

Pd Pincer Complex as a Probe To Index the Coordination Ability of Various Ligands

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An NCN pincer palladium complex was developed as a probe molecule to index the coordination ability of various monodentate ligands. Coordination constants of 27 monodentate ligands (L) with a pincer palladium complex to form complexes of the type $\text{ArPd}(\text{L})_2\text{Cl}$ were determined by ^1H NMR spectroscopy. This allowed the coordination ability of a wide variety of ligands, including P-coordinating ligands (phosphane, phosphite), as well as As-coordinating AsPh_3 ,

and N-coordinating pyridine, to be indexed. The differential between the highest/lowest coordination constants was 10^{12} . The relative coordination ability is described in a logarithmic manner, $\log(K_{\text{eq}}(\text{L})/K_{\text{eq}}(\text{PPh}_3))$, with respect to the value of PPh_3 to exhibit high linearity in the Hammett plot.

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Introduction

Transition-metal–ligand complexes have emerged as versatile and functional molecules in the domain of chemistry. Vast arrays of functional metal complexes have been developed in which ligands undergo drastic change and/or fine-tuning of their chemical and physical properties. Transition-metal-catalyzed organic transformations are the most commonly employed reactions where the choice of ligands is essential in controlling the catalytic reaction pathway. Coordination ability is one of the most fundamental and important properties of ligands and, therefore, quite a few studies have appeared that index the ligand coordination ability. However, to the best of our knowledge, no direct or precise method has appeared that allows the determination of the relative strength/weakness of the coordination ability of PPh_3 to palladium, for example, versus AsPh_3 , pyridine, PCy_3 , etc. Clearly, although pioneering strides have been made, additional studies on the ordering of the coordination abilities of ligands are warranted.

Because the coordination ability is controlled by both the electronic and steric properties of the ligand, this renders quantitative description difficult. Indeed, although the two controlling factors (electronic and steric) have been defined,^[1,2] all of the well-developed research on the determination of the coordination ability of various ligands has been limited to isolated reports.^[3] If a practical probe for the direct and exact observation of the coordination–dissociation equilibria of a wide range of ligands were developed,

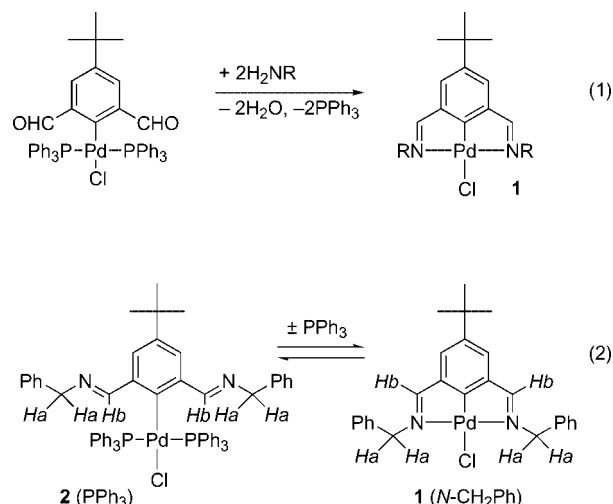
a scale of the coordination ability of various ligands would be achieved. This would provide fundamental and useful information for catalytic as well as organic, inorganic, organometallic, and materials research fields. We would like to propose pincer palladium complex **1** as a novel probe to titrate the coordination ability of various nonchelating ligands to palladium to form palladium complexes $\text{ArPd}(\text{L})_2\text{X}$. Many of these complexes are recognized as key intermediates in various palladium-catalyzed processes (e.g. cross-couplings, the Heck reaction, carbonylation, etc.).

Results and Discussion

We have previously prepared various NCN pincer palladium complexes^[4] by the ligand introduction route [Scheme 1, Equation (1)].^[5] From our detailed studies on the pincer complexation process, we found that intermediate complex **2** was in equilibrium with pincer complex **1**. The coordination–dissociation behavior of the PPh_3 ligand of intermediate complex **2** was observed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and the coordination constant $K_{\text{eq}}(\text{PPh}_3)$ was unambiguously determined by the ^1H NMR spectroscopic measurement of the intramolecular $\text{CH}=\text{NCH}_2\text{Ph}$ ligand groups [*Ha* and/or *Hb* indicated in Scheme 1, Equation (2)]. These observations led us to the conclusion that complex **1** would be a good probe to index the coordination abilities of various ligands. By using probe complex **1**, a wide range of coordination constants (the difference between the highest and lowest constants is 10^{12}) were determined with high accuracy by ^1H NMR spectroscopic measurements, which allowed the relative coordination ability of 27 different ligands to be indexed.

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Scheme 1. Preparation and substitution equilibrium of the pincer complex: (1) ligand introduction route to pincer complexation; (2) ligand substitution equilibrium.

A typical procedure for the equilibria study by NMR spectroscopy for PPh_3 is as follows: Complex **1** was dissolved in CD_2Cl_2 (12.7 mm) at 298 K and PPh_3 (2 mol equiv. to **1**) was added under a nitrogen atmosphere. The resulting mixture was analyzed by ^1H NMR spectroscopy, where the resonances of *Ha* for complexes **2** (phosphane complex) and **1** (pincer complex) were observed at $\delta = 4.50$ and 5.01 ppm, respectively, to provide $K_{eq}(\text{PPh}_3) = 2.06 \times 10^5 \text{ M}^{-2}$ in CD_2Cl_2 (298 K). The coordination constants of 27 ligands obtained by similar NMR spectroscopic experiments are shown in Table 1. Ligands, whose coordination constants could not be determined by the present method because their coordination ability was either too strong or too weak, are also listed in Table 1 to demonstrate the scope and limitation of this system. The coordination constants of $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-2-Me})$, $\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$, $\text{P}[\text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2]_3$, $\text{P}(\text{2-furyl})_3$, $\text{P}(\text{OPh})_3$, pyridine, and AsPh_3 were so small that the VT-NMR spectroscopic studies were performed at lower temperatures to observe both peaks of **1** and **2** (Table 1, Entries 22–28), and their $K_{eq(L)}$ values at 298 K were estimated by a van't Hoff plot (see Supporting Information). The relative coordination ability (RCA) is described in a logarithmic manner, $\log(K_{eq(L)}/K_{eq}(\text{PPh}_3))$, with respect to the value of PPh_3 .

Several representative and/or typical features obtained by this indexation include: (1) The coordination ability of ligands having the same cone angle was strictly determined by their electronic character (vide infra). (2) The coordination constant of AsPh_3 is 10^{10} smaller than that of PPh_3 . (3) $\text{P}(\text{OPh})_3$ exhibits a 10^7 smaller value than that of its carbon analogue $\text{P}(\text{CH}_2\text{Ph})_3$. (4) The order of the coordination ability of phosphane ligands bearing six-membered ring substituents is $\text{PCy}_3 > \text{PPh}_3 > \text{PPh}_2\text{Cy} > \text{PPhCy}_2$.^[6] (5) The coordination ability is significantly affected by the steric bulkiness of the ligand [e.g. PPh_3 versus $\text{PPh}_2\text{Tol-}o$ (Table 1, Entries 9 and 22)]. These features would be difficult to predict without direct observation of the K_{eq} values.

Table 1. Coordination constants of various ligands.^[a]

$\mathbf{1} + 2\text{L} \rightleftharpoons \mathbf{2}(\text{L})$			
Entry	Ligand	$K_{eq(L)} [\text{M}^{-2}]^{[b]}$	RCA ^[c]
1	$\text{P}(n\text{Bu})_3$	N/A	>3
2	$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-4-NMe}_2)$	2.38×10^7	2.06
3	$\text{P}(\text{C}_6\text{H}_4\text{-4-OMe})_3$	1.61×10^7	1.89
4	PCy_3	9.45×10^6	1.64
5	$\text{PhP}(\text{C}_6\text{H}_4\text{-4-OMe})_2$	4.58×10^6	1.35
6	$\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3$	2.20×10^6	1.03
7	$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-4-Me})$	1.04×10^6	0.703
8	$\text{P}(\text{C}_6\text{H}_4\text{-3-Me})_3$	8.15×10^5	0.597
9	PPh_3	2.06×10^5	0.00
10	$\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$	1.52×10^5	−0.132
11	PBN_3	1.27×10^5	−0.210
12	$\text{P}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_3$	1.16×10^5	−0.249
13	$\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3$	1.10×10^5	−0.272
14	Ph_3PCy	9.35×10^4	−0.343
15	$\text{P}(\text{C}_6\text{H}_4\text{-3-OMe})_3$	3.59×10^4	−0.759
16	PhPCy_2	1.63×10^4	−1.10
17	$\text{P}(\text{C}_6\text{H}_4\text{-4-Cl})_3$	1.39×10^4	−1.17
18	$\text{P}(\text{C}_6\text{H}_4\text{-3-Cl})_3$	2.07×10^3	−2.00
19	$\text{P}(\text{C}_6\text{H}_4\text{-3-F})_3$	1.30×10^3	−2.20
20	$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-2-OMe})$	1.73×10^2	−3.08
21	$\text{P}(\text{C}_6\text{H}_4\text{-4-CF}_3)_3$	1.28×10^2	−3.21
22 ^[d]	$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-2-Me})$	5.93	−4.54
23 ^[d]	$\text{Ph}_2\text{P}(\text{C}_6\text{F}_5)$	0.267	−5.89
24 ^[d]	$\text{P}[\text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2]_3$	0.120	−6.23
25 ^[d]	$\text{P}(\text{2-furyl})_3$	8.80×10^{-2}	−6.37
26 ^[d]	$\text{P}(\text{OPh})_3$	2.09×10^{-2}	−7.00
27 ^[d]	Pyridine	1.06×10^{-4}	−9.29
28 ^[d]	AsPh_3	2.49×10^{-5}	−9.92
29	$\text{P}(\text{C}_6\text{H}_4\text{-2-Me})_3$	N/A	<−10
30	$\text{P}(t\text{Bu})_3$	N/A	<−10
31	$\text{CyP}(t\text{Bu})_2$	N/A	<−10
32	$\text{Cy}_2\text{P}(t\text{Bu})$	N/A	<−10
33	$\text{PhP}(\text{C}_6\text{H}_4\text{-2-OMe})_2$	N/A	<−10
34	$\text{P}(\text{C}_6\text{F}_5)_3$	N/A	<−10
35	$\text{PhP}(\text{C}_6\text{F}_5)_2$	N/A	<−10
36	$\text{Cy}_2\text{P}(\text{2-biphenyl})$	N/A	<−10

[a] All titrations were performed by ^1H NMR spectroscopic measurements at 298 K. [b] Average of two or three measurements. [c] $\text{RCA} = \log(K_{eq(L)}/K_{eq}(\text{PPh}_3))$. [d] K_{eq} value was estimated by the van't Hoff plot obtained by VT-NMR spectroscopic experiments (see Supporting Information).

Figure 1 is the Hammett plot for the RCA values of various triarylphosphanes to quantify the electronic effect of the P substituents. Triarylphosphanes with *para* and *meta* monosubstituted aromatic groups having cone angles of 145° show excellent proportionality for the σ values^[7] of the aromatic groups. Thus, the RCA value decreased proportionally as the σ value of the aromatics increased and the RCA– σ relationship exhibits high linearity (Figure 1, black solid line: $R^2 = 0.9925$), which demonstrates the high accuracy of the RCA values measured by the present method. This observation should make the prediction of the RCA value of various triarylphosphane ligands having *para* or *meta* monosubstitution possible by inter-/extrapolation (dotted line), even if the RCA value is out of the measurement range with highly electron-rich or -deficient substituents. The RCA values of triarylphosphane ligands of the 147° cone angle were slightly smaller than those of the plot for the ligands of the 145° cone angle. Thus, $\text{P}(\text{C}_6\text{H}_3\text{-$

3,5-Me₂)₃ and P[C₆H₃-3,5-(CF₃)₂]₃ exhibited RCA values of -0.249 and -6.23, respectively (Table 1, Entries 12 and 24). More sterically demanding ligands gave lower RCA values (Table 1, Entries 20, 22, and 23).

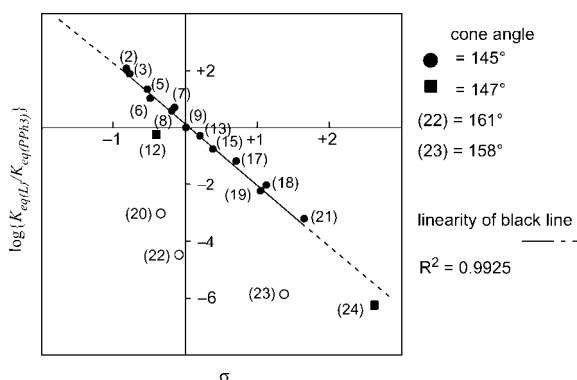


Figure 1. Hammett plot for the RCA values: $\log(K_{eq}(L)/K_{eq}(PPh_3))$ versus Taft's σ value of aromatic substituents of the triarylphosphane ligands. The numbers in parentheses correspond to the entry numbers in Table 1.

Conclusions

We have developed pincer palladium complex **1** as a novel probe for the determination of the coordination ability of various ligands to form $ArPd(L)_2Cl$, with the relative coordination abilities of 27 ligands being determined easily by ¹H NMR spectroscopic experiments. A two-dimensional analysis using probe complexes of different steric demands (with the use of various NR groups), as well as the application of the indexation protocol to ligands bearing other coordination sites, e.g. carbene, S, Sb, etc., are currently underway and will be reported in due course.

Experimental Section

General Equilibria Studies by NMR Spectroscopy: Complex **1** and a ligand (2 equiv.) were dissolved in [D₂]dichloroethane. The equilibrium constant, K_{eq} , was determined by the integration of the resonances: the resonance integration ratio $1/2 = x:y$; $K_{eq} = (1/4)[\{y(x + y)^2\}/x^3][1]_0^2$ (M⁻²). All NMR spectroscopic data (charts, chemical shifts, integration data, etc) are provided in the Supporting Information.

Supporting Information (see footnote on the first page of this article): ¹H NMR spectroscopic data with their measurement conditions for Table 1, Entries 2–28.

Acknowledgments

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- [6] The orders of steric and electronic factors of these phosphane ligands are reverse to each other [steric (small to large): $PPh_3 > PPh_2Cy > PPhCy_2 > PCy_3$; electronic (basicity): $PCy_3 > PPhCy_2 > PPh_2Cy > PPh_3$] and, therefore, the order of their coordination ability is difficult to predict. The spectroscopic direct observation of the coordination ability should be required to determine the order of their coordination ability.
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