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Note

Synthesis and thermochemical study of ligand substitution reactions of aminobis(phosphines), $Ph_2P(R)NPPh_2$, with $[Me_2Pt(COD)]$

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Abstract

The reactions of aminobis(phosphines), $Ph_2PN(R)PPh_2$ (R = H, Me, Et, ^{n}Pr, ^{n}Bu, Ph), with $Me_2Pt(COD)$ led to the formation of four-membered metallacycles in good yield. The enthalpies of the ligand substitution reactions are measured by the anaerobic solution calorimetry in THF at 30 °C.

Keywords: Aminobis(phosphines); Thermochemistry; Enthalpy; Platinum complexes

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1. Introduction

The utility of chelating bis(phosphine) ligands in organometallic chemistry and in homogeneous catalysis [1] is well documented. The platinum complexes of bis(phosphines) are of continuing interest owing to their potential use in processes such as coupling reactions [2], olefin reduction [3], and hydroformylation reactions [4,5]. In a homogeneous catalytic process, the reactivity at the metal center can be better understood by knowing the entropy of the system along with the metal–ligand bond disruption energy. The bond disruption energy value is a net effect of the stabilizing metal–ligand bond and the destabilizing strain energy caused by the formation of chelate ring. The thermochemical measurements can assess the metal–ligand interactions in organometallic systems effectively [6,7]. Nolan and coworkers [8–13] and others [14,15] have extensively studied the steric and electronic influences in the transition metal complexes containing tertiary phosphines and arsines using solution calorimetry. As a part of our interest in organometallic chemistry of phosphorus based ligands [16–21], we describe in this paper the synthesis and the solution calorimetric studies of platinum (II) complexes of $RN(PPh_2)_2$ (R = H, Me, Et, ^{n}Pr, ^{n}Bu, Ph) (see Scheme 1).

2. Experimental

2.1. General considerations

All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to

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Abbreviations: dpype, bis(dipyridylphosphino)ethane; dppf, bis(diphenyl-phosphino)ferrocene; diop, (2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene) bis(diphenylphosphine); dmpe, bis(dimethylphosphino)ethane; depe, bis(diethylphosphino)ethane; dcpe, bis(dicyclohexylphosphino)ethane

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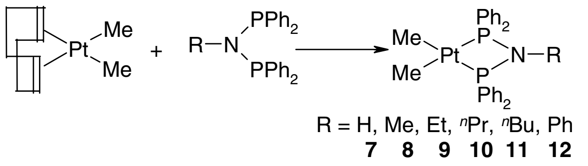

Scheme 1.

use. The aminobis(diphenylphosphines), RN$(PPh_2)_2$ (R = H, Me, Et, ^{n}Pr, ^{n}Bu, Ph), and $Me_2Pt(COD)$ were prepared according to the literature procedures. The ^{1}H and ^{31}P NMR spectra were recorded using Varian VXR 300, Bruker AMX 400, Gemini 300 and Oxford 400 spectrometers; Me_4Si was used as internal standard for the ^{1}H NMR and 85% H_3PO_4 as external standard for the ^{31}P NMR. Positive values indicate downfield shifts. 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 reaction [22] or the enthalpy of solution of KCl in water [23]. The calorimeter has been previously described [24,25]. The experimental enthalpies for these two standard reactions were compared very closely to literature values.

2.2. NMR titrations

Prior to every set of calorimetric experiments involving a new ligand, a precisely measured amount (±0.1 mg) of $(COD)PtMe_2$ was placed in an NMR tube along with THF and >1.2 equivalents of ligand. Both ^{1}H and $^{31}P\{^1H\}$NMR spectra were measured within 1 h of mixing; both indicated that the reactions were clean and quantitative. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all reactions investigated.

2.3. 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 glove box. A sample of $Me_2Pt(COD)$ (20.3 mg, 0.0609 mmol) was massed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A solution of $PPh_2N(^nBu)PPh_2$ (56.4 mg, 0.0128 mmol) in THF (4 mL) was added, and the remainder of the cell was assembled, removed from the glove box, 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 °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 (−22.4 ± 0.3 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 $(COD)PtMe_2$ (+6.25 ± 0.23 kcal/mol) in THF was determined using identical methodology.

Table 1
Spectral data for the complexes $[Me_2Pt\{Ph_2PN(R)PPh_2\text{-}\kappa P,\kappa P\}]$ (**7**–**12**)

R	δ_P (in ppm)	$^1J_{Pt–P}$ (in Hz)	δ CH_3 (in ppm)	$^2J_{Pt–H}$ (in Hz)
H (7)	19.3	3138	1.16	47.7
Me (8)	47.1	1519	0.83	40.3
Et (9)	46.7	1594	0.73	46.9
^{n}Pr (10)	47.7	1547	0.50	44.7
^{n}Bu (11)	47.8	1547	0.54	40.2
Ph (12)	49.3	4079	1.11	70.1

2.4. Syntheses

The complexes **7**–**12** were synthesized according to the following typical procedure.

A solution of $Ph_2PN(R)PPh_2$ (0.089 mmol) (R = H, Me, Et, ^{n}Pr, ^{n}Bu or Ph) in THF (7 mL) was added dropwise to a solution of $Me_2Pt(COD)$ (30 mg, 0.089 mmol) in the same solvent at 25 °C and the reaction mixture was heated to ~60 °C for 6 h. The volatiles were removed under reduced pressure and the residue was washed with *n*-hexane (3 × 5 mL). The colorless off-white solid was recrystallized in CH_2Cl_2-*n*-hexane (2:1) mixture at 0 °C. The spectral data of the complexes **7**–**12** are given in Table 1.

The NMR tube reactions of $Ph_2PN(R)PPh_2$ (0.059 mmol) (R = Et, ^{n}Pr, ^{n}Bu) with $Me_2Pt(COD)$ (20 mg, 0.059 mmol) in CH_2Cl_2 at 25 °C resulted in the formation of a mixture of complexes, $[Me_2Pt\{Ph_2PN(R)PPh_2\text{-}\kappa P,\kappa P\}]$ and $[Me_2Pt\{Ph_2PN(R)PPh_2\text{-}\kappa P\}_2]$ (R = Et, ^{n}Pr, ^{n}Bu) in ~25% and 75% yields, respectively. The ^{31}P NMR data are given in Table 2.

3. Results and discussion

The reactions of aminobis(phosphines), $PPh_2N(R)PPh_2$ (R = H, **1**; Me, **2**; Et, **3**; ^{n}Pr, **4**; ^{n}Bu, **5**; Ph, **6**), with equimolar quantity of $Me_2Pt(COD)$ in

Table 2
^{31}P NMR data for the complexes $[Me_2Pt\{Ph_2PN(R)PPh_2\text{-}\kappa P\}_2]$

R	$\delta_{P(Pt)}$ (in ppm)	$\delta_{P(un)}$ (in ppm)	$^1J_{Pt–P}$ (in Hz)	$^2J_{P–P}$ (in Hz)
Et	56.2	35.4	1345	34.7
^{n}Pr	53.1	32.4	1344	34.3
^{n}Bu	56.5	35.9	1348	34.8

THF at 60 °C gave mononuclear complexes **7**–**12**, respectively. In contrast, when the reactions were carried out in dichloromethane at room temperature a mixture of complexes with ligands exhibiting both chelating (**7**–**12**) and monodentate modes of coordination ($Me_2Pt\{Ph_2PN(R)PPh_2\text{-}\kappa P\}_2$ (R = Et, ^{n}Pr, ^{n}Bu)) was obtained; evidence from the ^{31}P NMR spectroscopic data [27]. The chemical shifts due to the coordinated phosphorus centers appear as doublets in the range of 53.1–56.5 ppm with Pt satellites, and the uncoordinated phosphorus centers also appear as doublets in the range of 32.4–35.9 ppm (see Table 2). The ^{31}P NMR spectra of the complexes 7–12 show single resonances (Table 1) with $^1J_{Pt-P}$ couplings in the range expected for cisplatinum (II) chelating complexes. The $^1J_{Pt-P}$ values for the *N*-alkyl derivatives are in the range of 1519–1594 Hz, whereas the NH and *N*-phenyl derivatives show larger values. Similar differences in the $^1J_{Pt-P}$ values were observed between *N*-phenyl- and *N*-methylaminobis(diphenylphosphites) in chelate complexes, $[Cl_2Pt\{P(OPh)_2\}_2NR]$ (R = Ph, $^1J_{Pt-P} = 3628$ Hz; R = Me, $^1J_{Pt-P} = 5041$ Hz), and obviously no clear explanation [26]. The ^1H NMR spectra of the complexes also support the formation of the complexes **7**–**12**.

3.1. Solution calorimetry

As determined by both ^1H and ^{31}P NMR spectroscopy, the reactions of aminobis(phosphines) (**1**–**6**) with $[Me_2Pt(COD)]$ appear quantitative for all ligands investigated by solution calorimetry at 30 °C in THF. The reaction of isopropyl amine derivative, $^iPrN(PPh_2)_2$, with $Me_2Pt(COD)$ was not clean under similar reaction conditions. The enthalpies for the reaction of Me_2Pt (COD) with aminobis(phosphines) to give the complexes **7**–**12** are presented in Table 3. These values include the enthalpy of solution of $Me_2Pt(COD)$ (+6.25 ± 0.23 kcal/mol) in THF. All the complexes of this series possess identical coordination environment around the platinum center as evidenced by the ^{31}P NMR spectroscopic data. Therefore, any variation in the structures and enthalpy of reaction should be mainly due to the steric/bite angle and electronic effects of the phosphine ligands employed in the study. As in all the complexes, the phosphorus environments are the same; the changes in the enthalpy value are attributed to the substituents on the nitrogen centers. As shown in Table 3, the enthalpy of substitution ranges from −20.7(3) kcal/mol for the complex **7** to −23.7(3) kcal/mol for the complex **8**. The overall order of stability is as follows: H < Et ∼ ^{n}Pr ∼ Ph < ^{n}Bu < Me. In other words, the reaction with the ligand having methyl substituent is more exothermic and the one with hydrogen substituent is least exothermic.

Table 3
Enthalpies of substitution in the reaction

$$Me_2Pt(COD)_{(Soln)} + P{\sim}P_{(Soln)} \xrightarrow[30\ ^{o}C]{THF} Me_2Pt(P{\sim}P)_{(Soln)} + COD_{(Soln)}$$

Complex	Ligands (P ∼ P)	ΔH (kcal/mol)
7	$Ph_2PN(H)PPh_2$	−20.7(3)
8	$Ph_2PN(Me)PPh_2$	−23.7(3)
9	$Ph_2PN(Et)PPh_2$	−21.4(3)
10	$Ph_2PN(^nPr)PPh_2$	−21.0(2)
11	$Ph_2PN(^nBu)PPh_2$	−22.4(3)
12	$Ph_2PN(Ph)PPh_2$	−21.4(3)

The present enthalpy data allow for comparison to prior thermochemical studies for the reaction of chelating aminobis(phosphines) in ruthenium complexes of the type, Cp′Ru(P ∼ P)Cl (Cp′ = η^5-C_5H_5, η^5-C_5H_5 [21]. The ligand **6** forms more stable complex with Cp′Ru(P ∼ P)Cl when compared to the ligand **2**, but the trend is exactly reverse with $Me_2Pt(COD)$. The reason may be the steric and electronic differences attributed to the other ancillary ligands. However, the results in the present study are comparable with the same in the analogous complexes containing bis(phosphines) such as dpype, dppf and diop with P–C–P framework [13]. It is observed that the better σ-donors such as dmpe, depe and dcpe form thermodynamically more stable complexes compared to the aminobis(phosphines).

4. Conclusions

The reaction enthalpies of aminobis(phosphines) are similar to the analogous bis(phosphines) with PCP framework [13]. The relative stability of the chelate complexes is influenced by the substituents present on the nitrogen center with better σ-donors inducing more thermodynamic stability to the complexes. The coordination behavior of the aminobis(phosphines) depends on the reaction conditions, the stoichiometry and the type of substituents present on both phosphorus and the nitrogen centers. The complexes of the type $[Me_2Pt\{Ph_2PN(R)PPh_2\text{-}\kappa P\}_2]$ can be used as synthons to design binuclear complexes and high nuclearity clusters. The research in this direction is in progress.

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