Carbon-13 Nuclear Magnetic Resonance Spectra of Polynuclear Carbonyls of Cobalt and Rhodium

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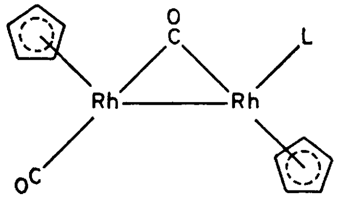
A variable-temperature ^{13}C n.m.r. spectroscopic study of the polynuclear carbonyls $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$, $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(PR_3)]$, $[Co_2(CO)_8]$, $[Rh_4(CO)_{12}]$, $[Rh_4(CO)_{11}(PPh_2R)]$ (R = Ph or Me), $[Co_4(CO)_{12}]$, $[Co_4(C_6H_5Me)(CO)_9]$, $[Co_4(RC_2R)(CO)_{10}]$ (R = CO_2Me or Ph), $[RhCo_3(CO)_{12}]$, and $[Rh_6(CO)_{15}I]^-$ has been carried out. Apart from $[Co_2(CO)_8]$, $[Co_4(RC_2R)(CO)_{10}]$, and $[Co_4(CO)_{12}]$, solution geometries have been established. A variety of CO-fluxional mechanisms have been observed and are discussed.

WHILE the structures of transition-metal carbonyl clusters can be determined in the crystal, the most commonly applied technique, i.r. spectroscopy, for deriving solution-state structures has often yielded ambiguous results. Carbon-13 n.m.r. spectroscopy is now well established as a convenient tool with which to study the structures of cluster carbonyls in solution.[1,2] Details of the rates and processes of carbonyl-site exchange can also be obtained by this means and, for example, rapid intramolecular ligand scrambling has been demonstrated for $[Rh_4(CO)_{12}]$ [3,4] and $[Fe_3(CO)_{12}]$.[5] Interconversion of terminal and edge-bridging carbonyls has been shown in a number of systems. The concerted pairwise process has been established for $[\{Fe(C_5H_5)(CO)_2\}_2]$ [6-9] and derivatives possessing a double bridge. In other circumstances, such as the presence of a single bridge, alternative mechanisms still allow site exchange.[10,11] We present a full report of our investigations of the structures and dynamics of polynuclear carbonyls of the cobalt triad using ^{13}C n.m.r. spectroscopy. Preliminary accounts of portions of this work have previously been communicated.[5-9]

RESULTS

Binuclear Complexes.—(*a*) $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ (1). This red crystalline complex has been demonstrated to possess one bridging and two terminal carbonyl groups in the crystal,[12] the two terminal carbonyls being in a *trans* orientation. Hydrogen-1 n.m.r. (303 K) and i.r. measurements indicated that only one isomer of (1) also of a *trans* geometry existed in solution.

Proton-decoupled ^{13}C n.m.r. spectra of a ^{13}CO-enriched sample of the complex were obtained in CD_2Cl_2 solution (Figure 1, Table 2) with the addition of 0.04 mol dm^{-3} $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) as relaxation agent.[13] At 293 K the carbonyl region of the spectrum showed only a sharp triplet, reflecting the rapid intermolecular site exchange of carbonyl groups. At 193 K the two resonances due to the separate environments were obtained, a triplet at δ 231.8 p.p.m. and a doublet at 191.8 p.p.m. of intensity ratio 1 : 2. Since $[Cr(pd)_3]$ at this concentration quenches most of the small Overhauser effects present, these two resonances should reflect the relative abundances. Hence, as indicated by the signal multiplicities, the downfield resonance is due to the bridging carbonyl and the doublet to the two terminal ones. The weighted average coupling constants and chemical shifts agree satisfactorily with those observed in the high-temperature limit at 293 K.



(1) L = CO

(3a) L = P(OPh)$_3$

(3b) L = PMe$_2$Ph

The fully labelled dimer would possess a XAMA′X′ spin system. This can be artificially divided into an XAA′X′ system for the terminal carbonyls and AA′M for the bridging. For the former system, a doublet would be observed

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if[14] ^1J(Rh–Rh) $\ll$ ^1J(Rh–C), ^2J(Rh–C). A maximum value for ^2J(Rh–C) of *ca.* 2 Hz can be set from these experimental conditions, and ^1J(Rh–Rh) also appears to be negligible (<1 Hz). At such high enrichment levels, ^2J(C–C) couplings should also affect the spectrum. The broad ($\Delta\nu_{\frac{1}{2}}$ *ca.* 10 Hz) linewidths of both carbonyl resonances at 193 K may be so caused. Even so, the ^2J(C–C) values are between 5 and 10 Hz. These values are still small by comparison to ^1J(Rh–C) and do not cause such complications to the spectra that isotopic enrichment need be avoided.

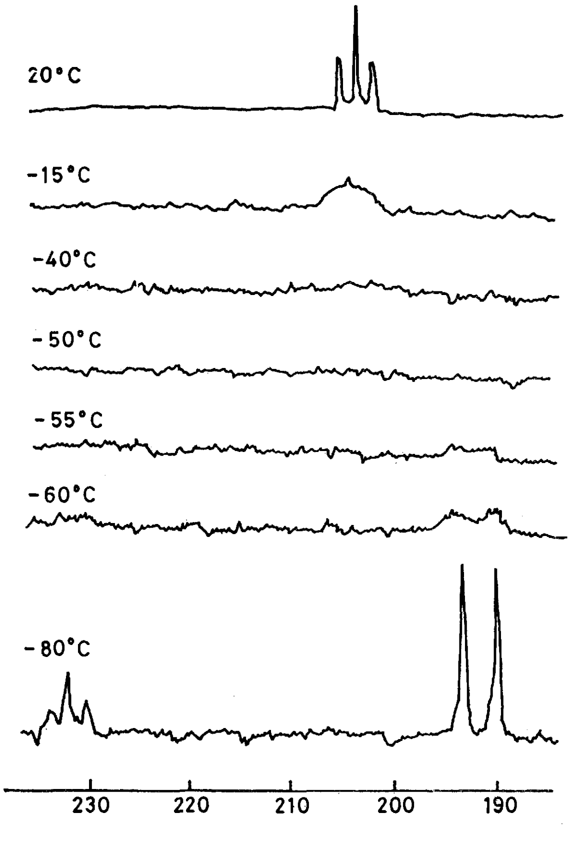

FIGURE 1 Carbon-13 n.m.r. spectrum of [$Rh_2(\eta\text{-}C_5H_5)_2(CO)_3$] in CD_2Cl_2

A coalescence temperature of 223 ± 5 K was determined for this exchange process. Using the method of Shanan-Atidi and Bar-Eli[15] for the coalescence of an unequal doublet (separation 1 008 Hz), the kinetic data in Table 1 could be estimated. Since the maximum concentration of [$Cr(pd)_3$] was 4×10^{-2} mol dm^{-3}, line-shape errors induced by this reagent are likely to be small.[16] When (1) was dissolved in trifluoroacetic acid a cationic complex (2) was observed. The ^1H n.m.r. spectrum of this solution exhibited two resonances; a singlet at τ 4.53 (10 H) and a triplet at τ 21.20 [1 H, *J*(Rh–H) 18 Hz]. This is consistent with the added proton adopting a bridging metal hydride position. However, the cation was too unstable to allow the recording of ^{13}C n.m.r. spectra, so the effect of protonation on the energy barrier to exchange was not determined.

TABLE 1

Kinetic data for carbon exchange in (1) at 223 K

Process	10^{-3} Rate constant (s^{-1})	$\Delta G^{\ddagger}$/kJ mol^{-1}
Terminal bridging	1.02	41.4 ± 1.3
Bridging terminal	2.04	40.2 ± 1.3

(b) [$Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(PR_3)$] (3). At 168 K, in $CHFCl_2$ solution, a low-temperature spectrum of (3a; R = OPh) was obtained (Table 2). By 188 K {in CD_2Cl_2 with added [$Cr(pd)_3$]} broadening of the resonances was observed and a coalescence temperature of 208 ± 10 K was recorded ($\Delta G^{\ddagger}$ 38 ± 1 kJ mol^{-1}). Observable at 298 K, the fast-exchange spectrum consisted of an eight-line multiplet. This demonstrates that intramolecular site exchange occurs rapidly at room temperature and also that the Rh–P bond remains intact throughout the process. This was further demonstrated by both ^{31}P and ^1H n.m.r. spectra of an unlabelled sample of (3a). Both the ^{31}P [in CD_2Cl_2; 141.2 p.p.m. downfield of H_3PO_4, d, *J*(Rh–P) 327 Hz] and ^1H n.m.r. spectra [in $CDCl_3$; τ 2.70 (m, 15 H), 4.41 (s, 5 H) and 5.32 (d, 5 H, *J* 2 Hz)] are temperature independent between 183 and 293 K.

Whilst the ^{13}C n.m.r. spectrum of (3b) consisted of one broad resonance at 169 K (CD_2Cl_2–$CHFCl_2$ solution) at δ 236.5 p.p.m., from 183 to 298 K an eight-line multiplet characteristic of an averaged bridge–terminal resonance was observed. Evidently, substitution of the more basic PMe_2Ph has lowered the barrier to bridge–terminal exchange. The chemical shift of this averaged resonance was markedly temperature dependent (Table 2), even allowing for solvent changes, suffering a 7 p.p.m. upfield shift in a 130 K range. At 300 K the ^1H n.m.r. spectrum of (3b) indicated that the two diastereotopic methyl groups on the phosphine were being averaged; this was still apparent down to the lowest temperature studied (193 K). Over the same temperature range the i.r. spectrum of (3b) is approximately invariant, but still suggests the presence of more than one isomer possessing bridging carbonyl groups.

(c) [$Co_2(CO)_8$] (4). As has been independently reported,[1] the ^{13}C n.m.r. spectrum of ^{13}CO-enriched [$Co_2(CO)_8$] exhibits one resonance at 193 K (δ 204 p.p.m., $\Delta\nu_{\frac{1}{2}}$ 15 Hz). At 213 K a similar spectrum was obtained, but by 243 K a small upfield shift and line broadening were discernible (δ 203.2 p.p.m., $\Delta\nu_{\frac{1}{2}}$ 22 Hz). By 293 K the resonance, now at δ 202.2 p.p.m., was very broad ($\Delta\nu_{\frac{1}{2}}$ 50 Hz). An upfield shift of a few p.p.m. would be anticipated from the increasing proportions of the non-bridged forms[17–19] at higher temperatures. The broadening is associated with the ^{59}Co nucleus, not an exchange process. Relaxation times decrease as the temperature decreases, due to more efficient relaxation by translational and rotational motions. When the relaxation time of the ^{59}Co nucleus is very short, coupling to the co-ordinated carbon is eliminated. At longer relaxation times this coupling takes effect and causes broadening of the ^{13}C resonances.

Carbonyl site exchange occurs very rapidly in this dimer ($k \gg 10^3$ s^{-1} at 193 K), presumably by a pairwise bridge-

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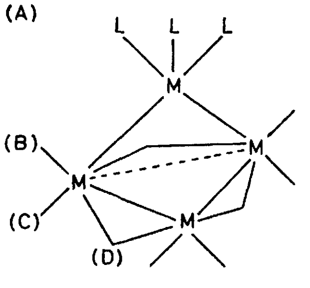
TABLE 2

Carbon-13 n.m.r. data for carbonyl complexes

Complex	Carbonyl [a]	Shift (δ/p.p.m.)	Multiplicity [b]
$[Rh(\eta\text{-}C_5H_5)_2(CO)_3]$ (1)	B	231.8	t (45)
In CD_2Cl_2 at 193 K	2 × T	191.8	d (83)
at 293 K	Av.	203.8	t (43)
$[(OC)(\eta\text{-}C_5H_5)Rh^1(CO)Rh^2(\eta\text{-}C_5H_5)\{P(OPh)_3\}]$ (3a)	B	239.4	m[$^1J(Rh^1\text{–}C)$ 41, $^1J(Rh^2\text{–}C)$ 50, $^2J(P\text{–}C)$ 19)]
In $CHFCl_2$ at 168 K	T	190.4	d[$^1J(Rh^1\text{–}C)$ 85]
In CD_2Cl_2 at 298 K	Av.	218.5	m[$J(Rh^1\text{–}C)$ 64, $J(Rh^2\text{–}C)$ 24, $J(P\text{–}C)$ 10)]
$[(OC)(\eta\text{-}C_5H_5)Rh^1(CO)Rh^2(\eta\text{-}C_5H_5)(PMe_2Ph)]$ (3b)			
In CD_2Cl_2–$CHFCl_2$ at 169 K	Av.	236.5	br
In CD_2Cl_2 at 83 K	Av.	235.4	m[$J(Rh^1\text{–}C)$ 60, $J(Rh^2\text{–}C)$ 26, $J(P\text{–}C)$ 8]
at 93 K		234.7	
at 213 K		232.2	
In $CDCl_3$ at 233 K		232.3	
at 298 K		229.5	
$[Co_2(CO)_8]$ (4)			
In CD_2Cl_2 at 193 K	Av.	204.0	s ($\Delta\nu_{\frac{1}{2}}$ 15)
at 243 K	Av.	203.2	s ($\Delta\nu_{\frac{1}{2}}$ 22)
at 293 K	Av.	202	s ($\Delta\nu_{\frac{1}{2}}$ 50)
$[Rh_4(CO)_{12}]$ (5)	3 × B (D)	228.8	t (35, $\Delta\nu_{\frac{1}{2}}$ 21)
In CD_2Cl_2 at 208 K	3 × T (A)	183.4	d (75, $\Delta\nu_{\frac{1}{2}}$ 14)
	3 × T (B or C)	181.8	d (64, $\Delta\nu_{\frac{1}{2}}$ 24)
	3 × T (B or C)	175.5	d (62, $\Delta\nu_{\frac{1}{2}}$ 22)
$[Rh_4(CO)_{11}(PPh_3)]$ (6a)	B	235.9	t (30)
In CD_2Cl_2 at 218 K	2 × B	234.8	t, br (33)
	6 × T	184.4	m
	T	181.7	d (63)
	T	178.9	d (67)
$[Rh_4(CO)_{11}(PMePh_2)]$ (6b)			
In CD_2Cl_2 at 191 K	B	249.0	m
	2 × B	242.6	m
	8 × T	188.9	m
In $C_6D_5CD_3$ at 333 K	Av.	199.6	br
$[Co_4(CO)_{12}]$ (7)	B	243.1	s ($\Delta\nu_{\frac{1}{2}}$ 10)
In CD_2Cl_2 at 213 K	T	195.9	s ($\Delta\nu_{\frac{1}{2}}$ 20)
	T	191.9	s ($\Delta\nu_{\frac{1}{2}}$ 20)
$[Co_4(C_6H_5Me)(CO)_9]$ (8)	3 × B	247.3	s
In CD_2Cl_2 at 203 K	3 × T	198.7	s
	3 × T	180.9	s
$[Co_4\{C_2(CO_2Me)_2\}(CO)_{10}]$ (9)	4 × Av.	211.2	s
In $CHFCl_2$ at 169 K	2 × Av.	198.2	s
	4 × Av.	191.3	s
In CD_2Cl_2 at 203 K	6 × Av.	203.2	s ($\Delta\nu_{\frac{1}{2}}$ 62)
	2 × Av.	197.7	s ($\Delta\nu_{\frac{1}{2}}$ 47)
	2 × Av.	190.1	s ($\Delta\nu_{\frac{1}{2}}$ 30)
In CD_2Cl_2 at 253 K	Av.	201	s ($\Delta\nu_{\frac{1}{2}}$ 300)
$[Co_4(C_2Ph_2)(CO)_{10}]$ (10)	4 × Av.	213.6	s
In $CHFCl_2$ at 183 K	2 × Av.	198.7	s
	4 × Av.	193.5	s
In CH_2Cl_2 at 223 K	6 × Av.	206.8	s ($\Delta\nu_{\frac{1}{2}}$ 100)
	2 × Av.	198.9	s ($\Delta\nu_{\frac{1}{2}}$ 45)
	2 × Av.	193.7	s ($\Delta\nu_{\frac{1}{2}}$ 50)
at 253 K	Av.	201.3	s ($\Delta\nu_{\frac{1}{2}}$ 500)
$[RhCo_3(CO)_{12}]$ (11)	B	251.2	s
In CH_2Cl_2 at 188 K	2 × B	238.3	d (38)
	2 × T	201.1	s
	2 × T	200.1	s
	2 × T	195.5	s
	T	188.2	d (78)
	T	183.1	d (51)
at 243 K	Av.	208.0	br, s
	Av.	186.2	d (72)
at 303 K	Av.	201.3	br, s
$[Rh_6(CO)_{15}I]^-$ (12)	2 × FB	245.3	m
In CD_2Cl_2 at 204 K	FB	239.2	q (28)
	FB	232.9	q (28)
	T	183.3	m

[a] FB = Face bridging, B = edge bridging, T = terminal, and Av. = averaged. [b] Values of $^1J(Rh\text{–}C)$ in Hz are given in parentheses.

opening and -closing process as in $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ [6,9] and its derivatives. This is consistent with the observation of one ^{59}Co n.m.r. resonance for the dimer.[20,21]



(5) M = Rh, L = CO
(7) M = CO, L = CO
(8) M = CO, $L_3 = C_7H_8$

Tetranuclear Clusters.—(a) $[Rh_4(CO)_{12}]$ (5). A limiting slow-exchange spectrum of four equally intense resonances was observed at 208 K for a 30-mg sample of 70% ^{13}CO-enriched (5) (Figure 2). This is entirely consistent with $[Rh_4(CO)_{12}]$ adopting the same structure in solution as in the crystal.[22] There is one bridging environment (D) and three terminal ones, apical (A), basal equatorial (B), and basal axial (C). As indicated above, the linewidths of the signals will be governed by ^2J(C–Rh–C). The apical carbonyl groups possess a simpler local spin system (AA′A″X) than either of the two basal-terminal environments (ABMM′X′) and would thus be expected to exhibit a narrower resonance. Hence the signal at δ 183.4 p.p.m. is assigned to the apical environment (A).

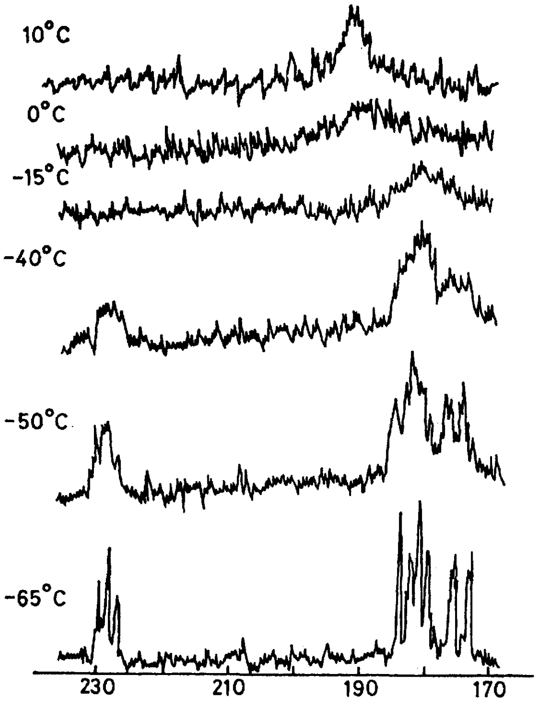


FIGURE 2 Carbon-13 n.m.r. spectrum of $[Rh_4(CO)_{12}]$ in CD_2Cl_2

Spectra were recorded at temperature intervals up to and above the coalescence temperature of 268 ± 5 K. At higher temperatures an averaged resonance at δ 190.7 p.p.m. was observed. On the basis of the slow-exchange spectrum, the limiting high temperature spectrum for an intramolecular process would consist of a quintet at δ 192.4 p.p.m. of splitting 16.9 Hz. This agrees satisfactorily with the reported values[3] (336 K, in $CDCl_3$; δ 189.5 p.p.m., *J* 17.2 Hz).

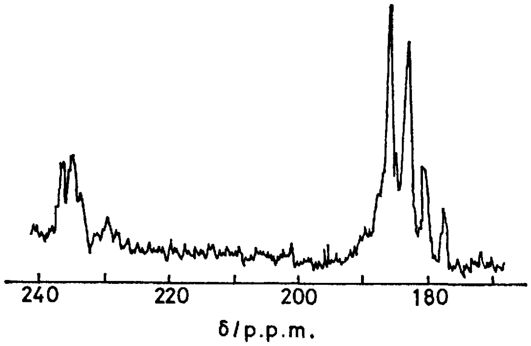


FIGURE 3 Carbon-13 n.m.r. spectrum of $[Rh_4(CO)_{11}(PPh_3)]$ in CD_2Cl_2 at −55 °C

(b) $[Rh_4(CO)_{11}(PPh_2R)]$ (6). A labelled sample of $[Rh_4(CO)_{11}(PPh_3)]$ (6a; R = Ph)[23] was prepared by treating the enriched sample of (5) used above with PPh_3. Due to the lower solubility and symmetry of the substituted cluster, long accumulation times were required to give satisfactory ^{13}C n.m.r. spectra of this material. That recorded at 218 K is illustrated in Figure 3 (Table 2). Two bridging-carbonyl resonances, of relative intensity 1 : 2, were observed and the more intense was the broader, probably from coupling to the phosphorus. This suggests that the substituent is in one of the basal-terminal portions, the basic structure of $[Rh_4(CO)_{12}]$ being retained. Spectra were also recorded at 263, 293, and 333 K. At 263 K, the signals were very broad and at 293 K they were infinitely broad. Hence the coalescence temperature was estimated as *ca.* 193 K. At 333 K a dark material precipitated from solution, probably either Rh metal or a hexanuclear cluster.

A similar spectrum was obtained for the more soluble $[Rh_4(CO)_{11}(PMePh_2)]$ (6b; R = Me) at 193 K. Broadening of bridging and terminal resonances occurred at 248 K and by 298 K yielded a broad averaged resonance. This sharpened somewhat by 333 K, but again sample decomposition prevented the recording of a limiting fast-exchange spectrum.

(c) $[Co_4(CO)_{12}]$ (7). Three carbonyl resonances, corresponding to one bridging and two terminal environments (Table 2), were observed for (7) in the range 173—213 K. All three exhibited approximately equal intensities, with or without added $[Cr(pd)_3]$ (Figure 4). If these intensities reflect

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the populations, this suggests that the structure of (7) is not that of C_{3v} symmetry as in the crystal,[24] but of D_{2d} symmetry.[25] However, both i.r.[26] and ^{59}Co n.m.r.[20,21,27] measurements indicate otherwise. The factors which influence the intensities of ^{13}C resonances in the presence of nuclei of high quadrupole moments are not well understood and an intensity distortion is conceivable. This was not noted in spectra reported below, or for $[Co_4(CO)_{11}\{P(OMe)_3\}]$.[27] Nevertheless, this spectrum of $[Co_4(CO)_{12}]$ has been obtained many times in two laboratories [27,28] and one is left with the explanation that in this particular case ^{59}Co-^{13}C coupling gives rise to intensity distortions.

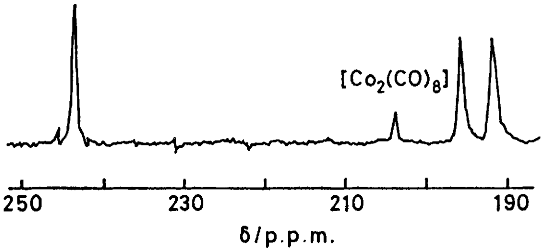

FIGURE 4 Carbon-13 n.m.r. spectrum of $[Co_4(CO)_{12}]$ in CD_2Cl_2 at −70 °C

A fast-exchange spectrum could not be obtained. Warming from 213 K caused line broadening and finally collapse (263 K) of the signals. Above 343 K decomposition ensued. This broadening was greater than for $[Co_2(CO)_8]$ and can be attributed, although not unambiguously, to a site-exchange process.

(d) $[Co_4(C_6H_5Me)(CO)_9]$ (8). Although complex (8) [29] could not be labelled directly, it was prepared from enriched precursors. Between 173 and 213 K the ^{13}C spectrum (Table 2) exhibited one bridging and two terminal resonances, all of equal intensity {with and without $[Cr(pd)_3]$}. This is consistent with the structure in the crystal [30] being maintained in solution. In this case no intensity distortion was evident. Once again, warming the solution caused broadening and the fast-exchange spectrum was not obtained.

(e) $[Co_4(RCCR)(CO)_{10}]$ [R = CO_2Me (9) *or* Ph (10)]. Enriched (70% ^{13}CO) samples of these ' butterfly ' clusters [31] were prepared by direct enrichment or from labelled precursors. Carbon-13 n.m.r. spectra of (9) and (10) were recorded between 168 and 313 K (Table 2). At 169 K for (9) and 183 K for (10) three resonances were observed in the ratio 2 : 1 : 2. As reported for (10),[32] between these temperatures and 203 and 223 K, for (9) and (10) respectively, an exchange process averages the low-field signal with half the high-field one to yield three resonances of intensity ratio 3 : 1 : 1. As the temperature is increased further all these resonances broaden and coalescence to a very broad resonance at δ 201 p.p.m. (253 K). Above 253 K no signals were detected. The low-temperature spectra do not correspond to those expected for the structure in the crystal,[33] in which there are five CO environments (four terminal and one bridging). A localised scrambling process persists at these temperatures which averages the bridging groups with two terminal ones to produce the low-field signal.

(f) $[RhCo_3(CO)_{12}]$ (11). At 188 K the ^{13}C n.m.r. spectrum of an enriched sample of (11) exhibited seven resonances of relative intensity 1 : 2 : 2 : 3 : 2 : 1 : 1 (Table 2, Figure 5),[34] and is thus entirely consistent with the structure proposed by Chini on the basis of the cluster's i.r. spectrum.[35] The rhodium atom occupies a basal position in the $[Rh_4(CO)_{12}]$ structure. Only one broad resonance was observable at 303 K (δ 201.3 p.p.m.) and examination of the intermediate revealed a complicated behaviour indicative of two exchange processes. At 213 K all the resonances were broadened by the lower-energy mechanism which has a coalescence temperature of *ca.* 228 K. By 243 K the spectrum consists of a broad resonance at δ 208 p.p.m. and a well resolved doublet at 186.2 p.p.m., resulting from the averaging of the two doublets at δ 188.2 and 183.1 p.p.m. (due to the two terminal carbonyl groups on the rhodium atom). On warming to 263 K these two resonances collapse again to yield the totally averaged signal at δ 208 p.p.m. at 303 K, which again is broadened from interaction with the cobalt nucleus.

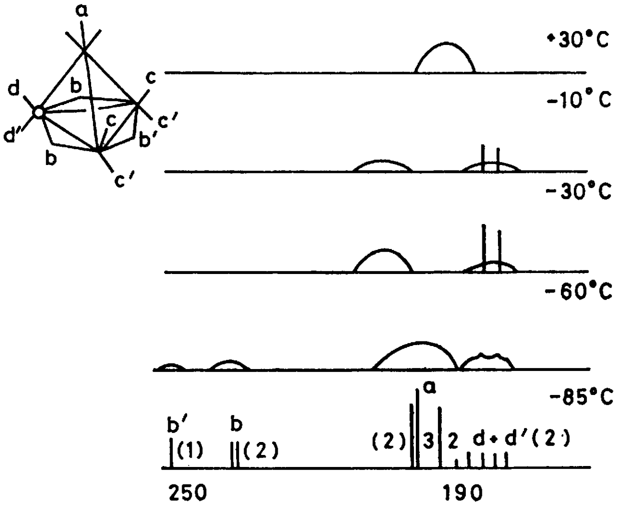

FIGURE 5 Diagrammatic ^{13}C n.m.r. spectrum of $[RhCo_3(CO)_{12}]$ in CH_2Cl_2

Hexanuclear Clusters.—$[Rh_6(CO)_{15}I]^-$ (12). Under the conditions reported for the preparation of the $[Rh_{12}(CO)_{30}]^{2-}$

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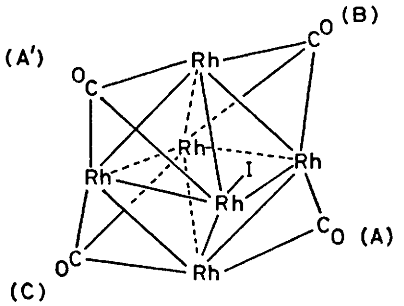
anion[36] from ^{13}CO-enriched [{Rh(CO)$_2$Cl}$_2$] but with $<$ 1 atm* pressure of ^{13}CO and with [NBu$^n{}_4$]I as precipitant, the brown anion [Rh$_6$(CO)$_{15}$I]$^-$ (12) [37] was produced containing *ca.* 60% ^{13}CO. The ^{13}C n.m.r. spectrum of (12) was recorded at 204 K in CD$_2$Cl$_2$ solution (Figure 6, Table 2). Three resonances due to the triply bridging CO groups were observed, as required by the C_s symmetry of the anion in the crystal.[38] The two quartets are due to the face bridges (B) and (C). However, the resonance due to (A) and (A′), related by the mirror plane, is not a pure quartet. These two CO groups are bonded to the iodide-substituted Rh atom and so the ^1J(Rh–C) coupling constant to that Rh nucleus may be markedly different from those to other two bonded Rh atoms; the observed multiplet structure results. It is noteworthy that the intensity of the terminal resonances is disproportionately high. Spectra were recorded at up to 303 K; site exchange was not evident.



(12)
(Terminal CO groups omitted)

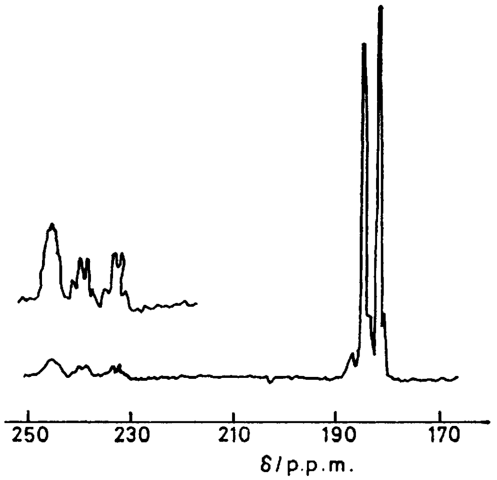


FIGURE 6 Carbon-13 n.m.r. spectrum of [Rh$_6$(CO)$_{15}$I]$^-$ in CD$_2$Cl$_2$ at 204 K

DISCUSSION

Carbonyl-scrambling Processes.—(*a*) *Binuclear complexes.* Evidence has been accumulated for the pairwise and connected bridge-opening and -closing mechanism in [{Fe(η-C$_5$H$_5$)(CO)$_2$}$_2$] and its derivatives.[7-9] Rotation about the metal–metal bond is hindered and so bridge–terminal interchange without isomerisation can occur for the *trans* isomer. It seems probable that this type of process is also involved in the rapid site exchange of [Co$_2$(CO)$_8$] (4). The absence of any verification of a direct 1 : 1 bridging for terminal exchange process has led Adams *et al.*[8] to propose that the exchange process in [Rh$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$] (1) is also pairwise, involving an intermediate with three bridging groups (Scheme 1) as has [Fe$_2$(CO)$_9$]. Closure of the two terminal groups yields the intermediate with the former terminal groups *trans*. For site exchange two *cis* bridges must be broken to give a *cis* isomer. So exchange by this process is *via* a *cis* isomer. No evidence for a second isomer was obtained, but this is mechanistically inconclusive.

The substituted complexes (3a) and (3b) do contain one bridging and one terminal CO group. Site exchange is rapid at room temperature and the spectra obtained unequivocally demonstrate a simple direct one for one exchange process. Because the Rh–P bond remains intact throughout this process, a mechanism involving a triply bridged intermediate with a bridging PR$_3$ group can be discounted. Since the two diastereotopic methyl groups in complex (3b; R$_3$ = Me$_2$Ph) are also averaged when CO scrambling occurs, it appears that chirality is lost at the substituted rhodium atom during the exchange process. Racemisation could occur either by the formation of a non-bridged intermediate for which free reaction around the metal–metal bond is allowed, or by a mechanism involving a synchronous process in which the ‘ old ’ and ‘ new ’ bridging groups are on opposite sides of the Rh–Rh(C$_5$H$_5$)(PMe$_2$Ph) co-ordination plane (Scheme 2). Whether the parent tricarbonyl complex (1) also follows this path cannot be determined. What is apparent is that the rate of exchange increases with the substitution of CO by a more electron-donating substituent [as shown by the CO stretching frequencies of complexes (1), (3a), and (3b)].

(*b*) *Tetranuclear clusters.* From the uniform collapse of the ^{13}C resonances of [Rh$_4$(CO)$_{12}$] all the carbonyl groups exchange by the same process. It is possible to envisage local scrambling of bridge and terminal groups around the basal plane but, in spite of the $\Delta G^{\ddagger}$ of this process being higher than the values for such processes in the binuclear complexes, this evidently does not occur. The entire cluster structure is important for considering exchange mechanisms and not just local factors. An exchange process has been postulated involving an intermediate isostructural with [Ir$_4$(CO)$_{12}$].[39] Since all the carbonyl groups are equivalent in this intermediate the resonances due to the four ligand environments would collapse uniformly. This would involve a change in the carbonyl polyhedron from icosahedral in the bridged structure to cuboctahedral in the intermediate.[40] However, a simpler process, of the type

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* Throughout this paper: 1 atm = 101 325 Pa.

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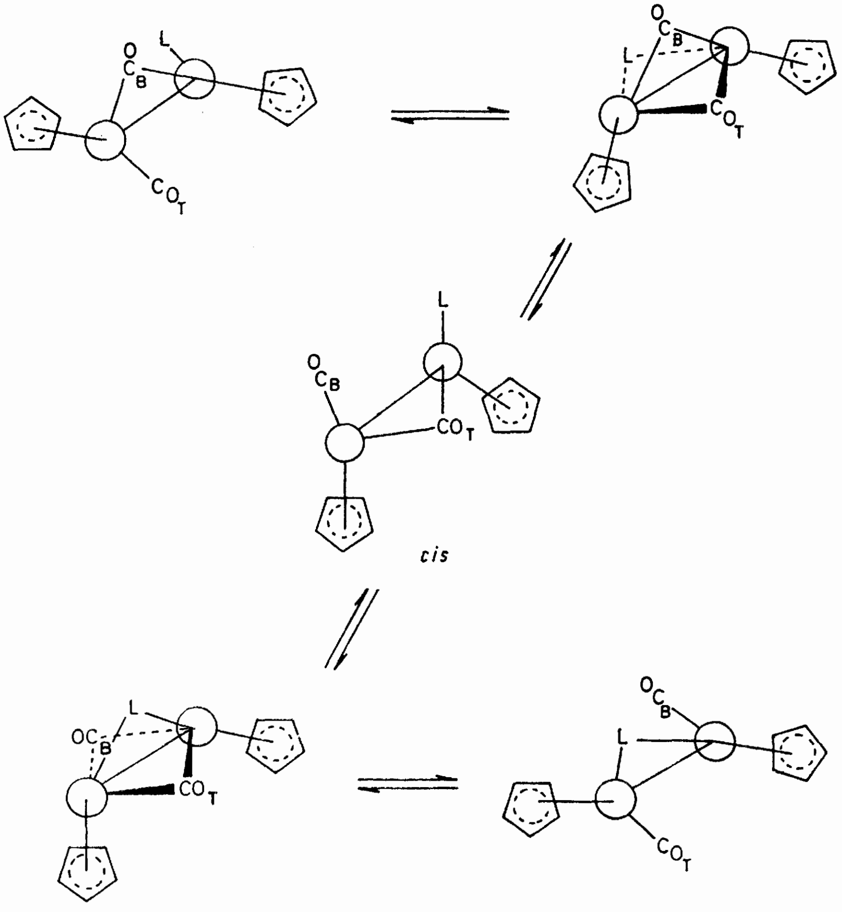
[38] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 678.

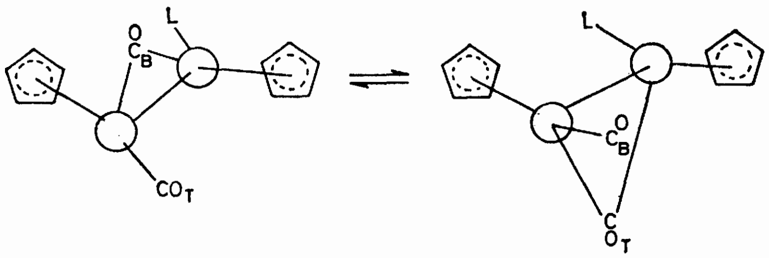
[39] F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1083.

[40] B. F. G. Johnson, *J.C.S. Chem. Comm.*, 1976, 211.

proposed for $[Fe_3(CO)_{12}]$,[41] would also account for the spectral changes with temperature. This would involve a small rotation of the Rh_4 tetrahedron within the icosahedron to give an unbridged intermediate of T symmetry. Again, since the carbonyl groups are all equivalent in this form, the four ^{13}CO resonances would broaden at the same rate. These two mechanisms differ in that only in the former do the ligands move relative to each other. In both mechanisms the ligands move relative to the metal core.



SCHEME 1



SCHEME 2 Synchronous exchange

The ligands of $[RhCo_3(CO)_{12}]$, however, must move relative to each other. Although the total ligand equilibration at high temperatures does not demonstrate this, the intermediate-exchange region, in which the two rhodium-only bound CO groups are averaged on the one hand and the remaining ten are interchanged on the other, is more informative. A rotation of the metal tetrahedron through 180°, maintaining the link of the rhodium atom with its two terminally bound carbonyl groups, would still leave four apparent carbonyl environments (of ratio 2 : 2 : 4 : 2), instead of the two observed. Even if this $Rh(CO)_2$ link were maintained through an icosahedral–cuboctahedral–icosahedral ligand motion, then a 2 : 8 : 2 spectrum would be obtained since the two ligands *para* to the $Rh(CO)_2$ pair (one of these is edge bridging and the other terminally bound to the apical cobalt) also only exchange with each other. At

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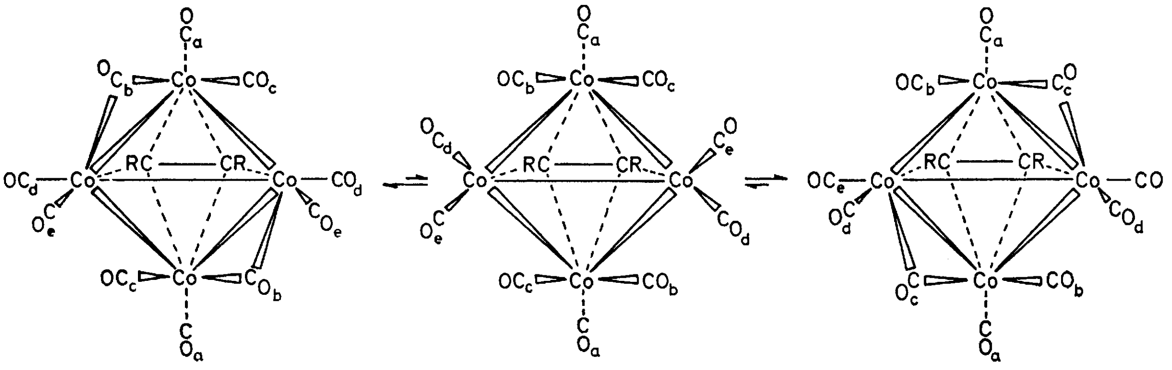
[41] B. F. G. Johnson, *J.C.S. Chem. Comm.*, 1976, 703.

188 K the ligands of the $Co(CO)_3$ moiety appear as one resonance, not two. If this is due to a rapid rotation of this unit at 188 K then the two *para* ligands would become averaged with the other eight by the icosahedral–cuboctahedral–icosahedral motion at 243 K. So unless the ligand motions are totally uncorrelated three processes are necessary to explain the temperature variation of the ^{13}C n.m.r. spectra of $[RhCo_3(CO)_{12}]$. It must be stressed that, while all the ligands in the cuboctahedral intermediate of $[Rh_4(CO)_{12}]$ would be terminally bound, this would not be the case for the mixed-metal cluster.*



SCHEME 3 R = CO_2Me (9) or Ph (10)

Three exchange processes have been identified for the $[Co_4(RCCR)(CO)_{10}]$ 'butterfly' clusters (Scheme 3). Even at the lowest temperature studied there is rapid exchange between the bridging and one terminal environment. It is probable that the shorter arm of the asymmetric bridge is retained and so exchange is with the terminal ligand (a). By *ca.* 210 K a second terminal environment is involved in the exchange, with total equilibration at higher temperatures. Two possibilities exist for the second process: exchange of (a), (b), and (c) or of (a), (c), and (d), with no means of differentiation.

EXPERIMENTAL

Carbon-13 and ^{31}P n.m.r. spectra were recorded on a Varian Associates XL-100-15 spectrometer and ^{1}H n.m.r. spectra on their HA-100 instrument. Infrared spectra were obtained on a Perkin-Elmer 257 and mass spectra on an A.E.I. MS12 spectrometer. The following complexes were all prepared according to published procedures: $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ (1),[12] $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(PR_3)]$ (3),[42] $[Rh_4(CO)_{12}]$ (5),[43] $[Rh_4(CO)_{11}(PPh_2R)]$ (6),[23] $[Co_4(CO)_{12}]$ (7),[44] $[Co_4(C_6H_6Me)(CO)_9]$ (8),[29] $[Co_4(RCCR)(CO)_{10}]$ [R = CO_2Me (9) or Ph (10)],[31] and $[RhCo_3(CO)_{12}]$ (11).[35] Unless otherwise stated, reactions were performed under nitrogen atmospheres.

Physical Details of the Complexes.—(1). Mass spectrum, parent ion at *m/e* 420. Some $[Rh_3(\eta\text{-}C_5H_5)_3(CO)_2]$ formed on the probe (Found: C, 37.75; H, 2.65. $C_{13}H_{10}O_3Rh_2$ requires C, 37.1; H, 2.40%). Infrared spectrum in cyclohexane: ν(CO) at 2 033w, 1 989s, and 1 841s cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 4.48 [d, *J*(Rh–H) 2 Hz].

(3a; R = OPh). Analysis: Found C, 50.55; H, 3.45; P, 3.9. $C_{30}H_{25}O_5PRh_2$ requires C, 51.3; H, 3.6; P, 4.4%. Infrared spectrum in cyclohexane: ν(CO) at 1 979 and 1 815 cm^{-1}. N.m.r. spectra: ^{1}H in $CDCl_3$, τ 2.70 (m, 15 H), 4.41 (s, 5 H), and 5.32 (d, *J* 2 Hz, 5 H); ^{31}P in CD_2Cl_2, 141.2 p.p.m. downfield of H_3PO_4, d, ^{1}J(Rh–P) 327 Hz.

(3b; R_3 = Me_2Ph). Infrared spectrum in CH_2Cl_2 at 201—300 K: ν(CO) at 1 950m, 1 796(sh), and 1 750s cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$ at 303 K: τ 2.25 (m, 2 H), 2.55 (m, 3 H), 4.61 (s, 5 H), 4.78 (s, 5 H), and 8.45 [d, *J*(PH) 10 Hz, 6 H].

Preparation of ^{13}CO*-enriched Complexes.*—(1). Complex (1) (38 mg) was stirred in CH_2Cl_2 solution under 2.58 mol of 88% ^{13}CO for 26 h yielding 81% enrichment. Infrared spectrum in cyclohexane: ν(CO) at 1 998w, 1 951s, and 1 798s cm^{-1}.

(3a). Complex (1) (32 mg) was stirred in $CHCl_3$ (2 cm^3) under 0.5 mmol ^{13}CO for 21 h to form a red solution. The solvent was removed and the degree of enrichment (50%) checked by i.r. spectroscopy. The product was dissolved in cyclohexane (4 cm^3) and a solution of $P(OPh)_3$ (2—4 mg) in cyclohexane (4 cm^3) added. This charge was stirred for 17 h and the cyclohexane then evaporated off. The enriched product (3a) was crystallised from CH_2Cl_2–hexane. Infrared spectrum in cyclohexane: ν(CO) at 1 986, 1 979, 1 838, and 1 814 cm^{-1}.

Complex (1) (35.1 mg) was stirred in $CHCl_3$ under ^{13}CO for 18 h and the solvent then removed. An i.r. spectrum of (1) indicated *ca.* 40% ^{13}CO incorporation. A solution of this solid in hexane (15 cm) was treated with PMe_2Ph (14 mg) and stirred for 1 h. The solvent was reduced in volume and the ^{13}CO-enriched sample of (3b) allowed to form as purple crystals overnight at −20 °C.

(5). Complex (5) (30 mg) in CH_2Cl_2 (25 cm^3) was stirred under 1.27 mmol of 88% ^{13}CO for 6 h; *ca.* 75% enrichment was achieved. Infrared spectrum of product in hexane: 2 090w, 2 074m, 2 068s, 2 057w, 2 047m, 2 037m, 2 030m, 2 027s, 2 020m, 2 014m, 2 010s, 2 001m, 1 994m, 1 988w, 1 915w, 1 907w, 1 888m, 1 862m, 1 851(sh), 1 846s, and 1 838w cm^{-1}.

(6a; R = Ph). The enriched sample of (5) (30 mg) and

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* A further consideration of these processes will be reported in a subsequent paper (B. F. G. Johnson and R. E. Benfield, *J.C.S. Dalton*, in the press).

[42] R. Hill and S. A. R. Knox, *J. Chem. Soc.* (*A*), **1969**, 500.

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[44] R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Shornberg, *J. Amer. Chem. Soc.*, **1955**, **72**, 3951.

PPh_3 (9.5 mg) were stirred in pentane (5 cm^3) for 1 h. A dark red precipitate was produced of enriched (6).

(6b; R = Me). Complex (5) (39.1 mg) was enriched to a 60% ^{13}CO level and dissolved in hexane (30 cm^3). A solution of $PMePh_2$ (10.5 mg) in hexane was added and the solution stirred for 50 h. Removal of the solvent yielded the ^{13}CO-enriched sample of (6b).

(7). Complex (7) (20 mg) was stirred under 0.73 mmol of 89% ^{13}CO for 24 h; *ca.* 50% ^{13}CO incorporation was achieved. Infrared spectrum in cyclohexane: 2 061(sh), 2 054s, 2 049s, 2 040(sh), 2 025m, 1 992m, 1 867m, and 1 822m cm^{-1}. ^{13}CO-enriched samples of $[Co_2(CO)_8]$ (4), (9), (10), and (11) were similarly prepared by direct exchange. Complex (8) was synthesised from a ^{13}CO-enriched sample of (7).

$[NBu_4][Rh_6(CO)_{15}I]$ (12). The complex $[\{Rh(CO)_2Cl\}_2]$ (233 mg) in $CHCl_3$ (10 cm^3) was stirred under 2.63 mmol of 89% ^{13}CO for 4 h; 57% ^{13}CO enrichment could be anticipated. The solvent was removed and the labelled material was dissolved in methanol (6.5 cm^3), frozen in liquid nitrogen, and allowed to warm up under 100 cm^3 of 89% ^{13}CO at s.t.p. Potassium acetate (260 mg) in methanol (1.3 cm^3) was added dropwise to the mixture. A dark precipitate formed, which redissolved on completion of the addition, to form a red solution. A solution of $[NBu_4]I$ (512 mg) in methanol (1.3 cm^3) and water (0.9 cm^3) was added and the charge stirred for 50 h. Filtration yielded the *product* (12) as a brown solid, which was washed with water and methanol and dried *in vacuo*. Infrared spectrum in CH_2Cl_2: 2 072(sh), 2 044s, 2 013s, 1 984m, 1 958m, 1 944m, and 1 744m, vbr cm^{-1}. The presence of iodine was confirmed by elemental analysis.

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