760 (10)	1 786 (sh)	1 943 (3.7)		2 076 (0.6, sh)	2 114 (1.6)
	MeCN		1 748 (10)		1 941 (4.7)			2 123 (2.4)
(*b*) Dienyl = C_5H_4Me								
Me	Xylene	1 729 (2.4)	1 758 (10)	1 788 (2.2)	1 940 (7.6)	1 985 (5.8)		2 145 (2.1)
	thf	1 729 (2.7)	1 756 (10)	1 786 (2.6)	1 939 (7.7)	1 980 (7.7)		2 149 (2.6)
	MeCN	1 718 (sh)	1 742 (10)	1 774 (1.9)	1 939 (7.7)	1 977 (6.2)		2 153 (4.1)
CH_2Ph	CS_2	1 710 (10.4)	1 752 (10)	1 786 (9.1)	1 942 (21.2)	1 983 (35.7)	*c*	*c*
	CS_2 (−78 °C)	1 710 (27.0)	1 745 (10)	1 784 (20.3)	1 943 (35.2)	1 983 (77)	*c*	*c*
	Xylene	1 714 (8.2)	1 758 (10)	1 779 (6.9)	1 943 (14.1)	1 986 (23.2)		2 122 (2.4)
	thf	1 712 (9.3)	1 757 (10)	1 789 (9.0)	1 941 (11.9)	1 980 (26.8)		2 123 (1.8)
(*c*) Dienyl = C_9H_7								
Me	Xylene	1 713 (1.9)	1 768 (10)	1 799 (2.1)	1 942 (11.2)	1 984 (9.1)		2 122 (4.0)
	thf	1 717 (2.6)	1 767 (10, br)	1 797 (2.5)	1 941(10.9)	1 980 (12.7)		2 126 (4.4)
	MeCN	1 712 (1.4)	1 758 (10)	1 789 (1.7)	1 941 (9.1)	1 978 (6.9)		2 133 (5.3)

[a] thf = Tetrahydrofuran. [b] Peak positions with relative peak heights in parentheses; br = broad. [c] Solvent absorption bands obscure this region of the spectra.

The absorption bands may be divided into Group I comprising B, F, G, and components of C and D, and Group II comprising A, E, and components of C and D. The relative intensities of absorption bands within each group are not greatly affected by RNC and η-dienyl ligands. However, these markedly influence the relative importances of Group I and II bands as measured by the ratio of the intensities of B : E or B : C in a particular solvent, *e.g.* hexane, at room temperature. Thus bands in Group I increase in importance, and Group II decline, along the series $R = Me < Et < Bu^n < Bu^i < Pr^i < Bu^s <$ *cyclo*-$C_6H_{11} < Bu^t$, $R = CH_2C_6H_4Cl$-*p* $< CH_2Ph < CH_2C_6H_4Me$-*p* $< CH_2C_6H_4Me$-*p* $< CH(Me)Ph < Me$, and dienyl = $C_5H_5 \sim C_5H_4Me < C_9H_7$.

Changes in solvent affect the Group I : Group II intensity ratios with the latter declining along the series hexane > xylene ~ tetrahydrofuran > acetonitrile; some typical spectra are given in Table 3. At the same time there are changes in the relative intensities of the absorption bands within each group. Along the same series, F in Group I declines with respect to G. This is most noticeable for the $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNBu^t)]$ derivatives. Also, although Group II declines, the intensity of E increases relative to that of D. This implies that the component of D which is part of Group II declines more rapidly than E which is due solely to Group II; *i.e.* if the Group I bands were absent the intensity ratio E : D would increase.

Decreasing the temperature of carbon disulphide solutions of $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_3(CNCH_2Ph)]$ causes the Group I absorption band B to decrease in intensity. At the same time there are marked changes in the shapes of A, D, and E which is consistent with changes in the relative intensities of their various components. It should be noted that, in contrast to the above, cooling carbon disulphide solutions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_{11})]$ causes the Group II bands A, C, and E to decrease in intensity, whilst the shape of B changes markedly.

DISCUSSION

It is clear that solutions of the $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ complexes contain a number of isomers. All have bridging and terminal carbonyl ligands. The absorption bands of Groups I and II are respectively attributed to species which also contain terminal or bridging isocyanide ligands. There is no evidence for tautomers without bridging CO or CNR groups.

It is probable that all the isomers have structures derived from *cis*- and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (Figure).[9,10] It is unlikely that replacement of a CO ligand by CNR would bring about any marked distortion in the overall geometry of the various species. Thus we assume that Fe–Fe–CO_t angles and the angles between the Fe(μ-CO)Fe planes are similar to those in the unsubstituted precursors (t refers to a terminally coordinated ligand, μ to one which bridges). These assumptions are consistent with the results of *X*-ray diffraction studies which have ascertained the structures of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ (R = Ph,[11] Bu^s,[12] or Bu^t [13]). We also assume that changes in the relative intensities of

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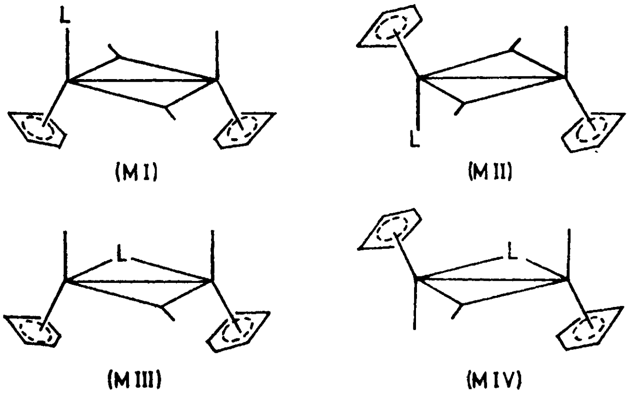
absorption bands are a reasonably accurate reflection of changes in isomer ratios.[14]

The presence of F and G or a corresponding single but asymmetric absorption band due to $\nu(CN_t)$ vibrations points unambiguously to the presence of *cis*- and *trans*-$[Fe_2(\eta\text{-dienyl})_2(\mu\text{-}CO)_2(CO)(CNR)]$, (MI) and (MII) in the Figure. The components may be resolved graphically by assuming that each is symmetrical. The intensity ratio G : F, as measured by (peak-height) × (band width at half peak-height), for $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_3(CNR)]$ declines from 3.4 : 1 for R = Me, through 1.95 : 1 for R = C_6H_{11}, to 1.05 : 1 for R = Bu^t. A similar series may be drawn up for the cyclopentadienyl complexes. If it is assumed that these changes are a reasonable reflection of changes in the ratios of the concentration of the two t-RNC isomers, it is clear that increasing the bulk of R causes one isomer to be destabilized with respect to the other. On the other hand, decreasing the temperature of solutions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNBu^t)]$ in dichloromethane or increasing the solvent polarity from hexane to acetonitrile for many other complexes causes the intensity of absorption band G to increase with respect to that of F.[15] It has been suggested that since the more polar solvents favour *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ at the expense of the *trans* species the same is true for the $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ complexes.[15] If that is the case then G is due to (MI) and F to the *trans* isomer (MII). However, the data available at present do not allow this assignment to be placed on a firmer footing.



The four isomers of the $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ complexes. Carbonyl groups and Fe atoms have been omitted for the sake of clarity. L = RNC

For the cyclopentadienyl and methylcyclopentadienyl derivatives each of the absorption bands due to the three C–O stretching vibrations of isomer (MI) is coincident with that due to the corresponding vibration of isomer (MII). Thus B is assigned to the antisymmetric $\nu(CO_\mu)$, the very weak component of C to the symmetric $\nu(CO_\mu)$, and a component of D to $\nu(CO_t)$ modes.* The two components of B are well resolved in the spectra of hexane solutions of $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_3(CNR)]$ {*cf.* $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [15] and $[Fe_2(\eta\text{-}C_9H_7)_2(CO)_4]$ [17]}. Thus the changes in the shape of B on cooling solutions of other complexes is also a reflection of changes in the concentration ratio [(MI)] : [(MII)].

There is no unambiguous direct evidence that both isocyanide-bridged isomers (MIII) and (MIV) are present in the solutions. However, absorption band A, which is due to $\nu(CN_\mu)$, is markedly asymmetric and has more than one component. That there are two is strongly suggested by the change in band shape with both temperature and solvent. Furthermore, when the Group I absorption bands are of little importance {*e.g.* for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNCH_2C_6H_4Cl\text{-}p)]$} the relative intensities of E and D are not consistent with a single *trans* isomer (MIV) or a *cis* species having Fe–Fe–CO_t angles similar to those of *ca.* 100° in *cis*- and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [9,10] and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ (R = Bu^s [12] or Bu^t [13]). They may best be explained by assuming that both (MIII) and (MIV) are present and that absorption band D is due to a coincidence of their antisymmetric $\nu(CO_t)$ vibrations whilst E results from the symmetric $\nu(CO_t)$ mode of (MIII).* The relative intensities of D and E imply that the *cis* species (MIII) are present in higher concentrations than the *trans*, (MIV), even in hexane solutions, and that the concentration ratio [(MIII)] : [(MIV)] increases as the solvent polarity is increased along the series hexane, xylene, tetrahydrofuran, and acetonitrile.

The various equilibria are affected by changes in the isocyanide ligand, RNC. We have endeavoured to separate the steric and electronic effects of R by preparing a number of complexes of alkyl isocyanide and $CNCH_2C_6H_4X\text{-}p$ ligands. It is clear that increasing the bulk of the alkyl group along the series R = Me, Et, Bu^n, Bu^i, Pr^i, Bu^s, cyclo-C_6H_{11}, and Bu^t shifts the equilibria from the species with bridging to those with terminal RNC groups. These observations may be rationalized if it is remembered that such ligands are linear when terminally co-ordinated, but bent when bridging with the R–N–C angle *ca.* 120° {*cf.* $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNPh)]$ [11] and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ [18]} and the α-carbon atom of R lying in the Fe_2C_μ–N_μ plane. Consequently, increasing the size of R, by alkyl-chain branching or to a lesser extent by increasing the chain length, will bring about an increase in the steric interactions between R and one $Fe(\eta\text{-dienyl})(CO_t)$ moiety. This destabilizes the μ-RNC with respect to the t-RNC species where similar interactions are likely to be less important.

In the complexes of the $CNCH_2C_6H_4X\text{-}p$ ligands it may be assumed that steric interactions are virtually constant, and that the changes observed are due largely to electronic effects. The importance of the isocyanide-bridged isomers increases along the series X = OMe < Me < H < Cl. This correlates well with the total electron-

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* The relative frequencies and intensities of absorption bands due to the ν(CO) vibrations of $Fe(CO_\mu)_2Fe$ and $[Fe(CO_t)]_2$ moieties have been discussed in detail in ref. 16.

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withdrawing ability of X, as measured by the Taft constant σ_p, which increases along the same series.[19] The observations may be rationalized using the currently accepted explanations of the bonding between transition metals and isocyanide or carbonyl ligands.[20] These predict that increasing donation of electrons from filled metal *d* orbitals into vacant C–O or C–N π^* orbitals results in lower C–O and C–N bond orders, lower ν(CO) and ν(CN) frequencies, and increased negative charge on the O or N atoms of the ligands. With bridging groups these negative charges are greater than if the same ligands were terminally bonded. Consequently, factors which enable a given carbonyl O or isocyanide N atom to accept this extra charge will tend to favour isomers in which that ligand occupies a bridging co-ordination position. Hence, an increase in the electron-withdrawing ability of the group R of the isocyanide would expect to stabilize μ-RNC at the expense of t-RNC species, as is observed in the present case. {The consequences of the interaction of $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with Lewis acids may be rationalized similarly.[21]} Furthermore, one would expect a decline in the electron-withdrawing ability of R, as measured by σ_p,[19] and hence in the importance of the μ-RNC tautomers, along the series $R = Me > Et > Pr^i > Bu^t$. Thus electronic effects reinforce the steric effects mentioned earlier. On the other hand, despite the relatively greater bulk of $R = CH_2Ph$ over $R = CH_2H$ or CH_2Me, the superior electron-withdrawing ability of the first group causes a swing in the equilibria towards the μ-RNC forms (MIII) and (MIV). The total absence of the t-RNC isomers (MI) and (MII) from solutions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNPh)]$ [15] may be attributed, at least in part, to the very powerful electron-withdrawing effect of the phenyl group. This gives rise to an energy barrier that is sufficient to prevent a ready μ-PhNC ⟶ t-PhNC conversion and which renders the phenyl isocyanide complex static at room temperature.[15] This conversion takes place readily for other fluxional $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ derivatives (see refs. 13 and 18, and refs. therein).

It is difficult to determine unambiguously the relative importances of the steric and electronic effects of R on the μ-RNC $\rightleftharpoons$ t-RNC equilibria in solutions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ complexes. However, a comparison of the spectra of those complexes where $R = CH_2Me$, $CHMe_2$, CH_2Ph, and CH(Me)Ph suggests that except for the most bulky group R, tertiary butyl, electronic effects are generally the more important but not overwhelmingly so. This contrasts markedly with the situation found for $[\{Co(CO)_3L\}_2]$ complexes (L = tertiary phosphine, arsine, or stibine) where the steric effects of L overwhelm its electronic effects.

In the solid state $[Fe_2(\eta\text{-dienyl})_2(CO)_3(CNR)]$ complexes are found as the CO-bridged forms (MI) or (MII) where R is an alkyl group. However, when $R = CH_2Ph$ or substituted benzyl the complexes crystallize as the isocyanide-bridged tautomers (MIII) or (MIV).

[7/2108 *Received*, 1*st December*, 1977]

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