(8) For leading references see S. Braverman and H. Mechoulam, *Tetrahedron*, **30**, 3883 (1974).

(9) For an explanation of the direction of this and other O → S 1,2 shifts see E. G. Miller, D. R. Rayner, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3139 (1966).

(10) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966); J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966); Q. N. Porter, *Aust. J. Chem.*, **20**, 103 (1967); R. D. Chambers and J. A. Cunningham, *Chem. Commun.*, 583 (1967); D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **32**, 3872 (1967).

(11) Pertinent evidence for a somewhat similar process, the concerted and reversible [2,3]-sigmatropic rearrangement of certain allylic sulfoxides to sulfenates, has been reported: S. Braverman and Y. Stabinsky, *Isr. J. Chem.*, **5**, 71p (1967); S. Braverman, *Int. J. Sulfur Chem., Part C*, **6**, 149 (1971); R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970).

(12) A. P. Boisselle and N. A. Meinhardt, *J. Org. Chem.*, **27**, 1828 (1962).

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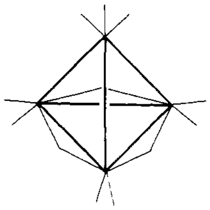
Received April 21, 1976

Solution Structures and Dynamics of $Ir_4(CO)_{12-x}(PPh_2Me)_x$ (x = 1–4)[1]

Sir:

Presently available evidence[2] suggests that the cluster compounds $M_4(CO)_{12}$ (M = Co, Rh, Ir) maintain the same structures in solution as in the solid state: **1** for $Co_4(CO)_{12}$[3] and $Rh_4(CO)_{12}$,[4] **2** for $Ir_4(CO)_{12}$.[4] However, the configurations adopted by their derivatives together with the occurrence and mechanisms of carbonyl mobility in such tetranuclear clusters remain problems of current interest. Complete scrambling of the carbonyl ligands over the tetrarhodium framework of $Rh_4(CO)_{12}$ has been demonstrated,[5] and the intermediacy of an unbridged form (**2**), as proposed by Cotton,[5,6] is consistent with available data.[7] However, spectral data reported for carbonyl scrambling in structurally related $RhCo_3(CO)_{12}$ are incompatible with the intervention of **2**, and concerted interchange of bridging and terminal carbonyls has been proposed.[8] Carbonyl mobility could not be established for $Co_4(CO)_{11}P(OMe)_3$[9] or $Co_4(CO)_{12}$[9,10] due to ^{59}Co quadrupolar effects. A previous study of some $Ir_4(CO)_8L_4$ derivatives demonstrated carbonyl site exchange, but the molecular configurations were not well established and no mechanistic evidence was forthcoming.[11] Following up on a new method for the preparation of derivatives of $Ir_4(CO)_{12}$,[12] we report here ^{31}P and ^{13}C NMR data that establish the solution structures of the series $Ir_4(CO)_{12-x}(PPh_2Me)_x$ (x = 1–4)[13] and present variable temperature ^{13}C NMR spectra that delineate the carbonyl scrambling processes in $Ir_4(CO)_{11}PPh_2Me$.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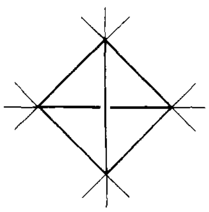
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Crystalline $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ adopt configurations **4** and **5**, respectively.[14] In **4** one PPh_3 ligand is in a radial position (P_2) with respect to the bridging carbonyls and one PPh_3 ligand (P_1) is axial. Configuration **5** has two radial ligands (P_2P_2') and one axial ligand (P_1). The $^{31}P\{^1H\}$ NMR spectrum[15] of $Ir_4(CO)_{10}(PPh_3)_2$ displays two resonances of equal intensity at −17.6 and 15.0 ppm and the spectrum of $Ir_4(CO)_9(PPh_3)_3$ shows two resonances of intensity 2:1 at −20.0 and 17.4 ppm. These data suggest that structures **4** and **5** are maintained in solution and that the radial phosphorus ligand signals appear at lower field than those of the axial phosphorus ligands. Accordingly, $Ir_4(CO)_{11}PPh_3$, which shows a ^{31}P signal at 13.0 ppm, is assigned structure **3** with an axial PPh_3 ligand.[16] $Ir_4(CO)_{11}(PPh_2Me)$ (31.5 ppm), $Ir_4(CO)_{10}(PPh_2Me)_2$ (5.7, 28.2 ppm, 1:1), and $Ir_4(CO)_9(PPh_2Me)_3$ (5.2, 25.0 ppm, 2:1) display completely analogous ^{31}P spectra and are assigned structures **3**, **4**, and **5**, respectively. $Ir_4(CO)_8(PPh_2Me)_4$ shows three resonances of intensity 1:2:1 (7.4, 39.8, 59.9 ppm), as previously reported.[11] Since the signal of relative intensity 2 is in the high field region associated with axial substitution, structure **6** is assigned.

Limiting $^{13}C\{^1H\}$ NMR spectra recorded for the PPh_2Me derivatives are fully consonant with these configurations (see Table I).[17,18] Certain general features of the data allow unusually detailed assignments for metal cluster carbonyl spectra. (i) Low-field resonances due to three bridging carbonyls (a, a′, b) are seen in each case. These signals shift ~10 ppm further downfield for each substitution at an adjacent iridium atom. (ii) Signals for terminal carbonyls positioned approximately in the basal plane (radial positions d, d′, f) are 7–15 ppm

Table I. ^{13}C NMR Data for $Ir_4(CO)_{12-x}(PPh_2Me)_x$, x = 1–4

Shift[a]	Mult (rel int)	Assign	Shift[a]	Mult (rel int)	Assign
	$Ir_4(CO)_{11}PPh_2Me$			$Ir_4(CO)_{10}(PPh_2Me)_2$	
206.8	m (2)	a,a′	217.6	m (1)	a′
196.2	m (1)	b	206.8	m (1)	a or b
173.2	d (1)[b]	f	205.6	m (1)	a or b
171.1	s (2)	d,d′	175.0	m (1)	f
158.3	s (2)	c,c′	172.6	d (1)[d]	d
157.1	s (2)	e,e′	160.9	s (1)	e,e′ or c
155.9	d (1)[c]	g	159.8	d (1)[e]	g
			159.7	s (1)	e,e′ or c
			158.7	d (1)[f]	c′
			156.3	s (1)	e,e′ or c
	$Ir_4(CO)_9(PPh_2Me)_3$			$Ir_4(CO)_8(PPh_2Me)_4$	
217.8	m (2)	a,a′	223.4	m (1)	b
217.1	m (1)	b	218.4	m (2)	a,a′
176.6	dt (1)[g]	f	178.2	dd (2)[j]	d,d′
165.7	d (1)[h]	g	171.1	dd (2)[k]	e,e′
160.7	d (2)[i]	c,c′	164.5	dd (1)[l]	f
159.9	s (2)	e,e′			

[a] Chemical shifts in ppm relative to internal Me_4Si. [b] $J(P\text{–}f) = 4$ Hz. [c] $J(P\text{–}g) = 26$ Hz. [d] $J(P_2\text{–}d) = 15$ Hz. [e] $J(P_1\text{–}g) = 24$ Hz. [f] $J(P_2\text{–}c') = 6$ Hz. [g] $J(P_2\text{–}f) = 14$ Hz, $J(P_1\text{–}f) = 9$ Hz. [h] $J(P_1\text{–}g) = 25$ Hz. [i] $J(P_2\text{–}c) = 3$ Hz. [j] $J(P_1\text{–}d) = 9$ Hz, $J(P_2\text{–}d) = 15$ Hz. [k] $J(P_1\text{–}e') = 32$ Hz, $J(P_3\text{–}e') = 4$ Hz. [l] $J(P_3\text{–}f) = 33$ Hz, $J(P_2\text{–}f) = 8$ Hz.

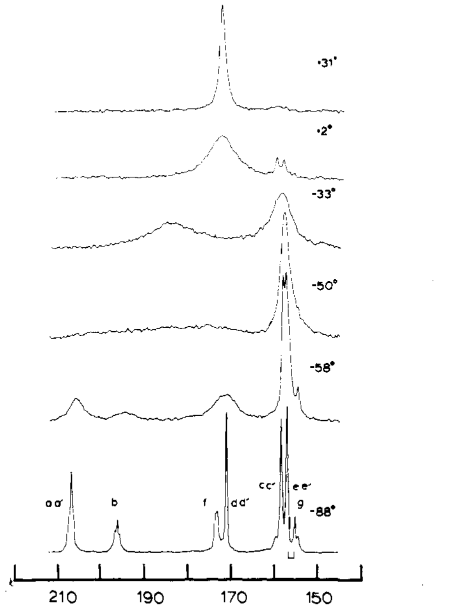
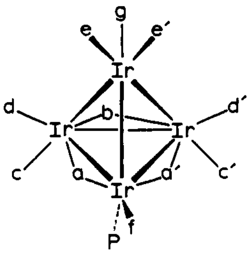


Figure 1. The 15-MHz ^{13}C NMR spectra (carbonyl region) obtained for $Ir_4(CO)_{11}PPh_2Me$. The position of the doublet due to carbonyl g (partially obscured at this frequency) is indicated by a bar.



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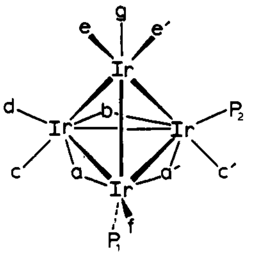

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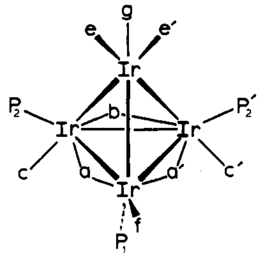

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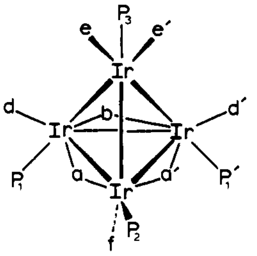

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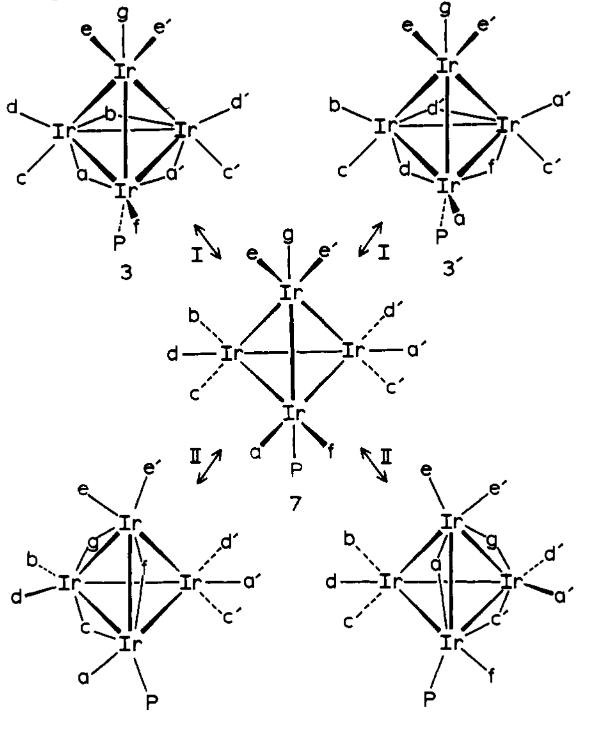
downfield of the signals for the remaining terminal carbonyls. (iii) Relatively large long-range carbon-phosphorus coupling constants are observed for certain stereochemical relationships. Thus, $^3J_{PC}$ = 24-34 Hz, when the ligands are trans to each other in apical and basal-axial positions (P_1-g in **3**, **4**, and **5**; P_3-f in **6**), and $^3J_{PC}$ = 14-15 Hz, when both ligands are in basal-radial positions (e.g., P_2/P_2'-f in **5**). However, the coupling is weaker for ligands attached to the same iridium atom, $^2J_{PC} \le 9$ Hz. For example, in the spectrum of $Ir_4(CO)_9(PPh_2Me)_3$ (six signals, 2:1:1:1:2:2, to increasing field), the signals corresponding to bridging carbonyls a, a', b (see **5**) are nearly coincident at ~217 ppm. The signal for the unique basal-radial carbonyl f (176.6 ppm) is a double triplet, due to coupling with the radial ligands P_2/P_2' (^3J = 14 Hz) as well as with the axial ligand P_1(^2J = 9 Hz). A doublet is observed for apical carbonyl g (165.7 ppm), coupled with basal-axial ligand P_1 (^3J = 25 Hz), but the resonance for apical carbonyls e/e' (159.9 ppm) is a singlet. Finally, the signal for axial carbonyls c/c' (160.7 ppm) appears as a narrow doublet, due to coupling with the radial ligands P_2/P_2' (^2J = 3 Hz).

The ^{13}C NMR spectra recorded for $Ir_4(CO)_{11}(PPh_2Me)$ at several temperatures are shown in Figure 1. Three distinct averaging processes can be observed as the temperature is raised from −88 °C. First, at −58 °C the resonances due to the bridging carbonyls (aa'b) and the basal radial carbonyls (dd'f) have broadened much more than the remaining resonances, and by −33 °C they have coalesced into a single broad peak at 185 ppm (calcd, 187.5). Secondly, the signals arising from carbonyls c,c',e, and e' begin to broaden by −50 °C and, as the temperature is raised further, they coalesce with the first set (aa'bdd'f) to give at 2 °C a single resonance at 174 ppm (calcd, 175.6). Finally, above 2 °C a third process averages the remaining doublet due to carbonyl g with the other signals.[19]

The Cotton mechanism (**1** ↔ **2**) suffices to explain the two lowest energy processes observed for $Ir_4(CO)_{11}PPh_2Me$. Process I (see Scheme I) involves formation from **3** of an unbridged intermediate such as **7**, followed by re-formation of the bridging carbonyls in the same plane to give **3'**. Further averaging (process II) requires formation of isomers such as **8** or **8'**, which have the PPh_2Me ligand in a radial position, and therefore are higher in energy than **3** or **3'**. However, trans ligand relationships (e.g., ad' or ce') are preserved through the course of the bridged-unbridged interconversions. Thus, carbonyl g, which is trans to the PPh_2Me ligand, is not equilibrated with the other carbonyls by the Cotton mechanism, in accord with the spectrum at 2 °C. However, complete averaging of all 11 carbonyls, which is well advanced at 31 °C, requires the operation of a different type of mechanism.

Scheme I



Each of the other derivatives show evidence for carbonyl site exchange, but at higher temperatures than required for $Ir_4(CO)_{11}PPh_2Me$. No low energy scrambling process such as **3** ↔ **7** ↔ **3'** is possible for structures **4**, **5**, or **6**, since each has a PPh_2Me ligand in a radial position. However, no mechanistically useful differential line broadening is observed in the intermediate exchange spectra for these derivatives. Furthermore, since each ultimately shows only one signal for all carbonyls, non-Cotton type scrambling mechanisms are indicated.

Acknowledgment. This work was supported by National Science Foundation Grant CHE 75-14460 to J.R.S. and a University of Illinois Fellowship to G.F.S. A loan of iridium trichloride from Engelhard Industries is also acknowledged.

References and Notes

(1) (a) Intracluster Ligand Mobility. 4. (b) Part 3: R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc.*, **98,** 7433 (1976).

(2) For a recent summary see F. H. Carre', F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, **15,** 380 (1976).

(3) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88,** 1821 (1966).

(4) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89,** 4792 (1967).

(5) F. A. Cotton, L, Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Am. Chem. Soc.*, **94,** 6191 (1972).

(6) F. A. Cotton, *Inorg. Chem.*, **5,** 1083 (1966).

(7) J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J. Chem. Soc., Chem. Commun.*, 807 (1973).

(8) B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Chem. Commun.*, 441 (1974).

(9) M. A. Cohen, D. R. Kidd, and T. L. Brown, *J. Am. Chem. Soc.*, **97,** 4408 (1975).

(10) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Am. Chem. Soc.*, **97,** 1245 (1975).

(11) P. E. Cattermole, K. G. Orrell, and A. G. Osborne, *J. Chem. Soc., Dalton Trans.*, 328 (1974).

(12) G. F. Stuntz and J. R. Shapley, *Inorg. Chem.*, **15,** 1994 (1976).

(13) $Ir_4(CO)_{11}PPh_2Me$ and $Ir_4(CO)_{10}(PPh_2Me)_2$ were prepared as previously reported.[12] $Ir_4(CO)_9(PPh_2Me)_3$ and $Ir_4(CO)_8(PPh_2Me)_4$ were prepared by further reaction with stoichiometric amounts of Me_3NO and PPh_2Me in refluxing benzene. The use of Me_3NO to promote substitution of carbonyl ligands in tetranuclear iridium clusters has proven to be a general reaction. These reactions will be reported separately.

(14) V. Albano, P. Bellon, and V. Scatturin, *Chem. Commun.*, 730 (1967).

(15) ^{31}P spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are referenced in parts per million from external 85% H_3PO_4, where a negative sign indicates downfield.

(16) Cf. K. J. Karel and J. R. Norton, *J. Am. Chem. Soc.*, **96,** 6812 (1974).

(17) ^{13}C spectra were obtained using samples enriched with ^{13}CO to a level of 30–50%, as judged by mass spectrometry. Spectra were obtained on a Jeol FX-60 spectrometer operating at 15.03 MHz. Coupling constants were confirmed by recording the spectra on a Varian XL-100 spectrometer operating at 25.15 MHz. $Cr(acac)_3$ (0.03 M) was added as a relaxation agent for the carbonyls.

(18) The ^{13}C NMR spectrum for $Ir_4(CO)_8(AsPh_2Me)_4$ has been reported: 223.7 (1), 220.3 (2), 175.5 (2), 169.1 (1), and 135.6 (2).[11] We feel that the signal at 135.6 ppm is very likely due to the phenyl carbons of the arsenic ligands.

(19) The doublet due to carbonyl g is observed to broaden, shift downfield, and decrease slightly in separation between −88 and 2 °C. We attribute these effects to a small but nonnegligible population of the radial isomer (e.g., **8**), whose relative proportion increases with temperature. (Similar effects have been observed for $H_4Ru_4(CO)_{11}P(OMe)_3$.[20]) We have not established another isomer from the limiting ^{1}H or ^{31}P NMR spectra (detection limits ca. 5%), but temperature-dependent chemical shifts also suggest exchange with an additional species. $Ir_4(CO)_{11}PPh_3$ shows essentially identical ^{13}C spectra over a similar range of temperatures, except that the doublet from carbonyl g shows much less perturbation with temperature up to the point equivalent to the 2 °C spectrum in Figure 1. Furthermore, separate isomers can be distinguished within the set of $PPhMe_2$ derivatives, indicating that the preference for axial substitution decreases in the order $PPh_3 > PPh_2Me > PPhMe_2$. This and other trends will be discussed in a full paper concerned with the complete set of compounds that we have studied.

(20) J. W. Koepke, Ph.D Dissertation, UCLA, 1974.

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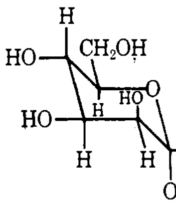
Some Experimental Observations on H···O Hydrogen-Bond Lengths in Carbohydrate Crystal Structures

Sir:

The completion of the neutron diffraction studies of of three crystal structures of carbohydrates with related configuration and conformation has revealed an unusually systematic relationship between the hydrogen-bond lengths and the type of O—H···O interaction. Although hydrogen bonds are the predominant cohesive forces in crystals of polyhydric organic compounds including the carbohydrates, many of which have been studied by x-ray diffraction, simple relationships involving the hydrogen-bond distances are not generally observed. This is because in these *molecular* crystals the hydrogen bonding depends not only upon the stereochemistry of the donor and acceptor groups involved but also upon the way in which the molecules as a whole can pack to form a regular three-dimensional lattice. The structure of a particular hydrogen-bonding scheme is not determined solely by the requirement of maximum hydrogen-bond energy, but rather represents a compromise between this and the optimization of the other intermolecular forces.

The three crystal structures are those of the monosaccharides methyl α-D-mannopyranoside (**1**),[1] methyl α-D-glucopyranoside (**2**),[1] and methyl α-D-altropyranoside (**3**),[2] in which there are representative examples of five different modes of interaction between donor hydroxyl groups and acceptor oxygen atoms.



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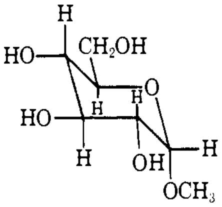

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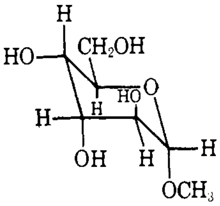

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As shown in Table I, each mode has associated with it two or more hydrogen-bond distances which appear to be characteristic within a relatively narrow range. These values fall into five distinct groups which are separated by about 0.1 Å.[3]

The shortest hydrogen bonds are those in which the hydroxyl oxygen is a hydrogen-bond acceptor, as well as functioning as a hydrogen-bond donor. This type of bonding is the most common in carbohydrate crystal structures and is responsible for the very frequent occurrence of chains of hydrogen bonds. This cooperative strengthening of hydrogen bonding has been predicted from theoretical studies of water polymers,[4] and is further discussed in the following communication.[5] In the absence of the acceptor function of the hydroxyl oxygens, the bonding is weaker, as shown by the two examples with significantly longer bond lengths. Hydrogen bonds from hydroxyls to the ring or glycosidic oxygens also occur in many carbohydrate structures but they are noticeably less common than those between two hydroxyls.[6] This is consistent with weaker bonding and the observed increase in the H···O bond distances. Bifurcated hydrogen bonds are even rarer, though the structure of methyl α-D-altropyranoside did provide two examples in which the H···O separations are less than the normal accepted sum of the van der Waals radii, 2.4 Å. Finally, there is an example of a nonbonding environment; however, the fact that the nearest neighbor atoms to the hydrogen are oxygens indicates that there may still be some specific H···O interactions not necessarily directional enough to be described as bonds.

With some exceptions, a similar distribution of hydrogen-bond lengths is found in the crystal structures of α-D-glucose[7] and sucrose,[8] for which the neutron diffraction data are also given in Table I. In the α-D-glucose structure the four donor-acceptor hydrogen-bond lengths have a longer mean value than in the methyl pyranosides by about 0.02 Å, but span a similar range of distances. The hydroxyl-to-ring oxygen hydrogen