"Mass Spectrometric Study of the Conversion of Rhenium Diolates to Metallaoxetanes and Carbenes. Coordination Number, Polar, and Steric Effects"

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Mass Spectrometric Study of the Conversion of Rhenium Diolates to Metallaoxetanes and Carbenes. Coordination Number, Polar, and Steric Effects

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A combination of mass spectrometric gas-phase ion−molecule reactions and density functional theory electronic structure calculations indicates that, at least in high-valent rhenium oxo complexes, a diolate complex can dissociate preferentially to form a carbene complex, which most likely proceeds via a metallaoxetane intermediate. The experimental study finds effects on the efficiency of carbene production due to coordination number, polar substituents, and steric hindrance. Both qualitative theory and DFT calculations confirm the central role played by coordination number and furthermore define the structural conditions under which the reaction sequence, diolate → metallaoxetane → carbene complex, should become favorable. The results are relevant, not only to oxidation chemistry but also for the initiation mechanism in some olefin metathesis catalysts.

Introduction

The chemistry of high-valent oxo complexes has been examined in connection with a wide range of stoichiometric and catalytic reactions. The oxo complexes are intermediates in epoxidation, dihydroxylation, aminohydroxylation, and other oxidation reactions.[1] Much of the chemistry has been developed around OsO_4, but other complexes, in particular MnO_4^-, CrO_2Cl_2, and $LReO_3$ (L = ligand), have shown similar reactivity. The diolates are often isolable intermediates from the reaction medium in oxidations of olefins by, for example, $Pb(OAc)_4$, permanganate, or, particularly, OsO_4. The mechanism for formation of the transition metal diolates has been furthermore controversial, with two routes, termed [3+2][2] and [2+2],[3] having been seriously considered. The two pathways from oxo complex to diolate differ in that the former is a concerted cycloaddition, whereas the latter is a stepwise reaction via an metallaoxetane intermediate (Scheme 1). Metallaoxetanes have been invoked as intermediates in aldehyde olefination by rhenium complexes,[4] as well as in the termination step of olefin metathesis, catalyzed by molybdenum or tungsten complexes, by aldehydes and ketones.[5] There is accordingly a manifold of reactions passing through five-membered ring intermediates and another manifold of reactions that proceed via four-membered
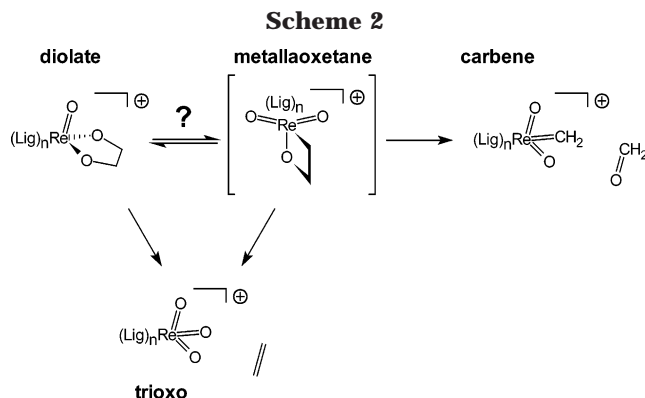
Scheme 1
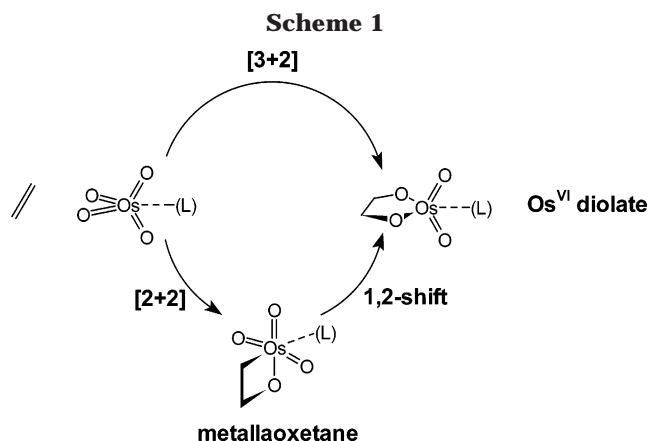
metallaoxetane

ring structures. An interconversion of high-valent transition metal diolates and the corresponding metallaoxetanes would be a "missing link" reaction between these two worlds. No compelling experimental evidence for a chemically plausible connection between these two manifolds has been presented to date, although a fair observer would find no reason a priori that a connection should not exist, at least under some circumstances. Given that stereoselection in the asymmetric dihydroxylation (AD) reaction[6] catalyzed by OsO_4 complexes in the presences of cinchona alkaloids occurs in the reactions that form the diolate, the mechanistic question assumes a considerable practical significance.

Whereas earlier computational work[7] shed doubt on the thermochemical plausibility of an intermediate metallaoxetane, not all structural possibilities were actually considered. Especially, the effect of low coordination number had not been adequately addressed.

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Scheme 2

In a preliminary report,[8] we showed evidence for the rearrangement of low-coordinate Re[V] diolate complexes to metallaoxetanes, followed by their dissociation to produce rhenium carbene complexes[9] and an aldehyde (Scheme 2).

The reaction even proceeded preferentially to the otherwise expected dissociation to an oxo complex and olefin. We report here experimental and computational studies of Re[V] diolates and Re carbene complexes that bear on the question of the interconversion of diolate and metallaoxetane complexes. The present results strongly suggest that specific circumstances with regard to substitution, coordination number, and ligand type render a metallaoxetane intermediate chemically plausible and that, moreover, the putative intermediacy may be established by the identification of at least one product, a carbene complex, which may be unambiguously associated with the metallaoxetane.

Experimental Section

The Re[V] diolates were prepared by a route analogous to that reported by Paulo et al.[10] by addition of 1 equiv of the appropriate diol (or epoxide) and the ligand to substitutionally labile *fac*-ReOCl$_3$(SMe$_2$)(OPPh$_3$)[11] or [(pyr)$_4$ReO$_2$]$^+$Cl$^-$ (pyr = pyridine)[12] complexes in CHCl$_3$ or CH$_2$Cl$_2$ solution at room temperature. The clean formation of the Re[V] diolate complex in solution can be confirmed by ^{1}H NMR (see Supporting Information). Often it is advantageous to precipitate the diolate from the CHCl$_3$ or CH$_2$Cl$_2$ solution with an excess of hexane so that excess reagents, e.g., ligand, may be separated off. The precipitate is then redissolved in polar solvent and used as before. Re[V] diolates have been prepared by similar methods by Davison[13] and have been fully characterized in that work. The diolates prepared in this work were used in the ESI-MS/MS experiments without further purification.

The complexes were typically diluted to 10^{-5} M with CH$_2$Cl$_2$ and electrosprayed on a modified Finnigan MAT TSQ-700 tandem mass spectrometer as has been previously described.[8,14−16] Mild desolvation conditions were used, e.g., tube lens ~80 V, although studies of sequential reactions

required more activation, e.g., tube lens up to 112 V, which is still rather soft. Collision-induced dissociation (CID) could be done in either the radio frequency (rf) 24-pole ion guide by collision with Xe (5−80 mTorr pressure) or in a gas-filled (~1 mTorr of either Xe or reagent gas) rf octopole ion guide. CID and ion−molecule reactions were all performed at low collision energy, i.e., −3 to −15 V in the laboratory frame.

Quantum mechanical calculations were performed with Titan 1.0.7[17] or Spartan '02[18] on a 1.3 GHz Pentium PC. After geometry optimizations, frequency calculations with numerical second derivatives were performed for each structure to confirm the number of negative frequencies, either zero or one, for minima and transition states. Moreover, the transition vector for each transition state was examined to confirm that it matched the expected reaction coordinate. All structures and energies in the Titan calculations were optimized with pseudospectral density functional theory (DFT) algorithms from the Jaguar[19] program. The B3LYP exchange−correlation functional,[20] comprised of the correlation functional of Lee, Yang, and Parr and exchange functional of Becke, was used with the LACVP** basis set.[21] The basis set is a polarized double-ζ basis set, equivalent to 6-31G** for the light elements, with an effective core potential (ECP) for the rhenium. The outermost core orbitals, comprising the 5s^{2}5p^6 configuration on rhenium, are not replaced by the ECP but are treated on an equal footing with the 5d, 6s, and 6p valence orbitals. The ECP also contains mass−velocity and relativistic effects in the potential.

Results

The gas-phase chemistry of the Re[V] diolates form the bulk of the results in this report. The syntheses of the diolates from a soluble Re[V] coordination complex, ligand, and a diol occur via simple ligand exchange and condensation reactions (bond formation with loss of H$_2$O) and are amply precedented in the literature. Mixtures of ligands and/or mixtures of diols produce libraries of

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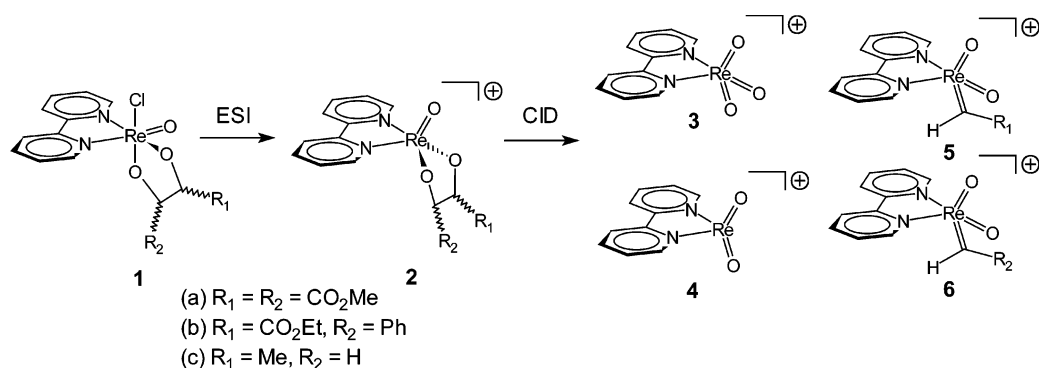(17) *Titan 1.0.7*, Schrödinger Inc.: 1500 SW First Ave., Suite 1180, Portland, OR 97201.

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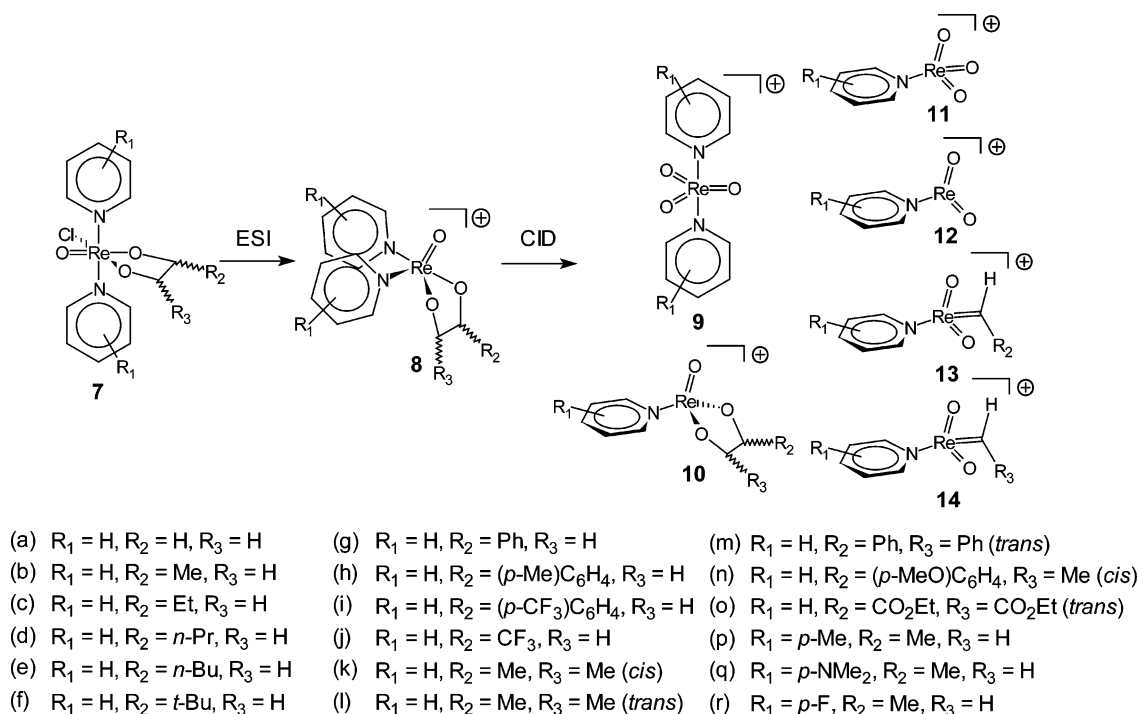(19) *Jaguar* version 3.5, release 42; Schrodinger, Inc.: Portland, OR, 1998.

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Scheme 3

(a) $R_1 = R_2 = CO_2Me$
(b) $R_1 = CO_2Et$, $R_2 = Ph$
(c) $R_1 = Me$, $R_2 = H$

Scheme 4

(a) $R_1 = H$, $R_2 = H$, $R_3 = H$	(g) $R_1 = H$, $R_2 = Ph$, $R_3 = H$	(m) $R_1 = H$, $R_2 = Ph$, $R_3 = Ph$ (*trans*)
(b) $R_1 = H$, $R_2 = Me$, $R_3 = H$	(h) $R_1 = H$, $R_2 = (p\text{-}Me)C_6H_4$, $R_3 = H$	(n) $R_1 = H$, $R_2 = (p\text{-}MeO)C_6H_4$, $R_3 = Me$ (*cis*)
(c) $R_1 = H$, $R_2 = Et$, $R_3 = H$	(i) $R_1 = H$, $R_2 = (p\text{-}CF_3)C_6H_4$, $R_3 = H$	(o) $R_1 = H$, $R_2 = CO_2Et$, $R_3 = CO_2Et$ (*trans*)
(d) $R_1 = H$, $R_2 = n\text{-}Pr$, $R_3 = H$	(j) $R_1 = H$, $R_2 = CF_3$, $R_3 = H$	(p) $R_1 = p\text{-}Me$, $R_2 = Me$, $R_3 = H$
(e) $R_1 = H$, $R_2 = n\text{-}Bu$, $R_3 = H$	(k) $R_1 = H$, $R_2 = Me$, $R_3 = Me$ (*cis*)	(q) $R_1 = p\text{-}NMe_2$, $R_2 = Me$, $R_3 = H$
(f) $R_1 = H$, $R_2 = t\text{-}Bu$, $R_3 = H$	(l) $R_1 = H$, $R_2 = Me$, $R_3 = Me$ (*trans*)	(r) $R_1 = p\text{-}F$, $R_2 = Me$, $R_3 = H$

different diolate complexes suitable for screening, although this particular feature of the synthesis was not exploited systematically in the present work.[22] The mass spectra of the unpurified diolate complexes show peaks derived from a single species. Spot checks with ^{1}H NMR, for example (see Supporting Information), for the diolates prepared from $ReOCl_3(SMe_2)$-$(OPPh_3)$, 2,2′-bipyridine, and either dimethyltartrate or ethylene glycol show only the expected (bipy)ReOCl-($-$O-bridge-O$-$) complexes analogous to those reported by Davison.[13]

When complexes **1** or **7** are prepared and diluted in CH_2Cl_2 and electrosprayed, the cations **2** or **8** in the small fraction of dissociated ion pairs in polar solution are transferred to the gas phase (Schemes 3 and 4). Depending on the tube lens potential, the complexes **8** can appear as either **8** or **10**. Any of these species, **2**, **8**, or **10**, can be mass-selected in the first quadrupole, usually as the isotopomer with [187]Re, for CID or reaction in the following octopole collision cell. The reactions are listed in Table 1 for the collision-induced dissociation (CID) of a selected ion with Xe at low collision energies. From previous work,[14] we know that these conditions correspond to a rather gentle CID process.

In cases where comparisons across differently substituted complexes were to be done, the spectra were taken sequentially with the conditions, especially the collision energy and pressure of collision gas, held constant.

The in situ preparation of the diolate complexes from a stoichiometric mixture of $ReOCl_3(O=PPh_3)$-(Me_2S), 2,2′-bipyridine, and racemic dimethyltartrate in CH_2Cl_2 proceeds quantitatively according to NMR, yielding the two expected diastereomers in approximately 1:1 ratio. As noted in entry 1 of Table 1, electrospray, selection of the isotopomer at $m/z = 535$, and then collision-induced dissociation (CID) produces a small but definite peak at $m/z = 447$ in addition to the major product at $m/z = 391$. The latter is the expected $[(bipy)\text{-}ReO_3]^+$ ion, while the former has the mass of the carbene complex $[(bipy)ReO_2(=CHCO_2Me)]^+$ produced by loss of an aldehyde. A similar experiment in which ethyl 3-phenylglycerate was used instead of dimethyltartrate yielded the comparable peak at $m/z = 461$, which

(22) By adding different concentrations of various substituted pyridines, for example, to compensate for gross differences in binding affinity, multiple complexes can be prepared in one pot. These can be electrosprayed and mass-selected. Zhang, X.; Chen, P., unpublished work.

Table 1. Listing of the Gas-Phase CID Experiments[a]

	starting complex (in soln)	selected ion	product ions after CID by xenon	comments
1	**1a**	**2a**	**3**, [**5a**]	isomer of **5a**
2	**1b**	**2b**	**3**, [**5b**]	isomer of **5b**; no **6b** formed
3	**1c**	**2c**	**3**	no other products
4	**7a**	**8a**	**9a, 10a, 11a**	**11a** is the major product
5	**7a**	**10a**	**11a, 12a, 13a**	**11a/13a** about 1:1; **12a** is minor product
6	**7b**	**8b**	**9b, 10b, 11b, 12b**	**10b, 11b** are the major products
7	**7b**	**10b**	**11b, 12b, 13b, 14b**	**13b/14b** (1:3) are the major products
8	**7c**	**8c**	**9c, 10c, 11c, 12c, 13c, 14c**	**10c, 11c** large; **13c, 14c** very small
9	**7c**	**10c**	**11c, 12c, 13c, 14c, [10c−18]**	**13c/14c** (1:2) are the major products
10	**7d**	**8d**	**9d, 10d, 11d, 12d, 13d**	**10d, 11d** large; **13d** very small
11	**7d**	**10d**	**11d, 12d, 13d, 14d**	**13d/14d** (1:1) are the major products
12	**7e**	**8e**	**9e, 10e, 11e, 12e, 13e, 14e**	**11e** large; **13e, 14e** very small
13	**7e**	**10e**	**11e, 12e, 13e, 14e**	**13e** is major product; **14e** is smaller, 1.4:1
14	**7f**	**8f**	**9f, 10f, 11f, 12f, 13f, 14f**	**10f** is major product; also small [**10f**−70]
15	**7f**	**10f**	**11f, 12f, 13f, 14f, [10f−18]**	unidentified ion at [**10f**−70] also seen
16	**7g**	**8g**	**9g, 10g, 11g**	**9g** is major products, **12g** not seen
17	**7g**	**10g**	**11g, 12g, [10g−18], [12g+79]**	**9g, 11g** is the major product
18	**7h**	**8h**	**9h, 10h, 11h, 12h, [12h+79]**	unidentified ion at [**8h**−151]
19	**7h**	**10h**	**11h, 12h, [12h−18], [10h−18]**	unidentified ions at [**10h**−75], [**10h**−97]
20	**7i**	**8i**	**9i, 10i, 11i, 12i, [12i+79]**	**9i, 11i** are major products, **12i** very small
21	**7i**	**10i**	**11i, 12i, [10i−18], [12i−18]**	unidentified ion at [**10i**−32]
22	**7j**	**8j**	**9j, 10j, 11j**	**11j** major, unidentified ion at [**8j**−153]
23	**7j**	**10j**	**11j, [10j−18]**	unidentified ion at [**10j**−27]; small [**10j**−18]
24	**7k**	**8k**	**9k, 10k, 11k, 12k, 13k**	**10k, 11k** are the major products
25	**7k**	**10k**	**12k, 13k**	**13k** is the major product; **11k** very small
26	**7l**	**8l**	**9l, 10l, 11l, 12l, 13l**	**10l, 11l** are major products, **13l** small
27	**7l**	**10l**	**11l, 12l, 13l, [10l−18]**	**13l, [10l−18]** major, **11l, 12l** very small
28	**7m**	**8m**	**9m, 11m**	**10m** is not observed
29	**7n**	**8n**	**9n, 10n, 11n, [12n+79]**	**9n, 11n** are the major products
30	**7n**	**10n**	**11n, 12n, [10n−18]**	**12n** major, unidentified ion at [**10n**−91]
31	**7o**	**8o**	**9o, 11o, 13o, [13o+79]**	several small unidentified ions
32	**7o**	**10o**	**11o, 12o, 13o**	unidentified ions at [**11o**+14], [**11o**+28]
33	**7p**	**8p**	**9p, 10p, 11p, 12p, 13p**	**13p** is very small
34	**7p**	**10p**	**11p, 12p, 13p, 14p**	carbene peaks are modest
35	**7q**	**8q**	**9q, 10q, 11q, 12q**	no carbene peaks at all, **11p** major
36	**7q**	**10q**	**11q, 12q, 13q, 14q**	carbene peaks are small
37	**7r**	**8r**	**9r, 10r, 11r, 12r, 13r, 14r**	**10r, 11r** are the major products
38	**7r**	**10r**	**11r, 12r, 13r, 14r, [10r−18]**	carbene peaks are large

[a] The solution-phase complex is listed from which the gas-phase species is sprayed or produced. The selected ion then undergoes CID with Xe to produce the listed products. Species in brackets have the mass of the nominal structure, but are likely to be an isomer. The mass spectra are given in the Supporting Information.

potentially could be assigned to the carbene complex $[(\text{bipy})\text{ReO}_2(=\text{CHCO}_2\text{Et})]^+$ if one were to consider the mass only. Curiously, no peak at $m/z = 465$ was observed, even though a putative rearrangement of the diolate could produce two different metallaoxetanes, each one potentially giving $[(\text{bipy})\text{ReO}_2(=\text{CHCO}_2\text{Et})]^+$ and $[(\text{bipy})\text{ReO}_2(=\text{CHPh})]^+$ upon CID. A possible selective depletion of $[(\text{bipy})\text{ReO}_2(=\text{CHPh})]^+$ by side reactions (in the gas phase) after formation in the CID experiment could be ruled out by independent preparation of the benzylidene complex from $(\text{pyr})_2(\text{bipy})\text{ReClO}_2$ and phenyldiazomethane in solution, followed by ESI-MS. Besides several species $[(\text{bipy})\text{ReO}_2(\text{pyr})_n]^+$ ($m/z = 375$, 454, 533) and the adduct ion $[(\text{bipy})\text{ReO}_2(\text{PhHC}=\text{N}_2)]^+$ ($m/z = 493$), there is a small but definite peak at $m/z = 465$, which corresponds to $[(\text{bipy})\text{ReO}_2(=\text{CHPh})]^+$, a benzylidene complex.[23] This result means that the benzylidene complex is stable enough so that if it were formed in the dissociation of a diolate complex, it would have been visible. That it was not seen in the dissociation of the corresponding diolate means most likely that it was not formed in the first place. While one can entertain this possibility, especially given that the potential surface for the rearrangement is still largely unexplored, the result casts some doubt on the structural assignment, which, after all, came primarily from the m/z ratio alone.

While the accuracy of the B3LYP/LACVP** calculations, depicted in Scheme 5, cannot be independently assessed, given the absence of suitable reference compounds, one can nevertheless draw an important conclusion.

Not only does the metallaoxetane appear to be too high energetically to play any significant role in the dissociation of the diolate, but a carboxyl group on the diolate opens a previously undiscussed product channel to a hydroxyenolate complex which, according to this calculation, would be favored kinetically and thermodynamically over either trioxo or carbene formation. The calculation is not wholly realistic in that the dissociation to any of the products comes out endothermic; we looked for the reverse reactions in the gas phase and did not find them, which suggests that, at least with regard to the product channels, the DFT calculation suffers from a systematic bias. It does, nevertheless, suggest mechanistic alternatives that can be further explored.

While the absolute energy differences from the calculation appear to have some problems,[24] the new structure is plausible and, moreover, has the same mass as the carbene complex. The possibility can be tested with a control experiment. As is evident from entry 3 in Table 1, depicted in Figure 1, the CID of complex **2c**,

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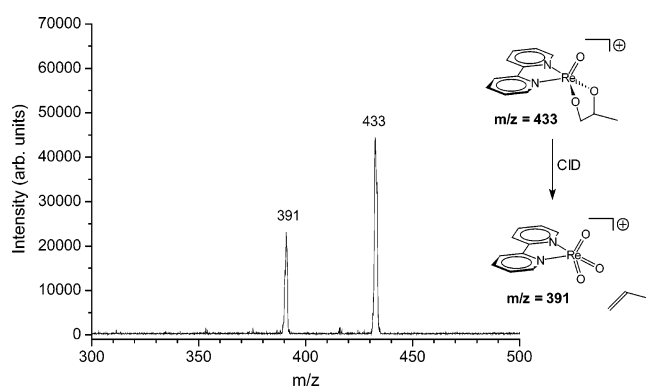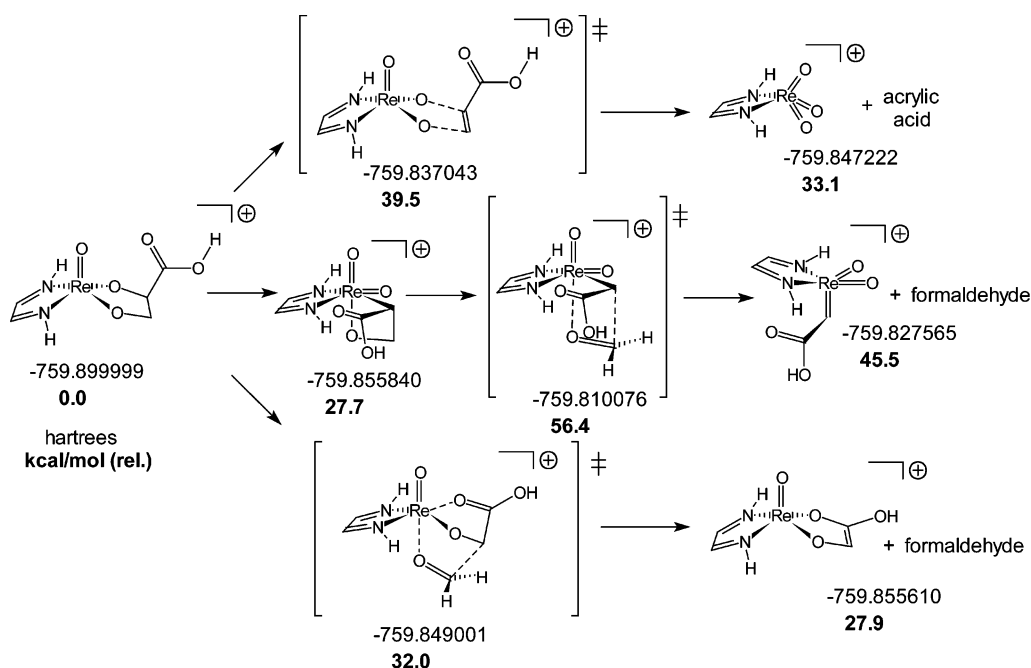(23) The ESI-MS is shown in the Supporting Information.

Scheme 5

Figure 1. Daughter spectrum obtained by electrospray of the $[(bipy)ReO_2(-OCH_2CHMeO-)]^+$, selection of a single isotopomer, and CID with Xe. Only one product channel is observed. The spectrum corresponds to entry 3 in Table 1.

$[(bipy)ReO(-OCH_2CHMeO-)]^+$, produces only a single ionic product, complex **3**, $[(bipy)ReO_3]^+$. In other words, the apparent production of carbene complexes from **2a** and **2b** (entries 1 and 2 in Table 1) is deceptive; the reaction most likely produces a noncarbene complex isomeric to **5a** or **5b**.

When the 2,2′-bipyridine ligand is replaced with two pyridines, the chemistry of the resulting ion with respect to CID changes in a fundamental way. New products arise because one pyridine may be lost from the complexes **8**: a route not available to **2**. The new products include ions with the mass of possible carbene complexes. Examination of Figures 3 and 4 shows that these putative carbene complexes are formed for many of the complexes **8**. The sequential reaction loss of first a pyridine from **8**, and then an aldehyde from **10**, to form a putative carbene complex is confirmed in all cases by the isolation of **10** by mass selection in the first
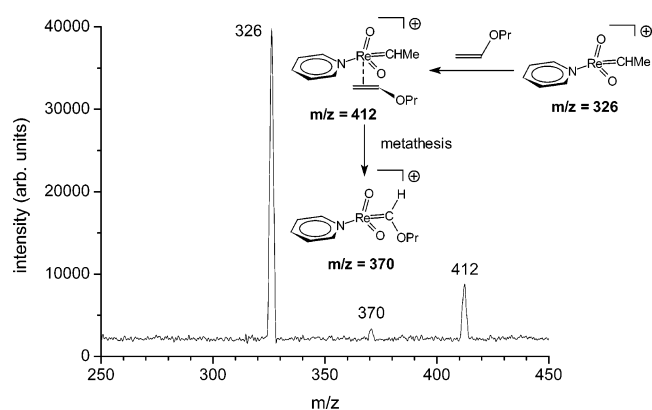
Figure 2. Daughter ion spectrum produced by mass selection of **13b** at $m/z = 326$ and reaction with *n*-propyl vinyl ether in the octopole collision cell. The formation of an adduct at $m/z = 412$, but more importantly, the formation of a product ion at $m/z = 370$, supports a carbene complex structure for **13b**.

quadrupole, followed by an ion−molecule reaction in the octopole collision cell. An exception is **8m**, entry 28 in Table 1, for which the loss of stilbene is so facilitated that loss of pyridine is not competitive. Because the mass of an ion does not alone provide convincing evidence for a carbene complex structure, **13** or **14**, gas-phase ion−molecule reactions must be used to see if the ion reacts like a carbene complex. When the ion at $m/z = 326$ in entry 7 of Table 1, for example, is selected by its mass, and then further reacted with either *n*-propyl vinyl ether or 1-hexene, the products are the adducts at $m/z = 412$ or 410 (which are not structurally informative) and, importantly, ions at $m/z = 370$ and 368 for the vinyl ether and hexene, respectively, albeit in low yield. The latter two masses are consistent with product ions $[(pyr)ReO_2(=CHOPr)]^+$ and $[(pyr)ReO_2-(=CHBu)]^+$, which would be the expected products of olefin metathesis. Olefin metathesis is the characteristic

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(24) One would expect, for example, on the basis of the computed surface that a gas-phase reaction of $(bipy)ReO_3^+$ with an olefin should produce the diolate. We could not observe any such reaction.
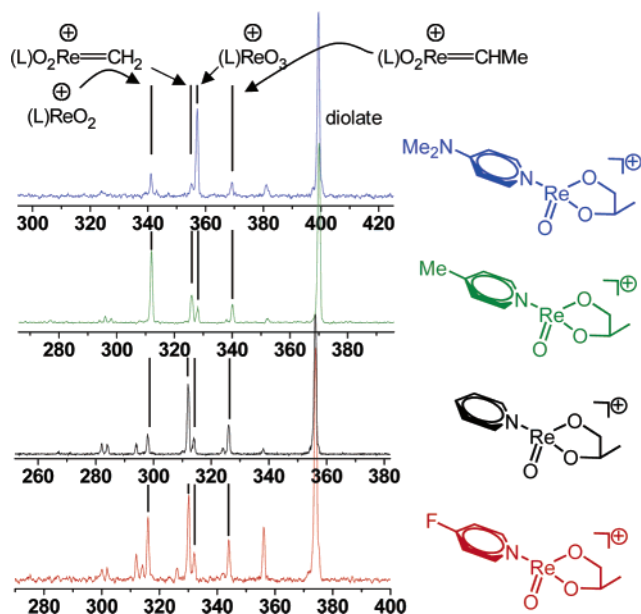
Figure 3. Stacked daughter spectra taken by electrospray of the diolate complex with different pyridine ligands, selection of the four-coordinate diolate complex, and the CID. One clearly sees that electron withdrawal on the pyridine favors the carbene products. The mass axes have been shifted so that comparable species line up with each other. The spectra correspond to entries 7, 34, 36, and 38 in Table 1.

reaction for carbene complexes. The reaction of the ion at $m/z = 326$ with a vinyl ether is shown in Figure 2.

Having found that reduction of the coordination number of the diolate complexes from 5 to 4 results in the formation of carbene complexes upon dissociation, we investigated structural effects on the efficiency of the reaction. In particular, comparisons of some of the mass spectra, taken under the same conditions, reveal trends as substituents are varied.

For example, a regular trend for the branching ratio between carbene products and the trioxo complex can be seen in Figure 3 as substituents on the pyridine ligand of the diolate are systematically changed. In a similar experiment, different alkyl groups on the diol moiety of the diolate complexes lead to a change in the branching ratio between the two possible carbene products, with the alkylidene complexes increasingly favored over the methylene complex as the alkyl group becomes larger, as shown in Figure 4. In contrast to the effect of substitution on the pyridine ligand, aryl groups, as well as electron-withdrawing groups, in general, on the diol moiety of the four-coordinate diolate complexes suppress formation of carbene complexes, as can be seen in entries 16−23 in Table 1 and the Supporting Information.

Discussion

The chemistry of Re^V diolates and the corresponding Re^{VII} oxo complexes[25] is closely related to that of OsO_4 and has been examined by other groups[10,13,26−28] in part as a model for the reactions of the latter complex, especially in connection to the catalytic asymmetric dihydroxylation reaction introduced by Sharpless and co-workers.[6] While the original mechanistic hypothesis by Böseken and Criegee,[2] termed the [3+2] mechanism,

had been accepted for decades, the mechanistic possibility of an alternative [2+2] mechanism[3] has been investigated at length by stereochemical,[29,30] kinetic,[31,32] isotope effect,[33,34] and computational[7,35−38] means. A direct observation, however, of a metallaoxetane intermediate in high-valent Re or Os chemistry, or products uniquely derived from metallaoxetanes, has remained outstanding. The rhenium carbenes, observed in this work, are the first experimental evidence for the intermediacy of metallaoxetane structures based on the observation of a product that may be uniquely associated with that intermediate. Furthermore, the results shed light on the activation reactions of metathesis reactions catalyzed by d^0 oxo complexes, for which the carbene formation step had been obscure.

Experimental Design. The choice of molecular system and experimental approach for demonstrating the intermediacy of an accessible metallaoxetane intermediate in the chemistry of high-valent oxo complexes requires some justification, especially given that, while the interest in the experiment was first kindled for osmium complexes, the project was executed with rhenium. The molecular system selected for a search for evidence of metallaoxetane intermediates was done on the basis of literature precedent; we chose to look where it appeared (at the onset of the project) likely to find something. The aldehyde olefination reaction catalyzed by methyl trioxorhenium (MTO) was proposed by Herrmann and co-workers[4] to proceed via a Re metallaoxetane intermediate which is formed by the reaction of a rhenium carbene complex with an aldehyde by [2+2] cycloaddition, as depicted in Scheme 6.

Recently, Kühn[39] has reported further experiments which were interpreted as supporting the Herrmann mechanism in the system under study. A further reason for looking at rhenium complexes comes from experiments on Re^V diolates in Scheme 7, which have been prepared and thermolyzed by Davison[13] and later Gable.[26,28] In all cases, the diolates gave clean rever-

(25) Rhenium oxo complexes have been reviewed. Romao, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197.

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(32) Göbel, T.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1329. Nelson, D. W.; Gypser, A.; Ho, P. T.; Kolb, H. C.; Kondo, T.; Kwong, H. L.; McGrath, D. V.; Rubin, A. E.; Norrby, P. O.; Gable, K. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 1840.

(33) Corey, E. J.; Noe, M. C.; Grogan, M. J. *Tetrahedron Lett.* **1996**, *37*, 4899.

(34) DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907.

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

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(37) 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.
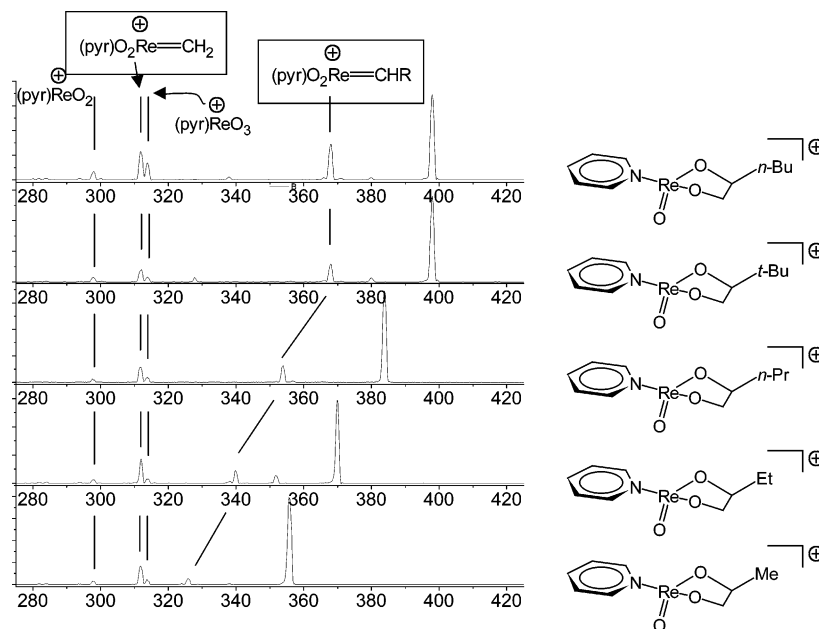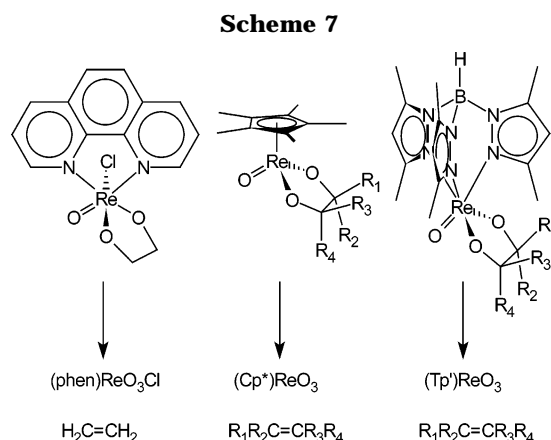
Figure 4. Stacked daughter spectra taken by electrospray of the diolate complex with different diols, selection of the four-coordinate diolate complex, and the CID. The branching ratio between the two carbene products shifts from the methylene complex to the alkylidene as steric bulk is increased. The spectra correspond to entries 7, 9, 11, 13, and 15 in Table 1.

Scheme 6

Scheme 7
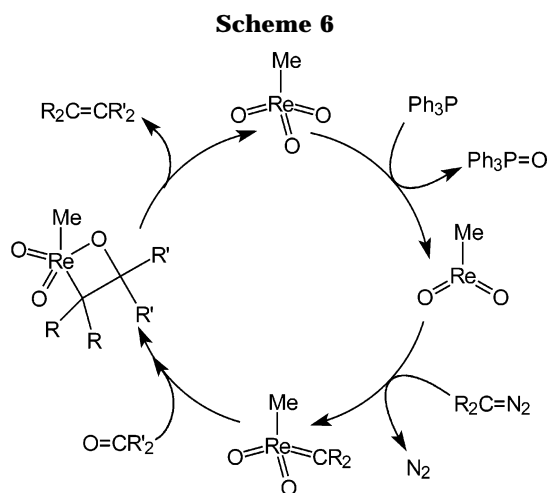
sion to coordinated rhenium trioxo species and an olefin. The reaction in the other direction, i.e., a trioxo complex reacting with at least some olefins to make a diolate, was reported by Davison in the same study for technecium[13] and, importantly, for $Cp*ReO_3$ by Gable.[26] Gable's secondary kinetic isotope effect studies on the $Cp*$ and Tp' Re diolates indicate that the cycloreversion to the Re trioxo complex and an olefin is at least highly asynchronous and potentially stepwise.[28]

Accordingly, we chose high-valent rhenium complexes as the likely arena in which experimental evidence for metallaoxetanes or their subsequent reaction products

(38) 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.

(39) Santos, A. M.; Romao, C. C.; Kühn, F. E. *J. Am. Chem. Soc.* **2003**, *125*, 2414.

might appear. Moreover, the appropriate rhenium complexes were inherently cationic, which made them better suited to the electrospray ionization technique than their neutral osmium relatives. On the basis of our previous work on aldehyde olefination,[16] we chose as supporting ligand simple nitrogen donors, such as 2,2′-bipyridine, which are, in any case, similar to the phenanthrene ligand used in Davison's work.

Given that species identification and selection is done by m/z ratio, an experimental probe must generate species of different mass. The gas-phase species that could potentially occur, with reactions that lead to and from each species, are shown in Scheme 8.
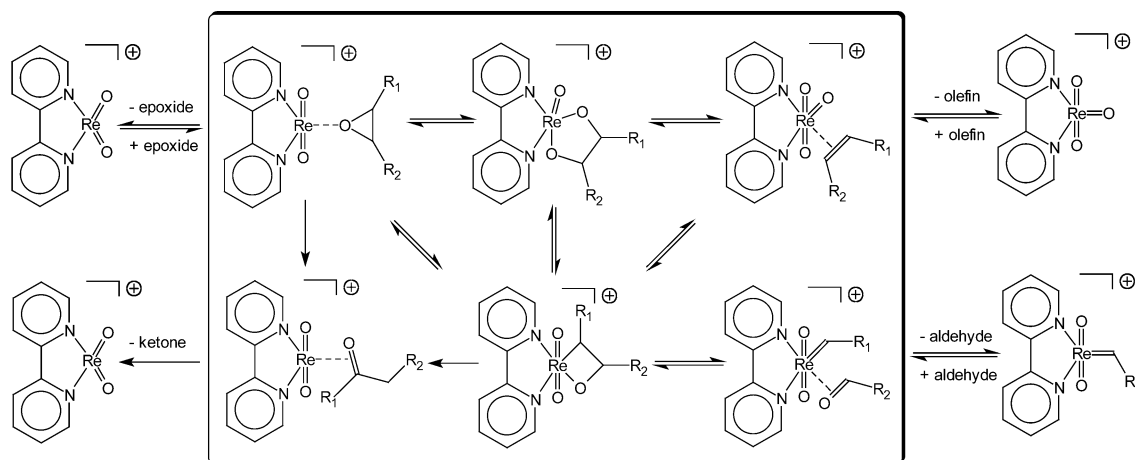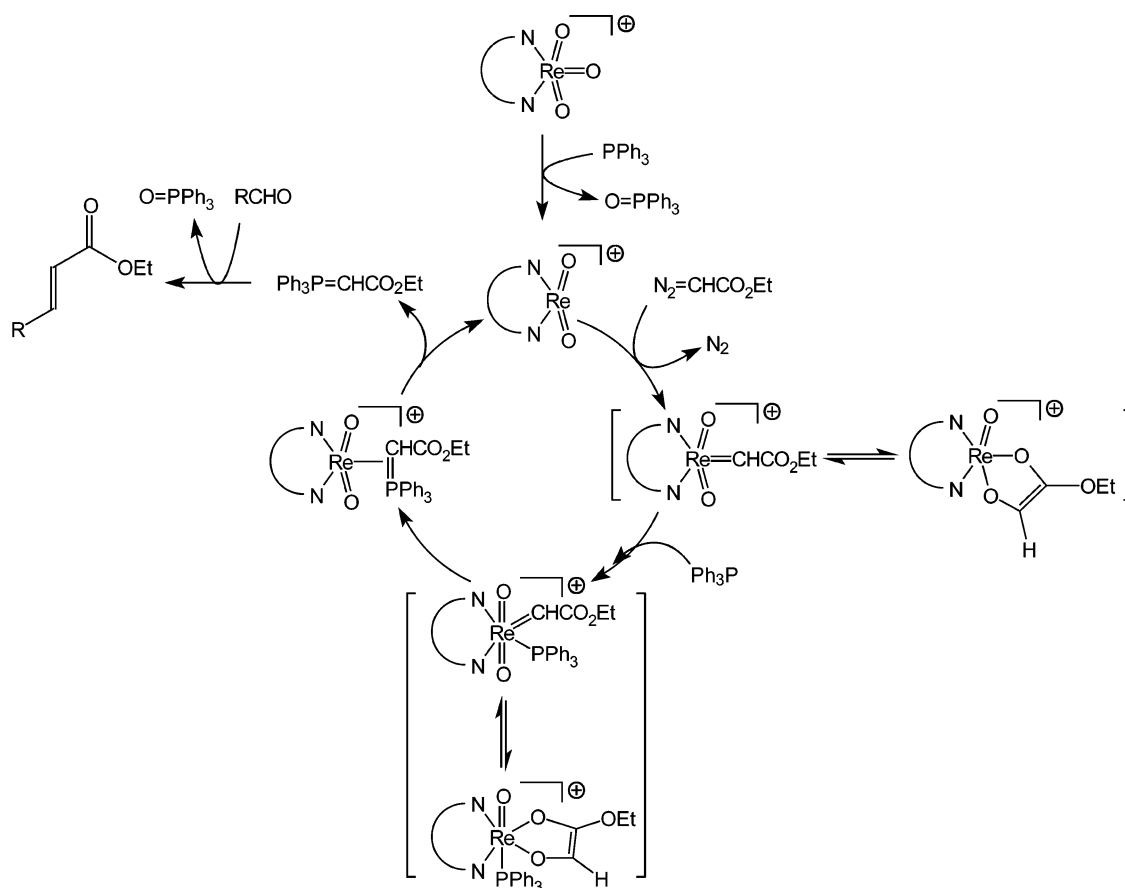
In principle, entry into the manifold of isobaric ions (in the box) through one reaction and exit through a different one could indicate the intermediacy of the metallaoxetane.

Aldehyde Olefination. A very direct piece of experimental evidence for the interconversion of diolate and metallaoxetane complexes could have been provided by the aldehyde olefination reaction. Reaction of a carbene complex with an aldehyde would produce, according to the Herrmann mechanism,[4] a metallaoxetane interme-

Scheme 8

Scheme 9

diate, for which one could imagine an isomerization to the corresponding diolate. Computational studies of the cationic (bipy)Re^V diolate complexes (vide infra) find a square-pyramidal equilibrium structure with an oxo ligand occupying the apical position in which the two carbons, one deriving from the carbene moiety and the other from the aldehyde, become (aside from substituents) equivalent. If the metallaoxetane and diolate were to interconvert reversibly, then a return out along the same reaction path along which the diolate was formed would produce a different carbene complex and a different aldehyde. Unfortunately for the original experimental design, a study of the gas-phase and solution-phase reactions of [(bipy)ReO$_3$]$^+$ under aldehyde olefination conditions show unambiguously that aldehyde

olefination, at least with this particular rhenium complex, proceeds by a wholly different mechanism, shown in Scheme 9, which never goes through a metallaoxetane at all.[16] Given the computational results in the present study, it is also possible—the experimental data neither support nor contradict the possibility—that the aldehyde olefination reaction with ethyl diazoacetate also involves species isomeric to the rhenium carbenes originally proposed.

Accordingly, the experimental results with regard to the aldehyde olefination reaction neither support nor contradict the possibility of an interconversion of metallaoxetane and diolate complexes.

Dissociation of Cationic (bipy)Re^V Diolates. An alternative entry into the manifold of structures would

be through the diolate complexes themselves, which can be synthesized simply by reaction of a Re[V] source, the ligand, and a diol. Whereas, Davison[13] and Gable[26,28] had obtained olefins and the Re[VII] trioxo complexes in the thermal decomposition of the diolates, one could imagine that a small yield of carbene complex could escape detection. Given the large dynamic range in the present mass spectrometric experiment,[40] even a small yield along the alternative product channel, carbene complex and aldehyde, could be detected. An unambiguous observation of these products would provide strong evidence for conversion of the diolate to the metallaoxetane; no other plausible path would lead to carbene products from the diolate. On the other hand, quantum chemical calculations for the closely related OsO_4, especially with inclusion of an additional amine ligand, have indicated almost uniformly that a possible metallaoxetane would lie too high in energy above the isomeric diolate to play any significant chemical role.[7] The transition states into and out from the metallaoxetane would lie accordingly higher, meaning that one might expect poor chances for a carbene product in the dissociation of a Re[V] diolate complex. The expectations from calculations for OsO_4 are, in fact, largely confirmed for Re analogues in our own calculations. Even at the modest B3LYP/LACVP** level, we find that the metallaoxetane lies 20−30 kcal/mol above the diolate. The initial observation of an ion that could have been a carbene proved, upon further experimentation, to be misleading in that control experiments and calculations strongly suggested that a lower-lying isomer of the desired carbene complex had been formed. The formation of the isomer requires the presence of a carboxyl group, or at least a carbonyl; experiments on diolates with only alkyl substituents show no evidence for a carbene mass among the products. One would conclude from the experimental observations, as well as the relative energetic ordering of species in the computation, that the metallaoxetane plays no role in the dissociation of these diolates.

Qualitative Theoretical Arguments. Computational studies, particularly those by Houk[37] and by Frenking,[7] have been converging toward a consensus that the metallaoxetane intermediate in the OsO_4-catalyzed dihydroxylation reaction, especially when ligand acceleration is operative, lies 10−30 kcal/mol above the isomeric diolate. The most useful qualitative explanation for trends in relative energies was given by Rappé,[35] who argued that four-coordinate d⁰ transition metal oxo complexes were "π-strained" when more than two of the ligands are strong π-donors. The prediction comes from the ligand field splitting of the d-orbitals; for a tetrahedral ligand field, there are only two low-lying d-orbitals with which π-bonds to a π-donor ligand may be made. OsO_4, for example, formally has four π-bonds, meaning that the last two pairs of π-electrons must go into substantially less bonding (or even non- or antibonding) orbitals.[41] By the simplest variant of this argument, formation of the diolate from OsO_4 is thermodynamically favored over formation of

Scheme 10
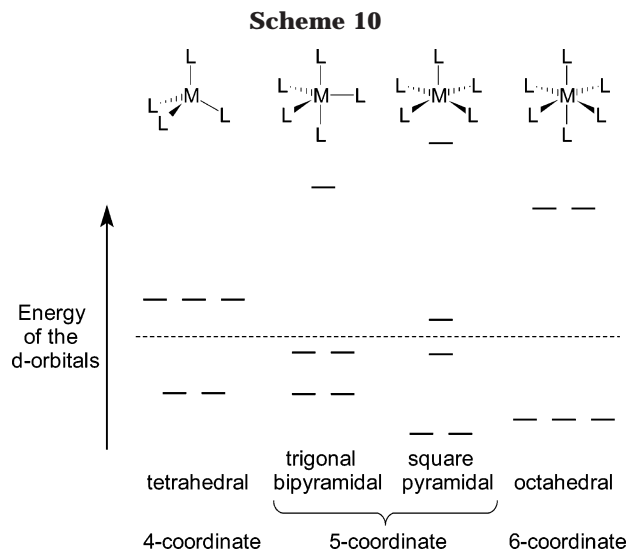
the metallaoxetane because two of the four π-bonds to the metal are removed in the former reaction as opposed to only one of the four in the latter, leading to greater relief of π-strain in the case of diolate formation. If one were to consider only π-strain, however, as a determinant of relative stability, a more complete view can be obtained by comparing the ligand field splittings, shown in Scheme 10, of the d-orbitals for model four-, five-, and six-coordinate complexes.

For four-, five-, and six-coordinate complexes, the maximum number of low-lying d-orbitals, i.e., the maximum number of strong π-bonds, is two, four, and three, respectively. Comparing the metallaoxetane to the isomeric diolate, one notices that both the coordination number and the number of π-bonds are one higher for the former than they are in the latter. That would mean, within the assumptions of Rappé's π-strain concept, that the metallaoxetane is disfavored relative to the diolate when the metallaoxetane and diolate are six- and five-coordinate, respectively; the effect should be substantially ameliorated, or even absent, however, when the two structures are five- and four-coordinate.

The computed energies of the fully optimized equilibrium geometries, shown in Figure 5, for [(bipy)ReO(−OCH₂CH₂O−)]⁺, [(bipy)ReO₂(−OCH₂CH₂−)]⁺, [(pyr)ReO(−OCH₂CH₂O−)]⁺, and [(pyr)ReO₂(−OCH₂CH₂−)]⁺ at the B3LYP/LACVP** level of theory confirmed this expectation, with the energy difference between metallaoxetane and diolate dropping from +29.9 to −1.0 as the ligand is changed from 2,2′-bipyridine to pyridine, i.e., when the coordination number dropped by one. Again, it should be emphasized that the level of theory is probably insufficient for fully quantitative results, but the result as the coordination number is dropped by one is likely to be genuine, given the magnitude of the change. If one assumes that transition states in and out from the metallaoxetane are comparably affected, then a lower coordination number should make the metallaoxetane a plausible intermediate and the [2+2] cycloaddition a plausible mechanism.

Dissociation of Low-Coordinate Cationic (pyr)-Re[V] Diolates. The theoretical results, both qualitative

(40) One should note that the dynamic range in a quadrupole mass spectrometer can reach 10⁶, which means that parts-per-million levels of a minor product can be detected. Product isolation, trapping, or NMR experiments in solution-phase experiments typically have difficulty already at the parts-per-thousand level.

(41) Green, J. C.; Guest, M. F.; Hillier, I. H.; Jarrett-Sprague, S. A.; Kaltsoyannis, N.; MacDonald, M. A.; Sze, K. H. *Inorg. Chem.* **1992**, *31*, 1588.
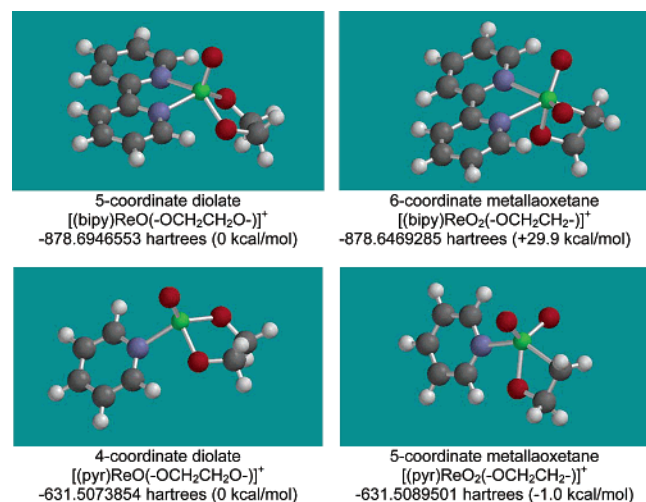
5-coordinate diolate
[(bipy)ReO(-OCH₂CH₂O-)]⁺
-878.6946553 hartrees (0 kcal/mol)

6-coordinate metallaoxetane
[(bipy)ReO₂(-OCH₂CH₂-)]⁺
-878.6469285 hartrees (+29.9 kcal/mol)

4-coordinate diolate
[(pyr)ReO(-OCH₂CH₂O-)]⁺
-631.5073854 hartrees (0 kcal/mol)

5-coordinate metallaoxetane
[(pyr)ReO₂(-OCH₂CH₂-)]⁺
-631.5089501 hartrees (-1.0 kcal/mol)

Figure 5. B3LYP/LACVP** optimized structure for five- and four-coordinate diolate complexes, as well as the isomeric metallaoxetanes with a coordination number one higher.

and semiquantitative, argue that the same test for the intermediacy of the metallaoxetane, i.e., formation of a carbene complex from dissociation of a diolate, should be repeated with a four- rather than five-coordinate diolate. Moreover, diolates carrying substituents with a carbonyl group should be avoided. The preparation of a low-coordinate diolate for a solution-phase experiment would be problematic; facile ligand exchange, the formation of dinuclear complexes with bridging ligands, and even coordination of solvent all contribute to difficulties. However, the gas-phase preparation involves only the change of ligand from 2,2′-bipyridine to pyridine, electrospray of the analogous [(pyr)₂ReO(−OCH₂CHRO−)]⁺ complex, and then (optionally) a first CID to remove one of the pyridine ligands. The experimental implementation of this plan gives clear evidence that a carbene complex is formed by loss of an aldehyde from a four-coordinate diolate complex. The carbene peaks can, in some cases, even become the major products. It is important to note that, in cases where more than one carbene can be formed, ions with masses corresponding to both possible carbene products are seen. Moreover, in ion−molecule reactions with olefins, the putative carbene complexes give products consistent with olefin metathesis, a reaction that is diagnostic for a carbene structure. As a point of reference for the structural argument based on carbene reactivity, it should be noted that a variety of metal carbene complexes have been prepared in the gas phase, and their reactions parallel those of their solution-phase congeners.[15,42]

If one accepts that carbene complexes have been formed from the four-coordinate diolates, then it is highly likely that the dissociation proceeded through the intermediacy of a metallaoxetane intermediate or transition state. Purely from the point of view of connectivity, it is difficult to find any plausible alternative to a metallaoxetane. Moreover, of all the previous arguments against metallaoxetane intermediates, the most convincing (or actually the least ambiguous) came from

quantum chemical calculations. A 10−30 kcal/mol difference between metallaoxetane and diolate would be decisive in excluding the intermediacy of the metallaoxetane. It should be pointed out, however, that the criterion based on Rappé's π-strain model says that a metallaoxetane is relatively more favorable when the coordination number is low and when at least one ligand is not a π-donor.[35] With the exception of those calculations in Rappé's report, no investigation has considered this situation to date. As even our admittedly modest calculations show, the effect of lowering the coordination number by one is dramatic: the metallaoxetane moves from being nearly 30 kcal/mol above the isomeric diolate to slightly below it in energy. Regardless of the limitations of the computation with regard to the absolute energies, the large change itself is good evidence that the qualitative orbital picture delivers a reliable prediction.

Although there is still no model that predicts detailed substituent effects, we observe that electron-withdrawing substituents on the diol moiety of the diolate complex shut down the product channel to the carbene complex; only trioxo product is seen. Conversely, mildly electron-donating alkyl substitution on the diolate increases the fraction of carbene products relative to trioxo. There is also a steric effect in addition to the polar effects on the product distribution. As the size of the alkyl substituent on the diol moiety is increased, i.e., from methyl to butyl, the balance between methylene and alkylidene complex shifts in favor of the alkylidene, as seen in Figure 4, although the effect appears to level off after *n*-propyl. Interestingly, Figure 3 shows that electron-withdrawing substituents on the pyridine ligand have the opposite effect in that they increase the amount of carbene products; electron donation on the pyridine shuts down the carbene channel again.

In principle, the effects can operate at the level of the metallaoxetane/diolate equilibrium, or they can derive from energetic movements among the product channels. The working hypothesis is that the [LReO₃]⁺ is more electron-deficient than [LReO₂(=CH₂)]⁺ and therefore relatively more destabilized by electron withdrawal. These issues must however be examined quantitatively by more extensive computational work. This is underway.

Relevance to Activation Reactions in ROMP. As mentioned earlier, the extant mechanism for the oxidation chemistry by high-valent oxo complexes was believed to go exclusively via intermediates with five-membered rings, i.e., the diolate complexes, while olefin metathesis was known to proceed by way of four-membered ring intermediates, i.e., metallacyclobutanes. Importantly, olefin metathesis, catalyzed by early-to-mid transition metal complexes, is typically terminated by addition of an aldehyde,[5] which if it reacts as a heteroalkene, would produce an intermediate metallaoxetane, so a connection to the present work should be possible. Moreover, while olefin metathesis can be performed by a preformed carbene complex, the original recipes involved alkylation of a metal center, followed by deprotonation of the metal alkyl by a strong base, to generate the active carbene species in situ.[43] There are, however, scattered reports of olefin metathesis catalyzed

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by transition metal complexes in which there is no obvious way by which a carbene moiety is generated. In the extreme case, the (pre)catalyst may have no metal−carbon bond at all. Among heterogeneous catalysts, Re_2O_7 on Al_2O_3 is a metathesis catalyst upon treatment with alkyl tin reagents, but even with no alkylating agent at all, the system is active.[44] Similarly, CH_3ReO_3 on Nb_2O_5 is active in metathesis, but it has been demonstrated experimentally that the carbene moiety in the active species comes from the olefin and *not* the methyl group.[45] Among homogeneous systems, Commereuc[46] has published a well-characterized complex that can formally be seen as either a ReO_3^+ moiety with an aluminate ligand or a perrhenate anion bound to an aluminum center. Regardless of how one sees the complex, it is a single-component metathesis catalyst completely lacking a metal−carbon bond. Last, OsO_4 alone has been reported to catalyze the ROMP of norbornene.[47] Given the computational and experimental results in the present work, one can speculate that the initiation of metathesis in each of these systems involves the reaction of the d^0 metal oxo complexes with the olefin to make either a metallaoxetane or a diolate. All of these systems share the structural feature that the diolates would be four-coordinate, meaning that the

theoretical argument advanced in this work would place the metallaoxetane energetically within reach as a chemical intermediate. The metallaoxetane could then split off an aldehyde and generate the carbene needed to initiate metathesis.

Conclusions

Gas-phase reactions of electrosprayed organometallic ions show that Re^V diolate complexes can produce carbene complexes, most likely through intermediate metallaoxetanes, for certain specific substitution patterns. Qualitative theoretical considerations, as well as DFT calculations, identify the structural conditions that favor a metallaoxetane structure such as low coordination number and at least one σ-donor ligand. The carbene complexes are identified, not only by their mass but also by characteristic reactivity. The structural motif identified in this work suggests that the asymmetric dihydroxylation reaction as it is commonly practiced does not involve metallaoxetane intermediates, but that their rearrangement and cleavage is of importance in the initiation of metathesis by catalysts for which there is otherwise no clear route to a carbene.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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