Synthesis and Mechanisms of Fluxionality of the Clusters $[Ir_4(CO)_{11}(PH_{3-n}Ph_n)]$ ($n = 1$ or 2)†

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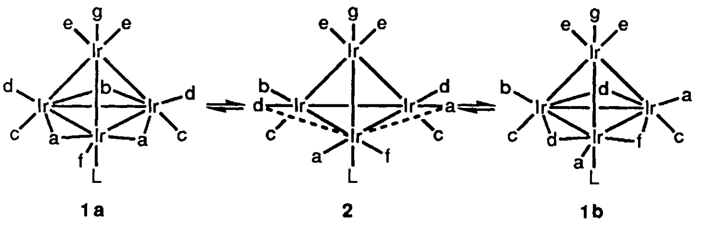
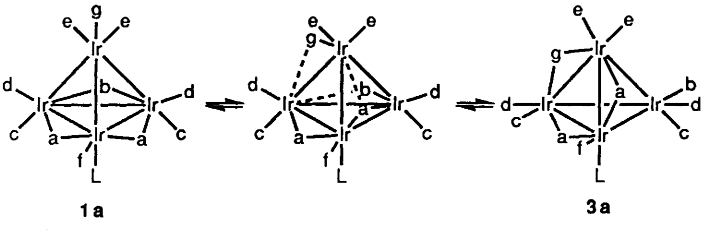
The carbonyl clusters, $[Ir_4(CO)_{11}(PH_2Ph)]$ and $[Ir_4(CO)_{11}(PHPh_2)]$, have been synthesised by replacement of the bromide in $[Ir_4(CO)_{11}Br]^-$ by the appropriate phosphorus ligand. It is shown that $[Ir_4(CO)_{11}(PH_2Ph)]$ and $[Ir_4(CO)_{11}(PHPh_2)]$ exist in solution predominantly as the all-terminal isomers, but there are small concentrations of the two carbonyl-bridged isomers, $[Ir_4(CO)_8(\mu\text{-}CO)_3(PH_2Ph)]$ and $[Ir_4(CO)_8(\mu\text{-}CO)_3(PHPh_2)]$, with the phosphorus ligand axial and equatorial to the bridged face. Carbon-13 magnetisation-transfer measurements were used to demonstrate carbonyl scrambling around the three inequivalent faces of the iridium tetrahedron in $[Ir_4(CO)_{11}(PH_2Ph)]$, and rates were determined. Interconversion of the three isomers of $[Ir_4(CO)_{11}(PHPh_2)]$ was demonstrated by ^{31}P magnetisation-transfer measurements. It was unambiguously shown that interconversion of the carbonyl-bridged isomers occurs *via* the all-terminal isomer.

There have been a number of investigations of the fluxionality of carbonyl groups on derivatives of $[Ir_4(CO)_{12}]$.[1] Two principal low-energy mechanisms have been identified. The original work on $[Ir_4(CO)_{11}(PMe_2Ph)]$ by Stuntz and Shapley[1a] interpreted the exchange mechanism on the basis of the Cotton merry-go-round mechanism. Subsequently, the original Cotton merry-go-round mechanism[2] has been modified for $[Ir_4(CO)_{11}(PEt_3)]$, so that complete bridge-opening is not required, see Scheme 1, L = PEt_3.[1c] A consequence of this modification is that carbonyl scrambling about each face has a different activation energy. The second mechanism of carbonyl scrambling on $[Ir_4(CO)_{11}L]$ derivatives involves face-bridged intermediates, see Scheme 2. This mechanism was originally identified in $[Ir_4(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$,[1d,1h] but has subsequently been shown to be applicable to $[Ir_4(CO)_{11}(PEt_3)]$[1c] and $[Ir_4(CO)_{11}Br]^-$.[1e]

We have now synthesised $[Ir_4(CO)_{11}(PH_2Ph)]$ and $[Ir_4(CO)_{11}(PHPh_2)]$. Both these compounds exist predominantly as terminal isomers and provide an opportunity to investigate carbonyl scrambling in $[Ir_4(CO)_{12}]$ derivatives where carbonyl bridges are disfavoured.



Scheme 1 Modified Cotton mechanism for carbonyl scrambling in $[Ir_4(CO)_{11}L]$. The lower-case letters refer to carbonyl ligands



Scheme 2 Face-bridged mechanism for carbonyl scrambling in $[Ir_4(CO)_{11}L]$ derivatives

Results and Discussion

NMR Spectra of $[Ir_4(CO)_{11}(PH_nPh_{3-n})]$ (n = 1 *or* 2).—$[Ir_4(CO)_{11}(PH_2Ph)]$. The ^{31}P NMR spectrum of $[Ir_4(CO)_{11}(PH_2Ph)]$ in CD_2Cl_2 at 20 °C consists of a broad singlet at δ −139.1. On cooling to −100 °C, three ^{31}P NMR signals are resolved at δ −81.0, −124.5 and −137.0, in the intensity ratio 0.016:0.012:1.00. The ^{13}C NMR spectrum of $[Ir_4(CO)_{11}(PH_2Ph)]$ in CD_2Cl_2 at 20 °C consists of a broad singlet at δ 157.3 and a broad doublet at 155.8, $J(^{31}P\text{–}^{13}C)$ 35 Hz, in the approximate intensity ratio 10:1. On cooling to −104 °C, the ^{13}C NMR spectrum splits into six strong signals at δ 159.8, $J(^{31}P\text{–}^{13}C)$ 4, $J(^{13}C\text{–}^{13}C)$ 11; 158.1, $J(^{13}C\text{–}^{13}C)$ 11; 155.3; 154.4, $J(^{31}P\text{–}^{13}C)$ 37; 154.3, $J(^{13}C\text{–}^{13}C)$ 11 and 153.8, $J(^{13}C\text{–}^{13}C)$ 12 Hz, in the intensity ratio 2:2:2:1:2:2, see Fig. 1. In addition very weak signals are resolved at δ 204.4, 203.6, 195.2, 171.6, 170.0 and 169.5, see Fig. 2. The absence of signals due to the major isomer at higher chemical shift than δ 160 is consistent with the major isomer having all terminal carbonyl groups, **4**, L = PH_2Ph. If there were bridging carbonyl groups, they would be expected to have chemical shifts of between δ 190 and 210 by analogy with known compounds.[1]

The ^{13}C NMR signals of isomer **4**, L = PH_2Ph, can be assigned by analogy with known compounds. Carbonyl g can be immediately assigned on the basis of $^3J(^{31}P\text{–}^{13}C)$ 37 Hz and the intensity of 1. It is now well established[1c] that, when there is a linear arrangement, $^3J(^{13}C\text{–}^{13}C)$ and $^3J(^{31}P\text{–}^{13}C)$ are substantial and this is used as a major assignment aid. The lack of a resolvable $^3J(^{13}C\text{–}^{13}C)$ on the signal at 155.3 permits its assignment to carbonyl d, which is the only carbonyl group which is linearly related to carbonyl d′, while all the other carbonyls are linearly related to another carbonyl or PH_2Ph. The signal at δ 159.8 shows $J(^{31}P\text{–}^{13}C)$ 4 Hz, which is consistent with it being due to carbonyl a. The remaining signals proved more difficult to assign. A $^{13}C\text{–}^{13}C$ correlation spectroscopy (COSY)-90 two dimensional NMR spectrum was recorded to establish the $J(^{13}C\text{–}^{13}C)$ connectivities, see Fig. 3. The experiment showed connectivities between the signals at δ 159.8 and 153.8 and between δ 158.1 and 154.4. The connectivity between the signals at δ 159.8 and 153.8 and the assignment of

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† *Non-SI unit employed:* cal = 4.184 J.

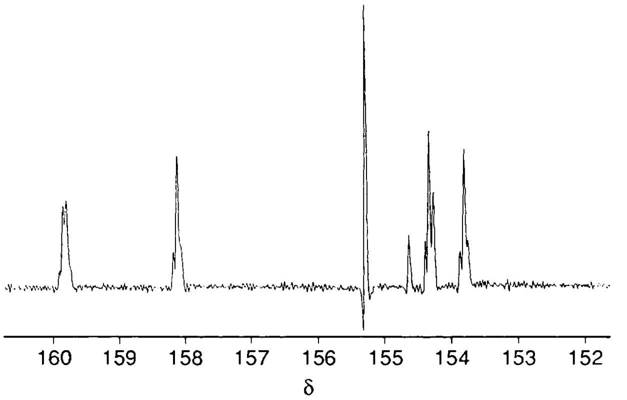


Fig. 1 Partial 100.62 MHz ^{13}C NMR spectrum of $[Ir_4(CO)_{11}(PH_2Ph)]$ in CD_2Cl_2 at −104 °C. The spectrum has been subjected to a Gaussian enhancement to improve the resolution of the ^{13}C satellites. The compound is *ca.* 25% enriched in ^{13}CO

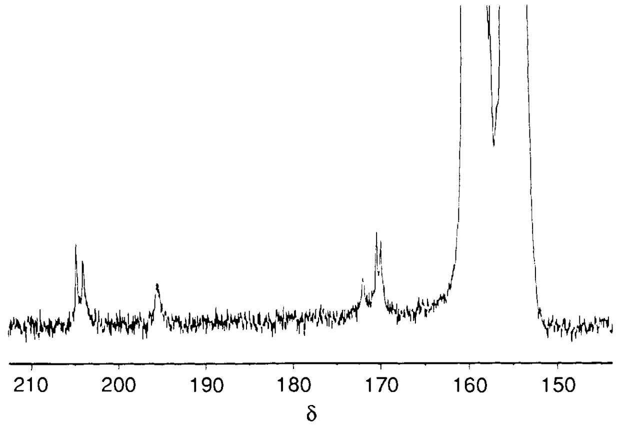
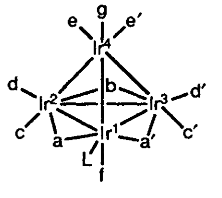


Fig. 2 Partial 100.62 MHz ^{13}C NMR spectrum of $[Ir_4(CO)_{11}(PH_2Ph)]$ in CD_2Cl_2 at −104 °C. The spectrum has been subjected to a line broadening of 3 Hz to enhance the signal : noise ratio. The gain has been adjusted for the signals due to the minor isomers to be visible. The carbonyl signals due to the major isomer are shown in Fig. 1. The compound is *ca.* 25% enriched in ^{13}CO



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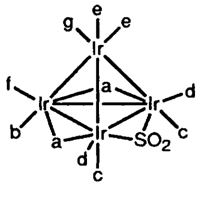

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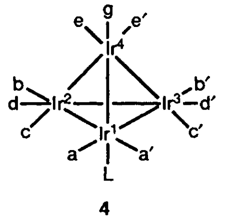

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the carbonyl at δ 159.8 to carbonyl a permits the assignment of the carbonyl at δ 154.4 to carbonyl b. The relative assignments of the carbonyls at δ 158.1 and 154.4 between the remaining unassigned carbonyls c and e is uncertain.

The minor isomers show ^{13}CO signals in the δ 190 to 210 region of the spectrum, and are due to the two carbonyl-bridged isomers **1** and **3**, L = PH_2Ph. These isomers are associated with the ^{31}P NMR signals at δ −81.0 and −124.5. It has been

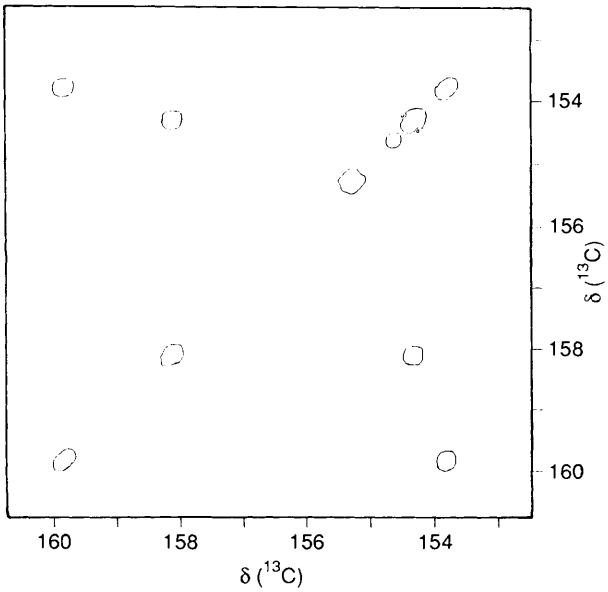
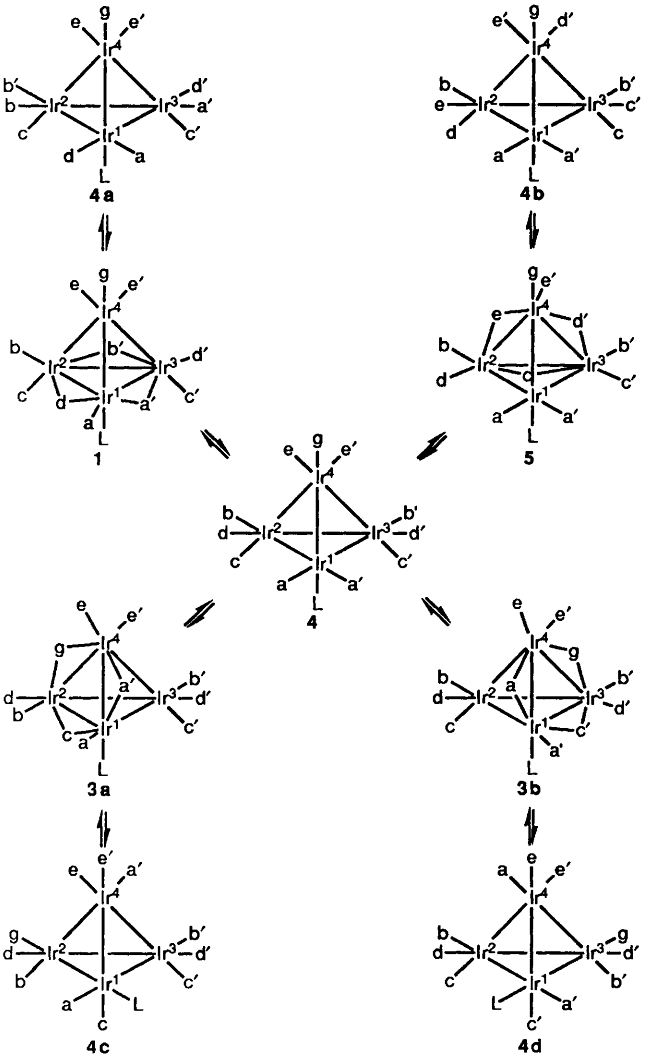


Fig. 3 Partial 100.62 MHz COSY-90 ^{13}C NMR spectrum of the major isomer of $[Ir_4(CO)_{11}(PH_2Ph)]$ in CD_2Cl_2 at −104 °C. The compound is *ca.* 25% enriched in ^{13}CO

previously established that δ(^{31}P) 28.7 for **3**, L = PEt_3 and 6.0 for **1**, L = PEt_3.[1b] On the basis of the relative ^{31}P chemical shifts when L = PEt_3, it is probable that for **1**, L = PH_2Ph, δ(^{31}P) −124.5 and **3**, L = PH_2Ph, δ(^{31}P) −81.0. This gives the isomer populations as **1**:**3**:**4** is 0.012:0.016:1.00. Hence the ΔG° values for the stability of **1** and **3**, relative to **4**, L = PH_2Ph, are 1.52 and 1.40 kcal mol^{-1} respectively. The ^{13}CO signals of the minor isomers can be partially assigned, δ 204.4 and 203.6 are assigned to carbonyl b, δ 195.2 to carbonyl a, and δ 171.6, 170.0 and 169.5 to carbonyl d and carbonyl f, but the relative assignments to isomers **1** and **3** are not made.

The mechanism of carbonyl exchange was investigated using magnetisation-transfer measurements at −93 °C, studied by applying a selective DANTE[3] pulse to the various carbonyls of the major isomer. It proved possible to carry out the measurements selectively inverting carbonyls at δ 159.8, 158.1 and 155.3. The carbonyls at δ 154.4 and 153.8 were not inverted, due to their mutual proximity. It was not possible to include the minor isomers on account of the low intensity of the signals and the consequential substantial broadening due to exchange. The data were initially analysed without applying any rate constraints, and then analysed assuming only the Cotton merry-go-round mechanism, see Scheme 3. There was no significant reduction in the quality of the fit and it is this fit that is presented here. On account of the uncertainty of assignment of carbonyls c and e, the data were fitted using both assignments, and the fit was 50% worse using the assignment carbonyl c at δ 154.4 and carbonyl e at δ 158.1, rather than carbonyl c at δ 158.1 and carbonyl e at 154.4, which is probably the correct assignment. Using this assignment, then carbonyl a and carbonyl c which are close to the PH_2Ph substituent are both moved to high frequency.

There are three different faces to the Ir_4 tetrahedron of $[Ir_4(CO)_{11}L]$ derivatives, namely the $Ir^1Ir^2Ir^3$ face, the $Ir^1Ir^2Ir^4$ face, which is equivalent to the $Ir^1Ir^3Ir^4$ face, and the $Ir^2Ir^3Ir^4$ face, see Scheme 3. Carbonyl scrambling about the $Ir^1Ir^2Ir^3$ face produces carbonyl exchange (a ⟷ a′ ⟷ d′ ⟷ b′ ⟷ b ⟷ d ⟷ a) at a rate k_{123} and about the $Ir^2Ir^3Ir^4$ face exchange (c ⟷ d ⟷ e ⟷ e′ ⟷ d′ ⟷ c′ ⟷ c) at a rate k_{234}. Exchange on the equivalent $Ir^1Ir^2Ir^4$ and $Ir^1Ir^3Ir^4$ faces produces exchange (a ⟷ a′ ⟷ c′ ⟷ d ⟷ e′ ⟷ b′ ⟷ b ⟷ e ⟷ d′ ⟷ c ⟷ a) at a rate $k_{124} = k_{134}$. Overall this produces the rate matrix in Table 1. The data were fitted using a previously published computer



Scheme 3 Possible Cotton merry-go-round mechanisms in $[Ir_4(CO)_{11}L]$ derivatives with an unbridged ground state

Table 1 The exchange matrix for carbonyl exchange in isomer **4**

	δ 159.8 CO_a	δ 158.1 CO_c	δ 155.3 CO_d	δ 154.4 CO_e	δ 153.8 CO_b
CO_a	—	$2k_{124}$	k_{123}	0	0
CO_c	$2k_{124}$	—	$2k_{124} + k_{234}$	0	0
CO_d	k_{123}	$2k_{124} + k_{234}$	—	$2k_{124} + k_{234}$	k_{123}
CO_e	0	0	$2k_{124} + k_{234}$	—	$2k_{124}$
CO_b	0	k_{234}	k_{123}	$2k_{124}$	

program[4] and the derived rates* at −93 °C are k_{123} = 10.7, k_{124} = 1.6 and k_{234} = 2.9 s^{-1}, corresponding to $\Delta G_{180}^{\ddagger}$ = 9.5, 10.2 and 10.0 kcal mol^{-1}, respectively.

$[Ir_4(CO)_{11}(PHPh_2)]$. The ^{31}P NMR spectrum of $[Ir_4(CO)_{11}(PHPh_2)]$ consists of three signals in CD_2Cl_2 at δ −16.5, −57.4 and 65.2 in the ratio 0.09:0.27:1.00 due to the three isomers **3**, **1** and **4**, L = $PHPh_2$.

Difficulties were encountered in obtaining a good ^{13}C NMR spectrum of $[Ir_4(CO)_{11}(PHPh_2)]$ on account of its lower solubility and the presence of several significant isomers. As a consequence, $^3J(^{13}C-^{13}C)$ was not resolved. The major isomer gave five signals of equal intensity at δ 161.1, 158.6, 155.6, 154.5 and 153.9. Only one half of the doublet due to carbonyl g was resolved at δ 154.2. As for $[Ir_4(CO)_{11}(PH_2Ph)]$, the absence of signals between δ 190 and 210 for the major isomer permits its assignment as **4**, L = $PHPh_2$ and, by analogy, the signals are assigned as carbonyl a at δ 161.1, carbonyl b at δ 155.6, carbonyl c and carbonyl e at δ 158.6 and 153.9, carbonyl d at δ 153.9 and carbonyl g at *ca.* δ 154.2. The ^{13}C NMR spectrum of **1**, L = $PHPh_2$ can be partially assigned by analogy with **1**, L = PEt_3 as carbonyl a at δ 205.1, carbonyl b at δ 195.3, carbonyl f at δ 172.5, carbonyl d at δ 170.0 and carbonyl c or carbonyl e at δ 156.9. The other ^{13}CO signals due to **1**, L = $PHPh_2$ were not well enough resolved to assign. The ^{13}C NMR spectrum of **3**, L = $PHPh_2$ can be partially assigned by analogy with **3**, L = PEt_3 as carbonyl a at δ 205.5, carbonyl b at δ 195.5 and carbonyl d at δ 170.7. The other ^{13}CO signals due to **3**, L = $PHPh_2$ were not well enough resolved to assign.

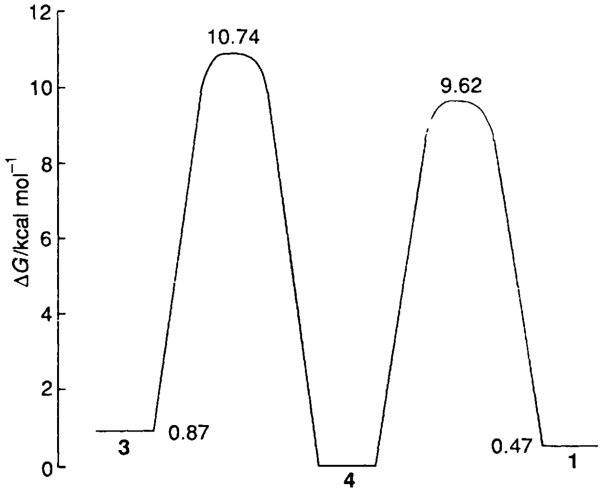


Fig. 4 Free-energy diagram for the interconversion of the isomers **1**, **3** and **4** of $[Ir_4(CO)_{11}(PHPh_2)]$ in CD_2Cl_2 at −93 °C

The ^{13}C NMR spectrum consisted of too great a number of overlapped signals between δ 153 and 162 to carry out magnetisation-transfer measurements, but the ^{31}P NMR spectrum was well resolved and magnetisation-transfer measurements were performed to determine the rate of exchange between the three isomers. Three separate magnetisation-transfer measurements were performed where each ^{31}P NMR signal was inverted at −93 °C using the DANTE pulse sequence. The resulting exchange data were fitted using a computer program which has been described previously to give rates of exchange from isomer **3** to **4** of 3.93 s^{-1}, corresponding to $\Delta G^{\ddagger}$ = 9.87 kcal mol^{-1} and from **1** to **4** of 28.85 s^{-1}, corresponding to $\Delta G^{\ddagger}$ = 9.15 kcal mol^{-1}. No significant rate was found for the direct exchange between **1** and **3** making the mechanism in Scheme 2 negligible for this compound in comparison with the Cotton bridge-opening-closing mechanism.[2] These values of $\Delta G^{\ddagger}$ combined with the ΔG° values for the equilibria between **1**, **4** and **3** have been used to derive a reaction profile for the interconversion of these isomers, see Fig. 4.

The Structure of $[Ir_4(CO)_{11}L]$ *Derivatives.*—The X-ray structures of a number of $[Ir_4(CO)_{11}L]$ derivatives have been determined. When L = CO, the ground state has all the carbonyls terminal, **4**, L = CO.[5] Similarly when L = $CNBu^t$ all the carbonyls are terminal.[6] In contrast, when L = $[SCN]^-$ or I^- there are three bridging carbonyls as in **1**.[7] In addition, the structure of $[Ir_4(CO)_{11}(SO_2)]$ has two bridging carbonyls and the SO_2 bridges, **6**.[8] Carbon-13 NMR spectroscopy has been used to characterise a number of other $[Ir_4(CO)_{11}L]$ derivatives. When L = tertiary phosphine, the ground state has bridging carbonyls with structure **1** predominating, structure **3** is significant for the smaller tertiary phosphines. When L = PPh_3, only isomer **1** is detected.[9] When L = PMe_2Ph, $PMePh_2$ or PEt_3, both isomers **1** and **3** are detected in the

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* The computer program does not produce error estimates, however, the variation in rates from one data set to another indicates that the errors are ±1 s^{-1}.

ratio 2:1, 15:1 and 7:1 respectively.[1b,1c,9] Hence among $[Ir_4(CO)_{11}L]$ complexes, the complexes $[Ir_4(CO)_{11}(PH_nPh_{3-n})]$, $n = 1$ or 2, are unique with isomer **4** being dominant. One cause is the small size of these ligands favouring the terminal structure.

Mechanism of Carbonyl Scrambling in $[Ir_4(CO)_{11}L]$ *Derivatives.*—Prior to this work, carbonyl scrambling in $[Ir_4(CO)_{11}L]$ derivatives was known to occur by three mechanisms: (*i*) the Cotton merry-go-round mechanism around face $Ir^1Ir^2Ir^3$, see Scheme 3, (*ii*) the Cotton merry-go-round mechanism around faces $Ir^1Ir^2Ir^4$ and $Ir^1Ir^3Ir^4$, see Scheme 3 and (*iii*) a mechanism involving a face-bridged intermediate/transition state, see Scheme 2. This work has established the significance of a fourth mechanism, a Cotton merry-go-round mechanism around face $Ir^2Ir^3Ir^4$, see Scheme 3. This work also establishes that the bridge-open isomer and the edge-bridged isomers are poor representations of the transition state for carbonyl scrambling in clusters based on $[Ir_4(CO)_{12}]$. The transition state must involve the carbonyls adopting positions intermediate between bridging and terminal. Previously, the difference in energy between the Cotton merry-go-round mechanism around face $Ir^1Ir^2Ir^3$ and around other faces was attributed to a small bridging interaction in the intermediate **4**, see Scheme 1.[1c] In the light of the present work, the difference in energy between the activation energies for the Cotton merry-go-round mechanism around different faces can equally well arise from differential stabilisation of the transition state, which is clearly well removed from either the carbonyl-bridged structures **1**, **3** or **5**, or the all-terminal structure **4**.

Experimental

Sodium hexachloroiridate(IV) hexahydrate (Johnson Matthey), tetrabutylammonium bromide and silver hexafluoroantimonate (Aldrich Chemical), phenyl- and diphenyl-phosphines (Strem Chemicals), Inc.) were used as received. The compound $[NBu^n_4][Ir_4(CO)_{11}Br]$ was prepared by the literature method.[7b,c] Samples of 25–30% ^{13}CO-enriched compounds were prepared starting from $[NBu^n_4][Ir_4(CO)_{11}Br]$. Manipulations were performed in Schlenk-type flasks under an atmosphere of nitrogen. Solvents were dried, freshly distilled and freed from dissolved oxygen by freeze degassing. TLC plates (20 × 20 cm, 2 mm; Merck) were used for the separations. The Ir_4 substituted species were stored under an inert atmosphere for they were found to be slightly air sensitive in the solid state.

The NMR spectra in CD_2Cl_2 were measured on a Bruker WM250 (^1H) and WH400 (^{13}C and ^{31}P) NMR spectrometer. The temperatures were measured using a Comark electronic thermometer, by replacing the sample with an NMR tube containing a thermocouple in CH_2Cl_2. Phosphorus-31 NMR chemical shifts were determined relative to external 85% H_3PO_4.

The following experimental procedure was employed to carry out the DANTE[3] measurements. A suitable temperature was chosen so that there was a little line broadening due to exchange. After the spectrometer had stabilized at that temperature, the T_1 values of the exchanging nuclei were estimated using the $10D_1$–π–D_1–$\frac{\pi}{2}$ pulse sequence, adjusting the delay, D_1, for the null signal. Subsequently, the relaxation delay was taken as $10D_1$. The DANTE pulse length was optimized for maximum signal inversion. The measurements were carried out using the pulse sequence: {[read free-induction decay (f.i.d.)–$\{10D_1$–$(D_2$–$P_1)_{30}$–D_3–$\frac{\pi}{2}$–acquire$\}_8$–write f.i.d.–change $D_3]_m$–reset exchange delay, $D_3\}_n$, with m typically 10 and n chosen to give adequate signal:noise ratio. Typical values are $D_1 = 3$ s, $D_2 = 0.2$ ms, $P_1 = 2.8$ μs (^{31}P), 1.2 μs (^{13}C), $D_3 = m$ values with the minimum one being 3 μs and the largest being $10D_1$ and $\frac{\pi}{2}$ pulse = 40.0 μs (^{31}P), 25 μs (^{13}C). The remaining times are chosen to give a spread over the exchange and relaxation times, typically 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2 and 0.4 s. This sequence has the advantage that any temperature drift during the experiment will be spread over all the measurements.

Mass spectra were obtained on a Kratos MS 902 by fast-atom bombardment using 3-nitrobenzyl alcohol as matrix. Infrared spectra were recorded on a Perkin-Elmer 1700 Fourier transform spectrophotometer. Microanalyses were performed at the Chemical Laboratories, University of Cambridge.

Preparation of $[Ir_4(CO)_{11}L]$ ($L = PH_2Ph$ *and* $PHPh_2$).[9,10]—A mixture of $[Ir_4(CO)_{12}]$ (221.0 mg, 0.2 mmol) and NBu^n_4Br (70.9 mg, 0.22 mmol) in tetrahydrofuran (30 cm^3) was heated under reflux for 1 h. After cooling to −40 °C, PH_2Ph (22.0 μl, 0.2 mmol) or $PHPh_2$ (34.8 μl, 0.2 mmol) was added to the mixture, which was allowed to warm to −20 °C and kept at this temperature for 1 h. The solvent was evaporated to dryness *in vacuo* and the residue taken up in dichloromethane (4 cm^3) and chromatographed on TLC plates. Elution with dichloromethane–hexane (3:7) gave one yellow fraction of $[Ir_4(CO)_{11}(PH_2Ph)]$ or $[Ir_4(CO)_{11}(PHPh_2)]$ that was recrystallized from hexane. $[Ir_4(CO)_{11}(PH_2Ph)]$ (225.5 mg, 95%) (Found: C, 17.5; H, 0.7; P, 2.5. $C_{17}H_7Ir_4O_{11}P$ requires C, 17.2; H, 0.6; P, 2.6%); M^{+} 1190 (calc. ^{193}Ir). IR, ν(CO) (hexane) at 2096m, 2058vs, 2040s, 2017m, 2007m, 2000m, 1980w, 1965vw, 1953vw, 1857vw and 1826vw cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.46 [d, $J(^{31}P-^1H)$ 376.7 Hz] and 7.60 (m, Ph). $[Ir_4(CO)_{11}(PHPh_2)]$ (224.8 mg, 89%) (Found: C, 21.7; H, 0.9; P, 2.4. $C_{23}H_{11}Ir_4O_{11}P$ requires C, 21.9; H, 0.9; P, 2.5%); M^{+} 1266 (calc. ^{193}Ir). IR ν(CO) (hexane) at 2093w, 2055vs, 2035m, 2012w, 1846vw and 1826vw cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4 [d, $J(^{31}P-^1H)$ 386.57 Hz], 7.45–7.49 and 7.55–7.63 (m, Ph).

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