

Synthetic, Structural, and Solution Calorimetric Studies of Pt(CH₃)₂(PP) Complexes[†]

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Received December 6, 1999

Reaction enthalpies of the complex (COD)PtMe₂ (**1**; COD = η^4 -1,5-cyclooctadiene) with an extensive series of bidentate phosphines (dpype, dppf, diop, dppe, dppb, dppp, dpmcb, depe, dmpe, dcpc) have been measured by solution calorimetry. The relative stabilities of the resulting complexes PtMe₂(PP) are determined by a combination of the donor and bite angle/steric properties of the bidentate phosphine ligand. In general, good σ donor ligands with small bite angles result in more thermodynamically stable complexes. Additionally, the molecular structures of **1**, Pt(Me)₂(pype) (**2**), Pt(Me)₂(dppf) (**3**), Pt(Me)₂(diop) (**4**), Pt(Me)₂(dppe) (**6**), Pt(Me)₂(dpmcb) (**9**), and Pt(Me)₂(Et₂dppp) (**13**) have been determined by single-crystal X-ray diffraction. No correlation between the thermochemical results and the structural parameters, e.g. M–P distance (as observed in other systems), is apparent in this class of complexes.

Introduction

Thermochemical measurements have been applied for some time to the quantitative assessment of metal–ligand interactions in organometallic systems.¹ We have been investigating the steric and electronic contributions present in tertiary phosphine and arsine based organoruthenium,² organorhodium,³ organoplatinum,⁴ and organoiron⁵ systems by means of solution calorimetry. We present in this paper the first thermochemical studies on a series of organoplatinum bis(phosphine) complexes formed by the general reaction given in Scheme 1. The complexes of the type (COD)PtRX (COD = η^4 -1,5-cyclooctadiene; R, X = aryl, alkyl, halide) are well-studied.⁶ The substitutional lability of COD renders these compounds convenient sources of organoplatinum fragments for coordination to phosphine ligands. Calorimetric measurements on related Pt(Me)₂(L)₂ (L = monodentate phosphine) complexes⁴ have been explained in terms of contributions from two separate

factors: a steric factor, typically Tolman's cone angle for the ligand involved, and an electronic factor which is highly dependent on the ligand.⁷ In light of these

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[†] Contribution No. 7838 from Du Pont.

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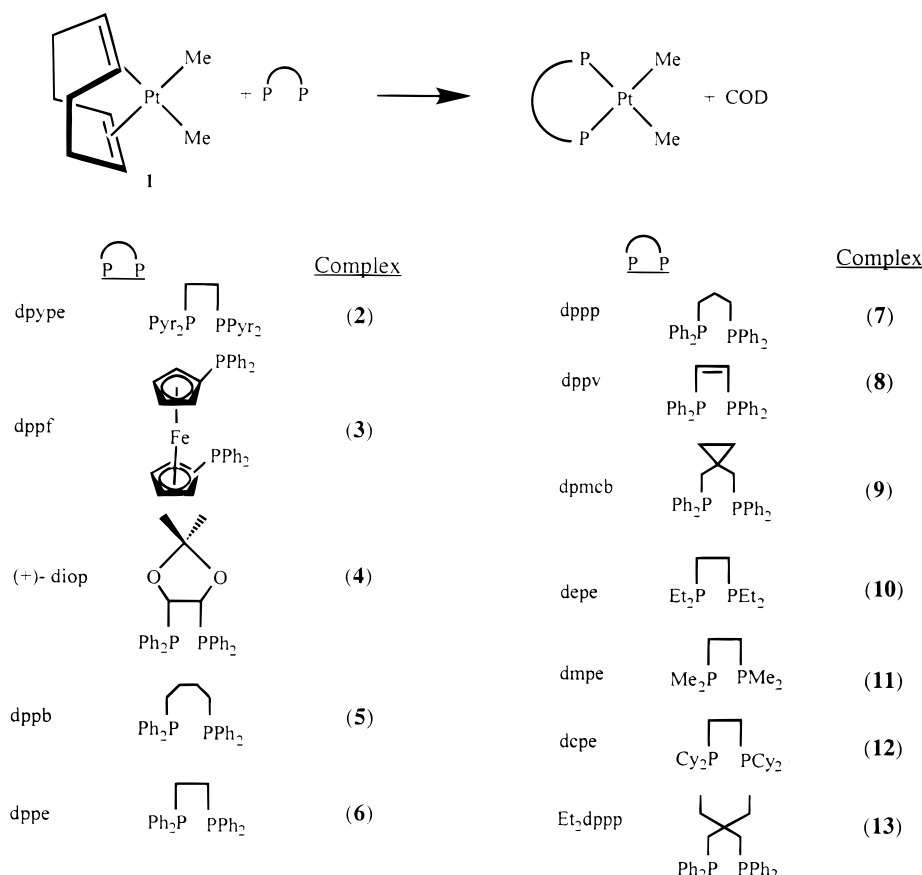
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Scheme 1



previous results on monodentate ligands, and the importance of chelating phosphorus ligands in coordination/organometallic chemistry and catalysis,⁸ we decided to conduct a thermochemical and structural study on the related bis(phosphine) PtMe_2 complexes. In this report, thermochemical measurements are compared to determine some of the possible factors affecting the structures and relative stability of the $\text{Pt}(\text{Me})_2(\text{PP})$ complexes.

Results and Discussion

Organoplatinum Syntheses. All organoplatinum complexes were prepared in a similar manner from $\text{PtMe}_2(\text{COD})$ (**1**) using a stoichiometric amount of the appropriate bis(phosphine) ligand in either CH_2Cl_2 or THF according to Scheme 1. In all cases, the reaction proceeded rapidly, except in the case of **13**, which required a slightly elevated temperature. All new compounds were found to be mononuclear complexes and are readily soluble in both THF and CH_2Cl_2 .

NMR Spectroscopy. Included in the Experimental Section are the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR data for all new compounds investigated in the present study. The multinuclear NMR data are typical of square-planar platinum with a *cis* arrangement of phosphine and methyl ligands. The $\text{Pt}-\text{C}_{\text{methyl}}$ resonances appear in ^1H spectra as phosphorus-coupled multiplets with ^{195}Pt satellites ($^2J_{\text{PtH}} = 69\text{--}72$ Hz), while $^{31}\text{P}\{^1\text{H}\}$ resonances

Table 1. Enthalpies of Substitution in THF at 30 °C for $\text{Pt}(\text{Me})_2(\text{COD}) + \text{P}\sim\text{P} \rightarrow \text{Pt}(\text{Me})_2(\text{P}\sim\text{P}) + \text{COD}$

complex	(P~P) ligand	ΔH_{rxn}^a (kcal/mol)	complex	(P~P) ligand	ΔH_{rxn}^a (kcal/mol)
2	dpype	-21.7(1)	8	dppv	-30.7(3)
3	dppf	-24.3(2)	9	dpmcb	-31.4(3)
4	(+)-diop	-25.7(1)	10	depe	-35.6(3)
5	dppb	-26.4(3)	11	dmpe	-36.4(2)
6	dppe	-29.9(1)	12	dcpe	-37.2(2)
7	dppp	-30.5(4)			

^a Enthalpy values are provided with 95% confidence limits.

are singlets with ^{195}Pt satellites ($^1J_{\text{PtP}} = 1779\text{--}2180$ Hz, within the typical range for *cis*-bis(phosphine) species).⁴ It is interesting to note that the $^{31}\text{P}\{^1\text{H}\}$ chemical shifts, $^1J_{\text{PtP}}$ values, and the $\text{Pt}-\text{C}_{\text{methyl}}$ chemical shifts are highly dependent on the identity of the chelating bis(phosphine) ligand. However, the $^2J_{\text{PtH}}$ coupling constants are insensitive to variation of the bis(phosphine) ligand. These observations are consistent with $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy studies on previously reported $\text{Pt}(\text{Me})_2(\text{PR}_3)_2$ complexes.⁴

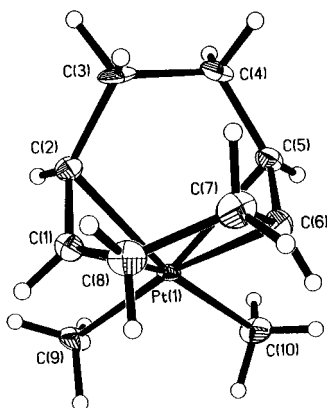
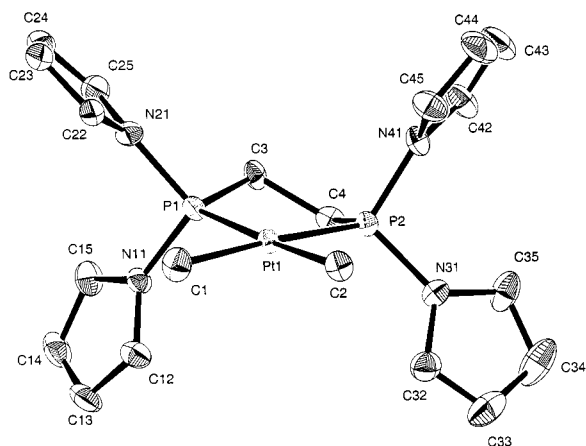
Structure Determination and Crystallographic Data. In an effort to clarify the relationship between phosphine ligand steric and electronic properties and the thermochemistry (see below), single-crystal X-ray diffraction analyses of *cis*-(COD) PtMe_2 **1**, and the bis(phosphine) adducts **2**–**4**, **6**, **9**, and **13** were performed. Crystallographic information for all seven compounds, including cell dimensions and details of the data collection, are given in Table 2. The ORTEP diagrams of **1**–**4**, **6**, **9**, and **13** are given in Figures 1–7. In their gross structural features, all *cis*- $\text{PtMe}_2(\text{PP})$ complexes

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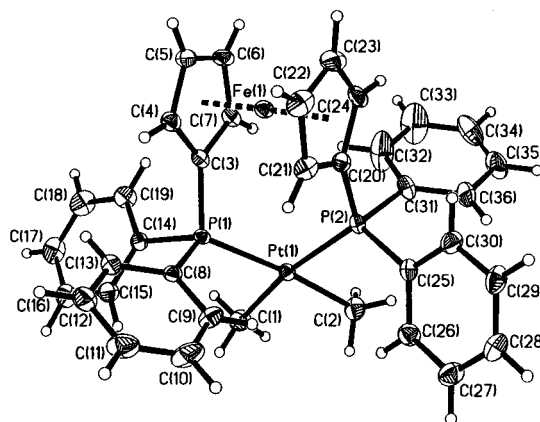
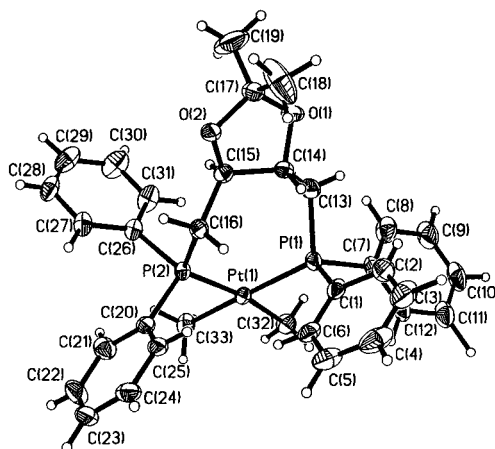
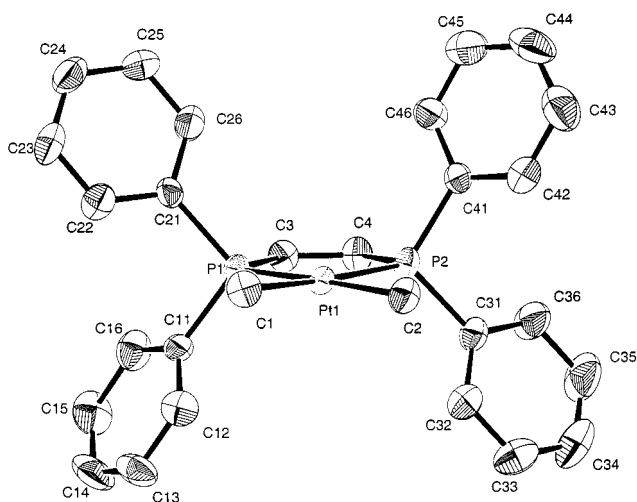
Table 2. Selected Bond Lengths and Angles in the Inner Coordination Sphere of the Complexes Pt(Me)₂(L)₂^a

complex	Pt–P, Å	Pt–C, Å	P–Pt–P, deg	trans-C–Pt–P, deg
2	2.241(1)	2.102(5)	84.73(5)	177.2(2)
	2.238(1)	2.114(5)		176.4(2)
3	2.2916(8)	2.094(3)	100.77(3)	173.42(11)
	2.2954(9)	2.102(4)		168.95(10)
4	2.2743(5)	2.1009(18)	98.022(18)	173.18(7)
	2.2954(5)	2.1066(19)		170.96(7)
6	2.246(2)	2.108(7)	86.01(7)	177.5(2)
	2.254(2)	2.112(6)		176.6(2)
9	2.261(1)	2.109(5)	95.39(5)	174.8(2)
	2.265(1)	2.106(6)		174.7(2)
13	2.2562(13)	2.156(4)	95.82(4)	172.99(11)
	2.2620(12)	2.258(4)		174.51(13)

^a Complete structural details are provided as Supporting Information.

**Figure 1.** ORTEP diagram of **1** with ellipsoids drawn at 50% probability.**Figure 2.** ORTEP diagram of **2** with ellipsoids drawn at 50% probability.

are typical for square-planar Pt(II) complexes. Average Pt–P bond lengths range from a maximum of 2.294 Å in **3** to a minimum of 2.240 Å in **2**, as shown in Table 2. All complexes investigated are rigorously square planar at platinum. Average Pt–C_{methyl} distances span a range from 2.098 Å (**3**) to 2.207 Å (**13**) and appear somewhat less sensitive to the identity of the phosphine ligand; however, the responses of P(1)–Pt–P(2) and C(1)–Pt–C(2) are opposite, as expected. For comparison, the Pt–C_{methyl} bond distances in the structure of PtMe₂(COD) (**1**) are 2.056(6) and 2.069(6) Å, and these distances are shorter on average than most of the bis(phosphine)

**Figure 3.** ORTEP diagram of **3** with ellipsoids drawn at 50% probability.**Figure 4.** ORTEP diagram of **4** with ellipsoids drawn at 50% probability.**Figure 5.** ORTEP diagram of **6** with ellipsoids drawn at 50% probability.

complexes. The P(1)–Pt–P(2) angle generally opens up with increasing chelate “bite” of the bis(phosphine) ligand accompanied by an increase in the Pt–P bond distance.

Solution Calorimetry. As determined by both ¹H and ³¹P{¹H} NMR spectroscopy, the reaction illustrated by Scheme 1 is notably fast, clean, and quantitative for a wide variety of chelating bis(phosphine) ligands at 30 °C. Of the 13 ligands examined for the reaction in

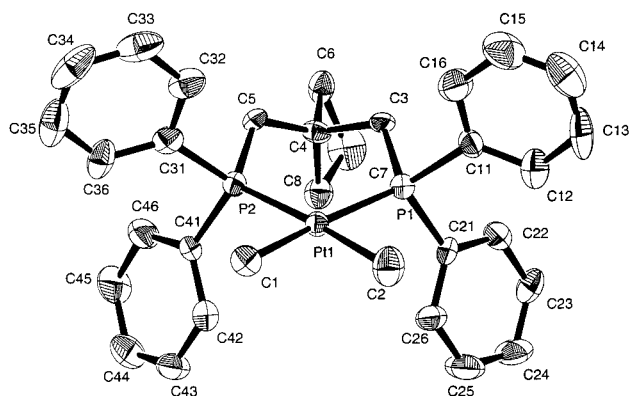


Figure 6. ORTEP diagram of **9** with ellipsoids drawn at 50% probability.

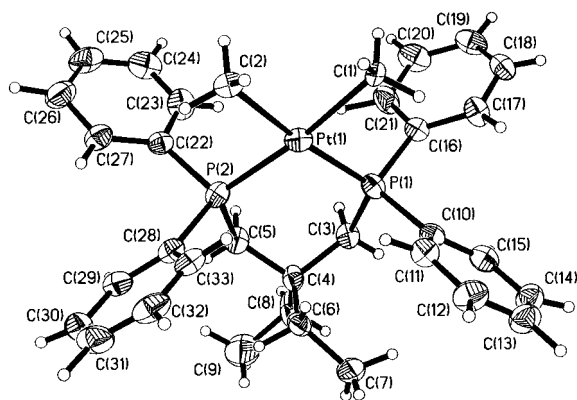


Figure 7. ORTEP diagram of **13** with ellipsoids drawn at 50% probability.

Scheme 1, forming the complexes $\text{PtMe}_2(\text{dppe})$ (**2**), $\text{PtMe}_2(\text{dppf})$ (**3**),⁹ $\text{PtMe}_2(+)\text{-diop}$ (**4**), $\text{PtMe}_2(\text{dppb})$ (**5**),^{10,11} $\text{PtMe}_2(\text{dppe})$ (**6**),^{10–12} $\text{PtMe}_2(\text{dppp})$ (**7**),^{10,11} $\text{PtMe}_2(\text{dppv})$ (**8**), $\text{PtMe}_2(\text{dpmcb})$ (**9**), $\text{PtMe}_2(\text{depe})$ (**10**),¹³ $\text{PtMe}_2(\text{dmpe})$ (**11**),^{14,15} and $\text{PtMe}_2(\text{dcpe})$ (**12**),¹⁶ only Et_2dppp failed to react under these conditions, requiring 24 h at 40 °C to give complete ligand substitution to form **13**. All complexes in this series possess identical coordination environments at platinum. Therefore, any variation in structures and the enthalpy of reaction should be due chiefly to the steric/bite angle and electronic effects of the phosphine ligand. As shown in Table 1, the enthalpies of substitution range from $-21.7(1)$ kcal/mol for **2** to $-37.2(2)$ kcal/mol for **12**. The overall order of stability is as follows: $\text{dppe} < \text{dppf} < (+)\text{-diop} < \text{dppb} < \text{dppe} < \text{dppp} < \text{dppv} < \text{dpmcb} < \text{depe} < \text{dmpe} < \text{dcpe}$. As the Tolman electronic scale⁷ predicts, the relative stabilities of the resulting complexes are strongly influenced by the electronic donor properties of the bidentate phosphine ligand if no larger steric factors are present. For example, better σ donors, e.g., dmpe , depe and dcpe , give

more thermodynamically stable complexes while the isosteric ligand dppe , which also possesses a five-membered ring, gives the lowest enthalpy of the series due to its weak donor properties. A similar enthalpic trend was observed for the related $\text{PtMe}_2(\text{PR}_3)_2$ complexes with monodentate phosphine ligands.⁴ Other trends are not well-defined and will require further investigation. For instance, it is notable that the two ligands with the largest bite angles ($\text{dppf} \approx (+)\text{-diop} \approx 100^\circ$) give reaction enthalpies 5–10 kcal/mol lower than the five- and six-membered-ring chelates. However, no relationship is found between the enthalpies of reaction and the average Pt–P bond lengths or P(1)–Pt–P(2) angles of the complexes, and no clear correlation between the C–Pt–C angle and the enthalpy is evident. Other relationships between the enthalpy of reaction and the metrical parameters are not straightforward, suggesting that other factors (e.g., steric, electronic, reorganization, or solvation) are operative and influence the structural chemistry of this system.¹⁷

Comparison between model bis(monodentate) and chelating ligand complexes can afford a gauge of the “strain energy” present in chelating systems.^{2a} In this platinum system, such a comparison involving (diphenylphosphino)ethylene and $(+)\text{-diop}$ with the $\text{Me}_2\text{Pt}(\text{PPh}_2\text{Me})_2$ complex (as a model system with no strain energy; since there is no metallacyclic structure, there is no strain) is possible. Any difference in enthalpy of reaction is then attributed to the strain energy in the metallacyclic complex. Observed differences between (diphenylphosphino)ethylene (-29.9 kcal/mol) and 2 equiv of PPh_2Me (-29.0 kcal/mol) is very small, indicating almost no strain in the metallacycle. On the other hand, $(+)\text{-diop}$ (-25.7 kcal/mol) shows signs of strain on the order of 3 kcal/mol. This strain energy is of the same order as that found for seven-membered metallacycles in the $(\text{PP})\text{Mo}(\text{CO})_4$ systems investigated by Hoff and co-workers.^{1b}

The present enthalpy data allow for comparison to prior thermochemical studies for reactions of a common chelating bis(phosphine) ligand in the $\text{Cp}^*\text{Ru}(\text{PP})\text{Cl}^{2g,h}$ ($\text{Cp}^* = \text{Cp} = \eta^5\text{-C}_5\text{Me}_5$ or $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and $(\text{PP})\text{Ru}(\text{allyl})_2$ (allyl = 2-methylpropenyl) systems. The relative order of stability of the resulting complexes in the $\text{Cp}^*\text{Ru}(\text{PP})\text{Cl}$,^{2g} $\text{CpRu}(\text{PP})\text{Cl}$,^{2h} and $(\text{PP})\text{Ru}(\text{allyl})_2$ ¹⁸ systems follow a similar trend as for the $\text{PtMe}_2(\text{PP})$ system. A good correlation ($R = 0.96$) is found for the plot of ΔH_{rxn} versus ΔH_{rxn} for a series of common PP ligand substitution reactions in the $\text{CpRu}(\text{PP})\text{Cl}$ and $\text{PtMe}_2(\text{PP})$ systems, and the plot is presented in Figure 8. Similarly, for reactions of the same PP ligand in the $\text{Cp}^*(\text{PP})\text{RuCl}$ and $\text{PtMe}_2(\text{PP})$ systems a good correlation ($R = 0.97$) is found and is illustrated in Figure 9. However, comparison of ΔH_{rxn} versus ΔH_{rxn} of the $\text{PtMe}_2(\text{PP})$ and the $(\text{PP})\text{Ru}(\text{allyl})_2$ systems only yields a fair correlation ($R = 0.91$), as illustrated in Figure 10; the reason for the weaker correlation may be due to the steric and electronic differences attributed to the ancillary ligands. Another informative system for comparison is the $(\text{PP})\text{-}$

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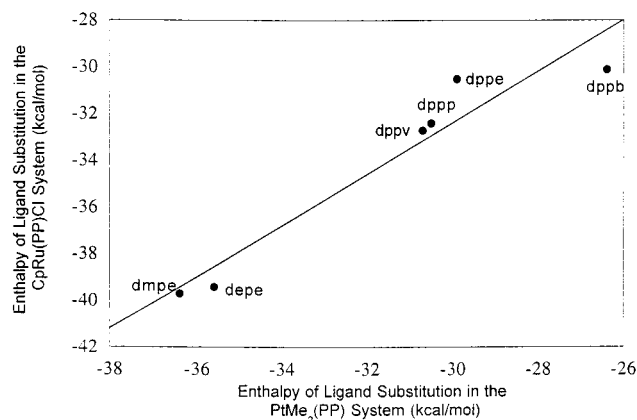


Figure 8. Comparison between enthalpies of ligand substitution in the CpRu(PP)Cl system and PtMe₂(PP) systems. $R = 0.96$; slope = 1.1 ± 0.2 .

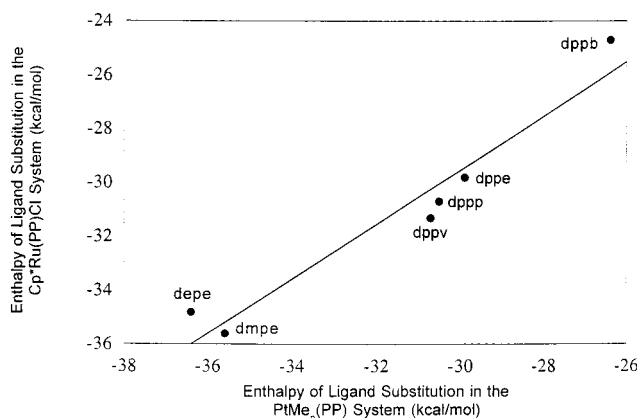


Figure 9. Comparison between enthalpies of ligand substitution in the Cp*Ru(PP)Cl system and PtMe₂(PP) systems. $R = 0.97$; slope = 1.0 ± 0.1 .

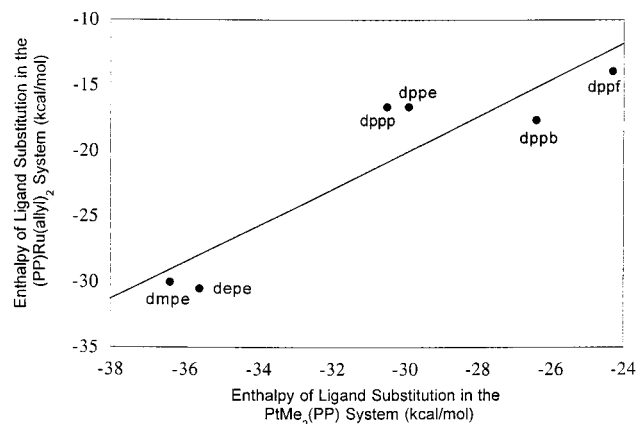


Figure 10. Comparison between enthalpies of ligand substitution in the (PP)Ru(allyl)₂ system and PtMe₂(PP) systems. $R = 0.91$; slope = 1.4 ± 0.3 .

Fe(CO)₃ system,¹⁹ since the chelating phosphine ligands should have similar steric environments about the metal center. As expected, the relative orders of stability of the resulting complexes of both PtMe₂(PP) and (PP)Fe(CO)₃ systems are similar. For reactions of common PP ligands in the (PP)Fe(CO)₃ and PtMe₂(PP) systems a good correlation ($R = 0.96$) is found. This linear relationship between ΔH_{rxn} for PP ligand substitution in the

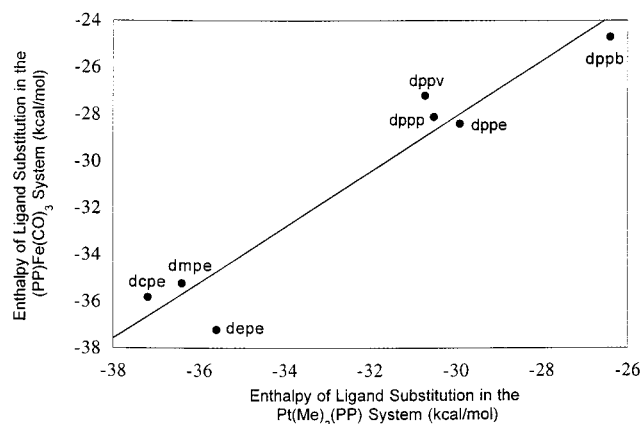


Figure 11. Comparison between enthalpies of ligand substitution in the (PP)Fe(CO)₃ system and PtMe₂(PP) systems. $R = 0.96$; slope = 1.2 ± 0.2 .

(PP)Fe(CO)₃ and PtMe₂(PP) systems is presented in Figure 11. Importantly, the thermochemical comparisons between these organoplatinum, organoruthenium, and organoiron systems illustrate that common electronic and steric factors of the bis(phosphine) ligands affect the thermodynamic stability of metallacyclic complexes.

Conclusion

Single-crystal X-ray diffraction studies of several PtMe₂(PP) systems have been performed in order to correlate structural parameters regarding the chelate bite of the bis(phosphine) ligand. Among this series of complexes, the reaction enthalpies correlate well with established donor properties of phosphine ligands.^{4,7} The relative stabilities of the resulting complexes are strongly influenced by the electronic donor properties of the bidentate phosphine ligand with better σ donors, resulting in more thermodynamically stable complexes. However, other relationships between the enthalpy of reaction and resulting metrical parameters are not forthright, suggesting that other factors influence the structural chemistry of this system.¹⁷

Experimental Section

General Considerations. All manipulations involving organoplatinum complexes were performed under an inert atmosphere of argon, using standard high-vacuum or Schlenk techniques, or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. Multinuclear NMR spectra were recorded using a Gemini 300 MHz or Oxford 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction²⁰ or the enthalpy of solution of KCl in water.²¹ The calorimeter has been previously described.^{22,23} The experimental enthalpies for these two standard reactions compared very closely to literature values. All phosphine

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Table 3. Crystallographic Data for the Complexes Pt(Me)₂(L~L)

	1	2	3	4	6	9·2.5THF	13
formula	C ₁₀ H ₁₈ Pt	C ₂₀ H ₂₆ N ₄ P ₂ Pt	C ₃₆ H ₃₄ FeP ₂ Pt	C ₃₃ H ₃₈ O ₂ P ₂ Pt	C ₂₈ H ₂₈ P ₂ Pt	C ₄₃ H ₅₆ P ₂ PtO _{2.5}	C ₃₃ H ₄₀ P ₂ Pt
fw	333.33	579.49	779.51	723.66	621.57	869.96	693.68
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> bcn	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	8.134 (2)	14.317(4)	9.3697(12)	10.9150(7)	8.521(5)	24.914(1)	11.1982(7)
<i>b</i> , Å	18.105(4)	8.981(1)	9.3757(12)	16.2899(11)	14.612(2)	13.850(1)	20.1754(13)
<i>c</i> , Å	7.3117 (19)	16.274(5)	18.135(2)	17.0011(11)	19.895(2)	22.694(1)	13.9257(9)
α, Å	90	90	92.089(3)	90	90	90	90
β, deg	115.708(5)	94.24(3)	104.105(3)	90	90.67(3)	90	112.011(2)
γ, deg	90	90	103.106(3)	90	90	90	90
<i>R</i> ^a	0.041	0.029	0.036	0.021	0.035	0.020	0.029
<i>R</i> _w ^a	0.114	0.025	0.081	0.031	0.028	0.020	0.060
goodness of fit	0.91	0.90	1.03	0.74	0.87	0.55	0.90

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|; R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2.$$

ligands used in these studies were purchased from Aldrich or Strem or prepared by the literature methods.^{24,25}

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, a precisely measured amount (±0.1 mg) of (COD)PtMe₂ was placed in an NMR tube along with CD₂Cl₂ and >1.2 equiv of ligand. Both ¹H and ³¹P{¹H} NMR spectra were measured within 1 h of mixing; both indicated the reactions were clean and quantitative. 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 145 °C, and then taken into the glovebox. A sample of (COD)PtMe₂ (20.2 mg, 0.0539 mmol) was massed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A solution of **7** (30.1 mg, 0.0751 mmol) in CH₂Cl₂ (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 platinum 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). Control reactions with Hg and phosphine show no reaction. The enthalpy of ligand substitution (−30.5 ± 0.4 kcal/mol) listed in Table 1 represents the average of at least three individual calorimetric determinations with all species in solution. The enthalpy of solution of (COD)PtMe₂ (+5.8 ± 0.1 kcal/mol) in CH₂Cl₂ was determined using identical methodology.⁴

Synthesis of Dimethylbis(phosphine)platinum(II) Complexes. Unless otherwise noted, all new complexes were prepared according to the following typical procedure. PtMe₂-(COD)²⁶ (**1**) and PtMe₂(dppf)⁹ (**3**) were prepared by literature methods.

Synthesis of PtMe₂(dpype) (2**).** In the glovebox, a Schlenk tube equipped with a magnetic stir bar was charged with (COD)PtMe₂ (77.9 mg, 0.234 mmol), dpype (82.8 mg, 0.234 mmol), and THF (5 mL). The vessel was sealed, removed from the glovebox, and interfaced to a Schlenk line, where the reaction mixture was stirred for ~2 h. The volatile components were removed in vacuo, and the residue was triturated several times with CH₂Cl₂ (3–5 mL) to ensure complete removal of cyclooctadiene. The colorless to off-white residue was then taken up in a minimum of CH₂Cl₂. Layering with pentane afforded orange prisms of **2** after 1 day. Yield: 106 mg (77.9%). ¹H NMR (CD₂Cl₂): δ 1.02 (m, 6 H, Pt(CH₃)₂, *J*_{PtCH₃} = 72 Hz),

2.15–2.25 (m, 4 H, PCH₂), 6.10–7.20 (m, 16 H, pyrl). ³¹P{¹H} NMR (CD₂Cl₂): δ 109.71 (s, pseudo d, *J*_{PtP} = 2180 Hz). Anal. Calcd for C₂₈H₂₈P₂Pt: C, 54.11; H, 4.54. Found: C, 54.19; H, 4.44.

Synthesis of PtMe₂((+)-DIOP) (4**).** Yield: 104 mg (73.6%) as yellow blocks. ¹H NMR (CD₂Cl₂): δ 0.187 (m, 6 H, Pt(CH₃)₂, *J*_{PtCH₃} = 69 Hz), δ 1.1 (s, 6 H, O₂CCH₃), 3.10–3.20 (m, 4 H, PCH₂), 3.70–3.85 (m, 2 H, OCH), 7.15–7.85 (m, 20 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ 9.23 (s, pseudo d, *J*_{PtP} = 1832 Hz). Anal. Calcd for C₃₃H₃₈O₂P₂Pt·H₂O: C, 53.44; H, 5.44. Found: C, 53.70; H, 5.39.

Synthesis of PtMe₂(dppv) (8**).** Yield: 144 mg (77.4%) as orange prisms. ¹H NMR (CD₂Cl₂): δ 0.667 (m, 6 H, Pt(CH₃)₂, *J*_{PtCH₃} = 71 Hz), 7.10–7.80 (m, 2 H, HC=CH; 20 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ 56.82 (s, pseudo d, *J*_{PtP} = 1779 Hz). Anal. Calcd for C₂₈H₂₈P₂Pt: C, 54.11; H, 4.54. Found: C, 54.19; H, 4.44.

Synthesis of PtMe₂(dpmcb) (9**).** Yield: 94 mg (61.7%) as colorless crystals. ¹H NMR (CD₂Cl₂): δ 0.17 (m, 6 H, Pt(CH₃)₂, *J*_{PtCH₃} = 69 Hz), 1.32 (t, 4 H, PCH₂), 1.2–1.4 (m, 4 H, (CH₂)₃), 1.52 (q, 2 H, (CH₂)₃), 7.05–7.89 (m, 20 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ 5.76 (s, pseudo d, *J*_{PtP} = 1821 Hz). Anal. Calcd for C₃₂H₃₆P₂Pt·2H₂O: C, 53.85; H, 5.65. Found: C, 54.33; H, 5.33.

Synthesis of PtMe₂(Et₂dppp) (13**).** The reaction mixture was heated to 50 °C for 18 h. Yield: 108 mg (60.1%) as colorless needles. ¹H NMR (CD₂Cl₂): δ 0.16 (m, 6 H, Pt(CH₃)₂, *J*_{PtCH₃} = 70 Hz), 2.30 (m, 4 H, PCH₂), 1.07 (q, 4 H, CH₂), 0.26 (s, 6 H, CH₃), 7.1–8.0 (m, 20 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ 4.25 (s, pseudo d, *J*_{PtP} = 1874 Hz). Anal. Calcd for C₃₃H₄₀P₂Pt: C, 57.14; H, 5.81. Found: C, 57.48; H, 6.04.

X-ray Structural Analyses of 1–4, 6, 9, and 13. For each compound, a suitable crystal was mounted on the glass fiber of a goniometer head in a random orientation and placed in the cold stream of N₂ in an automated diffractometer using Mo Kα radiation. The cell dimensions were determined in each case from at least 25 centered reflections, and data were collected. Standard reflections were monitored during data collection. An azimuthal absorption correction was applied in all structures. The structures of **1–4**, **9**, and **13** were determined from data collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a low-temperature apparatus (150 K), while the structure of **6** was determined on a Bruker Smart 1K CCD system with equipped with Mo Kα radiation and a low-temperature apparatus. The structures were solved by direct methods using either the SHELXS or MULTAN program. Each structure was refined in a full-matrix least-squares refinement on *F*, using anomalous terms for Pt and P, with all non-hydrogen atoms refined anisotropically. In each case, hydrogen atoms were located from a Fourier difference map and used as the basis of H atom positions in the final structure. All the structures have idealized and fixed H atoms, after attempts to refine them proved unsatisfactory. The absolute configuration of **4** was determined by refining a Flack parameter, which confirms the proper structural as-

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signment. ORTEP diagrams of each structure are given in Figures 1–7. Selected bond distances and angles are given in Table 2, and crystallographic data are given in Table 3. Positional and equivalent isotropic parameters for all non-hydrogen atoms are given in the Supporting Information.

Acknowledgment. S.P.N. acknowledges the National Science Foundation (Grant No. CHE-9985213)

and Du Pont (Educational Aid Grant) for financial support of this research.

Supporting Information Available: Details of the crystal structure determination for complexes **1–4**, **6**, **9**, and **13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM990962I