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Reactions of electrosprayed rhodium phosphine complexes in the gas phase: modeling homogeneous catalytic hydrogenation

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Abstract

Electrospray ionization tandem mass spectrometry is used to prepare low coordinate rhodium phosphine complexes related to the reactive intermediates in asymmetric homogeneous catalytic hydrogenation in solution. Each elementary step, or its functional equivalent, in at least one mechanism for the solution-phase reaction can be observed in the gas phase, although functional equivalency and structurally similarity do not necessarily go hand-in-hand. Additional restrictions on the catalyst structure for a gas phase hydrogenation catalyst are also found and evaluated. (Int J Mass Spectrom 185/186/187 (1999) 871–881) © 1999 Elsevier Science B.V.

Keywords: Electrospray; Homogeneous catalysis; Catalytic hydrogenation; Rhodium phosphine complexes

1. Introduction

We report the selective preparation, and subsequent gas-phase reactions, of $[Rh(PMe_3)_2]^+$ **3a**, and $[Rh(PMe_3)_2(H)_2]^+$ **7**, by electrospray ionization tandem mass spectrometry. The cationic rhodium complex **3a** structurally resembles the key reactive intermediate in the catalytic hydrogenation of reactions by rhodium or ruthenium complexes, and furthermore, exhibits gas phase ion–molecule chemistry with hydrocarbons and molecular hydrogen that shows parallels to solution-phase homogeneous catalytic hydrogenation [1,2]. To find the conditions to construct a gas-phase catalytic cycle, a combination of isotopic labeling and multistep reaction sequences is used to map two mechanistic pathways in the hydrogenation sequence and define the structural requirements for a gas-phase mimic of the solution-phase reaction.

Previous studies in this group have shown that gas-phase ion–molecule reactions of organometallic complexes can display surprising similarities to the corresponding reaction in solution, but there remain sufficient differences that it is not at all obvious that a known catalytic cycle in solution will work in the absence of solvent. In particular, low-coordinate reactive complexes that are the catalytically competent species are invariably stabilized by coordination of one or more solvent molecules, whose dissociation in a pre-equilibrium precedes addition of a substrate molecule. A gas-phase equivalent of the solvent coordination needs to be found if substantially similar chemistry would be run in the absence of solvent. In this study, we find that reversible cyclometalation in $[Rh(PMe_3)_2]^+$, transforming a trimethylphosphine li-

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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gand into an η^2-($Me_2P{=}CH_2$) ligand plus a hydrido ligand, fulfills the same function in the gas phase as solvent coordination in the condensed phase. The resulting stabilized complex serves as a reservoir for what is effectively the reactive two-coordinate cationic rhodium complex, that upon binding of hydrogen and/or an unsaturated hydrocarbon, reversibly transfers a hydride between the bound hydrocarbon ligand and the metal center.

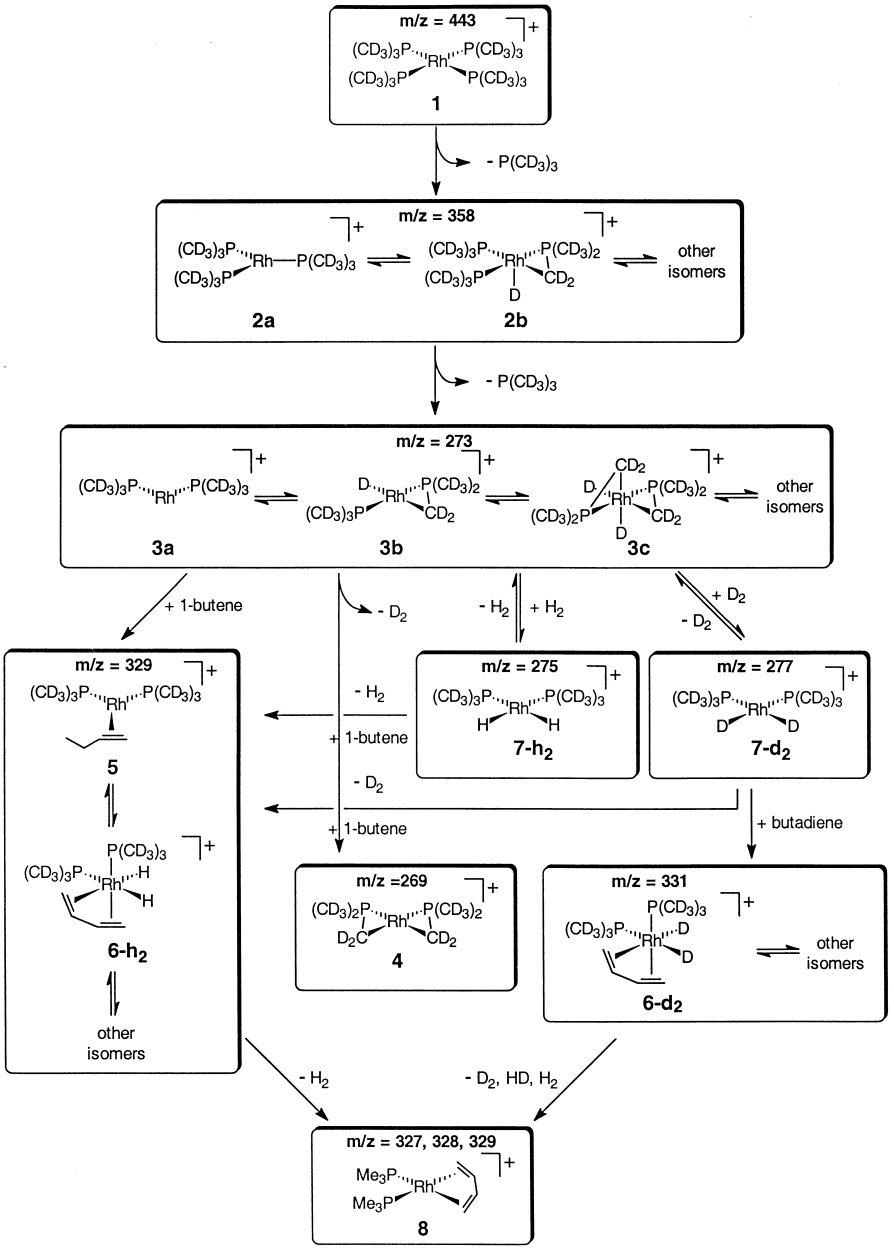
2. Experimental

The electrospray ionization [3,4] tandem mass spectrometric (ESI-MS/MS) experiment was performed in a modified Finnigan MAT TSQ-7000 mass spectrometer as described previously [5–8]. The spectrometer was set up with an octopole, quadrupole, octopole, quadrupole (O1/Q1/O2/Q2) configuration behind a conventional electrospray ion source. The extent of desolvation and collisional activation prior to thermalization, reaction, and/or analysis was controlled by the tube lens potential in the electrospray source, which sets the translational energy of the ions from the source into the first octopole where collisions can either thermalize and/or dissociate the initially produced ions; this potential was varied from low (30–44 V, lab frame) to medium (45–60 V) to high (60–80 V). The first octopole was fitted with an open cylindrical sheath around the rods into which a collision gas could be bled for thermalization or reaction at pressures up to 20 mTorr. Control experiments with $Mn(CO)_6^+$ have found that ~10 mTorr of Ar in O1 are sufficient [9] for thermalization of ions produced by the electrospray source to the 70 °C manifold temperature. The second octopole was operated as specified in the commercial instrument for MS/MS experiments with pressures ranging from 10^{-6} to 10^{-2} Torr. In the daughter-ion mode used in most of the experiments in this report, Q1 is used to mass-select ions of a single mass from among all of the ions produced in O1, which are then collided or reacted with a target gas in O2, and mass-analyzed by Q2. Monte Carlo modeling of ion motion in an octopole radio frequency field at a finite pressure assuming a Langevin cross section for collisions finds, for ~1 mTorr collision gas in O2 at 70 °C, up to 10,000 collisions for an ion introduced with low kinetic energy [8]. Thus O2 operates in a regime where it behaves more like an ion drift cell than a conventional collision-induced dissociation (CID) cell.

Organometallic precursor compounds were prepared and handled with conventional Schlenk techniques. $[Rh(P(CD_3)_3)_4(H)_2]^+PF_6^-$, $[Rh(PPh_3)_2(nbd)]^+PF_6^-$, and $[Rh(PMe_3)_3(nbd)]^+PF_6^-$ (nbd = norbornadiene) were prepared according to the procedure by Schrock and Osborn [10]. The complex [Rh(*S*,*S*-chiraphos)(nbd)]$^+$ ClO_4^- was purchased from Aldrich and used as received [*S*,*S*-chiraphos = (2*S*,3*S*)-(−)-*bis*(diphenylphosphino) butane]. $[Rh(R\text{-BINAP})(CH_3OH)_2]^+Cl^-$ was prepared by the reaction of two equivalents of *R*-BINAP with the chlorobridged dimeric complex $((C_2H_4)_2RhCl)_2$ in methanol, and used without isolation (*R*-BINAP = (*R*)-(+)-2,2′-*bis*(diphenylphosphino)-1,1′binaphthyl). Rhodium, rather than the ruthenium, complexes were investigated because rhodium has a single naturally occurring isotope, in contrast to the seven for ruthenium. While later applications would be unaffected by the isotopic distribution, the present mass spectrometric study would be substantially more complicated if ruthenium had been used.

3. Results

Typically, 10^{-5} *M* CH_2Cl_2 solutions of each complex were electrosprayed, cleanly giving the parent masses. When the tube lens potential in the ion source was progressively increased, sequential loss of ligands and/or hydrogen could be induced. While the structure of each intermediate ion is not directly addressed by the mass spectrometric experiments, tentative assignments, shown in Scheme 1, are made consistent with known rhodium chemistry, and with the reactivity observed in this experiment. The series of gas phase preparations of reactive low-coordinate complexes, and their subsequent reactions are shown in Table 1 with a brief description of each experiment. Most of the results were obtained in daughter-ion mode to eliminate ambiguities in the identity of the

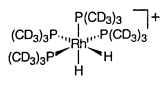
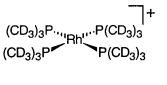
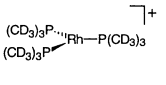
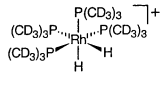
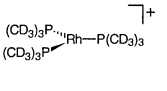
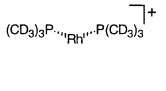
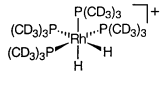
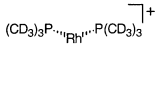
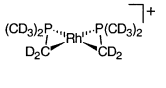
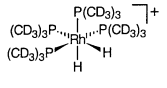
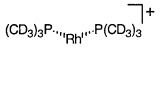
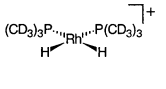
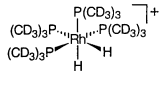
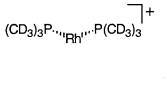
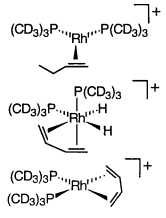
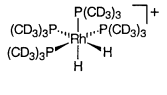
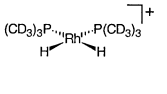
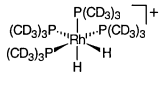
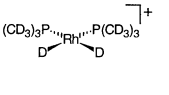
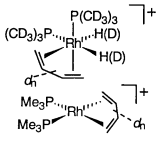
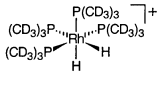
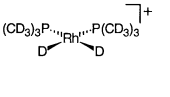
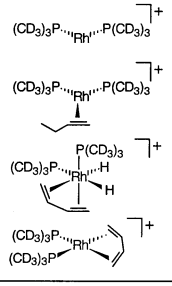


Scheme 1

reacting species. Three of the more important daughter-ion spectra are shown in Figs. 1 and 2. In Fig. 1, CID of **3** clearly leads to loss of D_2, producing **4**, indicative of the intermediacy of **3c**. Fig. 2 shows the daughter-ion spectra when **7-h$_2$** and **7-d$_2$** are collided with 1-butene and 1,3-butadiene, respectively.

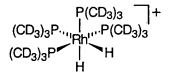
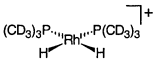
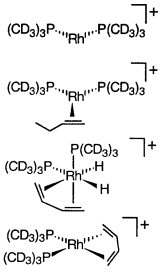
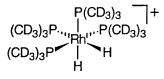
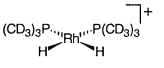
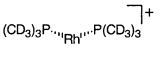
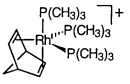
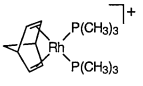
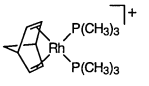
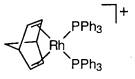
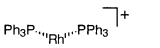
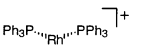
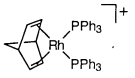
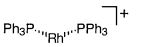
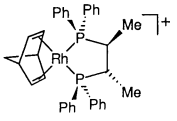
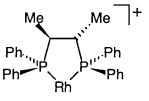
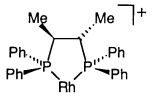
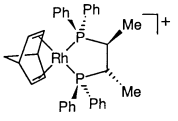
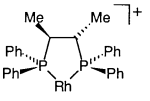
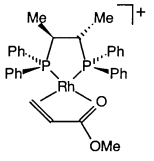
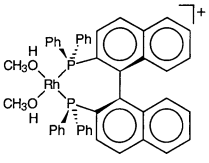
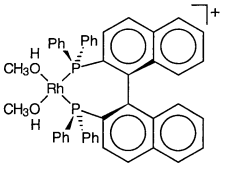
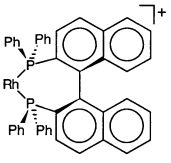
From the reactions described in Table 1, a series of observations about **3** and **7** may be made. The results are divided into four sections: the structure of **3**, the energetics of the various possible isomers of **3**, the formation and reactions of **6** as revealed by **8**, and further work pertaining to catalytic hydrogenation.

Table 1
Schematic description of the gas-phase tandem mass spectrometric experiments. O1 and Q1 are used to prepare and mass-select ions for the daughter-ion experiments in O2, with detection of products in Q2. Initial collision energies in O2 are set by the offset voltage between Q1 and O2, which is noted for each daughter-ion experiment above.

	Precursor:	is electrosprayed into O1 where there is:	producing in Q1, which is then mass-selected:	and collided in O2 with:	producing in Q2:	Comments:
1		N_2 / ~10 mTorr		Ar / 1.4 mTorr -40 V		plus small peaks corresponding to further phosphine loss.
2		N_2 / ~10 mTorr		Ar / 1.2 mTorr -20 to -50 V		At -40 eV, further loss of D_2 begins.
3		N_2 / ~10 mTorr		Ar / 1.3 mTorr -20 V		A *cis*-arrangement of phosphines is assumed. Parallel (<u>not</u> sequential) loss of CD_4 is also seen.
4		N_2 / ~10 mTorr		H_2 / 3 mTorr -1 V		The *bis*-phosphine adds H_2 readily.
5		N_2 / ~10 mTorr		1-butene 0.4 to 1.7 mTorr -1 to -4 V		Addition, followed by dehydrogenation is evident.
6		H_2 / ~10 mTorr		Ar / 0.6 mTorr -3 to -15 V		Only loss of H_2 and D_2 is observed.
7		D_2 / ~10 mTorr		1,3-butadiene 1.0 mTorr -2 to -9 V		H/D scrambling is indicated by observation of the products from loss of H_2, HD, and D_2.
8		D_2 / ~10 mTorr		1-butene 0.4 to 1.7 mTorr -1 to -4 V		Only a trace of H/D exchange is observed, as evidenced by the predominant loss of H_2 in forming the butadiene complex. This indicates that D_2 loss precedes addition of butene.

(*continued*)

Table 1 (*continued*)

9		H_2 / ~10 mTorr		1-butene 0.4 to 1.7 mTorr -1 to -4 V		Only final H_2 loss is seen (no HD or D_2 loss), H/D scrambling can be ruled out, as for the previous experiment.
10		H_2 / ~10 mTorr		methyl acrylate ≤ 1 mTorr -5 to -10 V		Either the acrylate was reduced or a simple CID process gave loss of H_2.
11		N_2 / ~10 mTorr		D_2 / 7.8 mTorr up to -40 V		Loss of norbornadiene is not facilitated by D_2.
12		N_2 / ~10 mTorr		Ar / 1.0 mTorr -36 V		At even higher collision energies, the complex loses a phosphine instead of H_2.
13		D_2 / ~10 mTorr		----	----	No addition of D_2 or loss of H_2 is observed to the *bis*-phosphine complex.
14		N_2 / ~10 mTorr		D_2 / 1.0 mTorr up to -36 V		No evidence for deuterium addition is found. No loss of H_2 is observed either.
15		N_2 / ~10 mTorr		methyl acrylate ≤ 1 mTorr -5 to -10 V		A methyl acrylate adduct does form with very low collision energies.
16		N_2 / ~10 mTorr		Ar / 2.2 mTorr -20 to -30 V		CID produces no evidence for H_2-loss.

3.1. Structures for **3**

The reaction **3** → **7** proceeds through structure **3a** (which can, in principle, be either an intermediate or a transition state), as evidenced by the absence of H/D scrambling in that reaction when it is run in both the forward and reverse direction. Structure **3c** cannot add H_2—it is an 18-e$^-$ complex—but the absence of detectable scrambling indicates H_2 addition to the 16-e$^-$ complex **3b** is not competitive with reversion

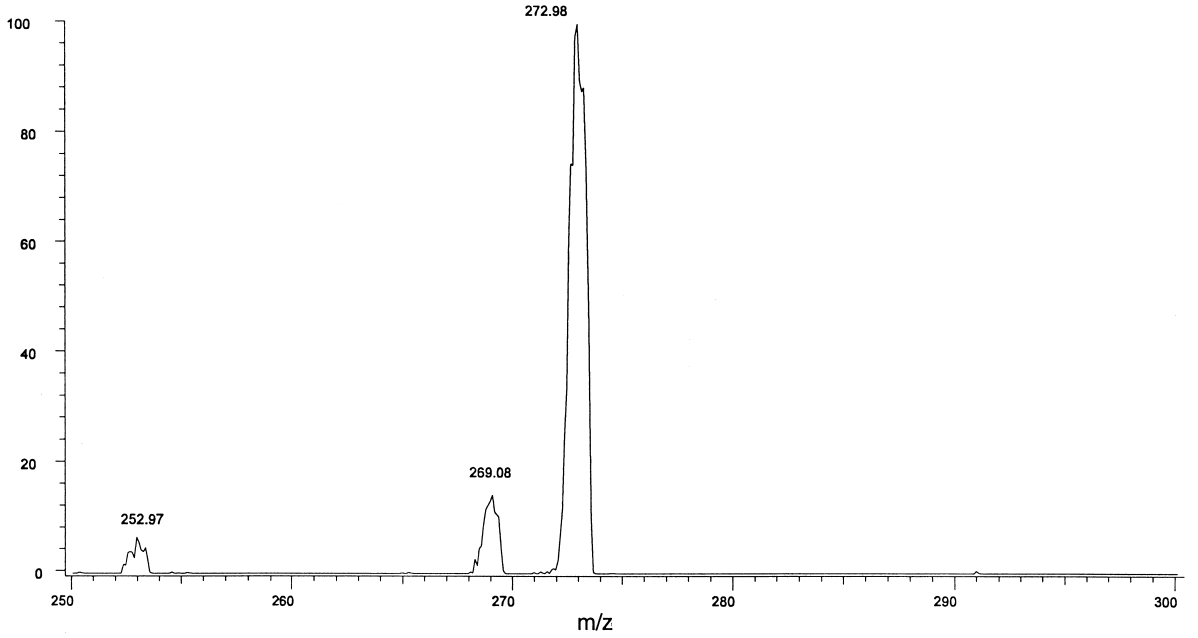


Fig. 1. Daughter-ion spectrum taken by CID of $[Rh(P(CD_3)_3)_2]^+$ **3a** at $m/z = 273$, yielding two parallel product channels. The peaks at $m/z = 269$ and 253 correspond to loss of D_2 and CD_4, respectively. No other peaks appear.

and subsequent reaction through **3a** [entries 4 and 6].

CID of **3** ($m/z = 273$) gives two parallel dissociation channels. The major channel is loss of D_2, forming **4** ($m/z = 269$). The loss of D_2 from **3** indicates that, in addition to structure **3a** above, a structure **3c** must be on the reaction coordinate. The minor channel, in which loss of CD_4 presumably forms a phosphido complex ($m/z = 253$), can be shown to be parallel rather than sequential to D_2-loss by performing a CID experiment on **4**, which produces only two further daughter ion peaks at $m/z = 237$ and $m/z = 233$, corresponding to loss of ethylene-d_4 and ethane-d_6, respectively [entry 3].

*3.2. Energetics of the isomers of **3***

The absence of phosphine loss in the collision-induced dissociation, **3** → (**4** + D_2), sets an upper-bound on the highest point along the reaction coordinate **3a** → **3b** → **3c**. It can be no more than the binding energy for a trimethylphosphine ligand above **3a** [entry 3].

Bergman has estimated that intermolecular C–H activation by a coordinatively unsaturated Rh(I) complex is ≥15 kcal/mol exothermic [11]. From our previous work on $[CpIr(PMe_3)(CH_3)]^+$ and $[CpIr(\eta^2\text{-}CH_2PMe_2)]^+$, one can estimate [12] the strain energy of the three-membered ring to be ~12 kcal/mol [13]. Assuming that the strain in the rhodium and iridium systems are comparable, we can therefore estimate that the reactions **3a** → **3b** and **3b** → **3c** are each mildly exothermic.

*3.3. Formation and reactions of **6** probed by isotopic scrambling in the formation of **8***

Direct reaction of **3** with 1-butene produces **6-h$_2$**, presumably via **5**, which then can go on to **8** by loss of H_2. Dehydrogenation of the hydrocarbon ligand is evidenced by exclusive loss of H_2, i.e. no HD or D_2, from **6-h$_2$** in the formation of **8** [entry 5].

Along the route, **3** → **7** → **6**, in which **7** is reacted with 1-butene, loss of H_2 or D_2 from **7-h$_2$** or **7-d$_2$**, respectively, largely precedes reversible hydrogen transfer to and from the hydrocarbon ligand, as

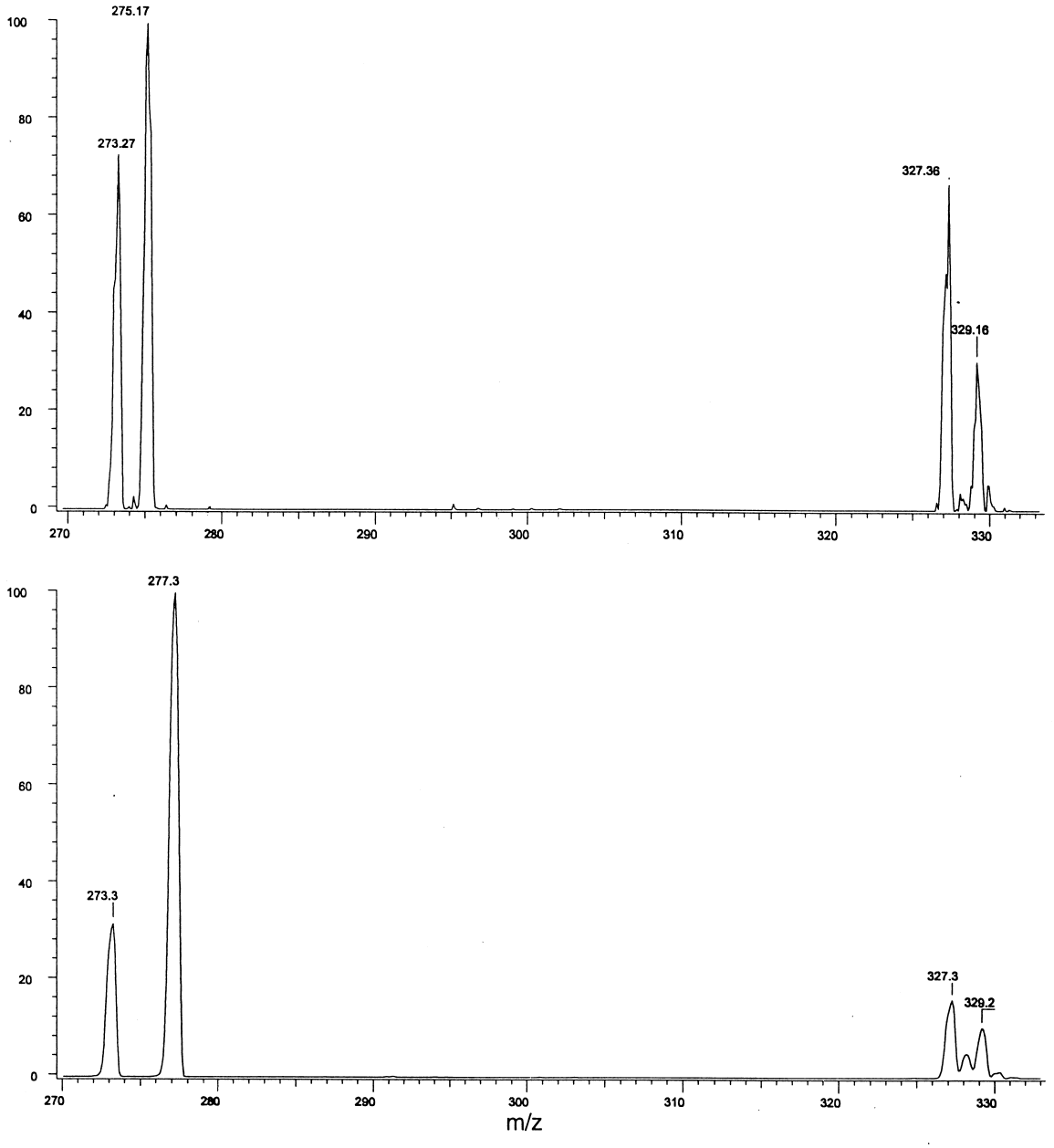


Fig. 2. Daughter-ion spectra taken by collision/reaction of **7-h$_2$** at m/z = 275 with 1-butene (upper trace), and **7-d$_2$** at m/z = 277 with 1,3-butadiene (lower trace).

evidenced by the very small amount of isotopic scrambling when **7-d$_2$** is used, i.e. **7-h$_2$** and **7-d$_2$** both revert to **3** before adding 1-butene, and then proceed to **8** as above [entries 8 and 9].

Along the route, **3** → **7** → **6**, in which **7-d$_2$** is reacted with 1,3-butadiene, one presumably forms the same intermediate complex **6**, except that **6** has two deuteride, rather than two hydride, ligands. In the formation of **8**, loss of H_2, HD, and D_2 from **6-d$_2$** (see Fig. 2) indicates that reversible hydrogen transfer

between the hydrocarbon ligand and the metal center precedes formation of **8**. The experiment does not distinguish between isotopic scrambling through a π-allyl intermediate and reversible interconversion of **5** and **6**, i.e. reversible transfer of either one or two hydrogens. Moreover, the barrier to reversible hydrogen transfer must be lower than that for loss of hydrogen to form **8**. A reaction **3** → **7** → **6** → **5** is formally one step in the homogeneous catalytic hydrogenation of butadiene via the "hydride" mechanism. Regeneration of **3** would require that the dissociation of butene from **5** have a lower barrier than reductive elimination of H_2 from **6**, which is evidently not the case [entry 7].

*3.4. Other reactions of **3** and **7**, and their analogs having aromatic phosphine ligands*

When methyl acrylate is used instead of butadiene in the reaction with **7**, one sees formation of **3**. This observation is suggestive, although not definitive, evidence for a reduction, followed by dissociation of methyl propionate, which would be more weakly bound that the butene-complex **5** [entry 10].

$[Rh(PMe_3)_2(nbd)]^+$ binds the diene very tightly. The triphenylphosphine and chiraphos complexes lose the diene more readily, presumably for a combination of electronic and steric reasons [entries 11, 12, 13, and 14].

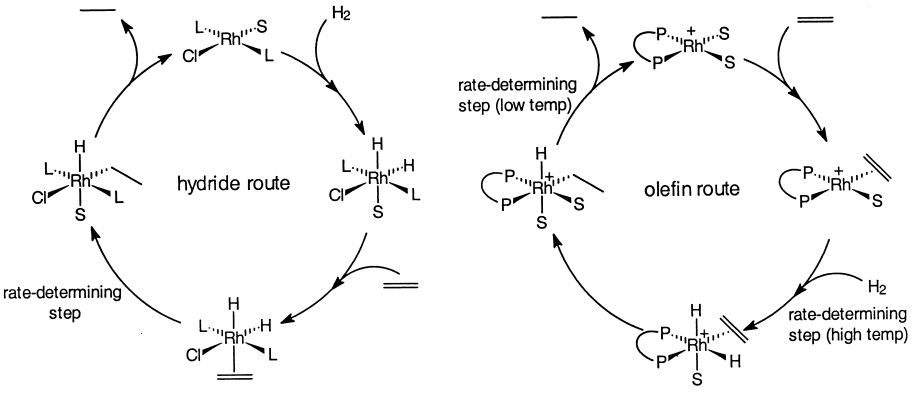
In contrast to the trimethyl phosphine complexes, $[Rh(PPh_3)_2]^+$, $[Rh(chiraphos)]^+$, and $[Rh(BINAP)]^+$ neither lose nor add H_2 or D_2, although they do form adducts with ligands such a methyl acrylate [entries 13, 14, 15, and 16].

4. Discussion

The application of electrospray ionization tandem mass spectrometry to organometallic reactions has only recently appeared. In this group, we have previously studied gas phase C–H activation [5] by $[CpIr(PMe_3)(CH_3)]^+$, oxo-transfer reactions [6] by $[O{=}Mn^V(salen)]^+$, the Ziegler–Natta polymerization [7] of α-olefins by $[Cp_2Zr{-}R]^+$, and olefin metathesis [8] (both acyclic and ROM) by $[Cl_2Ru(=CHPh)(Cy_2PCH_2CH_2NMe_3)_2]^{2+}$. Analytical applications of electrospray mass spectrometry to organometallics has been reported by other groups [14], most notably Colton and co-workers [15], as well. While small organometallic ions have been studied using a variety of mass spectrometric techniques [16,17], and metal-to-ligand or intraligand hydride transfer reactions [18–20], in particular, have been observed, the ability to bring complicated organometallic species from solution (where they have known reactivity patterns) into the gas phase has been generally lacking. Consequently, previous studies generally investigated gas phase complexes for which there was no solution-phase analog.

The interest in the reactions of L_2Rh^+ species, where L is a phosphine ligand, derives from the central role played by these complexes in the solution-phase homogeneous catalytic hydrogenation of olefins [1,2]. Solvent ligands, typically alcohols designated "S", are usually understood to be present, with the free complex formed in a preequilibrium step from the $L_2RhS_2^+$ reservoir species. The reactions of L_2Rh^+ and $L_2Rh(H)_2^+$ in the gas phase represent therefore important points of comparison to the known solution-phase chemistry.

Two general mechanistic pathways [21] have been documented by a combination of labeling, kinetics, and direct observation of intermediates for the catalytic hydrogenation of unsaturated organic compounds by these catalyst systems: the hydride route and the olefin route, which differ in the order in which molecular hydrogen and the olefin are bound to the complex. Halpern and co-workers [22] elegantly demonstrated that $L_2RhS_2^+$, where L is a phosphine ligand, catalyzes the asymmetric hydrogenation of α,β-unsaturated carbonyl compounds by the olefin route, and that, furthermore, stereoselection occurs in the hydride transfer step to the minor isomer of the olefin complex. Other complexes, such as the Wilkinson catalyst [23], on the other hand, operate by the hydride route. The mechanism operative in the ruthenium-BINAP catalysts from Noyori and co-workers [24] is less well characterized, although some studies have been carried out [25]. Clearly, both mechanisms



Scheme 2

are feasible, with the balance between the two determined by subtle features of structure and energetics. In this work, **3a** and **7** correspond to the L_2Rh^+ and $L_2Rh(H)_2^+$ intermediates, albeit without solvent ligands, for which the reactivity with H_2 (D_2) and olefins and/or dienes are presented here. With the exception of dissociation of the reduced product, each elementary step of the homogeneous catalytic hydrogenation of a diene according to the hydride route is evident in the gas-phase chemistry we observe (**3** → **7** → **6** → **5**). Moreover, the hydride transfers are specific—witness the key difference between **6-h$_2$** and **6-d$_2$**—in that complete scrambling of isotopic labels among the ligands is *not* seen. Interestingly, the role of solvent ligation, i.e. stabilization of the reactive two-coordinate active species, is taken over by reversible cyclometalation (see Scheme 2 [21]). The best estimate of the thermochemistry of the cyclometalation step makes it a few kcal/mol exothermic, coincidentally in the same range as solvent binding. Therefore, **3c** likely serves as the reservoir species, even though the subsequent intermolecular addition chemistry of **3** is exclusively that of **3a** (as either an intermediate or transition state).

The low reactivity of complexes like **8** or $[(Me_3P)_2Rh(nbd)]^+$ with H_2 or D_2 frustrated attempts to observe the olefin route for catalytic hydrogenation in this study. Furthermore, the surprising absence of either H_2 (D_2) addition to, or loss from, $[(Ph_3P)_2Rh]^+$, $[Rh(chiraphos)]^+$, and $[Rh(BINAP)]^+$ indicates that the aryl phosphine ligands have somehow interfered with the reactions of the two-coordinate complexes. While an *ortho*-metalation is certainly precedented [26], one would expect loss of H_2 to proceed from a doubly *ortho*-metalated complex, and this H_2 loss is definitely not observed. We believe the most likely explanation for the low reactivity of the two-coordinate aryl phosphine complexes of rhodium lies in the formation of a π complex between one of the pendant aryl groups and the metal center in which coordination of another substrate is blocked. In a recent report, Burk *et al*. [27] found ^{1}H nuclear magnetic resonance evidence for a $[(S,S\text{-Et-DuPHOS})Rh(\eta^6\text{-benzene})]^+$ complex to which they attribute the inhibition of Rh(DuPHOS)-catalyzed hydrogenation of enol esters in benzene solution. A analogous complex, but intramolecular, could be the cause of our results.

From these conclusions one can venture to predict what sort of complex should catalyze asymmetric hydrogenation in the gas phase. At higher pressures, where a reduced substrate can be displaced by incoming educt, turnover can be expected. Based on the mass spectrometric studies, a cationic rhodium complex of a C_2-symmetric chelating *bis*-phosphine with no conformationally mobile aryl groups would have to be used. There should be at least one alkyl group on the phosphine with a C–H bond β to phosphorus. The great majority of chiral *bis*-phosphines, BINAP [24] being only the most used one, will not function in the gas phase, according to the above criteria. Accordingly, the BPE and DuPHOS ligands from Burk [28], and the new PennPHOS ligands from Zhang and

co-workers [29], all of which lack pendant aryl groups on the phosphines, hold the most promise for a gas phase asymmetric hydrogenation. Studies on these systems are underway.

Acknowledgements

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