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Thomas C. Flood

University of Southern California, Los Angeles

Masanori Iimura

University of Southern California, Los Angeles

Jeremy M. Perotti

University of Southern California, Los Angeles, perotti@nova.edu

Arnold L. Rheingold

, University of Delaware, Newark

Thomas E. Concolino

, University of Delaware, Newark

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Oxidation of [(cyclic triamine)(1,5-cyclooctadiene)iridium]⁺ cations by hydrogen peroxide forms metallaoxetanes

Thomas C. Flood,^{*a} Masanori Iimura,^a Jeremy M. Perotti,^a Arnold L. Rheingold^b and Thomas E. Concolino^b

^a Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0744, USA.
E-mail: flood@chem1.usc.edu

^b Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522, USA

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Iridaoxetane **3** formed by oxidation of **1** with aqueous H₂O₂ is isolated and characterized, providing a rare example of formation of a metallaoxetane by direct oxidation of a metal–alkene complex.

Metallaoxetanes (1-metalla-2-oxacyclobutanes) have been invoked over the years as key intermediates in certain transition metal-mediated oxygen atom transfer reactions to olefins.^{1,2} A number of metallaoxetanes of transition metals have been prepared by indirect methods,³ but to our knowledge there is no example of isolation, or even spectroscopic detection, of a metallaoxetane from a catalytically oxidizing medium. Thus, their intermediacy has been the subject of much speculation and some debate over the past two decades.²

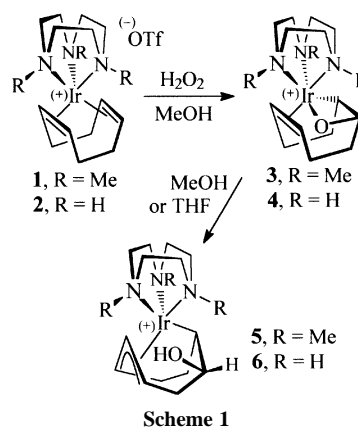
We are aware of only two reports of direct stoichiometric oxygenation of coordinated alkenes that result in formation of characterizable metallaoxetanes.^{4,5} One of these is the recent elegant work of Gal and coworkers⁵ on oxidation of olefins bonded to rhodium(I) bearing *fac*-coordinating triaza and tetraaza ligands. For example, [(N₄)Rh(C₂H₄)]⁺ [N₄ = *N,N,N*-tris(2-pyridylmethyl)amine] and H₂O₂ gave a rhodaoxetane which was isolated and an X-ray crystal structure determination was completed.

Over the last several years we have been developing the synthetic organometallic chemistry of CnIr- and Cn*Ir-containing molecules,[†] and we have observed that Ir^{III} in these ‘hard’ coordination environments binds olefins very strongly. We decided to check the reactions of [(Cn*/Cn)Ir(cod)]⁺ (**1/2**) and [(Cn*/Cn)Ir(C₂H₄)₂]⁺ with H₂O₂ and other oxidants. Perhaps iridaoxetane ‘intermediates’ would be stable enough to detect or isolate before rearrangement to some other species. Ideally, the chemistry of iridium might depart substantially from that reported of rhodium.

[Cn*Ir(cod)]OTf **1** is obtained in up to 86% yield as a light yellow precipitate from reaction of Cn* with [(cod)IrCl]₂ in THF in the presence of NaOTf. Off-white [CnIr(cod)]OTf **2** is similarly prepared in up to 73% yield. [Cn*Ir(cod)]Cl can also be isolated in the absence of NaOTf, but the yield is very variable because of formation of a byproduct of stoichiometry Cn*Ir₂(cod)₂Cl₂ and indeterminate structure. Both **1** and **2** are stable in the absence of air in DMSO, methanol or THF for days at 60 °C.

Treatment of **1** with an excess of aqueous H₂O₂ in methanol (Scheme 1), followed by precipitation with diethyl ether results in isolation of a pale-yellow solid. Various 1-D and 2-D NMR techniques were used to assign its iridaoxetane structure **3**.⁶ The ¹³C NMR spectrum contains 17 unique carbons, comprising of 3 CH₃, 10 CH₂ and 4 CH groups (DEPT). Despite considerable effort, X-ray quality crystals of **3** were not obtained.

After 2 days at 20 °C, a sample of **3** in MeOH-*d*₄ in a sealed NMR tube was unchanged. After 6 h at 60 °C, a new species, **5**, began to form, and after 24 h at 60 °C the conversion was quantitative. Since **5** is chiral (17 unique carbons) it cannot be the iridium analogue of the achiral rhodium product⁵ [Cn*Rh(oxabicyclononadiyl)]⁺. Rearrangement of **3** was repeated on a synthetic scale in THF. Removal of solvent after



16 h at reflux gave a beige powder for which DEPT NMR showed 3 CH₃, 9 CH₂ and 5 CH carbons. A ¹H–¹³C correlation NMR experiment was consistent with the assignment of Ir(III) hydroxycyclooctenediyl species **5**.⁷

[CnIr(cod)]⁺ **2** was also treated with aqueous H₂O₂ under conditions similar to those for **1**, but iridaoxetane **4** was not observed. Instead, the reaction proceeded directly to yield Ir(III)–hydroxycyclooctenediyl **6** in almost quantitative yield (Scheme 1). The structure was assigned by ¹H and ¹³C 1-D and 2-D NMR. An X-ray diffraction study of a single crystal of **6** grown from THF–pentane confirms its structure (Fig. 1).⁸ As expected, the hydroxy group is *endo* with respect to the iridium center, consistent with its origin in **4**. Formation of iridaoxetane intermediate **4** was established by low temperature NMR spectroscopy. A slight excess of aqueous H₂O₂ was added to **2** in MeOH-*d*₄ in an NMR tube immersed in liquid nitrogen. Reaction progress was monitored by NMR as the sample warmed. No change was seen below –20 °C, but at –10 °C formation of **4** was observed. After 10 min at –10 °C the resonances of iridaoxetane **4** had begun to be replaced by those of **6**, and conversion of **4** to **6** was rapid at 0 °C. Several attempts to isolate iridaoxetane **4** at low temperature were unsuccessful.

Complexes **1** and **2** were treated with other oxidants like pyridine *N*-oxide, iodosobenzene, and O₂ in aprotic solvents (MeNO₂, THF and CH₂Cl₂), all of which gave no reaction. *tert*-Butyl hydroperoxide and **2** generated **6**, but more slowly than H₂O₂. Dioxygen in methanol did form **3**, but the yield was much reduced and there was substantial decomposition during the reaction. We suspect that in the case of O₂ protic solvent is required to allow destructive oxidation of **1** and concomitant formation of H₂O₂ which then effects the usual oxidation of residual **1**. Treatment of [CnIr(C₂H₄)₂]⁺ with H₂O₂ or Bu^tOOH in methanol or THF gave uncharacterizable mixtures, and its oxidation was not pursued further.

Overall, the oxidation of **2** to **4** is qualitatively faster than that of **1** to **3**, and clearly the rearrangement of **4** to **6** is much faster than **3** to **5**. The reason(s) for the faster reactions of **2** and **4** are not obvious. Since we would have expected the presumably

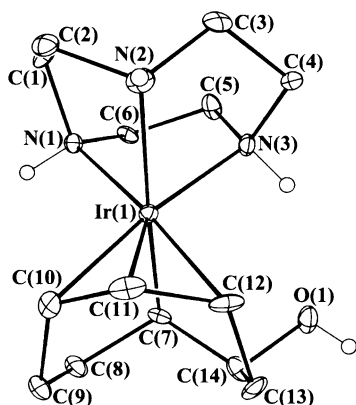


Fig. 1 Thermal ellipsoid plot (30% probability) of the cation of **6**. The OTf counter ion and hydrogen atoms, except H(1)–H(4) which were located, have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–N(1) 2.158(7), Ir(1)–N(2) 2.198(8), Ir(1)–N(3) 2.140(7), Ir(1)–C(7) 2.096(9), Ir(1)–C(10) 2.164(8), Ir(1)–C(11) 2.081(8), Ir(1)–C(12) 2.157(8); N(1)–Ir(1)–N(2) 80.0(3), N(2)–Ir(1)–N(3) 79.7(3), N(1)–Ir(1)–N(3) 79.4(3), N(1)–Ir(1)–C(12) 175.2(3), N(2)–Ir(1)–C(7) 171.5(3), N(3)–Ir(1)–C(10) 172.9(3), C(7)–Ir(1)–C(10) 81.3(4), C(7)–Ir(1)–C(12) 82.4(4).

more electron rich **1** to oxidize faster, steric differences may be the more likely explanation. Although we were not able to obtain X-ray quality crystals of either **3** or **4**, from the X-ray crystal structures of $[\text{CnIr}(\text{H})_2(\eta^2\text{-cyclooctene})]\text{OTf}$ and $[\text{Cn}^*\text{Ir}(\text{H})_2(\eta^2\text{-cyclooctene})]\text{Cl}$ we have observed average Ir–N distances of 2.15 and 2.20 Å, respectively, so the methyl groups have only a small effect on the Ir–N distances. Thus, the *N*-methyl groups cause considerably more crowding around the equator of the complex than the *N*-H groups. It may be that the methyl groups restrict conformational mobility of the oxidized ligand in **3** relative to that in **4** leading to a larger barrier for the rearrangement. Similarly, the slower oxidation of **1** compared to **2** may result from steric hindrance to attack by peroxide on the metal or on the coordinated alkene.

It is interesting that in the three cases where metallaoxetane species have been isolated from oxidation of coordinated olefins, the complexes contain ancillary ligands which coordinate to the metal *via* the relatively non-polarizable atoms oxygen and nitrogen. There is too little information as yet to conclude if this observation is significant.

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Notes and references

† Abbreviations used in this paper: Cn = 1,4,7-triazacyclononane, Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane.

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- 6 Data for **3**: ^1H NMR (DMSO- d_6 , 500 MHz): δ 0.78–2.47 (complex, 8H, cod), 2.41 (m, 1H, IrCH), 2.83–3.40 (complex, 12H, NCH₂), 2.68 (s, 3H, NCH₃), 2.95 (s, 6H, NCH₃), 5.17 (pseudo-d, 2H, –CH=), 5.56 (t, 1H, IrOCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 126 MHz) δ 0.88 (IrCH), 19.67, 24.52, 26.95, 34.17 (cod CH₂), 47.49, 49.12, 55.78 (NCH₃), 58.45, 58.60, 61.09, 61.63, 62.58, 64.13 (NCH₂), 78.34, 85.30 (cod –CH=), 88.04 (IrOCH). Anal. Calc. for C₁₈H₃₃N₃O₄F₃IrS•H₂O: C, 33.02; H, 5.39; N, 6.42. Found: C, 32.75; H, 5.25; N, 6.38%.
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- 8 *Crystallographic characterization of 6*: C₁₅H₂₇F₃IrN₃O₄S, *M* = 594.66, monoclinic, space group *P*2₁/*c*, *a* = 9.6533(3), *b* = 11.5159(4), *c* = 16.8150(4) Å, β = 98.6347(13)°, *V* = 848.09(16) Å³, *Z* = 4, *T* = 173(2) K, *D_c* = 2.137 g cm^{–3}, μ = 73.95 cm^{–1}, *R*(*F*²) = 0.0453, *wR*(*F*²) = 0.1078 for 4191 observed independent reflections. DIFABS absorption corrections were applied to the data set. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to the nitrogen atoms of the Cn ligand and the hydrogen atom of the hydroxy group were located from a difference map and allowed to refine. All other hydrogen atoms were treated as idealized contributions. CCDC 182/1731.