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CHEMISTRY OF IRIDIUM CARBONYL

I. CHEMICAL AND STRUCTURAL CHARACTERIZATION OF THE TETRANUCLEAR ANIONS $[Ir_4(\mu\text{-}CO)_3(CO)_8(COOR)]^-$ *

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Summary

1 The anions $[Ir_4(CO)_{11}(COOR)]^-$ (R = Me, Et) have been prepared by reacting $Ir_4(CO)_{12}$ with alkali alkoxides in dry alcohol and under an atmosphere of carbon monoxide. The reaction of $[Ir_4(CO)_{11}(COOMe)]^-$ with primary and secondary alcohols (EtOH, Pr^iOH) gives rise to specific alcoholysis. The anions $[Ir_4(CO)_{11}(COOR)]^-$ react with acids in THF solution to give quantitatively $Ir_4(CO)_{12}$. The chemical, spectroscopic and crystallographic characterization of the tetranuclear anions are reported.

Introduction

It is known that $Ir_4(CO)_{12}$ reacts with neutral and anionic ligands, resulting in the substitution of one or more terminal carbon monoxide groups [1]. The basic structure of $Ir_4(CO)_{12}$ [2] is retained only in the reaction with tert-butylisocyanide [3], while substitution with other neutral and anionic ligands significantly modifies the original arrangement of carbonyl ligands so that both bridging and terminal carbonyls appear [1,4,5]. As part of a study of the reactivity of iridium carbonyl, we recently reported the preparation and the structural characterization of a new series of anions of general formula $[Ir_4(\mu\text{-}CO)_3$-

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* Dedicated to the memory of Professor Paolo Chini (deceased, February 1980).

$(CO)_8X]^-$ (X = Cl, Br, I, SCN) [4]. We now report the synthesis and the chemical characterization of the new anions $[Ir_4(\mu\text{-}CO)_3(CO)_8(COOR)]^-$ (R = Me, Et), which are closely related to these anionic species. These new anions are obtained by nucleophilic attack of an alkoxide group RO^- (R = Me, Et) on a terminal carbon monoxide bonded to iridium.

Results

a) Synthesis of the $[Ir_4(CO)_{11}(COOR)]^-$ (R = Me, Et) anions

Dodecacarbonyltetrairidium reacts in dry methanol under a carbon monoxide atmosphere with an excess of sodium methoxide to give a yellow solution containing the new carboalkoxy anion according to the reaction:

$$Ir_4(CO)_{12} + MeONa \xrightarrow[CO]{MeOH} Na[Ir_4(CO)_{11}(COOMe)]$$

A carbon monoxide atmosphere is necessary to avoid decomposition of the carboalkoxy species, which in the absence of CO decomposes slowly to give a mixture of other iridium cluster anions presently under investigation. The reaction time is strictly related to the molar ratio between $Ir_4(CO)_{12}$ and RO^-, and to the particle size of the solid $Ir_4(CO)_{12}$ used. Usually the reaction is complete within six to eight hours when three or four moles of methoxide per mole of $Ir_4(CO)_{12}$ are used. The addition of such an excess of MeO^- usually does not give rise to any other product in the above-cited reaction time; only when a large excess of sodium methoxide is used, does one obtain a small amount of $[Ir(CO)_4]^-$. The analogous derivative containing an ethoxy group is obtained in similar conditions by reacting $Ir_4(CO)_{12}$ with EtONa in dry ethanol. Very poor yields of the anion are obtained with magnesium alkoxides. Slow formation of the carbomethoxy derivative is also observed by reacting $Ir_4(CO)_{12}$ in dry methanol with a large excess of anhydrous sodium or potassium carbonate.

We have spectroscopic evidence, to be described later, which shows that the carboalkoxy derivatives are the first compounds formed when $Ir_4(CO)_{12}$ is treated with alkaline agents in an alcohol medium. The yellow anion $[Ir_4(CO)_{11}(COOR)]^-$ can be isolated from the alcoholic solution by addition of aqueous solutions of bulky cations such as PPN^+ $[PPN^+ = (Ph_3P)_2N^+]$, $(PPh_4)^+$, $(AsPh_4)^+$, $(NMe_2Bz_2)^+$ (Bz = $CH_2C_6H_5$) and $[Co(\eta_5\text{-}Cp)_2]^+$. All these salts are very soluble in THF, dichloromethane and acetonitrile, sparingly soluble in methanol, ethanol and isopropanol, insoluble in water and aliphatic or aromatic hydrocarbons. They can all be recrystallized from THF/toluene; crystals of the dimethyldibenzylammonium salt, suitable for X-ray analysis, were obtained by layering heptane over a dichloromethane solution of the compound under a carbon monoxide atmosphere.

The structure of the dimethyldibenzylammonium salt, found by X-ray analysis (vide infra), shows both terminal and bridging carbonyl groups, in agreement with the IR spectra reported in Table 1. The IR spectrum of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ in THF solution is shown in Fig. 1 and features carbonyl stretching bands at 2065w, 2030vs, 2000s, 1985s, 1960m and 1825s cm^{-1} in the terminal and bridging CO stretching regions. In addition, weak absorption bands assignable to the carbomethoxy group appear at 1650 cm^{-1} and at 1045

TABLE 1

INFRARED [a] AND NMR SPECTRA [b]

Compound	CO stretching frequencies				^{1}H NMR δ (ppm)			
					$\mathrm{OC}H_3$	$\mathrm{OC}H_2\mathrm{CH}_3$	$\mathrm{OCH_2C}H_3$	Other resonances
$[\mathrm{NMe_2Bz_2}][\mathrm{Ir_4(CO)_{11}(COOMe)}]$	2070w 1645w	2035vs	2005s	1835s	3.1(s)			1.2–1.4(m), $\mathrm{C}H_3$, $\mathrm{C}H_2$ 8(m), $\mathrm{C_6}H_5$
$(\mathrm{PPh_4})[\mathrm{Ir_4(CO)_{11}(COOMe)}]$	2065w 1960m	2030vs 1825s	2000s 1650w	1985s	3.1(s)			8.0(m), $\mathrm{C_6}H_5$
$(\mathrm{AsPh_4})[\mathrm{Ir_4(CO)_{11}(COOMe)}]$	2060w 1960m	2020vs 1820s	2005s 1645w	1980s	3.1(s)			7.9(m), $\mathrm{C_6}H_5$
$(\mathrm{PPN})[\mathrm{Ir_4(CO)_{11}(COOMe)}]$	2070w 1830s	2040vs 1645w	2005s	1985s	3.1(s)			7.5(m), $\mathrm{C_6}H_5$
$[\mathrm{Co}(\eta^5\text{-}\mathrm{Cp})_2][\mathrm{Ir_4(CO)_{11}(COOMe)}]$	2065w 1830s	2035vs 1640w	1990s 1630w	1870w	3.1(s)			5.45(s), $\mathrm{C_5}H_5$
$(\mathrm{NMe_3Bz})[\mathrm{Ir_4(CO)_{11}(COOMe)}]$	2070w 1960m	2035vs 1830s	2005s 1645w	1990s	3.1(s)			1.1–1.4(m), $\mathrm{C}H_3$, $\mathrm{C}H_2$ 8.0(m), $\mathrm{C_6}H_5$
$(\mathrm{PPh_4})[\mathrm{Ir_4(CO)_{11}(COOEt)}]$	2060w 1875w	2030vs 1820s	1995s 1640w	1980s		3.85(q)	1.0(t)	7.8–8.2(m), $\mathrm{C_6}H_5$
$(\mathrm{PPN})[\mathrm{Ir_4(CO)_{11}(COOEt)}]$	2070w 1875w	2035vs 1820s	2000s 1640m	1985s		3.9(q)	1.0(t)	8.0(m), $\mathrm{C_6}H_5$
$(\mathrm{PPh_4})[\mathrm{Ir_4(CO)_{11}(COOPr^i)}]$ [c]	2065w 1965m	2025vs 1875w	1990s 1820s	1975s 1635w				4.96(se), $\mathrm{OC}H(\mathrm{CH_3})_2$ 1.33(d), $\mathrm{OCH(C}H_3)_2$ 7.8–8.2(m), $\mathrm{C_6}H_5$

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[a] THF solution, cm^{-1}, relative intensities w = weak, m = medium, s = strong, vs = very strong. [b] Acetone solution. Multiplicity s = singlet, d = doublet, t = triplet, q = quartet, se = septet, m = multiplet. [c] Chloroform solution.

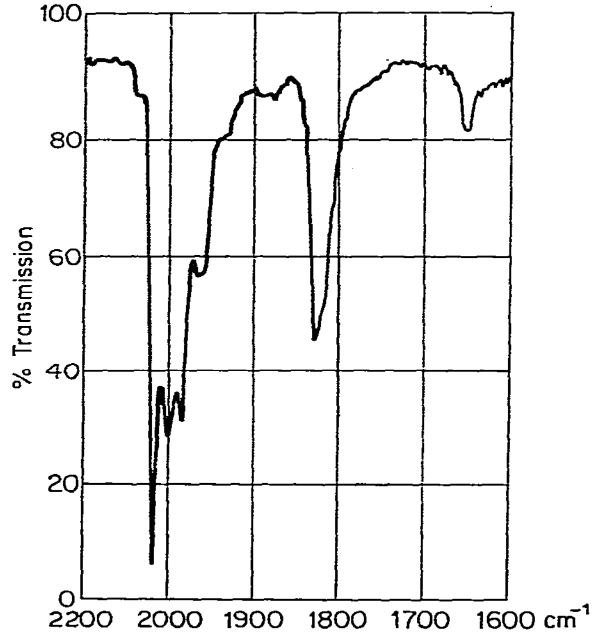

Fig. 1. Infra-red spectrum of $[PPh_4]^+[Ir_4(CO)_{11}COOCH_3]^-$ in THF solution.

cm^{-1} *, the latter being more easily observed in the Nujol mull spectrum. The ^1H NMR spectrum of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ (40°C, CD_3COCD_3) shows a singlet at $\delta = 3.1$ ppm (due to the resonance of the methyl group) with the correct intensity ratio (3 : 20) relative to the cation phenyl hydrogens at $\delta = 7.9$ ppm (Table 1).

b) Chemical characterization of the $[Ir_4(CO)_{11}(COOR)]^-$ anions

The $[Ir_4(CO)_{11}(COOR)]^-$ anions react with an excess of acids such as H_2SO_4 and CH_3COOH in methanol or in THF solution to give $Ir_4(CO)_{12}$ according to:

$$[Ir_4(CO)_{11}(COOR)]^- + H^+ \rightarrow Ir_4(CO)_{12} + ROH$$

This behaviour was already observed in the case of the analogous rhodium derivatives [6]. The alkali metal salts of the $[Ir_4(CO)_{11}(COOR)]^-$ anions react with sodium or potassium hydroxide in dry isopropanol to give the dianionic species $[Ir_4(CO)_{11}]^{2-}$ [7], but when the same reaction is carried out in wet isopropanol the dianion $[H_2Ir_4(CO)_{10}]^{2-}$ [8] is isolated instead. One interesting feature of these carboalkoxy anions is that they can undergo alcoholysis. The alkoxy group exchanges quickly and completely at 50°C with those of primary alcohols such as MeOH and EtOH, while exchange with secondary alcohols such as isopropanol is slower and incomplete (60% yield). No exchange has been observed with tertiary alcohols such as tertbutanol. From these data the replacement of the alkoxy group seems to depend essentially on the entering group and not on the leaving group.

The $[Ir_4(CO)_{11}(COOR)]^-$ anions are not very sensitive to water: in fact, they can be recovered without any modification after 24 hours from a THF or alco-

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* This was recorded with the $[CoCp_2]^+$ salt. The 1045 cm^{-1} band can only be seen if the cation contains no P—C bond, since the P—C stretching frequency is found at ~1030 cm^{-1}.

holic solution containing 2% water; such stability is quite surprising because the analogous rhodium derivatives are unstable under these conditions [6]. Another difference between the iridium and rhodium compounds is that no redox condensation between the carboalkoxy anions and $Ir_4(CO)_{12}$ can be observed, whereas this type of reaction takes place readily in the rhodium case [6]. The carboalkoxy anions react immediately in wet alcohols with Na_2CO_3 or K_2CO_3 under a carbon monoxide atmosphere to give the known anion $[HIr_4(CO)_{11}]^-$ [5].

Crystallographic section

$[NMe_2Bz_2]^+[Ir_4(CO)_{11}(COOCH_3)]^-$ crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell parameters: $a = 10.749(8)$, $b = 14.086(5)$, $c = 12.958(6)$ Å, $\alpha = 71.38(4)$, $\beta = 87.07(4)$, $\gamma = 108.17(2)°$; $V = 1742(1)$ Å^3, ρ(calcd) = 2.60 g cm^{-3} for $Z = 2$. A specimen of approximate dimensions 0.65 × 0.30 × 0.20 mm was used for the structure analysis. One hemisphere of data was collected on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo-K_α X-rays using an ω-scan mode up to a 2θ maximum of

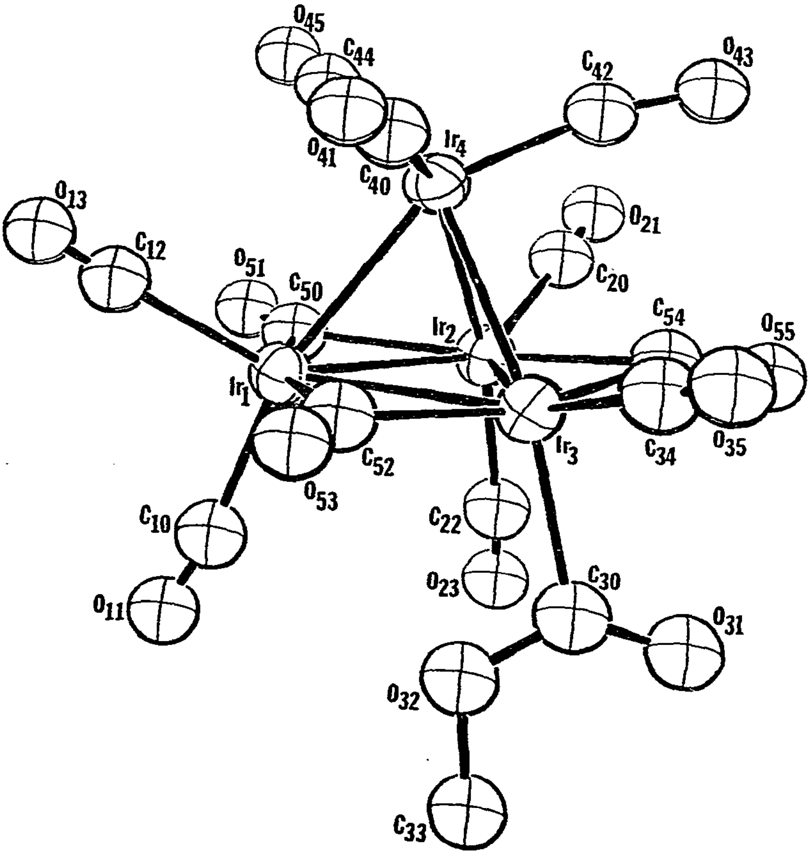

Fig. 2. Molecular plot of the anion in $[NMe_2Bz_2]^+[Ir_4(CO)_{11}COOCH_3]^-$.

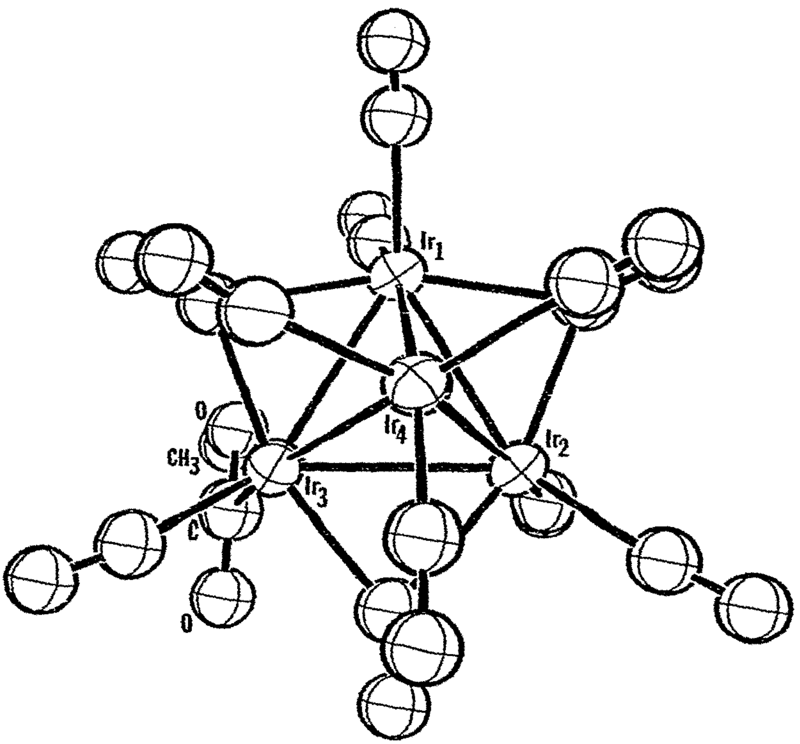

Fig. 3. An alternative view of the $[Ir_4(CO)_{11}COOCH_3]^-$ anion. Note that the carbomethoxy group is essentially planar and is roughly perpendicular to the basal $Ir_1Ir_2Ir_3$ plane of the cluster.

45°. Data processing (which included Lorentz, polarization and absorption corrections) reduced the 4241 independent reflections to 3211 having $I > 3\sigma(I)$. The structure was solved with standard heavy-atom methods, and refined to final agreement factors of R = 7.6% and R_w = 7.2%. Molecular plots of the $[Ir_4(CO)_{11}(COOCH_3)]^-$ anion are shown in Figs. 2 and 3, and listings of the final coordinates of all atoms and selected distances in the anion are given in Tables 2 and 3. Tables of the final thermal parameters and the interatomic angles are available [9].

As can be seen in the figures, the ligand arrangement in $[Ir_4(CO)_{11}(COOCH_3)]^-$ is significantly different from that in the parent compound $Ir_4(CO)_{12}$ [2]. In $Ir_4(CO)_{12}$ only terminal carbonyls are found, while in $[Ir_4(CO)_{11}(COOCH_3)]^-$ there are three bridging carbonyls situated on the edges of the Ir(1,2,3) face (the basal face) of the cluster. For purposes of comparison, in $[HIr_4(CO)_{11}]^-$ [10] and $[H_2Ir_4(CO)_{10}]^{2-}$ [8] there are two and three bridging CO ligands, respectively. The carbomethoxy group in $[Ir_4(CO)_{11}(COOCH_3)]^-$ is bonded to one of the basal atoms, Ir(3), and is situated approximately *trans* to the axial atom Ir(4). The non-hydrogen portion of the $-COOCH_3$ group is planar within experimental error, and is roughly perpendicular to the basal Ir(1,2,3) face (Fig. 3).

TABLE 2

FINAL ATOMIC COORDINATES FOR $[NMe_2Bz_2]^+[Ir_4(CO)_{11}(COOCH_3)]^-$

Atom	*x*	*y*	*z*
Ir(1)	0.4217(2)	0.3366(1)	0.1786(1)
Ir(2)	0.3395(2)	0.3830(1)	0.3509(1)
Ir(3)	0.3878(2)	0.1976(1)	0.3894(1)
Ir(4)	0.1729(2)	0.2250(1)	0.2938(1)
C(10)	0.614(7)	0.414(4)	0.134(4)
O(11)	0.709(4)	0.451(3)	0.101(3)
C(12)	0.369(4)	0.325(3)	0.031(3)
O(13)	0.340(4)	0.315(2)	−0.035(2)
C(20)	0.196(4)	0.423(3)	0.413(3)
O(21)	0.124(3)	0.451(2)	0.442(2)
C(22)	0.509(7)	0.490(4)	0.376(6)
O(23)	0.592(5)	0.532(4)	0.382(4)
C(30)	0.585(4)	0.240(3)	0.438(4)
O(31)	0.590(3)	0.226(2)	0.529(2)
O(32)	0.678(4)	0.292(3)	0.355(2)
C(33)	0.809(5)	0.337(5)	0.372(5)
C(34)	0.343(4)	0.054(4)	0.482(4)
O(35)	0.321(4)	−0.029(2)	0.527(3)
C(40)	0.150(5)	0.094(3)	0.256(3)
O(41)	0.148(3)	0.036(2)	0.224(2)
C(42)	0.049(5)	0.159(3)	0.426(4)
O(43)	−0.007(3)	0.122(3)	0.517(3)
C(44)	0.076(7)	0.317(5)	0.185(5)
O(45)	0.045(6)	0.364(4)	0.142(4)
C(50)	0.370(5)	0.473(3)	0.175(2)
O(51)	0.355(3)	0.540(2)	0.123(2)
C(52)	0.447(6)	0.185(2)	0.239(3)
O(53)	0.483(3)	0.133(2)	0.210(2)
C(54)	0.298(7)	0.243(3)	0.503(3)
O(55)	0.283(3)	0.231(2)	0.591(2)
N(5)	0.405(3)	0.811(2)	0.180(2)
C(60)	0.544(4)	0.805(2)	0.212(2)
C(61)	0.660(4)	0.909(3)	0.164(3)
C(62)	0.733(3)	0.931(2)	0.061(2)
C(63)	0.838(4)	1.027(3)	0.014(3)
C(64)	0.887(5)	1.104(3)	0.078(4)
C(65)	0.795(5)	1.078(3)	0.178(4)
C(66)	0.689(4)	0.986(3)	0.220(3)
C(70)	0.305(4)	0.702(3)	0.257(3)
C(71)	0.170(4)	0.693(3)	0.239(3)
C(72)	0.109(5)	0.640(3)	0.165(3)
C(73)	−0.013(6)	0.625(3)	0.143(4)
C(74)	−0.099(5)	0.662(4)	0.201(5)
C(75)	−0.047(5)	0.714(3)	0.268(3)
C(76)	0.087(5)	0.724(3)	0.299(3)
C(80)	0.374(3)	0.905(2)	0.206(3)
C(90)	0.405(4)	0.825(3)	0.058(3)

Discussion

The formation of the tetranuclear derivatives $[Ir_4(CO)_{11}(COOR)]^-$ is a clear example of the direct nucleophilic attack, in this case of an alkoxy group, on a positively polarized carbon atom of a carbon monoxide group bonded to a metal atom. The structural details of the $[Ir_4(CO)_{11}(COOR)]^-$ anion show that

TABLE 3

SELECTED DISTANCES (Å) IN THE $[Ir_4(CO)_{11}COOCH_3]^-$ ANION

Ir—Ir		*Ir—COOMe*	
Ir(1)—Ir(2)	2.700(2)	Ir(3)—C(30)	2.20(4)
Ir(1)—Ir(3)	2.733(2)	C(30)—O(31)	1.13(6)
Ir(1)—Ir(4)	2.706(2)	C(30)—O(32)	1.27(6)
Ir(2)—Ir(3)	2.717(2)	O(32)—C(33)	1.41(6)
Ir(2)—Ir(4)	2.722(2)		
Ir(3)—Ir(4)	2.750(2)		
Ir—C(terminal)		*Ir—C(bridging)*	
Ir(1)—C(10)	1.96(7)	Ir(1)—C(50)	2.15(4)
Ir(1)—C(12)	2.06(4)	Ir(1)—C(52)	2.14(4)
Ir(2)—C(20)	2.01(4)	Ir(2)—C(50)	2.17(3)
Ir(2)—C(22)	2.09(7)	Ir(2)—C(54)	2.20(4)
Ir(3)—C(34)	1.88(5)	Ir(3)—C(52)	2.10(3)
Ir(4)—C(40)	2.00(5)	Ir(3)—C(54)	2.08(4)
Ir(4)—C(42)	1.88(5)		
Ir(4)—C(44)	2.14(7)		

the carboalkoxy group is bonded to an iridium atom of the basal plane: the stability of this monoanion could be attributed to the delocalization of the negative charge (brought by the negatively charged alkoxy group) through the Ir_4 cluster unit. It also seems reasonable to assume that some polarization is maintained in the carboalkoxy group, in order to explain alcoholysis by attack of the entering nucleophile.

The $[Ir_4(CO)_{11}(COOR)]^-$ anion is the first compound formed when $Ir_4(CO)_{12}$ is treated with alkaline agents in an alcoholic medium, as for example in the synthesis of the $[HIr_4(CO)_{11}]^-$ anion. This can be proved by monitoring the IR spectrum of the solution, which shows that the characteristic 2035 cm^{-1} band due to the terminal CO's of $[Ir_4(CO)_{11}(COOR)]^-$ appears before the absorption band at 2010 cm^{-1} due to the $[HIr_4(CO)_{11}]^-$ anion. This is probably due to the reaction of $Ir_4(CO)_{12}$ with some alkoxide anion generated in solution according to the equilibrium:

$$OH^- + CH_3OH \rightleftharpoons CH_3O^- + H_2O$$

The formation of water and the excess of alkaline agents subsequently leads to the hydrolysis of the ester group with formation of the hydrido species. The mechanism of formation of the hydrido species can thus be rationalized by the following steps, both of which have been experimentally verified:

$$Ir_4(CO)_{12} + ROH + OH^- \rightarrow [Ir_4(CO)_{11}(COOR)]^- + H_2O$$

$$[Ir_4(CO)_{11}(COOR)]^- + OH^- + H_2O \rightarrow [HIr_4(CO)_{11}]^- + ROH + HCO_3^-$$

Experimental

All reactions were carried out under a carbon monoxide or nitrogen atmosphere. Solvents were purified and dried by standard methods. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer: the spectra were calibrated with polystyrene. Nuclear magnetic resonance spectra (Table 1) were recorded on a Varian Neva NV14 spectrometer at 60 MHz; chemical shifts (δ) are reported in ppm downfield from internal TMS. $Ir_4(CO)_{12}$ was prepared by the carbonylation of K_2IrCl_6 [7].

Synthesis of $[NMe_2Bz_2][Ir_4(CO)_{11}(COOCH_3)]$ *(I)*

a) From $Ir_4(CO)_{12}$ *and MeONa.* A suspension of $Ir_4(CO)_{12}$ (0.492 g, 0.44 mmol) in dry methanol (20 ml) was stirred at room temperature with 1.78 ml of a 1 *M* solution of MeONa in dry methanol [molar ratio $Ir_4(CO)_{12}$/MeONa = 4/1] until all the iridium carbonyl had reacted (~8 hours). The resulting orange-yellow solution was dropped into a stirred solution of $[NMe_2Bz_2]Cl$ (0.65 g) and KCl (0.5 g) in water (75 ml). The yellow precipitate which was obtained was collected by filtration, washed with water (3 X 10 ml) and vacuum dried. Yield 80%. Crystals can be obtained by layering heptane over a dichloromethane solution under a carbon monoxide atmosphere. The product is best stored under a carbon monoxide atmosphere. Analysis Found: C, 25.35; H, 1.53; Ir, 56.21; N, 0.98. Calcd. for $C_{29}H_{23}Ir_4NO_{13}$: C, 25.26; H, 1.70; Ir, 56.48; N, 1.02%. The $(PPh_4)^+$, $(AsPh_4)^+$, $(PPN)^+$, and $[Co(\eta_5\text{-}Cp)_2]^+$ salts were obtained similarly.

b) From $Ir_4(CO)_{12}$ *and* K_2CO_3. A suspension of $Ir_4(CO)_{12}$ (0.457 g, 0.41 mmol) in dry methanol (25 ml) was stirred with anhydrous K_2CO_3 (0.32 g, 2.31 mmol) until all the iridium carbonyl had reacted (about 12 hours). The resulting yellow solution was filtered and treated as above. Yield 75%.

Synthesis of $PPN[Ir_4(CO)_{11}(COOC_2H_5)]$

This compound was prepared as described for I but using dry ethanol (15 ml), $Ir_4(CO)_{12}$ (0.5 g, 0.45 mmol) and EtONa (1.03 *M*, 1.5 ml; molar ratio $Ir_4(CO)_{12}$/EtONa = 1/3.4). The reaction was complete after 10 hours. 75% yield.

Reaction of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ *with EtOH*

A suspension of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ (0.205 g, 0.14 mmol) in dry ethanol (40 ml) was stirred for 1 hour at 50°C. The hot solution was filtered, then cooled to —10°C. The resulting yellow crystals were filtered off, washed with cold ethanol (2 X 10 ml) and vacuum dried. The product was recovered in about 80% yield. The NMR spectrum ($CDCl_3$, 28°C) showed a complete conversion from the methyl to the ethyl derivative.

Reaction of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ *with* Pr^iOH

A suspension of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ (0.417 g, 0.28 mmol) in dry isopropanol (60 ml) was stirred for 90 minutes at 60°C under a nitrogen atmosphere. The hot solution was filtered and then cooled to —10°C. The yellow compound was filtered off, washed with cold isopropanol (3 X 10 ml) and vacuum dried. The product was recovered in about 80% yield. The NMR spectrum ($CDCl_3$, 28°C) showed both the methyl and isopropyl signals in a ratio consistent with a 65% conversion.

Reaction of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ *with acetic acid*

A solution of $(PPh_4)[Ir_4(CO)_{11}(COOMe)]$ (0.512 g, 0.35 mmol) in THF (50 ml) was treated with 5 ml of acetic acid and stirred for 30 minutes. A green-yellow precipitate of $Ir_4(CO)_{12}$ separated from the solution, which was filtered and washed with THF (5 X 10 ml) and n-hexane. Yield 95%.

Reaction of (PPN)[$Ir_4(CO)_{11}(COOMe)$] with K_2CO_3

A suspension of (PPN)[$Ir_4(CO)_{11}(COOMe)$] (0.986 g, 0.59 mmol) was stirred, under a carbon monoxide atmosphere, with K_2CO_3 (0.8 g, 5.8 mmol) in methanol (50 ml) containing 2% water. After 1 hour the product was separated by addition of a solution of KCl (0.5 g), (PPN)Cl (0.5 g) and MeOH (1 ml) in water (50 ml). The compound was filtered, washed with water (3 × 10 ml) and vacuum dried. Yield 95%. The product showed an IR spectrum identical to that of an authentic sample of (PPN)[$HIr_4(CO)_{11}$].

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9 Supplementary material has been deposited as a NAPS document. Order from NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only $0.00 for photocopies or $3.00 for microfiche. Outside the U.S. and Canada add postage of $3.00 for photocopy and $1.00 for microfiche.

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