Computational Study of Low-Coordinate Rhenium Diolates, Metallaoxetanes, Oxo Complexes, and Carbenes

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Summary: CCSD energies with a triple-ζ quality basis set at DFT geometries show that low coordination numbers favor metallaoxetane over diolate isomers in high-valent rhenium complexes. Minima and transition states are located and used to rationalize recently published experimental studies of the gas-phase chemistry of the title complexes. The experimental and theoretical studies shed light on the related chemistry of isoelectronic osmium complexes involved in catalytic asymmetric dihydroxylation.

Scheme 1

We report a combined density functional theory (DFT)/coupled cluster (CCSD) study of the interconversion between isomeric Re diolate and metallaoxetane complexes,[1] and their dissociation to either oxo or carbene products. The computational study accompanies experimental work we have recently reported, which shows that, contrary to the consensus opinion, certain structural features enable the rearrangement of Re[V] diolate complexes to the isomeric metallaoxetane, and the subsequent loss of an aldehyde to form a Re carbene complex, in competition with the otherwise expected loss of olefin.[2] The experimental work had been motivated in large part by earlier, albeit low-level and incomplete, calculations (reported therein) of the relative stability of diolate versus the isomeric metallaoxetane. Given the decisive role that computation had played in disqualifying metallaoxetanes as intermediates in the chemistry of OsO_4,[3] the present study seeks to show that this judgment depends on structural features in a simple way, with qualitative theory suggesting that the preference may be reversible by simple structural changes. The qualitative theory, which predicted an energetically plausible metallaoxetane intermediate, is confirmed in the present computational work, in which not only the equilibrium geometries but also the transition states connecting the various species have been found (Scheme 1).

Calculations were performed on the Re species using the ADF 2000.02 (Amsterdam Density Functional) package or Gaussian 2003 on Quant-X Alpha (Compaq Unix Tru64 5.3), HP Superdome with 64 PA8600 processors (HP/UX), and AMD Athlon (Red Hat Linux 7.1) machines. Given the relatively small size of the complexes, a full quantum-mechanical model was used in the DFT calculations,[4] as is described fully in the
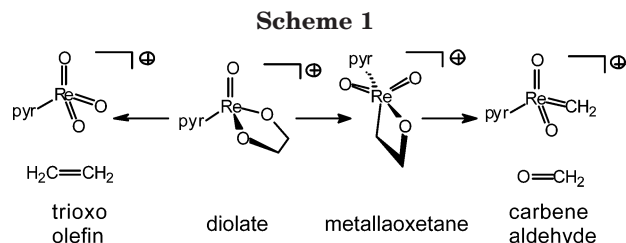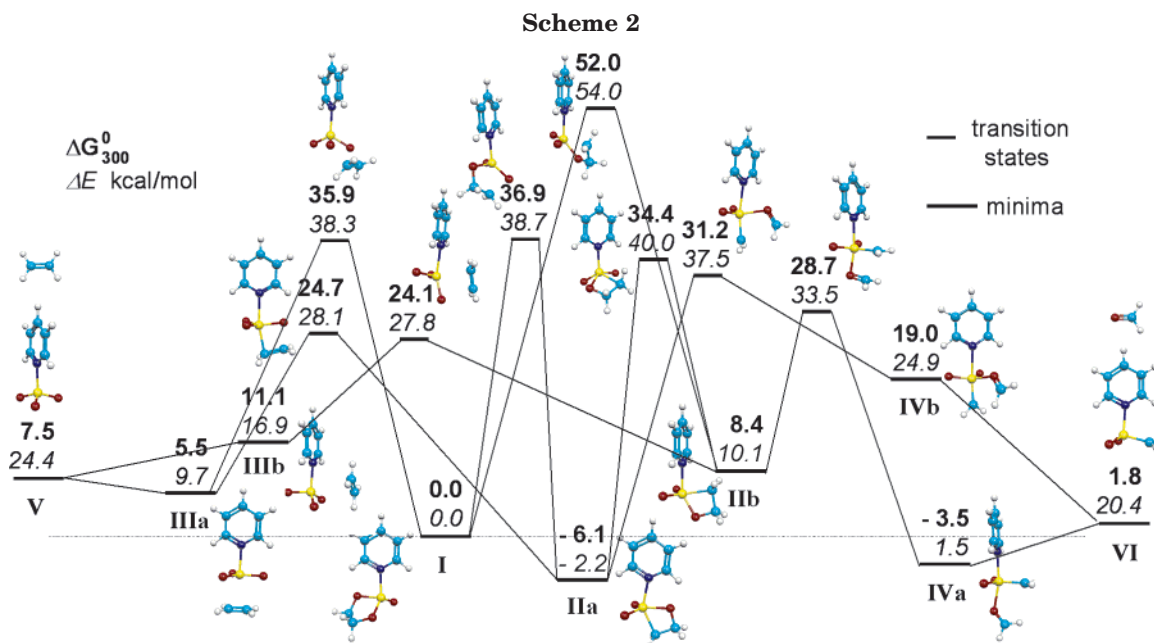
Supporting Information. All critical points were checked by frequency calculations to verify that they are minima or transition states. Transition states were localized approximately by linear transit and then optimized. Finally, intrinsic reaction coordinate (IRC) calculations were performed to verify that each optimized transition state indeed connected the minima in question. Each critical point was then recalculated using coupled-cluster theory (CCSD) with a polarized triple-ζ-quality basis set for the valence electrons and the Hay−Wadt effective core potential on rhenium. Checks at selected points showed that CCSD(T) did not bring any significant changes. Further details of the calculation, as well as the corrections of the internal energy to Gibbs free energy, were done as described in the Supporting Information. The corrections to the internal energy are necessary, even in a qualitative picture, because the surface spans a dissociation of one molecule into two. A temperature of 300 K was assumed in the corrections for the sake of illustration. Although we believe relative energies to be reliable to within about 5 kcal/mol, we cannot exclude systematic errors, given the paucity of tests against experiment for comparable reference systems.

The CCSD/TZP//BP86 internal energies and free energies are shown in Scheme 2. Coupled-cluster energies at DFT geometries have been claimed to give the best possible energetic results with current technology.[5]

(3) Haller, J.; Strassner, T.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 8031. Norrby, P. O.; Rasmussen, T.; Haller, J.; Strassner, T.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 10186. Pidun, U.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2817. Dapprich, S.; Ujaque, G.; Maseras, F.; Lledós, A.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1996**, *118*, 11660. Torrent, M.; Deng. L.; Duran, M.; Sola, M.; Ziegler, T. *Organometallics* **1997**, *16*, 13. Ujaque, G.; Maseras, F.; Lledós, A. *J. Am. Chem. Soc.* **1999**, *121*, 1317. Deubel, D. V.; Frenking, G. *J. Am. Chem. Soc.* **1999**, *121*, 2021. Gisdakis, P.; Rösch, N. *J. Am. Chem. Soc.* **2001**, *123*, 697. Deubel, D. V.; Schlecht, S.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 10085.

(4) Geometry optimizations for minima and transition states were done with BP86. Re was treated with the Hay-Wadt ECP; a polarized triple-ζ-quality basis set was used for the valence electrons. H, C, N, and O were treated with a polarized double-ζ-quality basis set in the DFT part. CCSD energies used a triple-ζ-basis set throughout.

(5) Niu, S.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 1360. Sekusak, S.; Frenking, G. *THEOCHEM* **2001**, *541*, 17.

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(1) A review of the rhenium and osmium work has appeared: Deubel, D. V.; Frenking, G. *Acc. Chem. Res.* **2003**, *36*, 645.

(2) Chen, X.; Zhang, X.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 3798. Zhang, X.; Chen, X.; Chen, P. *Organometallics* **2004**, *23*, 3427.

Scheme 2

Aside from the confirmation of the relative energies predicted by qualitative theory, the calculation finds olefin and aldehyde complexes whose binding energy relative to the separated components depend strongly on temperature. Upon activation by collision, the Re^V diolate rearranges by a concerted 1,2-shift to the more favorable metallaoxetane isomer in which the Re−O bond is cis to the pyridine ligand. The transition state for the 1,2-shift is energetically near-degenerate to the transition state for a retro-[3 + 2] cleavage of the diolate to the rhenium trioxo complex and an olefin. This initial competition should largely determine the product ratio in the overall dissociation reaction. The metallaoxetane has similar competing exit channels, one leading to the carbene and aldehyde product via an aldehyde σ-complex and the other to the trioxo and olefin product via a retro-[2 + 2] cleavage to the olefin π-complex. Because the lower energy metallaoxetane leads to the higher energy aldehyde σ-complex, there are two possible pathways to the carbene. One goes directly through the higher energy aldehyde complex. The other starts with a conversion of the trigonal-bipyramidal cis metallaoxetane to the higher energy trans isomer via a square-pyramidal transition state. The transition state for interconversion between the two isomeric metallaoxetanes comes out surprisingly high in energy, given the common wisdom that five-coordinate complexes are stereochemically fluxional.[6] Although we performed an extensive search through structural space, we cannot definitively exclude the possibility that a lower energy transition state exists. For all species in the calculation, one should note, however, that the calculated free energy refers to the free energy change at standard state. Conditions under which the dissociation has been studied experimentally would tilt the reaction more in favor of dissociation. Moreover, our experiments show that substitution greatly enhances the yield of carbene versus that of the trioxo complex; therefore, the computed surface in this report is a "worst" case scenario for carbene production.[7]

The most convincing argument against the intermediacy of metallaoxetanes in the asymmetric dihydroxy-

lation of olefins catalyzed by OsO$_4$ and chiral tertiary amines, i.e., the stepwise [2 + 2] versus concerted [3 + 2] mechanism, had been delivered by theory. Computational studies compared the energetics of Os^{VI} diolates and the isomeric osmaoxetanes and found that the metallaoxetanes were uniformly 10−30 kcal/mol higher in energy than the diolates.[3] If the transition states leading in and out of these structures were correspondingly higher, then one could conclude with reasonable certainty that the metallaoxetanes play no significant role in OsO$_4$-catalyzed dihydroxylation reactions.[8]

The relative ordering diolate < metallaoxetane was explained qualitatively by Rappé, who pointed out that, for a model tetrahedral d^0 complex such as OsO$_4$, a maximum of two strong ligand−metal π-bonds are possible.[9] Formally, OsO$_4$ has four ligand−metal π-bonds, which means that two electron pairs must go into much less bonding, or even slightly antibonding, orbitals. Rappé termed the effect "π-strain" and suggested that the formation of a diolate with attendant elimination of two π-bonds is favored over formation of the metallaoxetane, where the π-bond order decreases by only 1 because of greater relief of π-strain. Rappé's argument is a clever, qualitative explanation for the more quantitative DFT results in the literature. It neglects, however, one point. Examination of the metallaoxetane and isomeric diolate shows that the former always has a coordination number that is higher by 1 than that of the latter. A proper comparison of the π-strain for the isomers requires consideration of coordination number. At its simplest, qualitative theory predicts that the maximum number of strong π-bonds is set by the number of low-lying d orbitals in the idealized four-,

(6) Both pseudorotation and a turnstile mechanism are possible, but there are a large number of pathways for which the transition states were very difficult to localize. A review is given by: Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288.

(7) Preliminary calculations of the alkyl-substituted complexes show that the transition states to carbene products are selectively stabilized.

(8) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. Dupau, P.; Epple, R.; Thomas, A. A.; Fokin, V. V.; Sharpless, K. B. *Adv. Synth. Catal.* **2002**, *344*, 421.

(9) Pietsch, M. A.; Russo, T. V.; Murphy, R. B.; Martin, R. L.; Rappé, A. K. *Organometallics* **1998**, *17*, 2716.

five-, and six-coordinate geometries. For the kinds of systems computed in this study, i.e., complexes with the composition $[LReO_3^+H_2C{=}CH_2]$ or (as previously done) ligand-accelerated asymmetric dihydroxylation, one compares either a four-coordinate diolate to a five-coordinate metallaoxetane or a five-coordinate diolate to a six-coordinate metallaoxetane, respectively. In the former comparison, the diolate has two low-lying d orbitals versus three or four for the metallaoxetane. In the latter, the diolate has three or four low-lying d orbitals versus three for the metallaoxetane. Accordingly, with π-donor ligands, we predict that the energetic ordering diolate < metallaoxetane will apply for five-coordinate diolates and six-coordinate metallaoxetanes, as has been seen in all quantum-chemical calculations to date. Reducing the π-donor number and the coordination number by 1, however, should reverse the ordering. The Hammond postulate would predict that the transition states would be moved in a similar way. Scheme 2 shows that the expectation is fully confirmed. Our earlier, albeit lower level, calculations show that this inversion of stability does not occur when the coordination number is higher, i.e., the higher coordinate Re complexes behave like their Os analogues.[2]

The present study validates the predictions of qualitative theory that the number of π-donors and the coordination number control the relative energies of high-valent metal diolates and the isomeric metallaoxetanes. The conclusions in previous studies that metallaoxetanes lie energetically too high to play a significant role in oxidation chemistry must be therefore reexamined. Moreover, a rearrangement and dissociation of easily prepared diolate complexes to metathesis-active transition-metal carbenes promises new fundamental chemistry and applications.

Supporting Information Available: Tables giving coordinates, frequencies, and energies for all computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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