High-Valent Rhenium Oxo Chemistry

Metallaoxetanes and Carbenes from Diolates in High-Valent Rhenium Oxo Chemistry: The Importance of the Coordination Number**

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Dedicated to Professor Jerome A. Berson
on the occasion of his 80th birthday

We report an electrospray ionization tandem mass spectrometric study of the chemistry of Re^{V} diolate complexes in which the intermediacy of the isomeric metallaoxetane complexes is implicated by dissociation of the diolates to rhenium carbene complexes instead of the expected oxo species (Scheme 1). Not only is the chemistry unprecedented for well-defined diolate complexes, but the marked dependence of the preferred reaction path upon coordination number in the original diolate complex supports a qualitative molecular orbital argument based on π-strain[1] that may be able to guide further design of new catalysts.

The chemistry of Re^{V} diolates and the corresponding Re^{VII} oxo complexes is closely related to that of OsO_4, and has been examined by other groups[2–5] 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 coworkers.[6] While the original mechanistic hypothesis by Böseken and De Graaft, and by Criegee and co-

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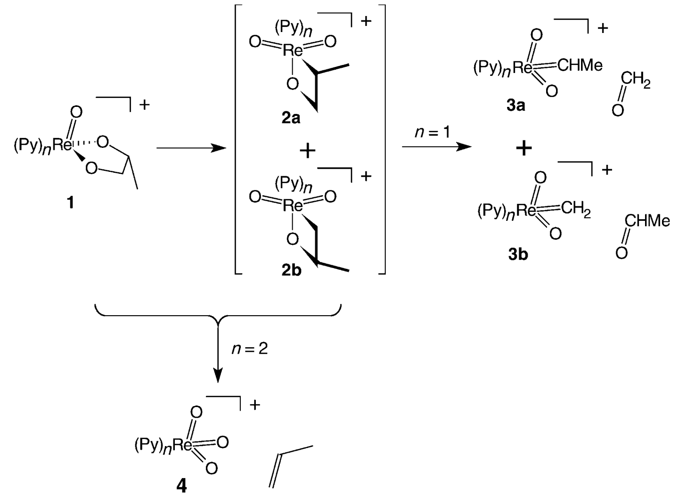

Scheme 1. Schematic diagram of CID products of $(Py)_{1-2}ReO(OCHCH_3CH_2O)$ cation upon the coordination number.

workers,[7] termed the [3+2] mechanism, had been accepted for decades, the mechanistic possibility of an alternative [2+2] mechanism[8] was investigated at length by stereochemical,[9,10] kinetic,[11,12] isotope effect,[13,14] and computational means.[1,15–17] 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 **3**, produced by dissociation of Re^{V} diolate **1**, are the first experimental evidence for the intermediacy of metallaoxetane intermediates based on 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.

The Re^{V} diolates were prepared by a route analogous to that reported by Paulo et al.[3] by the addition of one equivalent of the appropriate diol, 1,2-propanediol (in the work presented herein), and pyridine (in the first case) to $[ReOCl_3(SMe_2)(OPPh_3)]$ or $[(Py)_4ReO_2]Cl$ (Py = pyridine)[18] in CH_3Cl or CH_2Cl_2 solution at room temperature. The clean formation of the Re^{V} diolate complex in solution can be confirmed by ^1H NMR. Complex **1** was diluted to 10^{-5} M with CH_2Cl_2 and electrosprayed on a modified Finnigan MAT TSQ-700 tandem mass spectrometer as previously described.[19] The principal species in the electrospray mass spectrum is **1** ($n = 2$) when desolvation conditions are gentle, for example, tube lens ~80 V. Collision-induced dissociation (CID) of **1** ($n = 2$) in the radio-frequency (rf) 24-pole ion guide by collision with Xe under multiple collision conditions produces **1** ($n = 1$) and further daughter products such as **3** or **4**. Each of the species, **1** ($n = 2$), **1** ($n = 1$), or **3** can be selected by m/z (usually the ^{187}Re isotopomer) in the first quadrupole mass filter and then presented for CID or reaction in a gas-filled (0.1 mbar of either Xe or n-propyl vinyl ether) rf octopole ion guide to distinguish between primary and secondary reactions of each ion. The products are then analyzed in the second quadrupole. CID and ion-molecule reactions were all performed at low collision energy, that is, −10 to −15 V in the laboratory frame.

While a variety of diols have been used in this study so that structure-activity relationships and substituent effects may be quantified, the salient result for the intermediacy of metallaoxetanes can already be seen for the simple alkyl substituted diolate **1**. For the five-coordinate complex **1** ($n = 2$), CID with Xe induces two reactions: **1** ($n = 2$) loses either propene to form the Re^{VII} trioxo complex **4**, or pyridine to form **1** ($n = 1$). On the other hand, mass-selection of **1** ($n = 1$), followed by CID, leads to mass spectrum in Figure 1.

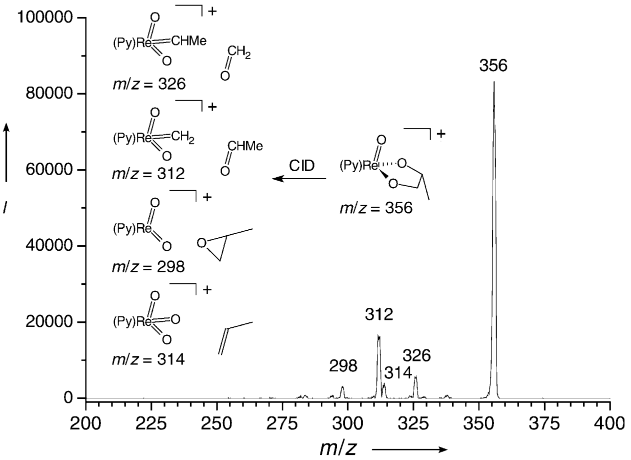

Figure 1. Daughter ion spectrum obtained by mass-selecting the ^{187}Re isotopomer of 1 ($n = 1$) at $m/z = 356$ and subjecting it to collision-induced dissociation with Xe at low collision energy. The major products at $m/z = 326$ and 312 are shown to be carbene complexes by their subsequent reaction with n-propyl vinyl ether. I = intensity, arbitrary units

As is evident from Figure 1, the CID of four-coordinate **1** ($n = 1$) gives ions with the masses of **3a**, $m/z = 326$, and **3b**, $m/z = 312$, as the major products, and a smaller amount of ions at $m/z = 298$ and 314, which are assignable without doubt to $[(Py)ReO_2]^+$ and $[(Py)ReO_3]^+$. To establish the identity of the putative carbene complexes, the ion at $m/z = 326$ was selected and reacted with n-propyl vinyl ether in the octopole ion guide to yield products at $m/z = 298$ and 370. The former ion is again $[(Py)ReO_2]^+$; the latter is consistent with an assignment of $[(Py)ReO_2({=}CHOPr)]^+$. From these ions, which would be the expected (ionic) products resulting from cyclopropanation and metathesis, respectively, of the vinyl ether, one can assign $m/z = 326$ to the carbene complex **3a**. The experimental result can be simply formulated. For the two possible dissociation pathways that a preformed Re^{V} diolate can take, formation of carbene complexes **3** or formation of trioxo complex **4**, the former is the predominant reaction for **1** ($n = 1$) and the latter for **1** ($n = 2$). The sharp dichotomy is striking.

The mechanism of diolate formation in the asymmetric dihydroxylation of olefins by OsO_4, either concerted [3+2] cycloaddition or stepwise by [2+2] cycloaddition followed by ring expansion, has been the subject of intense discussion.[9–17]

Arguments based on stereoselectivity, temperature effects, and isotope effects were made by both sides, with the interpretation of the same set of experimental results often diverging depending on one's point of view. The most convincing experimental study, a kinetic isotope effect study by using the method from Singleton, best fits expectations based on a [3+2] mechanism.[14] Quantum chemical calculations have been decisive in the entire story,[1,15–17] which have not only provided the basis for interpretation of experimentally determined isotope effects, but moreover predicted, in general, that the metallaoxetane intermediate in the [2+2] mechanism lay too high in energy, typically about 10–30 $kcal\,mol^{-1}$, above the isomeric diolate to be chemically significant. However, observation of the relevant metallaoxetane intermediates or products that could be uniquely associated has been wholly missing from the experimental side of the discussion. Recently, further experimental work on the closely related high-valent rhenium oxo complexes has provided some indirect support for the [2+2] mechanism.[5] Methyl trioxorhenium (MTO),[20] and other rhenium complexes[21,22] participates furthermore in a reaction, aldehyde olefination, for which a metallaoxetane intermediate has been proposed, although the intermediacy of metallaoxetanes in that reaction has been challenged by other experiments.[23,24]

Accordingly, we chose the chemistry of Re^{V} diolates as the most likely arena in which metallaoxetanes might appear. The Re^{V} diolates also allow a wide range of structural variation, which should be important if one wants to ultimately put together structure-activity models that may help clarify issues with OsO_4 and the corresponding Os^{VI} diolates. The observation of carbene complexes **3** from the diolate **1** ($n=1$) is unprecedented for well-defined complexes, although there have been reports of metathesis or ring-opening metathesis polymerization (ROMP) activity by Re_2O_7,[25] MTO,[26,27] some perrhenates,[28] and even OsO_4.[29] For Re_2O_7, an alkyl tin activator is not mandatory even though the "promoter" improves activity. For MTO, it was established definitively that the methyl group was not transformed into a carbene. For the perrhenates or OsO_4, there were no alkylating reagents to generate the metal alkyl that would be deprotonated to a carbene. It is difficult to establish the origin of the presumed carbene intermediates, especially given that there are only few reports of well-defined, high-valent rhenium carbenes.[30,31] The present experiment shows that simple Re^{V} diolates, which were shown[2] to be accessible by the reaction of Re^{VII} oxo complexes with olefins, can yield carbenes. By far the most probable mechanism involves the rearrangement of the diolate to a metallaoxetane, which then cleaves, that is, **1**→**2**→**3**. Observation of carbene products **3** therefore constitutes the best experimental evidence to date that metallaoxetanes are chemically significant intermediates in this manifold of structures. One should also note that the small amount of $[(Py)ReO_2]^+$ produced in the dissociation of **1** ($n=1$) is consistent with loss of an epoxide from either **1** ($n=1$) or **2** ($n=1$); epoxidation of olefins is a characteristic reaction of MTO, albeit in the presence of peroxides.[32] Lastly, the reaction sequence **4**→**2**→**3** or **4**→**1**→**2**→**3** provides a plausible mechanism for the metathesis activity of Re_2O_7, MTO, the perrhenates, and OsO_4.

It remains to explain why the observation of carbene products has remained outstanding up until now, and why the reactivity of **1** shows such a sharp dichotomy depending on whether one or two pyridine units are coordinated to the metal center. A rationale, which had in fact provided a part of the reasoning behind the experimental design, is inspired by a computational study by Rappé and co-workers.[1] For the reaction of an olefin with a model four-coordinate complex $LReO_3$, in which L ranges from a strong σ donor like $-CH_3$ to strong π donors, such as =O or Cp, Rappé and co-workers proposed that the thermodynamically favored product, either diolate or metallaoxetane, would be determined by release of π strain. They reasoned that the tetrahedral ligand field splits the d orbitals into bonding e_g and antibonding t_{2g} sets. With only two low-lying d orbitals, the complex can have only two strong π bonds to ligands. $LReO_3$ has either three or four π bonds, depending on the nature of L, so the electrons for the one or two "extra" π bonds necessarily go into antibonding (or at least substantially less bonding) orbitals. Accordingly, the more π-strained complexes, $LReO_3$, in which L is a π donor, prefer the product that reduces the total π bond order the most, that is, the diolate. For $LReO_3$, in which L is a σ donor, the preference for diolate over metallaoxetane is less, or perhaps even reversed. One additional point needs to be made. Whereas a four-coordinate tetrahedral ligand field gives only two low-lying d orbitals, both five-coordinate and six-coordinate complexes have at least three. Given that the coordination number of the metallaoxetane is one higher than that for the corresponding diolate, one expects therefore a relative stabilization of the metallaoxetane relative to the diolate when the two structures are five- and four-coordinate, respectively, as opposed to the case in which the metallaoxetane is six-coordinate and the diolate five-coordinate. Preliminary DFT calculations (B3LYPLACVP**, to be published) place **2** ($n=2$) approximately 30 $kcal\,mol^{-1}$ above **1** ($n=2$), but **2** ($n=1$) a few $kcal\,mol^{-1}$ below **1** ($n=1$), which is fully consistent with the expectations based on π strain, as well as the present experimental results. The working hypothesis says, therefore, that, the [2+2] mechanism is competitive with the [3+2] mechanism when the metallaoxetane is low enough in energy, which in turn requires a four-coordinate d^0 oxo complex, in which at least one of the ligands is a σ rather than π donor. While this is possible for $LReO_3$ systems, the [2+2] mechanism would not be competitive for OsO_4 with or without ligand acceleration.

We report a novel reaction in which Re^{V} diolate complexes cleave either to the Re^{VII} trioxo complex or a rhenium carbene, depending on the coordination number of the original diolate complex. The carbene complexes produced from diolates are the best experimental indication to date for intermediate metallaoxetanes, which would be the first-formed intermediate in [2+2] reactions of olefins with a d^0 oxo complex. The dichotomy in reactivity is surprisingly sharp and can be explained by a qualitative π-strain model. Further studies to investigate substituent and ligand effects are underway.

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Keywords: carbene ligands · diolate · mass spectrometry · reaction mechanisms · rhenium

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[1] M. A. Pietsch, T. V. Russo, R. B. Murphy, R. L. Martin, A. K. Rappé, *Organometallics* **1998**, *17*, 2716.
[2] R. M. Pearlstein, A. Davison, *Polyhedron* **1988**, *7*, 1981.
[3] A. Paulo, A. Domingos, A. Pires de Matos, I. Santos, M. F. N. N. Carvalho, A. J. L. Pombeiro, *Inorg. Chem.* **1994**, *33*, 4729.
[4] K. P. Gable, T. N. Phan, *J. Am. Chem. Soc.* **1994**, *116*, 833; K. P. Gable, J. J. J. Juliette, *J. Am. Chem. Soc.* **1995**, *117*, 955; K. P. Gable, J. J. J. Juliette, *J. Am. Chem. Soc.* **1996**, *118*, 2625; K. P. Gable, *Adv. Organomet. Chem.* **1997**, *41*, 127; K. P. Gable, A. AbuBaker, K. Zientara, A. M. Wainwright, *Organometallics* **1999**, *18*, 173.
[5] K. P. Gable, F. A. Zhuravlev, *J. Am. Chem. Soc.* **2002**, *124*, 3970.
[6] For a review, see: H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483; Recent progress is described in: P. Dupau, R. Epple, A. A. Thomas, V. V. Fokin, K. B. Sharpless, *Adv. Synth. Catal.* **2002**, *344*, 421.
[7] J. Böseken, C. De Graaft, *Recl. Trav. Chim. Pays-Bas* **1922**, *41*, 199; R. Criegee, *Justus Liebigs Ann. Chem.* **1936**, *522*, 75; R. Criegee, *Angew. Chem.* **1937**, *50*, 153; R. Criegee, *Angew. Chem.* **1938**, *51*, 519; R. Criegee, B. Marchand, H. Wannowius, *Justus Liebigs Ann. Chem.* **1942**, *550*, 99.
[8] K. B. Sharpless, A. Y. Teranishi, J. E. Bäckvall, *J. Am. Chem. Soc.* **1977**, *99*, 3120.
[9] E. J. Corey, M. C. Noe, S. Sarshar, *J. Am. Chem. Soc.* **1993**, *115*, 3828; E. J. Corey, M. C. Noe, *J. Am. Chem. Soc.* **1993**, *115*, 12579; E. J. Corey, M. C. Noe, *J. Am. Chem. Soc.* **1996**, *118*, 11038; E. J. Corey, J. Zhang, *Org. Lett.* **2001**, *3*, 3211.
[10] P. O. Norrby, H. C. Kolb, K. B. Sharpless, *J. Am. Chem. Soc.* **1994**, *116*, 8470; H. Becker, P. T. Ho, H. C. Kolb, S. Loren, P. O. Norrby, K. B. Sharpless, *Tetrahedron Lett.* **1994**, *35*, 7315.
[11] E. J. Corey, M. C. Noe, *J. Am. Chem. Soc.* **1996**, *118*, 319.
[12] T. Göbel, K. B. Sharpless, *Angew. Chem.* **1993**, *105*, 1417; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1329; D. W. Nelson, A. Gypser, P. T. Ho, H. C. Kolb, T. Kondo, H. L. Kwong, D. V. McGrath, A. E. Rubin, P. O. Norrby, K. P. Gable, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, *119*, 1840.
[13] E. J. Corey, M. C. Noe, M. J. Grogan, *Tetrahedron Lett.* **1996**, *37*, 4899.
[14] A. J. DelMonte, J. Haller, K. N. Houk, K. B. Sharpless, D. A. Singleton, A. A. Thomas, *J. Am. Chem. Soc.* **1997**, *119*, 9907.
[15] P. O. Norrby, H. C. Kolb, K. B. Sharpless, *Organometallics* **1994**, *13*, 344; P. O. Norrby, H. Becker, K. B. Sharpless, *J. Am. Chem. Soc.* **1996**, *118*, 35.
[16] J. Haller, T. Strassner, K. N. Houk, *J. Am. Chem. Soc.* **1997**, *119*, 8031; P. O. Norrby, T. Rasmussen, J. Haller, T. Strassner, K. N. Houk, *J. Am. Chem. Soc.* **1999**, *121*, 10186.
[17] G. Ujaque, F. Maseras, A. Lledós, *J. Am. Chem. Soc.* **1999**, *121*, 1317; D. V. Deubel, G. Frenking, *J. Am. Chem. Soc.* **1999**, *121*, 2021; P. Gisdakis, N. Rösch, *J. Am. Chem. Soc.* **2001**, *123*, 697.
[18] $[(Py)_4ReO_2]^+$ Cl^- is prepared as described by: M. S. Ram, J. T. Hupp, *Inorg. Chem.* **1991**, *30*, 130.
[19] C. Hinderling, D. A. Plattner, P. Chen, *Angew. Chem.* **1997**, *109*, 272; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 243; C. Hinderling, D. Feichtinger, D. A. Plattner, P. Chen, *J. Am. Chem. Soc.* **1997**, *119*, 10793; D. Feichtinger, D. A. Plattner, *Angew. Chem.* **1997**, *109*, 1796; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1718; D. Feichtinger, D. A. Plattner, P. Chen, *J. Am. Chem. Soc.* **1998**, *120*, 7125; C. Hinderling, C. Adlhart, P. Chen, *Angew. Chem.* **1998**, *110*, 2831; *Angew. Chem. Int. Ed.* **1998**, *37*, 2685; C. Hinderling, P. Chen, *Angew. Chem.* **1999**, *111,* 2393; *Angew. Chem. Int. Ed.* **1999**, *38*, 2253; Y. M. Kim, P. Chen, *Int. J. Mass Spectrom.* **1999**, *185-7*, 871; C. Hinderling, P. Chen, *Int. J. Mass Spectrom. Ion Processes* **2000**, *195/196*, 377; C. Hinderling, C. Adlhart, P. Chen, *Chimia* **2000**, *54*, 232; C. Adlhart, P. Chen, *Helv. Chim. Acta* **2000**, *83*, 2192; C. Adlhart, M. A. O. Volland, P. Hofmann, P. Chen, *Helv. Chim. Acta* **2000**, *83*, 3306; C. Adlhart, C. Hinderling, H. Baumann, P. Chen, *J. Am. Chem. Soc.* **2000**, *122*, 8204; M. A. O. Volland, C. Adlhart, C. A. Kiener, P. Chen, P. Hofmann, *Chem. Eur. J.* **2001**, *7*, 4621; G. Gerdes, P. Chen, *Organometallics*, in press; X. Zhang, P. Chen, *Chem. Eur. J.* **2003**, *9*, 1852–1859.
[20] W. A. Herrmann, M. Wang, *Angew. Chem.* **1991**, *103*, 1709; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1641; W. A. Herrmann, P. W. Roesky, M. Wang, W. Scherer, *Organometallics* **1994**, *13*, 4531.
[21] B. E. Ledford, E. M. Carreira, *Tetrahedron Lett.* **1997**, *38*, 8125.
[22] A. M. Santos, C. C. Romão, F. E. Kühn, *J. Am. Chem. Soc.* **2003**, *125*, 2414.
[23] O. Fujimura, T. Honma, *Tetrahedron Lett.* **1998**, *39*, 625; H. Lebel, V. Paquet, C. Proulx, *Angew. Chem.* **2001**, *113*, 2971; *Angew. Chem. Int. Ed.* **2001**, *40*, 2887; G. A. Mirafzal, G. Cheng, L. K. Woo, *J. Am. Chem. Soc.* **2002**, *124*, 176.
[24] X. Zhang, P. Chen, *Chem. Eur. J.* **2003**, *9*, 1852–1859.
[25] J. C. Mol, *Catal. Today* **1999**, *51*, 289.
[26] W. A. Herrmann, W. Wagner, U. N. Flessner, U. Volkhardt, H. Komber, *Angew. Chem.* **1991**, *103*, 1704; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1636; R. Buffon, A. Choplin, M. Leconte, J. M. Basset, R. Touroude, W. A. Herrmann, *J. Mol. Catal.* **1992**, *72*, L7; R. Buffon, A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J. M. Basset, W. A. Herrmann, *J. Mol. Catal.* **1992**, *76*, 287.
[27] Photochemical formation of a carbene tautomer of MTO has also been reported. L. J. Morris, A. J. Downs, T. M. Greene, G. S. McGrady, W. A. Herrmann, P. Sirsch, W. Scherer, O. Gropen, *Organometallics* **2001**, *20*, 2344.
[28] D. Commereuc, *J. Chem. Soc. Chem. Commun.* **1995**, 791; G. Doledec, D. Commereuc, *J. Mol. Catal. A* **2000**, *161*, 125.
[29] J. G. Hamilton, O. N. D. Mackey, J. J. Rooney, D. G. Gilheany, *J. Chem. Soc. Chem. Commun.* **1990**, 1600.
[30] R. Toreki, R. R. Schrock, *J. Am. Chem. Soc.* **1990**, *112*, 2448; R. Toreki, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1992**, *114*, 3367; R. Toreki, G. A. Vaughan, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1993**, *115*, 127; A. M. LaPointe, R. R. Schrock, *Organometallics* **1995**, *14*, 1875.
[31] M. Chabanas, A. Baudouin, C. Copéret, J. M. Basset, *J. Am. Chem. Soc.* **2001**, *123*, 2062.
[32] W. A. Herrmann, R. W. Fischer, W. Scherer, M. U. Rauch, *Angew. Chem.* **1993**, *105*, 1209; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1157; W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal.* **1994**, *86*, 243.