Structure and Reactivity Studies of the Unusual Peroxo-Bridged Complex, [Ir₂I₂(CO)₂(μ-O₂)(Ph₂PCH₂PPh₂)₂]: The First Compound Having a Peroxide Moiety Bridging a Metal–Metal Bond

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Abstract: Reaction of the diiodo complex [Ir₂I₂(CO)(μ-O)dpmm)] (1; dpmm = Ph₃PCH₂PPh₃) with oxygen gives an unusual peroxy-bridged complex, [Ir₂I₂(CO)₂(μ-O₂)dpmm] (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 SO₂ with 2 yields the sulfate-bridged complex [Ir₂I₂(CO)(μ-SO₂)dpmm)] (3), which is also produced in the reaction of 2 with CuSO₄ and in the protonation of 2 with H₂SO₄, with release of H₂O₂. Reaction of 2 with NO and NO affords the nitrate- and nitrosyl-bridged compounds [Ir₂I₂(CO)(μ-X)dpmm)](NO)₂ (X = NO (4a); NO (5)), respectively. The reaction with CO in CH₃Cl/CHOH yields two complexes together with CO₂. One of the species is identified as [Ir₂I₂(CO)(μ-CO)(μ-O₂)dpmm)] (6), formed by formal CO insertion into the Ir–Ir bond of 2. In contrast, isocyanides (RN₃; R = Pr, Bu) are not oxidized by 2; instead the hydroxide-bridged methoxycarbonyl species [Ir₂(CO)₃(μ-COOH)dpmm)] (7), (R = Pr (7); Bu (8)) are obtained through involvement of the methanol solvent. Reaction of 2 with HCl yields two tetrahedral isomers [Ir₂I₂(CO)₂(dpmm)] (9a,b). Attempted reactions with NO₃, HBF₄·OEt₂, and CH₃SO₃CF₃ gave rise to the hydroxide-bridged complex [Ir₂I₂(CO)(μ-O₂)(μ-CH₃SO₃CF₃)] (10), through involvement of adventitious water, although under dry conditions, reaction with NO₃ 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 P4₁2₁2, with a = 14.647(2) Å, c = 27.973(4) Å, V = 6001(1) Å³, and Z = 4 and has refined to R = 0.061 and R₁ = 0.019 on the basis of 2585 observations and 169 parameters varied. Complex 6 crystallizes in the orthorhombic space group Pna2₁, with a = 30.110(8) Å, b = 15.678(6), c = 12.020(6) Å, V = 5674(7) Å³, and Z = 4 and has refined to R = 0.056 and R₁ = 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 century¹–³ has stemmed in a large part from the importance of dioxygen complexation to biological systems⁴ and from the involvement of such complexes in the catalytic oxidation of organic substrates.⁵ In the large number of dioxygen complexes known, the O₂ ligand has demonstrated a variety of coordination modes (a–f). Although most species fit into the first four types, as classified by Vaska in 1976,¹⁶ a few examples of structural types g and h are also known.

With the exception of cobalt, for which a large number of binuclear complexes is known,⁶–⁸ most studies have dealt with mononuclear O₂ species. As part of a continuing study on the activation of small molecules by binuclear complexes, we discovered that the electron-rich complex [Ir₂I₂(CO)₂(dpmm)] (dpmm = Ph₃PCH₂PPh₃) 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...
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 \([\text{Ir}_2\text{I}_2(\text{CO})_2(\mu-\text{O})_2(\text{dpmp})]_2\) and a description of its chemistry. A preliminary report of some of this work has appeared.\(^3\)

### Experimental Section

All solvents were dried and distilled before use. Reactions were performed with use of standard Schlenk procedures unless otherwise noted. Dimethyl was passed through columns of Riddox 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\(_2\)CO\(_2\)F, and bis(diphenylphosphino)methane (dpmm) 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 \([\text{Ir}_2\text{I}_2(\text{CO})(\mu-\text{CO})(\text{dpmm})]_2\) (1) was prepared as previously reported.\(^8\)

The \(\text{H}, \text{H}^1\text{P}, \text{H}^3\text{P}, \text{H}^2\text{C}, \text{H}^2\text{Cl}\) NMR spectra were recorded on a Bruker AM-400 spectrometer, and infrared spectra were run on either a Nicolet 3100 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 1 \(\text{M}\) concentration. Elemental analyses were performed by the microanalytical service within the department.

(a) Preparation of \([\text{Ir}_2\text{I}_2(\text{CO})(\mu-\text{CO})(\text{dpmm})]_2\) (1). A CH\(_2\)Cl\(_2\) solution of \([\text{Ir}_2\text{I}_2(\text{CO})(\mu-\text{CO})(\text{dpmm})]_2\) (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\(_2\)Cl\(_2\) 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 vacuum. Anal. calc. for \(\text{Ir}_2\text{P}_4\text{O}_3\text{C}_5\text{H}_{14}\): 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\(_2\)Cl\(_2\) 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 \([\text{Ir}_2\text{I}_2(\text{CO})(\mu-\text{SO}_2)(\text{dpmm})]_2\text{CH}_2\text{Cl}_2\) (3) as a yellow-orange solid (95% yield). Anal. calc. for \(\text{Ir}_2\text{C}_2\text{SP}_2\text{O}_3\text{C}_5\text{H}_{14}\): C, 38.72; H, 2.82; I, 15.43; S, 1.95. Found: C, 38.48; H, 2.86, I, 15.3; S, 2.47.

(c) Reaction of 2 with H\(_2\text{SO}_4\). To a CH\(_2\)Cl\(_2\) suspension of 2 (60.0 mg, 0.040 mmol, in 10 mL) was added 1 eqv of H\(_2\text{SO}_4\) (1.1 mL in 3 mL of CH\(_3\)OH), 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 Cu\(_2\text{SO}_4\). The procedure was the same as in c, except 1 equiv of Cu\(_2\text{SO}_4\) 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 \([\text{Ir}_2\text{I}_2(\text{CO})(\mu-\text{NO}_2)(\text{dpmm})]_2\) (4a) was isolated as yellow microcrystals in 70% yield and was determined to be a 1:1 electrolyte in CH\(_2\)Cl\(_2\) (\(\Delta \text{m} = 81.1, 1.0 \text{~cm}^{-1}\) mol\(^{-1}\)). Anal. calc. for \(\text{Ir}_2\text{C}_2\text{P}_2\text{O}_2\text{N}_2\text{H}_{14}\): C, 37.35; H, 2.66; N, 1.68. Found: C, 37.67; H, 2.78; N, 1.67.

Table I. Spectroscopic Data*

<table>
<thead>
<tr>
<th>compd</th>
<th>IR (cm⁻¹)b</th>
<th>δ(¹³P/H)c</th>
<th>δ(¹H)d</th>
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<tr>
<td>[Ir₂Cl₂(CO)(μ-O₂)(dppm)₂] (2)</td>
<td>2005 (vs)</td>
<td>-24.4</td>
<td>5.30 (m, 2 H)</td>
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<td></td>
<td>1979 (st)c</td>
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<td>4.02 (m, 2 H)</td>
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<td>[Ir₂Cl₂(CO)(μ-SO₄)(dppm)₂] (3)</td>
<td>2038 (st)</td>
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<td>2026 (st)c</td>
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<td></td>
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<tr>
<td>[Ir₂Cl₂(CO)(μ-N₂O)(dppm)₂][NO] ᵐ (4a)</td>
<td>2049 (st, br)c</td>
<td>-20.0 (m)</td>
<td>5.91 (m, 2 H)</td>
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<td></td>
<td>1518 (med)</td>
<td>-26.1 (m)</td>
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<td><a href="BF%E2%82%84">Ir₂Cl₂(CO)(μ-N)=N</a> (4b)</td>
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<td>2025 (w)c</td>
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<td>2.80 (m, 2 H)</td>
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<td>[Ir₂(CN)₂(CO)(μ-N)=N][NO] (7)</td>
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<td>2193 (vs)</td>
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<td>2191 (v)b</td>
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<td>5.20 (m, 2 H)</td>
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<td></td>
<td>2037 (st)c</td>
<td></td>
<td>3.00 (q, 1 H)</td>
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</tbody>
</table>

*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, CH₂Cl₂ cast. c Versus 85% H₃PO₄, 25 °C, in CDCl₃. d Versus TMS, 25 °C, in CDCl₃. e (ν(CO)). f (ν(SO₄)). g (ν(N=O)). h (ν(C=N)). i (ν(C=O)). j (ν(C-O)). k See text.

(p) Reaction of 2 with NOPF₆. The procedure was the same as in o, except that 1 equiv of NOPF₆ was used, and compound 10c was obtained as the PF₆ salt.

(q) Reaction of 2 with PPh₃. To a mixture of 2 (60.0 mg, 0.04 mmol) and PPh₃ (5.5 mg, 0.021 mmol) in 10 mL of CH₂Cl₂ 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 OPP₃₃ (ca. 30% yield) was confirmed by ¹³P/H NMR (δ 27.5) and IR (ν(P=O) = 1187 cm⁻¹) spectroscopy.

X-ray Data Collection. (a) [Ir₂Cl₂(CO)(μ-O₂)(dppm)₂] (2). Dark-purple crystals of 2 were obtained by slow diffusion of atmospheric oxygen into a CH₂Cl₂ solution of [Ir₂Cl₂(CO)(μ-CO)(dppm)₂] (1). Although the crystals appeared as well-formed tetragonally elongated octahedral prisms, most did not diffrac 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 Kα 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 (00I, I ≠ 4n; 00I, h ≠ 2n) were consistent with the space groups P4₁2₁2₁ and P4₂12₁. 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 θ/2θ scan technique up to
Studies of [Ir2Cl(μ-O2)(μ-O)(P̄̄̄̄̄̄̄̄̄̄P̄̄̄̄̄̄̄̄̄C̄̄̄̄̄̄̄̄̄H̄̄̄̄̄̄̄̄̄P̄̄̄̄̄̄̄̄̄P̄̄̄̄̄̄̄)]

Table II. Crystallographic Data for [Ir2Cl(μ-O)(μ-O2)(ddppm)] (2) and [Ir2Cl(μ-O)(μ-O)(ddppm)]2CH2Cl2 (6).

<table>
<thead>
<tr>
<th>compd</th>
<th>formula</th>
<th>space group</th>
<th>temp (°C)</th>
<th>radiation (λ, Å)</th>
<th>cell parameters</th>
<th>crystal parameters</th>
<th>final no. of unique data</th>
<th>final no. of unique data used</th>
<th>R</th>
<th>Rf</th>
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<tbody>
<tr>
<td>2</td>
<td>C25H39ClO6P7Ir2</td>
<td>P42/n22</td>
<td>259</td>
<td>graphite-monochromated Mo Kα (0.71079)</td>
<td>a (Å) = 14.647(2) b (Å) = 15.675(6) c (Å) = 27.973(4) V (Å³) = 6001(1) Z = 4</td>
<td>π(calc'd) (cm⁻¹) = 1.655</td>
<td>116</td>
<td>0.061</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C25H39ClO6P7Ir2</td>
<td>Pnma</td>
<td>255</td>
<td>graphite-monochromated Mo Kα (0.71079)</td>
<td>a (Å) = 14.647(2) b (Å) = 15.675(6) c (Å) = 27.973(4) V (Å³) = 6001(1) Z = 4</td>
<td>π(calc'd) (cm⁻¹) = 1.655</td>
<td>116</td>
<td>0.061</td>
<td>0.056</td>
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</tbody>
</table>

2θ = 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, and corrections for Lorentz and polarization effects and for absorption were applied. Crystallographic data for 2 are shown in Table II. (b) [Ir2Cl(μ-O)(μ-O2)(ddppm)]2CH2Cl2 (6). Yellow crystals of 6 were obtained by slow diffusion of ether into a CH2Cl2 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 Kα, 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° ≤ 2θ ≤ 20.6°. The automatic peak search and reflection indexing programs generated an orthorhombic cell. The systematic absences (0kI, k + I = odd; 0hI, h = odd) led to the choice of space group as Pnma, or Pnna (a nonstandard setting of Pnma). Pnma was established as the probable one on the basis of the successful refinement of the structure.

Intensity data were collected using the θ/2θ scan technique to a maximum 2θ = 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 for p to downweight intense reflections. Corrections for Lorentz and polarization effects and for absorption, using the method of Walker and Stuart, were applied to the data. Crystallographic data for 6 are shown in Table II.

Structure Solution and Refinement. Both structures were solved in the respective space groups (P42/n22 for 2, Pnna for 6) by using direct methods. The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Full-matrix least-squares refinements proceeded, minimizing the function Σ |Fo - |Fσ|², where w = 4Fo²/σ²(Fo²). Atomic scattering factors and anomalous dispersion terms were taken from the usual tabulations. [9] 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 Rf = 0.093. Attempts to refine in the enantiomorphic space group P42/n22 resulted in higher residuals of R = 0.080 and Rf = 0.115, suggesting that P42/n22 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 Rf = 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 [Ir2Cl(μ-O)(μ-O2)(ddppm)] (2) is readily obtained by exposing solutions of [Ir2Cl(μ-O)(μ-O2)(ddppm)] (1) to air or pure oxygen. All spectroscopic data support the formulation shown for 2. In particular, the [31P31H] 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.

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 alkene-bridged products. However, in the context of O₂ 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 O₂ 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 O₂ 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). The resulting geometry at each metal is distorted octahedral, in which the major distortions result from the strain imposed by the small bridging O₂ 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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[11] Programs used were those of the Enraf-Nonius Structure Determination Package, in addition to local programs by R. G. Bull.
in the range from 1.40 to 1.50 Å.\textsuperscript{1,2b} 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 \( \eta^2 \) 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,\textsuperscript{1,17} 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_{2}Cl_{2} or benzene suspension of \( \text{C}_{2} \) 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 \( \text{2} \). The \( \text{3}^3 \text{P} \left( \text{H} \right) \) 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.\textsuperscript{19} By comparison, the analogous mononuclear complexes \( \left[ \text{IrX} \left( \text{SO}_{4} \right) \left( \text{CO} \right) \left( \text{PPh}_{3} \right)_{2} \right] \) (\( \text{X} = \text{Cl}, \text{Br}, \text{I} \)) showed sulfate bands at ca. 1300, 1170, 890, 860, and 670 cm\(^{-1}\), and the sulfate-bridged diplatinum species \( \left[ \text{Pt}_{2} \left( \mu-\text{OH} \right) \left( \mu-\text{SO}_{4} \right) \left( \text{PPh}_{3} \right)_{2} \right] \left[ \text{ClO}_{4} \right] \) displayed similar stretches at 1275, 1155, and 887 cm\(^{-1}\). On the basis of these data, the structure shown for \( \left[ \text{Ir}_{2} \left( \text{CO} \right) \left( \mu-\text{O}_{2} \right) \left( \text{PPh}_{3} \right)_{2} \right] \) (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 \( \text{H}_{2} \text{SO}_{4} \), with release of \( \text{H}_{2} \text{O} \), or by reaction of 2 with \( \text{CuSO}_{4} \). The \( \text{O}_{2} \text{adduct} \) (2) also reacts readily with \( \text{NO}_{2} \) to give the nitrate-bridged product \( \left[ \text{Ir}_{2} \left( \text{CO} \right) \left( \mu-\text{NO}_{2} \right) \left( \text{PPh}_{3} \right)_{2} \right] \left[ \text{NO}_{3} \right] \) (4a). The IR spectra of 4a show bands at 1518, 1259, 1040, and 790 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 \( \text{NaBF}_{4} \), yielding 4b. The bands for the coordinated nitrate group are comparable to those reported for a variety of related species.\textsuperscript{20,21} Although compounds 3 and 4 are rather analogous, the \( \text{3}^3 \text{P} \left( \text{H} \right) \) 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 carboxyl ligands shown in the sketch; the arrangement shown for 4 is as observed in the alkylene adducts of 1.\textsuperscript{1}
Compound 2 was found to be unreactive with carbon dioxide; after 24 h, suspensions of 2 in CH₂Cl₂ in the presence of a large excess of CO₂ showed the presence of only starting material. With CS₂, compound 2 reacted readily; however several species were obtained under a variety of conditions, and these products were not characterized.

Although the O₂ 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 diatomic reactants. Reaction of 2 with excess NO requires about 15 min for completion, yielding the nitrosyl-bridged product [Ir₂(CO)₆(NO)(dpmm)]²⁻[NO]⁻ (5). Compound 5 is a 1:1 electrolyte in CH₃NO₂ (A = 78.7 Ω⁻¹ cm⁻² mol⁻¹) but is weakly conducting in CH₂Cl₂ (A = 29.6 Ω⁻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 ³¹P{¹H} NMR spectrum is again typical of a symmetrical species. Dppm-bridged dirhodium or diphosphino nitrosyls have not previously been reported, but the above reaction is not without precedent. Treatment of [Ni(O₂)(BuNC)]²⁻ with NO in the presence of BuNC produced the nitrosyl complex [Ni(NO)₂(BuNC)]²⁻ also as a nitrate salt,²¹ although, in the related Pd and Pt species [M(O₂)(PPh₃)]²⁻ (M = Pd, Pt), formation of dinitro compounds was suggested instead,²⁰²¹ and reaction of a peroxo-bridged dicobalt complex yielded a nitrito-bridged product.²³

The oxidation of carbon monoxide by mononuclear dioxygen complexes generally yields carbones,²⁴ although the nickel complex noted above affords a dicarbonyl species and carbon dioxide.²¹² Compound 2 also reacts with CO, although in CH₂Cl₂ the reaction is slow, requiring more than 100 h. The same reaction in either a CH₃Cl/CH₃OH or a CH₂Cl₂/CH₃CN 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 [Ir₂(CO)₆(µ-1)(µ-2)(dpmm)]²⁻ and is presumably the metal-containing product in the reaction yielding CO₂. The other metal-containing product displays a singlet in the ¹³C{¹H} NMR spectrum at δ = 28.2 and shows bands in the IR spectrum at 266, 2036, 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 ¹³C 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..

The reaction of 2 with ¹³CO gives IR bands at 2040, 1993, and 1643 cm⁻¹, in which only one of the terminal carbonyl bands has shifted significantly. Furthermore, the ¹³C{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.²² In addition, when the totally ¹³CO-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 dpmm 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–Ir(III)/Ir(III) system. Such a description requires formulation of the bridging carbonyl as a formally diatomic group, which is consistent with formulation 6 as a dimetalloue ketone. Although this is not the normal formulation for a bridging carbonyl, it has previously been suggested²⁶ and is consistent with the geometry at this group, which suggests sp² 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 dpmm groups.²⁶²² 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 substrates 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 O₂ unit forms part of five-membered...

metallacycle. However this appears to be the first such metallacycle in which a carbonyl is a bridging group together with O.

Examples involving the oxidation of isocyanides by dioxirane compounds, as in the reaction of [NiO2{(BuNC)2}] with BuNC to give [Ni{(BuNC)2}],14 and 1BuNC0.24 are rare. In CH2Cl2/CH3OH (5:1), compound 2 reacts with excess (5–10 equiv) 1PrNC, 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(C(C(=O)CH3)(PrNC)(μ-OH))(μ-CO)(dpmm)]2.28 The 1H NMR 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 13CO-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 C==O of the methoxycarbonyl group.28 The O==H stretch of the hydroxyl 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 cm–1 in CH3NO2) is also lower than expected for a 1:2 electrolyte;25 this may result from the proposed hydrogen bonding. The hydroxide group of 7 readily undergoes proton exchange with H2O, 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 D2O.

The presence of the methoxycarbonyl group is further supported by the 13C{1H} and 1H NMR spectra of 7. In the 13C{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 (JHC = 7.1 Hz). This latter resonance falls at the high-field end of the range typically found (δ 158–215)24 for alkoxycarbonyl 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 13CO-enriched compound (JHC = 3.8 Hz). When CD3OD is used as solvent, no methyl signal is observed for the methoxycarbonyl protons, confirming that methanol is the origin of the methoxy moiety. The 1H NMR spectrum also shows the expected pattern of doublets and septets (JHH = 6 Hz) for the PrNC groups in the expected regions. The hydroxide resonance was not observed so is presumably obscured by the isocyanide resonances.

The analogous compound [Ir(CO2Me)(BuNC)2(μ-OH)(μ-CO)(dpmm)]2(8), shown above, is obtained in a similar manner by the reaction of 2 with BuNC and is characterized in the same way. Both compounds 7 and 8 appear to be fluxional, as shown by their 1H and 13C{1H} NMR spectra. However the nature of this fluxionality was not elucidated.

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Alkoxy carbonyl complexes are commonly prepared by the reaction of carbonyl complexes with the nucleophilic alkoxy anions. However their generation from weak nucleophiles such as alcohols is less common. 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, compound 2 reacts rapidly with protic acids, yielding H2O2, as detected iodometrically. Treatment of 2, either in solution or the solid state, with excess gaseous HCl yields [Ir2I4(CO)3(dppm)2](9a) immediately. This is shown by 31P{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 31P{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 diido complexes, so they are formulated as the isomers shown. The isomer with the good π-donor iodo ligand trans to the carbonyls is formulated 9b on the basis of the lower carbonyl stretch for this isomer. The isomer having inversion symmetry and one halide and one carbonyl on each side of the Ir2P2 plane are ruled out, since both 9a and 9b display two resonances for the CH2 protons of the dppm groups, indicating different environments on each side of this plane.

Protonation of 2 with 1 equiv of HBF4·Et2O 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 (JPH = 2.8 Hz), which simplifies to a singlet upon 31P decoupling. This product is formulated as [Ir2I4(CO)3(μ-Cl)(dppm)2][BF4] (10a) and apparently results from adventitious water, as has been previously observed in protonation reactions involving O2 complexes. Attempts to obtain this product more directly, by the oxidative addition of I2 to the known hydroxy-bridged [Ir2I4(CO)3(dppm)2] [BF4]26 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.

Initial attempts to prepare the nitrate-bridged complex 4b (as either the BF4 or PF6 salts) by reaction of 2 with NOBF4 or NOPF6 in CH2Cl2 instead gave rise to the hydroxide-bridged compounds 10a and 10c. Similar results have previously been obtained, even when precautions were taken to dry solvents and glassware. The above reaction proceeds more readily in the presence of added H2O and yields significant quantities of the OD-bridged product when D2O is added, as judged by the decrease in the OH resonance in the 1H NMR spectrum. When the reaction of 2 with NOBF4 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 peroxy compounds of group VIII metals are known to catalyze the oxidation of organic phosphines, no reaction was observed between 2 and PPh3, even after several days. However in the presence of 1 equiv of protic acid (e.g. HCl and CH3CO2H), PPh3 is readily oxidized to OPOPPh3, 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 peroxy group to yield the hydrogen peroxy anion occurs, and it is this anion which performs the oxidation. Such a mechanism has previously been proposed for the oxidation of PPh3 by Pt(PPh3)4.34

Dioxygen complexes are known to oxidize olefins and ketones. 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 [Ir2I4(CO)3(μ-O2)(dppm)2] (2) confirms this as the first example in which a peroxy 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 SO2 and NO2 yield the respective sulfate- and peroxy-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 [Ir2I4(CO)3(μ-NO)(dppm)2][NO3]. Reaction with carbon monoxide results in both oxidation of the substrate to give carbon dioxide and [Ir2I4(CO)3(μ-CO)(dppm)2][I] and CO- addition to yield the unusual carbonyl- and peroxy-bridged species [Ir2I4(CO)3(μ-O2)(μ-CO)(dppm)2]. Compound 2 in methanol reacts with isocyanides to give [Ir2(C≡N)2(MeCN)3(μ-OCO)(dppm)2][I]2, in which the methoxycarbonyl group has come from methanol through nucleophilic attack on a coordinated carbonyl. The bridging hydroxide group has originated through the peroxo 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 NOBF4 to give [Ir2I4(CO)3(μ-NO3)(dppm)2][BF4] in carefully dried solvents, the hydroxide-bridged species [Ir2I4(CO)3(μ-O2)(dppm)2][BF4] 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 peroxy ligand should not be viewed

References

as an exceptional occurrence. In this context, an Ir(II)/Ir(II), peroxy-bridged intermediate, previously formulated without an Ir–Ir bond, 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 \([\text{Ir}_2\text{L}_2(\text{CO})_2(\mu-\text{O}_2)(\text{dppm})_2]\) to give \([\text{Ir}_2\text{L}_2(\text{CO})_2(\mu-\text{O}_2)(\mu-\text{CO})-(\text{dppm})_2]\).

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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.