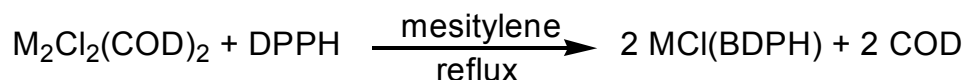


SECTION 3:

C-H INSERTION AND HYDROGEN-TRANSFER IN THE ALKYL BACKBONE OF RHODIUM BIS-PHOSPHINE COMPLEXES

Perhaps the most interesting, and noteworthy, feature of these rhodium bis-phosphine complexes is their ability to catalyze dehydrogenation reactions. While many such metal complexes are known to promote the homogeneous hydrogenation of olefins (Wilkinson's catalyst being the best known example), the reverse has been far less studied. However, it was discovered during the course of this work that electrospray mass spectrometry is an excellent tool for such a study, as it can both induce and detect the loss of H₂, H₂CO, or CH₃OH easily by simply increasing the cone voltage (see the Introduction for more information).

The first case of an alkane being homogeneously dehydrogenated by a metal site was actually that of an alkane anchored by two phosphorus atoms for the case:

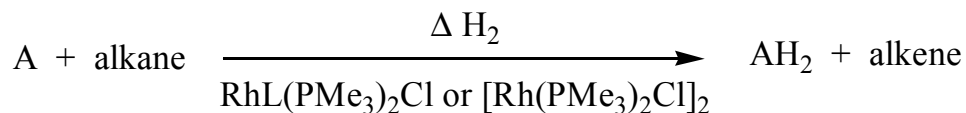


where M = Rh or Ir and BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene.¹ In studying the activation of C-H bonds it was discovered that the C₃ position of the alkyl chain in the straight chain phosphines P(C₃H₇)₃ and P(C₄H₉)₃ is much more activated than the other positions, giving rise to a favored five-membered ring intermediate.^{2,3} This led

Clark to research whether the other members of the diphosphine series $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 5, 7, 8$) and the diarsine, $\text{Ph}_2\text{As}(\text{CH}_2)_6\text{AsPh}_2$, would undergo the dehydrogenation reaction. However, after refluxing in mesitylene they found no evidence of dehydrogenation or metallation (a step suggested for the mechanism) for any of these ligands.¹

While C_3 is favored in these cases, other C-H activation studies have shown that almost any carbon-hydrogen bond can be activated under the proper conditions. Transition metals such as Ta, Cr, W, Ru, Co, Rh, Ir, Ni, Pd, Cu, and Hg have all been successfully used in C-H activation, palladium and ruthenium being the most common, followed by rhodium. Both aromatic and alkylic C-H bonds have been activated, sometimes involving cyclometallation, sometimes without.^{4,5,6,7,8,9,10}

Further work since Clark's studies has shown that alkane transfer-dehydrogenation systems are the foremost examples of organometallic-catalyzed alkane functionalization such as hydroformylation and polymerization. So instead of the direct loss of H_2 suggested by Clark for the formation of BDPH, one could also imagine the displaced COD acting as a hydrogen-acceptor to form both cyclooctene and cyclooctane. This type of reaction has been recently studied by Goldman et al with a variety of hydrogen-acceptors to give reactions of the type:¹¹



A similar situation is encountered for the $[\text{Rh}(\text{COD})(\text{bis-phosphine})]\text{BF}_4$ complexes studied in this work wherein COD can act as a hydrogen acceptor, allowing the dehydrogenation of the alkyl backbone. Although the samples are not heated, the energy imparted to them through increasing the cone voltage in ESMS and bombarding them with high-energy particles as in FAB mimics the process, leading to the formation of olefin-containing backbones. Of course using other types of energy besides thermal to induce reaction is nothing new. Recently, Loupy *et al.* used microwave radiation in a solvent-free system to effect chelation-assisted hydroacylation with rhodium(I) catalysts.¹²

Dehydrogenation of Complexes of the Type $[\text{Rh}(\text{COD})(\text{bis-phosphine})]\text{BF}_4$

The complexes synthesized in section 1 were studied by ESMS and FAB MS. For ESMS it was noted that at higher cone voltages, primarily 50 V and above, that loss of H_2 became a common process. In FAB the fragmentation pathway sometimes indicated loss of cyclooctene or cyclooctane in addition to H_2 . All these observations allow better understanding of the mechanism by which dehydrogenation of the alkane backbone occurs.

1,8-Bis(Diphenylphosphino)Octane

In the positive electrospray, upon increasing the cone voltage to 50 V a new species appears at $m/z = 581$ (Table 23). Rather than gradually appearing, this new species is actually the base peak and has been identified as $[\text{Rh}(\text{DPPO} - 2 \text{H}_2)]^+$. The

Table 23

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,8-bis(diphenylphosphino)octane (DPPO)^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 2 \text{H}_2]^+ - 581$	--	--	100	97.9 *	100
	$[\text{Rh}_2(\text{COD})_2\text{L}_2]^{2+} - 693$	100 *	100	15.9	✓	11.5
	$[\text{Rh}_2(\text{COD})_2\text{L}(\text{Cl})]^+ - 939$	3.8	25.1	99.9 *	100	64.1
	$[\text{Rh}_2\text{L}_2(\text{CH}_3\text{CN})(\text{BF}_4) - 2 \text{H}_2]^+ - 1294$	--	--	--	6.3	24.2
	$[\text{Rh}_2\text{L}_2(\text{CH}_3\text{CN})(\text{BF}_4)]^+ - 1298$	--	--	--	✓	25.6
	$[\text{Rh}_2(\text{COD})\text{L}_2(\text{BF}_4)]^+ - 1365$	--	--	11.6	26.4 *	9.7
	$[\text{Rh}_2(\text{COD})_2\text{L}_2(\text{BF}_4)]^+ - 1473$	15.1 *	27.5	61.6	7.4	6.4

L = 1,8-bis(diphenylphosphino)octane (DPPO)

✓ = Species present in small, undetermined amount

* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

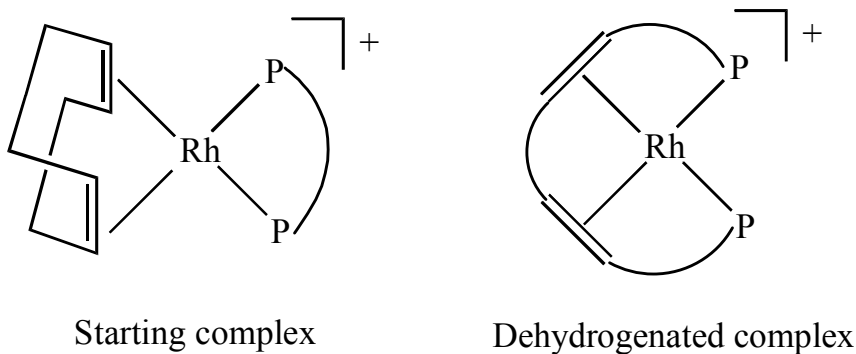
^b Data reported as % relative intensity.

previous base peak at 30 V was $[\text{Rh}_2(\text{COD})_2(\text{DPPPO})_2]^{2+}$ suggesting that most of this new species originated from it. This would make sense considering that the COD acted as a hydrogen-acceptor for the octanyl backbone to form an octadiene. This is believed to have occurred via a mechanism similar to that proposed by Clark for the dehydrogenation of DPPH (Figure 6), though with two dehydrogenations (Figure 25). This is ironic as Clark found no evidence of dehydrogenation with this same ligand after refluxing in mesitylene with $\text{M}_2\text{X}_2(\text{COD})_2$ ($\text{M} = \text{Rh}$, $\text{X} = \text{Cl}$ or Br ; $\text{M} = \text{Ir}$, $\text{X} = \text{Cl}$). Instead he obtained only an impure, difficult to isolate complex.¹

The first step in the mechanism is insertion in the C-H bond of C_3 via oxidative addition to form the favored five-membered ring (see above). This is followed by hydride transfer to cyclooctadiene. Next is β -hydrogen elimination of C_4 to form the first double bond between C_3 and C_4 , followed by reductive elimination to create cyclooctene. This is repeated starting with C_6 to form two five-membered rings, and eventually the second double bond between C_5 and C_6 , along with elimination of cyclooctane. The final product closely resembles that of the original species with *cis*-phosphine and COD, except that the COD has been replaced by the diolefin in the hydrocarbon backbone (Figure 26).

Figure 26

Structural Comparison of Starting $[\text{Rh}(\text{COD})(\text{DPPO})]^+$
Complex with Dehydrogenated Product



This mechanism is more complete than those previously proposed by Clark or Wharf, the primary difference being the addition of the two metallocyclopropane intermediates. Prior mechanisms did not explain in stepwise fashion how the carbon-carbon double bond formed, instead going directly from C-H insertion at C_3 to olefin formation. The mechanism herein proposed remedies this by proposing the formation of metallocyclopropanes between $\text{Rh}-\text{C}_3-\text{C}_4$ and $\text{Rh}-\text{C}_5-\text{C}_6$. Such metallocyclopropanes have precedence in literature for molybdenum and tungsten,^{13,14} zirconium,¹⁵ ruthenium,¹⁶ and even platinum(0) with disilene.¹⁷

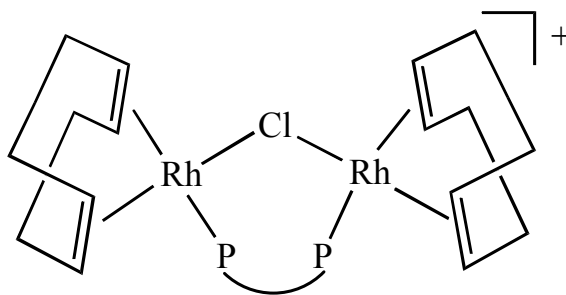
The intermediate, $[\text{Rh}(\text{COE})(\text{L} - \text{H}_2)]^+$, may also be present but as it has the same m/z (693) as the $[\text{Rh}(\text{COD})(\text{L})]^+$ it is difficult to distinguish. It is suspected that this intermediate would not be observed as the presence of COE would act as a hydrogen acceptor for two more hydrogen atoms, quickly inducing the second dehydrogenation.

Previous FAB work confirms much of this.¹⁸ In fact, the base peak was $[\text{Rh}(\text{DPPO} - 2 \text{H}_2)]^+$ at $m/z = 581$ resulting from double dehydrogenation of the bis-phosphine backbone and loss of cyclooctane. Link scans verified the loss of cyclooctane.

ESMS also observed another species at higher cone voltages that rivals $[\text{Rh}(\text{DPPO} - 2 \text{H}_2)]^+$ as the base peak. Having a m/z of 939 and a unique isotopic pattern from that of other rhodium phosphines, the species at first eluded identification. However, after noting the large intensity of the $(M+2)^+$ species the possibility of a chlorine-containing species was considered, knowing that the $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ starting material was formed from $[\text{Rh}(\text{COD})\text{Cl}]_2$. It was finally concluded that this peak was actually $[\text{Rh}_2(\text{COD})_2(\text{DPPO})(\text{Cl})]^+$, resulting from the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ impurities still present in the $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ starting material (Figure 27).

Figure 27

Possible Structure of $[\text{Rh}_2(\text{COD})_2(\text{DPPO})(\text{Cl})]^+$



Both are soluble in CH_2Cl_2 (the solvent used in ESMS) so this seems possible. This species probably arises from an unobservable neutral dichloride species. Higher cone voltages causes loss of one chloride, giving it a positive charge enabling it to be detected

by ESMS. The identification of this species has been confirmed by isotopic pattern (Figure 28). This same species has also been observed for DPPD and DPPDOD at higher cone voltages, though 28 amu higher in both cases to account for the two additional CH₂ units in each. The intensity, however, is much lower than in the DPPO case.

While this is an undesirable species, its effect on the other results is minimal for two reasons. One, it does not seem to compete with [Rh(COD)(CH₃CN)₂]BF₄ as the expected complex, [Rh(COD)(DPPO)]₂BF₄, remains the base peak at 20 V. Two, it does not come into play until fragmentation begins as it is not observed in ³¹P NMR. Thus, only at higher cone voltages will the loss of chloride occur and the possibility of bonding with the bis-phosphine be a factor. Since the studies at these high cone voltages primarily relate to C-H insertion and hydrogen-transfer reactions this is not a factor.

1,10-Bis(Diphenylphosphino)Decane

In the case of DPPD the sudden appearance of new peaks at 50 V indicating dehydrogenation was again observed (Table 24). The base peak at 50 V corresponds to loss of a single hydrogen molecule, while the peak for loss of two hydrogen molecules ($m/z = 609$) has an intensity of 53.0%. Figure 29 shows the resolution between the two peaks indicating how ESMS distinguishes between loss of multiple hydrogen molecules easily.

As the species at 611 has only gone through one dehydrogenation cycle, the presence of cyclooctene is expected. However, loss of this fragment is very possible at a cone voltage of 50 V. Upon increasing the cone voltage farther to 90 V the reaction does

Figure 28

Calculated and Observed Isotopic Patterns of
 $[\text{Rh}_2(\text{COD})_2(\text{DPPO})(\text{Cl})]^+$ in CH_2Cl_2 at 20 V

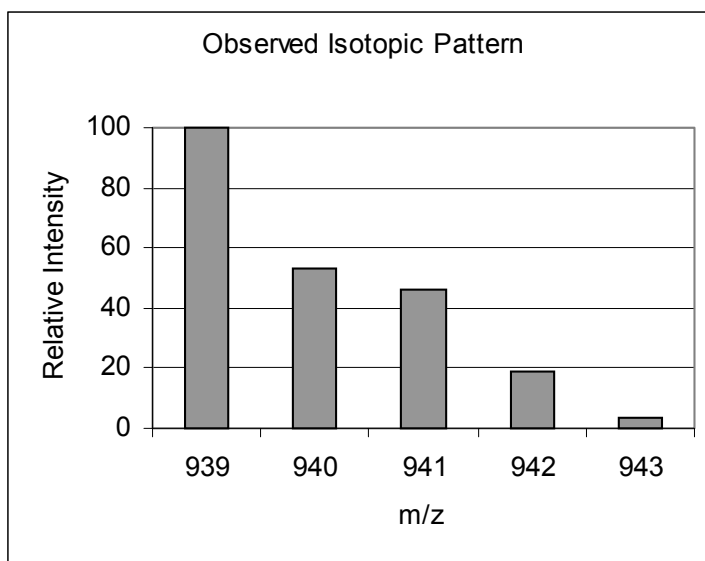
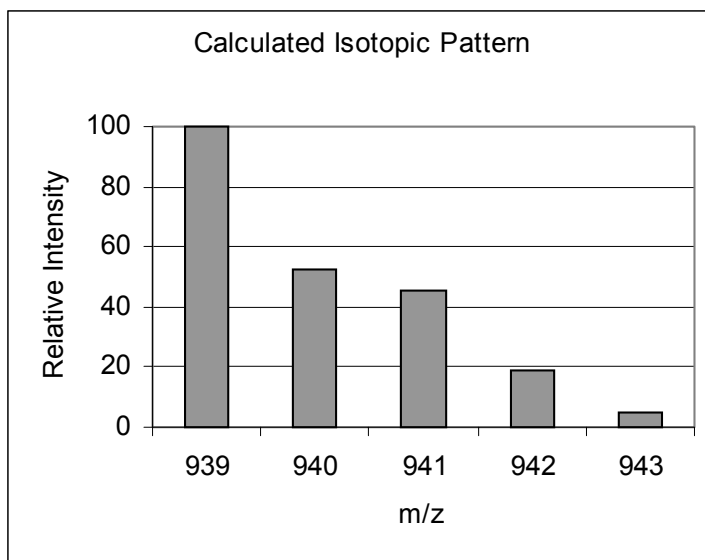


Table 24

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,10-bis(diphenylphosphino)decane (DPPD)^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 2 \text{H}_2]^+ - 609$	--	--	53.0	100	100
	$[\text{RhL} - \text{H}_2]^+ - 611$	--	--	100	97.5	89.2
	$[\text{Rh}(\text{COD})\text{L}]^+ - 722$	100	100	58.2	5.8	10.8
	$[\text{Rh}_2(\text{COD})_2\text{L}(\text{Cl})]^+ - 967$	2.5	4.6	33.2	28.1	39.8
	$[\text{Rh}_2(\text{COD})\text{L}_2(\text{BF}_4)]^+ - 1421$	--	--	4.0	9.4	4.5

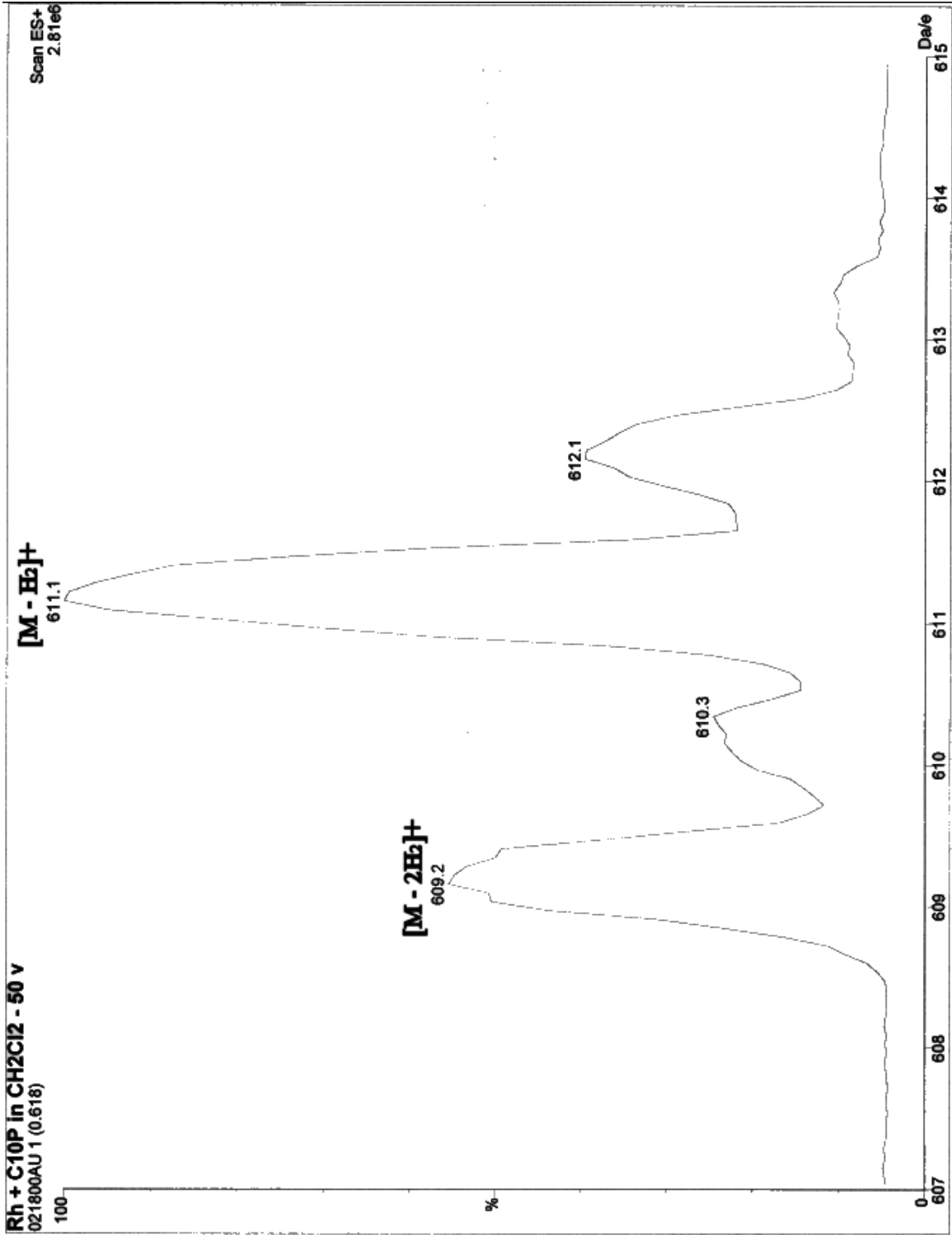
L = 1,10-bis(diphenylphosphino)decane (DPPD)

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Figure 29

ESMS Spectrum for $[\text{Rh}(\text{DPPD})]^+$ in CH_2Cl_2 at 50 V Indicating Loss of H_2 and 2H_2

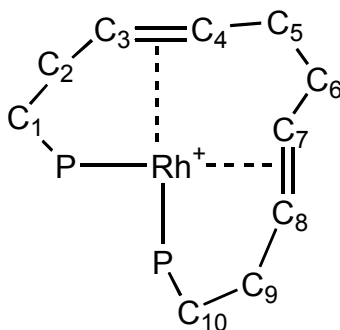


indeed proceed to completion and loss of two molecules of hydrogen ($m/z = 609$) becomes the base peak.

The mechanism for this loss is similar to that of DPPO, except after the first dehydrogenation cycle the next double bond should form between C_7 and C_8 . This seems likely as C_8 is three carbons from the phosphorus atom making it favored for C-H activation due to the formation of the five-membered ring (Figure 30).

Figure 30

Proposed Structure of Dehydrogenated $[\text{Rh}(\text{DPPD} - 2 \text{H}_2)]^+$



Again, previous FAB work¹⁹ confirms the ESMS results, while showing what a much harder ionization technique FAB is. The base peak was $m/z = 609$ which corresponds to loss of cyclooctane. However, ESMS did not detect this species as the base peak until reaching 90 V, and could actually detect the precursor at $m/z = 611$ for loss of one molecule of hydrogen. Link scans were done in an attempt to verify the loss of cyclooctane, but an inexplicable daughter ion at 610 resulted instead. This was not observed in ESMS.

1,12-Bis(Diphenylphosphino)Dodecane

Table 25 shows the ESMS results for DPPDOD. Again at 50 V dehydrogenation of the backbone begins, but with loss of only one molecule of hydrogen, presumably accompanied by loss of cyclooctene. The base peak, however, remains $[\text{Rh}(\text{COD})(\text{DPPDOD})]^+$. Upon increasing the cone voltage to 70 V the base peak now becomes the dehydrogenated species $[\text{Rh}(\text{DPPDOD} - 2 \text{H}_2)]^+$ at $m/z = 637$. In addition, also present are high-intensity peaks representing loss of three and four molecules of hydrogen. This was not previously observed for the shorter backbone ligands. By 90 V loss of four molecules of hydrogen is the dominant species. Since cyclooctadiene is no longer available to accept the two additional molecules of hydrogen lost it must be assumed they are simply eliminated as H_2 . The graph in Figure 31 displays the intensity of the four possible dehydrogenation species as a function of cone voltage. The final structure of the dehydrogenated backbone is probably similar to Figure 32, though it is unknown which of the olefins bonds with the rhodium center.

Figure 32

Proposed Structure of Dehydrogenated $[\text{Rh}(\text{DPPDOD} - 4 \text{H}_2)]^+$

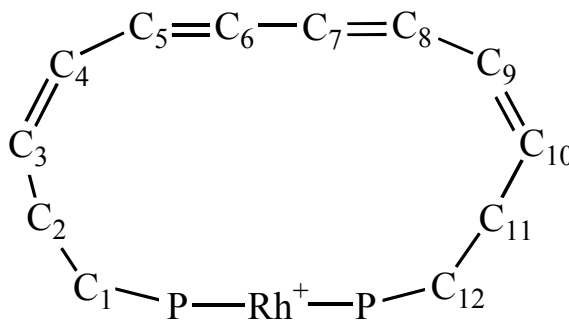


Table 25

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,12-bis(diphenylphosphino)dodecane (DPPDOD)^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 4 \text{H}_2]^+ - 633$	--	--	--	78.5	100
	$[\text{RhL} - 3 \text{H}_2]^+ - 635$	--	--	--	94.7	96.5
	$[\text{RhL} - 2 \text{H}_2]^+ - 637$	--	--	✓	100	87.9
	$[\text{RhL} - \text{H}_2]^+ - 639$	--	--	66.0 *	80.5	25.8
	$[\text{RhL}]^+ - 641$	--	--	✓	52.8	10.5
	$[\text{Rh}(\text{COD})\text{L}]^+ - 749$	100 *	100	100	9.4	10.3
	$[\text{Rh}_2(\text{COD})_2\text{L}(\text{Cl})]^+ - 995$	✓	✓	14.2	14.3	31.6

L = 1,12-bis(diphenylphosphino)dodecane (DPPDOD)

✓ = Species present in small, undetermined amount

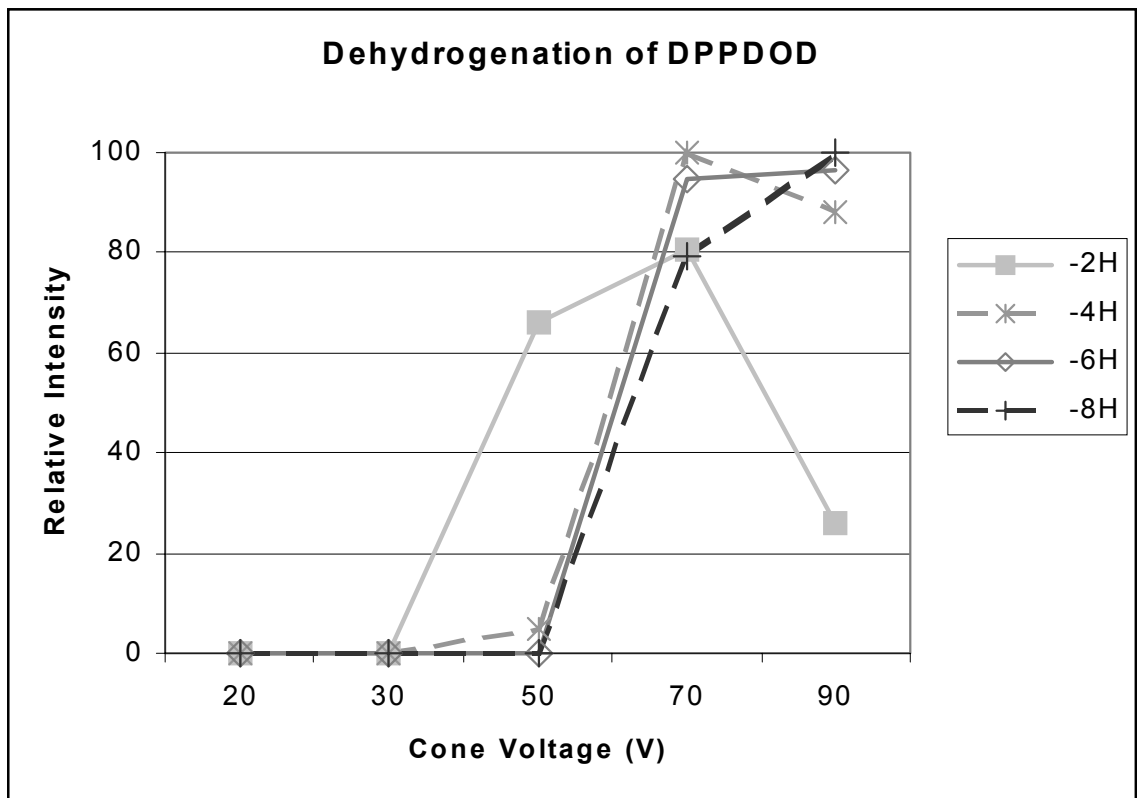
* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Figure 31

Dehydrogenation of DPPDOD as a Function of Cone Voltage in ESMS



The FAB studies²⁰ verified the results in ESMS, although some new difficulties were encountered. The loss of cyclooctene and not cyclooctane from $[\text{Rh}(\text{COD})(\text{DPPDOD})]^+$ was corroborated by link scans. This was followed by two successive losses of H_2 , but instead of losing a fourth molecule of hydrogen, link scans showed the loss of $\text{Ph}_2\text{PC}_6\text{H}_9$. A species at $m/z = 633$ ($- 4 \text{H}_2$) was not observed in FAB.

FAB also encountered intrabackbone fragmentation not seen in ESMS. Fragments containing 5, 6, 10, and 12 carbons were found. It appears that as the hydrocarbon chain length increases, so do the fragmentation possibilities.

1,4-Bis(Diphenylphosphino)Butane

DPPB, having a shorter hydrocarbon chain, displays significantly different species in ESMS and fragments in FAB than the previous cases (Table 26). The base peak remains the expected species $[\text{Rh}(\text{COD})(\text{DPPB})]^+$ up through 50 V, but past this point (70 V) it drops off to 25.0% and loss of COD predominates, with $[\text{Rh}(\text{DPPB})]^+$ becoming the new base peak. Also seen is a new peak at $m/z = 475$ which becomes the base peak upon increasing the cone voltage to 90 V. According to the isotopic pattern this species is $[\text{Rh}(\text{HPPH}_2)_2]^+$ indicating loss of C_4H_6 , presumably as 1,3-butadiene.

The mechanism by which this occurs is not well understood, but it may be that the first step involves loss of HPPH_2 followed by 1,3-butadiene. Formation of HPPH_2 is lent credence by the species at 343, attributed to $[\text{Rh}(\text{DPPB} - \text{HPPH}_2)]^+$. This is a fairly common species as well with a relative intensity of 77.9% at 50 V. Figure 33 shows the precursor at $m/z = 529$, as well as the structures of $m/z = 475$ and 343.

Table 26

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,4-bis(diphenylphosphino)butane (DPPB)^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{Rh}_2\text{L}]^{+2}$ - 316	--	--	--	--	6.6
	$[\text{RhL} - \text{HPPPh}_2]^+$ - 343	--	--	--	--	77.9 *
	$[\text{Rh}(\text{HPPPh}_2)_2]^+$ - 475	--	--	--	8.3	100 *
	$[\text{RhL}]^+$ - 529	--	--	37.2 *	100	92.3
	$[\text{RhL}(\text{CH}_3\text{CN})]^+$ - 570	7.1	3.8	--	--	--
	$[\text{RhL}(\text{CH}_3\text{CN})_2]^+$ - 611	5.4	--	--	--	--
	$[\text{Rh}(\text{COD})\text{L}]^+$ - 637	100 *	100	100	25.0	53.0

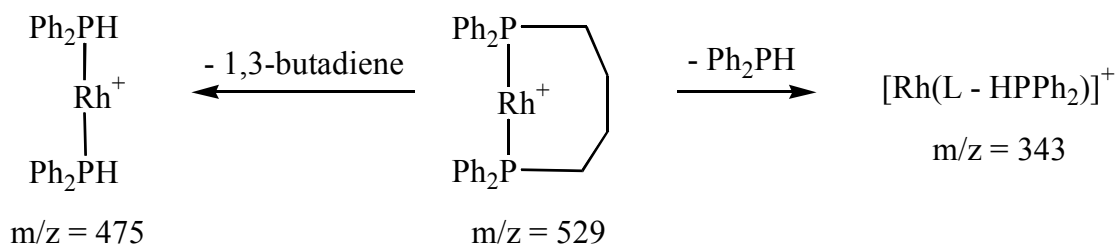
L = 1,4-bis(diphenylphosphino)butane (DPPB)

* = Species verified by isotopic pattern

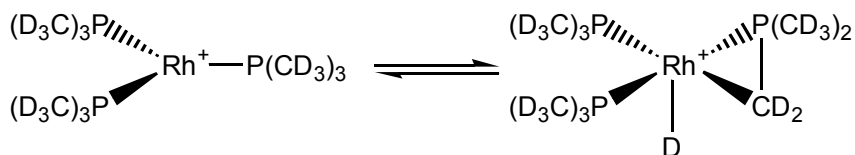
^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Figure 33

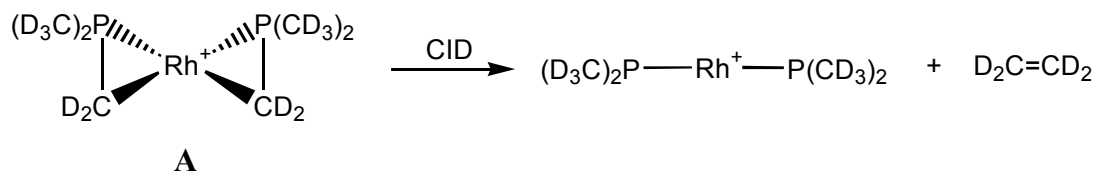
Precursor and Proposed Structures for $m/z = 475$ and 343 

Kim and Chen showed in 1999 that a similar type of reaction is possible in ESMS.²¹ Using electrospray ionization tandem mass spectrometry (see Introduction for a description of this technique) they prepared $[\text{Rh}\{\text{P}(\text{CD}_3)_3\}_4]^+$ and observed in daughter-ion mode that, upon loss of one or more phosphines, it was possible for the methyl carbons to attach to the rhodium center and transfer a deuterium atom.



After loss of two phosphines, $[\text{Rh}\{\text{P}(\text{CD}_3)_3\}_2]^+$ can lose D_2 to produce A below.

Collisionally induced dissociation (CID) (see Introduction) of A produced only two daughter ions corresponding to ethylene- d_4 (shown) and ethane- d_6 .



Based on this work, it seems reasonable to suggest a similar mechanism for the case studied here. One can imagine that, after loss of COD, the α -carbons in the alkyl backbone of DPPB attack the rhodium center, transferring H. This eventually leads to loss of 1,3-butadiene and transfer of the hydrogens to the PPh_2 groups to form HPPh_2 .

FAB²² concurs with some of the results seen in ESMS, giving a base peak of $[\text{Rh}(\text{COD})(\text{DPPB})]^+$ followed by loss of COD to produce a species at $m/z = 529$. This then loses HPPh_2 to form the species $[\text{Rh}(\text{DPPB} - \text{HPPh}_2)]^+$ at $m/z = 343$ as in the ESMS case. Both of these fragmentations were verified by link scans. Loss of 1,3-butadiene (C_4H_6) was not detected by FAB, but loss of C_4H_7 was.

1,6-Bis(Diphenylphosphino)Hexane

As discussed in Section 1, the ESMS results with DPPH are very different from the other ligands studied. The signal-to-noise ratio was poor, giving very few observable ions in solution. It is suspected that most of the rhodium species in solution are neutral, having formed ion-pairs. Therefore, what is seen is not representative of the overall solution and is only present in minor concentration. However, even the few peaks that are identifiable do show evidence of dehydrogenation. Even as low as 20 V species showing loss of H_2 are observed. As the cone voltage is increased the species at higher m/z begin to decrease and eventually disappear. This is to be expected as the additional energy imparted causes them both to fragment and lose weakly bound groups such as CH_3CN . No species losing more than one hydrogen molecule was detected.

FAB MS confirms this, showing only loss of a single hydrogen molecule. Link scans on $[\text{Rh}(\text{DPPH})(\text{COD})]^+$ produced two main daughter ions, $m/z = 557$ (loss of cyclooctadiene) and 555 (loss of cyclooctene). The loss of cyclooctane was not observed.

These results confirm what was expected, that DPPH only loses one molecule of hydrogen as this requires the formation of two stable five-membered rings. Clark previously showed this by refluxing DPPH together with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in mesitylene. They even isolated the dehydrogenated ligand and showed the double bond was between C_3 and C_4 as expected.¹ All of these results conclusively show that DPPH can and does lose only one molecule of hydrogen from its alkyl backbone. The proposed mechanism, based on Clark's work (Figure 6), is similar to that with DPPO (Figure 25) but ending with the first loss of H_2 and production of cyclooctene.

C-H Insertion and Hydrogen-Transfer of Complexes of the Type
 $[\text{Rh}(\text{CO})_2(\text{bis-phosphine})]\text{BF}_4$

The carbonyl species studied in section 2 were also examined at higher cone voltages in electrospray. In addition to dehydrogenation occurring, there is now the added possibility of the carbonyl group accepting a hydrogen molecule to form formaldehyde, H_2CO . There is also the prospect of the carbonyl group accepting two molecules of hydrogen to form methanol, CH_3OH . Each of these will be examined by ESMS, using the *in situ* species both after bubbling with carbon monoxide and purging with argon, and by FAB MS, studying only the isolated dicarbonyl.

1,8-Bis(Diphenylphosphino)Octane

Similar to what was seen for the $[\text{Rh}(\text{COD})(\text{DPPO})]^+$ case above, loss of H_2 began occurring at 50 V (Table 27). The base peak remains the carbonyl, $[\text{Rh}(\text{DPPO})(\text{CO})]^+$, but also seen was the formation of a species at $m/z = 581$ with an intensity of 44.8% corresponding to $[\text{Rh}(\text{DPPO} - 2 \text{H}_2)]^+$. Believing that most of this species in fact came from $[\text{Rh}(\text{DPPO})(\text{CO})]^+$, dehydrogenation of the backbone is expected to induce loss of methanol and not hydrogen or formaldehyde. However, the observed isotopic pattern for $m/z = 581$ does show a very small 4% increase above that calculated for 583 that may indicate some minor loss of formaldehyde or hydrogen directly. By 70 V this species at $m/z = 581$ becomes the base peak and remains so up through 90 V. Purging with argon gas had no significant effect at higher cone voltages (Table 28) and loss of two molecules of hydrogen in some fashion still predominates.

FAB studies¹⁸ also indicated the loss of CH_3OH from 613 to 581. No intermediate fragments displaying loss of H_2 or H_2CO were observed, seeming to back up the conclusion that methanol is formed and lost, not hydrogen and carbon monoxide.

Table 27

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,8-bis(diphenylphosphino)octane (DPPO) + CO^{a}

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 2 \text{H}_2]^+ - 581$	--	--	44.8 *	100	100
	$[\text{RhL}(\text{CO})]^+ - 613$	36.5 *	100	100	30.4	66.9
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 654$	100 *	✓	--	--	--
	$[\text{Rh}_2\text{L}_2(\text{BF}_4)]^+ - 1257$	25.0	25.4	38.3	--	--
	$[\text{Rh}_2\text{L}_2(\text{CO})_2(\text{BF}_4)]^+ - 1313$	--	✓	10.4	7.2	--
	$[\text{Rh}_2\text{L}_2(\text{CO})_3(\text{BF}_4)]^+ - 1341$	✓	6.9	12.5	✓	--
	Other			596(12.7)	1245(11.4)	

L = 1,8-bis(diphenylphosphino)octane (DPPO)

✓ = Species present in small, undetermined amount

* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Table 28

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,8-bis(diphenylphosphino)octane (DPPO) + CO + Ar^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 2 \text{H}_2]^+ - 581$	--	--	27.0	100	100
	$[\text{RhL}(\text{CO})]^+ - 613$	69.8	100	100	20.7	27.7
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 654$	100	✓	--	--	--
	$[\text{Rh}_2\text{L}_2(\text{BF}_4)]^+ - 1257$	41.7	16.7	20.7	✓	✓
	$[\text{Rh}_2\text{L}_2(\text{CO})_2(\text{BF}_4)]^+ - 1313$	--	--	--	--	--
	$[\text{Rh}_2\text{L}_2(\text{CO})_3(\text{BF}_4)]^+ - 1341$	✓	✓	✓	--	--
	Other					

L = 1,8-bis(diphenylphosphino)octane (DPPO)

✓ = Species present in small, undetermined amount

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

The mechanism for this is similar to that proposed earlier and is shown in Figure 34. In this instance the hydrogen acceptor is the carbonyl group instead of COD. First comes oxidative addition of the C-H bond on C₃ to form the favored five-membered ring (see above). Then there is hydride transfer to the carbonyl group followed by β -hydrogen elimination at C₄ to form the first double bond C₃ and C₄, as well as formaldehyde. This is then repeated, but with formaldehyde in place of carbon monoxide, until eventually methanol is reductively eliminated and a second double bond is formed between C₅ and C₆. The final product is believed to be the same as that shown previously in Figure 25.

1,10-Bis(Diphenylphosphino)Decane

ESMS of the DPPD complex shows corresponding results to that of DPPO (Table 29). At 30 V the base peak is $[\text{Rh}(\text{DPPD})(\text{CO})]^+$, but at 50 V a new species arises at $m/z = 609$ which is also now the base peak. This is identified again as the previous base peak after loss of hydrogen, either directly or in the form of formaldehyde or methanol. The isotopic pattern of the base peak ($m/z = 609$) at 50 V shows a prominent species at $m/z = 611$ as well (Figure 35). Subtracting out the contribution to this peak from 609, the intensity of the $m/z = 611$ peak is approximately 80%. Compared to 4% for the comparable species in DPPO, loss of methanol must no longer be the dominate process. Either greater amounts of formaldehyde are being lost, or carbon monoxide is being displaced and hydrogen lost directly from the backbone. This is not entirely unexpected as the formation of the second double bond involves formation of a five-membered and a seven-membered ring which would be less stable. Thus, loss of formaldehyde is favored

Figure 34

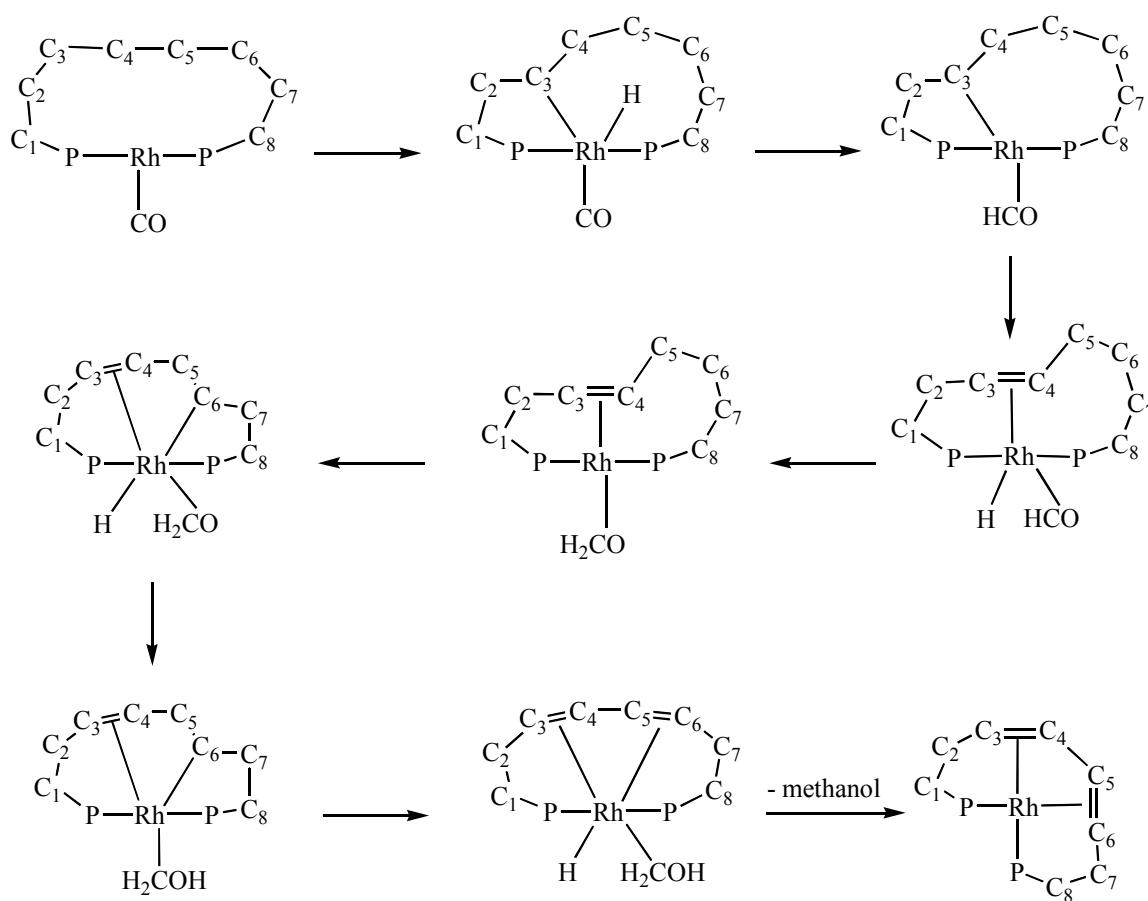
Dehydrogenation and Loss of Methanol from $[\text{Rh}(\text{CO})(\text{DPPO})]^+$ 

Table 29

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,10-bis(diphenylphosphino)decane (DPPD) + CO^{a}

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 2 \text{H}_2]^+ - 609$	--	--	100	100	100
	$[\text{RhL}(\text{CO})]^+ - 641$	5.6	100 *	82.6	11.7	9.4
	$[\text{RhL}(\text{CO})_2]^+ - 669$	6.3	22.7	7.0	✓	✓
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 682$	100 *	30.8	15.6	3.45	✓

L = 1,10-bis(diphenylphosphino)decane (DPPD)

✓ = Species present in small, undetermined amount

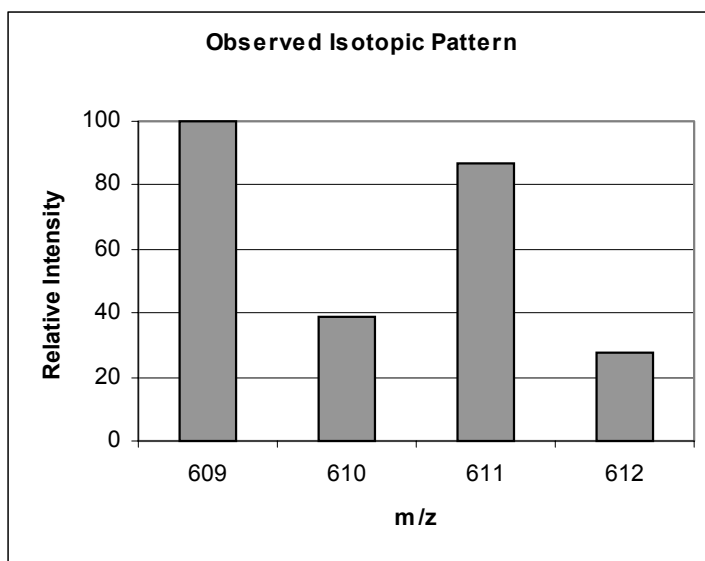
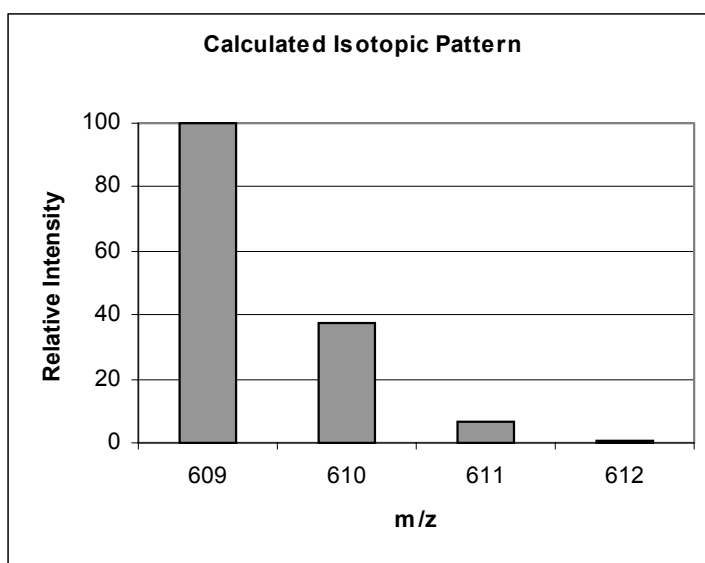
* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Figure 35

Calculated and Observed Isotopic Patterns of $[\text{Rh}(\text{DPPD} - 2 \text{H}_2)]^+$
in CH_2Cl_2 at 50 V



instead of the dominating loss of methanol seen in DPPO. Again, purging with argon gas had no significant effect on the ESMS results (Table 30).

The FAB studies¹⁹ again proposed loss of methanol. No fragment attributable to loss of H₂ was detected so it can be presumed that loss of two molecules of hydrogen predominates and this is the base peak ([Rh(DPPD - 2 H₂)]⁺). However, link scans were not performed to verify whether what was lost was actually two molecules of hydrogen or methanol. Also, as was noted for the DPPDOD case earlier in the beginning of this section, there is again fragmentation of the backbone for the ligands containing longer carbon chains. In this case species containing five and six carbon atoms were detected.

1,12-Bis(Diphenylphosphino)Dodecane

As in the case prior to adding carbon monoxide, loss of up to four molecules of hydrogen from the ligand backbone begins in ESMS at 50 V (Table 31). The base peak at 50 V remained the same as at 30 V, [Rh(DPPDOD)(CO)]⁺, but upon increasing the cone voltage to 70 V loss of one molecule of hydrogen dominates followed by two, three, and four in order. At 90 V the complete dehydrogenation of the backbone, loss of four molecules of H₂, becomes the most prevalent species in solution.

Table 30

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,10-bis(diphenylphosphino)decane (DPPD) + CO + Ar^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 2 \text{H}_2]^+ - 609$	--	--	44.2	100	100
	$[\text{RhL}(\text{CO})]^+ - 641$	4.2	100	100	15.7	10.7
	$[\text{RhL}(\text{CO})_2]^+ - 669$	--	--	--	--	--
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 682$	100	51.2	14.0	4.1	✓

L = 1,10-bis(diphenylphosphino)decane (DPPD)

✓ = Species present in small, undetermined amount

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Table 31

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,12-bis(diphenylphosphino)dodecane (DPPDOD) + CO^{a}

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 4 \text{H}_2]^+ - 633$	--	--	✓	10.1	100
	$[\text{RhL} - 3 \text{H}_2]^+ - 635$	--	--	19.2	38.3	80.8
	$[\text{RhL} - 2 \text{H}_2]^+ - 637$	--	--	26.8	63.0	35.3
	$[\text{RhL} - \text{H}_2]^+ - 639$	--	--	31.1	100 *	14.9
	$[\text{RhL}]^+ - 641$	--	--	27.9	23.6	3.4
	$[\text{RhL}(\text{CO})]^+ - 669$	4.8	100 *	100	17.1	9.7
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 710$	100 *	77.9	11.4	3.1	--

L = 1,12-bis(diphenylphosphino)dodecane (DPPDOD)

✓ = Species present in small, undetermined amount

* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Having seen for DPPO at 50 V that the base peak was the completely dehydrogenated species, the fact that here it was still the $[\text{Rh}(\text{DPPDOD})(\text{CO})]^+$ complex led to the conclusion that loss of hydrogen was not as facile for this ligand. Even at 70 V only loss of one molecule dominates and it is not until 90 V that all the expected dehydrogenation significantly occurs. Thus, formation of methanol would not be expected, but more likely formaldehyde followed by subsequent loss of hydrogen.

This makes sense upon considering the ring size necessary in order to add two molecules of hydrogen to CO. Not only would the desirable five-membered ring have to form, but also an additional nine-membered ring. Therefore, after addition of one molecule of hydrogen to create formaldehyde it most likely dissociates and subsequent loss of hydrogen is in the form of H_2 . Purging with argon gas again had no significant effect on the results (Table 32).

FAB work²⁰ verifies some of this by indicating fragments attributable to loss of formaldehyde and hydrogen. However, whether this loss occurred sequentially with formaldehyde lost first and then hydrogen cannot be proven. It may be that both formaldehyde and methanol were lost as seen in the DPPD case via ESMS. Link scans could have decisively determined this but were not performed.

1,4-Bis(Diphenylphosphino)Butane

ESMS again shows a process similar to the DPPB case before addition of carbon monoxide, whereby at higher voltages formation of HPPH_2 occurs, simultaneous with loss of C_4H_6 (Table 33). At 50 V this is not observed, but by 70 V the process has begun,

Table 32

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,12-bis(diphenylphosphino)dodecane (DPPDOD) + CO + Ar^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - 4 \text{H}_2]^+ - 633$	--	--	7.8	32.7	100
	$[\text{RhL} - 3 \text{H}_2]^+ - 635$	--	--	18.7	86.1	73.1
	$[\text{RhL} - 2 \text{H}_2]^+ - 637$	--	--	20.9	100	52.6
	$[\text{RhL} - \text{H}_2]^+ - 639$	--	--	19.0	45.4	22.5
	$[\text{RhL}]^+ - 641$	--	--	16.6	23.0	8.8
	$[\text{RhL}(\text{CO})]^+ - 669$	6.0	100	100	12.5	9.4
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 710$	100 *	70.6	10.9	4.01	--

L = 1,12-bis(diphenylphosphino)dodecane (DPPDOD)

* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

Table 33

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,4-bis(diphenylphosphino)butane (DPPB) + CO^{a}

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - \text{HPPH}_2]^+ - 343$	--	--	--	16.0	100
	$[\text{Rh}(\text{HPPH}_2)_2]^+ - 475$	--	--	--	29.7	48.1
	$[\text{RhL}]^+ - 529$	--	--	100 *	100	22.6
	$[\text{RhL}(\text{CO})]^+ - 557$	✓	100 *	19.8	8.3	10.5
	$[\text{RhL}(\text{CO})_2]^+ - 585$	100 *	52.4	✓	6.3	17.6
	$[\text{RhL}(\text{CH}_3\text{CN})(\text{CO})]^+ - 598$	15.0	✓	--	--	--
	$[\text{Rh}_2\text{L}_2(\text{BF}_4) - 4\text{H}]^+ - 1141$	--	4.8	3.3	3.2	15.2
	$[\text{Rh}_2\text{L}_2(\text{BF}_4)]^+ - 1145$	--	6.9	--	--	--

L = 1,4-bis(diphenylphosphino)butane (DPPB)

✓ = Species present in small, undetermined amount

* = Species verified by isotopic pattern

^a 10^{-3} M sample in pure CH_2Cl_2 .

^b Data reported as % relative intensity.

though $[\text{Rh}(\text{DPPB})]^+$ remains the base peak. After increasing the cone voltage to 90 V loss of HPPh_2 dominates (100%), followed by loss of 1,3-butadiene (48.1%). The mechanism for this is most likely the same as that for the DPPB case above without carbon monoxide. After purging with argon gas the results were largely unchanged (Table 34).

In the FAB work²² the base peak at $m/z = 459$ was unidentifiable, but possibly arose from the matrix as its weight is three times that of 3-nitrobenzyl alcohol (NBA). There is again seen loss of HPPh_2 and C_4H_7 , but not C_4H_6 , confirming at least part of the earlier proposal.

Conclusions

Mass spectrometric studies of rhodium bis-phosphine complexes using electrospray and fast atom bombardment have proven extremely useful in understanding the process by which loss of hydrogen from the hydrocarbon backbone occurs. ESMS, with the ability to vary the cone voltage, is especially useful as it allows the determination of the stability of the various intermediates and which fragments prevail.

Table 34

ESMS Data for 1:1 Study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,4-bis(diphenylphosphino)butane (DPPB) + CO + Ar^a

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{RhL} - \text{HPPPh}_2]^+ - 343$	--	--	--	11.2	100
	$[\text{Rh}(\text{HPPPh}_2)_2]^+ - 475$	--	--	--	35.0	42.3
	$[\text{RhL}]^+ - 529$	--	--	100	100	27.3
	$[\text{RhL}(\text{CO})]^+ - 557$	9.1	100	18.1	10.5	7.7
	$[\text{RhL}(\text{CO})_2]^+ - 585$	100	47.7	6.4	6.3	5.4
	$[\text{RhL}(\text{CH}_3\text{CN})(\text{CO})]^+ - 598$	9.8	✓	--	--	--

L = 1,4-bis(diphenylphosphino)butane (DPPB)

✓ = Species present in small, undetermined amount

^a 10^{-3} M sample in pure CH_2Cl_2 .

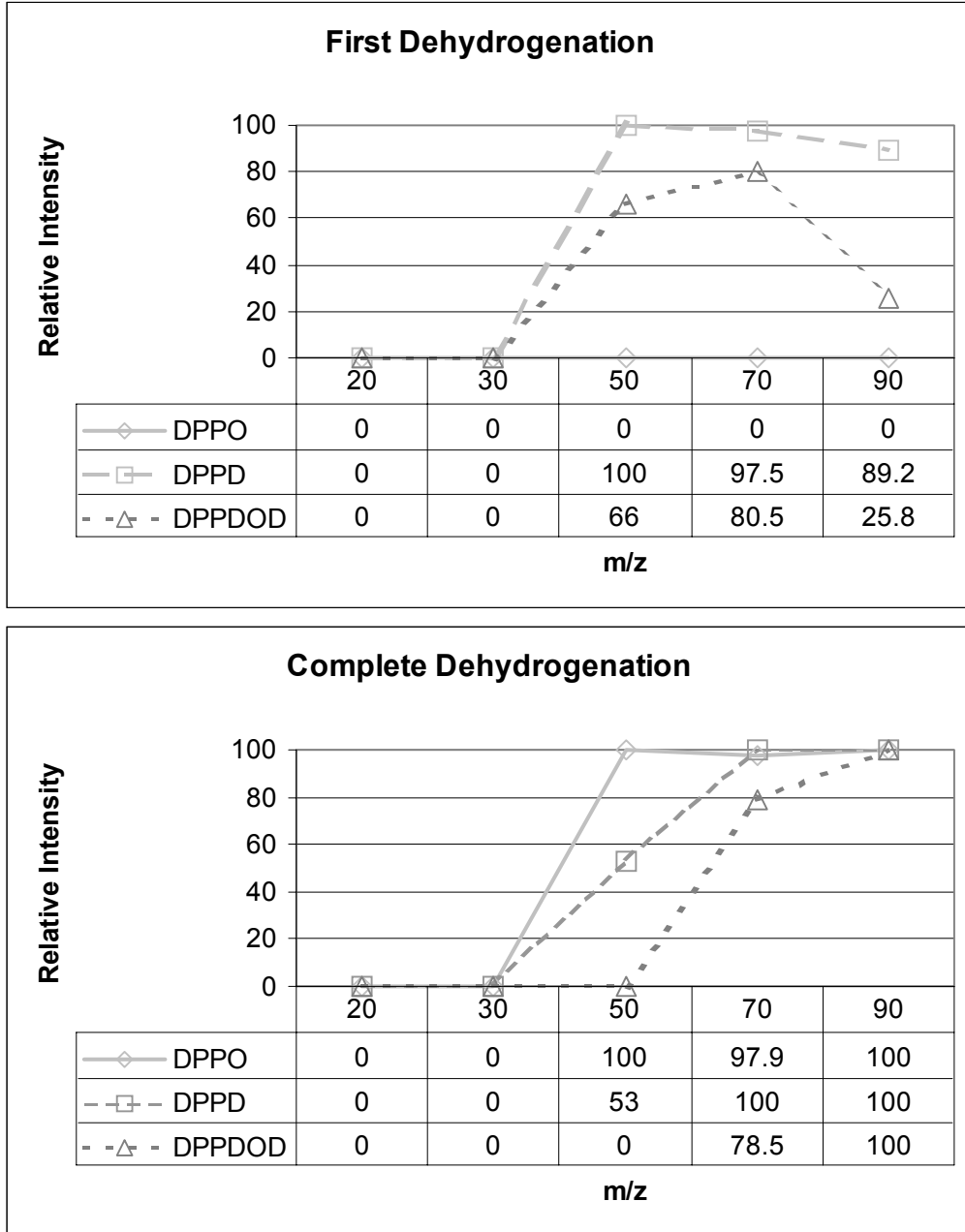
^b Data reported as % relative intensity.

First, consider just the long chain bis-phosphines (DPPO, DPPD, and DPPDOD) where multiple loss of hydrogen is possible. At 50 V dehydrogenation begins in every case, but the completely dehydrogenated product (i.e. loss of the maximum observed hydrogen, whether it be 2 or 4 molecules of H₂) is only the dominant species for DPPO (Figure 36). Upon increasing the cone voltage, the amount of hydrogen lost also increases until at 90 V complete dehydrogenation of all expected hydrogens was induced and this species became the base peak in every case.

This process of increasing the cone voltage has proven very useful in determining the favored loss products. For example, with DPPO complete dehydrogenation (loss of 2 molecules of hydrogen) occurs easily at 50 V making this the base peak. This is expected as COD is available to accept both molecules and the backbone must only form two very stable five-membered rings. However, in the DPPD case at 50 V the dominant species is only loss of one molecule of hydrogen while the complete dehydrogenation product has an intensity of only 53%. As DPPD must form both a five- and seven-membered ring to complete the process this is not unlikely. For DPPDOD the loss of one molecule of hydrogen at 50 V is only present in 66.0% and complete dehydrogenation is not observed. As this ligand would be required to form a five- and nine-membered ring, even less likely under mild conditions, these results make sense. Thus, it can be said that DPPO is the optimal case for dehydrogenation of the backbone as it alone can form two very stable, and highly favored, five-membered rings. As the length of the backbone increases the dehydrogenation process becomes more difficult. The following general trend for the ease of dehydrogenation of bis-phosphines is therefore observed:

Figure 36

Intensity vs Cone Voltage for First and Complete Dehydrogenation of Bis-Phosphine Ligands in CH₂Cl₂ According to ESMS



DPPO: First m/z = 583, Complete m/z = 581
 DPPD: First m/z = 611, Complete m/z = 609
 DPPDOD: First m/z = 639, Complete m/z = 633

DPPO > DPPD > DPPDOD

In studying the carbonyls similar results were observed, though loss of formaldehyde and methanol are now additional possible products. It appears again that where formation of a five-membered ring is easy, then methanol is formed, as this requires loss of two molecules of hydrogen. However, as the chain length increases, the amount of methanol (CH_3OH) formed decreases and the amount of formaldehyde (H_2CO) produced increases. This is again believed to be based upon the necessity of forming larger secondary rings to produce methanol. Thus, as the stability of these secondary rings decreases, so does the amount of methanol produced. The production of methanol, therefore, should follow the same trend as above for ease of dehydrogenation.

For the shorter chain bis-phosphines (DPPB, DPPH) the results are as expected. DPPH ideally can only lose one molecule of hydrogen as doing so requires the formation of two stable five-membered rings. Clark previously showed this to be the case upon refluxing in mesitylene and in fact isolated the dehydrogenated ligand where the double bond was between C_3 and C_4 .¹ ESMS and FAB link scans confirmed Clark's proposed mechanism, showing production of cyclooctene and loss of only one hydrogen molecule. DPPH is thus the intermediate between no dehydrogenation (DPPB) and loss of two or more molecules of hydrogen (DPPO).

The case of DPPB, having a backbone too short to form a stable five-membered ring, gives necessarily different results. Mimicking a similar ESMS observation by Kim and Chen,²¹ the primary products at higher cone voltage appear to be from loss of HPPH_2 and 1,3-butadiene. FAB verified the loss of HPPH_2 by link scans, but detected C_4H_7

instead of C_4H_6 .

In conclusion, it is easy to see the usefulness of both ESMS and FAB in studying the dehydrogenation and loss of formaldehyde and methanol in these systems. ESMS is especially informative as the gradual increase in energy applied to the sample provides more information than one spectra alone could. However, combined with FAB the results become even more conclusive and one begins to understand the mechanism by which these systems lose hydrogen.

References

1. Clark, P.W., *J. Organomet. Chem.*, **1977**, *137*, 235.
2. Masters, C., *J. Chem. Soc., Chem. Commun.*, **1973**, 191.
3. Kiffen, A.A., Masters, C., Raynand, L., *J. Chem. Soc., Dalton*, **1975**, 853.
4. Jun, C.-H., Moon, C.W., Lee, D.-Y., *Chem. Eur. J.*, **2002**, *8:11*, 2422.
5. Dyker, G., *Angew. Chem. Int. Ed.*, **1999**, *38*, 1698.
6. Wiley, J.S., Heinekey, D.M., *Inorg. Chem.*, **2002**, *41*, 4961.
7. Jun, C.-H., Moon, C.W., Kim, Y.-M., Lee, H., Lee, J.H., *Tet. Lett.*, **2002**, *43*, 4233.
8. Jun, C.-H., Chung, J.-H., Lee, D.-Y., Loupy, A., Chatti, S., *Tet. Lett.*, **2001**, *42*, 4803.
9. Bendorf, H.D., Colella, C.M., Dixon, E.C., Marchetti, M., Matukonis, A.N., Musselman, J.D., Tiley, T.A., *Tet. Lett.*, **2002**, *43*, 7031.
10. Lee, D.-Y., Kim, I.-J., Jun, C.-H., *Angew. Chem. Int. Ed.*, **2002**, *41:16*, 3031.
11. Wang, K., Goldman, M.E., Emge, T.J., Goldman, A.S., *J. Organomet. Chem.*, **1996**, *518*, 55.
12. Loupy, A., Chatti, S., Delamare, S., Lee, D.-Y., Chung, J.-H., Jun, C.-H., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1280.
13. Thomas, J.L., *J. Am. Chem. Soc.*, **1973**, *95*, 1838.
14. Alt, H.G., Thewalt, U., *J. Organomet. Chem.*, **1984**, *268*, 235.
15. Fryzuk, M.D., Duval, P.B., Rettig, S.J., *Can. J. Chem.*, **2001**, *79*, 536.
16. Wong, W.-K., Chiu, K.K., Statler, J.A., Wilkinson, G., *Polyhedron*, **1984**, *3:11*, 1255.
17. Sakaki, S., Ieki, M., *Inorg. Chem.*, **1991**, *30*, 4218.
18. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 130.
19. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 134.

20. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 139.
21. Kim, Y, Chen, P., *Int. J. of Mass Spec.*, **1999**, 185/186/187, 871.
22. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 113.