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

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Iridaoxetane 3 formed by oxidation of 1 with aqueous \( \text{H}_2\text{O}_2 \) 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. A number of metallaoxetanes of transition metals have been prepared by indirect methods, 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.

We are aware of only two reports of direct stoichiometric oxygenation of coordinated alkenes that result in formation of characterizable metallaoxetanes. One of these is the recent elegant work of Gal and coworkers on oxidation of olefins bonded to rhodium(ii) bearing fac-coordinating triaza and tetraaza ligands. For example, \( (\text{N}_4\text{Rh}(\text{C}_2\text{H}_4))^{+} \) \( [\text{N}_4 = \text{N},\text{N},\text{N},\text{N}-\text{tris}(2\text{-pyridylmethyl})\text{amine}] \) and \( \text{H}_2\text{O}_2 \) gave a rhodaoxetane which was isolated and characterized as an X-ray crystal structure determination was completed. Over the last several years we have been developing the synthetic organometallic chemistry of \( \text{CnIr} \) and \( \text{CnIr} \)-containing molecules, and we have observed that \( \text{Ir}^{III} \) in these ‘hard’ coordination environments binds olefins very strongly. We decided to check the reactions of \( [(\text{Cn}^{III}\text{Ir})(\text{C}_2\text{H}_4)]^{+} \) (1/2) and \( [(\text{Cn}^{IV}\text{Ir})(\text{C}_2\text{H}_4)]^{2+} \) with \( \text{H}_2\text{O}_2 \) 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 for rhodium.

\[ [\text{Cn}^{III}\text{Ir}(\text{cod})\text{OTf}] \] is obtained in up to \( 86\% \) yield as a light yellow precipitate from reaction of \( \text{Cn}^{IV} \) with \( [(\text{cod})\text{IrCl}] \), in THF in the presence of NaOTf. Off-white \( [\text{CnIr}(\text{cod})\text{OTf}] \) is similarly prepared in up to \( 73\% \) yield. \( [\text{CnIr}(\text{cod})\text{Cl}] \) can also be isolated in the absence of NaOTf, but the yield is very variable because of formation of a byproduct of stoichiometry \( \text{Cn}^{III}\text{IrCl}_2(\text{cod})\text{Cl}_2 \) and indeterminate structure. Both 1 and 2 are stable in the absence of air in DMSO, methanol or THF for days at \( 60^\circ \text{C} \).

Treatment of 1 with an excess of aqueous \( \text{H}_2\text{O}_2 \) in methanol (Scheme 1), followed by precipitation with diethyl ether results in isolation of a pale-yellow solid. Various l-D and 2-D NMR (Scheme 1) were treated with aqueous \( \text{H}_2\text{O}_2 \) under conditions similar to those for 1, but iridaoxetane 4 was not observed. Instead, the reaction proceeded directly to yield \( \text{Ir}^{III} \)-hydroxycyclooctenediyl species 5.

\([\text{CnIr} \text{(cod)}]^{2+}\) was also treated with aqueous \( \text{H}_2\text{O}_2 \) under conditions similar to those for 1, but iridaoxetane 4 was not observed. Instead, the reaction proceeded directly to yield \( \text{Ir}^{III} \)-hydroxycyclooctenediyl \( \text{6} \) in almost quantitative yield (Scheme 1). The structure was assigned by \( 1 \text{H} \) and \( 13 \text{C} \) 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). 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 \( \text{H}_2\text{O}_2 \) 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 \( -20^\circ \text{C} \), but at \( -10^\circ \text{C} \) formation of 4 was observed. After 10 min at \( -10^\circ \text{C} \) the resonances of iridaoxetane 4 had begun to be replaced by those of 6, and conversion of 4 to 6 was rapid at \( 0^\circ \text{C} \). Several attempts to isolate iridaoxetane 4 at low temperature were unsuccessful.

Complexes 1 and 2 were treated with other oxidants like pyridine \( \text{N} \)-oxide, iodosobenzene, and \( \text{O}_2 \) in aprotic solvents (MeNO\( d_2 \), THF and CH\( \text{Cl}_2 \)), all of which gave no reaction. tert-Butyl hydroperoxide and 2 generated 6, but more slowly than \( \text{H}_2\text{O}_2 \). 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 \( \text{O}_2 \) protic solvent is required to allow destructive oxidation of 1 and concomitant formation of \( \text{H}_2\text{O}_2 \) which then effects the usual oxidation of residual 1. Treatment of \( [\text{CnIr}(\text{CH}_2\text{Cl})]^{2+} \) with \( \text{H}_2\text{O}_2 \) or BuOOH 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

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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 [CnIr(H)2(η2-cyclooctene)]OTf and [Cn*Ir(H)2(η2-cyclooctene)]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-methyl groups cause considerably more crowding around the N–H groups. It may be that the methyl groups restrict conformational mobility of the oxidized metallaoxetane relative to that in the three cases where metalloxoetane 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.

6 Data for 3: 1H NMR (DMSO-d6, 500 MHz): δ 0.78–2.47 (complex, 8H, cod), 2.41 (m, 1H, IrCH), 2.83–3.40 (complex, 12H, NCH2), 2.95 (s, 6H, NCH3), 5.15 (pseudo-d, 2H, –CH=), 5.56 (t, 1H, IrOCH). 13C{1H} NMR (DMSO-d6, 126 MHz) δ 88.88 (IrCH), 19.67, 24.52, 26.95, 34.17 (codCH2), 47.49, 49.12, 55.78 (NCH2), 58.45, 58.60, 61.09, 61.63, 62.58, 64.13 (NCH3), 78.34, 85.30 (cod –CH =), 88.04 (IrOCH). Anal. Calc. for C18H33N3O4F3IrS: C, 36.77; H, 5.05; N, 3.48.
8 Crystallographic characterization of 6: C10H6F4Ir3N3O3S, M = 594.66, monoclinic, space group P21/c; a = 9.6533(3), b = 11.5195(4), c = 16.8150(4) Å, β = 98.6347(13°), V = 848.09(16) Å3, Z = 4, T = 173(2) K, D =, 2.137 g cm–3, μ = 73.95 cm–1, R(F) = 0.0543, wR(F) = 0.1078 for 4191 observed independent reflections. DIIFABS absorption corrections were applied to the data. 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.