

200. Intramolecular Dynamics of Tetranuclear Carbonyliridium Cluster Compounds

Part II¹⁾

Disubstituted Complexes with One Chelating Ligand. Crystal Structure of $[\text{Ir}_4(\text{CO})_7(\mu\text{-CO})_3(1,5\text{-cyclooctadiene})]$

by **Andrés Strawczynski**²⁾, **Renzo Ros**³⁾*, and **Raymond Roulet***

Institut de Chimie Minérale et Analytique de l'Université de Lausanne, 3, place du Château, CH-1005 Lausanne

and **Fabrizia Grepioni** and **Dario Braga***

Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, I-40126 Bologna

(16.IX.88)

The two complexes $[\text{Ir}_4(\text{CO})_{10}(\text{diarsine})]$ (**1**) and $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cyclooctadiene})]$ (**2**) bear a bidentate ligand chelating one metal atom of the basal face of the Ir_4 tetrahedron. However, they differ in fluxional behaviour as observed by 2D-exchange and variable-temperature $^{13}\text{C-NMR}$. The CO-site exchange with lowest activation energy proceeds *via* an unbridged intermediate in **2**, whereas that in **1** occurs *via* a concerted edge-bridging of CO's to an alternative face of the metal core. This difference is apparently related to different ground-state geometries: the basal CO's are symmetrically bridging in **2**, whereas two CO's are semi-bridging in **1**. The molecular structure of **2** was determined by single crystal X-ray diffractometry. The crystals are orthorhombic, space group *Pbca*, $a = 11.651(4)$, $b = 13.118(3)$, $c = 28.64(1)$ Å. The idealized molecular symmetry is C_2 . The diolefin chelates a basal Ir-atom replacing an axial and a radial CO group on the tetrahedral metal-atom framework.

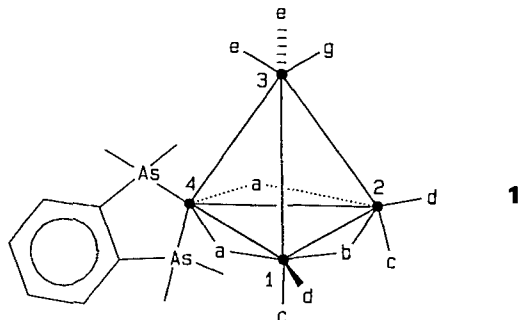
Introduction. – The substituted derivatives of $[\text{Ir}_4(\text{CO})_{12}]$ generally have CO ligands that either bridge two Ir-atoms or are terminal. The bridging CO's define the basal plane containing three Ir-atoms of the metal core. Terminal CO's are either apical if located on the fourth Ir-atom, radial when located more or less in the basal plane, or axial if approximately perpendicular to the basal plane. CO site exchange is a common feature of these cluster compounds.

The fluxional behaviour of five monosubstituted $[\text{Ir}_4(\text{CO})_{11}\text{L}]$ complexes has been examined to date (L = PEt_3 [1] [2], PMePh_2 [3], Br^- [4], $\mu\text{-SO}_2$ [5], and *t*-BuNC [6]). The PEt_3 and Br^- complexes have the same ground-state geometry with one axial L ligand, and behave similarly (the mechanism of CO exchange proposed in the first study on the PEt_3 complex has recently been reassessed [2], and is identical with that found for the Br^- complex). The latter two complexes have different ground-state geometries and present different fluxional processes.

¹⁾ Part I: [4].

²⁾ In part from the doctoral dissertation of A. S., University of Lausanne, 1988.

³⁾ Permanent address: Istituto di Chimica Industriale dell'Università, Via Marzolo 9, I-35131 Padova.



The disubstituted derivatives of $[\text{Ir}_4(\text{CO})_{12}]$ may have two monodentate L ligands, or a bidentate L-L ligand which either bridges two Ir-atoms, or chelates one metal atom. The present report deals with the fluxional behaviour of two cluster compounds of the latter, uncommon category.

NMR Study of $[\text{Ir}_4(\text{CO})_{10}(\text{diarsine})]$. – The complex $[\text{Ir}_4(\text{CO})_{10}(\text{diarsine})]$ (**1**) was first prepared by *Shapley et al.* [7], and its crystal structure was determined by *Churchill and Hutchinson* [8].

The ground state symmetry is C_s . The mirror plane contains the $\text{As}_2\text{C}_6\text{H}_4$ moiety along with atoms Ir(3) and Ir(4). The diarsine chelates to Ir(4). The molecule contains one symmetrically bridging CO across Ir(1)–Ir(2), and two symmetry-related semibridging CO groups (metal–CO distances in the latter are 2.012(25) and 2.257(22) Å [8]). The fluxional behaviour of **1** has been examined by *Shapley et al.* [7]. However, no kinetic parameters were reported, nor was any simulation of spectra undertaken to back up a proposed mechanism of site exchange involving a triply bridging CO. Their proposed mechanism is unprecedented and would require intermediates which do not follow the 18-electrons rule. Therefore, we have reexamined the fluxional behaviour of **1**, and for comparison we have completed a study of the fluxional behaviour of $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cyclooctadiene})]$.

In the ^{13}C -NMR spectrum of a ^{13}C -enriched sample of **1** in $\text{CD}_2\text{Cl}_2/\text{CHFCl}_2$ 4:1, all exchange processes are stopped at *ca.* 163 K. At this temperature, six CO resonances are observed at δ (relative to TMS) 213.9 (*a*), 200.1 (*b*), 173.1 (*d*), 159.4, 158.0 (*c* and *e*), and 154.0 (*g*) ppm with relative intensities 2:1:2:2:2:1. The assignment of the signals follows that of *Shapley et al.* [7], and the general observation that, in the ^{13}C - and ^{31}P -NMR spectra of Ir_4 cluster compounds, the δ 's of the ligands decrease in the positional sequence bridging > radial > axial \approx apical [9]. The four CO's *c* and *e* are undistinguishable, but this is of no importance for the following discussion.

The most obvious features observed in the variable-temperature ^{13}C -NMR spectra (*Fig. 1*) are that basal-apical CO exchange takes place, and that CO *a* is not involved in the site-exchange process. The first observation requires an edge-bridging of CO's on an alternative face of the tetrahedron containing the apical Ir-atom. The second observation requires the alternative face to be Ir(2)–Ir(3)–Ir(4), and the alternative edge-bridging of CO's to be 'synchronous', *e.g.* the process should not pass through an unbridged intermediate, since CO *a* is not involved.

The rate constant *k* of CO exchange was evaluated from line-shape analysis [10] of the variable-temperature ^{13}C -NMR spectra using the following *Kubo-Sack* matrix elements

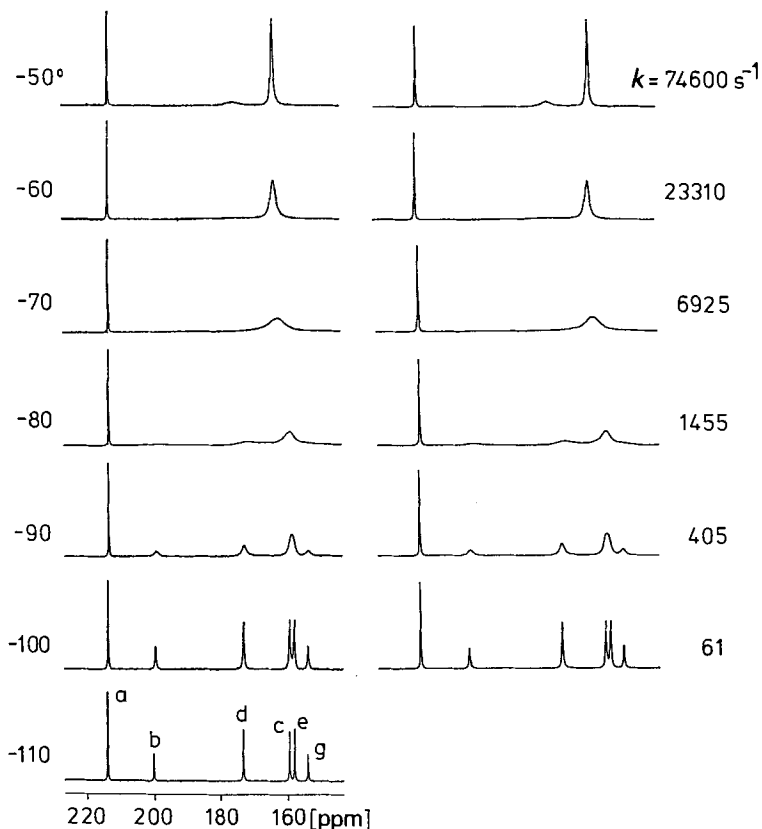
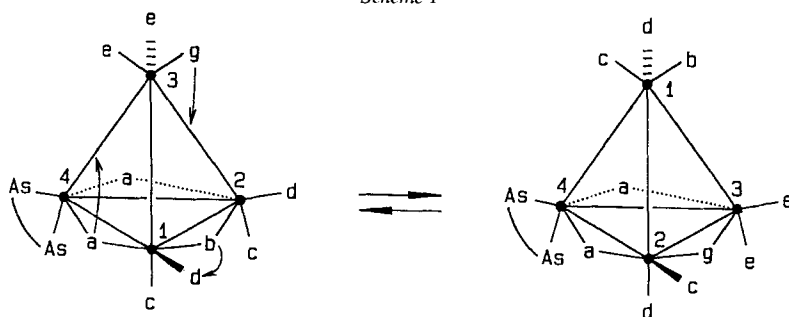


Fig. 1. Variable-temperature ^{13}C -NMR spectra of $[\text{Ir}_4(\text{CO})_{10}(\text{diarsine})]$ in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ 4:1

[11]: $(b, g) = (g, b) = k$; $(c, d) = (c, e) = (d, c) = (d, e) = (e, d) = (e, c) = k/2$; $(b, b) = (c, c) = (d, d) = (e, e) = (g, g) = -k$. The CO-exchange process has a ΔG_{298}^\ddagger of 29.8 ± 0.5 $\text{kJ} \cdot \text{mol}^{-1}$. This process requires the equilibration of the two As-atoms occupying a radial and an axial position of Ir(1). This is clearly observed in the ^1H -NMR spectrum of **1** at 160 K: two *singlets* at 2.02 and 1.52 ppm correspond to the two pairs of Me groups and coalesce upon raising the temperature. Line-shape analysis of this two site exchange gave, within experimental error, the same ΔG_{298}^\ddagger as that observed for the CO site exchange ($k_{193} = 1200 \text{ s}^{-1}$ is in agreement with the value reported in Fig. 1).

Among the fluxional processes already observed in Ir_4 cluster compounds [1–7], the ‘merry-go-round’ of basal CO’s can be excluded for **1**, since *a-d* site exchange is not observed. The absence of the ‘merry-go-round’ can be ascribed to the presence of an As-atom occupying a radial site. Likewise, for the process with lowest activation energy, the rotation for the three apical CO’s cannot be an alternative explanation, since it does not bring about apical-basal exchange. Therefore, the simplest mechanism satisfying the observations and consistent with the 18-electrons rule is a synchronous edge-bridging of CO’s to one alternative face of the tetrahedral metal core, not passing through unbridged intermediates, as illustrated in Scheme 1.

Scheme 1



NMR Study of $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cyclooctadiene})]$. – The complex $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cod})]$ (1,5-cod = 1,5-cyclooctadiene; **2**) was chosen as a second example of Ir_4 cluster with a chelating ligand also of C_s symmetry, but with three symmetrically bridging CO's (see below). It was first prepared from $[\text{Ir}_4(\text{CO})_{12}]$ and excess 1,5-cod [12], but may be obtained with better yields from $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ and 1,5-cod in the presence of AgBF_4 [13]. The ^{13}C -NMR spectrum of a ^{13}C -enriched sample of **2** in CD_2Cl_2 presents at 210 K six CO resonances at δ 208.6 (*a*), 196.4 (*b*), 171.2 (*d*), 157.9, 152.3 (*c* and *e*), and 151.8 (*g*) ppm with relative intensities 2:1:2:2:2:1. The assignment ambiguity concerning CO's *c* and *e* was resolved by the 2D-exchange ^{13}C -NMR at 210 K (Fig. 2). The cross peak (*a, c*) are more intense than the cross peaks (*a, e*), the latter being due to the two-step exchange $a \rightarrow c \rightarrow e$ (since the cross and diagonal peaks have the same sign, the former are indeed due to exchange and not to NOE). Therefore, the signals at 159.9 and 152.3 ppm can be assigned to *e* and *c*, respectively. The 2D-exchange and the variable-temperature ^{13}C -NMR spectra of **2** (Fig. 3) show a major difference when compared with those of **1**: CO *a* takes part in the fluxional process. Since apical-basal exchange is observed, and edge-bridging of CO's on an alternative face of the tetrahedron containing the apical Ir-atom must take place, but must be different from that of **1**. The 2D-exchange results for **2** are, in fact, in agreement with a mechanism first proposed by Shapley *et al.* for $[\text{Ir}_4(\text{CO})_{11}(\text{PMePh}_2)]$ [3]. A change of basal face must occur *via* the unbridged intermediate **II** (Scheme 2) to bring about the dynamic connectivities observed in the 2D-exchange spectrum: $a \rightarrow (a, c)$, $b \rightarrow g$, $c \rightarrow (a, e)$, $d \rightarrow (d, e)$, $e \rightarrow (c, d)$, and $g \rightarrow b$. The rate constant *k* of CO exchange was evaluated from line-shape analysis of the variable-temperature ^{13}C -NMR spectra using the following Kubo-Sack matrix elements: $(a, a) = (d, d) = -k/2$; $(b, b) = (c, c) = (e, e) = (g, g) = -k$; $(a, c) = (d, e) = (e, d) = (e, c) = (c, a) = (c, e) = k/2$; $(b, g) = (g, b) = k$. The CO-exchange process has a ΔG_{298}^\ddagger of $43.8 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$. The proposed mechanism requires the equilibration of the two C=C bonds of the coordinated diene. This is clearly seen in the ^1H -NMR spectrum of **2** in CD_2Cl_2 . At 190 K, three pairs of multiplets are observed at 4.55, 3.29, 3.00, 2.49, 2.15, and 2.00 ppm corresponding to the axially and radially located olefinic protons, and to the outer and inner CH_2 protons, respectively. On warming to 260 K, each pair coalesce to give three distinct signals at 3.98, 2.78, and 2.00 ppm, without interconversion between inner and outer CH_2 protons.

In conclusion, the disubstituted complexes **1** and **2** are fluxional on the NMR time scale. Both have C_s symmetry and a fluxional process involving edge-bridging of CO's on an alternative face of the tetrahedral metal core. However, the precise mechanism of

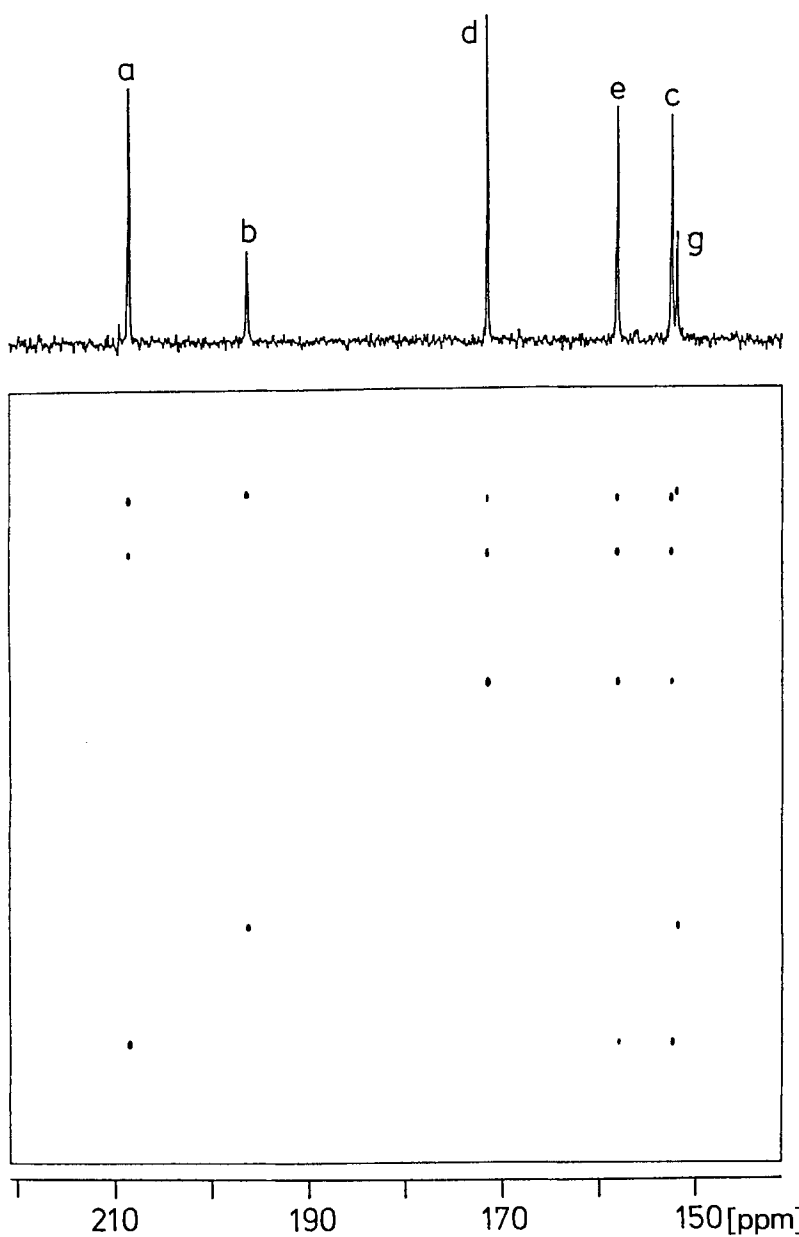


Fig. 2. 2D-exchange ^{13}C -NMR spectrum of $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cyclooctadiene})]$ in CD_2Cl_2 at 210 K (mixing time: 100 ms)

lowest activation energy for the CO site exchange is different: for **1**, the site exchange is synchronous and does not involve an unbridged intermediate; for **2**, the site exchange involves an unbridged intermediate. This difference may be related to a difference in the ground-state geometries of **1** and **2**: for **1**, two of the CO's are asymmetrically bridging;

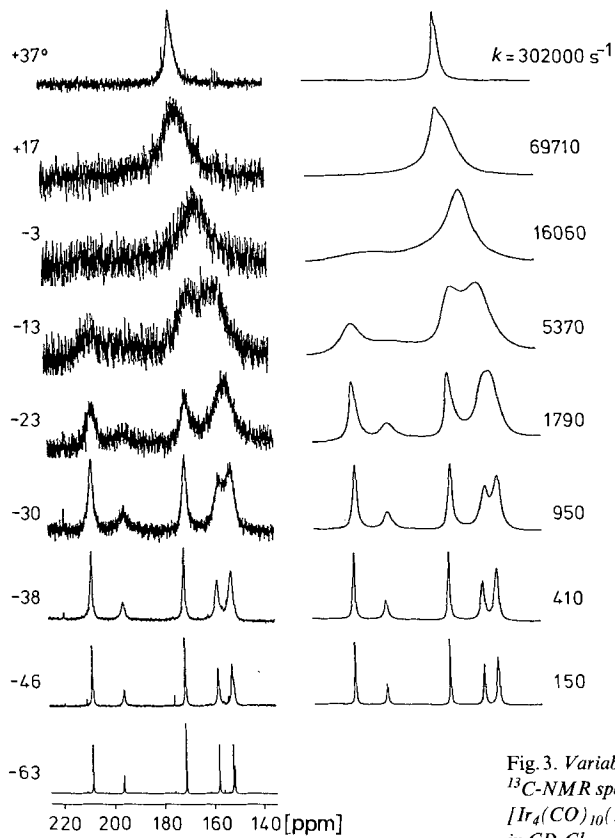
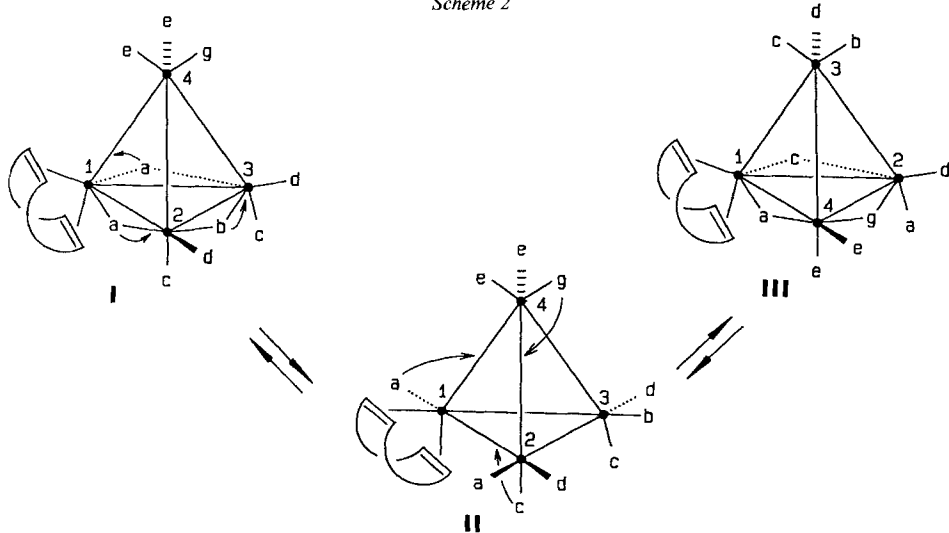


Fig. 3. Variable-temperature ^{13}C -NMR spectra of $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cyclooctadiene})]$ in CD_2Cl_2

Scheme 2



for **2**, all three CO bridges are symmetric. A possible general relationship between the ground-state structure and the fluxional mechanism may, therefore, be proposed. Further support is provided by our earlier report that the CO site exchange in $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$, which, like **1**, has two asymmetrically bridging CO's, is synchronous [4]. If one considers only intermediates that obey the 18-electrons rule, the absence of an unbridged intermediate, when the ground-state structure contains two asymmetrically bridging CO's, may be explained by the fact that its formation would require the rupture of one of the two short $\mu(\text{CO})\text{-Ir}$ bonds.

Crystal Structure of 2. – The molecular structure of **2** together with the atomic labelling is shown in *Fig. 4*. Relevant bond distances and angles are listed in *Table 1*. The four Ir-atoms define an almost regular tetrahedron. The overall ligand distribution is common to the majority of substituted Ir_4 -species with three edge-bridging CO's defining a basal plane of the metal polyhedron. The diolefin occupies the radial and axial sites on Ir(1) (see *Fig. 4*). The idealized molecular symmetry is C_s with the mirror plane bisecting

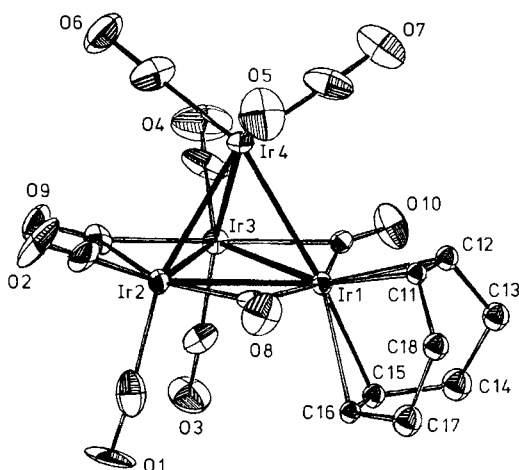


Fig. 4. Molecular structure of $[\text{Ir}_4(\text{CO})_{10}(1,5\text{-cyclooctadiene})]$

the 1,5-cod ligand, the middle of the opposite Ir–Ir bond, and including the remaining two Ir-atoms. Metal–metal bond distances range from 2.688(1) to 2.766(1) Å, average 2.726(1) Å. This average value is strictly comparable with those reported for most disubstituted Ir_4 derivatives such as **1** (2.723(2) Å) and for the species $[\text{Ir}_4(\text{CO})_9\text{L}(\text{norbornadiene})]$ (mean Ir–Ir 2.722(1) for L = PMe_2Ph ; and 2.735(1) Å for L = PPh_3 [14]).

The metal core of **2** is substantially larger than that present in $[\text{Ir}_4(\text{CO})_{12}]$ (mean Ir–Ir 2.68 Å [15]) and in all its derivatives which have the ' T_d -like' arrangement of CO-ligands [16]. Moreover, the CO-bridged Ir–Ir bonds of **2** are slightly longer (mean 2.737(1) Å) than the unbridged ones (mean 2.715(1) Å). This is in agreement with the general trend shown by most CO-bridged, ' C_{3v} -like' Ir_4 -species [16], although it contradicts the shortening effect usually attributed to μ_2 -CO-coordination on metal–metal bond lengths. A

Table 1. *Relevant Bond Distances [Å] and Angles [°] for 2 (standard deviations in parentheses)*

Ir(1)–Ir(2)	2.766(1)	Ir(1)–C(15)	2.26(2)
Ir(1)–Ir(3)	2.758(1)	Ir(1)–C(16)	2.24(2)
Ir(1)–Ir(4)	2.720(1)	C(1)–O(1)	1.12(2)
Ir(2)–Ir(3)	2.688(1)	C(2)–O(2)	1.15(2)
Ir(2)–Ir(4)	2.711(1)	C(3)–O(3)	1.10(2)
Ir(3)–Ir(4)	2.714(1)	C(4)–O(4)	1.09(2)
Ir(2)–C(1)	1.92(2)	C(5)–O(5)	1.10(2)
Ir(2)–C(2)	1.91(2)	C(6)–O(6)	1.12(2)
Ir(3)–C(3)	1.90(2)	C(7)–O(7)	1.14(2)
Ir(3)–C(4)	1.89(2)	C(8)–O(8)	1.17(2)
Ir(4)–C(5)	1.94(2)	C(9)–O(9)	1.15(2)
Ir(4)–C(6)	1.92(2)	C(10)–O(10)	1.13(2)
Ir(4)–C(7)	1.91(2)	C(11)–C(12)	1.43(3)
Ir(1)–C(8)	2.08(2)	C(12)–C(13)	1.47(3)
Ir(2)–C(8)	2.11(1)	C(13)–C(14)	1.53(3)
Ir(2)–C(9)	2.10(2)	C(14)–C(15)	1.50(3)
Ir(3)–C(9)	2.14(2)	C(15)–C(16)	1.43(2)
Ir(3)–C(10)	2.10(2)	C(16)–C(17)	1.49(3)
Ir(1)–C(10)	2.12(2)	C(17)–C(18)	1.48(3)
Ir(1)–C(11)	2.17(2)	C(11)–C(18)	1.48(3)
Ir(1)–C(12)	2.20(2)	Ir(2)–C(1)–O(1)	176(2)
Ir(2)–C(2)–O(2)	178(2)	Ir(1)–C(10)–O(10)	140(1)
Ir(3)–C(3)–O(3)	177(2)	Ir(3)–C(10)–O(10)	139(1)
Ir(3)–C(4)–O(4)	175(2)	C(11)–C(12)–C(13)	122(2)
Ir(4)–C(5)–O(5)	176(2)	C(12)–C(13)–C(14)	118(2)
Ir(4)–C(6)–O(6)	179(2)	C(13)–C(14)–C(15)	113(2)
Ir(4)–C(7)–O(7)	177(2)	C(14)–C(15)–C(16)	124(2)
Ir(1)–C(8)–O(8)	142(1)	C(15)–C(16)–C(17)	123(2)
Ir(2)–C(8)–O(8)	136(1)	C(16)–C(17)–C(18)	118(2)
Ir(2)–C(9)–O(9)	142(2)	C(17)–C(18)–C(11)	112(2)
Ir(3)–C(9)–O(9)	139(1)	C(18)–C(11)–C(12)	123(2)

further feature of the tetrahedral metal core is that while the Ir–Ir bond opposite to the Ir-atom which bears the diolefin is the shortest (2.688(1) Å), the other two basal Ir–Ir bonds are the longest (2.766(1), 2.758(1) Å).

The M–M bond distribution in the basal plane, however, appears to have no detectable effect on the geometry of the bridging CO's. These latter ligands are almost symmetric with no relevant differences in Ir–C bond length and Ir–C–O angles (*Table 1*). The Ir–Ir basal bonds, on the other hand, show a pattern similar to that observed for **2** with one 'short', symmetrically bridged bond (2.694(2) Å) opposite to the substituted Ir-atom, and two longer bonds (2.733(1) Å) spanned by the asymmetric CO ligands [8]. This Ir–Ir bond length distribution, while certainly determined by the presence of the substituent ligands, appears to be independent of the CO ligand geometry. Therefore, steric factors may be responsible for the differences in the bridging CO's distribution between **1** and **2**. The mean Ir–C and C–O bond distances are 1.91(2) and 1.12(2) Å, respectively. The chelating 1,5-cod ligand adopts a boat conformation and Ir–C(C₈H₁₂) distances fall in two distinct sets. The radial interactions (mean 2.19(2) Å) are slightly shorter than the axial ones (mean 2.25(2) Å). This probably arises from steric repulsions by the two axial CO groups. On the other hand, the C=C bond lengths are identical (1.43(2) Å) and agree

Table 2. *Crystal Data of 2*

Formula	C ₁₈ H ₁₂ O ₁₀ Ir ₄
Molecular weight	1157.2
Dimensions [mm]	0.2 × 0.1 × 0.15
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> [Å]	11.651(4)
<i>b</i> [Å]	13.118(3)
<i>c</i> [Å]	28.64(1)
<i>V</i> [Å ³]	4377
<i>Z</i>	8
<i>D</i> _{calc.} [g·cm ⁻³]	3.5
<i>μ</i> (cm ⁻¹)	234.2
Radiation	MoKα (λ = 0.71069)
<i>F</i> (000)	4062
Scan type	ω/2θ
Scan width [°]	0.80
Prescan speed [°min ⁻¹]	5
2θ limits [°]	2.5–25
Data collected	2818
Max. time for D.C. [sec]	120
Prescan acceptance σ(<i>I</i>)/ <i>I</i>	0.5
Requested σ(<i>I</i>)/ <i>I</i>	0.02
Minimum transmission factor for absorption correction	56%
Data in refinement (<i>F</i> ₀ > 4σ(<i>F</i> ₀))	2801
No. of variables	244
Solution method	direct methods
refinement method	least squares
<i>R</i>	0.039
$R_w = \Sigma(F_0 - F_c)w_{1/2} / \Sigma(F_0w_{1/2})$	0.042
$w = k/(\sigma^2(F) + g F^2)$	<i>k</i> = 1.0, <i>g</i> = 0.003

with the values expected for η² interactions with metal centres. The remaining C–C distances conform to the pattern shown by unsaturated cycles, e.g. in [Ir₄(CO)₅(C₈H₁₂)(C₈H₁₀)] [12] and the norbornadiene derivatives mentioned above [14].

We thank the *Swiss National Science Foundation* and the *Ministero della Pubblica Istruzione Italiana* for generous financial support, and Prof. *G. Bodenhausen* for stimulating discussions.

Experimental. – The complexes were prepared according to the literature methods [7] [13], starting with NEt₄[Ir₄(CO)₁₁Br] [14] enriched to ca. 30% ¹³C [4]. The ¹³C-NMR spectra were recorded on a *Bruker WH-360* (90.55 MHz) under atmospheric pressure. The 2D-exchange ¹³C-NMR spectra were obtained in CD₂Cl₂ at 210 K from NOESY experiments using TPPI. 256 *t*₁ increments with 2-K transients were acquired. The spectral width was 7246.4 Hz in the *F*₂ domain and 3623.2 Hz in the *F*₁ domain. The spectra were zero filled to 2K × 2K and a shifted squared sinus bell was applied in both domains prior to *Fourier* transformation.

Crystal Structure Determination. Crystal data and details of measurements are reported in *Table 2*. Diffraction intensities were collected at r.t. on an ENRAF-NONIUS *CAD4* diffractometer. Absorption correction was applied by azimuthal scanning of 12 reflections (χ > 80°). The structure was solved by direct methods and refined by full-matrix least-squares. For all calculations, the SHELX76 program was used [17]. The space group choice was based on systematic absences and confirmed by successful refinement. H-atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C-atoms. All atoms except the H-atoms were allowed to

vibrate anisotropically. A single isotropic thermal parameter was refined for the H-atoms (0.07 \AA^2). Residual peaks of about $1.5 \text{ e}^-/\text{\AA}^3$ were found in the final difference map in the proximity of the Ir-atoms. Fractional atomic coordinates, anisotropic thermal parameters, and a listing of interatomic distances and angles are available upon request.

REFERENCES

- [1] B. E. Mann, C. M. Spencer, A. K. Smith, *J. Organomet. Chem.* **1983**, *244*, C17.
- [2] B. E. Mann, B. T. Pickup, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1988**, in press.
- [3] G. F. Stuntz, J. R. Shapley, *J. Am. Chem. Soc.* **1977**, *99*, 607; A. Strawczynski, Doctoral dissertation, University of Lausanne, 1988.
- [4] A. Strawczynski, R. Ros, R. Roulet, *Helv. Chim. Acta* **1988**, *71*, 867.
- [5] D. Braga, R. Ros, R. Roulet, *J. Organomet. Chem.* **1985**, *286*, C8.
- [6] G. F. Stuntz, J. R. Shapley, *J. Organomet. Chem.* **1981**, *213*, 389.
- [7] J. R. Shapley, G. F. Stuntz, M. R. Churchill, J. P. Hutchinson, *J. Am. Chem. Soc.* **1979**, *101*, 7425.
- [8] M. R. Churchill, J. P. Hutchinson, *Inorg. Chem.* **1980**, *19*, 2765.
- [9] R. Ros, A. Scrivanti, V. G. Albano, D. Braga, L. Garlaschelli, *J. Chem. Soc., Dalton Trans.* **1986**, 2411.
- [10] EXCHANGE, program library, Computing Center, University of Lausanne.
- [11] C. S. Johnson, Jr., C. G. Moreland, *J. Chem. Educ.* **1973**, *50*, 477.
- [12] G. F. Stuntz, J. R. Shapley, C. G. Pierpont, *Inorg. Chem.* **1978**, *17*, 2596.
- [13] R. Ros, A. Scrivanti, R. Roulet, *J. Organomet. Chem.* **1986**, *303*, 273.
- [14] D. Braga, F. Grepioni, G. Guadalupi, A. Scrivanti, R. Ros, R. Roulet, *Organometallics* **1987**, *6*, 56.
- [15] M. R. Churchill, J. P. Hutchinson, *Inorg. Chem.* **1978**, *17*, 5328.
- [16] D. Braga, F. Grepioni, *J. Organomet. Chem.* **1987**, *336*, C9.
- [17] G. M. Sheldrick, SHELX76 System of Computer Programs, University of Cambridge, 1976.