Synthesis and Fluxional Character of Complexes of the Type $[M_2(cp)_2(CO)_3(CNR)]$ (M = Fe or Ru, cp = η-C_5H_5)

By **James A. S. Howell** * and **Anthony J. Rowan**, Department of Chemistry, University of Keele, Keele, Staffs. ST5 5BG

Infrared and ^{13}C and ^{1}H n.m.r. data for the complexes $[M_2(cp)_2(CO)_3(CNR)]$ [cp = η-C_5H_5, M = Fe, R = Me, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, or Ph; M = Ru, R = Me, C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$] show that, in solution, mixtures of isomers containing bridging and terminal isonitrile ligands exist; the n.m.r. results may be interpreted in terms of the Adams–Cotton mechanism. N.m.r. (^{1}H and ^{13}C) spectra for $[Os_2(cp)_2(CO)_4]$ have also been recorded. The protonated and alkylated derivatives $[M_2(cp)_2(CO)_3(CNHR)][PF_6]$ [M = Fe, R = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, or Ph; M = Ru, R = C_2H_5] and $[Fe_2(cp)_2(CO)_3(CNRR')][PF_6]$ [R = CH_3 or $CH(CH_3)_2$; R' = C_2H_5] have also been prepared and their ^{13}C and ^{1}H n.m.r. spectra recorded.

THE preparation and study of fluxional transition-metal carbonyl complexes continues to be of interest.[1] At least for bimetallic species containing doubly bridging carbonyl groups, the mechanism which has received most experimental support is that proposed by Adams and Cotton [2] involving symmetric bridge opening followed if necessary by internal rotation about the M–M bond of the non-bridged intermediate. Simultaneous bridge closing then regenerates a doubly bridged isomer which has undergone bridge–terminal carbonyl exchange and/or geometric isomerization {*e.g. cis* $\rightleftharpoons$ *trans* interconversion for $[Fe_2(cp)_2(CO)_4]$ (cp = η-C_5H_5)}. We report here our complete results on the preparation and fluxional behaviour of the related isonitrile complexes $[M_2(cp)_2(CO)_3(CNR)]$ [(1a)—(1e) M = Fe, R = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, or Ph; (2a)—(2d) M = Ru, R = CH_3, C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$], together with results on the complexes $[M_2(cp)_2(CO)_3(CNHR)][PF_6]$[(3a)—(3e) M = Fe, R = CH_3, C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$; (4) M = Ru, R = C_2H_5] and $[Fe_2(cp)_2(CO)_3(CNRR')][PF_6]$ [(5a) and (5b) R = CH_3 or $CH(CH_3)_2$, R' = C_2H_5] formed from electrophilic attack by H^+ or $C_2H_5^+$ on the neutral isocyanide derivative. Part of this work has been reported as preliminary communications.[3,4]

DISCUSSION

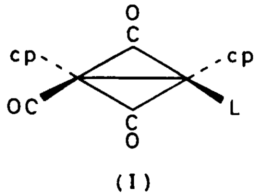
Synthesis.—Complexes (1a)—(1e) were prepared as described by Manning and co-workers.[5] Complex (1e) has previously been synthesized by tetrahydroborate reduction of [Fe(cp)(CO)(CNPh)I];[6] preliminary crystallographic results show that (1e) obtained from both reactions is identical.[7] The complex $[Ru_2(cp)_2(CO)_4]$ undergoes substitution slowly in refluxing xylene, and under the conditions described only monosubstitution is observed. Rapid decomposition of the ligand prevented preparation of $[Ru_2(cp)_2(CO)_3(CNPh)]$. The complex $[Os_2(cp)_2(CO)_4]$ did not undergo substitution under these conditions. Analytical data are in Table 1.

Infrared Spectra.—Infrared data are presented in Table 2. Since isonitriles may function either as bridging or terminal ligands, the four isomers (I)—(IV) are possible in principle.

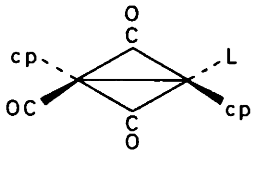
TABLE 1

Analytical data (%)

Compound	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
(2a)	40.3	3.1	3.3	39.4	2.8	3.1
(2b)	41.2	3.2	3.3	40.8	3.2	3.0
(2c)	42.0	3.5	3.2	42.1	3.5	2.9
(2d)	44.2	3.6	3.5	43.3	3.8	2.8
(3a)	34.9	2.7	2.8	35.1	2.7	2.7
(3b)	36.1	3.0	2.8	36.4	3.0	2.7
(3c)	37.7	3.0	2.7	37.5	3.3	2.5
(3d)	38.5	3.6	2.7	38.9	3.6	2.5
(3e)	42.1	2.7	2.8	41.7	2.8	2.4
(4)	31.7	2.6	2.7	31.1	2.6	2.3
(5a)	37.6	3.1	2.5	37.7	3.3	2.6
(5b)	39.7	3.5	2.7	40.1	3.9	2.5



(I)



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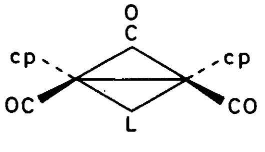

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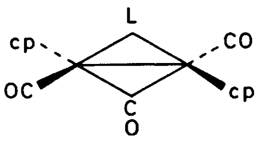


(IV)

Spectra of complexes (1a)—(1e) agree with those recently reported by Manning and co-workers,[5] and those of (2a)—(2d) can be assigned similarly. Thus, bands (A) and (B) are due to the terminal CN vibration of (I) and (II); band (C) may be assigned to the symmetric terminal CO vibration of (III), while band (D) is due to the incident asymmetric terminal CO vibrations of (III) and (IV) and the terminal CO vibrations of (I) and (II). Bands (F) and (G) are due to the coincident bridging CO vibrations of (III), (IV) and (I), (II) respectively, while bands (H) and (I) may be assigned to the bridging CN vibrations of (III) and (IV). The origin of the remaining terminal CO vibration (E) is not unambiguous, but a reasonable assignment is to the symmetric terminal CO vibration of (IV). Although inactive for $[Fe_2(cp)_2$-

(CO)$_4$],[8] it is well known that, both in solution [9] and the solid state,[6,10,11] bridging isonitrile ligands adopt a non-linear CN–R linkage (CN–R 125—130°), coupled possibly with a slight twist of the R group out of the plane defined by the Fe(μ-CO)(μ-CN)Fe moiety. Thus, the terminal symmetric CO vibration of (IV) may be allowed, although perhaps weakly.

The spectra indicate an increasing proportion of isomers (III) and (IV) in the order $C(CH_3)_3 < CH(CH_3)_2 < C_2H_5 < CH_3 <$ Ph, in agreement with n.m.r. results (see below). The order of the alkyl-substituted derivatives is consistent with the expected degree of steric interaction for an isonitrile in a bridging position, while the totally bridged isonitrile structure adopted by (1e) is undoubtedly a consequence of electronic rather than steric factors.[5] By comparison with (1a)—(1d), it can be seen that the ruthenium complexes show a much greater tendency towards occupation of the bridge position by isonitrile. Presumably, the need to bridge a longer M–M bond (1.24 *vs.* 1.36 Å in the parent dimers) [12,13] is more than compensated by relief of steric interaction between the cyclopentadienyl ligand and the alkyl substituent of the isonitrile. It should be noted that the spectrum of [Ru$_2$(cp)$_2$(CO)$_4$] in hexane reveals significant concentrations of both bridged [ν(CO) at 2 011, 1 964, and 1 794 cm^{-1}] and non-bridged forms [ν(CO) at 2 021, 1 972, and 1 943 cm^{-1}].[14] Bands of very low intensity at *ca.* 1 920, 1 930, and 1 964 cm^{-1} may possibly be assigned to very small concentrations of non-bridged isomers of (2a)—(2d), although no non-bridged isomers are evident in the n.m.r. studies. The equilibrium between bridged and non-bridged forms is very sensitive to ligand; thus, [Ru$_2$(C$_5$Me$_4$Et)$_2$(CO)$_4$],[15] [Ru$_2$(cp)$_2$(CO)$_3$(PPr$_3$)],[16] [Ru$_2$(cp)$_2$(CO)$_3$(CS)], and [Ru$_2$(cp)$_2$(CO)$_2$(CS)$_2$] [17] all adopt a totally bridged structure in solution, with thiocarbonyl functioning exclusively as a bridging ligand in the latter two complexes.

TABLE 2

Infrared data for (2a)—(2d) (hexane solution; values in cm^{-1} with relative intensities in parentheses)

Compd.	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)
(2a)	*b*	2 060 (5)	2 003 (95)	1 958 (100) 1 964 (sh)		1 808 (70)	1 772 (20)	1 729 (70)	
(2b)	2 124 (3)	*b*	2 004 (75)	1 958 (100) 1 963 (sh)	1 975 (10)	1 809 (55)	1 774 (15)	1 735 (25)	1 706 (15)
(2c)	2 110 (10)	2 090 (sh)	2 000 (95)	1 955 (100) 1 961	1 971 (10)	1 807 (80)	1 771 (35)	1 734 (20)	1 708 (50)
(2d)	2 120 (30)	2 075 (sh)	1 999 (5)	1 955 (70) [a]	1 973 (15)	1 804 (5)	1 775 (100)		

[a] CO vibration asymmetric, but assignment of shoulder not possible. [b] CN vibration asymmetric, but assignment of shoulder not possible.

Finally, it should be noted that both *cis* : *trans* ratios (I) : (II) and (III) : (IV) and the ratio of bridged to terminal isonitrile isomers are solvent dependent,[5,8] the proportion of the more polar isomers increasing with the polarity of the solvent. Direct comparison of isomer distributions derived from i.r. spectra (hexane solution) with those obtained from n.m.r. spectra (dichloromethane or toluene solutions) is therefore not valid.

Proton N.M.R. Studies of (1a)—(1e) *and* (2a)—(2d).—Proton n.m.r. data are given in Table 3. Since high-temperature limiting spectra were obtained for the iron complexes only at 60—80 °C, spectra were run in toluene solutions; ^{1}H spectra in CD$_2$Cl$_2$ at the low-temperature limit are included in the Table to enable comparison with ruthenium derivatives, and to confirm conclusions reached from the ^{13}C studies.

The proton spectrum of (1b) at −48 °C in the cyclopentadienyl region shows a single peak (δ 4.15) assignable to the equivalent cp ligands of (III), (IV) (assuming rapid nitrogen inversion), while the larger resonances at δ 4.29 and 4.27 may be assigned to the non-equivalent cp ligands of (I), (II). On the basis of intensities and decoupling experiments, the triplet and quartet resonances at δ 0.36 and 2.19 may be assigned respectively to the CH$_3$ and CH$_2$ resonances of (I), (II), while those at δ 1.39 and 3.71 may be assigned to (III), (IV). Although the apparent presence of only two isomers might be explained by depopulation of one bridging and one terminal isomer below the limits of detection, results on the analogous ruthenium complex indicate the true reason to be a coincidence of *cis* and *trans* signals. Thus the proton spectrum of (2b) at −85 °C shows complex multiplets at δ 3.5 and 1.1 assignable to CH$_2$ and CH$_3$ resonances respectively. Irradiation of the CH$_3$ multiplet reduced the CH$_2$ multiplet to a set of *four* singlets; the two at highest field may be assigned to *cis* and *trans* forms of the terminal isonitrile isomer, and the two at lower field to *cis* and *trans* forms of the bridging isonitrile isomer. No *cis*, *trans* distinction is, however, observed in the cyclopentadienyl region where the resonances at δ 5.09 and 5.19 may be assigned to the (I), (II) mixture and the resonance at δ 5.25 to the cp ligands of (III), (IV). For the iron complexes, only in the case of the phenyl derivative (1e) are separate resonances for (III) and (IV) observed.

Warming results in cyclopentadienyl site exchange in the resonances assigned to (I), (II) and bridge–terminal isonitrile exchange to yield finally the high-temperature limiting spectrum. The broadening and coalescence of resonances due to (III) and (IV) in the spectra of (1e) also demonstrates the presence of (III) $\rightleftharpoons$ (IV) interconversion.

The low-temperature spectra of (1a), (1c), (1d) and (2a), (2c), (2d) may be interpreted similarly, and show similar changes with temperature. The ratios of terminal : bridged isomers listed in Table 3 were derived from intensities of the cyclopentadienyl resonances in the low-temperature limiting spectrum, and the order is in agreement with the conclusions reached from i.r. studies.

Carbon-13 *N.M.R. Spectra of* (1a)—(1e) *and* (2a)—(2d).—Chemical-shift values are given in Table 4. Assignment of the spectrum of (1b) at −20 °C follows from chemical shifts and intensities, and is consistent with a mixture of bridged and terminal isonitrile isomers in which *cis*, *trans* differentiation is not observed. The only exception is (1e), where separate resonances due to (III) and (IV) are found.

TABLE 3

Variable-temperature ^1H n.m.r. spectra of (1a)—(1e) and (2a)—(2d) (δ relative to $SiMe_4$; multiplicities and coupling constants in parentheses)

Compound	θ_c/°C	Solvent	cp	Type of proton			Ratio of bridged : terminal isomers
				CH_3	CH_2	CH	
(1a)	−40	CD_2Cl_2	4.81	4.60			1 : 7
			4.67	2.85			
			4.54				
	−30	$C_6D_5CD_3$	4.27	1.69			1 : 4
			4.28				
			4.13	3.44			
	80	$C_6D_5CD_3$	4.31	2.55			
(1b)	−61	CD_2Cl_2	4.82	1.32 (t, 7.3)	3.89 (q)		1 : 16
			4.78	0.95 (t, 7.3)	3.22 (q)		
			4.57				
	−48	$C_6D_5CD_3$	4.29	0.36 (t, 7.1)	2.19 (q)		1 : 7
			4.27				
			4.16	1.39 (t, 7.1)	3.71 (q)		
	80	$C_6D_5CD_3$	4.32	0.72 (t, 7.1)	2.79 (q)		
(1c)	−40	CD_2Cl_2	4.81	1.19 (d, 6.5)		*a*	1 : 30
			4.68	1.01 (d, 6.5)		3.58 (s)	
			4.56				
	−30	$C_6D_5CD_3$	4.27	0.53 (d, 6.5)		2.73 (s)	1 : 13
			4.28				
			4.16	1.59 (d, 6.5)		*a*	
	64	$C_6D_5CD_3$	4.31	0.73 (d, 6.5)		3.04 (s)	
(1d)	−20	CD_2Cl_2	4.67	1.02			*b*
			4.55				
	−40	$C_6D_5CD_3$	4.30	1.72			*b*
			4.27				
	30	$C_6D_5CD_3$	4.31	1.77			
(1e) [c]	−22	CD_2Cl_2	4.66 [d]				*e*
			4.73				
	−28	$C_6D_5CD_3$	4.24 [d]				*e*
			4.11				
	50	$C_6D_5CD_3$	4.23				
(2a)	−90	CD_2Cl_2	5.26	3.20			3.4 : 1
			5.18	2.94			
			5.08				
	22	CD_2Cl_2	5.28	3.27			
(2b)	−85	CD_2Cl_2	5.27				2.3 : 1
			5.20	0.95—	3.15—		
			5.10	1.25 (m)	3.77 (m)		
	22	CD_2Cl_2	5.26	1.24 (t, 7.3)	3.53 (q)		
(2c)	−90	CD_2Cl_2	5.25			3.75 (s, br)	1.4 : 1
			5.19	1.11 (m)		3.35 (s, br)	
			5.09				
	20	CD_2Cl_2	5.24	1.25 (d, 6.4)		3.65 (s)	
(2d)	−90	CD_2Cl_2	5.20	1.02			*b*
			5.18				
	25	CD_2Cl_2	5.16	1.13			

[a] Septet not detected due to low abundance. [b] No bridging isomer detectable. [c] Aromatic multiplet at δ 7.05—7.49. [d] Two cyclopentadienyl peaks assignable to (III), (IV) in the ratio of 1 : 4 and 1 : 2.5 in CD_2Cl_2 and $C_6D_5CD_3$ respectively. [e] No terminal isomer detectable.

Values of 272.9 and 211.0 p.p.m. have been found for the bridging and terminal resonances of *cis*-[$Fe_2(cp)_2(CO)_4$] in CH_2Cl_2;[18] the only consistent variation found for (1a)—(1d) is a downfield shift of *ca.* 6 p.p.m. for the bridging CO resonance attributed to (I), (II). The average chemical-shift difference between bridging and terminal CO ligands for (1a)—(1e) (*ca.* 65 p.p.m.) is quite similar to that observed for the parent dimer (62 p.p.m.); the ruthenium complexes show on average a smaller chemical-shift difference between bridging and terminal positions (*ca.* 50 p.p.m.). The downfield shift of the isonitrile resonance on bonding as a bridging ligand is much larger (*ca.* 80 p.p.m. for both iron and ruthenium complexes).

Warming results in the onset of bridge–terminal carbonyl and isonitrile exchange, while changes in the alkyl and cyclopentadienyl region are consistent with those observed in the ^1H spectra. High-temperature limiting spectra were not obtained for the iron complexes due to limited solubility in toluene and slow decomposition at elevated temperatures. However, the spectrum of the ruthenium complex (2b) (Figure) shows clearly the high-temperature limiting spectrum obtained at 0 °C.

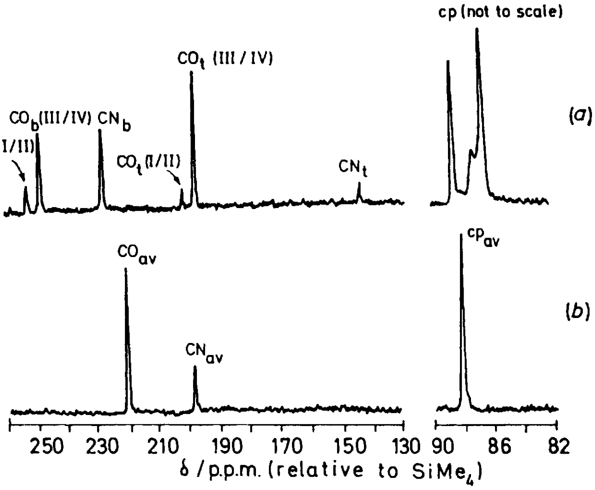
The ^{13}C spectrum of $[Ru_2(cp)_2(CO)_4]$ [18] in CH_2Cl_2 (34 °C) shows only one resonance at 216.9 p.p.m. which does not broaden down to −80 °C. Assuming values of 250 and 200 p.p.m. respectively for bridging and terminal Ru–CO resonances, the position of this averaged value corresponds approximately to a 1 : 1 mixture of bridged and non-bridged isomers in solution, in agreement with i.r. results. We have also determined the n.m.r. spectral parameters (0 °C, CD_2Cl_2) of $[Os_2(cp)_2(CO)_4]$[^{13}C, CO 185.3, cp 82.5; ^1H, cp 5.39 p.p.m.]; no dependence on temperature down to −80 °C is observed in either spectrum. The CO resonance is quite clearly in a position associated with a terminal Os–CO moety,[19] and is consistent with the i.r. spectrum [hexane (relative intensities in parentheses): 2 010 (15), 1 967 (93), and 1 931 (100) cm^{-1}] which shows that the osmium complex exists in solution solely as the non-bridged isomer.

TABLE 4

Carbon-13 n.m.r. spectra of (1a)—(1e) and (2a)—(2d) (CD_2Cl_2–CH_2Cl_2 solvent; chemical shifts in p.p.m. relative to $SiMe_4$)

Complex	θ_c/°C	CO_b	CN_b	CO_t	CN_t	cp	CH_3	CH_2	CH	C
(1a)	−24	278.8		211.8	158.4	85.9 84.9	29.3			
		272.6	246.6	209.9		86.9	34.8			
(1b)	−20	278.2		212.0	159.9	86.1 85.3	14.2	38.8		
		272.1	242.0	210.2		86.9	15.3	40.8		
(1c)	−20	278.5		211.8	158.4	85.8 84.0	21.9		47.4	
		272.8	239.7	210.1		86.9	23.0		*a*	
(1d)	−20	278.1		211.6	157.8	85.5 84.7	28.6			*b*
(1e) [c]	−20	270.1	252.6	209.7		86.4				147.9
		275.7		211.1		87.9				147.2
(2a) [d]	−70	247.7	227.0	197.8		89.0 87.2	46.9			
(2b)	−70	247.4	224.0	197.7		88.6 87.5	14.8	*a*		
		253.1		200.0	142.9	*e*	13.3	38.2		
(2c)	−70	247.7	220.4	197.8		88.6 86.8	22.5		63.5	
		252.9		200.6	142.6	*e*	21.2		44.3	
(2d)	−70	252.8		200.8	142.5	87.6 86.6	28.2			*b*

[a] Not detected; may be under solvent resonance at 53.9 p.p.m. [b] Probably under solvent resonance; chemical shift for quaternary carbon of free ligand is 51.2 p.p.m. (benzene solution). [c] Two sets of resonances due to (III) and (IV); those of higher intensity quoted first. *Para* and (*ortho* + *meta*) resonances at 112.0 and (119.0 + 127.8) p.p.m. [d] Resonances due to terminal isomers not detected. [e] Resonances due to terminal isomers obscured by bridging isomer resonances.



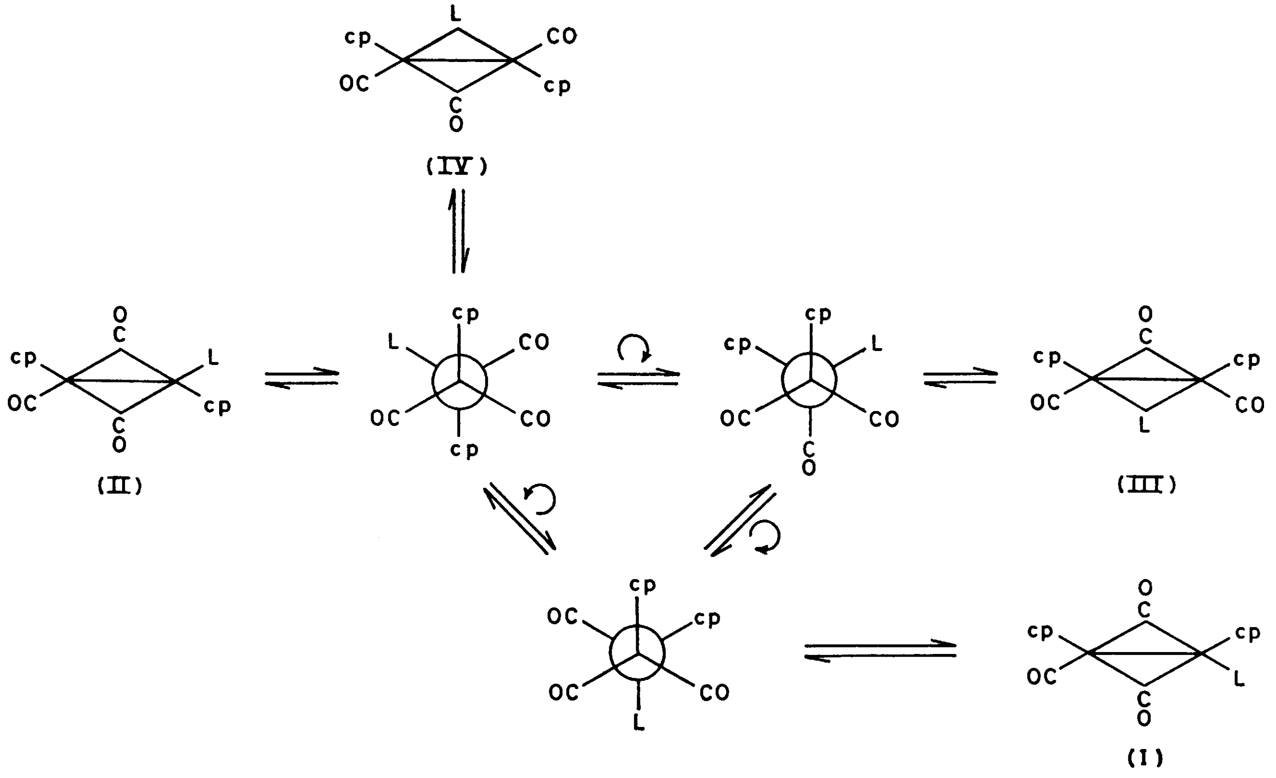
Carbon-13 n.m.r. spectra at (*a*) −70 and (*b*) 0 °C of $[Ru_2(cp)_2(CO)_3(CNEt)]$ in CH_2Cl_2–CD_2Cl_2 solution

In the low-temperature ^{13}C spectra of the ruthenium complexes (2a)—(2c), two cyclopentadienyl resonances are observed for the (III), (IV) mixture (although only a single peak in the ^1H spectrum). Since the two peaks are of equivalent intensity for all three complexes, assignment to *cis* and *trans* isomers seems unlikely, and it appears that at this temperature nitrogen inversion is also slow on the n.m.r. time scale, thus creating inequivalent cyclopentadienyl ligands. Even at temperatures down to −110 °C (CH_2Cl_2–CCl_3F solution), the cyclopentadienyl resonances of the iron complex (1e) show no sign of splitting and since the slowing of nitrogen inversion in the complex $[Fe_2(cp)_2(CO)_2(CNMe)_2]$ can be easily seen,[9] we assume that, in complexes (1a)—(1d), nitrogen inversion is still fast at −80 °C and has a lower activation energy than nitrogen inversion in the ruthenium complexes.

The CO and CN resonances in the high-temperature limiting spectra of (2a)—(2c) are not in the positions calculated from chemical-shift differences and relative isomer populations in the low-temperature spectra. The results indicate an increase in the population of the terminal isonitrile isomer with *increasing* temperature. In the absence of high-temperature limiting spectra for (1a)—(1c), we have studied the change in isomer population with temperature using variable-temperature i.r. spectroscopy. For (1b), (1c) in cyclohexane [(1a) is too insoluble at low temperatures] a decrease in temperature

(+20 to −55 °C) results in an increase in the intensity ratio of band G to band F, thus indicating an increasing proportion of terminal isonitrile isomer with *decreasing* temperature.

Finally, the results from the n.m.r. studies can be compared with predicted behaviour from the Adams–Cotton mechanism.



SCHEME 1 Mechanism for interconversion of (I) and (IV). L = CNR

(*i*) Scheme 1 shows that all of isomers (I)—(IV) may be interconverted by bridge opening–bridge closing. Only for the interconversion (II) $\rightleftharpoons$ (IV) may this be done without bond rotation of the unbridged intermediate, which is a requirement for the other five interconversions capable in principle of observation [(I) $\rightleftharpoons$ (II), (I) $\rightleftharpoons$ (III), (I) $\rightleftharpoons$ (IV), (II) $\rightleftharpoons$ (III), and (III) $\rightleftharpoons$ (IV)].

(*ii*) For any of the six possible exchange processes, a closed cycle may be drawn [as shown in Scheme 2 for (I) $\rightleftharpoons$ (III) exchange]. It can be shown for all six cycles that *cis–trans* isomerism or bridge–terminal isonitrile isomerism must be accompanied by bridge–terminal carbonyl exchange, and that where bridge–terminal isonitrile exchange occurs, this must be accompanied by cyclopentadienyl site exchange in the terminally bound isonitrile isomer (see Scheme 2). Although drawn as a closed loop, linking to other cycles occurs by one or more of the unbridged rotamers. All possible permutamers have not been shown, since in the absence of labelling of the metal atoms and/or the cyclopentadienyl ligands they are indistinguishable from those drawn.

It might therefore be expected that (II) $\rightleftharpoons$ (IV) interconversion would proceed with a lower activation energy, and that resonances assigned to these isomers would broaden and coalesce at a lower temperature, as observed for [Fe$_2$(cp)$_2$(CO)$_4$].[20] For the parent dimer, the difference between $\Delta G^\ddagger$ for the process involving M–M bond rotation and $\Delta G^\ddagger$ for the process simply involving bridge opening and closing is at least 4.5 kcal mol^{-1}.[*,†] In contrast, the difference in $\Delta G^\ddagger$ between processes involving and not involving M–M bond rotation in [Fe$_2$(cp)$_2$(CO)$_2$(CNMe)$_2$] is only 1.4 kcal mol^{-1} (the values are also much higher, being 17.5 and 18.9 kcal mol^{-1} respectively). The monosubstituted complex might be expected to fall at intermediate values. Examination of both iron and ruthenium ^{13}C spectra reveals an equivalent collapse of both CO and CN resonances, perhaps as expected in view of the anticipated small difference in $\Delta G^\ddagger$ between the two processes, and in view of the probable low population of isomer (II).

It is qualitatively obvious from the spectra that activation energies for exchange in the ruthenium complexes are lower. Perhaps the most meaningful comparison of $\Delta G^\ddagger$ values is for the cyclopentadienyl site

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[*] Throughout this paper: 1 cal = 4.184 J.

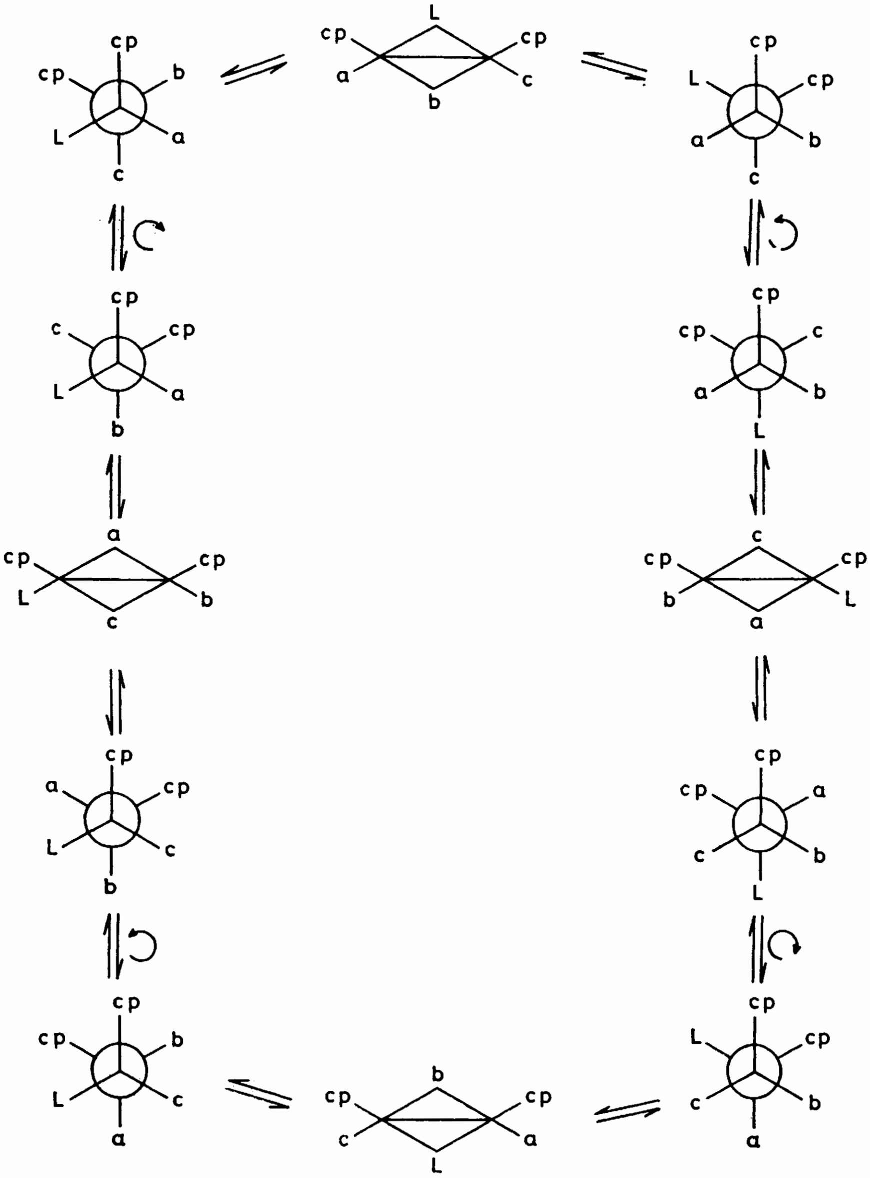
[†] Values for the two $\Delta G^\ddagger$ of 11.4 and 6.9 kcal mol^{-1} may be calculated from the data of ref. 18 assuming T_c values of 273 and 193 K respectively. The ΔG value is a minimum difference since the coalescence temperature for the latter process is lower than 193 K.

exchange of (1d) and (2d) where calculations* give values of 14.2 † and 10.9 kcal mol^{-1} respectively. It is apparent from comparison of i.r. spectra for the parent dimers that the bridged and non-bridged forms of $[Ru_2(cp)_2(CO)_4]$ are of more comparable stability, and the lower activation energies observed for isomer interconversion and site exchange are consistent with this.

Complexes (3a)—(3e), (4), *and* (5a), (5b).—Electrophilic attack by acid on the nitrogen of (1a) was first observed by Treichel *et al.*[21] While protonation of terminally co-ordinated isonitrile has been observed,[22] all results here indicate that protonation or alkylation results in isolation of only the bridged iminium derivative.

During the course of this work, several of these derivatives have been reported by Willis and Manning.[23,24] Although i.r. spectra are similar, the salts prepared by our methods do not contain solvent of crystallization (analytical data, Table 1). We have also achieved the protonation of (1d). Previously its non-reaction had been attributed to the considerable steric interaction of a Bu^t group in a bridging position; we have recently shown, however, that in the complex $[Fe_2(cp)_2(CO)_2(CNBu^t)_2]$ there is a small but significant concentration of the $[(OC)(cp)Fe(\mu\text{-}CO)(\mu\text{-}CNBu^t)\text{-}Fe(cp)(CNBu^t)]$ isomer.[25]

Proton and ^{13}C spectral data are given in Tables 5 and



SCHEME 2 Mechanism for *cis*-bridging $\rightleftharpoons$ *cis*-terminal [(I) $\rightleftharpoons$ (III)] exchange. L = CNR

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* Calculated using T_c values of 283 and 218 K for (1d) and (2d) respectively both in CD_2Cl_2.

† An activation energy of 14.4 kcal mol^{-1} has been determined for this process in CS_2 solution (R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, 1974, **13**, 257).

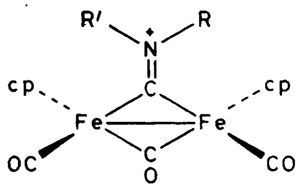
TABLE 5

Proton n.m.r. data for $[M_2(cp)_2(CO)_3(CNRR')][PF_6]$ [M = Fe, (3) and(5); Ru, (4)] complexes [$(CD_3)_2CO$ solution, −10 °C; chemical shifts relative to $SiMe_4$]

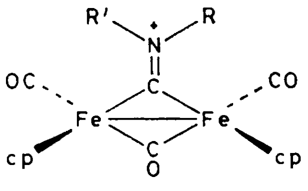
Compound	R	R′	CH_3'	CH_2'	CH_3	CH_2	CH	cp	NH
(3a)	CH_3	H			4.09			5.45	3.22 (br)
(3b)	CH_2CH_3	H			1.54 (t) J = 7.3 Hz	4.49 (q)		5.47	3.07 (br)
(3c)	$CH(CH_3)_2$	H			1.74 (d) 1.64 (d) J = 6.0 Hz		4.77 (s)	5.45	3.17 (br)
(3e) *	Ph	H						5.35	3.26 (br)
(4)	CH_2CH_3	H			1.45 (t) J = 7.3 Hz	4.23 (q) 4.24 (q)		5.87 5.78	3.03 (br)
(5a)	CH_3	CH_2CH_3	1.64 (t) J = 7.2 Hz	4.66 (q) 4.68 (q)	4.28			5.54 5.52	
(5b)	$CH(CH_3)_2$	CH_2CH_3	1.70 (t) J = 7.2 Hz	4.57 (q)	1.48 (d) 1.83 (d) J = 6.8 Hz		5.30 (s)	5.55 5.53	

* Aromatic multiplet at δ 7.71.

6. Slight decomposition even at −10 °C results in broadening of resonances in the ^1H spectra [particularly for (3d) for which a spectrum could not be obtained] which is undoubtedly responsible for the observation of only one cyclopentadienyl resonance for (3a)—(3c), (3e). Of particular interest is the doubling of the doublet resonances associated with the $CH(CH_3)_2$ groups of (3c) and (5b) and the quartet resonances associated with the CH_2 groups of (4) and (5a). This we attribute to a mixture of the two diastereoisomeric forms (V) and (VI) in equal proportions. The most obvious feature of the ^{13}C spectra is the large deshielding (*ca.* 75 p.p.m.) of the CN carbon compared to values for neutral bridging isonitrile. A similar, although smaller, deshielding (35 p.p.m.) of the bridging carbonyl resonance of $[Fe_2(cp)_2(CO)_4]$ has been observed on adduct formation with BCl_3 to yield $[(OC)(cp)Fe(\mu\text{-}CO{\cdot}BCl_3)_2Fe(cp)(CO)]$.[26] Inequivalence of the two iron atoms is evident only in the two cyclopentadienyl resonances observed for (3d) and the two terminal CO resonances of (5a). No fluxional process involving cyclopentadienyl site exchange is likely for the other complexes, and a simple coincidence of signals is postulated.



(V)



(VI)

TABLE 6

Carbon-13 n.m.r. data for $[Fe_2(cp)_2(CO)_3(CNRR')][PF_6]$ complexes [$(CD_3)_2CO$ solution, −10 °C; chemical shifts in p.p.m. relative to $SiMe_4$]

			^{13}C Nucleus									
Compound	R	R′	CO_b	CN_b	CO_t	cp	CH_3'	CH_2'	CH_3	CH_2	CH	C
(3a)	CH_3	H	255.5	320.6	208.2	89.9			44.3			
(3b)	CH_2CH_3	H	255.4	318.6	208.4	89.9			14.3	54.8		
(3c)	$CH(CH_3)_2$	H	255.3	315.4	208.5	89.9			22.0		64.0	
(3d)	$C(CH_3)_3$	H	254.3	314.1	209.2	89.9 90.3			*a*			63.7
(3e)	Ph [b]	H	255.2	321.7	208.6	90.1						143.7
(5a)	CH_3	CH_2CH_3	255.2	315.9	208.7 208.3	90.3	13.0	63.0	56.6			
(5b)	$CH(CH_3)_2$	CH_2CH_3	255.2	316.4	209.0	90.4	16.0	53.7	20.7		63.7	

[a] Not detected, but may be under solvent resonance at 29.2 p.p.m. [b] *Para* and (*ortho* + *meta*) resonances at 128.8 and (123.3 + 129.9) p.p.m.

EXPERIMENTAL

The isonitriles,[27-29] $[Ru_2(cp)_2(CO)_4]$,[17] and $[OEt_3][BF_4]$ [30] were prepared by literature methods; $[Os_2(cp)_2(CO)_4]$ was prepared asd escribed [31] using Tl[cp] instead of Na[cp] and purified by column chromatography. Other chemicals were purchased. Reactions were carried out under nitrogen in purified solvents.

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 1.0 mm NaCl cells, variable-temperature spectra using a Beckman-RIIC VLT-2 cell equipped with an automatic temperature controller. Proton and ^{13}C n.m.r. spectra were obtained using a JEOL FX-100 spectrometer, ^{13}C spectra in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate) as relaxation agent.

Preparations.—(*a*) $[Ru_2(cp)_2(CO)_3(CNMe)]$. The complex $[Ru_2(cp)_2(CO)_4]$ (0.5 g, 1.13 mmol) and CH_3NC (1.00 g, 2.2 mmol) were stirred in refluxing xylene (10 cm^3) for *ca.* 24 h until reaction was complete as judged by the i.r. spectrum. The solvent was removed under reduced pressure and the residue was chromatographed on grade II alumina using CH_2Cl_2. The complex $[Ru_2(cp)_2(CO)_4]$ was eluted first, followed by the product as a yellow band. Recrystallization from CH_2Cl_2–light petroleum (40 : 60) gave 0.25 g of orange crystals. Complexes (2b)—(2d) were prepared similarly.

(*b*) $[Fe_2(cp)_2(CO)_3(CNHMe)][PF_6]$. The complex $[Fe_2(cp)_2(CO)_3(CNMe)]$ (1.0 g, 2.6 mmol) was stirred in diethyl ether (25 cm^3) and enough CH_2Cl_2 added dropwise to bring it into solution. Hexaflorophosphoric acid (75% aqueous) was added dropwise until precipitation ceased. The deep red precipitate of (3a) was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 1.4 g). Complexes (3b)—(3e) and (4) were prepared similarly [(4), ν(CO) at 2 015, 1 995, and 1 835 cm^{-1}; ν(CN) at 1 585 cm^{-1} (Nujol mull)].

(*c*) $[Fe_2(cp)_2(CO)_3(CNMeEt)][PF_6]$. To a stirred solution of $[Fe_2(cp)_2(CO)_3(CNMe)]$ (1.0 g, 2.6 mmol) in diethyl ether (25 cm^3) was added an excess of $[OEt_3][BF_4]$. After 30 min, the red precipitate was filtered off, dissolved in the minimum of acetone, and added dropwise to a stirred aqueous solution of $[NH_4][PF_6]$. The resultant red precipitate was filtered off, washed with a small amount of cold ethanol followed by diethyl ether, and dried *in vacuo* (yield 1.11 g). Complex (5b) was prepared similarly [(5a), ν(CO) at 2 010, 1 985, and 1 825 cm^{-1}, ν(CN) at 1 575 cm^{-1}; (5b), ν(CO) at 2 015, 1 985, and 1 820 cm^{-1}, ν(CN) at 1 595 cm^{-1} (Nujol mull)].

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