

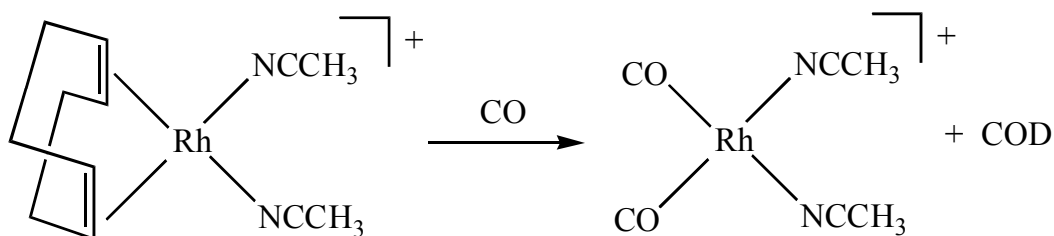
SECTION 2:

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

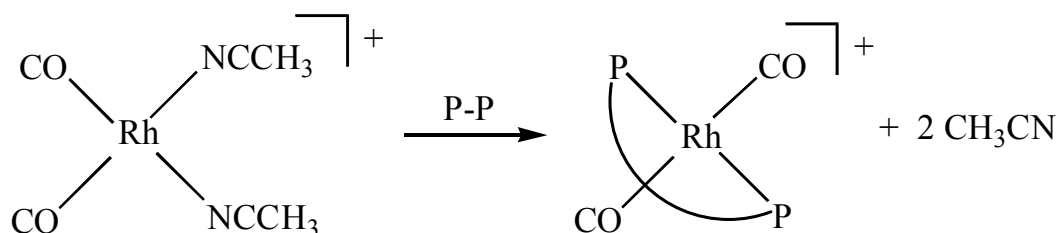
Variations of the complexes studied in section 1 were synthesized containing carbonyl ligands. The structures of these complexes were again examined using ^{31}P NMR, FAB MS, and ESMS along with infrared (IR) spectroscopy.

Synthesis of the Complexes

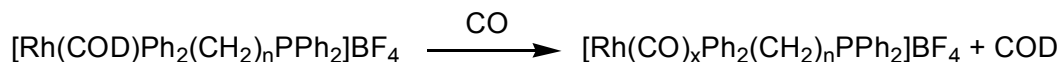
The starting material, $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$, has two types of ligands present: the diolefin and acetonitrile. The diolefin primarily acts as a π -acceptor, while acetonitrile can potentially be either a σ -donor or π -acceptor. It has been observed in the infrared spectra that the $\nu(\text{CN})$ resonances are higher for the coordinated CH_3CN than for the uncoordinated.¹ It can be induced from this that acetonitrile must primarily be acting as a σ -donor in this complex. The introduction of CO could in theory replace either of the ligands, but in fact replaces the ligand that is most like itself (a π -acceptor), cyclooctadiene.



This knowledge was used to create the isolated $[\text{Rh}(\text{CO})_2(\text{bis-phosphine})]\text{BF}_4$ complexes by first reacting $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ with CO to produce $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2]\text{BF}_4$. Knowing that phosphine ligands are strong σ -donors, and they replace acetonitrile as seen in section 1, reacting $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2]\text{BF}_4$ with the appropriate bis-phosphine ligand gave the desired product.



A slightly different method was used for the *in situ* complexes. Rather than first creating the $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2]\text{BF}_4$ complex, the phosphine-containing species already synthesized *in situ* in section 1, $[\text{Rh}(\text{COD})(\text{bis-phosphine})]^+$, had carbon monoxide gas bubbled through it at atmospheric pressure. Based on the observation above, it would be expected that CO should replace the π -acceptor cyclooctadiene to generate complexes of the type $[\text{Rh}(\text{CO})_x(\text{bis-phosphine})]\text{BF}_4$ ($x = 1, 2, \text{ or } 3$ depending on solvent), and this is in fact the case.



Schrock obtained similar results by bubbling carbon monoxide through a solution of $[\text{Rh}(\text{COD})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]^+$ to produce $[\text{Rh}(\text{CO})_x\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]^+$ ($x = 1, 2, \text{ or } 3$).^{2,3} Elsevier and coworkers synthesized $\text{HRh}(\text{CO})_2(\text{diphosphine})$ *in situ* by reacting 18 different phosphines with $\text{Rh}(\text{acac})(\text{CO})_2$ in benzene under syngas ($\text{CO}:\text{H}_2, 1:1$) pressure.⁴

Characterization of the Complexes

The phosphorus-31 NMR chemical shifts and rhodium-phosphorus coupling constants for the isolated $[\text{Rh}(\text{CO})_2(\text{bis-phosphine})]\text{BF}_4$ complexes are listed in Table 15.⁵ The coupling constant values, $^1\text{J}(\text{Rh-P})$, are all approximately 115-120 Hz leading us to conclude that the geometry is *trans* in every case.⁴ This was confirmed by infrared data that showed a strong band due to a $\text{C}\equiv\text{O}$ stretch in the region of 1989-1992 cm^{-1} for the isolated complexes.⁶ A *cis* arrangement, as in $[\text{Rh}(\text{CO})_2(\text{DPPE})]\text{BF}_4$, would have given two CO stretches (Table 16^{2,7,8}). It can therefore be concluded that the complexes have rearranged from *cis* to *trans* regardless of how they were synthesized (Figure 21).

This was interesting as Rh(I) dicarbonyls containing nitrogen donors or phosphine oxide ligands are always *cis*.^{9,10} The cause can most-likely be related to the well-known *trans*-effect seen for other square-planar d^8 systems. Carbonyl and phosphine are both strong π -acceptors and thus, are both strongly *trans*-directing. Amines and phosphine oxides are much weaker π -acceptors and thus less strongly *trans*-directing, actually preferring *cis*. For the amine and phosphine oxide case the carbonyl groups (π -acceptors) prefer to be *cis* so that they do not have to share π -electron density with one another through the d_{xy} , d_{xz} , and d_{yz} orbitals on rhodium. In the phosphine case, however,

Table 15

$^{31}\text{P}\{^1\text{H}\}$ NMR Data for the *Trans*-[Rh(CO)₂(Bis-Phosphine)]BF₄ Complexes

	Isolated Complex in d ₆ -acetone		
Ligand	δP^a	¹J(Rh-P)^b	% Composition
DPPB	+26.6	115.6	50
	+27.0	117.3	50
DPPO	+27.0	117.4	100
DPPD	+27.8	119.3	40
	+28.4	120.3	60
DPPDOD	+27.3	120.1	25
	+27.6	120.3	75

^a Relative to 85% H₃PO₄.

^b Measured in Hz. Measured in Hz.

Table 16

IR Data for Rh and Ir Carbonyl-Containing Phosphine Complexes

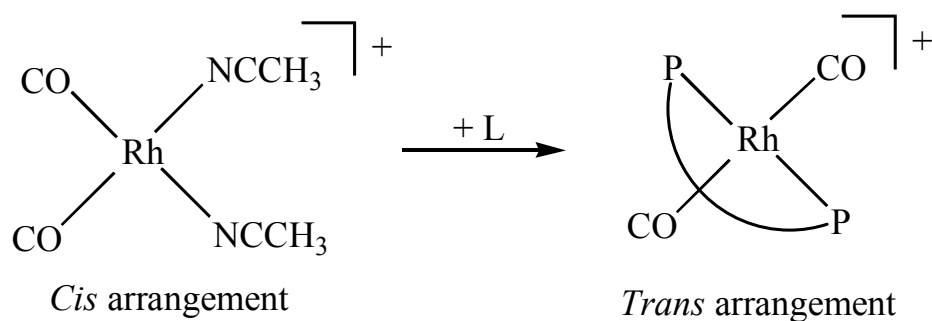
Complex	# of CO's	$\nu(\text{CO})^a$		
$[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4^b$	1	2029		
$[\text{Rh}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)\text{CH}_3)_3]\text{ClO}_4^b$	1	2023		
$[\text{Rh}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)\text{CH}_3)_3]\text{ClO}_4^b$	2	2027	1980	
$[\text{Rh}(\text{CO})_2(\text{DPPE})]\text{BPh}_4^b$	2	2100	2055	
$[\text{Ir}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2]\text{BPh}_4^c$	2	1990		
$[\text{Ir}(\text{CO})_2(\text{PPr}^i_3)_2]\text{BPh}_4^c$	2	1987		
$[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]\text{BPh}_4^c$	3	2074	2018	2010
$[\text{Rh}(\text{CO})_3(\text{PPh}_3)_2]\text{ClO}_4^b$	3	2023		

^a Reported in cm^{-1} .^b Obtained in CH_2Cl_2 .^c Obtained in CHCl_3 salt.

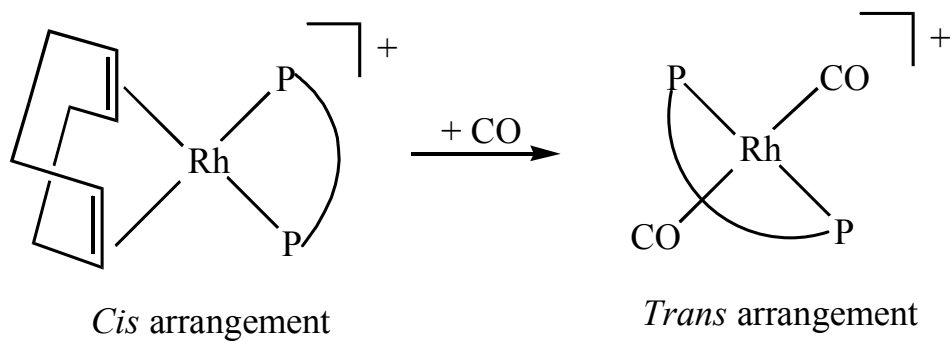
Figure 21

Trans to Cis Rearrangement of Carbonyl-Containing Rhodium Bis-Phosphines

Isolated Synthesis



In Situ Synthesis



they must compete for this electron density. Therefore, it is assumed that the energy minimum for the *trans* structure is significantly lower than for the *cis* leading to only the detection of *trans* and not a mixture of the two.

Although dicarbonyl cations of the type $[M(\text{CO})_2\text{L}_2]^+$ ($M = \text{Ir}, \text{Rh}, \text{L} = \text{tertiary phosphine}$) are fairly common for iridium,^{11,12} those with rhodium are much rarer. Schrock and Osborn² were able to isolate $[\text{Rh}(\text{CO})_3(\text{PPh}_3)_2]\text{ClO}_4$ in the solid state but could not isolate the dicarbonyl. Even in the solid state the complex slowly loses CO, but in solution it readily lost two moles of carbon monoxide to give $[\text{Rh}(\text{CO})(\text{solvent})(\text{PPh}_3)_2]^+$, with no dicarbonyl detected. They attempted the detection of the dicarbonyl in solvents such as dimethylformamide, dimethylacetamide, acetone, and acetonitrile without success. However, in the current work with bis-phosphines, dicarbonyl species were detected in both acetone and methylene chloride.

The ³¹P NMR spectrum for isolated $[\text{Rh}(\text{CO})_2(\text{DPPO})]\text{BF}_4$ in acetone exhibits only one doublet. This is expected to be the dimeric species and molecular weight and molar conductivities verify the assignment.¹³ In contrast, $[\text{Rh}(\text{CO})_2(\text{DPPD})]\text{BF}_4$ shows two doublets, +119.3 ppm assigned to the *trans*-chelated monomer and +120.3 ppm to the *trans*-chelated dimer. The monomeric species is present in 40% abundance, and the dimeric in 60%. $[\text{Rh}(\text{CO})_2(\text{DPPDOD})]\text{BF}_4$ also exhibits two doublets attributable to monomeric and dimeric species as in the DPPD case, although the amount of monomer formed (25%) is less for this ligand.

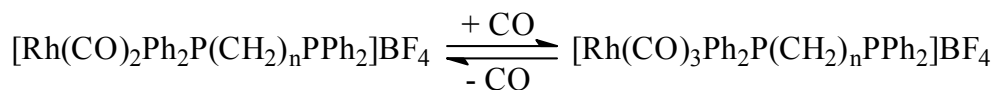
The case of $[\text{Rh}(\text{CO})_2(\text{DPPB})]\text{BF}_4$, however, appears contradictory. While molecular weight data leads to the conclusion of a dimeric complex, the phosphorus-31

NMR spectrum contains two doublets, each of equal intensity and each containing a coupling constant in the *trans* range. Similar results were obtained upon synthesizing the complex *in situ* from $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ and $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2]\text{BF}_4$. Unlike DPPD and DPPDOD, DPPB is too short for *trans*-chelation, as confirmed by the molecular weight data.

Others have also experienced unexpected results with this ligand. Anderson and Pignolet reported that the ^{31}P NMR of $[\text{Rh}(\text{DPPB})_2]\text{BF}_4$ in acetone at room temperature is a well-behaved doublet, but on cooling they observed a very complex spectrum which as yet is unexplained. In contrast to this, cooling $[\text{Rh}(\text{DPPP})_2]\text{BF}_4$ reveals an $\text{A}_2\text{B}_2\text{X}$ pattern due to coordination of acetone in the equatorial position.¹⁴

Addition of Carbon Monoxide Gas

The rhodium-phosphine complexes were also studied upon addition of carbon monoxide gas. The isolated complexes were dissolved in acetone, while the *in situ* were created in methylene chloride. In both cases, CO gas was bubbled through at room temperature and under atmospheric pressure. The yellow color of the solution lightens slightly in both instances upon this addition and a reversible reaction is believed to occur.



For the long chain bis-phosphines (n=8, 10, 12) the $^1J(\text{Rh-P})$ decreases from about 120 Hz to 75 Hz. One of the primary factors believed to influence rhodium-phosphorus coupling constants is the percent s-character in the bond. It is known that the orientation of the magnetic moment is primarily transmitted from one nucleus to another through the s orbitals as only they penetrate to the nucleus. Therefore, an increase in the s-character of either the metal or ligand atom should lead to an increase in the one-bond coupling constant. This has been proven for the silver-phosphorus case (Table 17).^{15,16}

Table 17

Coupling Constant Trends for Silver-Phosphorus

Ag-P Coordination	$^1J(\text{Ag-P})^a$	% s-Character	Orbital Type
1-coordinate	780	100	s
2-coordinate	470	50	sp
3-coordinate	310	33.3	sp ²
4-coordinate	224	25	sp ³

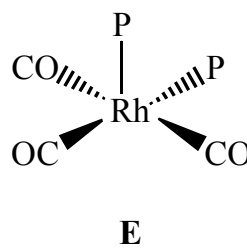
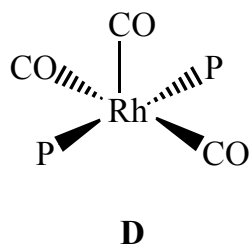
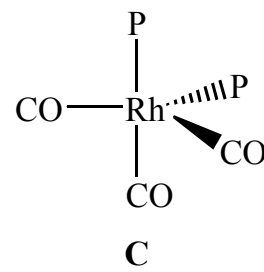
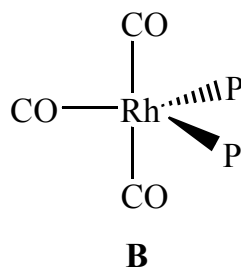
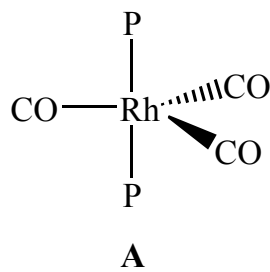
^a Measured in Hz.

Since the four-coordinate $^1J(\text{Rh-P})$ value is known to be approximately 120 Hz, the approximate 40% decrease to 75 Hz supports the proposal of a tricarbonyl, five coordinate species.

For these tricarbonyls with a $^1J(\text{Rh-P})$ of 75 Hz and no $^2J(\text{P-P})$, there must either be rapid intramolecular exchange of the phosphorus atoms since Rh-P coupling is not lost or both atoms must be in axial positions (structure A from Figure 22). As the $^1J(\text{Rh-P})$ is

Figure 22

Possible Structures for the Tricarbonyl Rhodium-Phosphine Species



75 Hz, it is most likely the latter, as phosphorus exchange would probably give a higher coupling constant between 80 and 115 Hz. Even at temperatures as low as -86°C , the spectrum of $[\text{Rh}(\text{CO})_3(\text{DPPO})]\text{BF}_4$ still exhibited two doublets with a coupling constant of 74 Hz.¹⁷ If intramolecular exchange is occurring it must be extremely fast compared to the NMR timescale.

1,8-Bis(Diphenylphosphino)Octane

Upon bubbling the solutions containing DPPO with carbon monoxide, it was found in both the isolated and *in situ* cases that the one doublet becomes two and the rhodium-phosphorus coupling constant decreases significantly (Table 18). For the isolated complex run in acetone, the new doublets have increased by +6 ppm and the coupling constants have decreased to the 75 Hz range seen above. Both of these observations indicate that the phosphorus atoms are in the axial positions as in structure A in Figure 22. As one doublet appears in 17% yield and the other in 83%, both monomer and dimer must have formed as the chemical shift difference (0.4 ppm) is not large enough to warrant an entirely new structure.

However, in the *in situ* case, something very interesting was noticed. Upon the addition of carbon monoxide, the expected decrease in rhodium-phosphorus coupling is still seen, but to 81 and 100 Hz. The peak at 81 Hz is most likely the expected axial-axial product as the coupling constant is similar to the isolated case (75 Hz) and the chemical shift increased by +4.8 ppm over that of the argon-purged values. However, the species at +23.0 ppm has a significantly larger coupling constant (100 Hz) and a slightly lower

Table 18

$^{31}\text{P}\{^1\text{H}\}$ NMR Data for the Reaction of *Cis*-[Rh(COD)(Bis-Phosphine)]BF₄ Complexes with CO.

		Isolated Complex in d ₆ -acetone			<i>in situ</i> Complex in CH ₂ Cl ₂ ^c		
Ligand		δP ^a	¹ J(Rh-P) ^b	% Composition	δP ^a	¹ J(Rh-P) ^b	% Composition
DPPB	+ CO	+22.3	120.8	100	+20.7 +22.9	119.3 123.6	45 55
	+ Ar	+22.3	118.5	59	+20.8	119.3	37
		+25.5	142.3	8	+22.3	122.2	63 ^d
+27.7		118.1	33	+22.9	122.0		
DPPO	+ CO	+32.1 +32.5	73.0 73.1	17 83	+23.0 +29.2	99.6 81.2	12 88
	+ Ar	+27.2	121.0	10	+24.4	113.5	100 ?
		+27.4	121.5	90			
DPPD	+ CO	+32.4 +35.1	74.9 74.8	34 66	+30.0 +31.3	70.4 72.6	36 ^e 64
	+ Ar	+27.7	122.2	23	+24.2	118.0	42 ^e
		+29.5	122.3	77	+24.6	113.5	58
DPPDOD	+ CO	+32.7 +33.6	74.2 76.1	30 70	+30.0 +31.6	71.5 74.2	22 78
	+ Ar	+27.9	120.7	24	+23.0	123.2	17
		+28.3	121.7	76	+24.8 +25.5	99.8 122.9	83 ^d

^a Relative to 85% H₃PO₄.

^b Measured in Hz.

^c CD₂Cl₂ added as lock solvent.

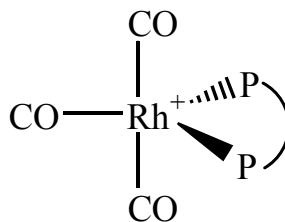
^d Combined value for both peaks

^e Approximate due to overlap of doublets

chemical shift than the argon purged values (-1.9 ppm). The most logical explanation for this is a new equatorial-equatorial structure similar to B in Figure 22 (Figure 23).

Figure 23

Structure of $[\text{Rh}(\text{CO})_3(\text{DPPO})]^+$ in CH_2Cl_2



$$\delta(\text{P}) \sim +23.0 \text{ ppm}$$

$$^1\text{J}(\text{Rh-P}) \sim 100 \text{ Hz}$$

Electrospray on the *in situ* complex determined the base peak at m/z of 654 to be $[\text{Rh}(\text{DPPO})(\text{CO})(\text{CH}_3\text{CN})]^+$ based on its isotopic pattern (Table 19).

Table 19

ESMS Data for Study of $[\text{Rh}(\text{COD})(\text{DPPO})]\text{BF}_4$ After Bubbling With Carbon Monoxide Gas and Purging With Argon.^a

		+ CO	+ Ar
Species - m/z	$[\text{RhL}(\text{CO})]^+$ - 613	36.5 *	100
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+$ - 654	100 *	✓
	$[\text{Rh}_2\text{L}_2(\text{BF}_4)]^+$ - 1257	25.0	25.4
	$[\text{Rh}_2\text{L}_2(\text{CO})_3(\text{BF}_4)]^+$ - 1341	✓	6.9

✓ = Species present in small, undetermined amount

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

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

This shows that indeed the acetonitrile present from the starting material does compete with the carbon monoxide in solution. In fact, in the ESMS loss of carbon monoxide appears to be a very easy process as no dicarbonyl or tricarbonyl species were detected in any appreciable quantities. This may be influenced from the ESI process itself where the droplets are volatilized by the nebulizing and bath gas (see Introduction) causing the concentration of carbon monoxide to decrease. As previously mentioned, Schrock found that his rhodium-phosphine tricarbonyl complexes easily lost two carbon monoxide groups to form $[\text{Rh}(\text{phosphine})(\text{CO})(\text{solvent})]^+$ which is similar to what is seen here, but with the displaced acetonitrile instead of the methylene chloride solvent.

The second most intense peak, $[\text{Rh}(\text{DPPO})(\text{CO})]^+$ (36.5%), is the base peak species with loss of the acetonitrile. Carbon monoxide would be expected to be the stronger coordinating ligand so loss of acetonitrile over CO is reasonable. The remaining

peak of interest is actually the dimer $[\text{Rh}_2(\text{DPPO})_2(\text{BF}_4)]^+$ (25.0%) without carbonyl or acetonitrile present.

Upon purging both the isolated and *in situ* samples with argon gas at atmospheric pressure a reversible reaction is observed where the extra carbon monoxide is lost and the dicarbonyl is reformed. The *in situ* shows only a doublet as expected, though its coupling constant is 113.5 Hz, slightly lower than expected, probably the result again of weak acetonitrile interaction. The isolated case shows the expected doublet for the dicarbonyl as well as another small doublet accounting for 10%. It may be that what is again being observed are monomer and dimer formation as in the precursor complex (see Section 1). However, it is unclear why this happens after addition of CO and purging with argon.

1,10-Bis(Diphenylphosphino)Decane

For the DPPD case the dicarbonyl starting material (isolated) displayed two doublets in a 40:60 ratio from the monomer and dimer formed (Table 18). Upon bubbling carbon monoxide through both the isolated and *in situ* solutions the two doublets are retained but they again shift downfield accompanied by a reduction in their rhodium-phosphorus coupling constants to 70-75 Hz. A five-coordinate structure with the phosphorus atoms in the axial positions as in structure A in Figure 22 is proposed for this case.

The lower coupling constants of 70.4 and 72.6 Hz in the *in situ* case indicates there was little to no interaction with the displaced acetonitrile in the NMR. However, the ESMS data shows the base peak to be $[\text{Rh}(\text{DPPD})(\text{CO})(\text{CH}_3\text{CN})]^+$ as in the DPPO case (Table 20).

Table 20

ESMS Data for Study of $[\text{Rh}(\text{COD})(\text{DPPD})]\text{BF}_4$ After Bubbling With Carbon Monoxide Gas and Purging With Argon.^a

		+ CO	+ Ar
Species - m/z	$[\text{RhL}(\text{CO})]^+$ - 641	5.6	4.2
	$[\text{RhL}(\text{CO})_2]^+$ - 669	6.3	--
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+$ - 682	100 *	100

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

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

One possible explanation may arise from the ESI process itself. After the solution is sprayed into the detector, the solvent is evaporated and the free ions left for detection. Since CH_2Cl_2 is more volatile, it may be lost first leaving behind the acetonitrile to coordinate with the rhodium complex. This, combined with loss of carbon monoxide from the combination of vacuum and gases, can account for both the lack of a tricarbonyl species and the identity of the base peak. Additionally, the isotopic pattern of the base peak was determined to be 100% monomer as it displayed no peaks at half-mass increments.

The other species of note in the electrospray upon bubbling with carbon monoxide were $[\text{Rh}(\text{DPPD})(\text{CO})_2]^+$ and $[\text{Rh}(\text{DPPD})(\text{CO})]^+$. Their intensity was very low though, only 6.3% and 5.6%, respectively. Both are entirely reasonable species for this complex.

After purging with argon gas, a phosphorus-31 spectra was again obtained almost identical to the dicarbonyl starting material for the solution created from the isolated complex. The coupling constants were 120.7 and 121.7 Hz, exactly where expected. The *in situ* complex also showed an increase in coupling constant upon loss of the third carbonyl group to 118.0 and 113.5 Hz. This is well within the normal range herein determined, but the second value is slightly lower, perhaps from weak interaction again with acetonitrile.

1,12-Bis(Diphenylphosphino)Dodecane

The DPPDOD case is quite similar to that of DPPD. The isolated DPPDOD dicarbonyl starting material displayed two doublets at +27.3 ppm and +27.6 ppm, each with an approximate $^1\text{J}(\text{Rh-P})$ of 120 Hz (Table 18). After bubbling the solution of the isolated complex with carbon monoxide, two doublets are retained, but they shift downfield to +32.7 ppm and +35.6 ppm. Each now also has a much reduced coupling constant around 75 Hz. This is most likely the result of a tricarbonyl species having a structure similar to that of structure A in Figure 22.

The *in situ* is also similar to the DPPD case in that it shows an increase in chemical shift to +30.0 ppm and +31.6 ppm, with a decrease in coupling constants to 71.5 and 74.2 Hz. Again no noticeable interaction with the displaced acetonitrile is observed based on ^{31}P NMR data.

The electrospray, however, again shows the base peak to be the rhodium species containing the bis-phosphine, one carbonyl group, and one acetonitrile, $[\text{Rh}(\text{L})(\text{CO})(\text{CH}_3\text{CN})]^+$ (Table 21). This was the most intense species for DPPO, DPPD, and DPPDOD. It can again be postulated that the formation of this acetonitrile containing species is formed via the mechanism described above for the DPPD case. The only other species observed at 20 V was $[\text{Rh}(\text{DPPDOD})(\text{CO})]^+$ with a relative intensity of 4.8%.

Table 21

ESMS Data for Study of $[\text{Rh}(\text{COD})(\text{DPPDOD})]\text{BF}_4$ After Bubbling With Carbon Monoxide Gas and Purging With Argon.^a

		+ CO	+ Ar
Species - m/z	$[\text{RhL}(\text{CO})]^+ - 669$	4.8	6.0
	$[\text{RhL}(\text{CO})(\text{CH}_3\text{CN})]^+ - 710$	100 *	100 *

^a Obtained at a cone voltage of 20 V.

^{a'} Run in CH_2Cl_2 as solvent.

After purging the solutions with argon gas, the isolated case again gave chemical shifts and coupling constants in the ^{31}P NMR very near to those of the starting dicarbonyl. The *in situ* complex in this case gave three doublets, two with coupling constants of approximately 120 Hz that are most likely from the monomer and dimer forms. The third doublet at +24.8 ppm overlapped with the one at +25.5 ppm and together had a combined integral amounting to 83% of the total. The coupling constant of this third doublet was 99.8 Hz suggesting this complex to be a dicarbonyl with some acetonitrile interaction (see the conclusion of this section for a more complete explanation).

1,4-Bis(Diphenylphosphino)Butane

As mentioned at the beginning of this section, DPPB has proven a perplexing ligand for ourselves and other groups. The appearance of two species with coupling constants in the *trans* range, despite the fact that DPPB is too short for *trans* bonding, is confusing. Upon the addition of carbon monoxide gas, the isolated complex displays only one doublet at +22.3 ppm with a coupling constant of 120.8 Hz (Table 18). Unlike the other cases, the chemical shift actually decreased by -5 ppm rather than increasing. The *in situ* case is no better. It displayed two doublets also in this chemical shift range and with approximately the same coupling constant. While it is reassuring to a degree that both methods gave similar results, the fact that they cannot be deciphered is troublesome.

Unlike the three previously mentioned cases, here the base peak in electrospray was $[\text{Rh}(\text{DPPB})(\text{CO})_2]^+$ rather than the monocarbonyl acetonitrile-containing species (Table 22). This species was detected, but at only 15%. $[\text{Rh}(\text{DPPB})(\text{CO})]^+$ was also present in minute quantities.

Table 22

ESMS Data for Study of $[\text{Rh}(\text{COD})(\text{DPPB})]\text{BF}_4$ After Bubbling With Carbon Monoxide Gas and Purging With Argon.^a

		+ CO	+ Ar
Species - m/z	$[\text{RhL}(\text{CO})]^+ - 557$	✓	9.1
	$[\text{RhL}(\text{CO})_2]^+ - 585$	100 *	100
	$[\text{RhL}(\text{CH}_3\text{CN})(\text{CO})]^+ - 598$	15.0	9.8
	1149	--	25.0

✓ = Species present in small, undetermined amount

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

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

After purging with argon gas, the base peak remains the dicarbonyl, but the second most intense species is a new one at a mass/charge ratio of 1149. It has a relative intensity of 25%. The only species that could be determined with a value even close to this was $[\text{Rh}_2(\text{DPPB})_2(\text{BF}_4)]^+$, but it has an m/z of 1145 and an isotopic pattern very different from that observed.

The ^{31}P NMR after purging with argon gave more confounding results. There are now three doublets, one at the same chemical shift as the species created by bubbling

carbon monoxide through it. The other two doublets are in the range of the starting dicarbonyl. However, the coupling constant for the doublet at +25.5 ppm is 142.3 Hz, the same as those of the *cis*-complexes without CO (Table 1). The most logical explanation is a four-coordinate structure where both phosphoruses are *cis* in equatorial positions.

Factors Affecting Monomer vs Dimer Formation

In examining the formation of monomer and dimer for the carbonyl complexes several points of interest were discovered. First, it should be noted that unlike the cyclooctadiene starting materials, no dimeric forms were detected in ESMS. Or at least none were observed with the expected half-mass separation down to the resolution limits. So if there was dimer formed it was present in a very small amount.

With DPPD it was noted that the isolated product varied from 10% to 40% monomer. For $[\text{Rh}(\text{CO})_2(\text{DPPDOD})]\text{BF}_4$ when prepared *in situ* from $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2]\text{BF}_4$, the amount of dimer was 41%. However, when synthesized from $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ 75% dimer was obtained. There was also a slight decrease observed in the coupling constant from 120.3 Hz to 116.8 Hz for the dimer and from 120.1 Hz to 116.3 Hz for the monomer.¹⁸ This may be caused by solvent association, as seen for the *in situ* cases above, leading to formation of a five-coordinate structure. This could be weak interaction with either the displaced acetonitrile or the acetone used as solvent. Based on what was noticed in the other *in situ* complexes studied it is probably the former. These variations in the percentage of monomer and

dimer formed indicate that reaction conditions play a large role in which structure is preferred and to what extent.

FAB vs ESMS

For the study of these carbonyl complexes using mass spectrometry, ESMS again shows itself to be far preferable to FAB. Electrospray routinely detected carbonyl-containing species in solution, including mono-, di-, and tricarbonyls. In fact, in every case the base peak was a carbonyl-containing species. After bubbling carbon monoxide through the *in situ* solutions of DPPO, DPPD, and DPPDOD the base peak was always found to be $[\text{Rh}(\text{bis-phosphine})(\text{CO})(\text{CH}_3\text{CN})]^+$. For DPPB the base peak was actually the dicarbonyl, $[\text{Rh}(\text{DPPB})(\text{CO})_2]^+$. These were not the only carbonyl-containing species observed; other mono- and dicarbonyls were detected (Tables 19-21).

After purging the solutions with argon gas, the base peak was still a carbonyl-containing species. For DPPO it was $[\text{Rh}(\text{DPPO})(\text{CO})]^+$, while for DPPD and DPPDOD it remained $[\text{Rh}(\text{bis-phosphine})(\text{CO})(\text{CH}_3\text{CN})]^+$. DPPB again showed $[\text{Rh}(\text{DPPB})(\text{CO})_2]^+$ as the base peak.

Comparing this to FAB it was seen that in a study of the isolated dicarbonyls having the general formula $[\text{Rh}(\text{bis-phosphine})(\text{CO})_2]\text{BF}_4$ the base peak never contained carbon monoxide.¹⁹ While some carbonyl-containing fragments were observed, they were always either of low relative intensity or part of an incomplete structure. In the DPPB case for example, the most intense carbonyl-containing fragment came at 11% relative intensity and for DPPO it was at 29%. In every case, the largest carbonyl-

containing species always had the formula Rh(bis-phosphine)(CO).

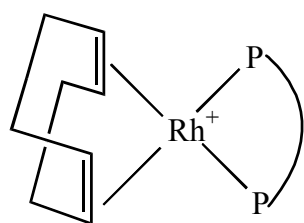
Also, phosphine oxides were observed in FAB for every case, and at intensities sometimes even above those of the carbonyl-containing fragments. In the DPPB case, for example, phosphine oxides were observed at 46%, 36%, and 20% while the most intense carbonyl-containing fragment was only 11%. Phosphine oxides were never observed in the ESMS spectra.

All of these observations lead us to conclude that electrospray is to be preferred over FAB in the identification of these rhodium bis-phosphine carbonyl complexes. With ESMS, relevant carbonyl-containing species are detected as the base peak. In FAB the base peak never even contained a carbonyl group. ESMS also detected both monomeric and dimeric forms of the complexes but FAB did not. Finally, FAB produces multiple phosphine oxide species that are simply not seen with ESMS.

Conclusions

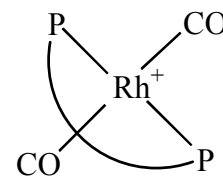
A summary of these findings, including the observed results and possible structures identified by ^{31}P NMR, are presented in Figure 24. First, it is noted that both monomeric and dimeric dicarbonyl species can be isolated and identified via ^{31}P NMR. These complexes contain *trans* phosphine groups with a square-planar structure (structure II). Upon bubbling these solutions with carbon monoxide, whether created *in situ* or first isolated and dissolved, tricarbonyl species are formed. In almost every case the structure is trigonal-bipyramidal with phosphorus in the axial positions, *trans* to one another (structure III).

Figure 24

³¹P NMR Data for Structures of Rhodium with Long Chain Bis-Phosphines

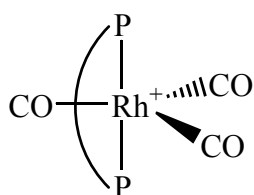
$$\delta \sim +18.0 - 20.0 \text{ ppm}^a$$

$$^1J(\text{Rh-P}) \sim 140-145 \text{ Hz}$$

I

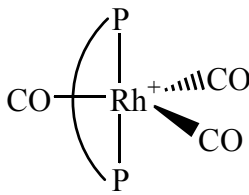
$$\delta \sim +27.0 - 28.5 \text{ ppm}^a$$

$$^1J(\text{Rh-P}) \sim 120 \text{ Hz}$$

II

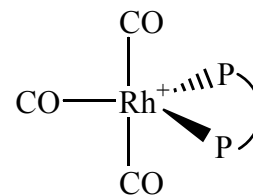
$$\delta \sim +32.0 - 35.0 \text{ ppm}^a$$

$$^1J(\text{Rh-P}) \sim 75 \text{ Hz}$$

IIIa

$$\delta \sim +29.0 \text{ ppm}^b$$

$$^1J(\text{Rh-P}) \sim 80 \text{ Hz}$$

IIIb

$$\delta(\text{P}) \sim +23.0 \text{ ppm}$$

$$^1J(\text{Rh-P}) \sim 100 \text{ Hz}$$

IV

^a Run in d₆-acetone. Relative to 85% H₃PO₄.

^b Run in CH₂Cl₂ with CD₂Cl₂ added as lock solvent. Relative to 85% H₃PO₄.

The first exception to this was with DPPPO *in situ* in methylene chloride which gave a trigonal-bipyramidal structure, but with one phosphorus in an axial position and one in an equatorial position (structure IV). The coupling constants for the non-equivalent phosphorus atoms are presented and can be rationalized if you consider this structure to be partway between II and III. Thus, $^1J(\text{Rh-P}_1)$ is 80 Hz, slightly above the 75 Hz average seen for axial phosphorus atoms *trans* to one another. $^1J(\text{Rh-P}_2)$ is 100 Hz, less than that of a square-planar complex (120 Hz) but well above an axial, trigonal-bipyramidal one (75 Hz).

The other exception was DPPB which gave confusing results in almost every case. (See the discussion above on this ligand for more details.)

After bubbling these solutions with argon gas, the structures return to a dicarbonyl form (structure II) as initially seen for the isolated complexes. The ^{31}P NMR values for both the isolated and *in situ* complexes agree well with the expected, having lower chemical shifts over the tricarbonyls and a coupling constant of approximately 120 Hz. The only exception was a small doublet in the *in situ* DPPDOD case having a coupling constant of 100 Hz. This is most likely from weak association with displaced acetonitrile present from the $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ starting material.

It is interesting to note that while Schrock could not isolate a dicarbonyl with rhodium and monodentate phosphines,² bis-phosphines readily form them. Although he could isolate a tricarbonyl with both $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$, they quickly lost two molecules of carbon monoxide in solution to form the monocarbonyl. Even under an atmosphere of carbon monoxide the dicarbonyl could not be isolated. This is not the case

for bis-phosphines. Apparently bidentate phosphines are stronger σ -donors than $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$, thereby stabilizing the rhodium center in the four-coordinate case allowing the dicarbonyl to be isolated. (For more information on the displacement of CO see Farrar's kinetic study of $\text{Ru}(\text{CO})_4(\eta^1\text{-diphosphine})$ to give $\text{Ru}(\text{CO})_3(\eta^2\text{-diphosphine})$ where diphosphine = DPPM, DPPE, DPPP, DPPB.²⁰)

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