π Effects Involving Rh–PZ₃ Compounds. The **Quantitative Analysis of Ligand Effects (QALE)**

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Through the quantitative analysis of ligand effects (QALE), we have probed π effects associated with Rh–P bond lengths, ν_{CO} , and $-\Delta H_{rx}$ for Rh(CO)(Cl)(PX₃)₂ and ν_{CO} and $-\Delta H_{rx}$ for Rh(acac)(CO)(PZ₃). It was found that π effects are complex and depend strongly on the nature of ancillary or other participatory groups. The results of the QALE analysis of $-\Delta H_{\rm rx}$ point out the importance of synergistic interactions between PZ_3 and other ancillary ligands in accord with theoretical computations. Literature data for Rh(CO)(Cl)(PZ₃)₂ have been supplemented with new values of $\Delta H_{\rm rx}$ for PMe₃ (-75.6 \pm 0.3 kcal/mol), P(i-Pr)₃ (-68.7 \pm 0.3 kcal/mol), and PCy₃ (-66.4 ± 0.4 kcal/mol) as well as crystal structures for Rh(CO)(Cl)- $(P(i-Pr_3))_2$ (Rh-P = 2.3488(3) Å) and $Rh(CO)(Cl)(PCy_3)_2$ (Rh-P = 2.3508(3)).

Introduction

Nolan and Moloy reported the heats of reaction $(-\Delta H_{\rm rx})$ of pyrrolylphosphines, PPh_i(Pyr)_{3-i} with two rhodium complexes, shown below.^{1,2} Interestingly, $-\Delta H_{\rm rx}$ for the two reactions show opposite trends for this set of phosphines.



R = Ph, i-Pr; COE = cyclooctene

ΔH_{rx} $[Rh(CO)_2Cl]_2 + 2PZ_3$ 2Rh(CO)(Cl)(PZ₃)₂ + 2CO



With decreasing "*i*", $-\Delta H_{\rm rx}$ for reaction 1 increases for PPh_i(Pyr)_{3-i}, whereas $-\Delta H_{rx}$ decreases for reaction

2. Recently, Landis³ et al. suggested that these opposing trends are explainable in terms of the synergy of σ -donor and π -acceptor ligands. In particular, they noted that the presence of π -donor ligands enhances Rh–PZ₃ π back-bonding. On the other hand, the presence of a π -acidic PZ₃ diminishes back-bonding to a π -acidic ligand such as CO.

The roles of σ and π bonding in the variations of physicochemical properties also can be evaluated empirically in terms of the QALE (quantitative analysis of ligand effects) model (vide infra). This is possible because we now have in hand values for a parameter $(\pi_{\rm p})$ that is a measure of the π acidity of PZ₃ compounds. These compounds include phosphites,⁴ pyrrolylphosphines,⁵ chlorophosphines,⁶ 2-cyanoethylphosphines,⁶ fluorinated phosphorus(III) compounds,⁷ and phosphines containing P-H bonds.⁶ Accordingly, for the first time, we address via the QALE model, the question of how the π acidity of PZ₃ affects the variations in a

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(2)



Figure 1. Molecular structure of Rh(CO)(Cl)[P(i-Pr)₃]₂.



Figure 2. Molecular structure of Rh(CO)(Cl)(PCy₃)₂.

variety of physicochemical properties. In this paper, we report our analyses of physicochemical properties, the results of which shed light on the aforementioned opposing trends in $-\Delta H_{\rm rx}$ for rhodium complexes. These properties include the Rh–P bond lengths, $\nu_{\rm CO}$, and $-\Delta H_{\rm rx}$ for Rh(CO)(Cl)(PZ_3)_2. Since there is insufficient data available for a QALE analysis of the properties of [RPNP]Rh(PZ_3) (see reaction 1), we included the analyses for $\nu_{\rm CO}$ and $-\Delta H_{\rm rx}$ for Rh(acac)(CO)(PZ_3)_2. We have supplemented the literature data for Rh(CO)(Cl)(PZ_3)_2 with new measurements from our laboratories.

Results

Molecular Structures of $Rh(CO)(Cl)[P(i-Pr)_3]_2$ and $Rh(CO)(Cl)(PCy_3)_2$. The molecular structures of complexes $Rh(CO)(Cl)[P(i-Pr)_3]_2$ and $Rh(CO)(Cl)(PCy_3)_2$ are shown in Figures 1 and 2, respectively. Both complexes occupy crystallographic centers of symmetry; this requires that the CO and Cl ligands are involved in a 1:1 disorder.⁸⁻¹¹ Selected bond lengths and angles



Bond Lengths				
Rh(1) - (Cl(1))	2.4041(16)	Rh(1)-P(1)	2.3488(3)	
Rh(1) - C(10)	1.698(5)	P(1) - C(1)	1.8448(16)	
P(1) - C(4)	1.8505(16)	P(1)-C(7)	1.8523(17)	
C(1) - C(2)	1.516(3)	C(1) - C(3)	1.518(3)	
C(4) - C(5)	1.525(3)	C(4) - C(6)	1.535(3)	
C(7)-C(8)	1.532(4)	C(7)-C(9)	1.522(3)	
C(10) - O(1)	1.152(5)			
	Bond	Angles		
Cl(1) - Rh(1) - Cl(1)	180.00	Cl(1) - Rh(1) - P(1)	89.43(5)	
Cl(1) - Rh(1) - P(1)	90.57(5)	Cl(1) - Rh(1) - P(1)	89.43(5)	
P(1)-Rh(1)-P(1)	180.00	Cl(1) - Rh(1) - C(10)	179.17(16)	
P(1) - Rh(1) - C(10)	90.08(12)	P(1) - Rh(1) - C(10)	89.92(12)	
Cl(1) - Rh(1) - C(10)	179.17(16)	P(1) - Rh(1) - C(10)	90.08(12)	
Rh(1) - P(1) - C(1)	110.87(5)	Rh(1) - P(1) - C(4)	113.39(5)	
C(1) - P(1) - C(4)	104.06(8)	Rh(1) - P(1) - C(7)	113.63(6)	
C(1) - P(1) - C(7)	103.77(8)	C(4) - P(1) - C(7)	110.28(9)	
P(1) - C(1) - C(2)	111.36(13)	P(1) - C(1) - C(3)	111.18(14)	
C(2) - C(1) - C(3)	110.10(18)	P(1)-C(4)-C(5)	112.35(16)	
P(1)-C(4)-C(6)	117.42(14)	C(5) - C(4) - C(6)	111.17(18)	
P(1)-C(7)-C(8)	111.86(16)	P(1)-C(7)-C(9)	117.01(15)	
C(8) - C(7) - C(9)	110.9(2)	Rh(1) - C(10) - O(1)	179.6(6)	

for the two structures appear in Tables 1 and 2. The Rh–C and Rh–Cl distances are approximately 0.03-0.10 Å shorter and longer, respectively, compared to complexes where no disorder is involved. This artifact is a consequence of the inability to completely resolve the effects of the disorder. Thus, these distances may not be used in detailed analyses of the structures. However, the Rh–P distances and related angles are unaffected by the disorder and provide useful parameters for our analyses as described below.

QALE Analyses. In Table 3, we present the stereoelectronic parameters of the PZ₃ that are considered in this paper. Literature data have been supplemented by new data for ν_{CO} , $-\Delta H_{rx}$ (see eq 2, L = PMe₃, P(i-Pr)₃, and PCy₃), and Rh–P bonds for Rh(CO)(Cl)(PZ₃)₂ (L = P(i-Pr)₃ and PCy₃). The new data are presented in Table 4. We have analyzed five physicochemical properties

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Rh(CO)(Cl)(PCy₃)₂ with esd's in Parentheses

	Bond L	engths	
Rh(1)-P(1)	2.3508(3)	$\breve{R}h(1)-Cl(1)$	2.3880(13)
Rh(1)-Cl(1)	2.3880(13)	Rh(1) - C(19)	1.745(5)
P(1) - C(1)	1.8595(12)	P(1)-C(7)	1.8482(12)
P(1) - C(13)	1.8579(12)	C(1) - C(2)	1.5287(18)
C(1) - C(6)	1.5300(17)	C(2) - C(3)	1.530(2)
C(3) - C(4)	1.514(3)	C(4) - C(5)	1.510(3)
C(5) - C(6)	1.530(2)	C(7)-C(8)	1.5347(19)
C(7) - C(12)	1.5319(17)	C(8) - C(9)	1.529(2)
C(9) - C(10)	1.522(3)	C(10) - C(11)	1.505(3)
C(11) - C(12)	1.527(2)	C(13) - C(14)	1.5325(18)
C(13)-C(18)	1.5369(18)	C(14) - C(15)	1.531(2)
C(15)-C(16)	1.514(3)	C(16)-C(17)	1.517(2)
C(17)-C(18)	1.527(2)	C(19)-O(1)	1.153(4)
	Bond	Angles	
P(1) - Rh(1) - P(1)	180.00	P(1) - Rh(1) - Cl(1)	91,39(3)
P(1) - Rh(1) - Cl(1)	88.61(3)	Cl(1) - Rh(1) - Cl(1)	180.00
P(1) - Rh(1) - C(19)	89.7(1)	P(1)-Rh(1)-C(19)	90.3(1)
Cl(1) - Rh(1) - C(19)	178.57(11)	P(1)-Rh(1)-C(19)	90.3(1)
P(1) - Rh(1) - C(19)	89.7(1)	Rh(1) - P(1) - C(1)	114.69(4)
Rh(1) - P(1) - C(7)	112.66(4)	C(1) - P(1) - C(7)	110.01(6)
Rh(1) - P(1) - C(13)	112.24(4)	C(1) - P(1) - C(13)	102.53(5)
C(7) - P(1) - C(13)	103.72(5)	Rh(1) - CL(1) - O(1)	172.0(6)
P(1) - C(1) - C(2)	113.25(9)	P(1) - C(1) - C(6)	117.98(9)
C(2) - C(1) - C(6)	109.86(11)	C(1) - C(2) - C(3)	110.67(13)
C(2) - C(3) - C(4)	111.73(15)	C(3) - C(4) - C(5)	111.17(16)
C(4) - C(5) - C(6)	111.60(15)	C(1) - C(6) - C(5)	110.21(13)
P(1) - C(7) - C(8)	114.22(9)	P(1)-C(7)-C(12)	116.39(9)
C(8) - C(7) - C(12)	110.66(11)	C(7) - C(8) - C(9)	109.97(13)
C(8) - C(9) - C(10)	111.99(14)	C(9) - C(10) - (11)	111.79(13)
C(10) - C(11) - C(12)) 111.29(14)	C(7)-C(12)-C(11)	110.21(12)
P(1)-C(13)-C(14)	113.85(9)	P(1)-C(13)-C(18)	110.21(8)
C(14) - C(13) - C(18)) 110.23(11)	C(13)-C(14)-C(15)	110.86(12)
C(14) - C(15) - C(16)) 111.11(13)	C(15)-C(16)-C(17)	110.82(13)
C(16) - C(17) - C(18)) 111.31(13)	C(13)-C(18)-C(17)	111.17(12)
Rh(1) - C(19) - O(1)	179.1(5)		

(Table 5). In each of the analyses, we began by examining the data graphically.¹² The details of this procedure can be found in the Supporting Information or on the QALE web site.¹³ Each set of data was subjected to statistical analysis in terms of the appropriate QALE parameters via either eq 3 or 4. In these equations, χ_d is the σ -donor capacity of the ligand;⁴ θ is Tolman's cone angle and is a measure of the size of the ligand;¹⁴ E_{ar} is an extra electronic effect, which was originally thought to be associated with aromatic pendent groups¹⁵ but is now thought to be more general;⁴ and π_p is a measure of π acidity.^{4–7} In eq 3, θ_{st} is the steric threshold¹⁶ and λ is the switching function that turns on the steric term after the size of the ligand surpasses the steric threshold.¹⁶ In the absence of a steric threshold this equation reduces to eq 4.

$$prop = a\chi_{d} + b(\theta - \theta_{st})\lambda + cE_{ar} + d\pi_{p} + e \quad (3)$$

$$prop = a\chi_{d} + b\theta + cE_{ar} + d\pi_{p} + e \qquad (4)$$

Our protocol for performing a QALE analysis is to test for the presence of a steric threshold graphically using the Steric Threshold Program.¹³ After the presence or

Table 3. Stereoelectronic Parameters of PZ₃^a

	ligand	χd	θ	$E_{\rm ar}$	π_{p}
1	P(OMe) ₃	17.9	107	1	2.8
2	PMe ₃	8.55	118	0	0
3	PPhMe ₂	10.6	122	1	0
4	P(OPh) ₃	23.6	128	1.3	4.1
5	PEt ₃	6.3	132	0	0
6	PPh ₂ (OMe)	14.8	132	2.3	0.9
7	PPh ₂ Me	12.1	136	2	0
8	$P(CH_2CH_2C_6F_{13})_3^b$	13.4	136	0	2.3
9	$PPh_2(CH=CH_2)$	13.65	140	-	0
10	$PPh_2(CH_2CH_2C_6F_{13})$	13.3	142	2	0.8
11	$P(p-MeOC_6H_4)_3$	10.5	145	2.7	0
12	$P(p-MeC_6H_4)_3$	11.5	145	2.7	0
13	$PPh_2(p-MeC_6H_4)$	12.8	145	2.7	0
14	$P(C_6H_5)_3$	13.25	145	2.7	0
15	$P(p-FC_6H_4)_3$	15.7	145	2.7	0
16	$PPh_2[p-(C_6F_{13})C_6H_4)]$	16.5	145	2.7	0
17	$P(p-ClC_6H_4)_3$	16.8	145	2.7	0
18	$PPh_2(Pyr)^c$	19.5	145	3.1	0.6
19	$PPh[p-(C_6F_{13})C_6H_4)]_2$	19.8	145	2.7	0
20	$P(p-F_3CC_6H_4)_3$	20.5	145	2.7	0
21	$P[p-(C_6F_{13})C_6H_4)]_3$	23.0	145	2.7	0
22	$PPh_2[Pyr-3,4-(CO_2Et)_2]^c$	23.2	145	3.1	0.7
23	$PPh(Pyr)_2^c$	25.7	145	3.2	1.3
24	$P(Pyr)_3^c$	31.9	145	3.3	1.9
25	$PPh[Pyr-3, 4-(CO_2Et)_2]_2^{c}$	33.1	145	3.2	1.4
26	$P[Pyr-3, 4-(CO_2Et)_2]_3^c$	43	145	3.3	2
27	$P(NC_4H_8)_3^d$	0.4	146	0	0
28	$P(m-MeC_6H_4)_3$	11.3	148	2.7	0
29	$P(i-Pr)_2(CH_2CH_2C_6F_{13})$	6.8	152	0	0.8
30	$PPh_2(o-MeC_6H_4)$	12.4	156	2.7	0
31	$PPh_2(C_6F_5)$	20.4	158	3.4	0
32	$PCy_2(CH_2CH_2C_6F_{13})$	5.4	159	0	0.8
33	P(i-Pr) ₃	3.45	160	0	0
34	$PPh(C_6F_5)_2$	27.6	171	3.7	0
35	PCy ₃	1.4	170	0	0
36	$P(\tilde{C}_6F_5)_3$	34.8	184	4.1	0

^a Taken from ref 7 and references therein. ^b Since our earlier report of the parameters for this ligand,⁷ the first vertical ionization potential and $-\Delta H_{\rm rx}$ for the protonation of the related compound $P(CH_2CH_2C_8F_{17})_3$ have become available.¹⁸ We assumed that the values of these properties for P(CH₂CH₂C₈F₁₇)₃ are very similar to those of $P(CH_2CH_2C_6F_{13})_3$. Thus, we recalculated the parameters for P(CH₂CH₂C₆F₁₃)₃ by combining these properties with those listed in ref 7. These new values are listed herein. ^c Pyr = pyrrolyl. d NC₄H₈ = pyrrolidinyl.

Table 4. New Physicochemical Data for $Rh(CO)(CI)(PZ_3)_2$

no.	PZ ₃	Rh-P bond length ^a	$\Delta H_{\rm rx}{}^b$	$\nu_{\rm CO}{}^c$
1	PMe3	2.308	-75.6	1966
2	P(i-Pr)3	2.349	-68.7	1947
3	PCy3	2.351	-66.4	1942

^{*a*}Å. ^{*b*} kcal/mol. ^{*c*} cm⁻¹ (methylene chloride).

absence of a steric threshold is established, each data set is subjected to regression analyses using the Minitab statistical program. Occasionally, within a set of data there is an outlier. A datum is identified statistically as an outlier in the following manner.¹⁷ The predicted values and the residuals of the property based on regression analysis were obtained where the suspect datum was omitted. Using the regression equation the predicted value of the suspect datum was calculated. If the difference between the predicted value and the experimental value is greater than 3.5 standard deviations from the set of residuals, then it is an outlier. Within the five data sets listed in Table 5 we found only three outliers out of 99 data. The final results of the

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Table 5. Systems, Properties, and Ligands Used in the QALE Analyses to Determine the Coefficients a-dof Eqs 1 and 2

				ligands	
no.	system	property	ligands used ^a	excluded	refs
1	Rh(CO)(Cl)(PZ ₃) ₂	$\nu_{\rm CO}$	1,2,3,4,5,8,7,10,11,12,14,20,16,17,18,20,21,22,	19	19-25
			23,24,25,26,27,29,31,32,33,34,35,36		
2	$Rh(CO)(Cl)(PZ_3)_2$	Rh–P bond length	2,3,7,9,8,10,12,14,15,24,27,33,35		8,9,20,22,26-35
3	$[(CO)_2RhCl]_2 + 4PZ_3 =$	$-\Delta H_{\rm rx}$	1, 2, 3, 4, 5, 7, 8, 10, 11, 12, 14, 15, 17, 18, 20, 22, 23, 25,	24	19 - 22, 24
	$2Rh(CO)(Cl)(PZ_3)_2 + 2CO$		26,29,32,33,35		
4	$Rh(acac)(CO)(PZ_3)$	$\nu_{\rm CO}$	3,4.7,11,12,13,14,15,17,18,20,23,24,28,30,33,35		36
5	$Rh(acac)(CO)_2 + PZ_3 =$	$-\Delta H_{rx}$	3,7,11,12,13,14,15,17,18,20,23,24,28,30,33,35	4	36
	$Rh(acac)(CO)(PZ_3) + CO$				

^a Numbers refer to the entry numbers in Table 3.

Table 6. Results of Regression Analyses (via Eqs 3 or 4) of the Physiochemical Properties Listed in
Table 5^a

no.	$a\chi_{ m d}$	bθ	$cE_{\rm ar}$	$d\pi_{ m p}$	е	$\theta_{\rm st}$	n	σ	r^2
1	1.7 ± 0.1	-0.24 ± 0.04	3.2 ± 0.8	6.9 ± 0.7	1980 ± 5		30	2.677	0.990
2	-0.0012 ± 0.0002	0.00066 ± 0.00008		-0.008 ± 0.002	2.25 ± 0.01		13	0.00387	0.967
3	-1.50 ± 0.08	-0.36 ± 0.04	-2.5 ± 0.6		132 ± 6		23	2.417	0.983
4	1.38 ± 0.09		1.3 ± 0.6	4.6 ± 0.5	1955.7 ± 0.8		17	1.149	0.995
5	-0.26 ± 0.09	-0.22 ± 0.02	-2.7 ± 0.4	2.9 ± 0.8	47 ± 4		16	0.816	0.961

^{*a*} The letters a-d are the regression coefficients of these equations. Entry numbers correspond to the entry numbers in Table 3. A missing value for a coefficient indicates that the coefficient was statistically indistinguishable from zero.

Table 7. Percent Contribution ^a that Each
Parameter Makes to the Variations in the
Physicochemical Properties Listed in Table 5

no.	χd	θ	$E_{\rm ar}$	$\pi_{ m p}$
1	+33	-10	+8	+49
2	-21	+26		-53
3	-57	-31	-12	-
4	+42		+5	+53
5	-12	-23	-15	+50

^{*a*} See text. The entry numbers correspond to the entry numbers in Table 4. Negative signs of the entries reflect the signs of the corresponding cofficients.

QALE analyses are presented in Table 6. The range of r^2 is 0.961–0.995.

To facilitate interpretation of the results of the QALE analyses, the percent contribution of each stereoelectronic property to the variations in the physicochemical property is presented in Table 7. These percent contributions are calculated in the following manner. We use a standard range of values for each of the QALE parameters. These values are 40, 90, 5, and 15 for χ_d , θ , E_{ar} , and π_{p} , respectively. The range for any parameter approximates the maximum range of that parameter for all the PZ₃ that we have studied. Each coefficient is multiplied by the range of the corresponding parameter, and the sum of the absolute values is taken. The product of each coefficient with its range is divided by this sum and multiplied by 100 to give the percent contributions. This procedure avoids the problem of having the ranges of the parameters depend on the collection of ligands in a particular data set. By using the standard set of ranges, we can compare the results of analyses of different data sets.

Discussion

The availability of the π_p parameters now allows us to incorporate π -acidic phosphorus(III) compounds into QALE analyses and thereby to probe the influence of phosphorus π bonding on physicochemical properties.

We begin by examining three disparate properties (Rh–P bond length, $-\Delta H_{\rm rx}$, and $\nu_{\rm CO}$) for Rh(CO)(Cl)-

 $(PZ_3)_2$. We have supplemented the literature data with new values of $-\Delta H_{rx}$ and ν_{CO} for PMe₃,P(i-Pr)₃, and PCy₃ as well as Rh–P bond lengths for Rh(CO)(Cl)(P(i-Pr₃))₂ and Rh(CO)(Cl)(PCy₃)₂ (Table 4). Examination of entries 1-3 in Tables 6 and 7 shows that these three properties respond differently to variations in the stereoelectronic properties of PZ₃; that is, the coefficients of the corresponding parameters of the three QALE equations are not proportional. Another way of showing that the properties respond differently to the parameters is by examining the percent contributions (Table 7) that each parameter makes to the variation in the properties. When we do this, we see that the percent contributions differ from property to property.

The signs of the coefficients of the QALE equation describing the variations in the Rh–P bond length seem reasonable (entry 2, Table 6). Thus, the negative coefficient of χ_d and the positive coefficient of θ indicate that the bond becomes longer as the σ -donor capacity and the size of PZ₃ increase. The negative coefficient of π_p indicates that increasing π acidity of PZ₃ shortens the bond. By examining the percent contributions of each parameter, we see that π_p dominates the variations in Rh–P bond length, with χ_d and θ making smaller and nearly equivalent contributions.

The analysis of $\nu_{\rm CO}$ for Rh(CO)(Cl)(PZ₃)₂ is also reasonable (entry 1, Table 6). The signs of the coefficients indicate that $\nu_{\rm CO}$ increases as PZ₃ becomes a poorer σ donor and a better π acid. Interestingly, $\nu_{\rm CO}$ is shifted to smaller values as the size of PZ₃ increases, although the effect is small. On the basis of the percent contributions, we see that the variations in $\nu_{\rm CO}$ are dominated by $\pi_{\rm p}$, although $\chi_{\rm d}$ also has a large effect.

The results of the analysis of $-\Delta H_{\rm rx}$ are insightful (entry 3, Tables 5–7). Thus, the coefficients of $\chi_{\rm d}$ and θ indicate that $-\Delta H_{\rm rx}$ becomes larger as PZ₃ becomes a better σ donor, and $-\Delta H_{\rm rx}$ becomes smaller as the size of PZ₃ increases, as expected. Surprisingly, $\pi_{\rm p}$ makes no statistically significant contribution to $-\Delta H_{\rm rx}$. We believe this result is real and has a rational explanation.

Clearly, the QALE analyses of Rh-P bond lengths and ν_{CO} for Rh(CO)(Cl)(PZ₃)₂ reveal that Rh–P backbonding is important. It is also obvious from the analysis of v_{CO} that Rh–P π back-bonding comes at the expense of Rh–CO π back-bonding. If the two effects almost balance, there would be only a small π effect in $-\Delta H_{rx}$: what is gained energetically in Rh–P π back-bonding is lost in Rh–CO π back-bonding.

In contrast, there ought to be a synergistic effect between a π -basic ligand and a π -acidic PZ₃ ligand.³ The electron acceptance from the metal by the π -acidic PZ₃ ligand would accentuate metal bonding with the π base. There is evidence that this is, indeed, the case. Unfortunately, not enough data are available to analyze the properties of the product of reaction 1, which should show this effect. Alternatively, we considered the properties of Rh(acac)(CO)(PZ₃) (entries 4 and 5 in Tables 5, 6, and 7). Analysis of $v_{\rm CO}$ shows a significant π effect as the π acidity of PZ₃ increases; this is comparable to the effect observed for Rh(CO)(Cl)(PZ₃)₂, where there are two PZ₃ present. The enhancement of the Rh–P π back-bonding again comes at the expense of Rh–CO π back-bonding. Although the π_p contribution to $-\Delta H_{\rm rx}$ (see eq 5) is negligible for $Rh(CO)(Cl)(PZ_3)_2$, the π_p contribution (+51%) to $-\Delta H_{\rm rx}$ is large and positive for $Rh(acac)(CO)(PZ_3).$

$$Rh(acac)(CO)_{2} + PZ_{3} \xrightarrow{\Delta H_{rx}} Rh(acac)(CO)(PZ_{3}) + CO$$
(5)

This suggests a synergistic interaction between the π -basic "acac" and the π -acidic PZ₃. The reported trend of $-\Delta H_{\rm rx}$ for reaction 1 then suggests that Rh–P π backbonding is also enhanced by the presence of the π -basic RPNP ligand.²

We note that the coefficient of χ_d becomes less negative for $-\Delta H_{rx}$ for Rh(acac)(CO)(PZ₃) than for Rh(CO)-(Cl)(PZ₃)₂. This observation suggests that Rh–P σ bonding is less important for a complex containing a π donor (e.g., $Rh(acac)(CO)(PZ_3)$) than for the complex containing a strong π acid (e.g., Rh(CO)(Cl)(PZ_3)₂). These observations seem to be in accord with the results of computations by Landis et al.,³ who noted that "...if a good π acceptor ligand is present (such as CO) then Rh–P bond strengths increase with phosphorus σ donor strength. If there is not a good π acceptor ligand, the Rh–P bond strength increases with π accepting capacity of phosphorus".

Conclusions

The QALE method is a tool that allows the evaluation of π effects in spectroscopic, thermodynamic, and kinetic data. The high quality of the analyses gives us confidence in the interpretations of the analyses. Clearly, π effects are complex and might appear in one property but not another for the same system. For example, Rh–P bond lengths and v_{CO} for Rh(CO)(Cl)(PZ₃)₂ show π effects, whereas $-\Delta H_{\rm rx}$ does not. It appears that the magnitude and the sign of the π effect are dependent on the presence of ancillary π -acidic or π -basic ligands. The QALE results are consonant with the theoretical results of Landis et al.

Experimental Section

General Considerations. All manipulations were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk line techniques, or in a glovebox containing less than 1 ppm oxygen and water. Solvents, including deuterated solvents for NMR analysis, were dried by standard methods³⁷ and distilled under nitrogen or vacuum transferred before use. NMR spectra were recorded using Varian Gemini 300 MHz or Varian Unity 400 MHz spectrometers. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80), which was periodically calibrated using the TRIS reaction³⁸ or the enthalpy of solution of KCl in water.³⁹ This calorimeter has been previously described,^{40,41} and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. [Rh-(CO)₂Cl]₂ was synthesized according to literature procedures.⁴² PMe₃, P(i-Pr)₃, and PCy₃ (Strem) were used as received.

Infrared Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (± 0.1 mg) of [Rh(CO)₂Cl]₂ was placed in a test tube fitted with a septum, and CH₂Cl₂ was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by infrared spectroscopy and found to be rapid, clean, and quantitative under experimental calorimetric (temperature and concentration) conditions necessary for accurate and meaningful calorimetric results. These conditions were satisfied for all organorhodium reactions investigated.

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NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount $(\pm 0.1 \text{ mg})$ of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was placed in an NMR tube along with CD_2Cl_2 and 4 equiv of ligand. A color change from red to yellow was immediate upon mixing. Both ¹H and ³¹P NMR spectra indicated the reactions were clean and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all reactions investigated.

Solution Calorimetry. In a representative experimental trial, the mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120° C, and then taken into the glovebox. A sample of $[Rh(CO)_2Cl]_2$ (13.2 mg, 34.0 μ mol) was weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A solution of PCy₃ (42.6 mg, 152 μ mol) in CH_2Cl_2 (4 mL) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no rhodium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (ca. 2 h), it was inverted, thereby allowing the reactants to mix. The reaction was considered complete after the calorimeter had once again reached thermal equilibrium (ca. 2 h). The vessels were removed from the calorimeter, and an infrared spectrum was immediately recorded. Conversion to Rh(CO)(Cl)(PCy₃)₂ was found to be quantitative under these conditions. Control reactions with Hg and phosphine show no reaction. The enthalpy of ligand substitution (-66.4 ± 0.4 kcal/mol) listed in Table 4 represents the average of at least three individual calorimetric determinations with all species in solution. The enthalpy of solution of $[Rh(CO)_2Cl]_2$ (8.6 \pm 0.2 kcal/mol) has been reported.¹⁹

X-ray Structure Determination of Rh(CO)(Cl)[P(i-Pr)₃]₂ and **Rh(CO)(Cl)(PCy**₃)₂. Crystallographic data for both compounds are summarized in Table 8. Data were collected on a Nonius CAD-4 Turbo diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).⁴³ Data were processed using the Nonius MolEN package;⁴⁴ structures were solved by the heavy atom method. Full-matrix least squares refinement was carried out using the Oxford University CRYSTALS-PC system.⁴⁵ Both compounds contain one-half molecule in the asymmetric

Table 8. Data for the X-ray Diffraction Studies of Rh(CO)(Cl)[P(i-Pr)₃]₂ and Rh(CO)(Cl)(PCy₃)₂^a

chemical formula	C19H42OClP2Rh	C37H66OClP2Rh
<i>a</i> , Å	8.1769(4)	9.9412(6)
<i>b</i> , Å	8.9312(3)	10.2413(5)
<i>c</i> , Å	16.6333(8)	10.7881(5)
α, deg	90	113.774 (4)
β , deg	93.402(4)	109.198(4)
γ , deg	90	90.786(4)
V, Å ³	1212.58(9)	935.55(9)
Ζ	2	1
fw	486.85	727.24
space group	$P2_1/c [C_{2h}^5; No. 14]$	$P\bar{1} [C_i^1; No. 2]$
T, °C	21(1)	21(1)
λ, Å	0.71073	0.71073
$\rho_{\rm calc}, {\rm g} {\rm cm}^{-3}$	1.333	1.291
μ , mm ⁻¹	0.939	0.632
transmn factors	b	0.936 - 1.00
R	0.0249	0.0235
$R_{ m w}$	0.0293	0.0268

 ${}^{a}R = \sum ||F_{0}| - |F_{0}||/\sum |F_{0}|; R = \{\sum w[|F_{0}| - |F_{0}|]^{2}/\sum w|F_{0}|^{2}\}^{1/2}.$ b Absorption correction not made for 1.

unit, which requires that the Cl and the CO ligands be involved in a 1:1 disorder. This is a common form of disorder in Rh-(CO)(Cl)(PZ₃)₂ systems^{10,11} and occurs in 14 Rh(CO)(Cl)(PZ₃)₂ structures of this type in the October 1998 version of the Cambridge Structural Data Base.⁴⁶ For both structures, all non-hydrogen atoms were refined using anisotropic displacement parameters; H atoms were placed in calculated positions and were not refined. Drawings were produced using the Oxford University Program CAMERON.⁴⁷ Full reports on both structures are available as CIF files.

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Supporting Information Available: Data for the structures of $Rh(CO)(Cl)[P(i-Pr)_3]_2$ and $Rh(CO)(Cl)(PCy_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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