$[ReO_3(bipy)]^+[X]^-$-Catalyzed Aldehyde Olefination: Carbene and Phosphorane Intermediates

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Abstract: The aldehyde olefination reaction, catalyzed by cationic high-valent oxorhenium complexes, shows evidence of the intermediacy of both carbene complexes and phosphoranes. The solution-phase reaction is facile and amenable to tuning and is, hence, likely to prove to be of practical significance. Individual steps in the catalytic cycle are observed in the gas phase. Catalytic competence of each of the putative intermediates can be demonstrated.

Keywords: carbene ligands · mass spectrometry · olefination · phosphoranes · reaction mechanisms · rhenium

Introduction

We report a convenient variant of Herrmann's aldehyde olefination reaction in which an electrospray mass spectrometric study indicates the existence of both rhenium carbene and phosphorane intermediates. The conversion of a C=O functional group into a C=C moiety is a fundamental synthetic transformation most commonly done with the Wittig reaction by way of a phosphorane intermediate. While of broad scope and versatility, the Wittig reaction suffers from the need for a strong base or nucleophile to generate the phosphorane. The aldehyde olefination reaction, in which catalytic amounts of a transition metal complex mediate the reaction of triphenylphosphine, an aldehyde, and ethyl diazoacetate, first reported by Herrmann and co-workers[1] for $[ReO_3(CH_3)]$ (methylrhenium trioxide: MTO),[2] offers a base-free alternative to the Wittig reaction. Subsequent work by Carreira[3] using $[ReOCl_3(PPh_3)_2]$, Fujimura[4] using $[RuCl_2(PPh_3)_3]$, Woo[5] using $[Fe^{II}(ttp)]$ (tpp = *meso*-tetra(*p*-tolyl)porphyrin), and Lebel[6] using $[RhCl(PPh_3)_3]$ and other complexes found that aldehyde olefination proceeds under mild conditions for a wide range of substrates with either diazoalkane or diazoesters and either phosphines or phosphites. Nevertheless, there has remained a mechanistic ambiguity: whereas Herrmann and Carreira have assumed that the reaction proceeds by way of a transition-metal carbene complex (and therefore, in the next step, a metallaoxetane), Lebel, Woo, and Fujimura suggest that the olefination step is performed by a phosphorane. In the latter case, the transition-metal complex plays a role only in the base-free, in situ formation of the phosphorane, which then reacts with the aldehyde as in the Wittig reaction. Lebel, however, presents experimental evidence against the intermediacy of metal–carbene intermediates, raising a question as to the origin of the phosphoranes. We report both a new variant of the aldehyde olefination reaction in which the catalyst is cationic, and, hence, amenable to study by electrospray mass spectrometry, as well as evidence for reduced oxorhenium complexes, rhenium carbenes, and phosphorane intermediates; the phosphoranes derive from carbene intermediates.

Results

Before mass spectrometric experiments could be done, it was necessary to establish the model system in conventional solution-phase reactions. While there is no guarantee that the same mechanism applies for all of the various Re, Rh, and Ru complexes that have been found to catalyze aldehyde olefination, the broad similarity of the reactions in all the reports suggest that they operate by a common reaction pathway. In any case, the Re_2O_7/bipyridine combination is certainly the least expensive option among the known choices, so it is perhaps appropriate that the mechanistic work is done for this system. It should be noted that these results are not fully optimized; most likely the Re_2O_7/ligand system can be substantially improved. The solution-phase results are summarized below in Table 1.

It should be noted that very similar results are seen when the catalysts are the isolated complexes[7] $[ReO_3(bipy)]^+[SbF_6]^-$, prepared by reaction of $[ReClO_3]$ with $Ag[SbF_6]$, or $[ReO_3(bipy)]^+[CF_3CO_2]^-$, prepared by reaction of Re_2O_7 with $(CF_3CO_2)_2O$ in the presence of bipyridine. This indicates that the perrhenate anion plays no major role, and

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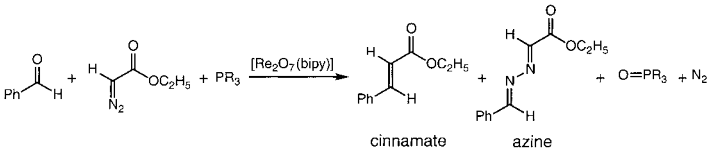
Table 1. Solution-phase aldehyde olefination reactions with $[ReO_3(bipy)]^+[ReO_4]^-$ as catalyst. The chemical yields are based on chromatographically isolated products and byproducts. The *E*/*Z* ratio is determined by NMR integration.



solvent	phosphine	mol% catalyst	reaction time [h]	*T* [°C]	% cinnamate	*E*/*Z* ratio	% azine	% recovered aldehyde
THF	PPh_3	3	44	25	86	38	2	12
THF	PPh_3	3	8	60	91	20	–	9
THF	PPh_3	0.7	22	60	75	31	6	19
THF	$P(OMe)_3$	3.6	94	25	14	3	–	54
CH_3CN	PPh_3	3	50	25	36	22	16	16
CH_3CN	$P(OMe)_3$	3.6	94	25	36	3	–	28
CH_2Cl_2	PPh_3	3	48	25	37	27	21	20

that the observed catalysis stems from reactions of the coordinated ReO_3^+ ion.

The time dependence of phosphine, phosphine oxide, and phosphorane (*cis* + *trans*) signals in the ^{31}P NMR spectrum is shown in Figure 1. Even without further kinetic analysis, it is easily seen that the phosphine decreases rapidly in correlation with the rise of the phosphorane, and that the phosphorane decays slowly in correlation with the rise of the phosphine oxide. The observation of the phosphorane by ^{31}P NMR spectroscopy is consistent with reports by Woo, Fujimura, and Lebel.

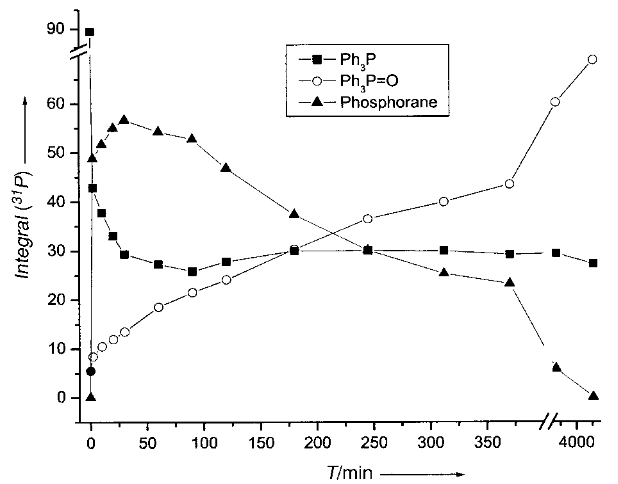


Figure 1. Time dependence of the ^{31}P integrations for a solution of benzaldehyde, triphenylphosphine, ethyl diazoacetate, and $[ReO_3(bipy)]^+[ReO_4]^-$ (1.0:1.2:0.9:0.07) in $[D_8]$THF. The integration for the *cis* and *trans* phosphoranes are summed together.

The *trans*/*cis* ratio of olefin product greatly depends on the phosphine or phosphite applied to this reaction, although a broad range of phosphite/phosphine compounds need to be tested. The *E*/*Z* ratio of >20 was obtained when triphenyl phosphine was used and about 3 for trimethyl phosphite. Similar *E*/*Z* ratios (ca. 20) for the olefin product were found for direct reaction between benzaldehyde and commercially available carbethoxymethylene triphenylphosphorane ($Ph_3P{=}CHCO_2Et$). If $[Re_2O_7(bipy)]$ (0.03 mmol) in THF (25 mL) was treated with PPh_3 (0.03 mmol), the originally colorless solution becomes purple after ≈10 min. Addition of PhCHO (1.0 mmol), $P(OMe)_3$ (1.1 mmol), and EDA (1.5 mmol; EDA = ethyl diazoacetate) gives the product ethyl cinnamate with an *E*/*Z* ratio of 2/1.

Based on the solution-phase experiments, the electrospray ionization mass spectrum of the solution was recorded as components were added one-at-a-time in concentrations comparable to those in preparative runs. Figures 2–4 show the positive ion mode spectra for $\sim 10^{-5}$ M solutions of bipyridine and Re_2O_7, bipyridine and Re_2O_7 with triphenylphosphine, and bipyridine and Re_2O_7 with triphenylphosphine and ethyl diazoacetate, respectively. Rhenium-containing species are easily identified by the characteristic pattern arising from the natural abundance of rhenium isotopes. The electrospray ionization mass spectra of solutions analogous to those used in the ^{31}P NMR experiment are fully consistent with the NMR results in that phosphine and diazo compound are converted rapidly to phosphorane in the presence of catalytic $[ReO_3(bipy)]^+$ ions in solution.

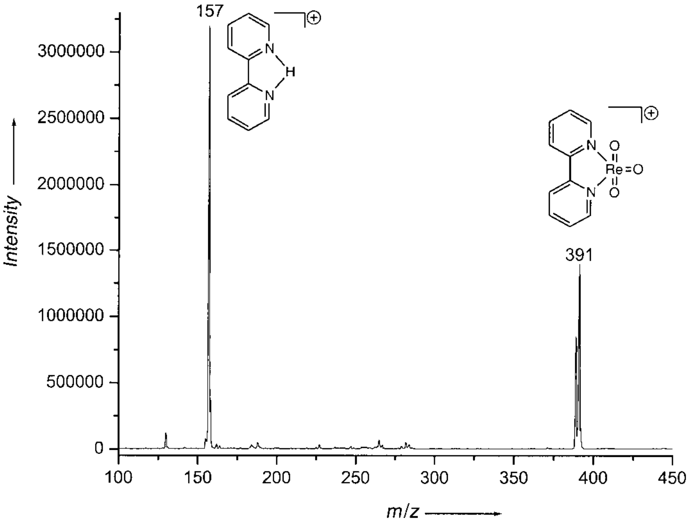


Figure 2. ESI-MS of a solution of Re_2O_7 and bipyridine in CH_2Cl_2; it shows the clean formation of $[ReO_3(bipy)]^+$, $m/z = 391$. The double peak for the complex is due to rhenium isotopes in their natural abundance (37.4% ^{185}Re, 62.6% ^{187}Re).

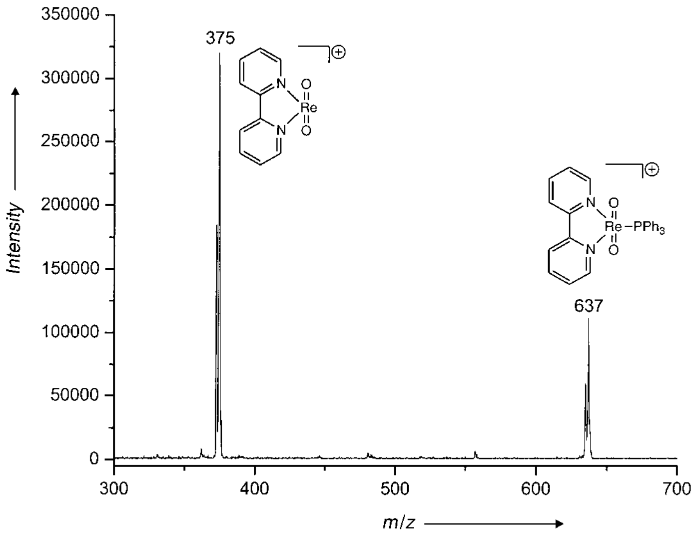


Figure 3. ESI-MS of a solution of Re_2O_7, bipyridine, and triphenylphosphine in CH_2Cl_2; it shows the formation of $[ReO_2(bipy)]^+$ ($m/z = 375$) and $[ReO_2(bipy)(PPh_3)]^+$ ($m/z = 637$). The double peaks for the complexes are due to rhenium isotopes in their natural abundance (37.4% ^{185}Re, 62.6% ^{187}Re).

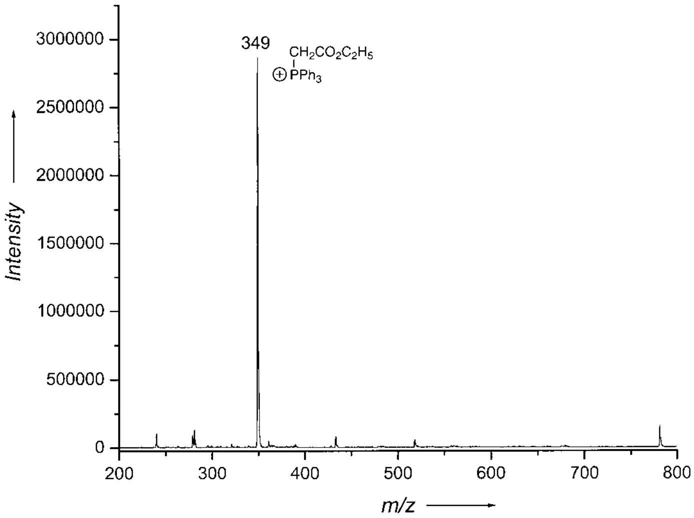


Figure 4. ESI-MS of a solution of Re_2O_7, bipyridine, triphenylphosphine, and ethyl diazoacetate in CH_2Cl_2; it shows the formation of the phosphorane, seen as the phosphonium cation after protonation.

Gas-phase ion–molecule reactions were then conducted in which $[ReO_3(bipy)]^+$ ($m/z = 391$), $[ReO_2(bipy)(PPh_3)]^+$ ($m/z = 637$), or $[ReO_2(bipy)]^+$ ($m/z = 375$) were produced in the ion source by electrospray of solutions of Re_2O_7 and bipyridine in CH_2Cl_2 (10^{-5} M), with or without PPh_3, to probe the otherwise invisible elementary steps in the catalytic cycle.

Reactions of these ions with ethyl diazoacetate in the octopole cleanly produce ions with mass-to-charge ratios $m/z = 461$, 723, and 809 as depicted in Figures 5 and 6, and Scheme 1. Simpler structural assignments can be made by a combination of the m/z value with chemical intuition. More complicated structures can be assigned on the basis of collision-induced dissociation of the selected ions with xenon in the rf (rf = radio frequency) octopole. For example, $m/z = 375$ is unquestionably the reduced $[ReO_2(bipy)]^+$ species. Reaction of the ion with $m/z = 375$ with EDA produces $m/z = 461$ as the sole product. With a clear assignment of the starting ion to a deoxygenated $[ReO_2(bipy)]^+$, the product is without doubt the rhenium carbene. Collision-induced dissociation (CID) experiments on the rhenium carbene show that it is stable against dissociation after collision with an inert gas atom under these relatively mild CID conditions. Reaction of the ion with $m/z = 461$, assigned above to the rhenium carbene, with excess PMe_3 produces two daughter ions, $m/z = 537$ and 613 (not shown). The masses indicate addition of either one or two molecules of the phosphine. In principle, the ion with $m/z = 537$ could be a five-coordinate phosphorane complex or

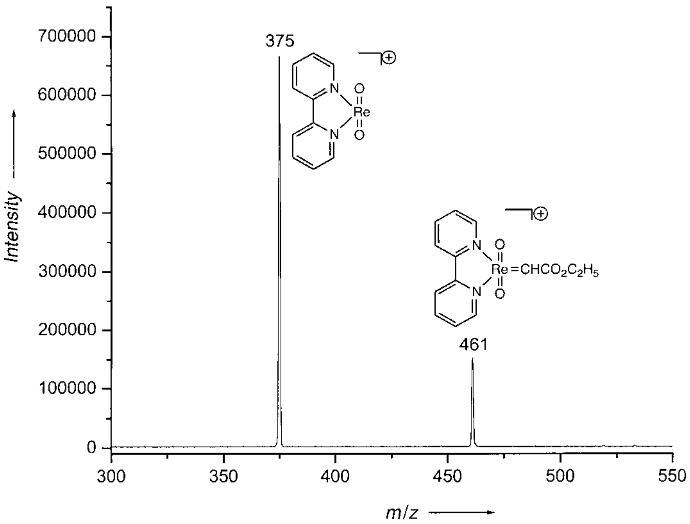


Figure 5. Daughter-ion spectrum produced by reaction of the mass-selected ion $[ReO_2(bipy)]^+$ ($m/z = 375$) with 0.38 mTorr ethyl diazoacetate in the octopole ion guide at low initial kinetic energy. The product ion at $m/z = 461$ can be assigned to $[ReO_2(bipy)(=CHCO_2Et)]^+$.

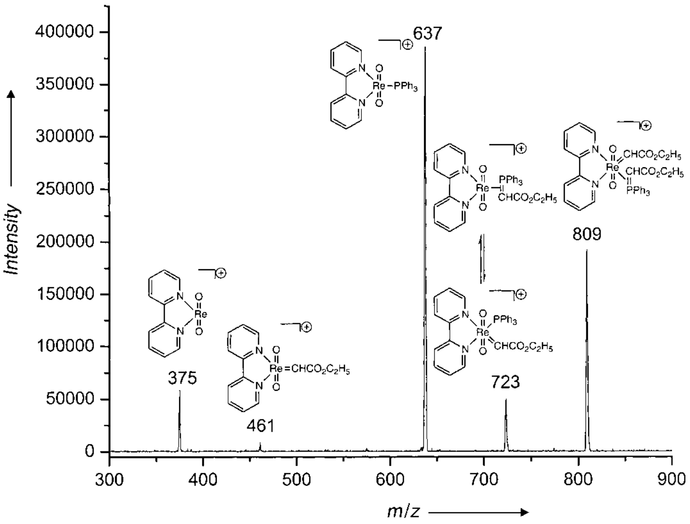
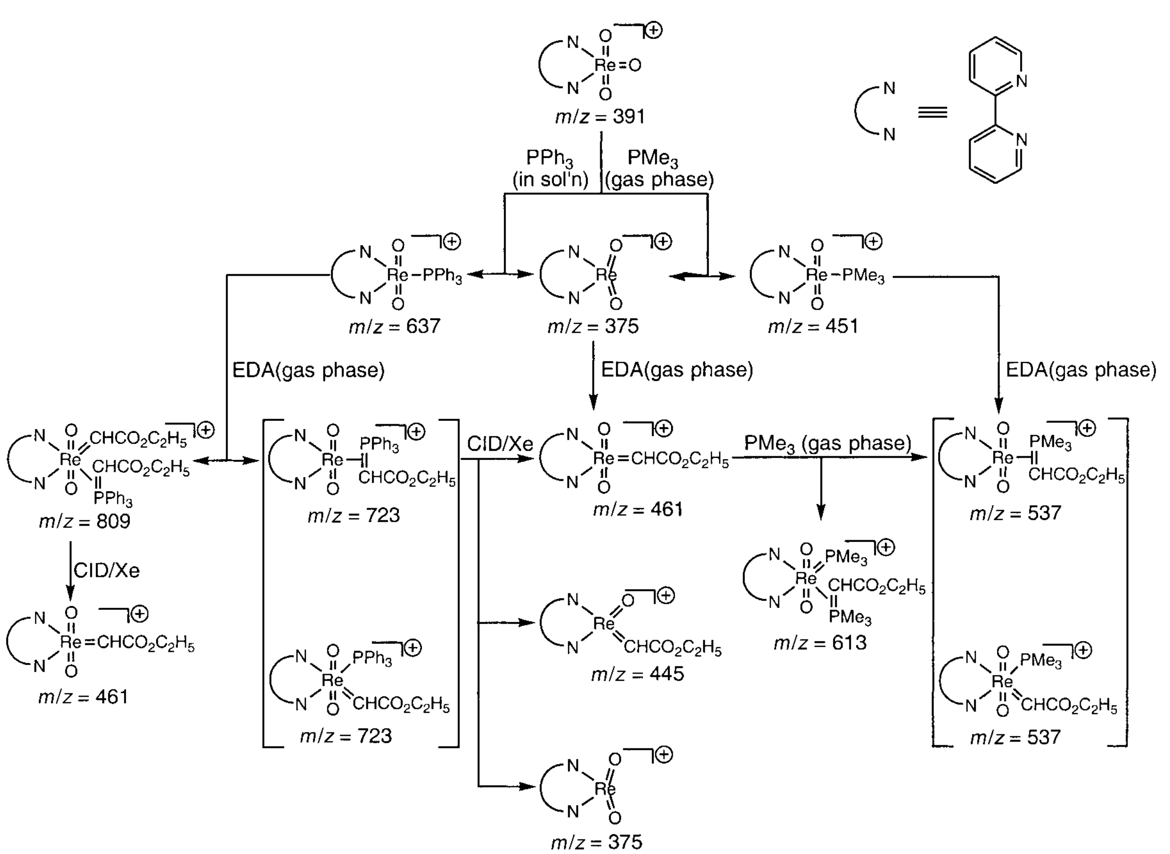


Figure 6. Daughter-ion spectrum produced by reaction of the mass-selected ion $[ReO_2(bipy)(PPh_3)]^+$ ($m/z = 637$) with 0.38 mTorr ethyl diazoacetate in the octopole ion guide at low initial kinetic energy. The product ion at $m/z = 375$, $[ReO_2(bipy)]^+$ comes from simple loss of PPh_3. The product ion at $m/z = 723$, is either a complex with a phosphine and a carbene ligand, or a phosphorane complex. The product at $m/z = 809$ must be a phosphorane complex with an additional carbene ligand. The small peak at $m/z = 461$ comes from either loss of PPh_3 from $m/z = 723$ or reaction of $m/z = 375$ with another molecule of ethyl diazoacetate.



Scheme 1. Reactions of the $[ReO_3(bipy)]^+$ ion ($m/z = 391$) in solution and in the gas phase as evidenced by ESI mass spectrometry.

a six-coordinate carbene/phosphine complex. For $m/z = 613$, there is no alternative other than a complex in which there is one phosphorane and one phosphine ligand.

In the experiment depicted in Figure 6, the ion with $m/z = 637$ is identifiable as a phosphine complex and not a phosphine oxide complex because collision-induced dissociation (CID) of $m/z = 637$ leads to loss of triphenylphosphine. It reacts with ethyl diazoacetate to form daughter ions at $m/z = 809$ and 723. Representative daughter ion spectra in which ions with $m/z = 809$ and 723 were generated in the 24-pole, mass-selected in the first quadrupole, and then collided with Xe in the octopole at low kinetic energy (0.38 mTorr, −2 to −7 eV laboratory frame) are shown in Figures 7 and 8, in which the CID results can be seen. The ion with $m/z = 809$, upon mass-selection and CID with Xe, dissociates by means of a single major channel, losing the phosphorane ligand as an intact unit. The ion with $m/z = 723$ yields three daughter ions corresponding to loss of triphenylphosphine, triphenylphosphine oxide, and the phosphorane. One accordingly assigns $m/z = 723$ to a mixture of phosphorane complex and phosphine–carbene complex, and $m/z = 809$ to a phosphorane–carbene complex.

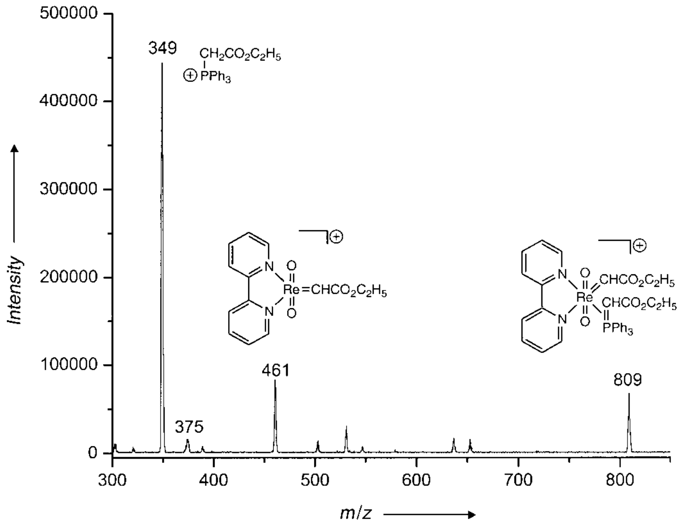


Figure 7. Daughter-ion spectrum produced by collision induced dissociation (CID) of $[ReO_2(bipy)({=}CHCO_2Et)(PPh_3{=}CHCO_2Et)]^+$ ($m/z = 809$) with xenon at low initial kinetic energy. The product ion at $m/z = 461$ comes from simple loss of the phosphorane ligand. The product ion at $m/z = 349$ is the phosphonium ion produced by protonation of the phosphorane.

Another series of gas-phase experiments was also done in which $[ReO_2(bipy)(PMe_3)]^+$, $m/z = 451$, was treated with ethyl diazoacetate to produce $[ReO_2(bipy)(Me_3P{=}CHCO_2Et)]^+$, $m/z = 537$, assigned in the previous experiment to a phosphorane complex, assuming analogous structures to those in the PPh_3 series. Together with the previously mentioned reaction of $m/z = 461$ with PMe_3 to produce $m/z = 537$, this experiment, and the analogues with PPh_3, demonstrates that the order of addition, that is, diazo compound first and then phosphine or visa-versa, does not matter. The gas-phase chemistry is summarized in Scheme 1.

The experiments show clearly that $[ReO_2(bipy)]^+$, produced in solution or in the gas-phase by deoxygenation of

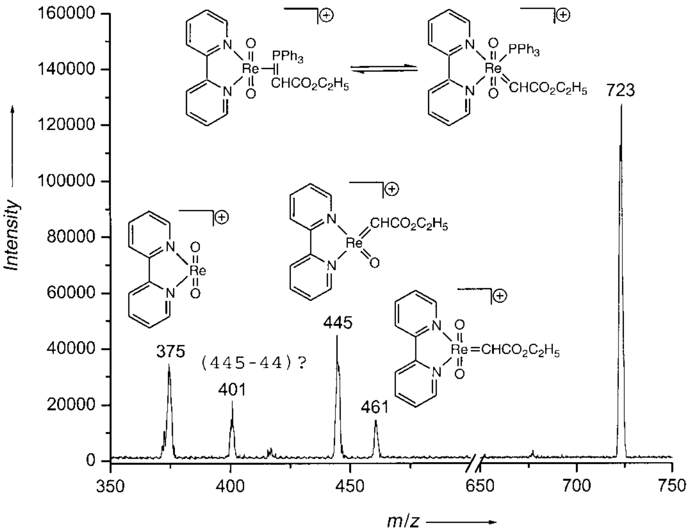
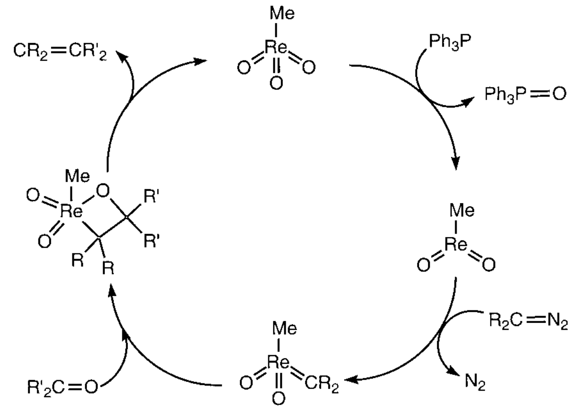


Figure 8. Daughter ion spectrum produced by collision induced dissociation (CID) of $m/z = 723$ with xenon at low initial kinetic energy. The product ion at $m/z = 375$ derives from loss of a phosphorane ligand and supports a structural assignment of $[ReO_2(bipy)(PPh_3{=}CHCO_2Et)]^+$ for $m/z = 723$. The product ions at $m/z = 461$ and 445 derive from loss of either triphenylphosphine or triphenylphosphine oxide and support a structural assignment of $[ReO_2(bipy)({=}CHCO_2Et)(PPh_3)]^+$, for $m/z = 723$. Accordingly, both species, likely interconvertible, are presumed to be present.



Scheme 2. Herrmann's mechanism for aldehyde olefination catalyzed by methyltrioxorhenium.

$[ReO_3(bipy)]^+$, reacts with a diazo compound to produce a carbene complex. If a phosphine ligand is present stoichiometrically or in excess, the carbene complex goes on to form a phosphorane complex.[8] The formation of phosphorane complexes from carbene complexes, at least for the case of ethyl diazoacetate, is the central result of the gas-phase experiments.

Discussion

While the original aldehyde olefination reaction displayed a number of desirable properties,[1] the reaction has found little application in synthesis for several reasons, among them the temperature of the reaction and the catalyst loading. The greatest limitation on the optimization of the reaction was, however, the catalyst; MTO, with limited possibilities for substitution, cannot be effectively tuned. Subsequent work by several groups found other transition-metal complexes that catalyzed aldehyde olefination;[3–6] some of these complexes were substantially cheaper and more flexible than the original MTO. Moreover, the introduction of trialkyl phosphites in place of triphenylphosphine simplified workup and purification.[3] Two different mechanisms for the aldehyde olefination reaction have been proposed, but investigations aimed at clarifying the course of the reaction have been hampered by the absence of effective analytical methods.

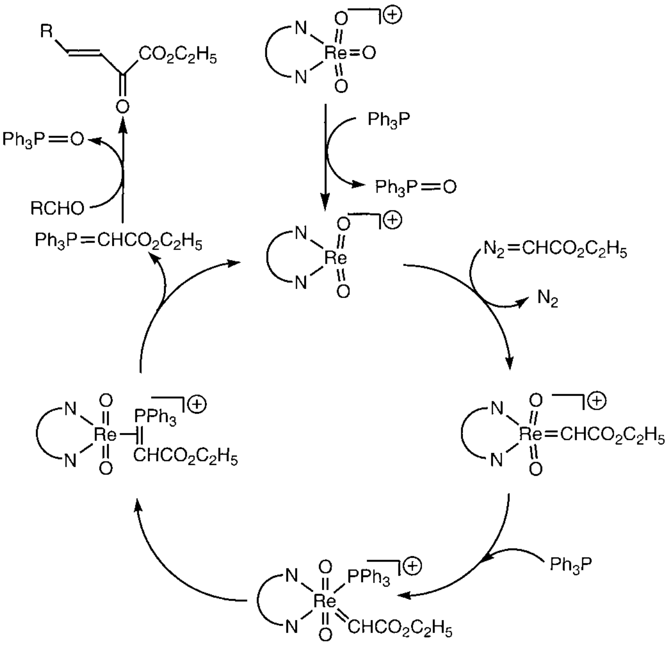
The initial step in the first possible mechanism, shown in Scheme 2, is deoxygenation of MTO, and has been studied computationally by Rösch and co-workers.[9] They report that the simple oxo transfer from MTO to PPh_3 is somewhat endothermic, but can be rendered exothermic if $MeReO_2$ dimerizes. Moreover, for other $[ReO_3(L)]$ complexes the Re=O bond is weaker, making oxo transfer more favorable. The subsequent steps in the putative mechanism have not been confirmed independently, although the reaction of a metal carbene with an aldehyde via a metallaoxetane is the usual formulation for the quenching of olefin metathesis by a carbonyl compound. The alternative mechanism was proposed by Lebel,[6] who suggested that aldehyde olefination proceeds by a base-free formation of a phosphorane, which then reacts as in the Wittig reaction. She discounted, however, the intermediacy of a carbene complex based on the poor catalytic activity for aldehyde olefination exhibited by Ru and Rh carbenes produced either in situ or as isolated compounds. The specific mechanism for phosphorane formation was not given, although it was presumed that the metal complex acted electrophilically to activate the diazo compound to displacement of N_2 by the phosphine. Lebel's mechanism would be consistent with the E/Z ratios in Table 1. If the sole role of the phosphine were to be deoxygenation of rhenium oxo complexes, then there would be no reason to expect a different E/Z ratio for the cinnamate ester product when $P(OMe)_3$ is used instead of PPh_3. On the other hand, if a phosphorane were to be formed, there is no reason to expect the same E/Z ratio for a phosphine versus a phosphite. As is evident from Table 1, the E/Z ratios from triphenylphosphine versus trimethylphosphite are approximately 30 and 3, respectively, suggesting (as indirect evidence) that Scheme 2 does not represent the mechanism, at least for this catalytic system. Consistent with this claim is the observation that Re^V, prepared in situ by stoichiometric reduction of Re^{VII} by one equivalent (relative to Re) of PPh_3, catalyzes the aldehyde olefination reaction with an E/Z ratio of 2/1 when $P(OMe)_3$ is subsequently added. A similar E/Z ratio (ca. 20) for the olefin product of the reaction of aldehyde with $Ph_3P{=}CHCO_2Et$ provides the direct evidence for the intermediate phosphorane.

Our solution-phase NMR studies confirm the observation of phosphorane intermediates made by Lebel,[6] Woo[5] and Fujimura,[4] and lead further to the conclusion that the original mechanism, depicted in Scheme 2, can already be ruled out because that mechanism would necessarily require phosphine oxide to be produced at the same rate that phosphine is consumed. The elimination of the original mechanism, and the direct observation of phosphoranes as intermediates, begs the question as to the mechanism by which the phosphoranes are formed. Are carbenes involved or not?

Having used electrospray ionization tandem mass spectrometry to study C–H activation, catalytic epoxidation, catalytic hydrogenation, Ziegler–Natta polymerization, and olefin metathesis,[10–12] we resolved to approach aldehyde olefination as a reaction in which we believed it possible that a discrete rhenium–carbene species might be observed. Reactions of metal–carbene complexes have been observed in the gas-phase by mass spectrometry,[13] but apart from the work from the present group, none of the previous studies prepared species that contain a phosphine ligand. Because electrospray requires a charged complex, and all of the reported catalysts for aldehyde olefination are neutral, a new catalyst was needed. Re_2O_7 is one of the transition-metal oxides that shows appreciable solubility in organic solvents. The solubility derives in large part from the facility by which Re_2O_7 can cleave heterolytically in polar, coordinating media such as THF or acetonitrile.[14][15] Accordingly, addition of a bidentate ligand, such as bipyridine (bipy), to Re_2O_7 in a variety of coordinating and noncoordinating solvents, was expected to produce the soluble ion-pair $[ReO_3(bipy)]^+[ReO_4]^-$. The $[ReO_3(bipy)]^+$ ion, a d^0 Re^{VII} complex, is easily observed mass spectrometrically by electrospray of a solution of the bipyridine and Re_2O_7 in CH_2Cl_2.

As is seen in Table 1, $[ReO_3(bipy)]^+[ReO_4]^-$ functions as a catalyst for the aldehyde olefination reaction. The reaction conditions are comparable to those for the original reaction, and the catalyst is certainly less expensive.[16] More importantly, the preparative-scale reactions define reaction conditions under which mass spectrometric experiments are sensible. While the best bulk results were obtained in THF, the results in CH_2Cl_2 were acceptable; the latter solvent is, however, much better for electrospray. Given the observation of phosphoranes by NMR spectroscopy, the mass spectrometric evidence for phosphoranes is not surprising. In contrast to the conclusion from Lebel's work, however, the gas-phase reactions of mass-selected carbene complexes and phosphine–carbenes indicates that carbene complexes are precursors to the observed phosphoranes. Our proposed catalytic cycle is shown in Scheme 3. The phosphorane produced at each turnover then goes on to react with aldehyde to produce the final olefin product. The catalytic cycle is based on two kinds of mass spectrometric evidence. Firstly, ESI-MS serves as a relatively straightforward analytical tool for the characterization of the ions in solution as the components are progressively added. Because Re_2O_7 by itself in a polar solvent shows no prominent ion signals, Figure 2 shows that coordination by a bidentate donor ligand suffices to induce heterolysis in solution.

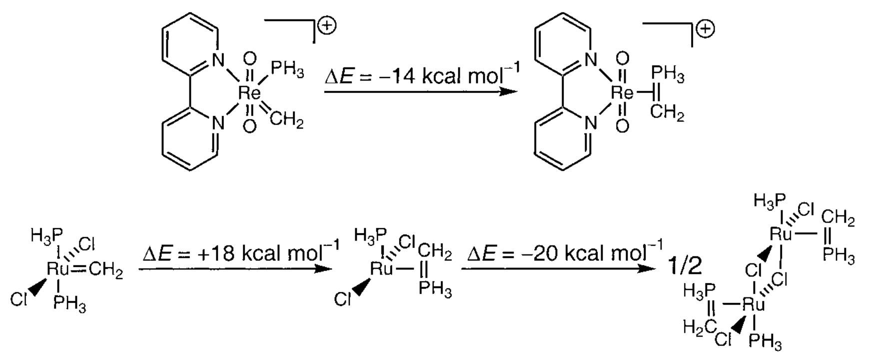
Figure 3 shows that addition of phosphine to the solution used for the measurment of spectrum shown in Figure 2 results in deoxygenation, that is, reduction, of the coordinated Re^{VII} species to Re^V. Addition of ethyl diazoacetate to the solution used for the measurment of spectrum shown in Figure 3 leads to the spectrum shown in Figure 4 if there is an adventitious proton source to protonate the rather basic phosphorane, rendering it visible in the ESI-MS. The mass spectrometric analyses of progressively constructed reaction solutions is informative in that we hope to directly observe the species in the catalytic cycle. However, we recall that, for a catalytic cycle at steady-state, the most abundant species-the resting state of the cycle-may be the only observable member of the cycle, and the phosphorane, being produced by much smaller amounts of catalyst, is present in high concentration. Other species would occur at much lower concentration.



Scheme 3. Proposed mechanism for aldehyde olefination catalyzed by cation trioxorhenium(VII) complexes $[Re_2O_7(bipy)]$.

Mere observation of species in solution does not constitute strong evidence for a mechanism. Proof of catalytic competence by reaction studies is needed. In the present work, the proof of competence is done by gas-phase reactions of mass-selected ions that correspond to elementary steps in the proposed catalytic cycle. Production of carbene species by reaction of Re^V complexes with diazo compounds is seen in Figures 5 and 6. Production of phosphorane complexes from carbene complexes and phosphines is seen in Figure 6, with CID evidence for the assigned structures in Figures 7 and 8. Additional work summarized in Scheme 1 show that the reactions with trimethylphosphine parallel those of triphenylphosphine.

The disagreement with Lebel's conclusion requires an explanation. While one would have expected that carbene complexes could be likely precursors to the phosphoranes, Lebel's argument that $[Ru{=}CH_2(Cl)(NO)(PPh_3)_2]$ and $[Rh_2(OAc)_4]$ proved to be poor aldehyde olefination catalysts raises doubts as to the competency of putative carbene intermediates. Moreover, if a coordinated phosphine group were to react efficiently with a carbene ligand on the same metal center, then the "first-generation" Grubbs metathesis catalysts[17] should have shown signs of isomerization. Moreover, the early ruthenium metathesis catalysts were prepared in situ by reaction of an $[RuCl_2(PPh_3)_3]$ complex with diazo compounds,[18] and no evidence for phosphorane formation



Scheme 4. Computed energetics of the carbene to phosphorane reaction.

was reported. Addressing this issue, DFT calculations reveal an interesting dichotomy (Scheme 4).

While the computational prediction of organometallic thermochemistry is still fraught with uncertainties, and the chosen level of theory—B3LYP/LACVP**—is reasonable but not spectacular, the computed difference between model rhenium and ruthenium complexes is large enough to give some confidence that there is a genuine reason to expect the two complexes to behave differently. According to the model calculation, phosphorane formation in the case of the rhenium complex is thermodynamically favorable. On the other hand, formation of a phosphorane ligand for the model ruthenium complex is strongly endothermic; even the expected dimerization of the coordinatively unsaturated product makes the overall transformation only approximately thermoneutral at best. Without the large exothermicity of the rhenium system, one may expect that phosphorane formation by ruthenium complexes may be strongly dependent on the particular phosphine, substitution on the carbene moiety, and even the concentration of the complex. Such factors may largely explain Lebel's observations. An explanation of the phenomenon, as well as full details of the calculation, will be subject of a subsequent publication, but it can be stated already that the high-valent oxorhenium complexes should generally produce phosphoranes. One should comment that an accessible transition state connecting a carbene with a coordinated ylide has been clearly shown in Milstein's recent synthesis of ruthenium carbenes by the reaction of [$RuCl_2(PPh_3)_3$] with sulfur ylides.[19] Similarly, ylides and carbenes on several other metal centers presumably interconvert,[20] although in those cases, one cannot say with absolute certainty that the phosphorane derived from a carbene as opposed to a halomethyl complex. Lastly, preliminary results[21] show that the addition of $Cy_3P{=}CHPh$ to [$RuCl_2(PPh_3)_3$] or [{$RuCl_2(cod)$}$_n$] in the presence of norbornene prepares in situ a highly active ring-opening metathesis (ROMP) catalyst. We can conclude that the interconversion of carbene and ylid complexes is plausible with the favored direction determined primarily by thermochemistry.

Conclusion

We find in the aldehyde olefination reaction, catalyzed by high-valent oxorhenium complexes, evidence for the intermediacy of both carbene complexes as well as phosphoranes. The solution-phase reaction is facile and amenable to tuning and is, hence, likely to prove to be of practical significance. Individual steps in the catalytic cycle are observed in the gas phase. Catalytic competence of each of the putative intermediates can be demonstrated. With the clean and facile reactions, it should be possible to explore the chemistry of rhenium carbenes in a systematic manner. Moreover, given the versatility of the rhenium complexes as catalysts, a variety of tandem reactions are conceivable. This work is underway.

Experimental Section

Based on structural work from a number of groups,[14] we expected that Re_2O_7 would be solubilized in a variety of organic solvents when a good bidentate ligand is introduced. The expectation was borne out when Re_2O_7 was treated with 2,2′-bipyridine (bipy) in a number of solvents. In toluene, a small solubility was achieved; in polar solvents such as CH_2Cl_2 or THF, the solution was completely homogeneous at the concentrations involved in the present study (<1 mM with respect to Re). While coordination of solvent molecules does not necessarily lead to cleavage of the Re_2O_7 moiety in the solid-state, a small but finite extent of heterolysis in polar solution occurred. For sufficiently strongly donating ligands, heterolysis can become the dominant process.[15] As will be seen below, electrospray mass spectrometry of Re_2O_7 and bipyridine in CH_2Cl_2 showed [ReO_3(bipy)]$^+$, $m/z = 391$, as the only metal-containing species in the positive ion mass spectrum.

For a typical solution-phase reaction, Re_2O_7 (14.5 mg, 1 equiv), bipyridine (5 mg, 1 equiv), triphenylphosphine (288 mg, 37 equiv), ethyl diazoacetate (EDA: 170 mg, 50 equiv), and benzaldehyde (106 mg, 33 equiv) were placed together in solvent (25 mL). The reaction mixture was then stirred at the specified temperature for a time varying between 8 and 96 hours. Workup by column chromatography (silica gel, hexane:ethyl acetate 95:5) and product identification by ^1H NMR spectroscopy and GC/MS resulted in the tabulated yields. The reaction solution with all components, or a subset thereof, was diluted to between 10^{-5} and 10^{-6} M in Re with CH_2Cl_2 and analyzed by electrospray mass spectrometry.

Mass spectrometric experiments were performed in a modified Finnigan MAT TSQ-700 spectrometer as described in earlier papers.[10–12] The tube lens potential—an indication of the severity of desolvation conditions at the exit of the transfer capillary—was typically kept at 70–120 V, which was found to be sufficient to desolvate the electrosprayed ions. The resulting ions were then passed through the a 38 cm long, jacketed, rf 24-pole ion guide[22] into which a partial pressure of up to 100 mTorr of a reagent gas had been introduced by a needle valve. Collisions with the reagent gas served to both thermalize the ions to the 70 °C manifold temperature and induce gas-phase reactions, the products of which were then mass-selected in the first quadrupole. The subsequent experiments on the mass-selected ions were performed in daughter-ion mode. The ions were introduced into the octopole collision cell with a nominal initial kinetic energy of 5 eV (laboratory frame), where they reacted with a second reagent (0.3–5 mTorr). Product ions were then mass-analyzed in the second quadrupole with a resolution $m/\Delta m \sim 2000$.

The details of the ion–molecule reactions in this study require discussion. The 24-pole and octopole function more like ion drift cells, as opposed to normal collision cells.[12] Monte–Carlo modeling, combined with experimental determinations of ion transit times through the octopole indicated that, under the conditions employed in this experiment, the ions underwent up to ~5000 collisions in the octopole; in the 24-pole, the number of collisions was considerably higher. Moreover, the initial kinetic energy of the ions was lost in the first several collisions. Although there was no applied longitudinal electric field, the continuous ion current into either ion guide created, by way of space-charge effects, a slight potential that drives the ions through. Otherwise, the procedure closely resembled that in previous publications. One concludes that the ions react under quasi-thermal conditions at the 70 °C manifold temperature.

Solution-phase NMR experiments were performed in a Varian Mercury 300 spectrometer operating at 121 MHz (for ^{31}P) on solutions prepared from [D$_8$]THF (0.7 mL), benzaldehyde (10 mg), triphenylphosphine (30 mg), ethyl diazoacetate (10 mg), and $[ReO_3(bipy)]^+[ReO_4]^-$ (4 mg) (1.0:1.2:0.9:0.07 mole ratio for the reagents). Under these conditions, four major species were observed in the ^{31}P NMR spectrum: the phosphine, phosphine oxide, and the *cis* and *trans* isomers of the phosphorane. Chemical shifts for the species were reported by Woo.[5] Very small signals ($\ll$5% total integration) were seen for other species. Control experiment for olefin *trans*/*cis* ratio directly using commercially available ylide (carbethoxymethylene triphenylphosphorane, $Ph_3P{=}CHCO_2Et$) with benzaldehyde was also done in an NMR tube. In-situ NMR measurement indicated that the reaction was finished in 24 hours at room temperature, and *trans*/*cis* ratio of product was about 20/1. Another experiment with the $[Re_2O_7(bipy)]$ (3%)/PPh_3 (3%)/$P(OMe)_3$ (1.1 mmol)/PhCHO (1.0 mmol)/EDA (1.5 mmol) system yielded 10% of the olefin with a *trans*/*cis* ratio of 2/1.

Density functional theory (DFT) calculations were done by using the Titan program package[23] running on a 1.2 GHz Athlon computer. All structures were fully optimized by using the B3LYP method with the LACVP** basis set. The LACVP** basis sets treat the 4s, 4p, and 4d, as well as the 3s and 3p, orbitals on ruthenium explicitly with a double-ζ basis; the inner electrons were treated with an effective core potential. It used 6-31G** for non-transition metal elements.

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