Carbon-13 Nuclear Magnetic Resonance Spectra and Mechanism of Bridge–Terminal Carbonyl Exchange in Di-μ-carbonyl-bis[carbonyl(η-cyclopentadienyl)iron](*Fe–Fe*) $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2]$; *cd*-Di-μ-carbonyl-*f*-carbonyl-*ae*-di(η-cyclopentadienyl)-*b*-(triethyl -phosphite)di-iron(*Fe–Fe*) $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_3P(OEt)_3]$,† and some Related Complexes

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A mechanism involving carbonyl-bridge breaking, rotation about the Fe–Fe bond, and bridge reformation is shown to account qualitatively for changes in the carbonyl region of the ^{13}C n.m.r. spectrum of the complex $[(cp)(OC)Fe(\mu\text{-}CO)_2Fe(cp)\{P(OEt)_3\}]$ and quantitatively for $[(cp)(OC)Fe(\mu\text{-}CO)_2Fe(CO)(cp)]$ (cp = η-cyclopentadienyl). The activation energy for this process, 49·0 ± 4 kJ mol^{-1} (11·7 ± 1 kcal mol^{-1}), is close to that reported for *cis–trans*-isomerization of the cp groups, in accord with this mechanism. Variable-temperature ^{13}C n.m.r. spectra of the complexes $[(cp)(OC)Ru(\mu\text{-}CO)_2Ru(CO)(cp)]$ and $[(cp)(OC)Fe(\mu\text{-}CO)_2Ni(cp)]$ are also reported.

THE variable-temperature ^{13}C n.m.r. spectrum of the complex $[(cp)(OC)Fe(\mu\text{-}CO)_2Fe(cp)L]$ (I; L = CO, cp = η-cyclopentadienyl) has been interpreted in terms of both bridge–terminal and *cis–trans*-carbonyl exchange.[1] Mechanisms have been recently published by Adams and Cotton,[2,3] which account for the fact that bridge–terminal exchange in the *trans*-isomer of complex (I) is much more facile than that in the *cis*-isomer. Carbonyl-bridge opening, followed by bridge closure, with no rotation of the non-bridged intermediate [equation (1)] accounts for bridge–terminal exchange in the *trans*-isomer. The *cis*-isomer, however, *cannot* undergo bridge–terminal exchange without simultaneous rotation about the metal–metal bond [equation (2)].

Before the Adams and Cotton papers appeared, we initiated an investigation of carbonyl exchange in the complex $[(cp)(OC)Fe(\mu\text{-}CO)_2Fe(cp)L]$ [I; L = $P(OEt)_3$] for which equation (1) is not applicable, because the phosphite ligand cannot reside in a bridging position. It was expected, therefore, that the *trans*-isomer would not exhibit bridge–terminal averaging independent of *cis–trans*-isomerization. We also sought to delineate the kinetics of exchange from the change in linewidths of carbonyl absorptions of complex (I; L = CO) as a function of temperature. Finally, we undertook brief investigations of the complexes $[(cp)(OC)Ru(\mu\text{-}CO)_2Ru(CO)(cp)]$, (II), and $[(cp)(OC)Fe(\mu\text{-}CO)_2Ni(cp)]$, (III). The results obtained are in full agreement with those of Adams and Cotton [2] with different ligands.

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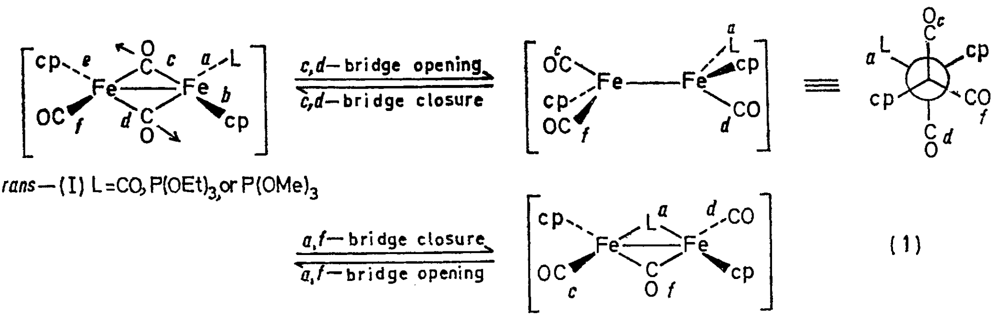
† Throughout the paper, only the name of the *cis*-isomer is given in full.

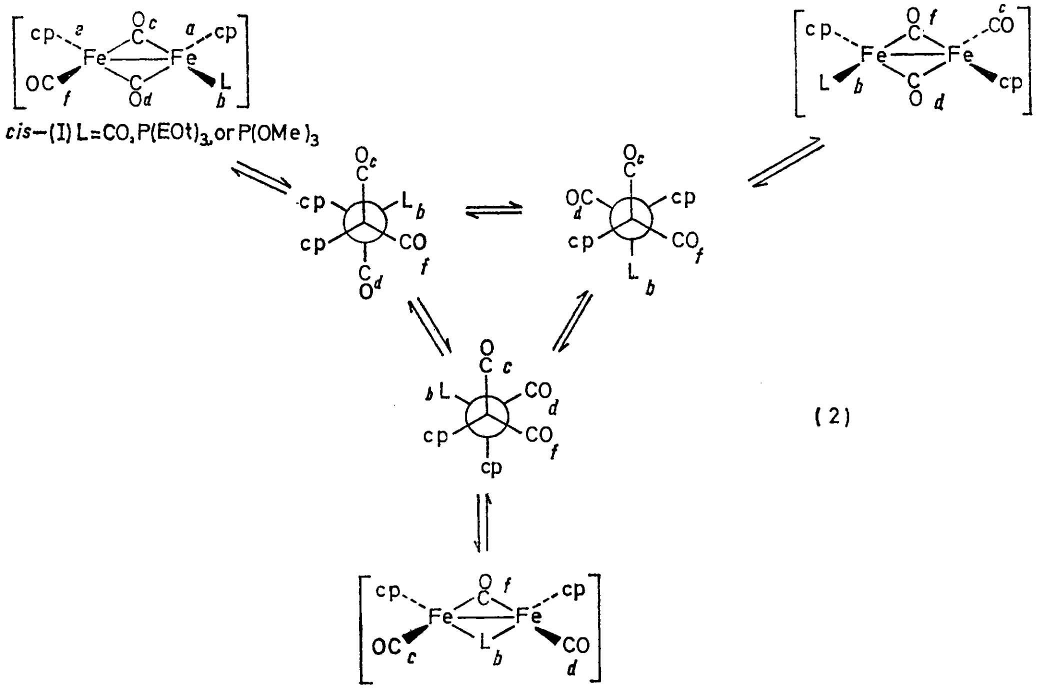
[1] O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, 1972, **94**, 2550.

[2] R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 1973, **7**, 153; *J. Amer. Chem. Soc.*, 1973, **95**, 6589.

[3] The same mechanisms were developed independently in this laboratory, *cf.* D. C. Harris, Ph.D. Thesis, California Institute of Technology, 1973, pp. 404—408.



(1)



(2)

EXPERIMENTAL

The complex [(cp)(OC)Fe(μ-CO)$_2$Fe(cp)L] (I; L = CO) was obtained from a commercial source and crystallized from ethanol. The method of Haines and DuPreez [4] was used to prepare the complexes [I; L = P(OMe)$_3$ and P(OEt)$_3$]. The complex [(cp)(OC)Ru(μ-CO)$_2$Ru(CO)(cp)], (II), was prepared by a procedure similar to Manning's [5,6] and sublimed twice, while [(cp)(OC)Fe(μ-CO)$_2$Ni(cp)], (III), was obtained by the method of Tilney-Bassett,[7] chromatographed on neutral alumina with 4 : 1 light petroleum (b.p. 30—60 °C)-benzene, and crystallized from 6 : 1 light petroleum-benzene.

^{13}CO *Enrichment*.—Complexes [I; L = CO or P(OEt)$_3$], (II), and (III), were stirred in benzene solutions under 90% ^{13}C-enriched carbon monoxide for 1 day at 45—50 °C. Enrichments were 14, 33, 48, and 36% respectively. The percent enrichment was determined from heights of the *m/e* 28 (^{12}CO) and 29 (^{13}CO) peaks in the 70 eV mass spectrum. All complexes other than (I; L = CO) reacted with CO to produce products in addition to enriched starting material. Thus, complex [I; L = P(OEt)$_3$] produced a mixture of 21% (I; L = CO) and 79% [II; L = P(OEt)$_3$]. This mixture was converted to pure [I; L = P(OEt)$_3$] by stirring it with excess of triethyl phosphite [the mole ratio of triethyl phosphite to (I; L = CO) was 5 : 1] in benzene at 60 °C *in vacuo* with periodic removal of the evolved CO by freeze–thaw degassing on a vacuum line. The purity was readily checked by ^{1}H n.m.r. spectroscopy (Table 1). Complex (II) was freed from unidentified ruthenium carbonyls produced by enrichment by crystallization from toluene. The carbonylation by-products of complex (III) included (I; L = CO) and a green volatile solid, presumably (cp)$_2$Ni. No attempt was made to remove complex (I; L = CO) from (III) after enrichment.

N.M.R. Spectra.—Fourier-transform ^{13}C n.m.r. spectra were recorded on our modified Bruker–Varian DFS-60 spectrometer operating at 15·09 MHz with deuterium lock and proton-noise decoupling. Chemical shifts are all in p.p.m. downfield of internal tetramethylsilane (tms). Temperatures were measured with a thermocouple or thermometer and were generally constant to ±2 °C. I.r.

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[4] R. J. Haines and A. L. DuPreez, *Inorg. Chem.*, 1969, **8**, 1459.

[5] A. R. Manning and P. A. McArdle, *J. Chem. Soc.* (*A*), 1970, 2128.

[6] An apparently superior synthesis has recently been published: A. P. Humphries and S. A. R. Knox, *J.C.S. Chem. Comm.*, 1973, 326.

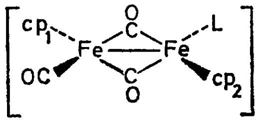
[7] J. F. Tilney-Bassett, *J. Chem. Soc.*, 1963, 4784.

spectra were obtained with a Perkin-Elmer 225 spectrometer. All reactions were carried out in atmospheres of nitrogen or argon. All solids, except (III), could be handled in the air without apparent harm, but were stored under a nitrogen atmosphere in a refrigerator. Solvents for the n.m.r. spectra were dried over Linde 4A molecular sieves and distilled *in vacuo* into the n.m.r. tubes. Solvents for other purposes were deoxygenated by bubbling a stream of nitrogen through them. Unless otherwise stated, all n.m.r. samples contained 0·08—0·10M-$Cr(acac)_3$ (acac = 2,4-pentanedionate) (crystallized from benzene–hexane, m.p. 212—213 °C) as relaxation reagent and were sealed under a N_2 atmosphere.

^1H Chemical shifts of all groups in complexes (I) were at significantly higher fields in benzene and toluene than in non-aromatic solvents (see Table 1). The ^{13}C shifts for triethyl phosphite are given in Table 2. Complex [I; L = $P(OMe)_3$] exhibited bridge and terminal carbonyl carbon absorptions of the predominant isomer at 282·0 ($J \approx 19$ Hz) and 215·4 p.p.m., respectively. Cyclopentadienyl carbon atoms appeared at 87·3 and 85·8 p.p.m., and the methyl carbons at 51·4 p.p.m. These data are for 1 : 1 $Cl_2C(D)C(D)Cl_2$–toluene solutions, 0·16M in complex [I; L = $P(OMe)_3$].

TABLE 1

^1H Chemical shifts (p.p.m.) and coupling data (J/Hz) for complexes (I)



L	Solvent	Chemical shift cp₁	Chemical shift cp₂	$J(^{31}P-^1H_2)$	Chemical shifts for L CH₂	Chemical shifts for L CH₃
CO	$MeCO_2H$	4·89				
	MeCN	4·83				
	C_6C_6	4·31				
	CD_2Cl_2	4·77				
$P(OMe)_3$	Me_3CO_2H	4·67	4·53	1·5		3·50
	$CDCl_3$	4·66	4·51	0·9		3·53
	CD_2Cl_2	4·67	4·52	1		3·52
	$(CD_3)_2CO$	4·67	4·56	1·0		3·50
	C_6H_6	4·46	4·36			3·30
$P(OEt)_3$ [a]	CH_2Cl_2	4·66	4·50	1·2	3·97	1·18
	C_6C_6	4·45	4·35	1·0	3·86	1·02
	$C_6H_6Me_3$	4·48	4·40	1·1	3·87	1·01

[a] For $P(OEt)_3$ in benzene, $\delta(CH_3)$ 1·12 and $\delta(CH_2)$ 3·81 p.p.m. [$J(^1H-^1H)$ 7, $J(^{31}P-CH_2)$ 7 Hz].

TABLE 2

Triethyl phosphite ^{13}C n.m.r. data [a]

Compound	Chemical shift/p.p.m. CH₂	Chemical shift/p.p.m. CH₃	$J(^{31}P-^{13}C)$/Hz CH₂	$J(^{31}P-^{13}C)$/Hz CH₃
$P(OEt)_3$	57·9	17·1	11·6	4·8
[I; L = $P(OEt)_3$] in CH_2Cl_2	60·8	16·2	4	6
[I; L = $P(OEt)_3$] in toluene	60·5	16	4	6

[a] All spectra were run at 30 ± 2 °C. Chemical shifts are referred to tms as zero. The triethyl phosphite sample consisted of triethyl phosphite (2 cm³), $CDCl_3$ (1 cm³), and tms (0·2 cm³).

RESULTS AND DISCUSSION

Complex [I; L = $P(OEt)_3$].—To test the proposed mechanism, both *cis*- and *trans*-isomers should be present in solution. From the work of Haines and DuPreez,[4] it is clear that both are present in cyclohexane, but an assignment of which isomer gives rise to which i.r. bands has never been made. In cyclohexane, we found two strong bands in the terminal metal–carbonyl stretching region at 1 964 and 1 944 cm⁻¹, logically taken to indicate the presence of both *cis*- and *trans*-isomers in this solution. In toluene, the bands were much broader and overlapped, yielding a maximum at 1 955 and a shoulder at 1 940 cm⁻¹. In dichloromethane, a second isomer was not evident from the i.r. spectrum, there

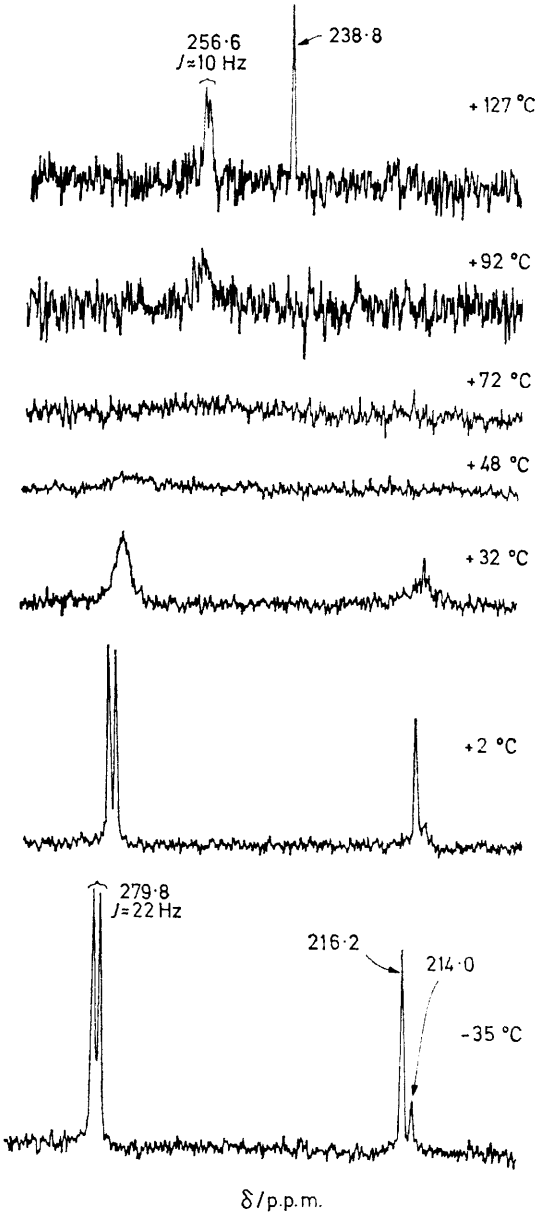


FIGURE 1 Variable-temperature Fourier-transform ^{13}C n.m.r. spectrum of a 0·13M solution of complex [I; L = $P(OEt)_3$] (33% enriched in ^{13}CO) with 0·08M-$Cr(acac)_3$ in toluene. The lower five traces represent 2 000 transients and the upper two 4 000. The 238·8 p.p.m. absorption belongs to an irreversibly formed thermal-decomposition product, probably (I; L = CO), which remains when the sample is cooled to 52 °C

being a nearly symmetrical peak at 1 952 cm^{-1}. Finally, the solid (KBr pellet) appeared to contain only one of the two isomers, the small splitting of the bands being a solid-state effect also seen in the individual isomers of complex (I; L = CO).[8]

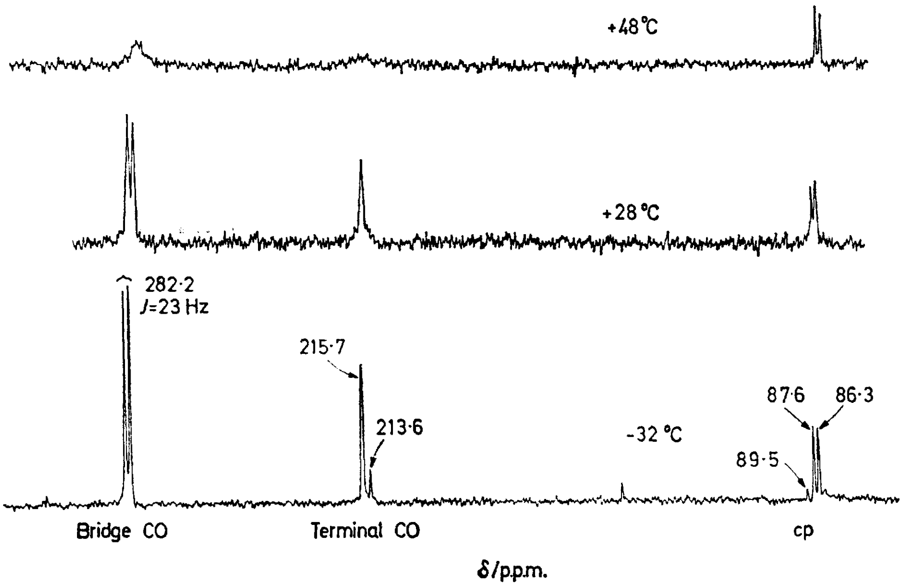


FIGURE 2 Variable-temperature Fourier-transform ^{13}C n.m.r. spectrum of a 0·17M solution of complex [I; L = P(OEt)$_3$] (33% enriched in ^{13}CO) with 0·09M-Cr(acac)$_3$ in dichloromethane. Each trace represents 2 000 transients

The low-temperature ^{13}C n.m.r. spectrum of complex [I; L = P(OEt)$_3$] in toluene (Figure 1) and dichloromethane (Figure 2) is very revealing. (We confirmed that no further changes took place in the spectrum below the lowest temperatures shown in Figures 1 and 2.) In the terminal-carbonyl region (*ca.* 215 p.p.m.), *both* solutions exhibited two isomers. The ratio of the latter was 4·4 (±1) : 1 in toluene and 5·9 (±1) : 1 in dichloromethane. As we expect the *cis*-isomer to be more polar than the *trans*-isomer, there should be more *cis*-isomer in dichloromethane than in toluene (or cyclohexane). On this basis, we believe the predominant isomer in all three solvents to be the *cis*-isomer.[9,*] In the bridging-carbonyl region, the isomers produced overlapping absorptions near 280 p.p.m. [J(^{31}P–^{13}C) 22 Hz]. In the cp region, the *cis*-isomer gave two peaks at 87·6 and 86·3 p.p.m. (Figure 3) with no observable ^{31}P–^{13}C coupling. A smaller peak at 89·5 p.p.m. is probably due to the *trans*-isomer, the other absorption of which must be under the *cis*-absorptions. This small *trans*-signal coalesced with the *cis*-signals at higher temperature. It is to be noted that phosphorus–carbon coupling was reduced when exchange was rapid amongst the carbonyl positions. The coalescence behaviour is fully consistent with the bond-rotation mechanism [equation (2)]. Bridge and terminal absorptions of the *cis*- and *trans*-isomers coalesced simultaneously with no discernible exchange occurring in one isomer before the other.

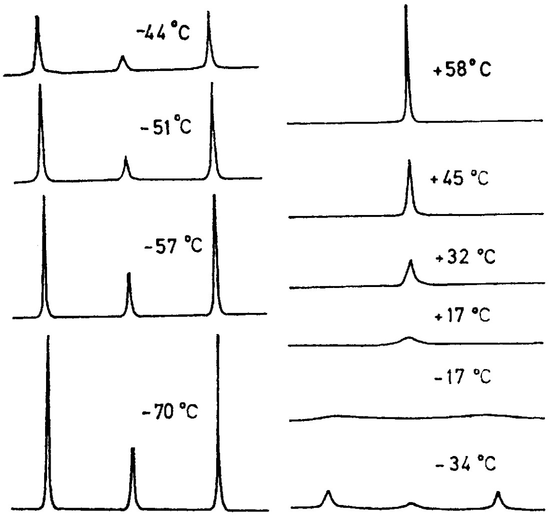


FIGURE 3 Calculated ^{13}C n.m.r. spectra as a function of exchange rates for complex (I; L = CO). Each curve was calculated using the rate constants of Table 3 at the indicated temperature

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[*] I.r. spectra of solutions of complex [I; L = P(OMe)$_3$] were similar to those of [I; L = P(OEt)$_3$], so we believe the *cis*-isomer is dominant here also: (cyclohexane)[4] 1 964s, 1 944m, and 1 750s; (chloroform) 2 056m, 2 010m, 1 963s, 1 773m, and 1 731s cm^{-1}. The solid may contain the *trans*-isomer because the KBr pellet spectrum showed bands at 1 983vw, 1 933vs, 1 887w, 1 770m, 1 733vs, and 1 707sh, m cm^{-1}. The KBr pellet of complex [I; L = P(OEt)$_3$] (2 075w, 2 008w, 1 957vs, 1 950vs, 1 906w, 1 766w, 1 739vs, 1 727vs, and 1 704w cm^{-1}) did not allow us to assign a configuration for it in the solid state, but the different wavenumbers of the terminal-carbonyl bands of complexes [I; L = P(OMe)$_3$ and P(OEt)$_3$] suggest that they possess different configurations in the solid state.

[8] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc.* (*A*), 1970, 3068.

[9] The same reasoning led to the first successful assignment of the isomers of complex (I; L = CO); A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319.

Complex (I; L = CO).—The spectrum of complex (I; L = CO) published by Gansow *et al.* was interpreted as follows.[1] At −85 °C, the *cis*- and *trans*-isomers are both static on the n.m.r. time scale. Each exhibits single absorptions for the bridge- and terminal-carbonyl groups but the signals accidentally overlap so that only one absorption is observed in each region. At −73 °C, the less-abundant *trans*-isomer exhibits bridge–terminal exchange, producing an averaged signal between the bridge and terminal signals of the *cis*-isomer. This averaged signal sharpens as the temperature is raised until, at −35 °C, all three signals begin to broaden and coalesce near −12 °C. In the high-temperature limit, only a single sharp absorption is observed in the bridge–terminal averaged position. The process stated to account for coalescence of the *cis*-isomer carbonyl signals is either bridge–terminal exchange within the isomer or *cis*–*trans*-isomerization.

We investigated spectra of complex (I; L = CO) using dichloromethane as solvent and our results are in agreement with those reported[1] with one exception: namely, the low-temperature absorption due to averaged carbonyl groups of the *trans*-isomer was not precisely midway between static carbonyl signals of the *cis*-isomer. At −73 °C, the averaged *trans*-signal was at 242·2 p.p.m., while bridge and terminal signals of the *cis*-isomer appeared at 272·9 and 211·0 p.p.m. This leads us to suggest that both bridge–terminal and *cis*–*trans*-isomerization occur rapidly at room temperature, because, if there were only separate bridge–terminal exchange for the *cis*- and *trans*-isomers (without *cis*–*trans*-isomerization), one would expect two peaks in the high-temperature limit. Our interpretation of the low-temperature spectrum differs from that of the earlier one[1] only in that we do not believe the low-temperature limit is reached at −85 °C. The observed spectrum at this temperature corresponds to an intermediate rate of *trans*-isomer bridge–terminal exchange whereby the signal is so broad that nothing is seen.

TABLE 3

Linewidths of carbonyl absorptions of complex (I; L = CO) and rate constants for exchange

	Linewidth/Hz			
t/°C	*cis*[a]	Averaged[b]	k_1[c]/s^{-1}	k_2[c]/s^{-1}
−70	9	12	8	13
−57	10	14	9	15
−51	13	23	16·5	18
−44	18	32	24	26
−34	38	61	47	65
−17	*d*	*d*	490[e]	490[e]
+17		*ca.* 130	7 400[e]	7 400[e]
+32		38	20 500	20 500
+39		24	33 500	33 500
+45		20	40 000	40 000
+51		15	58 000	58 000
+58		10	100 000	100 000

[a] Average value for bridge and terminal signals. Uncertainty is ±1 Hz. Only at −34 °C did the two linewidths differ by more than 1·0 Hz (bridge −41, terminal −36 Hz). [b] Below −17 °C this is the width of the single *trans*-absorption. Above −17 °C this is the width of the only signal in the carbonyl region. [c] Assuming intrinsic linewidths in the absence of exchange to be 2·0 Hz, these rate contants reproduce the observed linewidths within ±0·5 Hz. [d] Too broad to measure. [e] Rates estimated from an Arrhenius plot of the other data.

The cyclopentadienyl absorptions for the *cis*- and *trans*-isomers at −73 °C were 88·6 and 89·9 p.p.m., respectively. These coalesced below −44 °C and gave a single sharp peak at 89·0 p.p.m. at +60 °C.

Rates of *cis*–*trans*-isomerization and bridge–terminal exchange were determined by fitting measured carbonyl linewidths * to a series of theoretical linewidths corresponding to particular rate constants † (Table 3). Because spectra span only the region where bridge–terminal exchange of the *trans*-isomer is very rapid, only one averaged chemical shift was considered for this isomer. In equation (3), (A) and (B) correspond

$$\begin{tikzcd}
 & (C)_2 \arrow[dl, shift left, "k_{-1}"] \arrow[dr, shift left, "k_{-1}"] & \\
(A),(B) \arrow[ur, shift left, "k_1"] \arrow[rr, shift left, "k_2"] & & (B),(A) \arrow[ul, shift left, "k_1"] \arrow[ll, shift left, "k_{-2}"]
\end{tikzcd} \qquad (3)$$

to bridge and terminal carbonyl groups of the *cis*-isomer and (C) corresponds to those of the *trans*-isomer. Attempts to match linewidths at low temperature, with k_2 equal to zero, were not successful. Allowing k_1 and k_2 to vary, and using the measured ratio of *cis*- and *trans*-isomers to determine k_{-1},‡ a unique fit was obtained below −17 °C where there are two observed linewidths to fit with two rate constants. The values of k_1 and k_2 (Table 3) seem close enough to being equal to indicate essentially free rotation interconverting all three of the staggered non-bridged species in equation (2). Reproducing one linewidth with two rate constants at high temperature did not yield a unique solution, but the low-temperature fit seemed to justify assuming equal values of k_1 and k_2. With this assumption, the high-temperature fit was unique also. Simulated spectra using the rate constants of Table 3 are shown in Figure 3. An Arrhenius plot of the experimental rate constants was linear and yielded an activation energy of 49·0 ± 4 kJ mol^{-1} (11·7 ± 1 kcal mol^{-1}), as compared to 16·7 ± 1·6 kcal mol^{-1} calculated from *cis*–*trans*-isomerization

TABLE 4

^{13}C Chemical shifts[a] for complex (II)

Solvent	t/°C	CO	cp
C_6H_5Me	+37	212·8	88·2
C_6H_5Me	−10	215·5	89·1
C_6H_5Me	−47	219·2	90·3
CH_2Cl_2	+34	216·9	89·4
CH_2Cl_2	−42	222·6	90·8

[a] With tms as zero, positive shifts are downfield.

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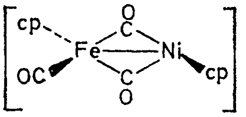
* We verified that 0·08M-Cr(acac)$_3$ does not affect carbonyl linewidths at −62 °C.

† Line-shape calculations were made with program DNMR3 written by D. A. Kleier and G. Binsch, Quantum Chemistry Program Exchange, Indiana University, 1969. We are grateful to Drs. F. A. L. Anet and W. Larson for helpful discussion concerning these calculations.

‡ From −72 to −34 °C, *trans* : *cis* = 0·25 : 1, within experimental error estimated at ±0·03.

followed by ^{1}H n.m.r. spectroscopy.[10] Significant deviations from a linear Arrhenius plot occurred only at our lowest temperature, -70 °C, where the calculated rate constants were too large. This could be due to breakdown of the assumption of infinitely rapid bridge–terminal exchange of the *trans*-isomer and general broadening of all lines in the spectrum, including solvent, at this low temperature.

Other Complexes.—For complex (II) there was a single sharp peak in the carbonyl region and one in the cp region (Table 4). Both had significantly temperature-dependent chemical shifts, consistent with the rapidly averaging set of *cis*- and *trans*-bridged and non-bridged isomers believed to be present in solution.[5,10] The mixed complex (III) gave a single carbonyl n.m.r. absorption at 237·0 p.p.m. at $+35$ °C, and at 238·1 p.p.m. at -62 °C in toluene, indicating rapid bridge–terminal exchange throughout this temperature range. Only one isomer has been detected in solutions of



(III)

complex (III),[11] but this does not preclude intermediacy of the other isomer in bridge–terminal exchange.

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[10] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 1972, **11**, 671; the authors state that their value of E_a may be too large.

[11] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1971, 717.