Ultrafast and Ultraslow Oxygen Atom Transfer Reactions between Late Metal Centers

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Abstract: Oxotrimesityliridium(V), (mes)$_3$Ir=O (mes = 2,4,6-trimethylphenyl), and trimesityliridium(III), (mes)$_3$Ir, undergo extremely rapid degenerate intermetal oxygen atom transfer at room temperature. At low temperatures, the two complexes conproportionate to form (mes)$_3$Ir−O−Ir(mes)$_3$, the 2,6-dimethylphenyl analogue of which has been characterized crystallographically. Variable-temperature NMR measurements of the rate of dissociation of the μ-oxo dimer combined with measurements of the conproportionation equilibrium by low-temperature optical spectroscopy indicate that oxygen atom exchange between iridium(V) and iridium(III) occurs with a rate constant, extrapolated to 20 °C, of $5 \times 10^4$ M$^{-1}$ s$^{-1}$. The oxotris(imido)osmium(VIII) complex (ArN)$_3$Os=O (Ar = 2,6-disopropylphenyl) also undergoes degenerate intermetal atom transfer to its deoxy partner, (ArN)$_3$Os. However, despite the fact that its metal–oxygen bond strength and reactivity toward triphenylphosphine are nearly identical to those of (mes)$_3$Ir=O, the osmium complex (ArN)$_3$Os=O transfers its oxygen atom 12 orders of magnitude more slowly to (ArN)$_3$Os than (mes)$_3$Ir=O does to (mes)$_3$Ir ($k_{OsOs}$ = $1.8 \times 10^5$ M$^{-1}$ s$^{-1}$ at 20 °C). Iridium–osmium cross-exchange takes place at an intermediate rate, in quantitative agreement with a Marcus-type cross relation. The enormous difference between the iridium–iridium and osmium–osmium exchange rates can be rationalized by an analogue of the inner-sphere reorganization energy. Both Ir(III) and Ir(V) are pyramidal and can form pyramidal iridium(V) with little energetic cost in an orbitally allowed linear approach. Conversely, pyramidalization of the planar tris(imido)osmium(VI) fragment requires placing a pair of electrons in an antibonding orbital. The unique propensity of (mes)$_3$Ir=O to undergo intermetal oxygen atom transfer allows it to serve as an activator of dioxygen in cocatalyzed oxidations, for example, acting with osmium tetroxide to catalyze the aerobic dihydroxylation of monosubstituted olefins and selective oxidation of allyl and benzylic alcohols.

Introduction

Oxygen atom transfer reactions (eq 1) are prototypical examples of two-electron inner-sphere redox reactions, with important applications in catalysis in organic synthesis and by metalloenzymes. In general, the net transfer of an oxygen atom requires two steps, with the formation of an intermediate where the oxygen atom is shared between the two redox centers. The thermodynamic requirements of such reactions have been extensively reviewed. Many rate measurements of oxygen atom transfer reactions between transition metal and main group species have been made, although in only a few cases has it been possible to analyze both steps. Kinetic studies of reactions between two different transition metal species have been carried out even more rarely, and so there is little systematic understanding of the factors that affect the rates of intermetal oxygen atom transfer. This situation is in stark contrast to the understanding of outer-sphere single-electron transfer rates provided by Marcus theory, which relates the facility of such reactions to their thermodynamic driving force ($\Delta G^\circ$), the degree to which the bonding environments of the metals must be altered to accommodate the redox change (the inner-sphere reorganization energy, $\lambda_i$), and the degree to which the solvent and counterions must reorganize to accommodate the redox change (the outer-sphere reorganization energy, $\lambda_o$).

$$\text{M}=\text{O} + \text{X} \rightleftharpoons \text{M}−\text{O}−\text{X} \rightleftharpoons \text{M} + \text{O=X} \quad (1)$$

Our desire to better understand the factors that govern intermetal oxygen atom transfer reactions was piqued by our earlier observation that Wilkinson’s iridium(V) oxo complex...

and Ir(mes)₃. When it had been determined by NMR that all of the and 0.3 mg of P(tol)₃ is oxidized to O₂, the (mes)₃Ir₃ and (mes)₃Ir=O were calculated using the measured total iridium concentration and the measured ratio of oxygen to iridium and the conproportionation Kₓ, which was calculated using AM² and AS° as adjustable parameters. Theoretical values for the absorbance at 513 nm were calculated using these concentrations, the measured extinction coefficients for (mes)Ir(920 M⁻¹ cm⁻¹) and (mes)Ir=O (1020 M⁻¹ cm⁻¹), and the extinction coefficient for (mes)Ir=O—Ir(mes), as a third adjustable parameter. The three adjustable parameters were allowed to vary, and the sum of [(Aₐₐₑₑ−Aₐ₅₅₅)/Aₛₛₛ] was minimized using Solver in Microsoft Excel. Optimized values for the parameters were ΔΔF = −5.14 ± 0.13 kcal/mol, ΔS° = −15.2 ± 0.7 cal/mol K, and ε₅₅₅ of (mes)Ir=O—Ir(mes) = 250 ± 300 M⁻¹ cm⁻¹, with estimated errors calculated as described in the literature.

Preparation of (2,6-Me₂C₆H₃)₃Ir=O. This compound has been described briefly in the literature. It was prepared by the same procedure used to prepare (mes)Ir=O₆, substituting 2,6-dimethylphenylmagnesium bromide (Aldrich) for mesitylmagnesium bromide. After purification by repeated chromatography on silica gel, eluting with 2% Et₃O/hexane, followed by crystallization from acetonitrile/water, (2,6-Me₂C₆H₃)₃Ir=O was isolated as dark blue crystals in 3.3% yield. H NMR (CD₂Cl₂): δ 2.50 (s, 18H, C₆H₃), 6.95 (d, 7H, 6H, m-ArH), 1.36 (s, 36H, para), 132.43 (meta), 147.58 (ipso), 130.43 (meta), 132.56 (ortho), 147.58 (ipso). UV—vis (CH₂Cl₂): λₘₐₓ = 616 nm, ε = 2040 M⁻¹ cm⁻¹. IR (evaporated film, cm⁻¹): 3049 (w), 2958 (w), 2922 (w), 2849 (w), 1442 (s), 1374 (w), 1234 (w), 1166 (w), 1025 (w), 844 (m), 763 (m), 667 (w). Anal. Calcd for (2,6-Me₂C₆H₃)₃Ir=O: C, 55.04; H, 5.21. Found: C, 55.26; H, 5.11.

X-ray Crystallography of (2,6-Me₂C₆H₃)₃Ir—O—Ir(2,6-Me₂C₆H₃)₃Ir=O. A solution of (2,6-Me₂C₆H₃)₃Ir=O in CD₂Cl₂ was treated with a stoichiometric amount of P(o-tol), very dark brown crystals of the μ-oxo complex grew when a sealed NMR tube containing this solution was allowed to stand in a −20°C freezer for several weeks. A 0.4 × 0.3 × 0.3 mm³ crystal was removed from the tube and placed in inert oil and transferred to the tip of a glass fiber in the cold N₂ stream of a Bruker Apex CCD diffractometer (T = −173°C). Data were reduced, correcting for absorption and decay, using the program SADABS. The crystal was cubic, and its space group was determined to be P2₁3 from the systematic absences. The structure was solved using Patterson methods, which located the iridium atom (on the crystallographic 3 axis) and oxygen atom (on the inversion center). The single crystallographically unique aryI group and the dichloromethane molecule (whose carbon atom was disordered about an inversion center, with the two chlorine atoms located on the 3 axis) were located on difference Fourier maps. Hydrogens were placed in calculated positions. Final full-matrix least-squares refinement on R² converged at R₁ = 0.0156 for 2042 reflections with Fc > 2σ(Fc), R₁ = 0.0177 for all 2186 unique reflections (wR₂ = 0.0385, 0.0396, respectively). All calculations used SHELXLT (Bruker Analytical X-ray Systems), with scattering factors and anomalous dispersion terms taken from the literature.

Measurement of (mes)Ir=O—Ir(mes)₃ Dissociation by ¹H NMR Line shape Analysis. Solutions of (mes)Ir=O in CD₂Cl₂ were partially

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reduced by allowing the solution to stand at room temperature in a sealed NMR tube for several days or by the addition of stoichio-
metric amounts of PPh₃. The composition of the solutions was analyzed by integration of the spectra at −110 °C (where the species give separate resonances) or by measurement of the chemical shifts at room temperature (where Ir(V) and Ir(III) give rise to weighted-average resonances).¹⁶ H NMR spectra were recorded between −80 °C and −110 °C on a Varian VXR-500 NMR spectrometer. The line shape of the para-methyl region was analyzed using the program gNMR¹⁶ to generate calculated lineshapes and superimpose them on the observed spectra, with optimization of the fit as a function of k_{obs} performed manually. The spectra were generally simulated assuming that the ratio of the concentrations of the two major iridium-containing species (mes)Ir=O=Ir(mes) and either (mes)Ir=O or (mes)Ir was as determined in the −110 °C spectrum and the concentration of the minor species (Ir(mes) if deoxygenation was <50% complete, (mes)Ir=O if deoxygenation was >50% complete) was negligible. Achieving satisfactory agreement of the chemical shift of the coalesced peaks in the higher-temperature spectra did sometimes require including small amounts of the minor species in the calculation, but never more than 5% of the total iridium concentration. Values of k_{obs} from different runs varied by <15% from the mean values, with no systematic deviations based on whether the solution was generated by autogenous reduction or by addition of PPh₃, or whether (mes)Ir=O or (mes)Ir was the major species exchanging with (mes)Ir=O=Ir(mes). Activation parameters were calculated by plotting ln(k_{obs}/T) vs 1/T in the range 170–193 K.

Kinetics of Reduction of (ArN)₂OIr=O with PPh₃. Solutions of (ArN)₂O=O were prepared in the drybox in dichloromethane (room temperature) or 1,2-dichlorobenzene (variable-temperature) in 1 cm quartz cells fitted with septum caps. The cells were inserted into the multicell transport block of a Beckman DU-7500 diode array spectrophotometer. The temperature was regulated by a thermostatted water/ethylen glycol mixture circulated through the cell block and was measured by a thermocouple inserted in the cell block. Solutions were allowed to equilibrate for 10 min at the desired temperature, and reactions were initiated by injecting 20–50 equiv of PPh₃ dissolved in a small volume of solvent. Reactions were monitored by measuring the decrease in absorbance at 610 nm. Pseudo-first-order rate constants were obtained from the slopes of plots of ln(A − A₀) vs time, which were linear over >4 half-lives. The observed pseudo-first-order rate constants were found to depend linearly on [PPh₃] in the range 0.002–0.010 M in CH₂Cl₂ at room temperature. Activation parameters were calculated from reactions measured in 1,2-dichlorobenzene by plotting ln(k_{obs}/T) vs 1/T over the range 288.6–330.6 K.

Preparation of (ArN)₂OIr=O (ArN = 4-Deuterio-2,6-diisopropyl-
phenyl), A sample consisting of 10 g of 2,6-diisopropylaniline (Acros) was washed twice with 1 mL of D₂O (Cambridge Isotope Laboratories). The aniline was then placed into a 500 mL glass bomb with 100 g of CH₃OD (Aldrich) and 8 mL of concentrated DCI in D₂O (Aldrich). The bomb was sealed, and the mixture was heated for 5 d at 60 °C. The solution was removed in vacuo and the solid was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether solution was dried with magnesium sulfate and concentrated in vacuo three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected. The ether concentrate was dissolved in water and rendered basic with sodium carbonate. The solution was extracted three times with ether, and the organic phases were collected.

Kinetics of Exchange Between Os(NAr)₃ and O=Os(NAr)₃. Reaction mixtures were prepared by weighing in the drybox 6–15 mg each of O=Os(NAr)₃ and deuterium-enriched Os(NAr)₃ (Ar = 2,6-diisopropylphenyl) into an NMR tube sealed to a ground glass joint. The solids were dissolved in dry CD₃CN, and the tube was flame-sealed under a vacuum. H NMR spectra were taken every day or two as the mixture was allowed to react at 20 °C, and the integrals for the protons in the para positions of the aromatic imido groups for each compound (Os=Os(NAr)₃, δ 6.89 ppm, Os(NAr)₃, δ 7.35 ppm) were measured. The fraction of osmium(VI) in the mixture was determined from the peaks for the (CH₃)₂CH—Ar septets (O=Os(NAr)₃, δ 3.48 ppm, Os-
(NAr)₃, δ 3.86 ppm) and remained constant at about 0.5 throughout the course of each reaction.

Kinetics were analyzed according to standard McKay exchange kinetics, with k_{obs} determined from the slope of the plot of ln([Os(VI)]/[[Os(VI)]−[unlabeled Os(VI)]/[total unlabeled Os]]) vs time.¹⁸ These plots curved significantly after ~1 half-life, apparently due to autocatalysis. The k_{obs} values determined over the first half-life were reproducible and were proportional to the total osmium concentration. The bimolecular rate constant was averaged over those observed in seven independent runs.

For two of these runs, the Ei mass spectra of two mixtures of O=Os(NAr)₃ and deuterium-labeled Os(NAr)₃ dissolved in CD₃CN, which had undergone complete isotopic scrambling as determined by H NMR, were acquired. The isotope envelope of the Os(NAr)₃ parent ion (m/z = 714–722) was fit using a combination of the d⁴, d⁵, d⁶, and d⁷ isotopomers using a locally written program.¹⁹

Measurement of K_{eq} for (mes)Ir=O + Os(NAr)₃ ⇌ Ir(mes) + O=Os(NAr)₃. O=Ir(mes) (1.75 mg) and Os(NAr)₃ (Ar = 2,6-
diisopropylphenyl) (10.0 mg) were mixed in an NMR tube sealed to a ground glass joint and dissolved in CD₃CN in the drybox. The tube was attached to a needle valve, evacuated at low temperature, and flame-sealed. The solution was allowed to react at room temperature for a few minutes until the system reached equilibrium. The tube was inserted into an NMR probe, and the H NMR spectrum was recorded. The sample was cooled in the probe of the NMR spectrometer, and spectra were recorded at temperatures from room temperature to ~30 °C at 5° intervals, allowing sufficient time at each temperature for the solution to reach equilibrium. The ratio [O=Os(NAr)₃]/[Os(NAr)₃] was determined at each temperature by measuring the relative integrals of the isopropyl methyl resonances. The ratio [Ir(mes) + O=Ir(mes)]/[Ir(mes) + O=Os(NAr)₃] was determined from the chemical shift of the aromatic H compared to its position in the spectra of authentic samples of (mes)Ir and (mes)Ir=O at the same temperature. (Formation of (mes)Ir=O=Ir(mes) is negligible at these temperatures and concentrations.)

Kinetics of (mes)Ir=O + Os(NAr)₃ − Ir(mes) + O=Os(NAr)₃. Freshly prepared solutions of O=Ir(mes) and Os(NAr)₃ in dry, deoxygenated CD₃CN were mixed under nitrogen in an NMR tube sealed to a ground glass joint and cooled to −78 °C. The NMR tube was evacuated and flame-sealed, and the solution was kept at −78 °C until it was inserted in the NMR probe, which was precooled to the desired temperature (~30 to −70 °C). The reaction was monitored by measuring the change in the chemical shift of the mesityl aromatic and ortho-CH₃ resonances over time. Since chemical exchange between O=Ir(mes) and Ir(mes), is rapid on the NMR time scale at these temperatures, a single set of mesityl resonances is seen for mixtures of O=Ir(mes), Ir(mes), and (mes)Ir=O=Ir(mes), and the peak positions shift upfield as the iridium is deoxygenated. In order to avoid precipitation of the sparingly soluble µ-oxo complex, the reactions were conducted using dilute solutions of iridium (~1.5 mg/0.6 mL) and

(16) Budzelaar, P. H. M. gNMR, v. 3.5.6.; Cherrwell Scientific Publishing: 1996.
were only monitored for the first 10–20% of reaction. Over this range of reaction, the chemical shift changes are linear with time. Second-order rate constants for this initial portion of the reaction were calculated from the slope of these curves, \(k_{\text{HOC}} = \frac{\partial \delta / \partial t}{\delta_{\text{HOC}}}\), according to eq 2:

\[
\frac{k_{\text{HOC}}}{K} = \frac{1 + K[\text{Ir}]}{\delta_{\text{HOC}}(\text{Ir}) + 2K[\text{Ir}]\delta_{\text{HOC}} - (1 + K[\text{Ir}]\delta_{\text{HOC}})} (2)
\]

where \(K\) is the equilibrium constant for the conproportionation of \((\text{mes})\text{Ir}\) and \((\text{mes})\text{Ir}^{2+}\) calculated from the thermodynamic parameters measured by optical spectroscopy in CHFCl\(_3\) and \(\delta_{\text{HOC}}(\text{Ir})\) are the chemical shifts of the resonances for pure \((\text{mes})\text{Ir}\), \((\text{mes})\text{Ir}^{2+}\), respectively, measured at (or in the case of \((\text{mes})\text{Ir}^{2+}\)) extrapolated to) the temperature of the kinetics run. Concentrations of iridium and osmium were corrected for thermal contraction of the solvent.12 Since the chemical shifts for the \(\mu\)-oxo complex can only be measured over a very narrow range of temperatures (−100 to −110 °C), this extrapolation is likely to be rather imprecise.

However, because the chemical shifts of the \(\mu\)-oxo complex are close to the average of the shifts of the iridium(II) and iridium(V) complexes, and because the mole fraction of iridium(V) is small at these concentrations and temperatures, the calculated rate constants are relatively insensitive to the treatment of the \(\mu\)-oxo complex, with calculated rate constants differing by no more than 10% from those where the formation of the \(\mu\)-oxo complex is completely neglected. Results from the shifts of the aromatic hydrogens agreed with those measured from the \(\sigma\)-CH\(_2\) resonances, and second-order rate constants calculated from eq 2 were independent of \([\text{Os}N\text{Ar}_3]\) in the range 0.007–0.016 M. Activation parameters were obtained from a plot of \(\ln(k/T)\) vs 1/T.

DFT Calculations on Iridium and Osmium Complexes. Calculations were performed on model complexes with the mesityl groups in the iridium complexes and the 2,6-Pr\(_2\)C\(_6\)H\(_3\) groups in the osmium complexes replaced by methyl groups. All structures were optimized using the hybrid B3LYP method, which has been successfully used in a number of studies involving transition metal complexes.20 A 6-311+G** basis set was used for the carbon, hydrogen, and oxygen atoms, while an SDD basis set was used on the iridium and osmium atoms. Stationary points were characterized by harmonic frequency analysis. Thermochemical corrections to the reported energies were calculated from the harmonic frequency analysis for a temperature of 293 K and a pressure of 1 atm, using a scaling factor of 0.9614.21 All calculations were performed using the G9822 and G0323 series of programs. The Kohn–Sham orbital24 representations were created in Molender using a contour value of 0.05.

Aerobic Dihydroxylation with \((\text{mes})\text{Ir}^{2+}O(C/H\text{H}_3)\text{N}\)O\(_2\). Represent-ative Procedure: Dihydroxylation of 1-Octene. Into a screw-capped NMR tube in the air were added \((\text{C/H}_3)\text{N}O\(_2\)(2.0 mg, 5.5 μmol, 20 mol %), \((\text{mes})\text{Ir}^{2+}O(C/H\text{H}_3)\text{N}O\(_2\)(3.1 mg, 5.5 μmol)\), and dimethyl terephthalate as an internal standard (0.5 mL of the (DHQD)\(_2\)PHAL/osmium solution was added to the NMR tube. Upon completion of the reaction (determined by NMR), the reaction mixture was diluted with Et\(_2\)O (8 mL), washed with saturated aqueous sodium sulfate to remove the metals, and dried over MgSO\(_4\). After the solvent was removed on the rotary evaporator, the diol was filtered through a small plug of silica gel using Et\(_2\)O/hexane (1:1) to give pure 1,2-dioctenediol. The two enantiomers were separated by chiral GC (J&W Scientific 112–2532, Cyclolex B; injection temperature 250 °C, detector temperature 300 °C, oven temperature 75 °C for 10 min followed by 2 °C/min to 145 °C for 5 min; retention times = 42.6 and 42.9 min).

Representative Procedure for the Oxidation of Benzylic and Allylic Alcohols: Oxidation of Benzy1 Alcohol. Into a 2.5 mL screw-capped vial was added a solution of \((\text{mes})\text{Ir}^{2=0}(4.5, 7.9 \text{ mmol}, 1 \text{ mol %}) and benzy1 alcohol (82 μL, 0.79 mmol) in 0.4 mL of THF. In an NMR tube, the osmium reagent was generated by adding allyl ethyl ether (12.0 μL, 0.106 mmol, 13.2 mol %) to a suspension of (quinuclidine)OsO\(_4\)(5.8 mg, 0.016 mmol, 2 mol %) in 0.1 mL of THF. After allowing this osmium-containing solution to stand for 40 s after addition of the alkene, the solution containing the substrate and iridium was added to the NMR tube. Oxygen gas, presaturated with THF by passing it through a gas dispersion tube in a 100 mL two-neck flask filled with THF, was admitted to the screw-cap NMR tube with a septum cap using a needle. Oxygen was bubbled through the reaction mixture at a moderate rate (~3 bubbles/s) and vented through a mineral oil bubbler. The reaction was complete in 3 days.

Results

Conproportionation of \((\text{mes})\text{Ir}^{2+}O(\text{mes})\text{Ir}\). Earlier we reported that solutions containing mixtures of Wilkinson’s homoleptic trimesityliridium(III), \((\text{mes})\text{Ir}^{2+}O(\text{mes})\text{Ir}(\text{mes})\text{Ir} = \text{2,4,6-tri-methylphenyl})\), and oxotrimesityliridium(IV), \((\text{mes})\text{Ir}^{2+}O^{2-}\) display only a single set of mesityl resonances in the \(1^H\) NMR at room temperature.6 This is due to fast intermolecular oxygen atom transfer between iridium(IV) and iridium(III) leading to chemical exchange of the two types of mesityl group (eq 3). Given the differences in chemical shift between \((\text{mes})\text{Ir}^{2+}O\) and \((\text{mes})\text{Ir}\) and the fact that only fairly sharp coalesced signals are seen at room temperature, this exchange must take place with \(k_{\text{HOC}} > 4 \times 10^5 \text{ M}^{-1} \text{s}^{-1}\).

\[
(\text{mes})\text{Ir}^{2+}O + \text{Ir}^{2+} \rightleftharpoons (\text{mes})\text{Ir} + \text{O}^{2-} + (\text{mes})\text{Ir} \quad (3)
\]

A logical intermediate in this oxygen atom transfer reaction is the iridium(IV) \(\mu\)-oxo complex \((\text{mes})\text{Ir}^{2+}O(\text{mes})\text{Ir}\). Results of the earlier study6 suggest that this conproportionation product is not present in significant concentrations at ambient temperatures. In particular, \((\text{mes})\text{Ir}^{2+}O\) is deoxygenated by oxygen atom acceptors such as triphenylphosphine or triphenylarsine in reactions which show clean pseudo-first-order kinetics (in the presence of excess reducing agent) over the entire course of the reaction. Substantial amounts of conproportionation would imply that the reaction would slow as \((\text{mes})\text{Ir}\) bound to the oxo complex \((\text{mes})\text{Ir}^{2+}O\), except in the unlikely event that the \(\mu\)-oxo complex was more readily deoxygenated than the terminal oxo complex.

Conproportionation is important at lower temperatures, however, as indicated by color changes when mixtures of \((\text{mes})\text{Ir}^{2+}O\) and \((\text{mes})\text{Ir}\) are cooled. Solutions of neither blue-green \((\text{mes})\text{Ir}^{2+}O\) nor yellow-brown \((\text{mes})\text{Ir}\) are thermochro-
ic, and optical spectra taken at room temperature of green solutions containing mixtures of the two compounds are simple.
The molecule therefore has crystallographic threefold axis with the bridging oxygen atom soluble dark brown compound, which was confirmed by X-ray warming the sample. Both the precipitation and the color change are reversed on temperature, a dark brown microcrystalline precipitate forms. Below room temperature, a color change from green to dark however, when dichloromethane solutions are cooled to well below room temperature, a color change from green to dark brown takes place. If the solutions are allowed to stand at low temperature, a dark brown microcrystalline precipitate forms. Both the precipitation and the color change are reversed on warming the sample.

By allowing a partially reduced sample of the 2,6-dimethylphenyl analogue (2,6-Me₂C₆H₃)₃Ir–O–Ir(C₆H₃-2,6-Me₂)₃, CD₂Cl₂ to stand at –20 °C, we were able to grow large single crystals of the sparingly soluble dark brown compound, which was confirmed by X-ray crystallography to be the μ-oxo complex (C₆H₃(C₂H₅)₃)Ir–O–Ir–(C₆H₃(Me₂C₆H₃)₃) (Figure 1). The compound crystallizes in the cubic space group Pa3 (Table 1), with the complex sitting on a 6 symmetry. In particular, the μ-oxo bridge is strictly linear, and the three-bladed propellers formed by the ary groups surrounding each iridium have opposing chirality.

A linear μ-oxo bridge was also seen in the isoelectronic neopentylrhodium(IV) complex (Me₃CCH₂)₃Rh–O–Rh(CH₂-CMe₃)₂. The geometry of the triaryliridium fragment (Ir–C distance of 2.007(2) Å, C–Ir–C angles of 106.43(5)°) is remarkably similar to what is found in both trimesityliridium-(III) (2.015 Å av, 107.5° av) and oxotrimesityliridium(V) (2.015 Å av, 108.9° av) (Table 2).

The change of color from green to brown on cooling solutions of partially reduced (mes)Ir=O can be analyzed quantitatively by low-temperature optical spectroscopy. As the temperature of solutions of (mes)Ir=O-(mes)Ir=O mixtures are lowered below about –60 °C, the absorbance of the solution increases at all wavelengths longer than 450 nm (Figure 2). The μ-oxo complex has a particularly strong absorption at 513 nm (ε = 25 400 M⁻¹ cm⁻¹) and also shows two other intense peaks at 560 and 632 nm, as well as shoulders at longer wavelengths (675, 736 nm). Similar behavior is observed in CH₂Cl₂ or in mixtures of

![Figure 1. SHELXTL plot (50% ellipsoids) of (2,6-Me₂C₆H₃)₃Ir–O–Ir–(C₆H₃-2,6-Me₂)₃.](image)

### Table 1. Crystallographic Details for (2,6-Me₂C₆H₃)₃Ir–O–Ir–(C₆H₃-2,6-Me₂)₃, CD₂Cl₂

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<th>Value</th>
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<td>C₆H₃(C₂H₅)₃Ir₂O</td>
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<td>λ (Å)</td>
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<td>No. of refined parameters</td>
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<td>R indices [I &gt; 2σ(I)]</td>
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<td>R indices (all data)</td>
<td>0.0177, wR2 = 0.0396</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.082</td>
</tr>
</tbody>
</table>

*References: 7. Numbers in parentheses represent estimated standard deviations in the last digits of single crystallographically measured values; values in brackets represent standard deviations in the average of the three independent measurements in the molecule. Values in italics are the results of DFT calculations on the (CH₃)₃Ir analogues of the triaryliridium complexes.

![Figure 2. Optical spectra of a mixture of (mes)Ir and (mes)Ir=O as a function of temperature (20:1 CHFCl₂/CD₂Cl₂, total [Ir] = 1.2 × 10⁻³ M, 0.2 mm path length). Temperatures are indicated on the left. Inset: Absorbance at 513 nm as a function of temperature. The solid line is the fit calculated on the basis of the thermodynamic parameters for conproportionation given in the text.](image)

<ref id="table1">

### Table 2. Selected Bond Lengths (Å) and Angles (deg) for (2,6-Me₂C₆H₃)₃Ir–O–Ir(C₆H₃-2,6-Me₂)₃, CD₂Cl₂, Compared with Corresponding Parameters in (mes)₃Ir=O and (mes)₃Ir=O²

<table>
<thead>
<tr>
<th></th>
<th>(mes)₃Ir=O</th>
<th>H₂Ir=O=IrH₂</th>
<th>(mes)₃Ir=O²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir–O, Å</td>
<td>n/a</td>
<td>1.9142(1)</td>
<td>1.725(9)</td>
</tr>
<tr>
<td>C–Ir–O, deg</td>
<td>n/a</td>
<td>112.36(4)</td>
<td>110[6] av</td>
</tr>
<tr>
<td>Ir–O–Ir, deg</td>
<td>n/a</td>
<td>180.0</td>
<td>170.5</td>
</tr>
</tbody>
</table>

<ref>
dichloromethane and CHFCl₂ (Freon-21), although the Freon mixture is preferred for quantitative studies because it remains fluid at the extremely low temperatures (∼140 K) needed to shift the equilibrium strongly toward the μ-oxo complex at the submillimolar concentrations required for optical spectroscopy. The rise in absorbance at 513 nm as the temperature is lowered is directly proportional to the concentration of the limiting reagent of eq 4, consistent with a 1:1 stoichiometry of (mes)₃Ir=O and (mes)₃Ir. Runs conducted at different iridium concentrations give consistent values for the $K_{eq}$ of eq 4, and analysis of the temperature-dependence of the absorbance from 135 to 220 K (inset, Figure 2) allows the determination of the thermodynamic parameters $\Delta H^\circ = -5.14 \pm 0.13$ kcal/mol and $\Delta S^\circ = -15.2 \pm 0.7$ cal/mol·K.

\[(\text{mes})_3\text{Ir}=\text{O} + \text{Ir(mes)}_3 \rightleftharpoons (\text{mes})_3\text{Ir}=\text{O} - \text{Ir(mes)}_3 \quad (4)\]

**Kinetics of Dissociation of (mes)₃Ir=O–Ir(mes)₃.** ¹H NMR spectra of equilibrium mixtures of (mes)₃Ir=O, (mes)₃Ir=O–Ir(mes)₃, and (mes)₃Ir recorded above about -80 °C show only a single set of mesityl resonances due to the rapid exchange of mesityl environments among the three species. Both aromatic hydrogens appear as a single resonance, as do both ortho-methyl groups. However, these resonances do show some broadening as the temperature is lowered to -80 °C, due to hindered Ir–C bond rotation in the three species. The iridium(III) complex was previously reported to exhibit a sizable barrier to Ir–C bond rotation ($\Delta G^\circ = 13.0$ kcal/mol, extrapolated to 163 K) and shows sharp, separate signals for the aromatic and ortho-methyl peaks even at -20 °C. In contrast, the oxo complex (mes)₃Ir=O shows a much faster Ir–C bond rotation. Even at -110 °C, the aromatic resonance, though slightly broadened, is still coalesced. However, at this low temperature the ortho-CH₃ resonances of (mes)₃Ir=O have decoalesced sufficiently to determine their chemical shifts (Figure S1), and this allows line shape analysis over the range -110 to -80 °C, giving thermodynamic parameters for Ir–C bond rotation in (mes)₃Ir=O (Figure S2) of $\Delta H^\circ = 5.73 \pm 0.04$ kcal/mol, $\Delta S^\circ = -9.80 \pm 0.24$ cal/mol·K, and $\Delta G^\circ$ (163 K) = 7.33 kcal/mol.

At temperatures above about -80 °C, the para-methyl resonance, which is insensitive to bond rotation but does change chemical shift with iridium oxidation state, remains a single sharp resonance in Ir(V)/Ir(IV)/Ir(III) mixtures. At temperatures below -80 °C, this resonance broadens and decoalesces as the rate of intermolecular exchange slows (Figure 3). The aromatic and ortho-methyl resonances likewise broaden and separate, although the detailed lineshapes of these resonances are complicated by the effects of intramolecular exchange due to Ir–C bond rotation. The low-temperature limiting spectra show only the μ-oxo complex (mes)₃Ir=O–Ir(mes)₃ and one of the monomeric iridium species, (mes)₃Ir or (mes)₃Ir=O, depending on whether more or less than half of the oxygen has been removed. At these concentrations and this low temperature, the position of the equilibrium strongly favors conproportionation. Note that the aromatic and ortho-methyl resonances of (mes)Ir=O–Ir(mes)₃ are well-separated, but still slightly broadened, at -110°, indicating that the barrier to Ir–C bond rotation in the μ-oxodiridium(IV) complex ($k_{rot} = 40$ s⁻¹, $\Delta G^\circ = 8.1$ kcal/mol at 163 K) is intermediate between that of Ir(III) and Ir(V). This correlation of rotation barrier with the electronic unsaturation at iridium, rather than with steric hindrance, substantiates our earlier contention that agostic interactions between iridium and the ortho-methyl groups are significant in (mes)₃Ir.⁵

The line shape of the para-methyl peaks can be analyzed in the temperature range -80 to -102.5 °C to determine the rate of dissociation of (mes)₃Ir=O–Ir(mes)₃ to give (mes)₃Ir=O and (mes)₃Ir (Figure 3; note that at these concentrations and temperatures conproportionation is highly favorable, so only one of (mes)₃Ir=O or (mes)₃Ir will be present in appreciable concentration, depending on whether the average oxidation state is greater than or less than +4). The rate constants $k_{diss}$ obtained by line shape analysis are independent within experimental error of whether the observed exchange is between Ir(IV) and Ir(V) or between Ir(IV) and Ir(III), and are independent of whether the mixture of oxidation states is generated by the slow spontaneous reduction of (mes)₃Ir=O in CD₂Cl₂ or by deliberate addition of substoichiometric PPh₃ (a process that has been shown to generate (mes)IrCl₃ cleanly⁶), substantiating a mechanism involving simple, unassisted dissociation of the μ-oxo dimer without participation of other species such as OPPPh₃ (if present). An Eyring plot (Figure S3) gives the activation parameters for the dissociation of the μ-oxo complex as $\Delta H_{diss}^{\circ} = 10.04 \pm 0.14$ kcal/mol, $\Delta S_{diss}^{\circ} = +8.6 \pm 0.8$ cal/mol·K. Combining these activation parameters with the thermodynamic parameters for the net reaction of eq 4 allows one to compute activation parameters for the forward direction of eq 4 (neglecting the difference between the 95% CHFCl₂ and 5% CD₂Cl₂ used for...
equilibrium measurements and the CD$_2$Cl$_2$ used for kinetics): $\Delta H^{\ddagger}_{\text{IrIr}} = 4.90 \pm 0.19$ kcal/mol, $\Delta S^{\ddagger}_{\text{IrIr}} = -6.6 \pm 1.1$ cal/mol-K, $\Delta G^{\ddagger}_{\text{IrIr}} (293 \text{ K}) = 6.83 \pm 0.36$ kcal/mol. Using these data to extrapolate the rate constant for bimolecular degenerate atom transfer to 293 K, where comproportionation is the rate-determining step in complete oxygen atom transfer, gives $k_{\text{IrIr}} = 5 \times 10^7$ M$^{-1}$ s$^{-1}$.

**Oxygen Atom Cross-Exchange Reactivity of (ArN)$_3$Os=O.** In order to better understand the features that make (mes)$_3$Ir=O so kinetically reactive toward oxygen atom self-exchange, we sought a system that might share a number of the unusual features of the (mes)$_3$Ir=O=(mes)$_3$Ir redox couple. The tris-imido osmium complexes (ArN)$_3$Os=O and (ArN)$_3$Os (Ar = 2,6-diisopropylphenyl), described by Schrock and co-workers, appeared to be an ideal comparison: Both pairs of complexes involve low-coordinate, late transition metal oxo complexes, and in both instances the reduced species are stable as three-coordinate monomers which do not readily bind additional ligands.

The osmium oxo complex (ArN)$_3$Os=O also appears to be similar to (mes)$_3$Ir=O in its reactivity toward main group oxygen atom acceptors. The osmium oxo complex undergoes clean reduction by triphenylphosphine to form OPP$_3$ and (ArN)$_3$Os in a reaction that is first-order in both reagents (eq 5). The activation parameters for this reduction (289–331 K, 1.2-dichlorobenzene, Figure S4), $\Delta H^{\ddagger} = 7.7 \pm 0.3$ kcal/mol, and $\Delta S^{\ddagger} = -30.3 \pm 1.1$ cal/mol-K, show the large negative activation entropy typical of bimolecular oxygen atom transfer reactions. At room temperature, the rate constant $k_{\text{Op}}$ is 1.30- (7) M$^{-1}$ s$^{-1}$ (25 °C, CH$_2$Cl$_2$), only three times smaller than the corresponding rate constant for iridium $k_{\text{IrP}} = 3.95 \times 10^7$ M$^{-1}$ s$^{-1}$.

$$(\text{ArN})_3\text{Os}=\text{O} + \text{PPh}_3 \rightarrow (\text{ArN})_3\text{Os} + \text{OPPh}_3$$ (5)

Even more remarkably, the osmium and iridium complexes have nearly equivalent thermodynamic propensities toward oxygen atom transfer. Within minutes at room temperature, intermetal oxygen atom transfer takes place between (mes)$_3$Ir=O and (ArN)$_3$Os to give an equilibrium mixture of both oxo complexes and both reduced species (eq 6), with $K_{\text{IrOs}} = 0.6$ in CD$_2$Cl$_2$ at 20 °C. The position of equilibrium is only slightly temperature-dependent, with a van’t Hoff plot between 243 and 288 K giving $\Delta H_{\text{IrOs}}^{\ddagger} = -0.86 \pm 0.03$ kcal/mol and $\Delta S_{\text{IrOs}}^{\ddagger} = -3.89 \pm 0.10$ cal/mol-K (Figure S5). In this temperature range the formation of the iridium(IV) µ-oxo complex is negligible, and there is no evidence by NMR for any interaction between (ArN)$_3$Os=O and (ArN)$_3$Os at any temperature. Since the bond dissociation enthalpies of the two bonds are nearly equal, with the Os=O bond having the greater BDE by 0.86 kcal/mol.

$$(\text{mes})_3\text{Ir}=\text{O} + (\text{ArN})_3\text{Os} \rightleftharpoons (\text{mes})_3\text{Ir} + (\text{ArN})_3\text{Os}=\text{O}$$ (6)

While the rate of cross-exchange (eq 6) is rapid at room temperature, rates can be measured between −70 and −30 °C by observing the growth of the resonances of (ArN)$_3$Os=O as well as the changes in the positions of the mesityl resonances, which shift upward as (mes)$_3$Ir=O is deoxygenated to an equilibrium mixture of (mes)$_3$Ir−O−Ir(mes)$_3$ and (mes)$_3$Ir. The measured initial rates of reaction are proportional to both [Ir] and [Os], and the variation of the observed second-order rate constants $k_{\text{IrOs}}$ with temperature (Figure S6) allows one to calculate activation parameters for the cross-exchange reaction of eq 6 (in the forward direction): $\Delta H_{\text{IrOs}}^{\ddagger} = 11.3 \pm 0.5$ kcal/mol and $\Delta S_{\text{IrOs}}^{\ddagger} = -15.3 \pm 2.4$ cal/mol-K.

**Oxygen Atom Self-Exchange of (ArN)$_3$Os:(ArN)$_3$Os=O.** Degenerate intermetal oxygen atom transfer between (ArN)$_3$Os and (ArN)$_3$Os=O is slow, with mixtures of the two osmium complexes showing sharp, separate, unperturbed NMR resonances for both complexes even at +100 °C in toluene-$d_8$. In order to measure exchange between the two species on the chemical time scale, we prepared the tris(imido)osmium(VI) complex labeled in the para position with deuterium, (ArN)$_3$-Os (Scheme 1).

Upon mixing Os(NAr)$_3$ with unlabeled (ArN)$_3$Os=O, growth of the para resonance of the osmium(VI) complex in the $^1$H NMR is exceedingly slow, requiring weeks to achieve equilibrium at room temperature. Kinetics of isotope exchange were measured in benzene, since (ArN)$_3$Os=O decomposes in dichloromethane at a significant rate on the extremely slow time scale of the reaction. The reactions exhibited a moderate degree of autocatalysis, with the apparent rate constants increasing after the first half-life or so. The origin of the autocatalysis is unknown, but it is not due to production of trace amounts of free aniline, since spiking the mixture with 2,6-diisopropylaniline does not accelerate exchange. However, reaction rates measured in the first half-life or so are reproducible, and redistribution of the deuterium conforms to the pseudo-first-order decay expected for exchange kinetics, regardless of the rate law. The fact that the observed rate constant is proportional to the total osmium concentration (Figure S7) indicates that the reaction is second-order, and from seven runs at 20 °C, the average rate constant $k_{\text{Ods}}$ is $(1.8 \pm 0.2) \times 10^{-5}$ M$^{-1}$ s$^{-1}$.

The NMR analysis of isotope exchange measures the rate at which the imido groups exchange environments between osmium(VI) and osmium(VIII) but cannot distinguish between oxygen atom transfer between (ArN)$_3$Os=O and (ArN)$_3$Os or direct imido group exchange between osmium centers. These two processes can be distinguished by mass spectrometry, since oxygen atom exchange retains the integrity of a tris(imido)-osmium unit, while imido exchange severs the correlation any individual imido group once had with its fellows in the Os-$(\text{NAr})_3$ fragment, and must therefore result in a completely

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**Scheme 1. Preparation of Labeled Os(NAr)$_3$**

1. CH$_3$OH, DCI/D$_2$O 60 °C, 5 d
2. H$_2$O/Na$_2$CO$_3$

3. DMAB, hexane

4. heptane, Δ

5. Os(NAr)$_3$ 82% D
statistical distribution of imido groups (Figure 4). The experimental data are highly nonstatistical and clearly exclude any significant amount of exchange of individual imido groups. Agreement with the groupwise exchange model is excellent, consistent with assignment of the observed exchange to an oxygen atom transfer process.

Application of Intermetal Oxygen Atom Transfer to Cocatalyzed Air Oxidations. Oxotrimesityliridium(V) is inert to all common organic functional groups, reacting only with very easily oxidized substrates such as phosphines and arsines. Thus, despite the fact that (mes)_3Ir activates O_2 readily to form the oxo compound, its use as a catalyst in air oxidations is limited. However, the great kinetic facility of (mes)_3Ir in intermetal oxygen atom transfer reactions suggests that it could be used in tandem with other oxometal reagents to allow greater scope for catalyzed air oxidations.

The goal of cocatalyzed air oxidation has been achieved using quinuclidine-ligated OsO_4 as a cocatalyst with (mes)_3Ir in two different reactions. First, this reagent combination mediates the well-known dihydroxylation of olefins using air and water as stoichiometric reagents. Air has been used as the terminal oxidant in dihydroxylations under organic/basic aqueous biphasic conditions, but no turnover is seen in organic solvents. However, in the presence of catalytic (mes)_3Ir=O, a variety of monosubstituted alkenes react with air and water in the presence of catalytic (C_8H_17N)OsO_4 and (mes)_3Ir=O to give 1,2-diols (eq 7). Diols are the sole product of oxidation of aliphatic alkenes, and functional group compatibility is good. Arylalkenes give lower yields of diols (75% for styrene to 1,2-phenylethanediol), presumably because of overoxidation of the benzylic alcohol in the product (see below).

Unfortunately, the rate of dihydroxylation is very low (5 turnovers/week), and the reaction is limited to monosubstituted alkenes. More highly substituted alkenes react readily with osmium to form glycolates, but these glycolates do not react with iridium at appreciable rates. Monitoring the reaction over time (Figure S8) indicates that the reaction slows down considerably as it progresses. This is not due to catalyst degradation, as the (mes)_3Ir=O and the osmium glycolate concentrations, as monitored by 1H NMR, are unchanged over the course of the reaction. Instead the slowdown is accounted for, quantitatively, by inhibition by the diol product.

1-Octene can be dihydroxylated enantioselectively with catalytic OsO_4 and (mes)_3Ir=O using (DHQD)_2PHAL. While the reaction occurs with a modest 45% ee, this is identical

Figure 4. Mass spectrometric analysis of the isotopic composition of Os(NAr)_3 after equilibration of deuterium-enriched Os(NArD)_3 and unlabeled Os(NAr)_3 (middle right). Isotope patterns of the parent ions of the 82% deuterated Os(NArD)_3 and natural-abundance Os(NAr)_3 are shown on the lower left. Isotope patterns calculated for the equilibrium mixture given the measured overall composition and assuming either an oxygen atom transfer mechanism (upper right) or an individual imido group transfer mechanism (lower right) are shown for comparison with the observed pattern.

to that shown by stoichiometric OsO4/(DHQD)2PHAL under the same conditions. The lower enantioselectivity than achieved under the optimized Sharpless conditions is attributed to the solvent (THF compared to BuOH/H2O). The equivalence of the selectivity under stoichiometric and catalytic conditions demonstrates that the (mes)3Ir=O does not participate directly in the osmylation of the olefin and acts solely as a reoxidant for the osmium.

Oxotrimetaloxiridium(V) can also cocatalyze the room-temperature air oxidation of benzyllic and allylic alcohols to the corresponding aldehydes and ketones. Here the cooxidant is (C6H4=CH)2OsO4 prereduced with a sacrificial alken e such as vinyl acetate or allyl ethyl ether, as was previously described using copper salts as the oxygen-activating component.29 Because alcohol oxidation is not inhibited by the product carbonyl compounds in the way that alkene oxidation is inhibited by the product diols, much higher turnover numbers can be achieved. Thus, complete oxidation of a variety of allyl and benzyl alcohols at atmospheric pressure is routinely achieved in 3 days in THF using 2 mol % of alkene-activated (C6H4=CH)2OsO4 and 1 mol % of O=Ir(mes)3. The scope (primary and secondary benzyllic and allylic alcohols, toleration of other oxidizable functional groups such as alkenes), selectivity (no overoxidation to the carboxylic acid, no oxidation of aliphatic alcohols), and limitations (1,2- and 1,3-diols prevent reaction) are the same as those discussed previously for the osmium/copper-catalyzed process, which requires only about 18 h to go to completion using similar catalyst loadings. In many cases conproportionation is favored and (m)-oxo complexes are the final observed products.30 Quantitative studies for the osmium/copper-catalyzed reactions31,32 and titanium complexes33 (TTP)Mo=O/(TTP)Mo=O are in rapid exchange by NMR even at −80 °C. Even highly exothermic oxygen atom transfer reactions, such as the ~70-kcal/mol downhill34 oxidation of PPh3 by [Ru(bpy)2-](py)(O)]2+ (k_Ru=O = 1.75 × 108 M−1 s−1),42 proceed at slower rates than this degenerate intermetal atom transfer. While there are examples of electron transfer and one-electron atom transfer reactions35 between transition metal centers that proceed at comparable (or faster) rates, the only two-electron atom transfer self-exchange reaction that approaches this rate is the degenerate transfer of Ir1 between [Cp*Ru]3+ and Cp*Ru (k ≈ 7 × 107 M−1 s−1, 20 °C, CD3CN),36 and the rapid rate in this case is contingent on the heavy halogen, with the chlorine analogue undergoing atom transfer at only 16.5 M−1 s−1.37

One obvious reason for the rapidity of the oxygen atom transfer process compared to other examples in the literature is that intrinsic rates are often obscured by rearrangements of the ancillary ligands that accompany the redox chemistry. The dithiocarbamate ligands in the molybdenum(VI) complex (dtc)2MoO must rearrange from trans to cis in order to form the molybdenum(V) μ-oxo complex (eq 8), and chloride transfer is required in addition to oxygen transfer in the porphyrinatochromium or -titanium reactions. Often, the complex in the lower oxidation state binds a ligand which must dissociate to open a site to accommodate the bridging oxygen.

In contrast, the (mes)3IrO/(mes)3Ir and (ArN)3OsO/(ArN)3Os redox couples examined here are well-suited to studying oxygen atom transfer free from complications of ligand dissociation or rearrangement. Both compounds exist in the lower oxidation state as stable, three-coordinate monomers. Oxygen atom transfer can take place near thermoneutrality among these complexes (Table 3), not only in the degenerate reactions but also in the cross-exchange reaction (k_{IrO=Ir}=0.6 at 293 K). Even conproportionation of (mes)3IrO with (mes)3Ir to form the μ-oxo complex (mes)3IrO=Ir=O=Ir(mes)3 is not strongly favored at room temperature (ΔG° = −0.69 kcal/mol at 293 K).

Comparison of the iridium and osmium systems demonstrates that ancillary ligand dissociation or rearrangement is not the only factor limiting oxygen atom transfer rates between metals. Despite the thermodynamic and structural similarities between the iridium and osmium systems, atom transfer in the two systems takes place at vastly differing rates. (ArN)3OsO=O transfers its oxygen atom to (ArN)3Os with a rate constant of

While these are not classical oxygen atom transfer reactions, since they involve only net one-electron transfer, they are related in that they involve electron transfer through an oxygen bridge. Rates range from 0.1 M−1 s−1 (Cr) to 240 M−1 s−1 (Ti).

Given these moderate rates, the extreme facility of oxygen atom transfer between (mes)3Ir=O and (mes)3Ir, with k_{Ir=O}=5 × 107 M−1 s−1 at 20 °C, is remarkable. Although the dearth of quantitative measurements makes comparison difficult, we know of no other examples where a metal oxo complex and its deoxy form are in rapid exchange by NMR at any temperature; (mes)Ir and (mes)3Ir=O are in rapid exchange by NMR even at −80 °C. Even highly exothermic oxygen atom transfer reactions, such as the ~70-kcal/mol downhill34 oxidation of PPh3 by [Ru(bpy)2-](py)(O)]2+ (k_Ru=O = 1.75 × 108 M−1 s−1),42 proceed at slower rates than this degenerate intermetal atom transfer. While there are examples of electron transfer and one-electron atom transfer reactions35 between transition metal centers that proceed at comparable (or faster) rates, the only two-electron atom transfer self-exchange reaction that approaches this rate is the degenerate transfer of Ir1 between [Cp*Ru]3+ and Cp*Ru (k ≈ 7 × 107 M−1 s−1, 20 °C, CD3CN),36 and the rapid rate in this case is contingent on the heavy halogen, with the chlorine analogue undergoing atom transfer at only 16.5 M−1 s−1.37

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The facility of oxygen transfer between iridium centers can be illuminated by an analysis of the bonding in the iridium-mesityl complex. For these reasons, and because of the inherent difficulties in calculations involving third-row transition metals, it is not expected that the computed thermodynamic values would be quantitatively accurate. Nevertheless, the agreement between the experimental and computed geometries (Table 2) indicates that the results from electronic structure calculations can be used in the qualitative arguments outlined above.

Note that the bonding here differs significantly from that in the tetrahedral monooxo complexes (silox)$_3$M=O (M = Nb, Ta), whose stereoelectronic requirements for oxygen atom transfer have been examined by Wolczanski and co-workers. These early metal oxo complexes are d$^3$, so their LUMOs are of $E$ symmetry, which requires a bent approach to allow oxygen atom transfer. This was experimentally demonstrated in the microscopic reverse direction, in that bulky Bu$_3$PO, which is...

sterically inhibited from attaining a bent geometry, is not deoxygenated, while Me₃PO is deoxygenated readily. But in d⁴ (mes)₂Ir=O the lowest e level is filled, and the symmetry-induced barrier to a linear approach is lifted because of the a₁ symmetry of both the (mes)₂Ir=O LUMO and (mes)₂Ir HOMO. The bonding situation in the μ-oxo complex (mes)₂Ir=O-Ir-(mes)₂ also differs from that of the phosphine oxide complex (Ph₃PO)Ir(mes)₃ that is the presumed intermediate in the oxidation of Ph₃P by O=Ir(mes)₃. In the phosphine oxide complex, the electronic differences between iridium and phosphorus favor localization of the HOMO on iridium rather than phosphorus (in contrast to its delocalization over both iridiums in (mes)₂Ir=O-Ir(mes)₃). This filled d₂ orbital would interact unfavorably with the filled orbitals on the oxygen, and in fact the donor complex (Ph₃P)Ir(mes)₃ is observed to have a sawhorse geometry, with a substantial barrier to phosphine binding on the threefold axis. This destabilization of the pseudo-tetrahedral geometry of (Ph₃PO)Ir(mes)₃ as initially formed by atom transfer has been suggested as one factor contributing to the modest rate of oxidation of PPh₃ by (mes)₂Ir. oxidation of (mes)₂Ir, in contrast, can form the stable linear μ-oxo complex directly.

While Os(NAr)₃ is a three-coordinate, late-metal complex like (mes)₂Ir, the osmium complex is planar rather than pyramidal. When the Os(NAr)₃ fragment pyramidalizes to accept the oxygen atom, the d₂ orbital overlaps with the a₁ combination of nitrogen p orbitals (Figure 6). In fact, all the d orbitals are π-antibonding with respect to a pyramidal M(NR)₃ fragment. Since a μ-oxo complex of the form (ArN)₃Os=O–Os(NAr)₃ must accommodate a pair of d electrons somewhere, this pair of electrons must be π* in character and the μ-oxo complex is expected to be a high-energy, effectively 20-electron intermediate. This is consistent with the large barrier to degenerate oxygen atom transfer observed in the osmium system. Computationally, all attempts to find a μ-oxo complex (MeN)₃Os=O–Os(NMe)₃ as a stable minimum or even a first-order saddle point failed; a scan of the Os=O distance from 3 Å to 2.35 Å with all other coordinates fully optimized leads to a monotonic rise in energy of 10 kcal/mol (Figure S9).

Another way of thinking about these electronic influences on the rate of oxygen atom transfer is to consider them as an inner-sphere reorganization energy. Barriers to single electron transfer in the Marcus framework are principally ascribed to the effects of driving force and reorganization energy λ. The reorganization energy can be further partitioned into an outer-sphere term, λₒ, involving rearrangement of solvent and counterions, and an inner-sphere term, λᵢ, which encompasses the changes in bond lengths and angles upon electron transfer. The effect of the λᵢ term on electron-transfer rates has been extensively explored.

Viewed from this perspective, the (mes)₃Ir fragment supports exceptionally rapid oxygen atom transfer because it has an exceptionally small inner-sphere reorganization energy. Indeed, crystallographic results on all three oxidation states reveal a (mes)₃Ir fragment whose Ir–C bond lengths and angles are identical within experimental error (Table 2). The only significant bonding change on oxygen transfer takes place along the Ir=O–Ir axis (as it must in order to achieve atom transfer). In contrast, the reduced osmium complex, Os(NAr)₃, is planar, while that fragment is pyramidal in O=Os(NAr)₃. Because of the d₇−π₇ repulsions on pyramidalization, this bonding change is expected to be energetically costly, and thus Os(NAr)₃ is expected to have a substantial inner-sphere reorganization energy and correspondingly slow rates of oxygen atom transfer.

If the bonding changes on atom transfer can be considered analogous to inner-sphere reorganization energy in electron-transfer reactions, then the analogy between the present study and explorations of the Marcus cross-relation is evident. This is the first example where self-exchange and cross-exchange kinetics of oxygen atom transfer have been measured in a system where the thermodynamics of cross-exchange are known. The cross relation has been applied to other one-electron inner-sphere reactions, such as hydrogen atom transfer, as well as to proton transfer, but this appears to be the first example of any multielectron atom transfer reaction to have been examined in this way. For example, while rates have been measured for the two-electron pseudo-self-exchange reactions between nitrido-metal and chlorometal porphyrins (both Mn(V)/Mn(III) and Cr(V)/Cr(III)) and the corresponding Mn/Cr cross-exchange, the cross-reactions are irreversible and the driving force is unknown. A similar situation is found in the two-electron halogen transfer reactions between Cp₂RuX⁺ and Cp₂OsX³⁺.

The Marcus cross-relation, if applied to the iridium–oxygen atom transfer reaction studied here, predicts that ΔG°ₐ₀ = ΔG°ₐₙ + ΔG°ₐₐₙ + ΔG°ₓ₈.⁴⁷ The activation barrier for cross-exchange calculated in this way is 15.3 ± 0.4 kcal/mol, in excellent agreement with the observed barrier of 15.8 ± 0.9 kcal/mol. While it is far too early to decide whether the Marcus-style analysis of oxygen atom transfer will be generally applicable, its success in this case is part of a growing number of studies that suggest that many of the same principles that govern outer-sphere electron transfer are useful in understanding the rates of atom transfer. In particular, effects of inner-sphere reorganization, whose importance in atom transfer is dramatically illustrated by the system described here, have been applied to explain rates of hydrogen atom transfer, and proton-transfer reactions can in many cases be rationalized by inner-sphere reorganization energy, as in cases where slow proton transfers into other states dominate the overall rate.
from carbon or from metal hydrides have been attributed to the need to change the geometry and bonding at the center bound to the proton. One is accustomed to thinking of inner-sphere reactions in terms of the electronic details of how bonds can be made and broken. The electronic contrast between the iridium system, where transfer of the oxygen atom in a linear fashion is orbitally allowed, and the osmium system, where it is not, is in line with these expectations. Yet the orbital effects can be viewed as simply another way of expressing inner-sphere reorganization: the (mes)Ir fragment is unchanged in the three oxidation states because the bonding changes to oxygen do not affect the metal-carbon bonds, and the electronic difficulties in achieving a μ-oxo complex of osmium are reflected in the energetic cost of pyramidalizing the Os(NAr)3 fragment.

The reorganization energy is certainly not the only factor in atom transfer reactions. Clearly, a key distinction between oxygen atom transfer and both outer-sphere electron transfer and one-electron inner-sphere processes such as hydrogen atom transfer is the presence of an intermediate in oxygen atom transfer reactions. If this intermediate is high in energy, oxygen atom transfer is slow regardless of the degree of inner-sphere reorganization. For example, main group oxygen atom transfer partners such as phosphines and phosphine oxides have structurally similar R3P fragments, yet direct atom transfer between main group partners is usually vanishingly slow because of the marked instability of a putative μ-oxo intermediate such as R3P-O-PR3. Similarly, the fact that (mes)Ir=O and (ArN)Os=O both oxidize triphenylphosphine at very similar rates contradicts simple predictions based on reorganization energy, which would imply much slower rates of reaction with osmium.

The instability of a pseudo-tetrahedral intermediate (mes)Ir(OOPPh3) (the phosphine adduct (mes)Ir(PPh3)) is over 12 kcal/mol lower in free energy in its saddle-shaped geometry than as a tetrahedron6) may contribute to the barrier for phosphine oxides by iridium in this case.

The thermodynamic instability of the μ-oxo osmium complexes (ArN)Os=O-MX3 is an adequate qualitative explanation for the slower rate of intermetal oxygen transfer involving osmium. The kinetic effects in intermetal oxygen atom transfer, however, are not negligible: for iridium, essentially thermoneutral formation of the μ-oxo intermediate nevertheless has a 6.8 kcal/mol barrier. The quantitative agreement between the observed and calculated cross-reaction rates suggests that not only the thermodynamic effects on the stability of the intermediate but also the kinetic effects in its formation scale linearly on progressing from iridium to osmium.

Use of (mes)Ir=O as an “Innocent” Dioxide Activator. Trimesityliridium(III) undergoes extremely rapid oxygen atom transfer with oxotrimesityliridium(V), but this reaction is degenerate and therefore cannot be harnessed to achieve net chemical change. The ability of the (mes)Ir fragment to mediate intermetal oxygen atom transfer extends to nondegenerate intermetal atom transfer reactions as well, as demonstrated by the ability of (mes)Ir=O to oxidize Os(NAr)3 at respectable rates (kO2 = 10 M−1 s−1, extrapolated to 293 K). Combining the ability of (mes)Ir to activate O2 to form (mes)Ir=O with the ability of (mes)Ir=O to transfer its oxygen atom rapidly to other metal centers raises the intriguing possibility of a general scheme for cocatalyzed air oxidation (Scheme 2). Many reagents can oxidize organic substrates but are kinetically unable to be reoxidized by dioxygen. If they were able to accept an oxygen atom from (mes)Ir=O, then the addition of catalytic amounts of oxotrimesityliridium could transform an otherwise stoichiometric organic oxidation to a catalytic one using dioxygen as the stoichiometric oxidant, with potential advantages in cost and environmental impact. Furthermore, since the iridium would interact only with the oxidant and not with the substrate, the selectivity of the oxidation would be that of the stoichiometric reagent and would be unaffected by the iridium.

Use of oxotrimesityliridium(V) as a cocatalyst in air oxidations has been demonstrated in two systems: with amine-ligated osmium tetroxide in the dihydroxylation of terminal alkenes26 and with osmium(VI) esters in the oxidation of allyl and benzyl alcohols to aldehydes.29 Both reactions require stoichiometric osmium in the absence of iridium but can use air as the stoichiometric oxidant in the presence of catalytic (mes)Ir=O. The “innocence” of the iridium (the fact that it is not involved in substrate oxidation) is demonstrated in the first reaction by the observation that the enantiomeric excess of 1,2-octanediol using (DHQD)2PHAL as a chiral ligand is identical in the stoichiometric oxidation and cocatalytic oxidations.

Osmium/iridium-cocatalyzed dihydroxylations are strongly inhibited by the 1,2-diol product (Figure S8), which limits the number of turnovers (~5 per week) and the scope of the reaction (more substituted alkenes, whose diols bind more tightly, do not turn over). The product inhibition supports a mechanism in which reversible loss of diol occurs from the observed osmium(VI) diolate resting state preceding rate-determining oxygen atom transfer from iridium to the osmium complex produced by loss of diol. Assignment of this unobserved osmium species as “OsO4” (or a ligated form thereof) is plausible, given the stability of isoelectronic Os(NAr)3 and its proven ability to accept an oxygen atom from (mes)Ir=O. Little can be said about the reoxidation step in the alcohol oxidation; it is unknown even whether reoxidation takes place at the Os(VI) or Os(V) oxidation state.

In neither of these particular reactions does use of (mes)Ir=O represent a practical advance as an oxygen activator, since dioxygen use in both dihydroxylations and alcohol oxidations using osmium is cocatalyzed equally effectively with much cheaper copper salts, and indeed under certain conditions aerobic oxidations of alkenes and alcohols can take place without a cocatalyst (albeit the selectivity in the latter reaction is different from that observed here). Still, the fact that (mes)Ir=O can be used as an efficient activator of dioxygen in catalytic

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reactions has potentially important consequences. First, the well-defined nature of the (mes)₃Ir=O/(mes)₃Ir redox couple and its inertness to most reactions other than intermetal oxygen atom transfer may make it a suitable cooxidant in delicate systems where copper salts would be unsuitable. For example, many late-metal complexes have been prepared which activate hydrocarbons, but linking this reactivity with dioxygen reduction to achieve catalytic selective hydrocarbon oxidation remains a challenge. In these and other organometallic systems, the inertness of its supporting ligands and its reluctance to undergo outer-sphere electron transfer may make trimesityliridium a more attractive cooxidant than, say, copper salts. Second, the analysis presented here highlights some of the reasons for the reactivity of the (mes)₃Ir=O/(mes)₃Ir couple toward oxygen atom transfer, notably the importance of minimizing inner-sphere reorganization energy. The use of these principles may aid in the development of new, perhaps cheaper or more reactive, oxygen atom transfer agents for use in catalysis.

Conclusions

Oxotrimesityliridium(V), (mes)₃Ir=O, undergoes degenerate oxygen atom transfer with trimesityliridium(III), (mes)₃Ir, at unprecedentedly fast rates (k_{IrIr} = 5 \times 10^7 \text{M}^{-1}\text{s}^{-1}, extrapolated to 293 K). In contrast, the osmium(VIII) oxo complex (ArN)₃Os=O, with an essentially identical metal–oxygen bond strength, transfers its oxygen to (ArN)₃Os 12 orders of magnitude more slowly (k_{OsOs} = 1.8 \times 10^{-5} \text{M}^{-1}\text{s}^{-1}). Cross-reaction takes place at intermediate rates, in quantitative agreement with a Marcus-type analysis. The unusual facility of the iridium oxygen atom transfer can be explained by orbital alignment (both the HOMO of (mes)₃Ir and the LUMO of (mes)₃Ir=O have \sigma symmetry, making atom transfer allowed in a linear geometry) and by low inner-sphere reorganization energy (the triaryliridium geometry is structurally identical in the III, IV, and V oxidation states). The ability of (mes)₃Ir to activate dioxygen and then transfer an oxygen atom to another metal has been demonstrated in catalytic cycles involving osmium complexes as the substrate-activating species to achieve alkene and alcohol oxidation.

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Supporting Information Available: Complete refs 22 and 23; variable-temperature NMR spectra of (mes)₃Ir=O; Eyring plots of bond rotation in (mes)₃Ir=O; dissociation of (mes)₃Ir=O→Ir(mes)₃, deoxygenation of (ArN)₃Os=O by PPh₃, and oxygen atom transfer from (mes)₃Ir=O to Os(NAr)₃; van’t Hoff plot of oxygen atom transfer from (mes)₃Ir=O to Os(NAr)₃; kinetic traces for oxygen atom transfer between (ArN)₃OsO and (Ar₃N)₃Os and for (mes)₃IrO/(quinuclidine)OsO₄-cocatalyzed air oxidation of octene; Cartesian coordinates, energies, and thermal corrections of all optimized structures; and a plot of energy vs distance scan for (CH₃N)₃Os=O→Os(NCH₃)₃ (PDF format); and crystallographic data for (Me₂C₆H₃)₃Ir=O→Ir-(C₆H₅CH₃)₃;CD₂Cl₂ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.