

rhombic than that calculated. This discrepancy cannot be attributed to the anisotropy in g , which is allowed for in the above expression. Moreover, alternative spin distributions in which unpaired spin was spread over the carbonyl ligands led to smaller, rather than larger, values of E . We conclude that there must be a substantial spin-orbit contribution to the fine-structure tensor D . A similar situation arose for radical pairs of $\text{Fe}(\text{CO})_4^-$ detected³¹ in single crystals of $[\text{PPN}][\text{HFe}(\text{CO})_4]$, where the tensors were markedly nonaxial and experimental D values were in considerable excess of the purely dipolar contribution. Unfortunately, it is not possible to estimate the importance of spin-orbit contributions to D without knowledge of the singlet-triplet energy gap in the excited states which connect to the ground singlet and triplet states via spin-orbit coupling.³¹

Conclusions

Analysis of the g tensors for the free-radical products of γ -irradiation of $[\text{PPN}][\text{HSM}_2(\text{CO})_{10}]$ ($M = \text{Cr}, \text{W}$) leads

to assignments to the radical anions arising from hydrogen atom loss. The molecular orbital occupied by the single unpaired electron in these species resembles that in SO_2^- : it has an important component from the S $3p_x$ orbital that is directed perpendicular to the plane containing the sulfur and metal atoms and smaller components from metal 3d orbitals. Weak satellite spectra present in the radiation-damaged Cr-containing compound are due to pairs of radicals ($S = 1$) located in certain nearest-neighbor sites.

Acknowledgment. We are indebted to R. Dutrisac of these laboratories for technical assistance.

Registry No. $[\text{PPN}][\text{HSCr}_2(\text{CO})_{10}]$, 77310-17-9; $[\text{PPN}][\text{HSW}_2(\text{CO})_{10}]$, 112680-81-6; $[\text{Cr}(\text{CO})_5]_2\text{S}^-$, 130011-53-9; $[\text{W}(\text{CO})_5]_2\text{S}^-$, 130011-54-0.

Supplementary Material Available: Full tables of bond distances and angles, anisotropic thermal parameters, and positional parameters of hydrogen atoms for $[\text{PPN}][\text{HSCr}_2(\text{CO})_{10}]$ (4 pages); a table of structure factors (30 pages). Ordering information is given on any current masthead page.

Synthesis and Crystal Structure of $[\text{PPh}_4]_2[\text{Ir}_4(\text{CO})_{10}(\text{CH}_2\text{COOMe})_2]$ and $[\text{PPh}_4][\text{Ir}_4(\text{CO})_{11}(\text{CH}_2\text{COOMe})]$. First Examples of Iridium Clusters Bearing an Alkyl-like Ligand

Fabio Ragaini and Francesca Porta*

Dipartimento di Chimica Inorganica e Metallorganica and CNR Center, v. Venezian 21, 20133 Milano, Italy

Francesco Demartin*

Istituto di Chimica Strutturistica Inorganica and CNR Center, v. Venezian 21, 20133 Milano, Italy

Received February 9, 1990

The reaction of $\text{Na}[\text{Ir}(\text{CO})_4]$ ($[\text{Na}]1$) with given amounts of $\text{BrCH}_2\text{COOMe}$ in THF, followed by treatment with PPh_4Cl , gave high yields of the two novel clusters $[\text{PPh}_4]_2[\text{Ir}_4(\text{CO})_{10}(\text{CH}_2\text{COOMe})_2]$ ($[\text{PPh}_4]_22$) and $[\text{PPh}_4][\text{Ir}_4(\text{CO})_{11}(\text{CH}_2\text{COOMe})]$ ($[\text{PPh}_4]3$). The reaction takes place in two steps; the first compound formed is 2, which then reacts, in a slower reaction, with excess $\text{BrCH}_2\text{COOMe}$ to afford 3. To the best of our knowledge, 2 and 3 are among the first examples of clusters bearing an alkyl or alkyl-like substituent. X-ray diffraction analysis of the clusters was carried out on crystals obtained by using PPh_4^+ as a counteranion. Compound $[\text{PPh}_4]_22$ is triclinic, space group $P\bar{1}$, with $a = 11.163$ (2) Å, $b = 12.807$ (2) Å, $c = 22.849$ (3) Å, $\alpha = 84.76$ (1)°, $\beta = 88.76$ (1)°, $\gamma = 73.53$ (1)°, $Z = 2$, $R = 0.034$, and $R_w = 0.042$ for 6373 independent reflections with $I > 3\sigma(I)$. Compound $[\text{PPh}_4]3$ is monoclinic, space group $P2_1/c$, with $a = 13.155$ (4) Å, $b = 24.593$ (5) Å, $c = 38.401$ (8) Å, $\beta = 91.00$ (3)°, $Z = 12$, $R = 0.065$, and $R_w = 0.069$ for 5227 independent reflections with $I > 3\sigma(I)$. Both anions contain a tetrahedron of iridium atoms with three bridging CO ligands around a triangular basal face of the metal tetrahedron, the alkyl-like substituents being axially bonded to the iridium atoms of this face. The reactivity of the sodium salt of $[\text{Ir}(\text{CO})_4]^-$ with $\text{BrCH}_2\text{COOMe}$ was quite different from that, already reported by us, of the same anion with PPN^+ ($\text{PPN}^+ = (\text{PPh}_3)_2\text{N}^+$) as a counteranion. This latter reaction forms only mononuclear species. The possible role of Na^+ in the formation of the clusters is discussed.

Introduction

It has often been claimed that cluster compounds are possible models for heterogeneous catalysis and have even been proposed as homogeneous catalysts themselves.¹ Metal-alkyl species are often supposed to form at the active metal sites in many heterogeneously catalyzed reactions, but, to the best of our knowledge, only a few osmium or rhenium clusters bearing alkyl or alkyl-like lig-

ands have been reported,² although many clusters with μ -carbene or carbyne groups are known.

(2) (a) Zoet, R.; van Koten, G.; Vrieze, K.; Jansen, J.; Goubits, K.; Stam, C. H. *Organometallics* 1988, 7, 1565. (b) Bassner, S. L.; Morrison, E. D.; Geoffroy, G.; Rheingold, A. *Organometallics* 1987, 6, 2207. (c) Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1986, 108, 4669. (d) Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. *Organometallics* 1986, 5, 408. (e) Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* 1986, 108, 1316. (f) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* 1978, 17, 1291. (g) Masters, A. F.; Mertis, K.; Gibson, J. F.; Wilkinson, G. *Nouv. J. Chim.* 1977, 1, 389. (h) Edwards, P. G.; Felix, F.; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1979, 361. (i) Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* 1978, 1334. (j) A $\sigma + \pi$ alkenyliridium cluster has also been reported: Pierpont, C. G. *Inorg. Chem.* 1979, 18, 2972.

(1) Gates, B. C.; Guzzi, L.; Knozinger, H., Eds.; *Metal Clusters in Catalysis; Studies in Surface Science and Catalysis* 29; Elsevier: Amsterdam, 1986.

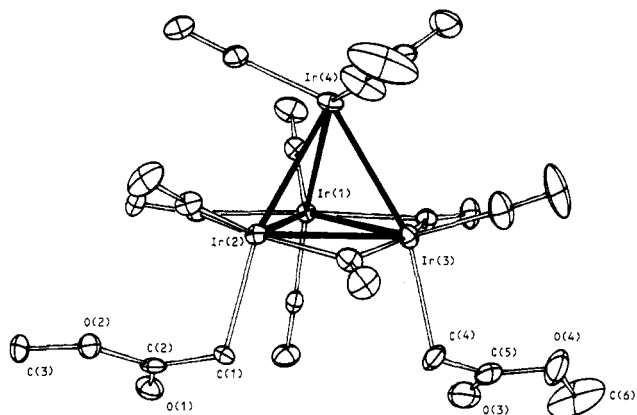


Figure 1. ORTEP drawing of the $[\text{Ir}_4(\text{CO})_{10}(\text{CH}_2\text{COOMe})_2]^{2-}$ anion. Thermal ellipsoids are drawn at 30% probability.

In this paper we report the syntheses and crystal structures of two clusters, $[\text{PPh}_4]_2[\text{Ir}_4(\text{CO})_{10}(\text{CH}_2\text{COOMe})_2]$ ($[\text{PPh}_4]_2\mathbf{2}$) and $[\text{PPh}_4][\text{Ir}_4(\text{CO})_{11}(\text{CH}_2\text{COOMe})]$ ($[\text{PPh}_4]\mathbf{3}$), bearing respectively two and one $-\text{CH}_2\text{COOMe}$ group with direct metal-carbon σ bonds.

Results and Discussion

When a THF solution of $\text{Na}[\text{Ir}(\text{CO})_4]$ ($[\text{Na}]\mathbf{1}$), prepared as in ref 3, was repeatedly treated under a dinitrogen atmosphere with small amounts of $\text{BrCH}_2\text{COOMe}$ until complete disappearance of the IR band at 1896 cm^{-1} (due to the starting compound), an orange solution containing a cluster as the only detectable product (by IR spectroscopy) was obtained. The cluster had main absorption bands in the IR spectrum (in THF) at 2027 (m) , 1996 (vs) , and $1960\text{ (vs)}\text{ cm}^{-1}$. No intermediate compound was observed by IR spectroscopy during the reaction, which also gave a white precipitate (NaBr). The cluster, isolated in a pure form as the PPh_4^+ or PPN^+ salts (see Experimental Section), is, in the solid state, indefinitely stable under a dinitrogen atmosphere. The IR spectrum of the isolated material shows an absorption pattern (ν_{CO} in THF for the PPN^+ salt: 2027 (mw) , 1983 (vs) , 1947 (vs) , 1922 (w) , 1835 (vw) , 1800 (w) , $1764\text{ (m)}\text{ cm}^{-1}$) similar to that of $[\text{Ir}_4(\text{CO})_{10}\text{H}_2]^{2-}$ with the addition of a band at 1687 cm^{-1} attributable to the COOMe groups.⁵

Crystals suitable for X-ray diffraction analysis were obtained by slowly diffusing a PPh_4Cl -saturated 2-propanol solution into an acetone solution of $[\text{PPh}_4]_2\mathbf{2}$.⁶ The X-ray structure determination showed $\mathbf{2}$ to be $[\text{Ir}_4(\text{CO})_{10}(\text{CH}_2\text{COOMe})_2]^{2-}$ with the two $-\text{CH}_2\text{COOMe}$ groups σ -bonded to two different iridium atoms (see Figure 1).

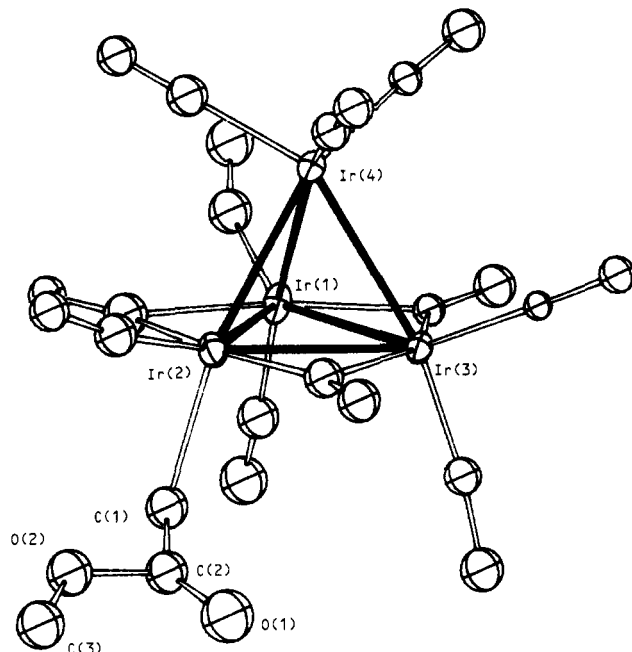
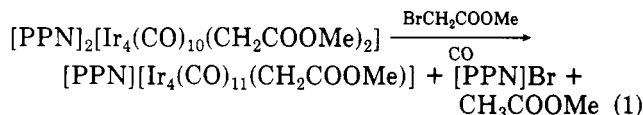


Figure 2. ORTEP drawing of the $[\text{Ir}_4(\text{CO})_{11}(\text{CH}_2\text{COOMe})]^-$ anion. Thermal ellipsoids are drawn at 30% probability.

When a solution of isolated $[\text{PPN}]_2\mathbf{2}$ in THF is treated with a large excess (5:1) of $\text{BrCH}_2\text{COOMe}$ under a CO atmosphere, a further reaction takes place, giving, with no detectable intermediate, a yellow cluster with IR bands in THF at $\nu_{\text{CO}} = 2066\text{ (w)}$, 2026 (vs) , 1999 (m) , 1989 (m) , 1834 (mw) , and $1819\text{ (mw)}\text{ cm}^{-1}$. These are typical for clusters of composition $[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$.⁷ An absorption band was also noted at 1702 cm^{-1} due to the COOMe group (eq 1).



Some $[\text{PPN}]\text{Br}$ precipitated as a white powder. Gas chromatographic analysis of the reacted solution showed the presence of methyl acetate and of the excess $\text{BrCH}_2\text{COOMe}$. No coupling products such as $\text{MeOOCCH}_2\text{CH}_2\text{COOMe}$ or $\text{MeOOCCH}_2\text{C(O)CH}_2\text{COOMe}$ could be detected. This cluster was also obtained directly from $\text{Na}[\text{Ir}(\text{CO})_4]$ ($[\text{Na}]\mathbf{1}$) by adding a large excess of the alkylating agent. Under these conditions a small amount of $[\text{IrBr}_2(\text{CO})_2(\text{CH}_2\text{COOMe})_2]^-$ ($\mathbf{4}$)⁸ was also formed. The exchange of the Na^+ counteranion with PPN^+ was accomplished by adding a $[\text{PPN}]\text{Cl}$ 2-propanol solution to the THF solution. The resulting solution was filtered to remove the NaCl and was then evaporated in vacuo. As $[\text{PPN}]\mathbf{3}$ is slightly soluble in benzene, the excess $[\text{PPN}]\text{Cl}$ and all other impurities can be removed by repeated extractions of the residue with this solvent up to its complete dissolution. (Although $[\text{PPh}_4]\mathbf{3}$ is less soluble in benzene than the PPN homologue, the above procedure is still viable but requires higher amounts of solvent.) Evaporation of the benzene solution gives the analytically pure compound. Like $[\text{PPN}]_2\mathbf{2}$, $[\text{PPN}]\mathbf{3}$ is indefinitely stable in the solid state under a dinitrogen atmosphere. Crystals suitable for X-ray diffraction analysis were obtained by

(3) Garlaschelli, L.; Chini, P.; Martinengo, S. *Gazz. Chim. Ital.* **1982**, *112*, 285.

(4) Ciani, G.; Manassero, M.; Albano, V. G.; Canziani, F.; Giordano, G.; Martinengo, S.; Chini, P. *J. Organomet. Chem.* **1978**, *250*, C17.

(5) (a) The low value of the C=O stretching frequency of the COOMe moiety is typical of unsaturated groups bearing a transition metal in the β -position and has also been found in monomeric compounds related to these clusters.⁷ This shift has been given the name of β -effect.^{5b,c} (b) Green, M. L. H. In *Organometallic Compounds*; Coates, G. E., Green, M. L. H., Wade, K., Eds.; Methuen: London, 1968; Vol. II. (c) Flood, T. C.; Di Santi, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

(6) The saturation of the 2-propanol layer with PPh_4Cl decreased the solubility of the cluster in the mixed solution and led to larger crystals than were obtained by using neat 2-propanol. To the best of our knowledge this procedure, which takes advantage of the high solubility of phosphonium halogenides in both 2-propanol and acetone, has never been reported. Such a procedure can be useful when the compound to be crystallized displaces an appreciable solubility in the acetone/2-propanol mixture, and it represents a valid alternative to the use of solvents of lower polarities such as hexane or toluene, which often give rise to oily precipitates (this is precisely what happened in the present case).

(7) Garlaschelli, L.; Martinengo, S.; Chini, P.; Canziani, F.; Bau, R. *J. Organomet. Chem.* **1981**, *213*, 379.

(8) Porta, F.; Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1990**, *9*, 929.

slow diffusion of *n*-hexane into a THF solution of [PPh₄]₃. (PPN⁺ salts were mostly used throughout the present work; however, crystals suitable for X-ray studies could not be obtained with this cation. Of those cations tried, only PPh₄⁺ gave acceptable crystals.)

The composition of **3** is [Ir₄(CO)₁₁(CH₂COOMe)]⁻, and its structure is similar to that of **2**, but there is only one organic substituent (see Figure 2).

The ¹H NMR spectra of [PPN]₂**2** and [PPN]**3** were also recorded. Besides the signals of the aromatic protons of the counteranion [PPN]₂**2** showed only two absorptions (in CDCl₃) at δ 1.66 (s, 4 H, CH₂) and δ 3.61 (s, 6 H, CH₃), in accordance with the equivalence of the two -CH₂COOMe groups. [PPN]**3** showed similar signals at δ 1.76 (s, 2 H, CH₂) and δ 3.64 (s, 3 H, CH₃). These values must be compared with those already reported for [PPN][IrBr(CO)₂(CH₂COOMe)] ([PPN]**5**; δ_{CH₂} = 2.18, δ_{CH₃} = 3.44, in CD₃COCD₃) and [PPN][IrBr₂(CO)₂(CH₂COOMe)₂] ([PPN]**4**; δ_{CH₂} (mean value) = 2.98, δ_{CH₃} = 3.62, in CDCl₃),⁸ in which the iridium atoms have formal oxidation states of I and III, respectively. The oxidation state of the iridium atoms in both **2** and **3** is zero; therefore, the protons of the CH₂ groups are more shielded than those of either of the mononuclear compounds. Until now no such mononuclear Ir⁰ alkyl complexes have ever been reported and, furthermore, it is difficult to even imagine their synthesis. These clusters therefore represent, at least for the moment, a unique opportunity to have an alkyl group bound to an iridium atom in such a low oxidation state.

Neither cluster reacts with CO (1 atm, 25 °C) to any detectable extent (IR evidence). This behavior is not surprising because electron-withdrawing substituents (such as COOMe) depress CO insertion into the M-C bond.

Also, [PPN]**3** does not react with additional [M][Ir(CO)₄] or [M][Rh(CO)₄] (M = PPN or Na). An attempt was made to favor the reaction of [PPN]**3** with [PPN][Ir(CO)₄] (in THF) by increasing the temperature to 50 °C, but this led only to the formation of [Ir₆(CO)₁₅]²⁻⁹ (IR evidence) instead of the desired higher nuclearity alkyl cluster.

BrCH₂COOMe was chosen as a substrate because the electron-withdrawing character of the COOMe group makes it a reactive compound toward nucleophiles and, at the same time, stabilizes the M-C bond in the product. This last characteristic is useful when the cluster is isolated but hinders further reactivity. Accordingly, we attempted to effect reaction 1 using PhCH₂Br or CH₃I in place of BrCH₂COOMe. Unfortunately, both these compounds are less reactive than methyl bromoacetate and the resulting clusters are probably less stable. The main product of these reactions was, therefore, [Ir₆(CO)₁₅]²⁻⁹ and only small quantities of some other, difficult to isolate, clusters were obtained. Efforts are being made to increase the yields of these clusters and to characterize them.

We have already reported⁸ that when the reaction of [Ir(CO)₄]⁻ with BrCH₂COOMe is conducted using PPN⁺ as a counteranion, instead of Na⁺, no clusters are formed. In this case the first product obtained in solution is *cis*-[IrBr(CO)₂(CH₂COOMe)]⁻ (**5**) which then reacts with more BrCH₂COOMe to form *ull-cis*-[IrBr₂(CO)₂(CH₂COOMe)₂]⁻ (**4**). The second oxidative addition is more rapid than the first, and **5** never accumulates to any extent. Although no intermediate species was observed during the formation of **2**, the fact that some **4** is also obtained, when a large excess of BrCH₂COOMe is added to the Na[Ir(CO)₄] solution at the beginning, seems to imply that **5** interme-

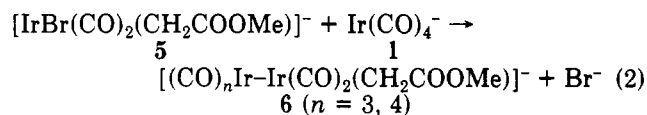
Table I. Crystallographic Data

	[PPh ₄] ₂ [Ir ₄ (CO) ₁₁ (CH ₂ COOCH ₃) ₂] ⁻	[PPh ₄] ₂ [Ir ₄ (CO) ₁₀ (CH ₂ COOCH ₃) ₂] ⁻
formula	C ₃₈ H ₂₆ Ir ₄ O ₁₃ P	C ₆₄ H ₅₀ Ir ₄ O ₁₄ P ₂
fw	1489.39	1873.85
cryst syst	monoclinic	triclinic
space group	P2 ₁ /c	P1
a, Å	13.155 (4)	11.163 (2)
b, Å	24.593 (5)	12.807 (2)
c, Å	38.401 (8)	22.849 (3)
α, deg		84.76 (1)
β, deg	91.00 (3)	88.76 (1)
γ, deg		73.53 (1)
V, Å ³	12422 (9)	3119 (1)
Z	12	2
D _{calc} , g cm ⁻³	2.389	1.995
μ(Mo Kα), cm ⁻¹	128.66	85.85
min transmissn factor	0.41	0.77
scan mode	ω	ω
ω-scan width, deg	1.2 + 0.35 tan θ	1.0 + 0.35 tan θ
θ range, deg	3-21	3-23
octants of reciprocal space explored	±h, +k, +l	±h, ±k, +l
no. of measd rflns	17 173	10 308
no. of unique obsd rflns	5227	6373
with I > 3σ(I)		
final R and R _w indices ^a	0.065, 0.069	0.034, 0.042
no. of variables	732	517
ESD ^b	1.897	1.443

^a R = [Σ(F_o - k|F_c|)/ΣF_o]; R_w = [Σw(F_o - k|F_c|)²/ΣwF_o²]^{1/2}. ^b ESD = [Σw(F_o - k|F_c|)²/(N_{observns} - N_{variables})]^{1/2}; w = 1/(σ(F_o))²; σ(F_o) = [σ²(I) + (0.04I)²]^{1/2}/2F_cLp.

diately forms even in this case. A study of the [PPN]-[Rh(CO)₄]-BrCH₂COOMe¹⁰ reaction further substantiates this assumption. In this case, in fact, the rapid formation of [RhBr(CO)₂(CH₂COOMe)]⁻ and its much slower reaction with the excess Rh(CO)₄⁻ to afford a cluster are clearly evident.

With regard to the second step of the reaction, one must consider that the halide ligands in [IrX₂(CO)₂]⁻ (X = halide) are known to be very labile and readily exchange with other halides during the time of mixing.¹¹ Since **5** is very similar to [IrX₂(CO)₂]⁻, it is reasonable to suppose that the second step of the reaction is a nucleophilic displacement of the bromide anion of **5** by Ir(CO)₄⁻:



The subsequent dimerization of **6**, with eventual CO loss, would yield compound **2**. Although this mechanism is speculative, the steps are reasonable and consistent with what is known about related reactions.^{8,10,11}

The counteranion probably influences reaction 2, and in fact, this step requires the coming together of two negatively charged species. It is presumed that this approach is favored by Na⁺'s ability to form ionic couples.¹²

(10) Ragaini, F.; Porta, F.; Fumagalli, A.; Demartin, F. Work in progress.

(11) Forster, D. *Inorg. Chem.* 1972, 11, 1686.

(12) An alternative explanation of the influence of Na⁺ can be derived from the reactivity of the related complex Co(CO)₄⁻. The PPN⁺ salt of Co(CO)₄⁻ reacts with CH₃I to afford [CH₃CoCoI(CO)₃]⁻,¹³ while the Na⁺ salt affords the neutral complex CH₃Co(CO)₄.¹⁴ Probably the formation of an ionic couple with Na⁺ deactivates the I⁻ and prevents attachment to the cobalt atom. Obviously if a complex such as MeOOCCH₂Ir(CO)₄ were formed, this would be more easily attacked by Ir(CO)₄⁻ than would the anionic **5**. (When Rh(CO)₄⁻ is protonated by a strong acid under 1 atm of CO, it immediately clusterizes.¹⁵) However, the fact that **4** is also formed during the reaction seems to imply that **5** is indeed an intermediate and the influence of the counteranion must be found in a subsequent stage of the reaction.

(13) (a) Roper, M.; Shieren, M. *J. Organomet. Chem.* 1986, 299, 131.

(b) Roper, M.; Kruger, C. *J. Organomet. Chem.* 1988, 399, 159.

(9) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Martinengo, S.; Canziani, F. *J. Chem. Soc., Chem. Commun.* 1980, 903.

Table II. Selected Bond Lengths (Å)

	[PPh ₄][Ir ₄ (CO) ₁₁ -(CH ₂ COOCH ₃) ₂] ^a		[PPh ₄] ₂ [Ir ₄ (CO) ₁₀ -(CH ₂ COOCH ₃) ₂]
Ir(1)-Ir(2)	2.739 (3)	2.735 (2)	2.704 (1)
Ir(1)-Ir(3)	2.704 (2)	2.707 (2)	2.723 (1)
Ir(1)-Ir(4)	2.719 (2)	2.733 (2)	2.738 (1)
Ir(2)-Ir(3)	2.741 (2)	2.749 (2)	2.748 (1)
Ir(2)-Ir(4)	2.728 (3)	2.728 (2)	2.755 (1)
Ir(3)-Ir(4)	2.720 (2)	2.714 (2)	2.758 (1)
Ir-Ir ^b	2.725	2.728	2.738
Ir-C _{term} ^b	1.83	1.81	1.86
C-O _{term} ^b	1.18	1.17	1.15
Ir(1)-C(12)	2.24 (5)	2.14 (4)	2.15 (1)
Ir(2)-C(12)	1.98 (5)	1.94 (4)	2.02 (1)
Ir(1)-C(13)	2.03 (4)	2.05 (4)	2.19 (1)
Ir(3)-C(13)	2.09 (4)	2.06 (4)	1.97 (1)
Ir(2)-C(23)	1.94 (4)	1.97 (3)	2.08 (1)
Ir(3)-C(23)	2.32 (4)	2.27 (3)	2.12 (1)
C-O _{bridg} ^b	1.19	1.23	1.18
Ir(2)-C(1)	2.15 (5)	2.22 (3)	2.192 (8)
Ir(3)-C(4)			2.181 (10)
C(1)-C(2)	1.35 (5)	1.40 (4)	1.48 (1)
C(2)-O(1)	1.31 (5)	1.18 (3)	1.22 (1)
C(2)-O(2)	1.48 (5)	1.38 (4)	1.36 (1)
O(2)-C(3)	1.50 (5)	1.52 (4)	1.47 (1)
C(4)-C(5)			1.51 (1)
C(5)-O(3)			1.21 (2)
C(5)-O(4)			1.24 (2)
O(4)-C(6)			1.74 (2)

^aTwo ordered independent anions. ^bAverage value.

Little can be said about the reaction of **2** with BrCH₂COOMe. As the products are **3**, [PPN]Br, and methyl acetate, a radical mechanism probably operates. Such a reaction of a complex bearing a pseudoalkyl ligand with BrCH₂COOMe is not without precedent, since we have already reported⁸ that [RhBr(CO)₂(CH₂COOMe)]⁻ decomposes to [RhBr₂(CO)₂]⁻ and methyl acetate when treated with BrCH₂COOMe. Available data are, however, insufficient to allow a description of the mechanism of this reaction.

Description of the Structures of Compounds [PPh₄]₂ and [PPh₄]3**.** Perspective views of the [Ir₄(CO)₁₀(CH₂COOMe)₂]²⁻ and [Ir₄(CO)₁₁(CH₂COOMe)]⁻ anions are shown in Figures 1 and 2, respectively. Selected molecular parameters for both anions are reported in Table II; the atomic coordinates have been deposited as supplementary material.

Crystals of [PPh₄][Ir₄(CO)₁₁(CH₂COOMe)] ([PPh₄]**3**) derive from the packing of tetraphenylphosphonium cations and [Ir₄(CO)₁₁(CH₂COOMe)]⁻ anions, separated by normal van der Waals interactions, and the asymmetric unit consists of three cations and three anions. This unusual number of independent molecules in the space group *P*2₁/*c* might give rise to the suspicion that the crystal structure of [PPh₄]**3** could have been described in an alternative space group in which the three independent anions and cations are mutually related by a crystallographic symmetry element. An inspection of the crystal packing and the conformational parameters of the anions excludes the possibility of some kind of correlation, further supported by the considerations that will be discussed later. As a consequence of packing effects, the conformational parameters of the CH₂COOMe appendages of two of the three anions are slightly different while the remaining anion appears disordered in the solid state. The refined model for this disordered anion consists of two

interpenetrating tetrahedra with a common vertex, surrounded by mostly well-resolved ligands. The iridium atom shared by the two tetrahedra displays a thermal parameter higher than those of the remaining metal atoms, and this is indicative that this position is also affected by disorder and should have split into two positions. Unfortunately these positions are so close that they cannot be refined separately. Such a disordered orientation of the metallic framework within an almost regular disposition of ligands is not uncommon in this kind of compound.¹⁶ The unfavorable ratio between the number of significant reflections and the number of collected data (see Table I) is directly related to this disorder in the crystal structure.

The values of the geometrical parameters for the anion, reported in Table II, relate to the two nondisordered anions. The structure of the [Ir₄(CO)₁₁(CH₂COOMe)]⁻ anion contains a tetrahedron of iridium atoms bearing eight terminal and three edge-bridging CO ligands and a -CH₂COOMe moiety. The ligand stereochemistry is that typical of Ir₄(CO)₁₂ substituted derivatives with poor π-acceptor ligands or with ligands that are sterically more demanding than CO, i.e. with three bridging CO's around a triangular "basal" face of the metal tetrahedron and with the substituent bonded to an iridium atom of the basal plane. As usual, two of the three bridging CO's are asymmetric with a short interaction toward the substituted Ir(2) atom, the remaining CO being almost symmetric. The observed values for Ir-Ir, Ir-C, and C-O bond lengths are in line with those typical for Ir₄(CO)₁₂ substituted derivatives, a compilation of which is reported in ref 17. The Ir-C(1) bond length of 2.18 Å is comparable to that found for the σ-bonded acyl ligand in [Ir₄(CO)₁₁(COOMe)]⁻, 2.20 (4) Å.⁷

The molecular geometry of the [Ir₄(CO)₁₀-(CH₂COOMe)₂]²⁻ dianion, with idealized C_s symmetry, may be derived from that of the monoanion by replacing a carbonyl, in an axial position with respect to the basal face of the tetrahedron, with a second -CH₂COOMe ligand. One effect of disubstitution is a slight change in the Ir-C_{bridging} bond lengths: again two asymmetric CO ligands are observed; the shorter bond connects the ligands to the substituted Ir atoms, and the almost symmetric CO bridge spans the Ir(2)-Ir(3) bond, i.e. the bond between the iridium atoms bearing the -CH₂COOMe substituents.

Experimental Section

General Procedure. Unless otherwise stated, all reactions and manipulations were conducted at room temperature under a dinitrogen atmosphere with a standard Schlenk-tube apparatus. All solvents were dried, degassed, and stored under dinitrogen before use. The organic reagents were commercial products and were used as received. THF solutions of Na[Ir(CO)₄] were prepared by reducing Ir₄(CO)₁₂ with sodium metal as in ref 3. IR spectra were recorded on a Perkin-Elmer 781 infrared spectrophotometer; ¹H NMR spectra were recorded on a Bruker VP 80 spectrometer. Elemental analyses were performed in the Analytical Laboratories of the University of Milan.

Synthesis of the Complexes. [PPN]₂[Ir₄(CO)₁₀-(CH₂COOMe)₂] ([PPN]₂**2**). An 18-mL portion of a Na[Ir(CO)₄] solution, prepared from 400 mg of Ir₄(CO)₁₂ in 40 mL of THF, is placed in a Schlenk tube under a N₂ or CO atmosphere. The yield of the synthesis of Na[Ir(CO)₄] is about 50–60%. This complex is very air-sensitive and, although the exact titer of the solution can be measured by atomic absorption spectroscopy, the

(14) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* **1984**, *59*, 203.
(15) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249.

(16) (a) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1821. (b) Wei, C. H.; Wilkes, G. R.; Dahl, F. L. *J. Am. Chem. Soc.* **1967**, *89*, 4972. (c) Wei, C. H. *Inorg. Chem.* **1968**, *8*, 2384. (d) Della Pergola, R.; Garlaschelli, L.; Demartin, F.; Manassero, M.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1990**, 127.
(17) Braga, D.; Grepioni, F. *J. Organomet. Chem.* **1987**, *336*, C9.

quantity of $[\text{Ir}(\text{CO})_4]^-$ can change during storage. The preferred procedure is to add $\text{BrCH}_2\text{COOMe}$ stepwise, in decreasing amounts, by a microsyringe. The first addition corresponds to half the molar amount necessary to complete the reaction, supposing a 50% yield in the synthesis of $\text{Na}[\text{Ir}(\text{CO})_4]$ (7.5 μL , 0.081 mmol in the present case). The reaction is then followed by IR spectroscopy until the complete disappearance of the band at 1896 cm^{-1} due to the starting material. (To ensure that all the added $\text{BrCH}_2\text{COOMe}$ has reacted, it is necessary to let the solution stand, with stirring, for 2 h after each addition.) Stepwise addition is, in any case, necessary to avoid the partial formation of **3** or **4**. The reaction results in a yellow-orange solution and a white crystalline precipitate (NaBr), which is filtered off. A solution of $[\text{PPN}]\text{Cl}$ (186 mg, 0.324 mmol) or $[\text{PPh}_4]\text{Cl}$ (121 mg, 0.324 mmol) in 2-propanol (10 mL) is added and the resulting suspension evaporated in vacuo until almost all the THF has been eliminated. The residue is then filtered off, washed with 2-propanol (2×5 mL), and dissolved in THF. Drying the THF solution affords the analytically pure compound as an orange, crystalline material (180 mg, PPN^+ salt). Anal. Calcd for $\text{C}_{88}\text{H}_{70}\text{N}_2\text{Ir}_4\text{O}_{14}\text{P}_4$: C, 46.5; H, 3.1; N, 1.2. Found: C, 46.7; H, 3.3; N, 1.2. As the exact quantity of $\text{Na}[\text{Ir}(\text{CO})_4]$ is not known, precise yields cannot be calculated. No trace of any byproduct was revealed by IR spectroscopy; thus, the reaction can be considered almost quantitative. A small loss of material does, however, occur during the workup. $[\text{PPN}]_2$ is very soluble in THF when freshly prepared; however, letting the solution stand for a few days causes complete precipitation of the complex. Redissolution of the precipitate in acetone affords the original cluster; the precipitation is probably due to the formation of a different crystalline form, with some clathrated THF. This does not happen when PPh_4^+ is used as a counteranion.)

$[\text{PPN}][\text{Ir}_4(\text{CO})_{11}(\text{CH}_2\text{COOMe})]$ ($[\text{PPN}]\mathbf{3}$). (a) From $[\text{PPN}]_2[\text{Ir}_4(\text{CO})_{10}(\text{CH}_2\text{COOMe})_2]$ ($[\text{PPN}]_2\mathbf{2}$). $[\text{PPN}]_2$ (100 mg, 0.044 mmol) was placed in a Schlenk tube under a CO atmosphere and dissolved in THF (10 mL). $\text{BrCH}_2\text{COOMe}$ (20.4 μL , 0.22 mmol) was then added by a microsyringe, and the solution was stirred for 2 h. The color of the solution changed from orange to yellow, and a white precipitate ($[\text{PPN}]\text{Br}$) formed. Gas chromatographic analysis of the solution at this stage (packed column, Chromosorb 103) showed the presence of methyl acetate and $\text{BrCH}_2\text{COOMe}$ as the only detectable products. To ensure the complete elimination of $[\text{PPN}]\text{Br}$ (most was filtered off) and of any unreacted starting material, the solution was evaporated to dryness in vacuo and the residue extracted repeatedly with benzene until the solvent remained colorless (60 mL). Evaporating the benzene solution to dryness afforded analytically pure $[\text{PPN}]\mathbf{3}$ (66 mg, 90% yield). Anal. Calcd for $\text{C}_{50}\text{H}_{35}\text{N}\text{Ir}_4\text{O}_{13}\text{P}_2$: C, 36.9; H, 2.2; N, 0.8. Found: C, 37.0; H, 2.2; N, 0.8.

(b) From $\text{Na}[\text{Ir}(\text{CO})_4]$ ($[\text{Na}]\mathbf{1}$). An 18-mL portion of a $\text{Na}[\text{Ir}(\text{CO})_4]$ solution, prepared from 400 mg of $\text{Ir}_4(\text{CO})_{12}$ in 40 mL of THF, was placed in a Schlenk tube under a CO atmosphere (see also the synthesis of $[\text{PPN}]_2\mathbf{2}$). $\text{BrCH}_2\text{COOMe}$ (0.11 mL, 1.2 mmol) was then added by a microsyringe, and the reaction was followed by IR spectroscopy. After about 1 h the reaction was

complete (total disappearance of the IR bands of both **1** and **2**). A solution of $[\text{PPN}]\text{Cl}$ (93 mg, 0.16 mmol) or $[\text{PPh}_4]\text{Cl}$ (60 mg, 0.16 mmol) in 2-propanol (10 mL) was added, and the resulting solution was evaporated to dryness in vacuo. Purification was afforded as in method a (yield about 100 mg). What was said concerning the yields in the synthesis of $[\text{PPN}]_2\mathbf{2}$ is also valid here. Loss of material during the workup is most certainly higher; IR analysis of the residue after extraction showed the presence of some $[\text{PPN}][\text{IrBr}_2(\text{CO})_2(\text{CH}_2\text{COOMe})_2]$ ($[\text{PPN}]\mathbf{4}$).

X-ray Data Collection and Structure Determination. Crystal data and other experimental details are summarized in Table I. The diffraction experiments, with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), were carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature. The dimensions of the crystals used were $0.1 \times 0.1 \times 0.3$ mm for $[\text{PPh}_4]_2\mathbf{2}$ and $0.05 \times 0.05 \times 0.01$ mm for $[\text{PPh}_4]\mathbf{3}$. The diffracted intensities were corrected for Lorentz, polarization, and absorption (empirical correction),¹⁸ but not for extinction. Scattering factors and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from ref 19. The structure of compound $[\text{PPh}_4]\mathbf{3}$ was solved by direct methods (MULTAN), while that of compound $[\text{PPh}_4]_2\mathbf{2}$ was solved by Patterson and Fourier methods. Both structures were refined by full-matrix least squares, minimizing the function $\sum w(F_o - k|F_c|)^2$. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.²⁰ Anisotropic thermal factors were refined only for the iridium atoms in compound $[\text{PPh}_4]\mathbf{3}$, while for $[\text{PPh}_4]_2\mathbf{2}$ anisotropic thermal factors were assigned to all the atoms of the anion and to the phosphorus atoms of the cations. For compound $[\text{PPh}_4]_2\mathbf{2}$, hydrogen atoms were introduced into the model of the cations at calculated positions with C-H = 0.95 \AA and not refined. The final difference Fourier synthesis showed maximum residuals of 1.3 and 0.6 $e/\text{\AA}^3$ for $[\text{PPh}_4]\mathbf{3}$ and $[\text{PPh}_4]_2\mathbf{2}$, respectively.

Acknowledgment. We wish to thank the Fondazione G. Donegani for the scholarship given to F.R. We also thank Profs. S. Cenini and L. Garlaschelli for their helpful suggestions and the Progetto Finalizzato Chimica Fine II for financial support.

Registry No. $[\text{Na}]\mathbf{1}$, 56625-78-6; $[\text{PPN}]_2\mathbf{2}$, 130031-67-3; $[\text{PPh}_4]_2\mathbf{2}$, 130143-22-5; $[\text{PPN}]\mathbf{3}$, 130013-50-2; $[\text{PPh}_4]\mathbf{3}$, 130062-33-8; $\text{BrCH}_2\text{COOMe}$, 96-32-2.

Supplementary Material Available: Listings of fractional atomic coordinates, thermal parameters, and all bond lengths and angles for $[\text{PPh}_4]_2\mathbf{2}$ and $[\text{PPh}_4]\mathbf{3}$ (34 pages); tables of observed and computed structure factor moduli (80 pages). Ordering information is given on any current masthead page.

(18) North, A. C.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* 1968, 24, 351.

(19) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham; U.K., 1974; Vol. IV.

(20) B. A. Frenz and Associates, SDP Plus Version 1.0, Enraf-Nonius, Delft, The Netherlands, 1980.