

commodate the observed product ratios; other combinations of the various transients are also conceivable.

Formation of aglycon dimers from reduction of the 11-deoxyanthracyclines (aclacinomycin A,¹⁷ 11-deoxydaunomycin,¹⁸ and menogaril¹⁹) results from slow, nonradical coupling of quinone methides, one quinone methide serving as a nucleophile and the other as an electrophile. Formation of aglycon dimers from reduction of daunomycin under anaerobic conditions is not observed because of the much shorter lifetime of the quinone methide state due to rapid tautomerization to form 7-deoxydaunomycinone (7).^{4,20,21}

Earlier, Bachur¹⁰ and Sinha¹¹ proposed that covalent binding of the aglycon to biological macromolecules occurred via a free-radical pathway involving combination of **11** with a radical site on the macromolecule. The semiquinone methide was thought to result from glycosidic cleavage at the semiquinone redox state.^{10,11,22,23} Substantial evidence now establishes that semiquinone does not undergo glycosidic cleavage, at least in vitro.^{4,17-20} The results described here indicate that the potentially important semiquinone methide is biologically accessible from reaction of the quinone methide, from glycosidic cleavage at the hydroquinone state, with molecular oxygen.

Supplementary Material Available: A reverse-phase HPLC chromatogram showing retention times of the products, ¹H NMR data showing chemical shifts and splittings for products **3-6**, **8**, and **9**, and MS data for products **5**, **6**, **8**, and **9** (3 pages). Ordering information is given on any current masthead page.

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First Example of a Peroxo-Bridged Complex Having an Accompanying Metal-Metal Bond

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Transition-metal dioxygen complexes have attracted a great deal of interest owing to their importance in biological systems¹⁻⁴ and because of their involvement in the oxidation of organic substrates.⁵⁻⁸ Although many complexes have been characterized in which the dioxygen molecule bridges the two metals,⁹ primarily involving cobalt, there are no examples of which we are aware in which the bridging O₂ moiety is accompanied by a metal-metal bond, to give a cyclic dimetallo-peroxide grouping. In this report

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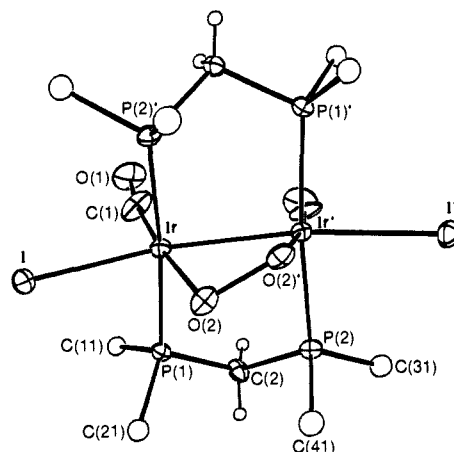


Figure 1. An ORTEP representation of $[\text{Ir}_2\text{I}_2(\text{CO})_2(\mu\text{-O}_2)(\text{dppm})_2]$ (**1**) in which only the ipso carbons of the phenyl rings are shown. Primed atoms are related by unprimed ones by a crystallographic 2-fold axis bisecting the Ir-Ir' and the O(2)-O(2)' bonds. Thermal ellipsoids are at the 20% level except for methylene hydrogens, which are arbitrarily small. Selected bond distances (Å): Ir-Ir', 2.705 (1); Ir-I, 2.764 (1); Ir-C(1), 1.82 (2); Ir-O(2), 2.04 (1); O(2)-O(2)', 1.58 (2). Interatomic angles (deg): Ir'-Ir-O(2), 71.7 (3); Ir-O(2)-O(2)', 102.0 (4); Ir'-Ir-C(1), 101.3 (7); I-Ir-C(1), 97.8 (7); I-Ir-O(2), 89.4 (3).

we outline the preparation, characterization, and some preliminary chemistry of such a species.

The compound in question, $[\text{Ir}_2\text{I}_2(\text{CO})_2(\mu\text{-O}_2)(\text{dppm})_2]$ (**1**)¹⁰ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), is readily and irreversibly obtained in greater than 70% yield as very insoluble dark purple crystals after exposure of a CH_2Cl_2 solution of $[\text{Ir}_2\text{I}_2(\text{CO})(\mu\text{-CO})(\text{dppm})_2]$ ¹¹ to air or pure dioxygen for several hours. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** indicates that all four phosphorus nuclei are chemically equivalent, and the increase in the carbonyl stretching frequencies, from 1948 and 1741 cm^{-1} in the precursor to 2005 and 1979 cm^{-1} in **1**, is consistent with oxidation of the metal centers; no O-O stretch can be unambiguously identified. Confirmation that the complex contains coordinated O₂ comes from the X-ray structure determination (see Figure 1), which shows that the dioxygen ligand bridges the two metals.¹² The short Ir-Ir' separation of 2.705 (1) Å clearly supports the μ -peroxo formulation in which the two Ir(II) centers are joined by an Ir-Ir bond. Although the Ir-O(2) distance (2.04 (1) Å) is normal, the O(2)-O(2)' separation, at 1.58 (2) Å, is extremely long; only $[\text{La}_2(\text{N}(\text{SiMe}_3)_2)_4(\text{O}_2)(\text{OPPh}_3)_2]$ ¹³ appears to have a longer O-O separation (1.65 (4) Å). By comparison, the O-O distance in Na_2O_2 is 1.49 Å¹⁴ and O-O distances are usually found in the range from 1.40 to 1.50 Å in other μ -peroxo compounds.^{9,15} The

(10) $[\text{Ir}_2\text{I}_2(\text{CO})_2(\mu\text{-O}_2)(\text{dppm})_2]$: ¹H NMR (CD_2Cl_2) δ 7.1-7.8 (m, 40 H), 5.3 (m, 2 H), 4.0 (m, 2 H); ³¹P{¹H} NMR (CD_2Cl_2 , vs 85% H_3PO_4) δ -24.4 (s); IR (Nujol) $\nu(\text{CO})$ 2005, 1979 cm^{-1} . Anal. Calcd for $\text{Ir}_2\text{I}_2\text{P}_4\text{O}_4\text{C}_{32}\text{H}_{44}$: C, 41.77; H, 2.97. Found: C, 41.44; H, 2.91.

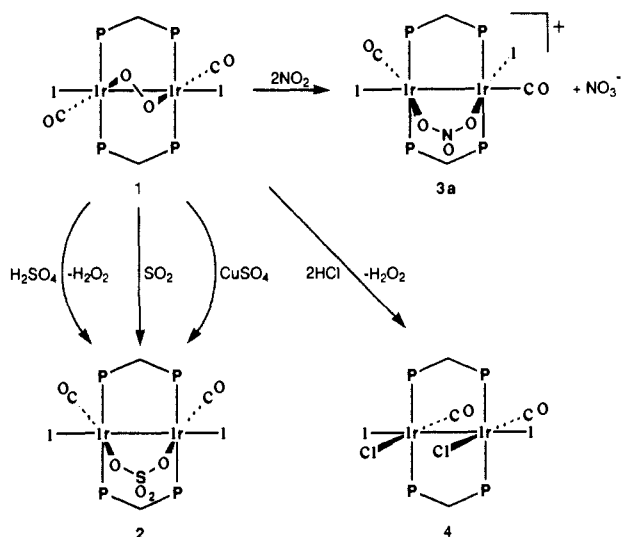
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(12) Crystal data for **1**, $\text{Ir}_2\text{I}_2\text{P}_4\text{O}_4\text{C}_{32}\text{H}_{44}$ (FW = 1495.03): space group $P4_21_2$, $a = 14.647$ (2) Å, $c = 27.973$ (4) Å, $Z = 4$, $V = 6001.4$ Å³. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation. Solved by using direct methods (MULTAN) and refined by using full-matrix least-squares techniques to $R = 0.061$ and $R_w = 0.093$ for 3585 unique observations with $F_o^2 \geq 3\sigma(F_o^2)$. The data were corrected for Lorentz and polarization effects and for absorption. The molecule occupies the crystallographic 2-fold axis.

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Scheme 1



Ir-O(2)-O(2') angle (102.0 (4)°) is smaller than observed (ca. 120°) in other μ -peroxo compounds,⁹ probably because of the strain introduced by the presence of the Ir-Ir bond. As in most such complexes, the Ir-O(2)-O(2')-Ir' moiety is not planar but displays a torsion angle about the O(2)-O(2') bond of 34.6°; again, this twist is less than in other bridged cases owing to the metal-metal bond. It is to be emphasized that compound **1** represents a new type of μ -peroxo compound in which the two metal centers are not independent but are connected by a metal-metal bond. It is significant that a related peroxo-bridged complex containing two Ir(II) centers has been postulated as an intermediate in an oxygen-atom transfer to an olefin.⁸ Although this intermediate was shown without a metal-metal bond, the present study suggests that it could be reformulated as having an accompanying Ir-Ir bond.

The long O(2)-O(2') separation in **1** suggests that this bond is weak and should be readily cleaved. Consequently the reactions of **1** with several small molecules have been investigated, and the preliminary results are summarized in Scheme 1; in all cases the reactions are characterized by a rapid color change from deep purple to yellow or orange. Compound **1** reacts with SO₂ to yield the sulfate-bridged product [Ir₂I₂(CO)₂(μ -SO₄)(dppm)₂] (**2**)¹⁶ through facile oxygen transfer to the SO₂ molecule. This product appears to be quite analogous to **1**, containing two Ir(II) centers linked by an Ir-Ir bond, and with the bridging peroxo group replaced by sulfate. Similarly, reaction of **1** with 2 equiv of NO₂ yields the nitrate-bridged species [Ir₂I₂(CO)₂(μ -NO₃)(dppm)₂][NO₃] (**3a**);¹⁷ the ³¹P{¹H} NMR spectrum suggests that a rearrangement between carbonyl and iodo ligands at one of the metal centers may have occurred to give an asymmetric species as shown in the scheme. Confirmation of the ionic nature of **3a** is obtained from conductivity measurements and by replacement of the NO₃⁻ anion by BF₄⁻ to give [Ir₂I₂(CO)₂(μ -NO₃)(dppm)₂][BF₄] (**3b**).¹⁸ Compound **1** also reacts with the protic

acids HCl and H₂SO₄ to yield [Ir₂I₂Cl₂(CO)₂(dppm)₂] (**4**)¹⁹ and **2**, respectively, with simultaneous formation of H₂O₂, which can be detected with use of aqueous KI solution in the presence of starch. Attempts to observe intermediates in which protonation of the coordinated O₂ moiety has occurred were unsuccessful. The sulfate-bridged product **2** can also be prepared through reaction of **1** with CuSO₄. Compound **1** also reacts with nitric oxide, hexafluoroacetone, and much more slowly (several days), with carbon monoxide, and also with acids such as HBF₄·Et₂O having only weakly coordinating conjugate bases; these and other reactions are being investigated.

The structure determination of **1** confirms that this compound is the first member of a new type of species in which a peroxo ligand bridges a metal-metal bond. It will be of interest to determine if the resulting strain introduced in the μ -peroxo unit by this metal-metal interaction, and the exceptionally long O-O distance, will result in unusual reactivity of this species.

Our preliminary studies show that the related dichloro species, [Ir₂Cl₂(CO)₂(dppm)₂], also reacts with O₂, and this reaction is being investigated to determine if a similar metal-metal-bonded, μ -peroxo complex is obtained.

Acknowledgment. We thank the National Science and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support and NSERC for partial support of the diffractometer and for funding of the PE883 IR spectrometer.

Supplementary Material Available: Tables of X-ray data, atomic coordinates, isotropic thermal parameters, and bond distances and angles for **1** (7 pages). Ordering information is given on any current masthead page.

(19) [Ir₂I₂Cl₂(CO)₂(dppm)₂]: ¹H NMR (CD₂Cl₂) δ 7.2-7.8 (m, 40 H), 5.7 (m, 2 H), 5.0 (m, 2 H); ³¹P{¹H} NMR (CD₂Cl₂, vs 85% H₃PO₄) δ -23.0 (s); IR (Nujol) ν (CO) 2028 cm⁻¹. Anal. Calcd for Ir₂I₂Cl₂P₄O₂C₅₂H₄₄: C, 40.71; H, 2.90; Cl, 4.62. Found: C, 40.51; H, 2.95; Cl, 4.59.

Unusual Reactions of Amino Acid Derivatives: N-Nitrooxazolones and N-Nitroamino Acids

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Amides are "activated" to attack by nucleophiles via N-nitrosation;¹ the resulting nitrosoamides ($\lambda_{\max} \sim 400$ nm) have proved to be useful substrates for enzymes, particularly since suitably constructed ones can also serve as irreversible inhibitors.² The present study is based on examining N-nitroamides³ as

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(16) [Ir₂I₂(CO)₂(μ -SO₄)(dppm)₂]: ¹H NMR (CD₂Cl₂) δ 7.1-7.9 (m, 40 H), 4.9 (m, 4 H); ³¹P{¹H} NMR (CD₂Cl₂, vs 85% H₃PO₄) δ -17.7 (s); IR (Nujol) ν (CO) 2085, 2037, 2028 cm⁻¹; ν (SO₄) 1250, 1140, 952, 800 cm⁻¹. Anal. Calcd for Ir₂I₂SP₄O₆C₅₂H₄₄: C, 40.06; H, 2.84; I, 16.28; S, 2.06. Found: C, 38.48; H, 2.86; I, 15.13; S, 2.47.

(17) [Ir₂I₂(CO)₂(μ -NO₃)(dppm)₂][NO₃]·CH₂Cl₂: ¹H NMR (CD₂Cl₂) δ 7.0-8.0 (m, 40 H), 5.9 (m, 2 H), 4.4 (m, 2 H); ³¹P{¹H} NMR (CD₂Cl₂, vs 85% H₃PO₄) δ -20.0 (m), -26.2 (m); IR (Nujol) ν (CO) 2049 cm⁻¹ (br); ν (μ -NO₃) 1518, 1259, 1040, 780 cm⁻¹; ν (NO₃) 1350, 1023, 700 cm⁻¹. Conductivity Λ (1 \times 10⁻³ M, CH₃NO₂) 81.1 Ω^{-1} cm² mol⁻¹. Anal. Calcd for Ir₂I₂Cl₂P₄O₈N₂C₅₂H₄₆: C, 37.35; H, 2.66; N, 1.68. Found: C, 37.67; H, 2.78; N, 1.67.

(18) [Ir₂I₂(CO)₂(μ -NO₃)(dppm)₂][BF₄]: ¹H NMR (CD₂Cl₂) δ 7.0-7.9 (m, 40 H), 5.9 (m, 2 H), 4.3 (m, 2 H); ³¹P{¹H} NMR (CD₂Cl₂, vs 85% H₃PO₄) δ -20.0 (m), -26.2 (m); IR (Nujol) ν (CO) 2048 cm⁻¹ (br); ν (NO₃) 1519, 1260, 780 cm⁻¹. Anal. Calcd for Ir₂I₂P₄F₄O₈NC₅₂BH₄₄: C, 38.75; H, 2.75; N, 0.87; I, 15.75. Found: C, 39.09; H, 2.76; N, 0.99; I, 16.07.

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