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Structure Expansion of the Ir_4 Cluster Core Induced by the Short Bite of the 2-(Diphenylphosphino)pyridine Ligand. Reaction of $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ with $[Cu(NCCH_3)_4]BF_4$ and $AgPF_6$ Leading to Higher-Nuclearity Ir_4Cu and Ir_4Ag Cluster Compounds

Carmela G. Arena,[1a] Dario Drommi,[1a] Felice Faraone,*[,1a] Maurizio Lanfranchi,[1b]
Francesco Nicolò,[1a] and Antonio Tiripicchio[1b]

Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare dell'Università, Salita Sperone 31, Villaggio S. Agata, I-98166 Messina, Italy, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, Viale delle Scienze, I-43100 Parma, Italy

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$[Ir_4(CO)_{11}Br]NEt_4$ reacts with Ph_2PPy, in the molar ratio 1:2, in dichloromethane solution, to give $[Ir_4(CO)_{10}(Ph_2PPy)_2]$, **1**. In this compound the tetrahedral Ir_4 cluster can be seen also as a trigonal pyramid with the three basal edges bridged by carbonyls lying roughly in the basal plane. The two Ph_2PPy act as monodentate P-bonded ligands and are coordinated at two basal iridium atoms occupying an axial and an equatorial position, respectively. The occurrence in $CDCl_3$ solution, at room temperature, of a scrambling process of the Ph_2PPy ligands between equatorial and axial positions was evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. At lower temperature this process is frozen. Compound **1** was structurally characterized by an X-ray study. The complex **1** reacts with $[Cu(NCCH_3)_4]BF_4$ and $AgPF_6$, in dichloromethane solution, in the molar ratio 1:1, affording, almost quantitatively, the ionic compounds $[Ir_4M(CO)_{10}(Ph_2PPy)_2]Y$ (**2**, M = Cu, Y = BF_4; **3**, M = Ag, Y = PF_6). The reaction of **1** with $[Au(tht)]PF_6$ (tht = tetrahydrothiophene) proceeds similarly, but the reaction product was not fully characterized. A full characterization of the acetone solvate of **2** was obtained by an X-ray crystal structure analysis. The cation of **2** consists of a trigonal bipyramid Ir_4Cu core, with the copper atom in an axial position; the copper atom is formally five-coordinated being bonded to three iridium atoms and to two nitrogen atoms of the Ph_2PPy ligands.

Introduction

Homo- and heterobimetallic complexes containing the metal centers held close together by the geometric requirements of the bridging short bite of the 2-(diphenylphosphino)pyridine (Ph_2PPy) ligand can give rise to transfer of ligands from one metal to the other, intramolecular redox processes, cooperation between the metal centers in the substrate activation, and making or breaking of the metal−metal bond.[2−11] Starting from the mononuclear complexes *trans*-$[Rh(CO)(Ph_2PPyOMe)_2Cl]$ or *cis*-$[Rh(CO)_2(Ph_2PPyOMe)Cl]$ (in equilibrium in solution with the species *trans*-$[Rh(CO)(Ph_2PPyOMe)(\mu\text{-}Cl)]_2$), in which the $Ph_2PPyOMe$ ($Ph_2PPyOMe$ = 2-(diphenylphosphino)-6-methoxypyridine) acts as monodentate P-bonded ligand, by reacting with $[Cu(NCCH_3)_4]BF_4$, we synthesized[12] the compound $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4{\cdot}CH_2Cl_2$. This compound contains two rhodium atoms linked by a double chloride bridge; the copper and rhodium atoms are not involved in a metal−metal bond, and the copper center is almost linearly coordinated by the pyridine nitrogen atoms of the $Ph_2PPyOMe$ ligands. Now we find that the presence of monodentate P-bonded Ph_2PPy ligands on two metal atoms of a tetrahedral cluster may induce the insertion of a group 11 metal ion into the cluster core; the coordination of pyridine nitrogen atoms to a group 11 metal ion promotes the process of expansion of the cluster core to higher nuclearity. To our knowledge, such a process has not been reported to date.

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Experimental Section

Established methods were used to prepare the compounds $[Ir_4(CO)_{11}Br]NEt_4$,[13a] $[Ir_4(CO)_{10}(PPh_2CH_3)_2]$,[13b] $[Cu(NCCH_3)_4]BF_4$,[14] [Au(tht)Cl][15] (tht = tetrahydrothiophene), and Ph_2PPy.[2] All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as Nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX R300.

^1H NMR spectra were referenced to internal tetramethylsilane, and $^{31}P\{^1H\}$ spectra, to external 85% H_3PO_4; positive chemical shifts are for all nuclei to higher frequency. Elemental analyses were performed by Redox snc, Cologno Monzese, Milano, Italy.

Syntheses. $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ (1). A mixture containing $[Ir_4(CO)_{11}Br]NEt_4$ (100 mg, 0.077 mmol) in dichloromethane (50 mL) was cooled to −10 °C, and then Ph_2PPy (40.78 mg, 0.155 mmol) in the same solvent (20 mL) was added. The mixture was stirred for about 40 min. During this time the solution turns yellow-orange. Then the temperature was slowly raised to 0 °C and the volume of the solution was reduced to ca. 5 mL by removing the solvent at reduced pressure. The solution was chromatographed on a SiO_2 column saturated with hexane. A yellow orange band was eluated with a 1:4 CH_2Cl_2−hexane mixture; then using methanol a yellow fraction containing $[Ir_4(CO)_{11}Br]NEt_4$ was separated. The yellow orange solution was evaporated at reduced pressure to give the product. Yield: 75% (90.99 mg; 0.058 mmol).

Anal. Calc for $C_{44}H_{28}N_2Ir_4O_{10}P_2$: C, 33.54; H, 1.79; N, 1.78. Found: C, 33.92; H, 1.89; N, 1.52%. IR (Nujol): ν_{CO} 2063, 2034, 1986, 1984, 1861, 1813, and 1780 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 10.44 ppm and −20.89; ^1H ($CDCl_3$) δ 8.7 ppm (6-H, Py).

$[Ir_4Cu(CO)_{10}(Ph_2PPy)_2]BF_4$ (2). To a dichloromethane solution (50 mL) containing $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ (160 mg, 0.101 mmol) was added a solution (20 mL) of $[Cu(NCCH_3)_4]BF_4$ (31.72 mg, 0.101 mmol). The solution was stirred for 0.5 h. The solution color turns from yellow to red orange. The volume of the solution was reduced to ca. 5 mL in vacuo; by addition of petroleum ether (bp 40−60 °C), an orange solid was formed. This was separated by filtration, washed with benzene, and recrystallized from CH_2Cl_2−hexane (1:3) to give the product. Yield: 92% (174.5 mg; 0.093 mmol).

Anal. Calc for $C_{44}H_{28}N_2BCuF_4Ir_4O_{10}P_2$: C, 30.62; H, 1.64; N, 1.62; F, 4.4. Found: C, 30.75; H, 1.53; N, 1.63; F, 4.36. IR (Nujol): ν_{CO} 2077, 2048, 2038, 2020, 2002, 1841, and 1795 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 1.51 ppm; ^1H ($CDCl_3$) δ 8.9 ppm (6-H, Py).

$[Ir_4Ag(CO)_{10}(Ph_2PPy)_2]PF_6$ (3). This compound was obtained similarly to **2**, as a yellow solid, starting from $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ and $AgPF_6$. Yield: 82%.

Anal. Calc for $C_{44}H_{28}N_2AgF_6Ir_4O_{10}P_3$: C, 28.90; H, 1.54; N, 1.53; F, 6.23. Found: C, 29.51; H, 1.53; N, 1.32; F, 6.16. IR (Nujol): ν_{CO} 2074, 2030, 2018, 2001, 1991, 1840, and 1819 cm^{-1}. NMR: $^{31}P\{^1H\}$ ($CDCl_3$) δ 0.11 ppm; ^1H ($CDCl_3$) δ 8.82 ppm (6-H, Py).

Reaction of 1 with $[Au(tht)]PF_6$. $AgPF_6$ (23.76 mg, 0.094 mmol) was added to a stirred dichloromethane solution (20 mL) of [Au(tht)Cl] (30.13 mg, 0.094 mmol); after 0.5 h the precipitated AgCl was separated by filtration. To the resulting solution was added $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ (148.3 mg, 0.094 mmol), in the same solvent (60 mL). The mixture was stirred for 2 h. After this time the volume of the solution was reduced to ca. 10 mL and petroleum ether was added to give a brown orange solid. This was separated by filtration and washed with diethyl ether (30 mL) and dried in vacuo. Analytical and spectroscopic data indicate that the crude product is a mixture of almost two compounds which we are not able to separate.

Table 1. Crystal Data and Structure Determination Summary for 1 and $2\cdot0.5C_3H_6O$

	1	$2\cdot0.5C_3H_6O$
formula	$C_{44}H_{28}N_2O_{10}P_2Ir_4$	$C_{44}H_{28}CuIr_4N_2O_{10}P_2\cdot BF_4\cdot0.5C_3H_6O$
fw	1575.42	1754.93
cryst dimens, mm^3	0.15 × 0.16 × 0.10	0.12 × 0.18 × 0.21
cryst form	yellow, spheric	deep red, prismatic
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a, Å	14.082(3)	47.376(4)
b, Å	17.802(4)	10.036(2)
c, Å	17.901(4)	21.288(3)
β, deg	95.66(2)	98.68(2)
V, Å^3	4466(2)	10006(3)
Z	4	8
$F(000)$	2896	6480
T, °C	23	23
ρ_{calcd}, g/cm^3	2.343	2.330
μ, mm^{-1}	12.012 (Mo Kα)	21.788 (Cu Kα)
rel transm	0.875−0.273	1.000−0.763
λ(graphite monochrom), Å	0.710 73 (Mo Kα)	1.5418 38 (Cu Kα)
2θ range, deg	3−52 ($2\theta-\omega$ scan)	6−130 ($\theta-2\theta$ scan)
no. of measd reflcns	9913 ($\pm h,k,l$)	9294 ($\pm h,k,l$)
no. of unique reflcns	8823	8519
no. of obsd reflcns	3788 [$F \geq 7\sigma(F)$]	2758 [$I \geq 2\sigma(I)$]
no. of variables	559	311
R^a	0.0407	0.0608
R_w	0.0913^b	0.0647^c
GOF^d	1.06	1.09

^{a} $R = [\sum|F_o| - |F_c|]/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. ^{d} GOF $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$.

X-ray Data Collection and Structure Refinement of $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ (1) and $[Ir_4Cu(CO)_{10}(Ph_2PPy)_2]BF_4\cdot0.5C_3H_6O$ ($2\cdot0.5C_3H_6O$). Suitable crystals of the complexes **1** and $2\cdot0.5C_3H_6O$ have been obtained by slow evaporation of CH_2Cl_2−hexane and acetone solutions respectively. Diffraction data were collected on a Siemens R3m/V diffractometer (using graphite-monochromated Mo Kα radiation) for **1** and on a Siemens AED diffractometer (using graphite-monochromated Cu Kα radiation) for $2\cdot0.5C_3H_6O$. Lattice parameters were obtained from least-squares refinement of the setting angles of 50 (**1**) and 30 ($2\cdot0.5C_3H_6O$) accurately centered reflections with 18° ≤ 2θ ≤ 32° (**1**) and 36° ≤ 2θ ≤ 66° ($2\cdot0.5C_3H_6O$). A summary of the crystallographic data and the structure refinements is listed in Table 1. The intensities of three (**1**) and one ($2\cdot0.5C_3H_6O$) standard reflections, monitored after every 197 (**1**) and 100 ($2\cdot0.5C_3H_6O$) measurements, showed only statistical fluctuations for **1** and a decay of 22% for $2\cdot0.5C_3H_6O$. The reflection intensities were evaluated by the learnt-profile[16a] (**1**) and Lehmann and Larsen[16b] ($2\cdot0.5C_3H_6O$) procedures; then they were corrected for Lorentz−polarization effects. An absorption correction was applied by fitting a pseudo-ellipsoid to the azimutal scan data of 20 high-χ reflections[17a] for **1**, and an empirical absorption correction[17b] was applied for $2\cdot0.5C_3H_6O$.

The structure of **1** was solved by Patterson and Fourier methods and refined by full-matrix least squares, first by using

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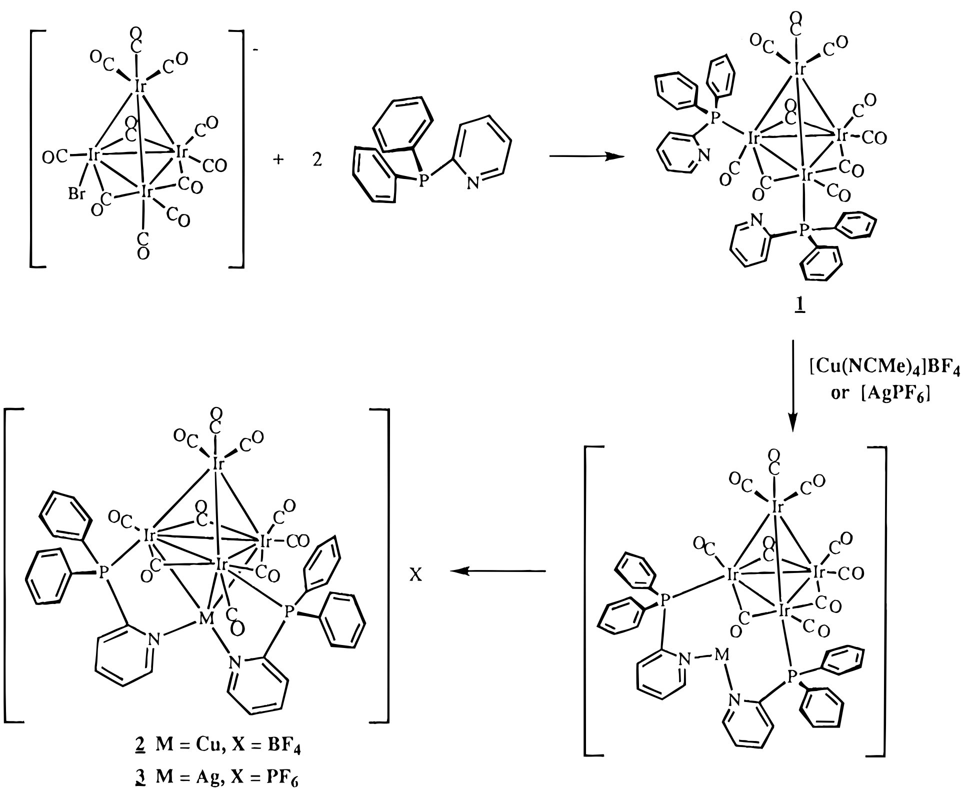
Scheme 1



SHELXTL-PLUS[18] and then SHELXL-93[19a] based on the F^2 values. The structure of $\mathbf{2}\cdot0.5C_3H_6O$ was solved by Patterson and Fourier methods and refined by full-matrix least squares, by using SHELX-76 and SHELXS-86.[19b,c] In the last cycles all the non-hydrogen atoms (**1**) and only the metals and the phosphorus atoms ($\mathbf{2}\cdot0.5C_3H_6O$) were refined anisotropically. The hydrogen atoms, apart those of the solvent of $\mathbf{2}\cdot0.5C_3H_6O$, were placed at their calculated positions and refined "riding" on the corresponding carbon atoms. The final weighting scheme was $w = \{\sigma^2(F_o^2) + [0.0171(\max(F_o^2,0) + 2F_c^2)]^2\}^{-1}$ for **1** and $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ (with $K = 0.698$ and $g = 0.0015$ at convergence) for $\mathbf{2}\cdot0.5C_3H_6O$. The highest remaining peak in the final difference map (close to the Ir atoms) was equivalent to about 2.03 (**1**) and 1.05 e Å^{-3} ($\mathbf{2}\cdot0.5C_3H_6O$). The final fractional coordinates are given as Supporting Information. Neutral-atom scattering factors and anomalous dispersion corrections for both compounds come from ref 20.

The final geometrical calculations were carried out with the PARST program[21] for both compounds.

Calculations for **1** were carried out with the Siemens package,[18] and for $\mathbf{2}\cdot0.5C_3H_6O$ on the Gould Powernode 6040 and Encore 91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Results

The reactions described are summarized in Scheme 1.

Synthesis of the Compounds. Treatment of $[Ir_4(CO)_{11}Br]NEt_4$ with Ph_2PPy in the molar ratio 1:2, in dichloromethane solution, afforded $[Ir_4(CO)_{10}(Ph_2PPy)_2]$, **1**, which was isolated as an orange solid, nonconducting in benzene solution and soluble in benzene and chlorinated solvents to give air-stable solutions. In **1** the Ir_4 cluster can be seen as a tetrahedron or alternatively as a trigonal pyramid with the three basal edges bridged by carbonyl groups lying roughly in the basal plane. The two Ph_2PPy act as monodentate P-bonded ligands and are coordinated at two basal iridium atoms occupying an axial and an equatorial position, respectively. In accordance, the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, shows two signals; they are broad at room temperature owing to the occurrence of a scrambling process of the ligands between equatorial and axial positions. At lower temperature this process is frozen; at 238 K two singlets at δ 10.44 and -20.89 ppm are observed. The scrambling process very likely can be related to a merry-go-round rotation of the bridging and equatorial carbonyl groups. A similar process has been observed, for example, in some Co_4 and Ir_4 carbonyl clusters.[22]

The IR spectrum of **1**, Nujol mull, shows both terminal and bridging carbonyl stretching frequency indicating that the compound retains the structure of the starting anion $[Ir_4(CO)_{11}Br]^-$.

In the compound **1** the uncoordinated pyridine nitrogen atoms of the Ph_2PPy ligands should act as donors toward coordinatively unsaturated metals or naked metal ions. This bridge-assisted synthetic strategy is very well established and was successfully used.[23] We

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tested this possibility considering the reactions of **1** with group 11 metal complexes able to give the corresponding naked metal ions.

The reaction of **1** with $[Cu(NCCH_3)_4]BF_4$ or $AgPF_6$, in dichloromethane solution, in the molar ratio 1:1, afforded, almost quantitatively, orange compounds, conducting in methanol solution (10^{-4}–5×10^{-4} M) as an 1:1 electrolyte. Analytical and spectroscopic data support their formulation as the ionic compounds $[Ir_4M(CO)_{10}(Ph_2PPy)_2]Y$ (**2**, M = Cu, Y = BF_4; **3**, M = Ag, Y = PF_6). The reaction of **1** with $[Au(tht)]PF_6$ (tht = tetrahydrothiophene) proceeds similarly, but we are not able to isolate an analytically pure product.

A full characterization of **2** was obtained by a X-ray crystal structure analysis. The cation consists of a Ir_4-Cu trigonal bipyramid cluster core, with the copper atom occupying an axial position; the copper atom results formally five-coordinated being bonded to three iridium atoms and to the pyridine nitrogen atoms of the coordinated Ph_2PPy ligands.

The IR spectra, Nujol mull, of **2** and **3** are different from those of **1**, in the carbonyl stretching region; significantly the bridging carbonyl stretching frequencies of **2** and **3** are shifted to higher wavenumbers with respect to **1**. The crystal structure of **1** evidences that the Ir–C distances of bridging CO (and consequently the corresponding stretching frequencies) are affected by the presence of coordinated phosphorus on the iridium atoms bearing the bridging CO. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3**, in $CDCl_3$ solution, show a singlet at δ 1.51 and 0.11 ppm, respectively; the spectra are not temperature dependent in the range 298–238 K, indicating the lack of a scrambling process. In the absence of a fluxional process, the $^{31}P\{^1H\}$ NMR spectra support for **2** and **3** a symmetric structure with both Ph_2PPy ligands in an axial or equatorial position. Significantly, in the ^1H NMR spectrum, in $CDCl_3$ solution, the 6-hydrogen of the pyridine ring is shifted to higher frequency with respect to **1**, as usually observed when the pyridine nitrogen atom is coordinated to a metal center.

Crystal Structure of $[Ir_4(CO)_{10}(Ph_2PPy)_2]$ (1). A view of the molecular structure of **1** with the corresponding atom-labeling scheme is shown in Figure 1; selected bond distances and angles are given in Table 2. The Ir_4 cluster can be seen as a tetrahedron or alternatively as a trigonal pyramid with the three edges of the Ir(1)Ir(3)Ir(4) basal face bridged by carbonyl groups lying roughly in the basal plane (maximum deviation is 0.33 Å). The Ir–Ir distances and the Ir–Ir–Ir angles range from 2.704(1) to 2.781(1) Å and from 58.61(3) to 61.81(3)°, respectively. The Ir(2) atom, 6-coordinated, is bound to three terminal CO groups and to the basal Ir atoms which are 7-coordinated. The Ir(3) completes its coordination with two terminal carbonyls, whereas Ir(1) and Ir(4) are coordinated with a terminal carbonyl and a P atom from the Ph_2PPy molecule acting as monodentate ligand (the two P atoms being in an equatorial and an axial position with respect to the Ir(1)Ir(3)Ir(4) triangle). The Ir–C bonds involving terminal CO groups range from 1.77(3) to 1.96(3) Å and are much shorter than the corresponding ones for the bridging carbonyls (in the range 2.02(2)–2.20(2) Å). The shortest Ir–C bonds of the three (one symmetrical and two asymmetrical) bridging CO involve the Ir atoms carrying the P atoms. The two P atoms of the Ph_2PPy ligands are displaced by 2.073(5) and 0.723(6) Å, respectively, on opposite sides, with respect to the Ir(1)–Ir(3)–Ir(4) triangle.

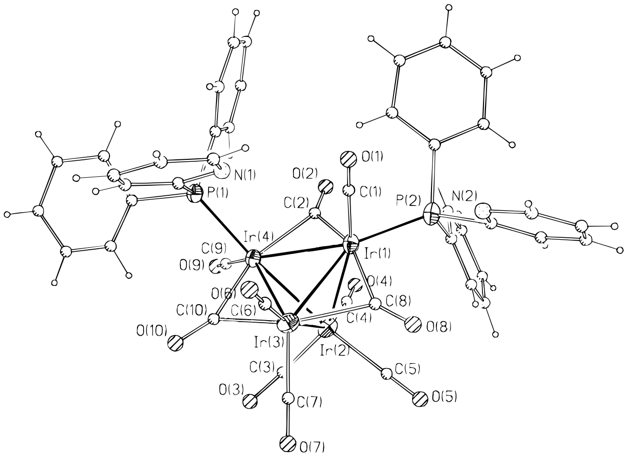

Figure 1. ORTEP view of the structure of the cluster **1** with the atomic numbering scheme. The ellipsoids for the Ir, P, and N atoms are drawn at the 40% probability level. The remaining atoms are drawn isotropically with arbitrary radii.

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Esd's for Non-Hydrogen Atoms of 1

Ir(1)–C(1)	1.87(2)	Ir(1)–C(8)	2.02(2)
Ir(1)–C(2)	2.07(2)	Ir(1)–P(2)	2.303(6)
Ir(1)–Ir(3)	2.709(1)	Ir(1)–Ir(4)	2.753(1)
Ir(1)–Ir(2)	2.760(1)	Ir(2)–Ir(3)	2.704(1)
Ir(2)–Ir(4)	2.711(1)	Ir(3)–Ir(4)	2.781(1)
Ir(2)–C(3)	1.79(3)	Ir(2)–C(4)	1.83(3)
Ir(2)–C(5)	1.96(3)	Ir(3)–C(6)	1.82(2)
Ir(3)–C(7)	1.87(2)	Ir(3)–C(10)	2.19(3)
Ir(3)–C(8)	2.20(2)	Ir(4)–C(9)	1.77(3)
Ir(4)–C(10)	2.07(3)	Ir(4)–C(2)	2.08(2)
Ir(4)–P(1)	2.319(5)		
Ir(3)–Ir(1)–Ir(2)	59.26(3)	Ir(3)–Ir(1)–Ir(4)	61.21(3)
Ir(3)–Ir(2)–Ir(4)	61.81(3)	Ir(4)–Ir(2)–Ir(1)	60.43(3)
Ir(3)–Ir(2)–Ir(1)	59.43(3)	Ir(4)–Ir(1)–Ir(2)	58.90(3)
Ir(2)–Ir(3)–Ir(1)	61.30(3)	Ir(2)–Ir(3)–Ir(4)	59.21(3)
Ir(1)–Ir(3)–Ir(4)	60.18(3)	Ir(2)–Ir(4)–Ir(1)	60.67(3)
Ir(2)–Ir(4)–Ir(3)	58.98(3)	Ir(1)–Ir(4)–Ir(3)	58.61(3)

The structure of **1** is, as expected, strictly comparable to that of $[Ir_4(CO)_{10}(PPh_3)_2]$,[24] where two PPh_3 replace the PPh_2Py ligands.

Crystal Structure of $[Ir_4Cu(CO)_{10}(Ph_2PPy)_2]BF_4 \cdot 0.5C_3H_6O$ ($2 \cdot 0.5C_3H_6O$). In the crystals of $2 \cdot 0.5C_3H_6O$, $[Ir_4Cu(CO)_{10}(Ph_2PPy)_2]^+$ cations, BF_4^- anions, and Me_2CO molecules of solvent are present. A view of the molecular structure of the cationic cluster with the corresponding atom-labeling scheme is shown in Figure 2; selected bond distances and angles are given in Table 3. This cationic cluster, in which the Ir_4Cu core can be described as a trigonal bipyramid, can be derived from the starting compound **1**, with the insertion of a Cu^+ cation capping the basal face carrying the three bridging carbonyls and the migration of one PPh_2Py ligand from an equatorial to an axial position in such a way to allow both ligands the coordination of the pyridinic nitrogens to the copper atom.

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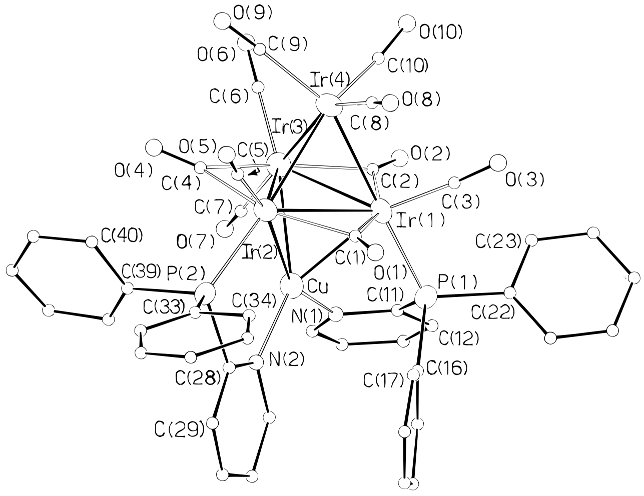

Figure 2. ORTEP view of the cationic cluster of $2\cdot0.5C_3H_6O$ with the atomic numbering scheme. The ellipsoids for the metal and P atoms are drawn at the 30% probability level. The remaining atoms are drawn isotropically with arbitrary radii.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex $2\cdot0.5C_3H_6O$

Ir(1)−Ir(2)	2.860(2)	Ir(1)−C(1)	2.06(4)
Ir(1)−Ir(3)	2.796(3)	Ir(1)−C(2)	2.10(3)
Ir(1)−Ir(4)	2.739(2)	Ir(1)−C(3)	1.79(5)
Ir(2)−Ir(3)	2.789(3)	Ir(2)−C(1)	2.14(4)
Ir(2)−Ir(4)	2.757(2)	Ir(2)−C(4)	2.07(4)
Ir(3)−Ir(4)	2.728(2)	Ir(2)−C(5)	1.92(4)
Ir(1)−Cu	2.713(5)	Ir(3)−C(2)	2.16(3)
Ir(2)−Cu	2.786(5)	Ir(3)−C(4)	2.22(4)
Ir(3)−Cu	2.733(5)	Ir(3)−C(6)	1.93(5)
Ir(1)−P(1)	2.336(10)	Ir(3)−C(7)	1.87(4)
Ir(2)−P(2)	2.319(8)	Ir(4)−C(8)	1.92(4)
Cu−N(1)	2.13(3)	Ir(4)−C(9)	2.01(4)
Cu−N(2)	1.99(2)	Ir(4)−C(10)	1.81(5)
Ir(4)−Ir(1)−Cu	108.2(1)	Ir(2)−Ir(3)−Cu	60.6(1)
Ir(3)−Ir(1)−Cu	59.5(1)	Ir(2)−Ir(3)−Ir(4)	60.0(1)
Ir(3)−Ir(1)−Ir(4)	59.0(1)	Ir(1)−Ir(3)−Cu	58.8(1)
Ir(2)−Ir(1)−Cu	59.9(1)	Ir(1)−Ir(3)−Ir(4)	59.4(1)
Ir(2)−Ir(1)−Ir(4)	59.0(1)	Ir(4)−Ir(3)−Cu	108.0(1)
Ir(2)−Ir(1)−Ir(3)	59.1(1)	Ir(2)−Ir(4)−Ir(3)	61.1(1)
Ir(1)−Ir(2)−Cu	57.4(1)	Ir(1)−Ir(4)−Ir(3)	61.5(1)
Ir(1)−Ir(2)−Ir(4)	58.3(1)	Ir(1)−Ir(4)−Ir(2)	62.7(1)
Ir(1)−Ir(2)−Ir(3)	59.3(1)	Ir(2)−Cu−Ir(3)	60.7(1)
Ir(4)−Ir(2)−Cu	105.7(1)	Ir(1)−Cu−Ir(3)	61.8(1)
Ir(3)−Ir(2)−Cu	58.7(1)	Ir(1)−Cu−Ir(2)	62.7(1)
Ir(3)−Ir(2)−Ir(4)	58.9(1)	N(1)−Cu−N(2)	102.5(11)
Ir(1)−Ir(3)−Ir(2)	61.6(1)		

Apart from the Ir(1)−Ir(2) bond, 2.860(2) Å, all values of the the Ir−Ir and Ir−Cu bonds are comparable ranging from 2.713(5) to 2.789(3) Å. The three carbonyl groups bridging the Ir(1)Ir(2)Ir(3) triangle are slightly pushed toward the axial Ir(4) atom with maximum deviation of 0.13(4) Å for C(4). Ir(1) and Ir(2) complete their coordination with a terminal CO and a P from Ph_2PPy, Ir(3) and Ir(4) with two and three terminal carbonyls, respectively. The Ph_2PPy molecules act as bidentate ligands through the P and N atoms bridging the Ir(1)Cu and Ir(2)Cu edges but with a different conformation. The five-membered-ring CuIr(2)P(2)C(28)N(2) is nearly planar with Ir(2) out of the mean plane of the other four atoms by 0.632(2) Å, while in the CuIr(1)P(1)C(11)N(1) ring the Ir(1) atom is out of the mean plane by 1.516(2) Å. The copper atom is 5-coordinate being bonded to three Ir atoms and to two pyridine N atoms, but the geometrical environment is difficult to describe: it could be seen as a severely distorted trigonal bypiramid with the equatorial positions occupied by the N(2), Ir(1), and Ir(3) atoms and the axial ones by the N(1) and Ir(2) atoms (the N(1)-CuIr(2) angle of 157.1(8)° is really very large).

The Ir−P bonds, 2.336(10) and 2.318(8) Å, are similar to those of the starting compound **1**, 2.303(6) and 2.319(5) Å, and the values of the Ir−C bonds of the bridging carbonyls follow the same trend of **1**.

Discussion

The results of the solid-state structure of **2** clearly show that the new Ir_4Cu and Ir_4Ag clusters are formed in the reaction of **1** with $[Cu(NCCH_3)_4]BF_4$ and $AgPF_6$. It is reasonable to assign to compound **3** a trigonal bipyramid arrangement of the Ir_4Ag core with the silver atom in axial position, considering that **3** shows the same spectroscopic properties as **2**. Few compounds containing the Cu or Ag atoms together with group VIII metals in a cluster, showing a trigonal bipyramid structure, have been reported, but in them the copper or silver atoms are in an almost tetrahedral arrangement.[25,26]

Some insights into the pathway of formation of **2** or **3** emerge considering that $[Ir_4(CO)_{10}(PPh_2CH_3)_2]$ does not react with $[Cu(NCCH_3)_4]BF_4$ to give an Ir_4Cu cluster; this indicates it is not the basicity of the metal framework but the presence of the coordinated Ph_2PPy monodentate ligands in **1** that is the factor that induces the formation of the Ir_4Cu or Ir_4Ag clusters.

The reaction of **1** with $[Cu(NCCH_3)_4]BF_4$ or $AgPF_6$, in CH_2Cl_2 solution, occurs rapidly and produces **2** and **3** almost quantitatively; with monitoring of the reaction course by NMR and IR spectroscopy, no intermediates have been detected. Very likely the first reaction step is the coordination of the naked Cu or Ag ions to pyridine nitrogen atoms of the Ph_2PPy ligands. In this transient intermediate the cluster core is not modified with respect to **1**, but the scrambling process between equatorial and apical Ph_2PPy ligands stops owing to pyridine nitrogen coordination to Cu or Ag ions; the Ph_2PPy ligands assume an apical position to favor the coordination of the metal ion to both the ligands.

An analogous step was evidenced[12] in the reaction of *trans*-$[Rh(CO)(Ph_2PPyOMe)_2Cl]$ or *cis*-$[Rh(CO)_2(Ph_2PPyOMe)Cl]$ (in equilibrium, in solution, with the species *trans*-$[Rh(CO)(Ph_2PPyOMe)(\mu\text{-}Cl)]_2$) with $[Cu(NCCH_3)_4]BF_4$. The reaction product $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$ contains two rhodium atoms linked by two bridging chloride ligands whereas the copper and rhodium atoms are not involved in metal−metal bonds; the copper center is almost linearly coordinated by the pyridine nitrogen atoms of the $Ph_2PPyOMe$ ligands.

In the intermediate, the coordinated copper or silver ions are involved in metal−metal bonds and cap a triangular face of the starting Ir_4 cluster to afford an Ir_4Cu or Ir_4Ag trigonal bipyramidal cluster. In complex **1**, the Ph_2PPy monodentate P-ligands act as arms; they

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bind the metal ions and bring them to Ir_4 cluster. To our knowledge the expansion of the cluster core to higher nuclearity induced by the presence of pendant ligands is not a process reported to date. The methods available for the introduction of fragments containing the silver or copper atoms into a tetrahedral polynuclear framework involve reaction of an anionic tetrahedral cluster with a group 11 metal containing cationic complex. The driving force of these reactions seems to be the interaction between the cation and anion species. Our attempts to introduce fragments containing group 11 metals into the Ir_4 carbonyl cluster core raising the basicity of the metal centers by substitution of CO with PPh_2Me failed; in fact, we have verified that $[Ir_4(CO)_{10}(PPh_2CH_3)_2]$ does not react with the species $[Cu(NCCH_3)_4]BF_4$, $[Cu(PPh_3)]PF_6$, $[Au(tht)]PF_6$, and $[Au(PPh_3)]PF_6$.

Braunstein and co-workers reported[26] that the cluster anions $[MCo_3(CO)_{12}]^-$ (M = Fe, Ru) react with $[\{Cu(PPh_3)Cl\}_4]$ and $[Au(PPh_3)Cl]$ to give $[MCo_3(CO)_{12}\{\mu_3\text{-}Cu(PPh_3)\}]$ and $[RuCo_3(CO)_{12}\{\mu_3\text{-}Au(PPh_3)\}]$, respectively. The derivative $[FeCo_3(CO)_{12}\{Au(PPh_3)\}]$ has been prepared[27] by the direct reaction of the cluster anion $[FeCo_3(CO)_{12}]^-$ with an equivalent amount of (triphenylphosphine)gold(I) nitrate. The structures of these pentametallic clusters consist of a trigonal bipyramid with the copper or gold atoms situated at one apex. The anionic clusters $[Fe_4(AuPEt_3)(CO)_{13}]^-$ and $[Fe_4(CuPPh_3)(CO)_{13}]^-$ have been also synthesized[28] starting from $[Fe_4(CO)_{13}]^{2-}$. The X-ray strucure shows that, in the solid state, the copper derivative adopts a tetrahedral arrangement for the iron atoms with the copper atom from $CuPPh_3$ capping one face, while in the gold derivative a butterfly Fe_4 core butterfly is present containing μ-CO; interconversion between tetrahedral and μ-CO-containing butterfly clusters was detected in solution. It is worthwhile mentioning[25] that in $[Ru_4(MPPh_3)(H)_3(CO)_{12}]$ (M = Cu, Ag, Au), the copper− and silver−tetraruthenium clusters adopt a trigonal bipyramid arrangement, with Cu and Ag in axial positions, while the gold derivative adopts a structure in which $AuPPh_3$ bridges an edge of an Ru_4 tetrahedron. Very likely the reaction of **1** with $[Au(tht)]PF_6$ gives a mixture of structural isomers which we were not able to separate.

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Supporting Information Available: Tables S1−S12, giving fractional atomic coordinates and *U* values for the non-hydrogen atoms, hydrogen atom coordinates, anisotropic thermal parameters, and complete bond lengths and bond angles for compounds **1** and **2** (19 pages). Ordering information is given on any current masthead page.

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