Preparation and Nuclear Magnetic Resonance Investigation of Some Stereochemically Non-rigid Derivatives of Dodecacarbonyltetrairidium

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The complexes $[Ir_4(CO)_8L_4]$ [L = Ph_2PMe, $PhPMe_2$, Ph_2PEt, Ph_2AsMe, $(PhO)_3P$, and $\frac{1}{2}(Ph_2PCH_2)_2$] have been prepared by direct reaction of $Ir_4(CO)_{12}$ with the ligand. All contain bridging carbonyl groups and in solution at ambient temperatures have one of two structures which differ in the number of bridging carbonyl groups. At temperatures above ambient the complexes were shown by ^1H and ^{13}C n.m.r. spectroscopy to be stereochemically non-rigid by virtue of an intramolecular carbonyl scrambling process. They dissolve in acids to give mainly diprotonated species which were also stereochemically non-rigid, probably involving both carbonyl and proton intramolecular scrambling. Evidence is presented for initial formation of monoprotonated species for some complexes.

THE complex $Ir_4(CO)_{12}$ is generally considered to be rather unreactive, but recently it has been found to react with base[1,2] and, under vigorous conditions, with tertiary phosphines and phosphites.[3-5] Addition of triphenylphosphine to the carbonyl anions $[Ir_4(CO)_{11}H]^-$ and $[Ir_8(CO)_{20}]^{2-}$ yields $[Ir_4(CO)_{10}(PPh_3)_2]$ and $[Ir_4(CO)_9(PPh_3)_3]$ respectively.[1] It has been shown[6] that in these complexes the Ir_4 tetrahedral cluster is retained and is supported both by bridging carbonyl groups and by metal–metal bonds. This is in contrast to the structure of $Ir_4(CO)_{12}$ in which the Ir_4 cluster is held together solely by metal–metal bonds.[7] This paper describes the preparation, by direct reaction of the metal carbonyl and the ligand under mild conditions, of some tetrasubstituted phosphine and arsine complexes of $Ir_4(CO)_{12}$ and their structural characterisation by spectroscopic methods. Particular interest is focused on the n.m.r. spectral evidence for stereochemical non-rigidity in solution of neutral complexes and of protonated species formed when the neutral complexes are dissolved in acid.

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EXPERIMENTAL

The complex $Ir_4(CO)_{12}$ was prepared by a modification of the method of Malatesta *et al.*[8] Hydrated iridium trichloride (1·0 g) was dissolved in boiling water (15 cm^3) and added to a suspension of sodium hydrogen carbonate (2·0 g) and potassium iodide (2·0 g) in methanol (200 cm^3). This mixture was placed in a glass liner in a stainless steel autoclave and stirred at 60 °C for 48 h under a pressure of carbon monoxide (40 atm). On opening the autoclave yellow crystals were found adhering to the liner and to the stirrer. The crystals were isolated, washed with water (50 cm^3), then methanol (25 cm^3), and dried *in vacuo* (0·01 mmHg, 24 h). The product was identified by i.r. spectroscopy. The yield was in the range 65—75%.

A typical preparation of a tetrasubstituted complex involved $Ir_4(CO)_{12}$ (250 mg, 0·23 mmol) suspended in dry, degassed toluene (50 cm^3) and to which an excess (>2 mmol) of the ligand was added under an atmosphere of nitrogen. The mixture was heated under reflux until all the $Ir_4(CO)_{12}$ had dissolved. The resultant orange solution was cooled, filtered, and evaporated to low bulk under reduced pressure. Addition of hexane (50 cm^3) and cooling to -70 °C precipitated the crude product which was filtered off and dried *in vacuo*. Purification was effected by column chromatography on Florisil using toluene or toluene–hexane mixtures as eluant. One band was eluted although some dark-coloured material remained at the top of the column and could not be removed by even the most polar solvents. The eluate was evaporated to low volume (10—15 cm^3) and, after addition of hexane (50 cm^3) and cooling to -70 °C, the product was filtered off and dried *in vacuo* (0·05 mmHg, 24 h). The complex $[Ir_4(CO)_8\{P(OPh)_3\}_4]$ decomposed on the chromatography column and for purification the crude solid was dissolved in toluene, the solution filtered and the solid precipitated on addition of hexane.

TABLE 1

Yields, melting temperatures, molar masses, and analytical results (%)

			M		Analyses					
					Found			Calc.		
Ligand	Yield (%)	M.p.(t/°C)	Found	Calc.	C	H	P or As	C	H	P or As
PPh_2Me	52	129—131	1 867	1 793	40·4	3·05	6·85	40·15	2·90	6·90
$PPhMe_2$	48	153 (decomp.)	1 598	1 545	31·1	2·90	7·95	31·05	2·85	8·00
PPh_2Et	50	122—126 (decomp.)	1 869	1 849	41·65	3·40	6·75	41·55	3·25	6·70
$AsPh_2Me$	60	102—103	1 958	1 968	36·8	2·60	15·05	36·55	2·65	15·2
$AsPhMe_2$	70	157—158	1 758	1 720	27·95	2·65	17·4	27·9	2·55	17·4
$(Ph_2PCH_2)_2$	67	170—185 (decomp.)	1 790	1 789	40·3	2·80	6·60	40·25	2·70	6·95
$P(OPh)_3$	57	178—179	2 332	2 233	43·85	2·75	5·55	43·0	2·70	5·55

TABLE 2

I.r. spectroscopic results (cm^{-1}) for the complexes [a]

Ligands	PPh_2Me [b]	$PPhMe_2$ [b]	PPh_2Et [b]	$AsPh_2Me$ [c]	$AsPhMe_2$ [b]	$(Ph_2PCH_2)_2$ [d]	$P(OPh)_3$ [d]
δ(CO)(terminal)	2 064vw 2 000m 1 980s 1 968s 1 932m	2 068w 1 994m 1 958s,b 1 930sh	2 040w 1 996m 1 985s 1 972sh 1 964s 1 938sh	2 040sh 2 008ms 1 975sh 1 967s 1 943sh	2 067vw 2 031vw 1 998m 1 959s,b	2 064vw 2 004vs 1 979vs 1 958vs	2 054w,sh 2 032m 2 020sh 2 002vs
δ(CO)(bridging)	1 756m,vb	1 810vw 1 770m,b	1 823vw 1 783sh 1 773s	1 831vw 1 783m,b	1 827w 1 760vs,b	1 830m 1 776s 1 752s	1 861w 1 806s

[a] s = Strong, m = medium, w = weak, b = broad, and v = very. [b] In hexane. [c] In cyclohexane. [d] In chloroform.

Microanalyses were performed at the Microanalytical Laboratory of the National Physical Laboratory and by A. Bernhardt. Molar masses were determined using a Mechrolab vapour-pressure osmometer with benzene as solvent. Melting temperatures were determined on a Kofler block apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, using a scale expansion of 2·5, ^1H n.m.r. spectra at 100 MHz using a JEOL MH-100 spectrometer, and ^{31}P and ^{13}C spectra at 36·43 and 22·63 MHz respectively using a Bruker HFX-13 Fourier transform spectrometer. Unless otherwise stated all n.m.r. spectra of the neutral complexes were recorded using solutions of the complexes in $CDCl_3$. ^{13}C Spectra, based on up to 30 000 pulses (7 μs) and a delay time of 2 s, were obtained from concentrated solutions of the complexes (*ca.* 25% w/w) in $CDCl_3$ containing $Cr(acac)_3$ (*ca.* 2% w/w). Tetramethylsilane was used as an internal reference for ^1H and ^{13}C spectra and 85% w/w H_3PO_4 for ^{31}P spectra.

RESULTS AND DISCUSSION

Complexes of the type $[Ir_4(CO)_8L_4]$ [L = Ph_2PMe, Ph_2PEt, $PhPMe_2$, Ph_2AsMe, $PhAsMe_2$, $(PhO)_3P$, and $\frac{1}{2}(Ph_2PCH_2)_2$] were prepared in good yield by reaction of the ligand with a suspension of $Ir_4(CO)_{12}$ in boiling toluene. Purification by chromatography on Florisil using toluene or toluene–hexane mixtures as eluant enabled the complexes to be recovered as orange or yellow solids. All the complexes are air-stable solids for which satisfactory elemental analytical results have been obtained (Table 1). Molar masses were determined

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[8] L. Malatesta, G. Caglio, and M. Angoletta, *Inorg. Synth.*, 1972, **13**, 95.

osmometrically in benzene and indicated that the Ir_4 cluster is preserved in the tetrasubstituted complexes. In contrast to results obtained by Drakesmith and Whyman [3,9] with alkyl phosphines, we did not find any evidence from molar-mass measurements for dissociation of the complexes in benzene. I.r. spectra of the complexes in the carbonyl-stretching region show absorptions which can be attributed to terminal and bridging carbonyl groups (Table 2), and so the structures of the substituted species differ from that of the parent carbonyl. The overall absorption pattern for the complexes is very similar to reported spectra of analogous complexes with alkyl phosphines.[9] Little definite structural information can be deduced from the number or intensity of the carbonyl absorptions because of the relatively low symmetry of possible structures and to the correspondingly large number of i.r.-active vibrations expected.

N.M.R. Spectral Results.—$[Ir_4(CO)_8(PhEMe_2)_4]$ (E = P *or* As). Ambient-temperature ^1H n.m.r. studies indicated that the Group V ligands were not all chemically equivalent in the complexes. For the $PhPMe_2$ complex the ^1H spectrum showed four doublet absorptions of equal intensity, attributable to methyl groups, centred at δ 2·25 ($^2J_{P-H}$ 10·5), 1·95 ($^2J_{P-H}$ 9·5), 1·60 ($^2J_{P-H}$ 9·5), and 1·40 p.p.m. ($^2J_{P-H}$ 9·0 Hz) relative to tetramethylsilane (δ 0). The $PhAsMe_2$ complex exhibited an analogous spectrum with four singlet absorptions of equal intensity at δ 2·12, 1·78, 1·50, and 1·28 p.p.m.

The ^{13}C n.m.r. spectrum of the arsine complex at ambient temperature in the presence of the relaxation reagent [10] $Cr(acac)_3$ confirms the presence of both bridging and terminal carbonyl groups. The absorption at 221·2 p.p.m., relative to tetramethylsilane at 0 p.p.m., may be assigned to bridging carbonyl groups and the absorptions at 176·6, 169·6, and 137·2 p.p.m. to terminal carbonyl groups.[11] If it is assumed that $Cr(acac)_3$ undermines the nuclear Overhauser effect of all carbonyl carbons, the measured intensities of the carbonyl bands should reflect relative abundances and permit determination of the relative numbers of bridging and terminal carbonyl groups in the molecule. The intensity ratio of 2 : 6 between the two sets of absorptions indicates two symmetrically equivalent bridging and six terminal carbonyl groups in the complex. This suggests that for the two bridging carbonyl groups to be symmetrically equivalent we must have at least either a C_2 axis or a plane of symmetry in the molecule. This leads to two types of chemically distinct iridium atoms, namely those (*a*) with two terminal carbonyl groups and one Group V ligand attached, and (*b*) those with one terminal carbonyl group and one Group V ligand attached. The structure containing the C_2 axis is favoured in view of its fulfilment of the 2 : 2 : 2 intensity distribution of the terminal carbonyl bands in the ^{13}C spectrum, whereas a structure of C_s symmetry would require a 2 : 2 : 1 : 1 intensity distribution. The absorptions at 17·0, 16·5, 15·6, and 13·5 p.p.m. in the ^{13}C n.m.r. spectrum and the four methyl absorptions in the ^1H spectrum must arise from magnetic non-equivalence of the pair of methyl groups within each Group V ligand because of the absence of a plane of symmetry relating these pairs of methyl groups. Four structures with Ir(1) and Ir(3) of type (*a*) and Ir(2) and Ir(4) of type (*b*) contain a C_2 axis and accommodate the spectral results. The bridging carbonyl groups link Ir(1) to Ir(2) and Ir(3) to Ir(4). The structures differ in respect of the relative positions of the terminal groups although some will be less probable from steric considerations.

$[Ir_4(CO)_8(Ph_2EMe)_4]$ (E = P *or* As). The ^1H n.m.r. spectrum of the complex $[Ir_4(CO)_8(Ph_2PMe)_4]$ at ambient temperatures showed three broad bands attributable to methyl groups between δ 2·7 and 1·3 p.p.m. which sharpened at −30 °C to three doublets centred at δ 2·70 ($^2J_{P-H}$ 10·0), 2·26 ($^2J_{P-H}$ 9·0), and 1·35 p.p.m. ($^2J_{P-H}$ 9·0 Hz) of relative intensity 1 : 1 : 2 respectively. The ^{31}P spectrum of this complex at ambient temperature showed absorptions centred at δ −8·4, −40·6, and −61·6 p.p.m. relative to H_3PO_4 (δ 0), of approximate intensity 1 : 2 : 1 respectively. The ^1H n.m.r. spectrum of the complex $[Ir_4(CO)_8(Ph_2AsMe)_4]$ at ambient temperatures showed three singlet absorptions attributable to methyl groups at δ 2·43, 2·11, and 1·24 p.p.m. of relative intensity 1 : 1 : 2 respectively. Variable-temperature studies from ambient temperature down to −60 °C using a variety of solvents failed to indicate any further splitting of any of these absorptions, showing that two of the four methyl groups were not accidentally isochronous but were exactly so by virtue of molecular symmetry.

The ^{13}C n.m.r. spectrum at ambient temperature of the $AsPh_2Me$ complex showed a broad band at 15·1 p.p.m. arising from the two unresolved singlets of the non-equivalent methyl groups, and a sharp singlet at 14·1 p.p.m. from the two isochronous methyl groups, confirming the assignment of the ^1H n.m.r. spectrum. Terminal carbonyl groups in the complex showed absorptions in the ^{13}C spectrum at 175·5, 169·1, and 135·6 p.p.m. in an intensity ratio 2 : 1 : 2, and the presence of bridging carbonyl groups is also confirmed with absorptions at 223·7 and 220·3 p.p.m. in an intensity ratio 1 : 2. Using the same assumptions as previously, three bridging carbonyl groups are indicated, two in one, and one in another environment. To accommodate this we must postulate a structure with a plane of symmetry for which a number of stereochemistries are possible. If the three bridging carbonyl groups are located on the edges of the triangle formed by Ir(1), Ir(2), and Ir(3) then, by analogy with complexes of type $[Ir_4(CO)_8(PhEMe_2)_4]$, Ir(4) is of type (*a*) and Ir(1), Ir(2), and Ir(3) are of type (*b*). Eight structures are possible differing in the relative positions

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[9] A. J. Drakesmith and R. Whyman, *J.C.S. Dalton*, 1973, 362.

[10] O. A. Gansow, A. R. Burke, and G. N. La Mar, *J.C.S. Chem. Comm.*, 1972, 456.

[11] J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1973, 79.

of the terminal groups but two are favoured on steric grounds and from their similarity to the known structure[6] for the complex $[Ir_4(CO)_9(PPh_3)_3]$.

Very little useful information can be obtained about the structures of the other complexes due either to the complexity of the ^1H n.m.r. spectrum or to solubility problems. The ^1H n.m.r. spectrum of the complex $[Ir_4(CO)_8(Ph_2PEt)_4]$ shows an intensity distribution of 1 : 1 : 2 for the methylene group absorptions at δ 2·9, 2·4, and 1·6 p.p.m. and so may possibly have a structure related to $[Ir_4(CO)_8(Ph_2PMe)_4]$.

Variable-temperature studies. At temperatures above ambient the ^1H n.m.r. spectra of the four complexes with L = $PhEMe_2$ and Ph_2EMe showed a marked alteration, the methyl bands first broadening and then sharpening to a single absorption. As has been observed in other systems[12] all the bands do not appear to broaden in a uniform manner. The Ph_2PMe complex has the lowest coalescence temperature at *ca.* 100 °C with a doublet absorption at δ 1·96 ($^2J_{P-H}$ 9·3 Hz) for the methyl groups. The weighted mean of the spectrum at −30 °C is δ 1·92. The ^1H methyl absorptions for the other complexes had coalesced by *ca.* 120 °C at the following positions: $PPhMe_2$, δ 1·88 ($^2J_{P-H}$ 9·6 Hz); $AsPh_2Me$, δ 1·80; and $AsPhMe_2$, δ 1·68 p.p.m. This indicates that, in solution, the molecules are stereochemically non-rigid and that carbonyl, and possibly Group V ligand, scrambling is occurring at the higher temperatures. The ^{13}C n.m.r. spectrum of the $PhAsMe_2$ complex at 100 °C showed single absorptions for the methyl groups at 16·2 p.p.m., for the $\geqslant$C–As carbon atoms at 139·4 p.p.m., and a single absorption at 176·1 p.p.m. for the carbonyl groups. The carbonyl resonance compares well with the expected value of 176·2 p.p.m. from the mean of the carbonyl resonances at ambient temperature. This confirms that intramolecular carbonyl scrambling is occurring in the complexes at the higher temperatures. Addition of Ph_2PMe to a solution of the complex $[Ir_4(CO)_8(Ph_2PMe)_4]$ produced separate signals in the ^1H n.m.r. spectrum, at all temperatures, due to the complex and to the free ligand, indicating that if the exchange process involves phosphine scrambling, then it must be intramolecular rather than intermolecular. Similar results were obtained by use of the complex $[Ir_4(CO)_8(Ph_2AsMe)_4]$ and added arsine. However in the light of recent observations with tetranuclear complexes of cobalt[13] and rhodium[14] we consider carbonyl scrambling only to be the more probable explanation. This present work is the first report of stereochemical nonrigidity in a tetrairidium complex.

In all these spectral studies certain difficulties were encountered due to the presence of trace impurities and to decomposition of the sample in solution. The spectra contained some very minor bands, some of which were temperature dependent, and may have arisen from decomposition reactions or possibly another complex which was not separable by conventional techniques. Some decomposition occurred whilst heating the samples to record the spectra at the fast-exchange limit; this was particularly noticeable for the ^{13}C n.m.r. spectra where high temperatures had to be maintained for long periods in order to perform the r.f. pulse accumulation technique.

Protonation studies. All the complexes were protonated in acids such as sulphuric (98% w/w) or trifluoroacetic to give species which exhibited very high field ^1H n.m.r. signals in the range δ −15 to −21. In sulphuric acid protonation was very rapid but the very high field signal was broad and complex, and yielded little structural information. In trifluoroacetic acid the protonation process was slower, the limiting spectrum being reached within 24 h; also better resolution of all signals was possible such that fine structure could be discerned in the very high field signals of the phosphorus compounds. Where relative areas could be measured reliably the spectra indicated that two protons were associated with the iridium cluster. This is in accordance with studies of $Ir_4(CO)_{12}$ which has been reported[15] to dissolve in acids to give $[Ir_4(CO)_{12}H_2]^{2+}$. All the protonated species appear to be undergoing scrambling processes, probably involving the hydrogen atoms and the carbonyl groups, with the process being rapid even at ambient temperatures. Cooling solutions of the complexes in trifluoroacetic acid to −15 °C, in an attempt to observe the limit of the fast exchange process, produced no change in the spectrum. Attempts to obtain the spectrum at still lower temperatures by use of the acids FSO_3H and F_2PO_2H were unsuccessful because of the broadness of the signals, probably as a result of decomposition of the complexes in these acids.

$[Ir_4(CO)_8(PhEMe_2)_4]$ (E = P or As). The ^1H n.m.r. spectrum of the arsine complex in trifluoroacetic acid immediately after dissolution of the solid showed broadening and reduction in intensity of the four methyl bands of the neutral complex; a sharp absorption appeared at δ 2·29 p.p.m., together with a single sharp absorption at δ −17·9 p.p.m. A spectrum taken after 46 min showed the methyl absorptions of the neutral complex to have disappeared and subsequent spectra showed no further changes. The single absorption at δ 2·29 p.p.m. can be assigned to methyl groups of a protonated species which is undergoing a rapid scrambling process.

With the phosphine complex in trifluoroacetic acid the limiting ^1H n.m.r. spectrum showed a doublet absorption in the methyl region, δ 2·37 p.p.m. ($^2J_{P-H}$ 11·0 Hz) and no initial broadening of the bands was observed. In the very high field region of the spectrum a signal consisting of a symmetrical disposition of five bands (δ −17·5 p.p.m.) was observed. If this signal

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[12] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1971, **93**, 4701.

[13] D. Labroue and R. Poilblanc, *Inorg. Chim. Acta*, 1972, **6**, 387.

[14] F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1972, **94**, 6191.

[15] J. Knight and M. J. Mays, *J.C.S. Dalton*, 1972, 711.

is interpreted as a symmetrical binomial quintet ($^2J_{\mathrm{P-H}}$ 5·6 Hz) this would indicate spectroscopic equivalence in the phosphorus and proton spin systems which could only occur if there was rapid intramolecular scrambling of the protons and the carbonyl groups. Interpretation of this signal as an incompletely resolved triplet of triplets is also feasible ($^2J_{\mathrm{P-H}} \approx 6{\cdot}4$, $^2J_{\mathrm{P-H}} \approx 4{\cdot}8$ Hz). This would require the protons to be located on the edges of the tetrahedron of iridium atoms between pairs of symmetrically equivalent phosphorus atoms [*i.e.* on the edges joining Ir(1)–Ir(3) and Ir(2)–Ir(4)], and precludes intramolecular exchange of the two protons.

[$\mathrm{Ir_4(CO)_8(Ph_2EMe)_4}$] (E = As or P). A freshly prepared solution of the arsine complex in trifluoroacetic acid exhibited two singlet absorptions in the very high field region of the ^{1}H n.m.r. spectrum at δ −17·5 and −20·8 p.p.m. The former signal increased in intensity at the expense of the latter until after *ca.* 2 h the latter signal was not observable. In the methyl region of the spectrum there was initial broadening and movement of all the signals, with the absorption at δ 1·24 p.p.m. experiencing the greatest change and moving to lower field. A singlet, which appeared at δ 2·48 p.p.m. and grew in intensity as the intensity of the other methyl absorptions diminished, can be assigned to the methyl groups of the fully protonated species. For the phosphine complex the doublet band due to the two equivalent methyl groups exhibited appreciable low-field shift on protonation and a new doublet δ 2·72 p.p.m. ($^2J_{\mathrm{P-H}}$ 10·2 Hz), ascribable to fully protonated species, appeared. The ^{31}P n.m.r. spectrum of the protonated species showed a single absorption at δ −21 p.p.m., relative to $\mathrm{H_3PO_4}$ (δ 0). In the very high field region of the ^{1}H n.m.r. spectrum two signals were observed initially, at δ −17·5 and −21 p.p.m. with the latter the more intense. Both signals were broad and fine structure could not be fully resolved. A spectrum recorded after 24 h showed that the δ −21 p.p.m. signal had vanished; the band at δ −17·5 p.p.m. had gained in intensity and showed the fine structure of a binomial quintet ($^2J_{\mathrm{P-H}}$ 5·5 Hz). We suggest that all the above observations can be explained on the basis of rapid initial formation of a monoprotonated species giving a very high field signal around δ −20 p.p.m. The subsequent diminution of intensity of this signal and the gain in intensity of a signal around δ −17·5 p.p.m. may be associated with formation of the more stable diprotonated species. The appreciable low-field movement of the band due to the two equivalent methyl groups may be attributed to a single proton associated either with the edge or with the face of the iridium tetrahedron which is bisected by the plane of symmetry.

The complexes [$\mathrm{Ir_4(CO)_8\{P(OPh)_3\}_4}$] and [$\mathrm{Ir_4(CO)_8(Ph_2PCH_2CH_2PPh_2)_2}$] also dissolved in acids to give protonated species but the very high field signals were too weak for any reliable conclusions to be drawn. In the absence of air and moisture acid solutions of all the complexes can be kept for several days without decomposition, and the neutral complexes can be recovered by cautious addition of the acid solution to water. Attempts to isolate the protonated complexes as hexafluorophosphate salts were not successful.

In conclusion, n.m.r. studies have shown that for the four complexes studied in detail, two structural types appear to be formed, differing in the number of bridging carbonyl groups present. It is generally considered that the main factor governing the occurrence of bridging carbonyl groups is the metal–metal bond distance in the carbonyl complex. Contrary to this is the fact that bridging carbonyls are present in $\mathrm{Rh_4(CO)_{12}}$ but not in $\mathrm{Ir_4(CO)_{12}}$ although the metal–metal distance[7] in $\mathrm{Ir_4(CO)_{12}}$ (268 pm) is less than it is in $\mathrm{Rh_4(CO)_{12}}$ (273 pm). Clearly both electronic and steric factors control formation of bridging groups in the carbonyl complexes of these metals. All the complexes readily undergo carbonyl scrambling indicating facile interchange between terminal and bridging groups in the molecules. In order to account for the chemical equivalence of the ligands at high temperature we must conclude that there is carbonyl scrambling concomitant with a $\mathrm{Ir\widehat{Ir}E}$ deformation which causes the Group V ligands to occupy symmetrically equivalent sites with respect to the $\mathrm{Ir_4}$ cluster and thus experience identical chemical shifts. This work appears to be a further example of carbonyl scrambling which is becoming established as a general phenomenon in polynuclear metal carbonyls.[11,14] The ^{13}C n.m.r. technique is obviously of great potential importance in probing this phenomenon, because of the sensitive dependence of carbonyl chemical shifts on magnetic environment.[16] This point is apparent in the present work where the carbonyl bands occur over a chemical shift range of *ca.* 90 p.p.m. For the present complexes further ^{13}C n.m.r. studies on the neutral complexes at the fast-exchange limit and on the protonation process, together with line-shape studies in the ^{1}H n.m.r. spectra, may give more indication as to the mechanism of the scrambling process.

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