

APPENDIXES

- APPENDIX I: Raw ESMS data for bidentate ligand complexation studies of rhodium(I) bis-phosphines alone and upon addition of carbon monoxide. Unidentifiable peaks below 10% are not included. Base peak in italics.
- APPENDIX II: Isotopic pattern comparison program written by Dr. Paul Norgaard to determine the percentage of monomer and dimer present in solution from the observed isotopic pattern.

APPENDIX I

Table 40

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
	$[\text{RhL} - \text{HPPH}_2]^+$ - 343	--	--	--	--	77.9 *
	$[\text{Rh}(\text{HPPH}_2)_2]^+$ - 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
	Other					

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.

Table 41

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	$[\text{RhL} - \text{HPPPh}_2]^+ - 343$	--	--	--	16.0	100
	$[\text{Rh}(\text{HPPPh}_2)_2]^+ - 475$	--	--	--	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	--	--	--
	Other					732(17.6) 808(11.8)

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.

Table 42

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	$[\text{RhL} - \text{HPPH}_2]^+ - 343$	--	--	--	11.2	100
	$[\text{Rh}(\text{CO})_2\text{L} - \text{HPPH}_2]^+ - 399$	--	--	--	--	20.4
	$[\text{Rh}(\text{HPPH}_2)_2]^+ - 475$	--	--	--	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	✓	--	--	--
	??? - 1149	25.0	15.7	4.9	5.0	9.3
	Other					

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.

Table 43

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

		Cone Voltage (V) ^b				
		20	30	50	70	90
Species - m/z	$[\text{Rh}_2(\text{L-H}_2)(\text{COD})]^{+2}$ - 382	31.5	31.6	54.2	25.3	15.0
	- 617	--	--	✓	6.6	28.3
	- 836	--	--	--	✓	38.3
	- 864	21.1	43.3	48.6	11.0	7.9
	$[\text{Rh}_2(\text{L-H}_2)(\text{COD})_2(\text{BF}_4)]^+$ - 961	22.3	15.8			
	- 968	--	--	35.9	100	100
	- 1097	11.9	20.6	33.9	10.6	✓
	$[\text{Rh}_2\text{L}_2(\text{COD})_2]^+$ - 1330	100	100	100	24.7	✓
	$[\text{Rh}_3(\text{L-H}_2)_2(\text{COD})_2(\text{CH}_3\text{CN})_3(\text{BF}_4)_2]^+$ - 1726	97.1	44.2	18.4	✓	--
	Other					

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

✓ = 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 44

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
	Other				710(15.0)	1403(16.5)

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 45

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 46

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.

Table 47

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
	Other					

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

* = Species verified by isotopic pattern

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

^b Data reported as % relative intensity.

Table 48

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	✓
	Other					

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.

Table 49

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	✓
	Other					

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 50

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
	Other					

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.

Table 51

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}

Redone twice and no $[\text{Rh}(\text{CO})_2\text{L}]^+$ detected.

		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	--
	Other					

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.

Table 52

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	--
	Other					

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.

APPENDIX II

Isotopic pattern comparison program written to determine the percent of monomer and dimer present in solution from the observed isotopic pattern.

```

REM *****
REM *** Isotope comparator program by Paul Norgaard ***
REM *** Last updated June 29, 1999 ***
REM *****

REM The next line clears the computer screen
CLS

REM The next line makes several arrays, each with 9 elements
DIM MZ(9), A(9), B(9), U(9), M(9)

REM          MZ = m/z values
REM          D = Dimer intensities
REM          M = Monomer intensities
REM          U = Observed intensities (U for unknown)
REM          MIX = intensities for mixed case

REM The next line sets the starting m/z value for the first
REM peak in the isotope pattern
MZ(1) = 589

REM The next 'FOR' loop defines the rest (2-9) of the m/z
REM values
FOR x = 2 TO 9
  MZ(x) = MZ(x - 1) + .5
NEXT

REM The theoretical intensity values for the Dimer
D(1) = 47.16
D(2) = 34.39
D(3) = 100
D(4) = 66.89
D(5) = 64.19
D(6) = 35.18
D(7) = 11.61
D(8) = 2.64
D(9) = .45

REM The theoretical intensity values for the Monomer
M(2) = 0
M(4) = M(2)
M(6) = M(2)
M(8) = M(2)
M(1) = 100
M(3) = 36.46
M(5) = 99.38
M(7) = 34.62

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```

M(9) = 6.05

REM This 'FOR' loop lets the user enter in the observed
REM intensities for the isotopic pattern
FOR x = 1 TO 9
  PRINT "What is the "; MZ(x); " percentage for the unknown?"
  INPUT U(x)
NEXT

REM The next line defines a very high starting error
VALUE = 1234567890

REM This 'FOR' loop goes through percentages to find the best
REM mixed case for the observed peaks
REM          AMTD = Amount of dimer    (percent)
REM          AMTM = Amount of monomer  (percent)
FOR PERCENT = 0 TO 100
  AMTD = PERCENT
  AMTM = 100 - AMTD

REM This 'FOR' loop goes through each peak in the isotopic
REM pattern and determines what the mix intensity should be
FOR x = 1 TO 9
  MIX(x) = D(x) * AMTD + M(x) * AMTM
  MIX(x) = MIX(x) / 100
NEXT

REM At this point the calculated mixed isotopic pattern is not
REM normalized, so now we must normalize it before it is
REM compared with the observed pattern.

REM We need to find the maximum peak in the isotopic pattern
REM to normalize the peaks. So first we set MAX to a very low
REM number.

MAX = .001

REM This 'FOR' loop looks at each peak in the pattern to find
REM the
REM largest one.
FOR x = 1 TO 9
  IF MIX(x) > MAX THEN MAX = MIX(x)
NEXT

REM Once we know the largest peak, we can make a modifier
REM that can multiply each peak intensity to normalize it.
IF MAX > 0 THEN MAX = 100 / MAX

REM Now we go through each peak in the pattern and normalize it.
FOR x = 1 TO 9
  MIX(x) = MIX(x) * MAX
NEXT

```

```

REM Now that we have the normalized isotopic pattern intensities
REM for a given percentage of dimer, we need to see how far off
REM that is from the observed pattern in order to determine the
REM percentage that gives the best fit

```

```

REM We need to look at each peak in the pattern to see how far
REM each one is off. NUMB will equal the difference in
REM intensities of each peak in the mixed and observed isotopic
REM patterns

```

```

REM The next 'FOR' loop adds up the difference in intensities
REM (between mixed and observed) for each peak in the patterns.

```

```

NUMB = 0
FOR x = 1 TO 9
  TEMP = 0
  TEMP = ABS(MIX(x) - U(x))
  NUMB = NUMB + TEMP
NEXT

```

```

REM Find the average difference in the peaks by
REM dividing by the number of peaks (9)
NUMB = NUMB / 9

```

```

REM Now let us find the best fit....
REM     HERE will be the percentage of dimer to give the best fit
REM     VALUE will be the error in that best fit
REM We will first set a high starting error

```

```

IF VALUE > NUMB THEN HERE = PERCENT
IF VALUE > NUMB THEN VALUE = NUMB

```

```

PRINT "For "; PERCENT; "% Dimer the unknown is off by "; NUMB;
" percent."
NEXT

```

```

PRINT "Best %age is "; HERE; " which is only off by "; VALUE

```