

II. RESULTS AND DISCUSSION

SECTION 1:

RHODIUM(I) CYCLOOCTADIENE COMPLEXES WITH LONG CHAIN BIS-PHOSPHINE LIGANDS

The structural and compositional characterization of complexes of the type *cis*-[Rh(COD)(bis-phosphine)]BF₄ has been a pursuit of this group for some time. Studies have been made using a variety of techniques, primarily ³¹P nuclear magnetic resonance (NMR) and fast atom bombardment (FAB) mass spectrometry. These produced good results, but proved less than 100 percent conclusive in determining the solution-state structure of the complexes. Bursley even demonstrated in 1983 that while FAB was preferred over techniques such as field desorption (FD) for singly-charged species, there was no clear method of choice for multiply-charged species.¹ In fact, since first conducting this work, Arakawa and co-workers have noted that techniques such as FAB, FD, secondary ion mass spectrometry (SIMS), and laser desorption mass spectrometry (LDMS) produce only singly-charged ions for coordination compounds.² The exception to this are doubly-charged ions of a ruthenium-bidentate ligand complex observed in FAB by carefully selecting an appropriate matrix, or combination of matrices.^{3,4,5,6,7}

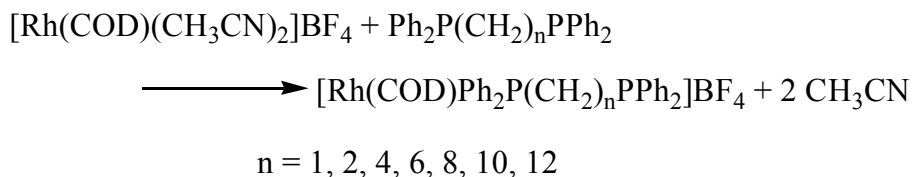
With the advent of electrospray mass spectrometry (ESMS) it seemed the proper time to revisit this work in the hopes of determining the structures of these complexes. Since it allows the easy transfer of ions from solution to the gas phase it seemed an ideal

choice for these potentially dimeric Rh^I complexes. And unlike the FAB studies of organometallic and coordination compounds where side processes such as proton extraction and formation of oxidized species complicate the mass spectra,² these are not generally observed in ESMS.

Synthesis of the Complexes

Green and co-workers first reported the [Rh(COD)(CH₃CN)₂]BF₄ starting material used in this work in 1970.⁸ As expected, the coordinatively unsaturated d⁸ [Rh(COD)₂]BF₄ system is kinetically labile and useful for the synthesis of new cationic derivatives of Rh^I. By reacting [Rh(COD)₂]BF₄ with acetonitrile donor ligands, they obtained the desired product, [Rh(COD)(CH₃CN)₂]BF₄. This is believed to occur because the entering π-acceptor group weakens the metal-olefin bond, leading to its displacement.⁹ They then discovered that coordinated acetonitrile, a σ-donor, could be readily displaced by stronger σ-donor groups such as PPh₃ or (Ph₂PCH₂)₂. However, while phosphines also have significant π-bonding ability and will displace cyclooctadiene, the rate is much slower.

This work has been extended to create complexes of the type *cis*-[Rh(COD)(bis-phosphine)]BF₄ (empirical formula), where bis-phosphine = Ph₂P(CH₂)_nPPh₂ (n = 1, 2, 4, 6, 8, 10, and 12). These were synthesized by the reaction of [Rh(COD)(CH₃CN)₂]BF₄ with the appropriate ligand in methylene chloride solution under an argon atmosphere. For the *in situ* case, the reactants were weighed out and the degassed solvent added to them. For the isolated case, the ligand was added dropwise over about one hour to a solution of the rhodium starting material.



The *in situ* complexes have been characterized by ³¹P NMR and electrospray mass spectrometry and the results compared to those of the isolated complexes and their characterization by ³¹P NMR and FAB mass spectrometry. The complexes are extremely hygroscopic and unstable in air, especially in solution, so must be handled under an argon atmosphere.

Characterization of the Complexes

The phosphorus-31 NMR chemical shifts, rhodium-phosphorus coupling constants, and percent compositions for both the isolated¹⁰ and the *in situ* complexes are listed in Table 1. As cyclooctadiene is a *cis*-chelating ligand, the geometry of all the complexes are confined to *cis*. This is proven by the ¹J(Rh-P) values which are in the

Table 1

$^{31}\text{P}\{^1\text{H}\}$ NMR Data of Studied Cis-[Rh(COD)(Bis-Phosphine)]BF₄ Complexes.

Ligand	Isolated Complex in CDCl ₃			<i>in situ</i> Complex in CH ₂ Cl ₂ ^c		
	$\delta\text{P}^{\text{a}}$	$^1\text{J}(\text{Rh-P})^{\text{b}}$	% Composition	$\delta\text{P}^{\text{a}}$	$^1\text{J}(\text{Rh-P})^{\text{b}}$	% Composition
DPPB	+24.8	143.0	100	+24.3 +26.4	143.4 149.2	58 42
DPPH	+17.3 +20.0	145.8 140.8	76 24	--	--	--
DPPO	+18.1 +19.9	142.2 142.4	33 67	+17.8 +18.0 +19.5	142.3 143.1 142.7	36 64
DPPD	+19.4	143.0	100	+18.9	135.9	100
DPPDOD	+19.4	142.2	100	+18.9	140.7	100

^a Relative to 85% H₃PO₄.

^b Measured in Hz.

^c CD₂Cl₂ added as lock solvent.

approximate range of 140-150 Hz, agreeing well with other known *cis*-[Rh(COD)(bis-phosphine)]⁺ complexes,¹¹ including the previously synthesized¹² [Rh(COD)(DPPB)]BF₄ (Table 2).

Table 2

³¹P{¹H} NMR Data of *Cis*-[Rh(COD)(Bis-Phosphine)]BF₄ Complexes in CH₂Cl₂.^a

Complex	δP ^b	¹ J(Rh-P) ^c
[Rh(COD){P(C ₆ H ₅) ₂ CH ₂ } ₂]ClO ₄ ·CH ₂ Cl ₂ ¹¹	-10.4	141
[Rh(COD)(DPPE)]ClO ₄ ¹¹	-54.6	161
[Rh(COD)(DPPB)]BF ₄ ¹²	23.5	144

^a CD₂Cl₂ added as lock solvent.

^b Relative to 85% H₃PO₄.

^c Measured in Hz.

All the raw electrospray data are presented in Appendix I. The reference spectrum of the [Rh(COD)(CH₃CN)₂]⁺BF₄⁻ starting material is presented in Figure 16. The electrospray data for the determination of monomer vs dimer of the *in situ* complexes is presented in Table 3. As the m/z value for both monomer and dimer would be the same without a counter-ion, the only way to determine the percentage of monomer and dimer for the species is by calculating it based on the isotopic pattern. This was done using a program designed by Norgaard¹³ that compares the possible combinations of isotopic patterns for monomer and dimer mixtures and determines which one matches the observed (Appendix II). Basically, the isotopic patterns of the monomer and dimer are

Figure 16

ESMS Spectrum of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$
Starting Material in CH_2Cl_2 at 20 V

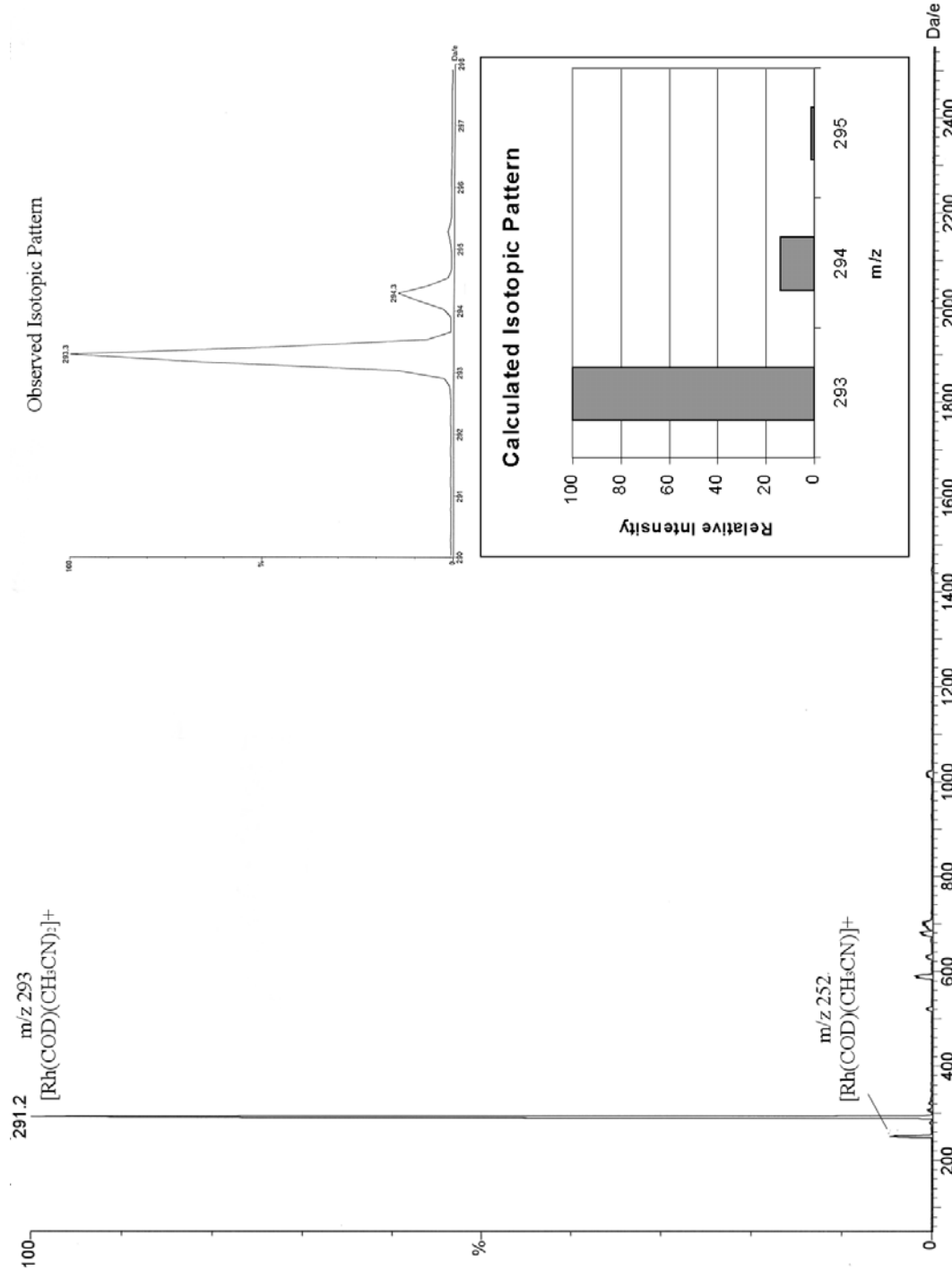


Table 3

ESMS Data for *in situ* *Cis*-[Rh(COD)(Bis-Phosphine)]BF₄ in CH₂Cl₂ at 20V.^a

Ligand	Base Peak (Intensity)	% Monomer ^b	% Dimer ^b
DPPB	[Rh(COD)]L ⁺ (100)	100	0
DPPH	[Rh(COD)]L ⁺ (100)	--	--
DPPO	[Rh(COD)L] ⁺ (100)	10	90
DPPD	[Rh(COD)L] ⁺ (100)	69	31
DPPDOD	[Rh(COD)L] ⁺ (100)	82	18

^a Compiled from Tables 5-8.

^b Calculated using program from Appendix II.

mathematically combined in different ratios until a match is found for the peak of interest's isotopic pattern. This ratio is then reported as the percentage of monomer and dimer.

In a study of $[\text{Ag}(\text{DPPM})]^+$ Norgaard found that fragmentation of dimer into monomer did not occur until ~ 35 V (Figure 17).¹⁴ A cursory look at the data in Appendix I show a similar trend, with fragmentation not beginning until the 30 or 50 V studies. This allows us to assume that all monomers present in these 20 V spectra are indeed actually present in solution, and not the result of dimer fragmentation. However, it must be remembered that any neutral ion-paired species present in solution will not be observed in the electrospray so the percentage of monomer-dimer determined is only valid for the particular species studied and not quantitative for the system as a whole.

Table 4 displays the FAB MS data¹⁵ for the isolated complexes, including the intensity of the $[\text{Rh}(\text{COD})\text{L}]^+$ species and the identity of the base peak species, if different. Agreeing with the earlier mentioned observations of Arakawa,² the FAB MS showed only monocharged species, primarily monomeric, for all cases. Though the discharged dimer was never observed, it is assumed that one process that can occur is the fragmentation of the dimer to the monomer.

Figure 17

Plot of % Monomer vs Cone Voltage for $[\text{Ag}(\text{DPPM})]^+$ as Determined by Isotopic Pattern in ESMS

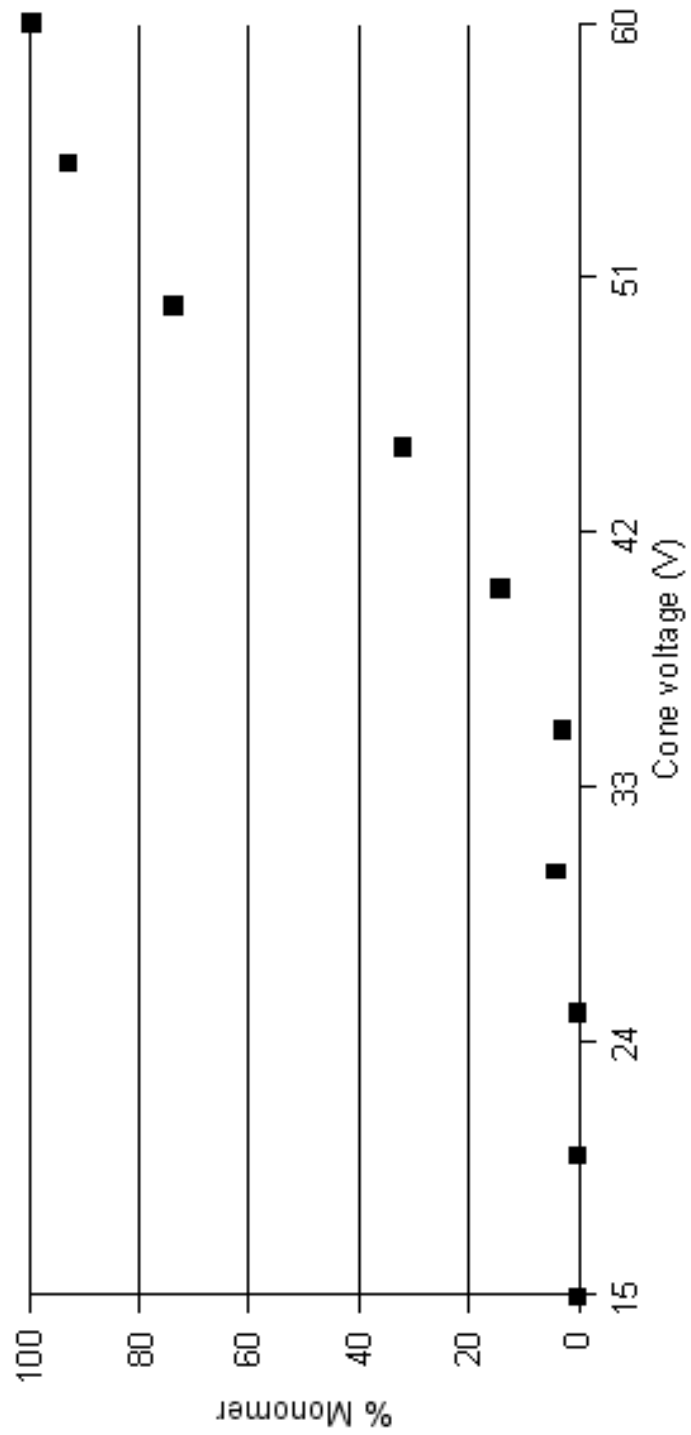


Table 4

FAB MS Data for Isolated *Cis*-[Rh(COD)(Bis-Phosphine)]BF₄.^a

Ligand (L)	Intensity of [Rh(COD)L] ⁺	Base Peak
DPPB	100	[Rh(COD)L] ⁺
DPPH	7	[RhL - H ₂] ⁺
DPPO	36	[RhL - 2 H ₂] ⁺
DPPD	24	[RhL - 2 H ₂] ⁺
DPPDOD	64	[RhPC ₆ H ₄] ⁺

^a 3-Nitrobenzyl alcohol used as matrix.

However, while the majority of the peaks were monomeric, some dimeric species containing BF₄⁻ or F⁻ counter-ions to produce +1 ions were observed in small amounts for all the ligands having a carbon chain length of six or more. For example, a FAB study of [Rh(COD)(DPPH)]⁺ showed species such as [Rh₂(COD)₂L₂BF₄]⁺ (2%), [Rh₂(COD)L₂BF₄]⁺ (1%), and [Rh₂(COD)L₂F]⁺ (1%) to be present.¹⁶ This clustering with anions to form +1 cations has also been observed in FAB studies of Cu(I) and Cu(II) chelates.¹⁷ This too may account for the relative lack of observed dimeric species since clustering with two anions would render the complex neutral and unobservable by FAB.

1,4-Bis(Diphenylphosphino)Butane

The phosphorus-31 NMR spectrum (Table 1) for the isolated complex shows only one doublet present at +24.8 ppm. The *in situ* shows two doublets at +24.3 ppm and +26.4 ppm in an approximately 60:40 ratio. These differences will be discussed below.

Electrospray (Figure 18) shows the 100% peak to be the anticipated $[\text{Rh}(\text{COD})(\text{DPPB})]^+$ species, as seen in Table 5.

Table 5

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

		Relative Intensity
Species - m/z	$[\text{RhL}(\text{CH}_3\text{CN})]^+$ - 570	7.1
	$[\text{RhL}(\text{CH}_3\text{CN})_2]^+$ - 611	5.4
	$[\text{Rh}(\text{COD})\text{L}]^+$ - 637	100 *

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

* = Species verified by isotopic pattern

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

^{a'} Obtained at a cone voltage of 20 V.

^{a''} Only relevant peaks are shown.

The only other species of any significance are two solvent-containing species, $[\text{RhL}(\text{CH}_3\text{CN})]^+$ and $[\text{RhL}(\text{CH}_3\text{CN})_2]^+$, with 7.1% and 5.4% relative intensities respectively. The isotopic pattern for the $[\text{Rh}(\text{COD})(\text{DPPB})]^+$ species showed there to be only monomer present (Table 6).

Figure 18

Typical ESMS Spectrum for 1:1 $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and 1,4-bis(diphenylphosphino)butane (DPPB) in CH_2Cl_2 at 20 V

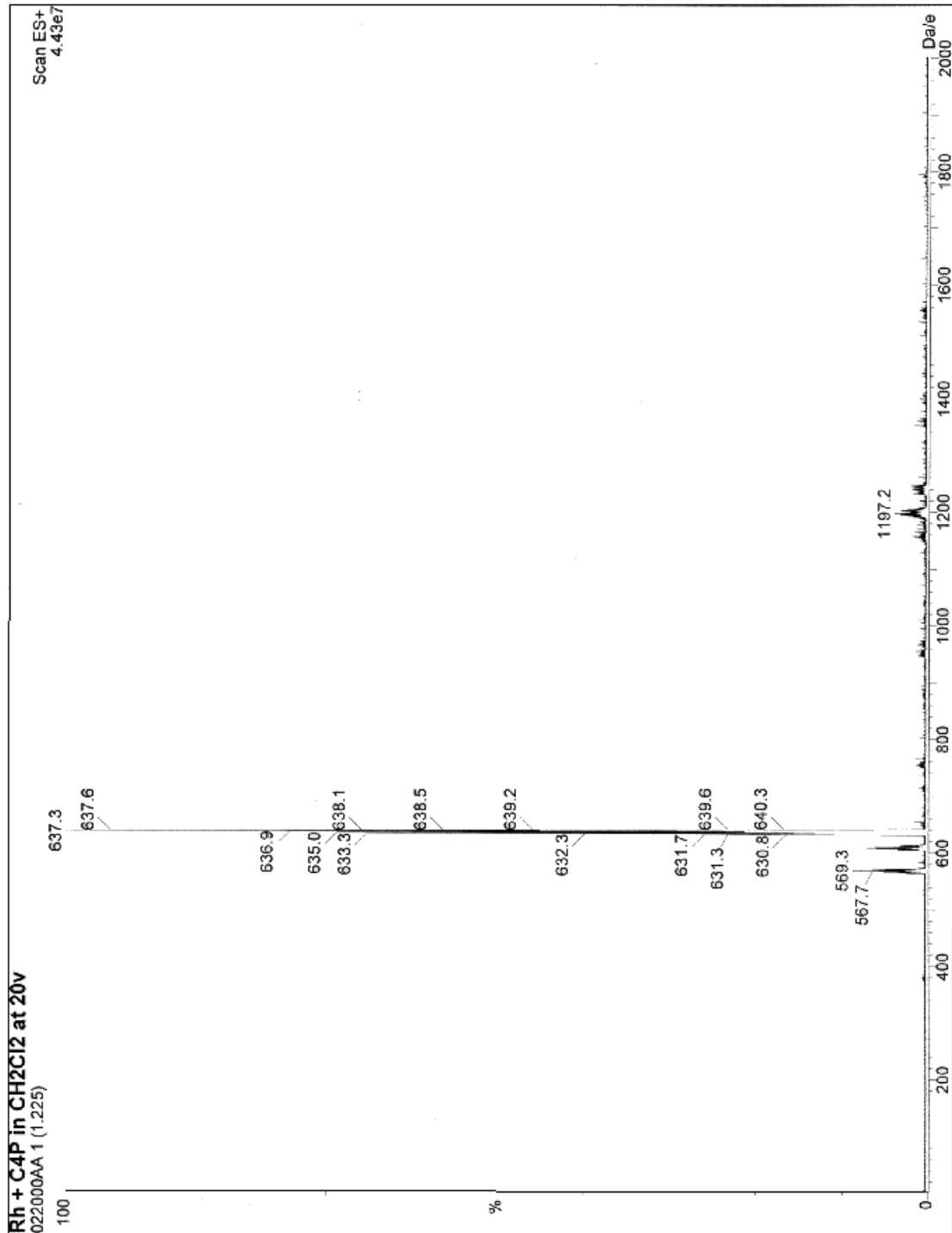


Table 6

Calculation of Percentage of Monomer and Dimer for *in situ* $[\text{Rh}(\text{COD})(\text{DPPB})]_x^{+x}$
Based on ESMS Data in CH_2Cl_2 at 20 V.^a

m/z	Monomer	Experimental	Dimer
637.0	100	100	100
637.5	0	0	78.7
638.0	39.3	36.4	30.5
638.5	0	0	7.8
639	7.6	7.25	1.4
Results: 100% Monomer, 0% Dimer			

^a Calculated using program from Appendix II.

FAB MS agrees with electrospray in this case, establishing $[\text{Rh}(\text{COD})(\text{DPPB})]^+$ as the base peak.¹⁸ The lack of other fragments in greater intensity is attributed primarily to the shortness of the hydrocarbon chain in the backbone. Observations of the complexes of differing chain length by FAB MS demonstrates that the longer the hydrocarbon chain, the more varied the fragmentations that are possible.²³ Another possible reason for the intensity of the $[\text{Rh}(\text{COD})(\text{DPPB})]^+$ species is the absence of dimer in the original sample which means one less source for monomeric fragments.

These results indicate that the monomeric species is the most favored for DPPB. ESMS, FAB MS, and ^{31}P NMR all demonstrate the presence of monomer, although the phosphorus-31 NMR of the *in situ* does show a secondary species. Present in 40% abundance, it is most likely a dimeric species. The 2.1 ppm chemical shift difference between monomer and dimer is similar to that observed for other systems. The fact that the dimeric species is not observed in electrospray, even at a cone voltage of 20 V, seems to indicate that $[\text{Rh}(\text{COD})(\text{DPPB})]_2^{+2}$ is very unstable and much prefers to be a monomer if given the chance.

1,6-Bis(Diphenylphosphino)Hexane

The phosphorus-31 NMR spectrum of the isolated complex shows two doublets in an approximately 75:25 ratio (Table 1). Since both phosphorus atoms are magnetically equivalent, monomer and dimer were assigned based on a comparison to the monodentate phosphine ⁿBuPPh₂ that could only form monomers. The ³¹P chemical shift of [Rh(COD)(ⁿBuPPh₂)₂]BF₄ in the same solvent was +18.4 ppm,¹⁹ letting us assign the +17.3 ppm peak as the *cis*-monomer species and +20.0 ppm as *cis*-dimer.

FAB MS data²⁰ shows both monomeric and dimeric species, with the dimeric being present as BF₄⁻ or F⁻ clusters but only in 1-3% relative abundance.¹⁶ [Rh(COD)(DPPH)]⁺ is present but in only 7% relative intensity. The base peak at m/z = 555 is [Rh(DPPH - H₂)]⁺, which has lost both COD and a hydrogen molecule. In fact, every major peak above 25% displays fragmentation, none contain COD and all show loss of at least two hydrogen atoms, presumably from the backbone. Apparently loss of COD and hydrogen are both facile processes for this ligand system.

Electrospray results for DPPH are the most confusing of all the ligands studied (Table 7). Unlike the others which showed clean spectra with few peaks, the DPPH case gives multiple peaks with a poor baseline. Even rerunning the spectra with a completely new batch of rhodium starting material and ligand in a different solvent gave a poor signal-to-noise ratio. The raw signal intensity for the base peak in the DPPH sample is 4.06x10⁶, while that of DPPB is 4.4x10⁷ - over 10x stronger. This led to the belief that most of the rhodium-containing species have ion-paired with BF₄⁻ to form neutral, inobservable species.

Table 7

ESMS Data for 1:1 study of $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and
1,6-bis(diphenylphosphino)hexane (DPPH)^a

		Relative Intensity
Species - m/z	$[\text{Rh}_2(\text{L}-\text{H}_2)(\text{COD})]^{+2}$ - 382	31.5
	- 617	--
	- 836	--
	- 864	21.1
	$[\text{Rh}_2(\text{L}-\text{H}_2)(\text{COD})_2(\text{BF}_4)]^+$ - 961	22.3
	- 968	--
	- 1097	11.9
	$[\text{Rh}_2\text{L}_2(\text{COD})_2 - 2\text{H}]^+$ - 1328	100
	$[\text{Rh}_3(\text{L}-\text{H}_2)_2(\text{COD})_2(\text{CH}_3\text{CN})_3(\text{BF}_4)_2]^+$ - 1726	97.1
	Other	

L = 1,6-bis(diphenylphosphino)hexane (DPPH)

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

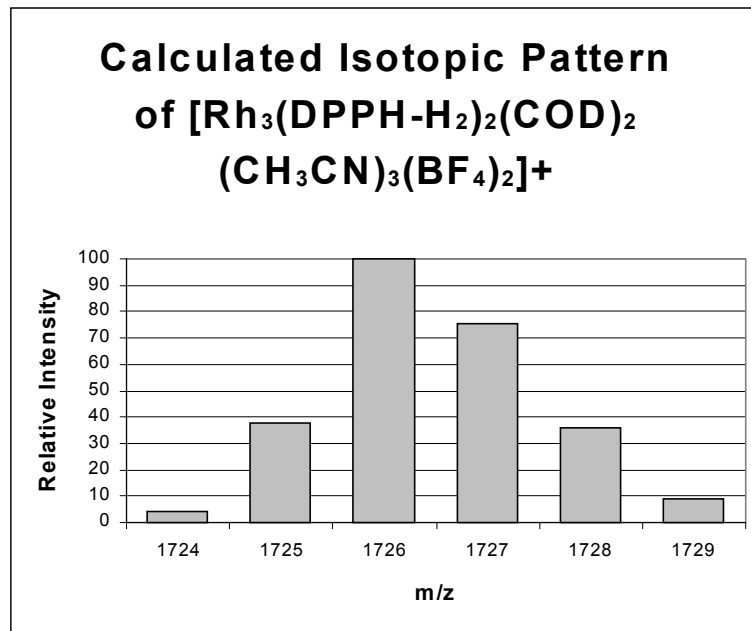
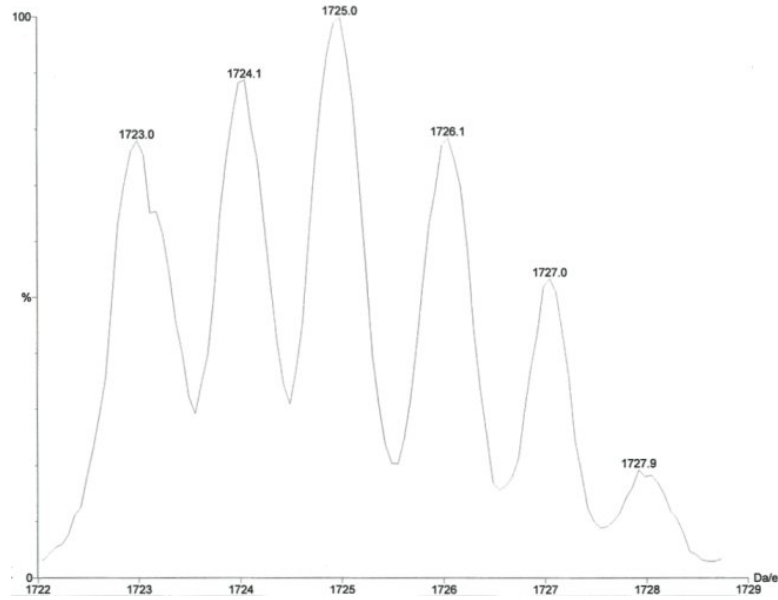
This can be explained by pointing to this system's strong preference for dimer over monomer. Such dicharged species would have a higher positive charge than monomers making them more likely to ion-pair. This is supported in three ways. First, of the peaks that were detected and identified, all are dimeric or possibly even trimeric (see below). Second, DPPH was the only ligand that showed any dimers when studied by FAB indicating that they are very prevalent. Third, even increasing the cone voltage to 90 V could not remove the dimeric species; the base peak was still identified as $[\text{Rh}_2(\text{DPPH-H}_2)(\text{COD})_2(\text{BF}_4)]^+$.

The three most intense peaks in the ESMS were identified as follows: The base peak at $m/z = 1328$ is the exact mass of $[\text{Rh}_2(\text{DPPH})_2(\text{COD})_2 - 2\text{H}]^+$. However, this should be a dicharged species and thus appear at $m/z = 664$, so its appearance at 1328 suggests the loss of hydrogen must bring the overall charge down to +1. The same complex run in acetonitrile seems to confirm this, as the base peak is now $m/z = 1369$, $[\text{Rh}_2(\text{DPPH} - \text{H}_2)_2(\text{COD})_2(\text{CH}_3\text{CN})]^+$. Again this should have +2 charge, so the loss of hydrogen must not be simply forming hydrogen molecules. There is no clear explanation for this. The next peak in intensity, nearly equal to the base peak at 97.1%, comes at $m/z = 1726$. It is identified as $[\text{Rh}_3(\text{DPPH} - \text{H}_2)_2(\text{COD})_2(\text{CH}_3\text{CN})_3(\text{BF}_4)_2]^+$, a trimeric species where one COD has already left, picking up a hydrogen molecule from each DPPH to form cyclooctane (see Section 3). The isotopic pattern is not conclusive, but other species such as loss of only one hydrogen molecule ($m/z = 1728$) may be interfering (Figure 19). The third most intense peak comes at $m/z = 380$ which is identified as $[\text{Rh}_2(\text{DPPH})(\text{COD})]^{+2}$, again a dimeric species. As seen in the FAB study, loss of both COD and H_2 are obviously facile processes for DPPH, even at low cone voltages.

While the ESMS results are not as beneficial as in the other cases, some useful information can be gleaned. It is not possible to calculate a percentage of monomer vs dimer because of the low signal-to-noise ratio and numerous dimeric species present, but it can be definitely said that dimer is formed and even favored for DPPH.

Figure 19

Calculated and Observed Isotopic Patterns of
 $[\text{Rh}_3(\text{DPPH} - \text{H}_2)_2(\text{COD})_2(\text{CH}_3\text{CN})_3(\text{BF}_4)_2]^+$ in CH_2Cl_2 at 20 V



1,8-Bis(Diphenylphosphino)Octane

The phosphorus-31 NMR spectrum for the isolated complex shows two doublets in an approximately 35:65 ratio (Table 1). Based on the $[\text{Rh}(\text{COD})(^i\text{BuPPH}_2)_2]\text{BF}_4$ results mentioned above, the +18.1 ppm peak is assigned as the *cis*-monomer species and the +20.0 ppm as *cis*-dimer.

For the *in situ* complex there are now three doublets, with the two at +17.8 ppm and +18.0 ppm nearly overlapping. However, the ratio of the combined intensity of these two doublets to the larger doublet at +19.5 ppm is again approximately 35:65, identical to that of the isolated complex. The doublet at +19.5 ppm is believed to be from the *cis*-dimer while the two smaller doublets are both *cis*-monomer species – most likely two different conformers of the backbone. Dapporto and Sacconi observed a similar result with $[\text{Ni}(\text{POOP})\text{I}_2]$ possessing more than one conformer of the chelate backbone.²¹ Both their system with POOP and this one with DPPO would produce 11-membered chelate rings making this comparison even more valid. This explains the results seen here as the difference in chemical shifts for the two complexes would be minimal and indeed only a 0.2 ppm deviation was observed. Such an effect would not be seen in the isolated case as only the most thermodynamically stable backbone conformer would be crystallized.

The electrospray data in Table 8 shows the base peak to be the discharged dimer $[\text{Rh}_2(\text{COD})_2(\text{DPPO})_2]^{2+}$.

Table 8

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

		Relative Intensity
Species - m/z	$[\text{Rh}_2(\text{COD})_2\text{L}_2]^{2+}$ - 693	100 *
	$[\text{Rh}_2(\text{COD})_2\text{L}(\text{Cl})]^+$ - 939	3.8
	$[\text{Rh}_2(\text{COD})_2\text{L}_2(\text{BF}_4)]^+$ - 1473	15.1 *

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

* = Species verified by isotopic pattern

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

^{a'} Obtained at a cone voltage of 20 V.

^{a''} Only relevant peaks are shown.

The percentage of monomer and dimer has been calculated from the isotopic pattern of this ion to be 10% and 90% respectively (Table 9). The rest of the spectrum contains only one other noteworthy species, $[\text{Rh}_2(\text{COD})_2(\text{DPPO})_2(\text{BF}_4)]^+$, which is present in 15.1% abundance. This is a dimeric species with a BF_4^- counter-ion, similar to that observed in FAB MS. This actually makes the percentage of dimer even higher if factored into the amount calculated from the base peak.

This is different from the NMR percentages of approximately 35% monomer and 65% dimer. It is unclear why the two differ, though it must be remembered that electrospray is unable to see any neutral species that could have been formed from ion-pairing with BF_4^- . Apparently some ion-pairing is occurring, as seen by the presence of $[\text{Rh}_2(\text{COD})_2(\text{DPPO})_2(\text{BF}_4)]^+$, but to what extent is unknown. Also, the mathematical

Table 9

Calculation of Percentage of Monomer and Dimer for *in situ* $[\text{Rh}(\text{COD})(\text{DPPO})]_x^{+x}$
Based on ESMS Data in CH_2Cl_2 at 20 V.^a

m/z	Monomer	Experimental	Dimer
693.0	100	100	100
693.5	0	79.2	87.6
694.0	43.7	37.1	37.8
694.5	0	11.7	10.7
695	9.4	3.0	2.2
Results: 10% Monomer, 90% Dimer			

^a Calculated using program from Appendix II.

functions used to measure the intensities in the isotopic patterns, such as smoothing and background subtracting, will no doubt induce error. An additional possibility could involve the electrospray technique itself. As ESMS involves the transfer of the ions from solution into the gas phase, as well as the induction of the cone voltage, one of these may account for the discrepancy (see the Introduction). Despite the difference, however, it can be conclusively stated that DPPO does form both monomeric and dimeric species in solution.

FAB MS data²² shows the expected $[\text{Rh}(\text{COD})(\text{DPPO})]^+$ species to be present, but only 36% relative to the 100% $[\text{Rh}(\text{DPPO} - 2\text{H}_2)]^+$ ion. This is not unexpected as FAB MS is a much harder technique compared to the soft electrospray method (see Introduction). It is also known that with longer carbon chains, intrabackbone fragmentation occurs in FAB²³ which reduces the intensity of the $[\text{Rh}(\text{COD})\text{L}]^+$ species.

1,10-Bis(Diphenylphosphino)Decane

The phosphorus-31 NMR spectra for both the isolated and *in situ* complexes show only one doublet (Table 1). The isolated comes at +19.4 ppm and the *in situ* at +18.9 ppm. The small difference of 0.5 ppm is not surprising considering the two different solvents the results were obtained in.

The electrospray data in Table 10 again shows the base peak to be the expected $[\text{Rh}(\text{COD})(\text{DPPD})]^+$ species. No other species of significant intensity were detected. The percentage of monomer and dimer has been calculated to be 69% and 31% respectively, as shown in Table 11. This differs from the one species seen in NMR, but

again the fragmentation caused by all MS techniques may account for this discrepancy.

(See the discussion above for DPPO.)

Table 10

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

		Relative Intensity
Species - m/z	$[\text{Rh}(\text{COD})\text{L}]^+ - 722$	100
	$[\text{Rh}_2(\text{COD})_2\text{L}(\text{Cl})]^+ - 967$	2.5

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

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

^{a'} Obtained at a cone voltage of 20 V.

^{a''} Only relevant peaks are shown.

FAB MS data²⁴ again shows only the monomeric fragments, without any of the expected dimer. $[\text{Rh}(\text{COD})(\text{DPPD})]^+$ is present, but only in 24% relative abundance.

The most intense peak is the $[\text{Rh}(\text{DPPD} - 2\text{H}_2)]^+$ ion. This is due to the dehydrogenation of the backbone which will be discussed later in Section 3.

Table 11

Calculation of Percentage of Monomer and Dimer for *in situ* $[\text{Rh}(\text{COD})(\text{DPPD})]_x^{+x}$
Based on ESMS Data in CH_2Cl_2 at 20 V.^a

m/z	Monomer	Experimental	Dimer
721.0	100	100	100
721.5	0	28.4	91.8
722.0	45.9	41.2	41.7
722.5	0	2.82	12.7
723.0	10.4	6.46	2.7
723.5	0	--	0.5
724.0	1.5	1.22	0.1
Results: 69% Monomer, 31% Dimer			

^a Calculated using program from Appendix II.

1,12-Bis(Diphenylphosphino)Dodecane

The phosphorus-31 NMR spectra for the isolated complex shows only one doublet at +19.4 ppm. The *in situ* displays a similar spectrum, though the lone doublet comes at +18.9 ppm. The slight difference in chemical shift is no doubt due to solvent as the isolated complex was run in CDCl₃ and the *in situ* in CH₂Cl₂. A similar upfield shift was seen in every case.

The electrospray data in Table 12 again shows the 100% peak to be the expected [Rh(COD)(DPPDOD)]⁺ species.

Table 12

ESMS data for 1:1 study of [Rh(COD)(CH₃CN)₂][BF₄] and 1,12-bis(diphenylphosphino)dodecane (DPPDOD)^a

		Relative Intensity
Species - m/z	[Rh(COD)L] ⁺ - 749	100 *
	[Rh ₂ (COD) ₂ L(Cl)] ⁺ - 995	✓

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 CH₂Cl₂.

^{a'} Obtained at a cone voltage of 20 V.

^{a''} Only relevant peaks are shown.

No other species of significant intensity were observed. The percentage of monomer and dimer for the base peak has been calculated to be 82% and 18% respectively (Table 13).

This will be discussed in more detail in the conclusion for this section.

Once again, FAB MS data²⁵ shows only the monomeric fragments, without any of the expected dimeric. $[\text{Rh}(\text{COD})(\text{DPPDOD})]^+$ is present in 64% relative abundance and the 100% peak is the $[\text{Rh}(\text{PC}_6\text{H}_4)]^+$ ion. This species is believed to be a product of the fragmentation of the monomer common to all ligands as it is seen in every case, though generally in smaller amounts.

Conclusions

Previous work has shown *cis*-monomers to be very common for $[\text{Rh}(\text{diolefin})(\text{bis-phosphine})]^+$ species, although there are some examples of *cis*-dimers, eg.

$[\text{Rh}(\text{nbd})(\text{DPF})_2](\text{BF}_4)$ where DPF = 2,5-bis(diphenylphosphino)furan.²⁶ In this work, the *cis*- $[\text{Rh}(\text{COD})(\text{bis-phosphine})]\text{BF}_4$ complexes are seen to form both monomeric and dimeric structures. This has been verified by both ³¹P NMR and ESMS.

DPPB, having the shortest carbon backbone at four carbons, tends to form almost exclusively monomer as expected. Phosphorus-31 NMR, electrospray, and FAB MS all support this. Though some dimer was seen in the ³¹P NMR for the *in situ* species, it seems very unstable.

DPPH, being two carbons longer than DPPB, would be expected to form more dimer. ³¹P NMR, electrospray, and FAB MS support this, all showing dimeric species to be present. In fact, electrospray gave almost exclusively dimeric species.

Table 13

Calculation of Percentage of Monomer and Dimer for *in situ* $[\text{Rh}(\text{COD})(\text{DPPDOD})]_x^{+x}$
Based on ESMS Data in CH_2Cl_2 at 20 V.^a

m/z	Monomer	Experimental	Dimer
749.0	100	100	100
749.5	0	17.8	96.2
750.0	48.1	49.0	45.8
750.5	0	--	14.3
751.0	11.4	10.2	3.5
751.5	0	--	0.6
752.0	1.7	1.35	0.1
Results: 82% Monomer, 18% Dimer			

^a Calculated using program from Appendix II.

The bis-phosphines with longer hydrocarbon backbones, such as DPPO, DPPD, and DPPDOD, tend to form both monomeric and dimeric species, though in differing amounts. DPPO seems to prefer dimer over monomer, as seen in both ^{31}P NMR and electrospray. However, the results for DPPD and DPPDOD are more dependent upon the technique used to study them.

In the phosphorus-31 NMR spectra, the lone doublets observed were previously attributed to dimer based on the expected pattern of increasing chain length leading to increasing dimer. For example, if the doublets for DPPD and DPPDOD were indeed dimer, then the amount could be said to increase from 0% (DPPB) to 24% (DPPH) to 67% (DPPO) to 100% (DPPD and DPPDOD). However, observations in the electrospray showing DPPH and DPPO to be almost exclusively dimer, while DPPD and DPPDOD are majority monomer, makes the assignment of the doublets as conclusively dimer questionable. It may be that the lone doublets observed for DPPD and DPPDOD are in reality from monomeric species.

Nevertheless, it is also true that the electrospray, despite being generally regarded as a soft technique, is significantly harder than NMR. As was seen in the DPPB case the *in situ* phosphorus-31 NMR showed some dimer present, but this same sample showed none in the electrospray. Thus, it can be assumed the dimer was much less stable and fragmented into monomer.

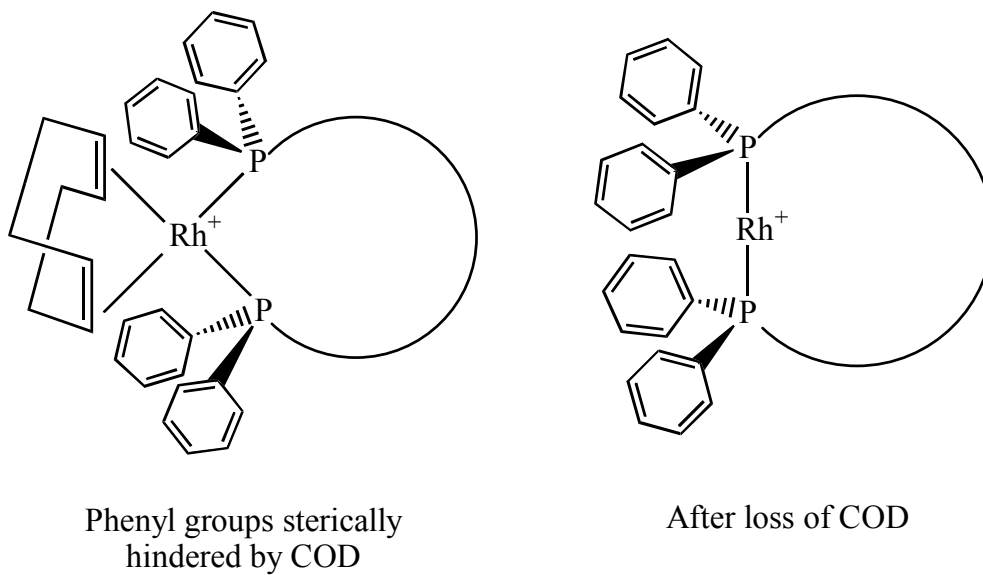
It may also be that the discharged dimer, containing a higher positive charge, is more apt to ion-pair with the BF_4^- counter-ions to form neutral species making it inobservable by electrospray. This would explain the lack of dimer seen in the DPPD

and DPPDOD cases as well. However, the DPPH and DPPO cases would have to be exceptions to this. For instance, electrospray of DPPO shows it to be present as 90% dimer, along with the 15.1% abundant dimeric $[\text{Rh}_2(\text{COD})_2(\text{DPPO})_2(\text{BF}_4)]^+$.

A final explanation for the increase in the amount of monomer in the ESMS case is based on steric considerations. One could imagine it being difficult for ligands with fairly bulky phenyl groups and long backbones like DPPDOD to attach *cis* with a COD ligand also attached *cis* (Figure 20). In order for the ligand to bind *cis* the backbone would be crowded and the phenyl groups would be forced into the space occupied by the bidentate COD ligand. Thus, a dimeric configuration would be preferred with long chain ligands. However, since COD is easily lost in ESMS the bis-phosphine can more easily attach *cis* without having to fold its backbone into a sterically constrained conformation and without phenyl-COD interaction. This could explain the increase in amount of monomer in ESMS as facile loss of COD is not seen in NMR, but this theory is not directly provable since $[\text{RhL}]^+$ cannot be studied in the NMR.

Figure 20

Steric Hindrance of $[\text{Rh}(\text{COD})\text{L}]^+$ Complexes for
Long Chain Bidentate Diphenyl Phosphines



However, the effects of steric interaction are seen indirectly by ^{31}P NMR in the formation of two backbone conformers for the *in situ* monomeric DPPO case (see above). This only seems to be a problem with ligands capable of forming 11-membered chelate rings, as seen also by Dapporto and Sacconi with $[\text{Ni}(\text{POOP})\text{I}_2]$ (discussed earlier).²¹ Evidently ligands with shorter and longer backbones do not have a significant problem forming monomers as this has only been reported for the 11-membered chelate ring case. Also, metals with larger ionic radii such as palladium(II) only show one conformer supporting this being a steric effect since larger metals would mean less ligand crowding about the metal center.²⁷

All of these results make us conclude that % monomer-dimer depends on several factors, including the solvent used for characterization and the precise reaction conditions. For example, depending on conditions, in some cases the isolated products with DPPO were as high as 100% dimer.²⁸ So while it can be said that both monomer and dimer are present in solution for the bis-phosphines DPPH, DPPO, DPPD, and DPPDOD, the exact ratios are elusive.

FAB vs ESMS

A final comparison between the utility of FAB vs ESMS is warranted. ESMS has proven itself to be far superior in the study of these rhodium-phosphine complexes. In every instance but DPPH, the most abundant species observed via ESMS (at 20 V) was the expected $[\text{Rh}(\text{COD})(\text{bis-phosphine})]^+$ or $[\text{Rh}_2(\text{COD})_2(\text{bis-phosphine})_2]^{2+}$. However, with FAB, the base peak varied for each ligand studied (Table 14).

Table 14

Observed Base (100%) Peak in ESMS vs FAB

Ligand	ESMS ^a	FAB ^b
DPPB	[Rh(COD)L] ⁺	[Rh(COD)L] ⁺
DPPH	[Rh ₂ (COD) ₂ L ₂ - 2H] ⁺	[RhL - 2H] ⁺
DPPO	[Rh ₂ (COD) ₂ L ₂] ²⁺	[RhL] ⁺
DPPD	[Rh(COD)L] ⁺	[RhL - 4H] ⁺
DPPDOD	[Rh(COD)L] ⁺	[RhPC ₆ H ₄] ⁺

^a Run in CH₂Cl₂ as solvent.^b Run in NBA matrix.

Additionally, ESMS detects both monomeric and dimeric species easily. These can be seen directly in ESMS through ion-pairing with the BF₄ counter-ion. For example, in the DPPO case [Rh₂(COD)₂L₂(BF₄)]⁺, [Rh₂L₂(CH₃CN)(BF₄)]⁺, [Rh₂(COD)L₂(BF₄)]⁺, and [Rh₂(COD)₂L₂(BF₄)]⁺ were observed at various cone voltages. Unlike FAB where such species were present at 1-3%, if at all, in ESMS they are observed at 15% or more.

Finally, and perhaps most importantly, ESMS allows the detection of both monocharged and dicharged species. For example, in the DPPO case [Rh₂(COD)₂L₂]²⁺ was observed at 100% relative intensity at a cone voltage of 20V. In FAB no dicharged species were observed. In fact, the dominant species for the DPPO case were [RhL]⁺ and fragmentation products, including phosphine oxides formed by interaction with the matrix.

In conclusion, it seems obvious that ESMS is the mass spectrometric method of choice for these type of complexes. It allows the easy determination of the most abundant species in solution. It also detects both monomeric and dimeric species with ease. Finally, it can discern both mono- and dicharged species.

References

1. Cerny, R. L., Sullivan, B. P., Bursey, M. M., Meyer, T. J., *Anal. Chem.*, **1983**, *55*, 1954.
2. Arakawa, R., Matsuo, T., Ito, H., Katakuse, I., Nozaki, K., Ohno, T., Haga, M., *Org. Mass Spectrom.*, **1994**, *29*, 289.
3. Bojesen, G., *Org. Mass Spectrom.*, **1983**, *20*, 413.
4. Miller, J. M., Balasanmugan, K., Nye, J., Deacon, G. B., Thomas, N. C., *Inorg. Chem.*, **1987**, *26*, 560.
5. Didier, P., Jacquet, L., Mesmaeker, A. K., Hueber, R., Van Dorsselaer, A., *Inorg. Chem.*, **1992**, *31*, 4803.
6. Argazzi, R., Bignozzi, C. A., Bortolini, O., Traldi, P., *Inorg. Chem.*, **1983**, *32*, 1222.
7. Denti, G., Serroni, S., Sindona, G., Uccella, N., *J. Am. Soc. Mass Spectrom.*, **1983**, *4*, 306.
8. Green, M., Kuc, T.A., Taylor, S.H., *Chem. Comm.*, **1970**, 1553.
9. Cocevar, C., Mestroni, G., Camus, A., *J. Organomet. Chem.*, **1972**, *35*, 389.
10. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 85.
11. Schrock, R.R., Osborn, J.B., *J. Am. Chem. Soc.*, **1971**, *93*, 2397.
12. Anderson, M.P., Pignolet, L.H., *Inorg. Chem.*, **1981**, *20*, 4101.
13. Norgaard, P.D., Ph.D. Dissertation, Auburn University, **1999**, 217.
14. Norgaard, P.D., Ph.D. Dissertation, Auburn University, **1999**, 117.
15. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, pp. 113, 124, 130, 134, 139-40.
16. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 128.
17. Cerny, R.L., Bursey, M.M., Jameson, D.L., Malachowski, M.R., Sorrel, T.N., *Inorg. Chim. Acta*, **1984**, *89*, 89.
18. Wharf, Rosalind M., Ph.D. Dissertation, Auburn University, **1988**, 113.

19. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 85.
20. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 124.
21. Dapporto, P., Sacconi, L., *J. Chem. Soc. A*, **1971**, 1914.
22. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 130.
23. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 144.
24. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 134.
25. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 139.
26. Brown, J.M., Canning, L.R., *J. Chem. Soc. Chem. Commun.* **1983**, 460.
27. Hill, W.E., Taylor, J.G., Falshaw, C.P., King, T.J., Beagley, B., Tonge, D.M., Pritchard, R.G., McAuliffe, C.A., *J. Chem. Soc., Dalton Trans.*, **1986**, 2289.
28. Wharf, R.M., Ph.D. Dissertation, Auburn University, **1988**, 86.