Structure and Reactivity Studies of the Unusual Peroxo-Bridged Complex, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(Ph_2PCH_2PPh_2)_2]$: The First Compound Having a Peroxide Moiety Bridging a Metal–Metal Bond

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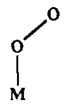
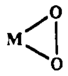
Abstract: Reaction of the diiodo complex $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**; dppm = $Ph_2PCH_2PPh_2$) with oxygen gives an unusual peroxo-bridged complex, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**), in which the bridging dioxygen group is accompanied by a metal–metal bond. The reactivity of this species has been investigated. Thus, reaction of SO_2 with **2** yields the sulfate-bridged compound $[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]$ (**3**), which is also produced in the reaction of **2** with $CuSO_4$ and in the protonation of **2** with H_2SO_4, with release of H_2O_2. Reaction of **2** with NO_2 and NO affords the nitrate- and nitrosyl-bridged compounds $[Ir_2I_2(CO)_2(\mu\text{-}X)(dppm)_2][NO_3]$ (X = NO_3 (**4a**); NO (**5**)), respectively. The reaction with CO in CH_2Cl_2/CH_3OH yields two compounds together with CO_2. One of the species is identified as $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dppm)_2][I]$, while the other one is shown to be a dioxygen compound, $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]$ (**6**), formed via formal CO insertion into the Ir–Ir bond of **2**. In contrast, isocyanides (RNC; R = ^iPr, ^tBu) are not oxidized by **2**; instead the hydroxide-bridged methoxycarbonyl species $[Ir_2(CO_2CH_3)(RNC)_3(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (R = ^iPr (**7**); ^tBu (**8**)) are obtained through involvement of the methanol solvent. Reaction of **2** with HCl yields two tetrahalide isomers $[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ (**9a**,**b**). Attempted reactions with NO^+, $HBF_4{\cdot}OEt_2$, and $CH_3SO_3CF_3$ gave rise to the hydroxide-bridged complex $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2]^+$ (**10**), through involvement of adventitious water; although under dry conditions, reaction with NO^+ yields **4**, with the appropriate anion. The structures of **2** and **6** have been determined by X-ray crystallography. Complex **2** crystallizes in the tetragonal space group $P4_12_12$ with $a = 14.647(2)$ Å, $c = 27.973(4)$ Å, $V = 6001(1)$ Å^3, and $Z = 4$ and has refined to $R = 0.061$ and $R_w = 0.093$ on the basis of 3585 observations and 169 parameters varied. Complex **6** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 30.110(8)$ Å, $b = 15.678(6)$, $c = 12.020(6)$ Å, $V = 5674(7)$ Å^3, and $Z = 4$ and has refined to $R = 0.056$ and $R_w = 0.064$ on the basis of 2598 observations and 328 parameters varied.

Introduction

The enormous interest in transition-metal dioxygen complexes over the past half century[1-3] has stemmed in a large part from the importance of dioxygen complexation to biological systems[2] and from the involvement of such complexes in the catalytic oxidation of organic substrates.[3] In the large number of dioxygen complexes known, the O_2 ligand has demonstrated a variety of coordination modes (**a**–**f**). Although most species fit into the first four types, as classified by Vaska in 1976,[1d] a few examples of structural types **e**[4] and **f**[5] are also known.


(**a**)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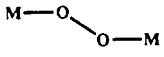
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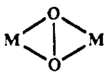
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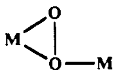
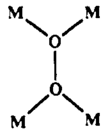

(**e**)


(**f**)

With the exception of cobalt, for which a large number of binuclear complexes is known,[2b,6] most studies have dealt with mononuclear O_2 species. As part of a continuing study on the activation of small molecules by binuclear complexes, we discovered that the electron-rich complex $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) formed a novel dioxygen adduct in which the dioxygen coordination mode did not belong to one of those previously noted (**a**–**f**). Instead a new bonding mode (**g**) was observed, in which the bridging peroxo moiety was

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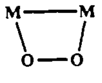
(g)

accompanied by a metal–metal bond.[7] It was therefore of interest to investigate the reactivity of this new structural class. In this paper we present the complete details of the structural determination of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ and a description of its chemistry. A preliminary report of some of this work has appeared.[7]

Experimental Section

All solvents were dried and distilled before use. Reactions were performed with use of standard Schlenk procedures unless otherwise noted. Dinitrogen was passed through columns of Ridox and type 4A molecular sieves before use, to remove traces of oxygen and water, respectively. Hydrated iridium(III) chloride was purchased from Johnson Matthey; $NOBF_4$, $NOPF_6$, $CH_3SO_3CF_3$, and bis(diphenylphosphino)methane (dppm) were obtained from Aldrich, and *i*-propyl isocyanide and *tert*-butyl isocyanide from Strem. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc. The compound $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) was prepared as previously reported.[8]

The ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer, and infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl windows, 0.5-mm path length) unless otherwise indicated. Spectral parameters for the compounds prepared are found in Table I. Conductivity measurements were carried out on a Yellow Springs Instruments Model 31 conductivity bridge, with solutions of approximately 10^{-3} M concentration. Elemental analyses were performed by the microanalytical service within the department.

(a) Preparation of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (2). A CH_2Cl_2 solution of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) (100 mg, 0.078 mmol, in 25 mL) was stirred in a flask open to air for several hours, during which time a dark-purple microcrystalline solid precipitated. The red-orange solution was transferred to another flask, while the purple solid was washed with two 5-mL portions of CH_2Cl_2 and the washings added to the mother liquor. The solution was again stirred for several hours and a second crop of the purple solid collected in the same manner as the first. This process was repeated several times, ultimately yielding compound **2** in about 70% yield. The compound could also be prepared by passing dioxygen through the solution. Anal. calcd for $Ir_2I_2P_4O_4C_{52}H_{44}$: C, 41.78, H, 2.97. Found: C, 41.44; H, 2.91.

(b) Reaction of 2 with SO_2. Sulfur dioxide was passed through a CH_2Cl_2 suspension of **2** (60 mg, 0.040 mmol, in 10 mL) at a rate of ca. 0.2 mL/s, causing an immediate color change from dark purple to bright yellow. After being stirred for an additional 0.5 h, the solution was concentrated to ca. 2 mL followed by addition of 10 mL of diethyl ether, resulting in the precipitation of $[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]\cdot CH_2Cl_2$ (**3**) as a yellow-orange solid (95% yield). Anal. calcd for $Ir_2I_2Cl_2SP_4O_6C_{53}H_{46}$: C, 38.72; H, 2.82; I, 15.43; S, 1.95. Found: C, 38.48; H, 2.86; I, 15.13; S, 2.47.

(c) Reaction of 2 with H_2SO_4. To a CH_2Cl_2 suspension of **2** (60.0 mg, 0.040 mmol, in 10 mL) was added 1 equiv of H_2SO_4 (1.1 μL in 3 mL of CH_3OH), causing an immediate color change to yellow-orange. The solution was stirred for 0.5 h, and the solvents were then removed under vacuum. The resultant product was spectroscopically identified as **3** (90% yield).

(d) Reaction of 2 with $CuSO_4$. The procedure was the same as in c, except 1 equiv of $CuSO_4$ was used. Compound **3** was isolated in 85% yield.

(e) Reaction of 2 with NO_2. The procedure was the same as in b, except that 2 equiv of NO_2 was used. An immediate color change to orange was observed. The product $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][NO_3]\cdot CH_2Cl_2$ (**4a**) was isolated as yellow microcrystals in 70% yield and was determined to be a 1:1 electrolyte in CH_3NO_2 ($\Lambda = 81.1\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. calcd for $Ir_2I_2Cl_2P_4O_8N_2C_{53}H_{46}$: C, 37.35; H, 2.66; N, 1.68. Found: C, 37.67; H, 2.78; N, 1.67.

(f) Preparation of $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][BF_4]$ (4b). To a CH_2Cl_2 solution of **4a** (79.0 mg, 0.050 mmol, in 10 mL) was added 55.0 mg of $NaBF_4$ (0.50 mmol, in 3 mL of CH_3OH). The mixture was stirred for 0.5 h followed by filtration. Concentration of the solution followed by washing with distilled water and addition of diethyl ether resulted in the isolation of **4b** in ca. 90% yield. Anal. calcd for $Ir_2I_2P_4F_4O_5NC_{52}BH_{44}$: C, 38.75; H, 2.75; N, 0.87; I, 15.75. Found: C, 39.09; H, 2.67; N, 0.99; I, 16.07.

(g) Reaction of 2 with NO. Nitric oxide was placed over a CH_2Cl_2 suspension of **2** (60.0 mg, 0.040 mmol, in 10 mL), causing the formation of a deep-orange solution in ca. 15 min. The solution was stirred for an additional 0.5 h, the volume was then reduced to ca. 2 mL, and a yellow-orange solid was precipitated upon addition of diethyl ether (75% yield). The product, $[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$ (**5**), was determined to be weakly conducting in CH_2Cl_2 ($\Lambda = 29.6\ \Omega^{-1}\ cm^2\ mol^{-1}$) but a normal 1:1 electrolyte in CH_3NO_2 ($\Lambda = 78.7\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. calcd for $Ir_2I_2P_4O_6N_2C_{52}H_{44}$: C, 40.16; H, 2.86; N, 1.80; I, 16.32. Found: C, 39.79; H, 3.08; N, 1.82; I, 16.81

(h) Reaction of 2 with CO. A stream of CO was passed through a CH_2Cl_2/CH_3OH (30 mL, 5:1) suspension of **2** (100.0 mg, 0.067 mmol) for 4 h, during which time a yellow solution was formed. The solvents were then removed under vacuum. Crystallization from CH_2Cl_2/diethyl ether afforded two distinctive crystalline solids. The yellow microcrystals were spectroscopically identified as $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$, and the pale-yellow crystals as $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (**6**). The two compounds were the only products observed by NMR spectroscopy; the relative yields of the two species varied from 1:1 to 1:3. Elemental analyses, even on hand-picked crystals of **6**, were highly variable owing to CH_2Cl_2 loss.

(i) Reaction of 2 with ^iPrNC. In a typical experiment, 36 μL (0.40 mmol) of ^iPrNC was added to compound **2** (60.0 mg, 0.040 mmol) in 25 mL of CH_2Cl_2/CH_3OH (5:1). A yellow solution was formed in ca. 5 h; concentration of the solution followed by addition of diethyl ether precipitated $[Ir_2(CO_2CH_3)(CN^iPr)_3(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (**7**) as a yellow crystalline solid (50% yield). Anal. calcd for $Ir_2I_2P_4O_4N_3C_{65}H_{69}$: C, 45.43; H, 4.06; N, 2.45. Found: C, 44.88; H, 4.27; N, 2.57.

(j) Reaction of 2 with ^tBuNC. The procedure was the same as for **7**, except ^tBuNC was used. The product, $[Ir_2(CO_2CH_3)(CN^tBu)_3(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (**8**), was isolated from CH_2Cl_2/diethyl ether as yellow crystals (70–75% yield). Anal. calcd for $Ir_2I_2P_4O_4N_3C_{68}H_{75}$: C, 46.39; H, 4.30; N, 2.39. Found: C, 46.68; H, 4.42; N, 2.49.

(k) Reaction of 2 with Excess HCl. Gaseous HCl was bubbled through a CH_2Cl_2 suspension of **2** (60.0 mg, 0.040 mmol, in 10 mL) for 1 min, causing the immediate formation of a yellow solution. After being stirred for an additional 0.5 h, the solution was concentrated to ca. 3 mL followed by addition of diethyl ether, resulting in the precipitation of $[Ir_2Cl_2I_2(CO)_2(dppm)_2]\cdot CH_2Cl_2$ (**9a**) as a microcrystalline solid (80% yield). Anal. calcd for $Ir_2I_2C_4P_4O_2C_{53}H_{46}$: C, 36.60; H, 2.67; Cl, 8.16; I, 14.59. Found: C, 36.53; H, 2.84; Cl, 8.09; I, 15.56.

Compound **9a** was also produced by reacting the solid **2** with HCl. The dark-purple solid immediately turned to orange upon purge with HCl.

(l) Reaction of 2 with 2 equiv of HCl. The procedure was the same as for **9a**, except that only 2 equiv of HCl (2.0 mL, 0.04 mmol) was syringed into a CH_2Cl_2 solution of **2** (60.0 mg, 0.040 mmol, in 20 mL). Isomer **9b**, $[Ir_2Cl_2I_2(CO)_2(dppm)_2]$, was obtained as a yellow solid 75–80% yield. Anal. calcd for $Ir_2I_2Cl_2P_4O_2C_{52}H_{44}$: C, 40.71; H, 2.90; Cl, 4.62. Found: C, 40.51; H, 2.95; Cl, 4.59.

(m) Reaction of 2 with $HBF_4\cdot OEt_2$. To a benzene suspension of **2** (60.0 mg, 0.040 mmol, in 10 mL) was added 1 equiv of $HBF_4\cdot OEt_2$ (5.7 μL). The mixture was stirred overnight, during which time the suspension turned to orange. Concentration followed by addition of diethyl ether afforded $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ (**10a**) as a yellow solid.

(n) Attempted Reaction of 2 with $CH_3SO_3CF_3$. The procedure was the same as for **10a**, except that 2 equiv of $CH_3SO_3CF_3$ (ca. 9 μL) was used, yielding $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][SO_3CF_3]$ (**10b**).

(o) Attempted Reaction of 2 with $NOBF_4$. To a mixture of **2** (100.0 mg, 0.67 mmol) and $NOBF_4$ (7.8 mg, 0.67 mmol) was added 10 mL of CH_2Cl_2. The mixture was stirred for ca. 3 h, during which time an orange solution was formed. Compound **10a** was obtained as a yellow solid in 85% yield.

The same compund was also produced in the presence of water. The procedure was the same as above except that, following addition of CH_2Cl_2, ca. 4 μL of H_2O was added to the mixture. A color change to orange was observed in ca. 10 min.

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Table I. Spectroscopic Data[a]

compd	IR (cm^{-1})[b]	NMR $\delta(^{31}P\{^1H\})$[c]	 $\delta(^1H)$[d]
$[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**)	2005 (vs) 1979 (st)[e]	−24.4	5.30 (m, 2 H) 4.02 (m, 2 H)
$[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]$ (**3**)	2038 (st) 2026 (st)[e] 1245 (w) 1140 (st) 952 (med) 800 (w)[f]	−17.6	4.92 (m, 4 H)
$[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][NO_3]$ (**4a**)	2049 (st, br)[e] 1518 (med) 1259 (w) 1040 (w) 780 (w)[g] 1340 (vs) 1023 (w) 700 (w)[h]	−20.0 (m) −26.1 (m)	5.91 (m, 2 H) 4.40 (m, 2 H)
$[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][BF_4]$ (**4b**)	2048 (vs)[e] 1519 (med) 1260 (w) 780 (w)[g]	−20.0 (m) −26.2 (m)	5.86 (m, 2 H) 4.32 (m, 2 H)
$[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$ (**5**)	2051 (vs) 2025 (w)[e] 1518 (s)[i] 1340 (vs) 1028 (w) 700 (w)[h]	−14.3 (s)	5.32 (m, 2 H) 4.44 (m, 2 H)
$[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]$ (**6**)	2048 (st) 2038 (st) 1645 (med)[e]	−28.2	3.94 (m, 2 H) 2.80 (m, 2 H)
$[Ir_2(CN^iPr)_3(CO_2CH_3)(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (**7**)	3190 (med)[k] 2193 (vs) 2180 (vs)[j] 1653 (st) 1625 (st)[e] 1036 (med)[l]	−8.1 (br) −11.8 (br)	4.42 (br, 2 H) 3.58 (br, 2 H) 3.31 (spt, 1 H) 3.23 (spt, 1 H) 3.18 (spt, 1 H) 2.60 (s, 3 H) 0.82 (d, 6 H) 0.78 (d, 6 H) 0.72 (d, 6 H)
$[Ir_2(CN^tBu)_3(CO_2CH_3)(\mu\text{-}CO)(\mu\text{-}OH)(dppm)_2][I]_2$ (**8**)	3188 (med)[k] 2181 (vs) 2174 (vs)[j] 1655 (vs) 1625 (vs)[e] 1070 (med)[l]	−9.1 (br) −12.1 (br)	3.50 (br, 4 H) 2.58 (s, 3 H) 0.83 (s, 9 H) 0.78 (s, 9 H) 0.75 (s, 9 H)
$[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ (**9a**)	2066 (st) 2031 (st)[e]	−13.9 (s)	4.97 (m, 2 H) 4.50 (m, 2 H)
$[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ (**9b**)	2025 (vs)[e]	−23.0 (s)	5.70 (m, 2 H) 5.03 (m, 2 H)
$[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ (**10a**)	3550 (w)[k] 2064 (st) 2032 (vs)[e]	−13.8 (s)	5.20 (m, 2 H) 4.17 (m, 2 H) 3.06 (q, 1 H)
$[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][SO_3CF_3]$ (**10b**)	3550 (w)[k] 2063 (st) 2031 (st)[e]	−13.7 (s)	5.22 (m, 2 H) 4.21 (m, 2 H) 3.07 (q, 1 H)
$[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][PF_6]$ (**10c**)	3550 (w)[k] 2062 (st) 2037 (st)[e]	−13.8 (s)	5.20 (m, 2 H) 4.05 (m, 2 H) 3.00 (q, 1 H)

[a] Abbreviations used: vs = very strong, st = strong, med = medium, w = weak, m = multiplet, q = quintet, d = doublet, s = singlet, spt = septet. [b] Nujol mull except compounds **10a–c**, CH_2Cl_2 cast. [c] Versus 85% H_3PO_4, 25 °C, in CD_2Cl_2. [d] Versus TMS, 25 °C, in CD_2Cl_2. [e] $\nu(CO)$. [f] $\nu(SO_4)$. [g] $\nu(\mu\text{-}NO_3)$. [h] $\nu(NO_3)$. [i] $\nu(NO)$. [j] $\nu(CN)$. [k] $\nu(OH)$. [l] $\nu(C\text{–}O)$. [m] See text.

(p) Reaction of 2 with NOPF$_6$. The procedure was the same as in o, except that 1 equiv of NOPF$_6$ was used, and compound **10c** was obtained as the PF$_6$ salt.

(q) Reaction of 2 with PPh$_3$. To a mixture of **2** (60.0 mg, 0.04 mmol) and PPh$_3$ (5.5 mg, 0.021 mmol) in 10 mL of CH_2Cl_2 was syringed ca. 0.5 mL (0.02 mmol) of gaseous HCl. After the reaction mixture was stirred for 1 h, the solvent was removed under vacuum. A mixture of several species was formed, but the appearance of OPPh$_3$ (ca. 30% yield) was confirmed by $^{31}P\{^1H\}$ NMR (δ 27.5) and IR (ν(P=O) = 1187 cm^{-1}) spectroscopy.

X-ray Data Collection. (a) $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (2). Dark-purple crystals of **2** were obtained by slow diffusion of atmospheric oxygen into a CH_2Cl_2 solution of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**). Although the crystals appeared as well-formed tetragonally elongated octahedral prisms, most did not diffract well; even the crystal chosen after many recrystallization attempts was of poorer diffraction quality than desired. The crystal was wedged into a capillary tube which was flame-sealed. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C using Mo K_α radiation. Unit cell parameters were determined from a least-squares refinement of the setting angles of 25 reflections in the range 19.9° ≤ 2θ ≤ 23.7°. Automatic peak search and reflection indexing programs established a tetragonal crystal system. The systematic absences ($00l$, $l \neq 4n$; $h00$, $h \neq 2n$) were consistent with the space groups $P4_12_12$ and $P4_32_12$. The former was established as the probable one on the basis of a successful refinement of the structure.

Intensity data were collected by using the $\theta/2\theta$ scan technique up to

Table II. Crystallographic Data for $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**) and $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (**6**)

compd	**2**	**6**
formula	$C_{52}H_{44}O_4P_4I_2Ir_2$	$C_{55}H_{48}Cl_4O_5P_4I_2Ir_2$
fw	1495.03	1692.91
space group	$P4_12_12$	$Pna2_1$
temp (°C)	22	–85
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)	
cell parameters		
a (Å)	14.647(2)	30.110(8)
b (Å)		15.678(6)
c (Å)	27.973(4)	12.020(6)
V (Å^3)	6001(1)	5674(7)
Z	4	4
ρ(calcd) (g cm^{-3})	1.655	1.982
no. of unique data collcd	4751 (*hkl*)	5407 (*hkl*)
no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	3585	2598
final no. of params refined	169	328
R	0.061	0.056
R_w	0.093	0.064

$2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak width on either side of the peak scan. Three reflections were chosen as intensity standards, being remeasured after every 120 min of X-ray exposure time. The mean decrease in the intensity was 11.3%, and a correction was applied assuming linear decay. The data were processed in the usual way with a value of 0.04 for *p* to downweight intense reflections,[9] and corrections for Lorentz and polarization effects and for absorption were applied.[10,11] Crystallographic data for **2** are shown in Table II.

(b) $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (6). Yellow crystals of **6** were obtained by slow diffusion of ether into a CH_2Cl_2 solution of the compound. A suitable crystal was mounted on a glass fiber with epoxy and optically centered in the X-ray beam of an Enraf-Nonius CAD4 automated diffractometer. The crystal was cooled to approximately –85 °C, using a cold-air stream apparatus (Air Jet Model XR-85-1, FTS Systems, Inc.), and all measurements were made at this temperature using Mo K_α radiation. The unit cell parameters were obtained at –85 °C from a least-squares refinement of the setting angles of 25 reflections in the range $13.5° \leq 2\theta \leq 20.6°$. The automatic peak search and reflection indexing programs generated an orthorhombic cell. The systematic absences ($0kl$, $k + l$ = odd; $h0l$, h = odd) led to the choice of space group as $Pna2_1$ or *Pnam* (a nonstandard setting of *Pnma*). $Pna2_1$ was established as the probable one on the basis of the successful refinement of the structure.

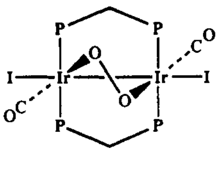
Intensity data were collected using the $\theta/2\theta$ scan technique to a maximum $2\theta = 50°$. Backgrounds were measured by extending the scan by 25% on each side of the calculated range. One reflection was chosen as a standard reflection, being remeasured at 120-min intervals of X-ray exposure time. The intensity of this reflection was found to fluctuate about its mean, suggesting movement of the crystal in the cold stream, but otherwise no decrease was noted; therefore no decay correction was applied. The data were processed in the usual way with a value of 0.04 used for *p* to downweight intense reflections.[9] Corrections for Lorentz and polarization effects and for absorption, using the method of Walker and Stuart, were applied to the data.[10,11] Crystallographic data for **6** are shown in Table II.

Structure Solution and Refinement. Both structures were solved in the respective space groups ($P4_12_12$ for **2**, $Pna2_1$ for **6**) by using direct methods.[12] The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Full-matrix least-squares refinements proceeded, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/(\sigma^2(F_o^2))$. Atomic scattering factors and anomalous dispersion terms were taken from the usual tabulations.[13–15] Positional parameters for the hydrogen atoms were calculated from the geometries of their attached carbon, using C–H distances of 0.95 Å. All hydrogen atoms were included in the calculations with fixed thermal parameters 1.2 times those of the attached atoms and were constrained to ride on the attached atoms.

The final model for complex **2**, with 169 parameters varied, converged to values of $R = 0.061$ and $R_w = 0.093$. Attempts to refine in the enantiomorphic space group $P4_32_12$ resulted in higher residuals of $R = 0.080$ and $R_w = 0.115$, suggesting that $P4_12_12$ was the correct choice. In the final difference Fourier map, the 10 highest peaks were in the range 1.788–1.188 e/Å^3 and were primarily located near the phenyl carbon atoms. The final model for complex **6**, with 328 parameters varied, converged to values of $R = 0.056$ and $R_w = 0.064$. The 10 highest peaks in the final difference Fourier map were in the range 2.48–1.37 e/Å^3 and were primarily located near the iridium atoms.

Results and Discussion

The peroxo-bridged complex $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**) is readily obtained by exposing solutions of $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) to air or pure oxygen. All spectroscopic data support the formulation shown for **2**. In particular, the $^{31}P\{^1H\}$ NMR spectrum displays a singlet, indicating the chemical equivalence of all phosphorus nuclei, and the carbonyl stretches in the IR spectrum (2005, 1979 cm^{-1}) show the frequency increase expected upon oxidizing **1** (ν(CO) = 1948, 1741 cm^{-1}) to a binuclear Ir(II)/Ir(II) species.



(2)

A close inspection of the IR spectra for compounds **1** and **2** has failed to identify a band that can be unambiguously attributed to the O–O stretch in **2**, and attempts to obtain Raman spectra of **2** failed, owing to decomposition in the laser beam. The Ir(II)/Ir(II) formulation shown for **2** is not unusual in the context of small-molecule additions to binuclear Ir(I) complexes and is not unlike related alkyne-bridged products.[16] However, in the context of O_2 complexes, this peroxo-bridged formulation is unprecedented in requiring the presence of a metal–metal bond; no previous example was known in which a bridging peroxo unit was accompanied by a metal–metal bond. In order to confirm this unusual formulation and to determine whether the strain imposed on the bridging O_2 moiety by the metal–metal bond would result in unusual structural consequences within the complex, we undertook a structural determination of **2** by X-ray techniques.

The structure of **2**, shown in Figure 1, clearly confirms the peroxo-bridged formulation. Selected distances and angles for the compound are given in Tables III and IV. The complex has crystallographic 2-fold symmetry in which the 2-fold axis bisects the O_2 moiety and the Ir–Ir bond. As is typical for dppm-bridged complexes, both dppm ligands bridge the metals in a trans arrangement, and most parameters associated with these groups are normal.

The formulation of **2** as a peroxo-bridged species requires an Ir(II)/Ir(II) formulation and an Ir–Ir single bond. Consistent with these ideas, the Ir–Ir separation, at 2.705(1) Å, is short and clearly indicates that the metals are bonded; this distance is over 0.1 Å shorter than that observed in the precursor (2.8159(5) Å).[8] The resulting geometry at each metal is distorted octahedral, in which the major distortions result from the strain imposed by the small bridging O_2 group. As a result of the short Ir–Ir separation, the two halves of the complex are significantly staggered, with torsion angles about the Ir–Ir bond ranging from 16.4° to 20.7°.

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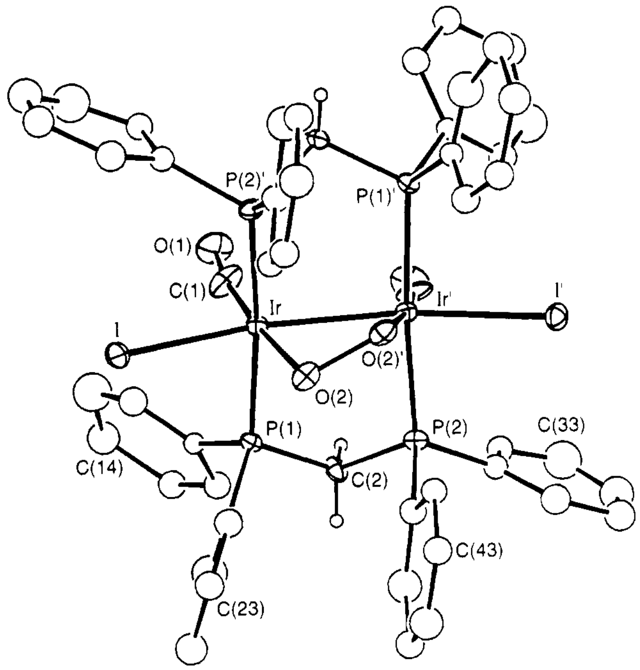


Figure 1. Perspective view of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**). Thermal ellipsoids are shown at the 20% level except for hydrogen atoms, which are shown artificially small for the methylene groups and omitted for the phenyl groups.

Table III. Selected Bond Distances (Å) in $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**)

	(a) Bonded Distances		
Ir–Ir′	2.705(1)	Ir–O(2)	2.04(1)
Ir–I	2.764(1)	Ir–C(1)	1.82(2)
Ir–P(1)	2.377(4)	O(1)–C(1)	1.22(2)
Ir′–P(2)	2.367(4)	O(2)–O(2)′	1.58(2)
	(b) Nonbonded Distances		
P(1)–P(2)	2.996(6)	Ir–I(2)′	2.83(1)

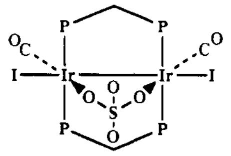
Table IV. Selected Angles (deg) in $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**)

	(a) Bond Angles		
Ir′–Ir–I	160.66(3)	P(1)–Ir–P(2)′	174.8(2)
Ir′–Ir–P(1)	94.6(1)	P(1)–Ir–O(2)	89.5(3)
Ir′–Ir–P(2)′	90.5(1)	P(1)–Ir–C(1)	89.6(6)
Ir′–Ir–O(2)	71.7(3)	P(2)′–Ir–O(2)	92.2(3)
Ir′–Ir–C(1)	101.3(7)	P(2)′–Ir–C(1)	89.5(6)
I–Ir–P(1)	88.5(1)	O(2)–Ir–C(1)	172.7(7)
I–Ir–P(2)′	86.6(1)	Ir–O(2)–O(2)′	102.0(4)
I–Ir–O(2)	89.4(3)	Ir–C(1)–O(1)	171(4)
I–Ir–C(1)	97.8(7)		
	(b) Torsion Angles		
P(1)–Ir–Ir′–P(2)	−16.4(2)	C(1)–Ir–Ir′–C(1)′	−17(1)
P(1)–Ir–Ir′–P(1)′	163.7(2)	Ir–O(2)–O(2)′–Ir′	−34.6(9)
O(2)–Ir–Ir′–O(2)′	−20.7(7)		

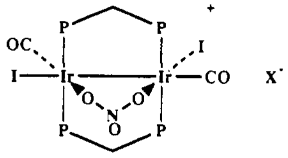
The Ir–I distance of 2.764(1) Å lies intermediate between the values of 2.6811(7) and 2.8032(8) Å in the precursor.[8]

Although the Ir–O(2) distance (2.04(1) Å) is normal, agreeing closely with such distances (2.00–2.07 Å) in mononuclear iridium peroxo complexes,[1d] as well as with those in some peroxo-bridged diplatinum species, such as $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]$,[17] the O(2)–O(2)′ separation, at 1.58(2) Å, is extremely long. Only $[La_2(N(SiMe_3)_2)_4(O_2)(OPPh_3)_2]$ appears to have a longer O–O distance (1.65(4) Å).[18] Typically peroxides, such as Na_2O_2 and BaO_2, display O–O distances of ca. 1.49 Å,[1e] and the O–O separation for binuclear peroxo-bridged compounds generally falls in the range from 1.40 to 1.50 Å.[1e,2b] Although it is tempting to attempt to rationalize this extremely long O–O distance on the basis of its bonding in the compound, the thermal ellipsoids associated with the oxygen atoms and the relatively poor diffraction quality of the crystal suggest that this abnormally long separation may be an artifact arising from systematic errors in the data. The contact between Ir and the distal oxygen of the O_2 unit (Ir–O(2)′), at 2.83(1) Å, is well outside of bonding distance, as expected for an $\eta^1{:}\eta^1$ peroxo binding mode. As is typical of peroxides, this unit is skewed about the O–O bond, yielding an Ir–O(2)–O(2)′–Ir′ torsion angle of 34.6°. This torsion angle is much less than is normally observed in peroxo-bridged compounds, where values between 60° and 80° appear more typical,[1e,17] and appears to be restricted by the presence of the Ir–Ir bond. This Ir–Ir bond also gives rise to an angle at O(2) (102.0(4)°) which is less than the range typically observed (110–120°) in the absence of metal–metal bonding.

It was of obvious interest to investigate the reactivity of this unusual peroxo moiety on the assumption that the inherent strain associated with this unit might give rise to unusual reactivity, either at the O_2 moiety or at the metal–metal bond. Passing SO_2 through a CH_2Cl_2 or benzene suspension of **2** causes an immediate reaction, as evidenced by the color change from dark-purple to yellow, and the complete dissolution of the otherwise rather insoluble precursor **2**. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of only **3**, as a symmetric species in which all phosphorus nuclei are chemically equivalent. Elemental analyses, which indicate one sulfur atom per complex molecule, and the IR spectrum, which shows three sulfate bands at 1245, 1140, and 952 cm^{-1}, suggest the presence of a bridging sulfate group.[19] By comparison, the analogous mononuclear complexes $[IrX(SO_4)(CO)(PPh_3)_2]$ (X = Cl, Br, I) showed sulfate bands at ca. 1300, 1170, 890, 860, and 670 cm^{-1},[20] and the sulfate-bridged diplatinum species $[Pt_2(\mu\text{-}OH)(\mu\text{-}SO_4)(PPh_3)_4][ClO_4]$ displayed similar stretches at 1275, 1155, and 887 cm^{-1}. On the basis of these data, the structure shown for $[Ir_2I_2(CO)_2(\mu\text{-}SO_4)(dppm)_2]$ (**3**), in which the $\mu\text{-}O_2$ unit is replaced by $\mu\text{-}SO_4$, is proposed. Compound **3** can also be obtained by reaction of **2** with H_2SO_4, with release of H_2O_2, or by reaction of **2** with $CuSO_4$.



(3)



X = NO_3 (**4a**), BF_4 (**4b**)

The O_2 adduct (**2**) also reacts readily with 2 equiv of NO_2 to give the nitrate-bridged product $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][NO_3]$ (**4a**). The IR spectra of **4a** show bands at 1518, 1259, 1040, and 780 cm^{-1} associated with the coordinated nitrate group and bands at 1340, 1023, and 700 cm^{-1} associated with the free nitrate anion. These latter three bands disappear upon replacement of the nitrate ion by tetrafluoroborate anion resulting from reaction of **4a** with $NaBF_4$, yielding **4b**. The bands for the coordinated nitrate group are comparable to those reported for a variety of related species.[20,21] Although compounds **3** and **4** are rather analogous, the $^{31}P\{^1H\}$ NMR spectra of **4a**,**b** show an AA′BB′ pattern, indicating that the two metal centers are inequivalent. This inequivalence most likely results from the arrangement of iodo and carbonyl ligands as shown in the sketch; the arrangement shown for **4** is as observed in the alkyne adducts of **1**.[8]

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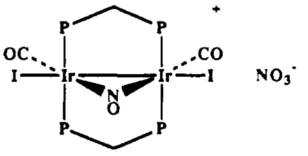
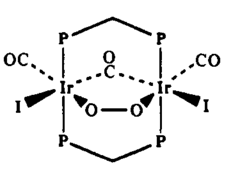
Compound **2** was found to be unreactive with carbon dioxide; after 24 h, suspensions of **2** in CH_2Cl_2 in the presence of a large excess of CO_2 showed the presence of only starting material. With CS_2, compound **2** reacted readily; however several species were obtained under a variety of conditions, and these products were not characterized.

Although the O_2 adduct of closely-related mononuclear dioxygen compounds are reported to be inert to reaction with nitric oxide or carbon monoxide,[20] our binuclear analogue **2** reacts with both of these diatomics. Reaction of **2** with excess NO requires about 15 min for completion, yielding the nitrosyl-bridged product $[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$ (**5**). Compound **5** is a 1:1 electrolyte in CH_3NO_2 ($\Lambda = 78.7\ \Omega^{-1}\ cm^2\ mol^{-1}$) but is weakly conducting in CH_2Cl_2 ($\Lambda = 29.6\ \Omega^{-1}\ cm^2\ mol^{-1}$). The IR spectrum shows two carbonyl bands at 2051 and 2025 cm^{-1} and a strong band at 1518 cm^{-1}, due to the bridging nitrosyl group, as well as bands typical of the nitrate anion. The nitrosyl stretch falls in the range (1400–1600 cm^{-1}) typical of bridged nitrosyls.[22] The $^{31}P\{^1H\}$ NMR spectrum is again typical of a symmetrical species. Dppm-bridged diiridium or dirhodium nitrosyls have not previously been reported, but the above reaction is not without precedent. Treatment of $[Ni(O_2)(^tBuNC)_2]$ with NO in the presence of ^tBuNC produced the nitrosyl complex $[Ni(NO)(^tBuNC)_3][NO_3]$ also as a nitrate salt,[21a] although, in the related Pd and Pt species $[M(O_2)(PPh_3)_2]$ (M = Pd, Pt), formation of dinitro compounds was suggested instead,[20,21b] and reaction of a peroxo-bridged dicobalt complex yielded a nitrito-bridged product.[23]



(**5**)

The oxidation of carbon monoxide by mononuclear dioxygen complexes generally yields carbonates,[1e] although the nickel complex noted above affords a dicarbonyl species and carbon dioxide.[21a] Compound **2** also reacts with CO, although in CH_2Cl_2 the reaction is slow, requiring more than 100 h. The same reaction in either a CH_2Cl_2/CH_3OH or a CH_2Cl_2/CH_3CN solvent mix is complete within 4 h. In all cases the same two products are obtained, together with carbon dioxide, which can be detected by using an aqueous sodium carbonate/phenolphthalein solution, which turns from pink to colorless in the presence of **2** and CO.[24] One of the complexes is readily identified as the previously characterized $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$[8] and is presumably the metal-containing product in the reaction yielding CO_2. The other metal-containing product displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −28.2 and shows bands in the IR spectrum at 2048, 2038, and 1645 cm^{-1}. Although it originally appeared that the low-frequency stretch arose from a carbonate group, subsequent studies have shown that it results from a carbonyl which has inserted into the Ir–Ir bond of **2** to give **6**. This is the only product in this study which reacts via ligand insertion into the metal–metal bond, while leaving the peroxo moiety intact, and presumably this reaction is driven in a large part by the relief of strain that results upon expanding the four-membered dimetallo peroxide ring to a five-membered ring. It can also be shown by ^{13}CO labeling that it is one of the originally bound carbonyls that moves to the bridging position and that direct insertion of free CO into the Ir–Ir bond does not occur.



6

The reaction of **2** with ^{13}CO gives IR bands at 2040, 1993, and 1643 cm^{-1}, in which only one of the terminal carbonyl bands has shifted significantly. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of this product shows only one carbonyl resonance at δ 164.4, in the region typical of terminal carbonyls, although it is noteworthy that carbonate carbons have also been found to resonate in this region.[25] In addition, when the totally ^{13}CO-enriched **6** is prepared, the two resonances at δ 224.5 and 164.4, integrating as 1:2, confirm that the high-field resonance results from the terminal carbonyls. As was the case with compound **2**, the IR spectrum of **6** displays no obvious O–O stretch and the Raman spectrum again could not be obtained owing to decomposition.

The structural formulation of **6** has been confirmed by an X-ray structure determination. A drawing of the compound is given in Figure 2, and relevant bond lengths and angles are shown in Tables V and VI. Compound **6** has the expected geometry in which both dppm groups bridge the metals in a trans arrangement. The most obvious difference in the geometry of these groups results from cleavage of the metal–metal bond with a concomitant increase in the Ir–Ir separation to 3.388(2) Å. The geometries at the metals are distorted octahedral, characteristic of an Ir(III)/Ir(III) system. Such a description requires formulation of the bridging carbonyl as a formally dianionic group, which is consistent with formulating **6** as a dimetallo ketone. Although this is not the normal formulation for a bridging carbonyl, it has previously been suggested[26] and is consistent with the geometry at this group, which suggests sp^2 hybridization of carbon, as indicated by the wide Ir(1)–C(2)–Ir(2) angle of 110(2)°. This formulation is also consistent with the low IR stretch for this group. This class of bridging carbonyl, not accompanied by a metal–metal bond, is uncommon but is found in several examples in which the metals are also bridged by dppm groups.[26b,27] Cleavage of the Ir–Ir bond in **2** to give **6** has resulted in a relaxation of the strain at the peroxo bridge. Therefore the angles at the oxygens (Ir(1)–O(4)–O(5) = 110(2)° and Ir(2)–O(5)–O(4) = 108(2)°) have opened up slightly from the value of 102.0(4)° in **2**. Similarly the Ir(1)–O(4)–O(5)–Ir(2) torsion angle of 61(2)° is also closer to the values observed in other peroxo-bridged species. The widening of the Ir–Ir separation in **6** has also resulted in less repulsion between the substituents on both metals, so although the two octahedra are staggered slightly about the Ir–Ir vector, the associated torsion angles (av 9.2°) are about half the values in **2**.

The O(4)–O(5) separation in **6** (1.43(3) Å) is normal for an O–O single bond and is shorter than the exceptionally long distance found in **2**. Whether this shortening is of chemical significance is of doubt; as noted, we suspect that the distance in **2** is artificially long.

Compound **6** is one of several examples of peroxo-bridged complexes in which the O_2 unit forms part of five-membered

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(27) See for example: (a) Cowie, M.; Vasapollo, G.; Sutherland, B. R.; Ennett, J. P. *Inorg. Chem.* **1986**, *25*, 2648. (b) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632. (c) Brown, M. P.; Keith, A. N.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem. Acta* **1979**, *34*, L223. (d) Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *31*, 1425. (e) Mague, J. T. *Inorg. Chem.* **1983**, *22*, 45.

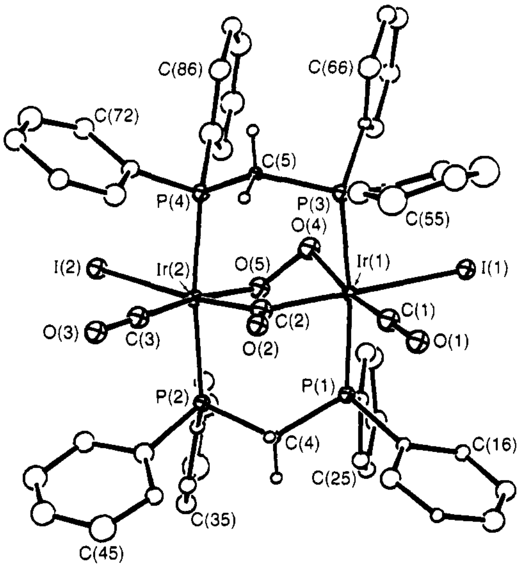


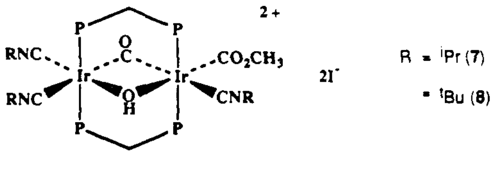
Figure 2. Perspective view of $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]$ (**6**). Thermal ellipsoids are shown at the 20% level except for hydrogen, which are shown artificially small for the methylene groups but are not shown at all for the phenyl groups.

Table V. Selected Distances (Å) in $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (**6**)

	(a) Bonded Distances		
Ir(1)–I(1)	2.822(3)	Ir(2)–P(4)	2.378(9)
Ir(1)–P(1)	2.363(9)	Ir(2)–O(5)	2.01(2)
Ir(1)–P(3)	2.350(9)	Ir(2)–C(2)	2.12(3)
Ir(1)–O(4)	2.05(2)	Ir(2)–C(3)	1.80(4)
Ir(1)–C(1)	1.86(4)	O(1)–C(1)	1.16(4)
Ir(1)–C(2)	2.03(4)	O(2)–C(2)	1.11(4)
Ir(2)–I(2)	2.821(2)	O(3)–C(3)	1.18(4)
Ir(2)–P(2)	2.347(9)	O(4)–O(5)	1.43(3)
	(b) Nonbonded Distances		
Ir(1)–Ir(2)	3.388(2)	Ir(1)–O(5)	2.87(2)
P(1)–P(2)	3.13(1)	Ir(2)–O(4)	2.81(2)
P(3)–P(4)	3.14(1)		

metallocycle.[1e,2b–d,g] However this appears to be the first such metallocycle in which a carbonyl is a bridging group together with O_2.

Examples involving the oxidation of isocyanides by dioxygen compounds, as in the reaction of $[Ni(O_2)(^tBuNC)_2]$ with ^tBuNC to give $[Ni(^tBuNC)_4]$ and ^tBuNCO,[21a] are rare. In CH_2Cl_2/CH_3OH (5:1), compound **2** reacts with excess (5–10 equiv) ^iPrNC, yielding a product containing three isocyanide ligands. However no evidence for oxidation of the isocyanide is observed, and all of the added isocyanide is accounted for in the ^1H NMR spectrum by the three coordinated groups and that remaining unreacted. The product is formulated as the hydroxide-bridged methoxycarbonyl complex $[Ir_2(C(O)OCH_3)(^iPrNC)_3(\mu\text{-}OH)(\mu\text{-}CO)(dppm)_2][I]_2$ (**7**). The IR spectrum of **7** displays two



strong absorptions at 2193 and 2180 cm^{-1}, assignable to the coordinated isocyanide ligands. Two low-frequency bands at 1653 and 1625 cm^{-1} can be assigned to the bridging carbonyl and to the carbonyl group of the methoxycarbonyl ligand. Bridging carbonyls in the absence of metal–metal bonds have been shown to display stretches in this region, as shown by compound **6**, and this range is also common for alkoxycarbonyl ligands.[28] The ^{13}CO-enriched compound displays the expected shift of these two bands (to 1614 and 1592 cm^{-1}), ruling out the possibility that they may arise from an isocyanide group. An additional band at 1036 cm^{-1} can be assigned to ν(C–O) of the methoxycarbonyl group.[28] The O–H stretch of the hydroxy group appears as a broad band at 3190 cm^{-1}. This is at slightly lower frequency than expected, possibly due to hydrogen bonding involving the iodide ion, as has been observed in other hydroxy halide compounds.[29] The conductivity of **7** (120.0 Ω^{-1} cm^2 mol^{-1} in CH_3NO_2) is also lower than expected for a 1:2 electrolyte;[30] this may result from the proposed hydrogen bonding. The hydroxide group of **7** readily undergoes proton exchange with H_2O, even in the solid state, as evidenced by the appearance of O–H and O–D bands (3190, 2360 cm^{-1}) when the compound is prepared in the presence of D_2O.

Table VI. Selected Angles (deg) in $[Ir_2I_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2)(dppm)_2]\cdot 2CH_2Cl_2$ (**6**)

	(a) Bond Angles		
Ir(2)–Ir(1)–I(1)	146.61(7)	Ir(1)–Ir(2)–P(4)	83.4(2)
Ir(2)–Ir(1)–P(1)	82.9(2)	Ir(1)–Ir(2)–O(5)	57.8(6)
Ir(2)–Ir(1)–P(3)	90.5(2)	Ir(1)–Ir(2)–C(3)	124(1)
Ir(2)–Ir(1)–O(4)	56.0(7)	I(2)–Ir(2)–P(2)	94.4(2)
Ir(2)–Ir(1)–C(1)	126(1)	I(2)–Ir(2)–P(4)	91.5(2)
I(1)–Ir(1)–P(1)	89.6(2)	I(2)–Ir(2)–O(5)	89.2(6)
I(1)–Ir(1)–P(3)	95.5(2)	I(2)–Ir(2)–C(2)	177.9(8)
I(1)–Ir(1)–O(4)	92.3(6)	I(2)–Ir(2)–C(3)	90(1)
I(1)–Ir(1)–C(1)	87(1)	P(2)–Ir(2)–P(4)	173.6(3)
I(1)–Ir(1)–C(2)	171.1(9)	P(2)–Ir(2)–O(5)	81.3(7)
P(1)–Ir(1)–P(3)	173.4(3)	P(2)–Ir(2)–C(2)	83.5(9)
P(1)–Ir(1)–O(4)	93.3(7)	P(2)–Ir(2)–C(3)	92(1)
P(1)–Ir(1)–C(1)	95(1)	P(4)–Ir(2)–O(5)	96.3(7)
P(1)–Ir(1)–C(2)	82.4(9)	P(4)–Ir(2)–C(2)	90.6(9)
P(3)–Ir(1)–O(4)	82.4(7)	P(4)–Ir(2)–C(3)	91(1)
P(3)–Ir(1)–C(1)	90(1)	O(5)–Ir(2)–C(2)	90(1)
P(3)–Ir(1)–C(2)	92.8(9)	O(5)–Ir(2)–C(3)	173(1)
O(4)–Ir(1)–C(1)	172(1)	C(2)–Ir(2)–C(3)	91(3)
O(4)–Ir(1)–C(2)	92(1)	Ir(1)–C(2)–Ir(2)	110(2)
C(1)–Ir(1)–C(2)	89(1)	Ir(1)–O(4)–O(5)	110(2)
Ir(1)–Ir(2)–I(2)	145.5(1)	Ir(2)–O(5)–O(4)	108(2)
Ir(1)–Ir(2)–P(2)	90.3(2)		
	(b) Torsion Angles		
I(1)–Ir(1)–Ir(2)–I(2)	−11.1(2)	C(1)–Ir(1)–Ir(2)–C(3)	10(2)
P(1)–Ir(1)–Ir(2)–P(2)	8.8(2)	Ir(1)–O(4)–O(5)–Ir(2)	61(2)
P(3)–Ir(1)–Ir(2)–P(4)	6.8(4)		

The presence of the methoxycarbonyl group is further supported by the $^{13}C\{^1H\}$ and ^1H NMR spectra of **7**. In the $^{13}C\{^1H\}$ NMR spectrum the bridging carbonyl appears as a broad singlet at δ 228.1 and the methoxycarbonyl appears as a triplet at δ 150.6 ($^2J_{PC}$ = 7.1 Hz). This latter resonance falls at the high-field end of the range typically found (δ 158–215)[28] for alkoxycarbonyls and related groups. The methoxy protons appear as a singlet at δ 2.60 in the ^1H NMR spectrum, changing to a doublet in the ^{13}CO-enriched compound ($^3J_{HC}$ = 3.8 Hz). When CD_3OD is used as solvent, no methyl signal is observed for the methoxycarbonl protons, confirming that methanol is the origin of the methoxy moiety. The ^1H NMR spectrum also shows the expected pattern of doublets and septets ($^3J_{HH}$ = 6 Hz) for the ^iPrNC groups in the expected regions. The hydroxide resonance was not observed so is presumably obscured by the isocyanide resonances.

The analogous compound $[Ir_2(CO_2Me)(^tBuNC)_3(\mu\text{-}OH)(\mu\text{-}CO)(dppm)_2][I]_2$ (**8**), shown above, is obtained in a similar manner by the reaction of **2** with ^tBuNC and is characterized in the same way. Both compounds **7** and **8** appear to be fluxional, as shown by their ^1H and $^{31}P\{^1H\}$ NMR spectra. However the nature of this fluxionality was not elucidated.

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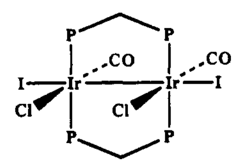
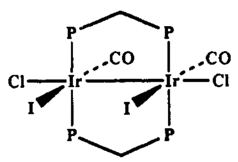
Alkoxycarbonyl complexes are commonly prepared by the reaction of carbonyl complexes with the nucleophilic alkoxide anions.[28] However their generation from weak nucleophiles such as alcohols is less common.[31] Significantly compound **2** itself does not react with methanol, even after several days. It may be that iodide substitution by the isocyanide ligands renders the carbonyls more electrophilic because of the resulting dipositive charge on the complex, leading to nucleophilic attack by methanol. However it should be pointed out that we have no mechanistic information on this reaction, and although we assume that protonation of the dioxygen moiety by methanol occurs, we are unable to comment on the stage at which this occurs, on the fate of the oxygen atom which is lost, or on the possible role of adventitious water.

As with other dioxygen complexes,[1e] compound **2** reacts rapidly with protic acids, yielding H_2O_2, as detected iodimetrically. Treatment of **2**, either in solution or the solid state, with excess gaseous HCl yields $[Ir_2I_2Cl_2(CO)_2(dppm)_2]$ (**9a**) immediately.



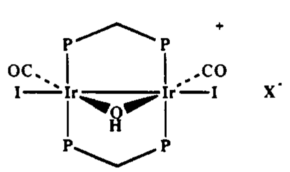
9a



9b

This species is shown by $^{31}P\{^1H\}$ NMR to be a symmetric species (singlet δ −13.9) and has two carbonyl bands at 2066 and 2031 cm^{-1}. If **2** is instead treated with only 2 equiv of HCl, a different species, **9b**, is obtained, having a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −23.0 and a carbonyl band at 2025 cm^{-1}. Elemental analyses indicate that both **9a** and **9b** are dichloro diiodo complexes, so they are formulated as the isomers shown. The isomer with the good π-donor iodo ligands trans to the carbonyls is formulated as **9b** on the basis the lower carbonyl stretch for this isomer. The isomers having inversion symmetry and one halide and one carbonyl on each side of the Ir_2P_4 plane are ruled out, since both **9a** and **9b** display two resonances for the CH_2 protons of the dppm groups, indicating different environments on each side of this plane.

Protonation of **2** with 1 equiv of $HBF_4{\cdot}Et_2O$ yields a symmetric species having two carbonyl bands at 2064 and 2032 cm^{-1} in the IR spectrum and a weak absorption at 3550 cm^{-1} attributed to the OH stretch of a hydroxide group. The ^1H NMR spectrum displays a quintet at δ 3.06 ($^2J_{PH}$ = 2.8 Hz), which simplifies to a singlet upon ^{31}P decoupling. This product is formulated as $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ (**10a**) and apparently results from adventitious water, as has been previously observed in protonation reactions involving O_2 complexes.[17] Attempts to obtain this product more directly, by the oxidative addition of I_2 to the known hydroxy-bridged $[Ir_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$,[29a] *did* yield **10a** in about 30% yield together with other unidentified products, adding support to its formulation. Attempts to detect intermediates containing coordinated hydroperoxo groups in these protonation reactions were not successful, even when the reactions were attempted at low temperature. In addition, attempts to alkylate the peroxo moiety of **2** by reaction with methyl triflate were also unsuccessful; again the only product detected was the hydroxide-bridged **10b** (having a triflate anion), the result of adventitious water.



X = BF_4 (**10a**)
= SO_3CF_3 (**10b**)
= PF_6 (**10c**)

Initial attempts to prepare the nitrate-bridged complex **4b** (as either the BF_4^- or PF_6^- salts) by reaction of **2** with $NOBF_4$ or $NOPF_6$ in CH_2Cl_2 instead gave rise to the hydroxy-bridged compounds **10a** and **10c**. Similar results have previously been obtained, even when precautions were taken to dry solvents and glassware.[32] The above reaction proceeds more readily in the presence of added H_2O and yields significant quantities of the OD-bridged product when D_2O is added, as judged by the decrease in the OH resonance in the ^1H NMR spectrum. When the reaction of **2** with $NOBF_4$ is carried out in carefully dried THF, the major product *is* the nitrate-bridged species **4a**, although **10a** is still observed in varying amounts.

Although peroxo compounds of group VIII metals are known to catalyze the oxidation of organic phosphines,[3a,33] no reaction was observed between **2** and PPh_3, even after several days. However in the presence of 1 equiv of protic acid (e.g. HCl and CH_3CO_2H), PPh_3 is readily oxidized to $OPPh_3$, along with the formation of other unidentified species. The amount of oxidation depends directly on the amount of acid added and is therefore not catalytic in acid. It appears therefore that protonation of the peroxo group to yield the hydrogen peroxide anion occurs, and it is this anion which performs the oxidation. Such a mechanisn has previously been proposed for the oxidation of PPh_3 by $Pt(PPh_3)_4$.[34]

Dioxygen complexes are known to oxidize olefins and ketones.[1e] However compound **2** was found to be unreactive with the few substrates that we investigated; no reaction was observed with ethylene, tetrafluoroethylene, tetrachloroethylene, *cis*-1,2-dichloroethylene, or acetone. Although **2** did react with hexafluoroacetone, several species were obtained under a variety of conditions, and this has not been pursued.

Conclusions

The structural determination of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (**2**) confirms this as the first example in which a peroxo moiety bridges two metals which are linked by a metal–metal bond. Although such a coordination mode of dioxygen is unprecedented, this is not unusual for other related unsaturated substrates. It is therefore likely that such species will become more prevalent as the chemistry of binuclear, group VIII complexes with dioxygen is expanded. For the most part the chemistry of **2** with small molecules is as expected. Therefore reactions with SO_2 and NO_2 yield the respective sulfate- and nitrate-bridged products. However compound **2** does exhibit a significant variety of unusual reactivities with other small molecules. With nitric oxide, oxidation occurs to give the unusual nitrosyl-bridged species as the nitrate salt $[Ir_2I_2(CO)_2(\mu\text{-}NO)(dppm)_2][NO_3]$. Reaction with carbon monoxide results in *both* oxidation of the substrate to give carbon dioxide and $[Ir_2(CO)_2(\mu\text{-}CO)(dppm)_2][I]$ *and* CO-addition to yield the unusual carbonyl- and peroxo-bridged species $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-}CO)(dppm)_2]$. Compound **2** in methanol reacts with isocyanides to give $[Ir_2(C(O)OMe)(CNR)_3(\mu\text{-}OH)(\mu\text{-}CO)(dppm)_2][I]_2$, in which the methoxy carbonyl group has come from methanol through nucleophilic attack on a coordinated carbonyl. The bridging hydroxide group has originated through protonation of the peroxy group either by methanol or adventitious water. Adventitious water was found to play a role in a number of reactions, so although **2** reacted with $NOBF_4$ to give $[Ir_2I_2(CO)_2(\mu\text{-}NO_3)(dppm)_2][BF_4]$ in carefully dried solvents, the hydroxide-bridged species $[Ir_2I_2(CO)_2(\mu\text{-}OH)(dppm)_2][BF_4]$ was also obtained, sometimes as the major or sole product depending on the wetness of the solvent.

As suggested earlier, the presence of a metal–metal bond accompanying the bridging peroxide ligand should not be viewed

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as an exceptional occurrence. In this context, an Ir(II)/Ir(II), peroxo-bridged intermediate, previously formulated without an Ir–Ir bond,[3f] should probably be reformulated. Assuming that this dimeric formulation is correct, we would suggest that it represents another example in which the peroxide bridge is accompanied by a metal–metal bond.

It appears that the presence of a metal–metal bond should influence the reactivity of the peroxide group through the added strain in the four-membered dimetallo peroxide moiety. Although it is difficult to confirm such a postulate on the basis of the chemistry of one species, a clear example showing one consequence of this strain is the CO-insertion into the metal–metal bond of $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ to give $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(\mu\text{-}CO)(dppm)_2]$.

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Supplementary Material Available: Tables of positional parameters for all atoms, thermal parameters for the anisotropic atoms, idealized hydrogen parameters, and bond distances and angles within the phenyl rings and solvent molecules for **2** and **6** (17 pages); listings of observed and calculated structure factors for **2** and **6** (32 pages). Ordering information is given on any current masthead page.