Syntheses and Theoretical Study of Palladium(II) Complexes with Aminophosphines as 7-Membered Chelate Rings

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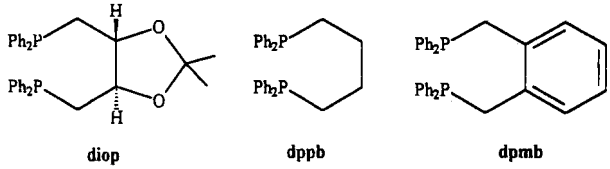
Nature of palladium(II) complexes with 7-membered chelates was studied by experimental and theoretical methods on a $Pd(L)Cl_2$ system, where L is $Ph_2PNHCH_2CH_2NHPPh_2$(L1), $Ph_2PNHC_6H_4NHPPh_2$(L2). The palladium(II) complexes were prepared and characterized by elemental analysis, IR, UV, ^1H, and ^{31}P NMR spectroscopy. *Ab initio* calculations with geometry optimizations were also performed for related model systems, $Pd(L)Cl_2$; L=$R_2PNH(CH_2)_2NHPR_2$(L3), $R_2PNHC_6H_4NHPR_2$(L4), $R_2P(CH_2)_4PR_2$(L5), $R_2PCH_2(C_6H_4)CH_2PR_2$ (L6); R=H, CH_3.

Introduction

Trivalent phosphorus donor ligands, PR_3 play a major role in coordination and organometallic chemistry. Especially, diphosphine complexes of palladium (0 or II) have been widely used in catalytic reactions including hydroformylation,[1] hydrogenation,[2] and C-C coupling.[3] Examples of these catalytic reactions often involve aryl halides activation and Heck reaction,[4] as well as cross-coupling chemistry that forms carbon-carbon bonds. Transition metal catalyzed hydroformylation is one of the most versatile methods for the functionalization of C=C bonds and, consequently, can be used as a very powerful synthetic tool for the preparation of fine chemicals. One special class of carbonylation reaction concerns the co-polymerization of alkenes and carbon monoxide, leading to the formation of polyketones, a reaction which was known to be very efficiently catalyzed by the type $Pd(L)X_2$ (L is a chelating phosphorus[5] or nitrogen ligand,[6] X is a weak or mono coordinating anion). Especially, the transition metal complexes with 7-membered chelate ring have higher optical activity than which have smaller chelate ring in hydroformylation reaction.[7] Transition metal complexes of bidentate phosphine ligands (Scheme 1) with 7-membered chelate such as diop, dppb, and dpmb often show structural and spectroscopic features, as well as reactivity patterns, which differ significantly from those of bidentate phosphines forming smaller chelate.[8]

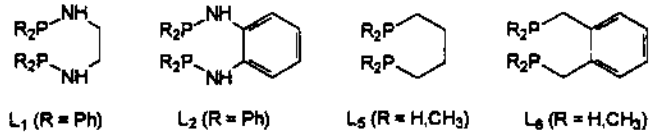
Although there have been a lot of studies for this subject, a systematic study of structure and reactivity relationships in a closely related set of complexes has not appeared. For this purpose, one needs a chelating aminophosphine ligand forming 7-membered chelates which could be easily modified their syntheses and, at same time, would have only limited conformational flexibility.



Scheme 1.

In previous work, the synthesis and spectroscopic properties of the palladium(II) complexes, $[Pd(L)X_2]$ (L=1,2-bis {(diphenylphosphino)amino}propane and *trans*-1,2-bis {(diphenylphosphino)amino}cyclohexane) as well as theoretical study were reported.[9,10]

In this work, in order to understand the nature of the π-effects on aminophosphine, we carried out a combination of experimental and theoretical study. Based on the strong trans effect of the phosphines ligands, and the lability of the Pd-X bond, we have synthesized new palladium(II) complexes, $[Pd(L)X_2]$ which are similar to dppb and dpmb in complex formation. Where, L is $Ph_2PNHCH_2CH_2NHPPh_2$ (L1) and $Ph_2PNHC_6H_4NHPPh_2$ (L2). All of them have been characterized by means of elemental analysis, UV, IR, ^1H and ^{31}P NMR spectroscopy.



The identification of conformational isomer of palladium (II) complex with aminophosphine (L1, L2) were studied by theoretical calculation[10c] due to the limitation of spectrosopic method; in the theoretical study, the calculation was expended to L3, L4, L5 and L6. Also, the quantum chemical value calculated to predict the catalytic activity of palladium(II) complexes. *Ab initio* calculations have been performed on $[Pd(L)Cl_2]$, (L=$R_2PNH(CH_2)_2NHPR_2$ (L3), $R_2PNHC_6H_4NHPR_2$ (L4), $R_2P(CH_2)_4PR_2$ (L5), $R_2PCH_2(C_6H_4)CH_2PR_2$ (L6), R=H, CH_3).

Experiment and Calculation

General. All operations were performed under N_2 atmosphere by vacuum line and Schlenk technique.[11] Solvents were dried and deoxygenated prior to use. Elemental

analyses were performed by a Perkin-Elmer Model 240. IR spectra were recorded on a Perkin-Elmer 1330 and Hitachi 270-50 instrument on a KBr or CsI discs. UV spectra were recorded on a Hitachi 320 UV/vis spectrophotometer in chloroform solution. ^{1}H NMR (reference from TMS) and ^{31}P NMR (reference from external 85% H_3PO_4) were recorded on a Bruker ARX 300 MHz in $CDCl_3$. The ligands were identified by GC/mass (Hewlett Packard 5890 II(GC)/ 5971 A(mass) model by FFAP(Carbox 20) column). Melting points were measured by an electrothermal melting point apparatus.

1,2-Bis{(diphenylphosphino)amino}ethane (L1). To a solution of diaminoethane (0.025 mol in 100 mL benzene), triethylamine (0.05 mol) and chlorodiphenylphosphine (0.05 mol) were added with stirring under a nitrogen atmosphere over a period of 30 min. The mixture was continuously stirred for 12 h at an ambient temperature and the precipitate was filtered off. The crude solution was evaporated under reduced pressure to give an oilly product. Yield 67%. IR (KBr, cm $^{-1}$): 3400-3380 (s), 1185 (s), 1432 (w), 1120 (s).

1,2-Bis{(diphenylphosphino)amino}benzene (L2). was prepared by the same procedure. Yield 58%. IR (KBr, cm^{-1}): 3400-3380 (s), 1434 (w), 1185 (s), 1110 (s).

[1,2-Bis{(diphenylphosphino)amino}ethane]dichloropalladium(II), Pd(L1)Cl$_2$. A solution of L1 (1 mmol, 5 mL benzene) was added to stirred equimolar solution of $Pd(PhCN)_2Cl_2$[12] (1 mmol) in benzene. After 2 h, a pale-yellow precipitate was formed. The product was filtered and dried. The precipitate was recrystallized from CH_2Cl_2 and diethyl ether. Yield 84%. mp 158-159 °C. Anal. calcd. for $Pd(C_{26}H_{26}N_2P_2)Cl_2$: C 51.55, H 4.33, N 4.62. Found: C 51.41, H 4.55, N 4.22. IR (CsI, cm^{-1}): 3405-3380 (s), 1388 (w), 1115s (sh), 1098 (s), 980 (t, s), 288, 282 (m).

[1,2-Bis{(diphenylphosphino)amino}benzene] dichloropalladium(II), Pd(L2)Cl$_2$. The Pd(L2)Cl_2 was prepared in 79% yield by analogous method. mp 162-163 °C. Anal. calcd. for $Pd(C_{30}H_{26}N_2P_2)Cl_2$: C 55.11, H 4.01, N 4.28. Found: C 54.98, H 3.87, N 4.69. IR (CsI, cm^{-1}): 3405-3378 (s), 1118 (s), 1106 (s), 980 (t, s) 294, 288 (m).

Calculation Methods. *Ab initio* molecular orbital calculations have been carried out for the model system [Pd(L)Cl_2] using the Gaussian 94 packages[13] on the Sun SPARC workstation and Intel Pentium Pro processors (200 MHz) under the Linux operation system. Effective core potential (ECP) including relativistic contributions are used to represent 28 innermost (up to 3d) electrons of the Pd atom (LANL1DZ),[14] and standard 3-21G* basis sets are used for other atoms except Cl, where 3-21G basis sets[15] are used because optimized bond length of Pd-Cl (2.3 Å) in Pd (diphosphine)Cl_2 is in good agreement with experimental value.

Results and Discussion

Synthesis and Characterization. A series of potential 7-membered chelating aminophosphine were prepared in high yield by the reaction of diamine with chlorodiphenylphosphine in benzene. These ligands were identified by IR, ^{1}H and ^{31}P NMR spectra, and GC/mass (M^+/z; L1=428, L2=442). The ligands easily form [Pd(L)X_2] by the reaction of ligand with appropriate metal compounds, Pd $(PhCN)_2Cl_2$. The physical and spectroscopic data of a series of the palladium(II) complexes, Pd(L)X_2 are listed in Table 1.

Table 1. Color, ^{1}H, and ^{31}P NMR Data of [Pd(L)Cl_2] Complexes

Compound	Color	^{1}H NMR	δ (^{31}P) ppm
L1	colorless	1.08-1.13 (t, 4H, CH_2), 3.34-3.41 (q, 2H, NH), 7.14-7.25 (m, 20H, C_6H_5)	63.7
L2	colorless	2.47 (s, 2H, NH), 7.16-7.46 (m, 24H, CH & C_6H_5)	93.4
Pd(L1)Cl_2	pale yellow	1.18-1.23 (t, 4H, CH_2), 3.44-3.51 (q, 2H, NH), 7.26-7.75 (m, 20H, C_6H_5)	32.5
Pd(L2)Cl_2	pale yellow	2.57 (s, 2H, NH), 7.27-7.94 (m, 24H, CH & C_6H_5)	79.4

In the IR spectra, all complexes exhibit bands corresponding to the palladium(II) complexes with aminophosphines. In [Pd(L)X_2] complexes, the υ(C-N) frequencies were observed in the range 1098-1106 cm^{-1} as a strong intensity. The υ(C-N) frequencies of the complexes were shifted 10 cm^{-1} to lower frequencies compared to those of the free ligand. The υ(P-N) frequencies were observed at 1114 cm^{-1} for L1 and 1120 cm^{-1} for L2 with medium intensity. These υ(P-N) frequencies of the complexes were shifted about 70 cm^{-1} toward lower frequencies compared to those of the free ligand, and might be overlapped with the υ(C-N) frequency at 1110 cm^{-1}. The two υ(Pd-Cl) frequencies are observed at 288, 282 cm^{-1}, indicating that the complexes have cis configuration. This fact may be related to a decrease in the υ(P-N) and υ(C-N) bond strength upon coordination.[9]

Electronic absorption bands ($^1A_{2g} \leftarrow {}^1A_{1g}$) for both [Pd(L)$Cl_2$] complexes are observed in 335 nm (L1), 340 nm (L2), respectively. The variation in the absorption maxima and extinction coefficient for complexes were similar to that of palladium(II) complexes Pd(L)Cl_2 with $Ph_2PNHCH(CH_3)CH_2NHPPh_2$.[9]

The ^{1}H NMR of the free ligands and the complexes were measured to get information about the binding site and structural changes. The changes of chemical shift ($\delta_{complex}$-δ_{ligand}) for each proton are shown in table 1 for comparision. Most resonances are shifted about 0.1 ppm towards down-field, phenyl proton signals are shifted about 0.4 ppm. These results are consistent with phosphorus atom coordinated to Pd(II).

Furthermore, the proton decoupled ^{31}P NMR spectra of free ligands display only one signal, 63.7 ppm for L1 and 93.4 ppm for L2. And, those of both palladium(II) complexes as well as Pd(L)Cl_2 show a signal at 32.5 (L1), 79.4 ppm (L2), which is indicating that the complexes have *cis* configuration. In the Pd(L)Cl_2 complexes, these signals are shifted to up-field by about 31.2 ($\Delta\delta$, L1) and 14.0 ($\Delta\delta$, L2) ppm which are in consistent with their structural differences. The differences in the chemical shift are probably due to the fact that the electron density of P atom in Pd(L1)Cl_2 complex is shifted to Pd atom. The extent of this electron

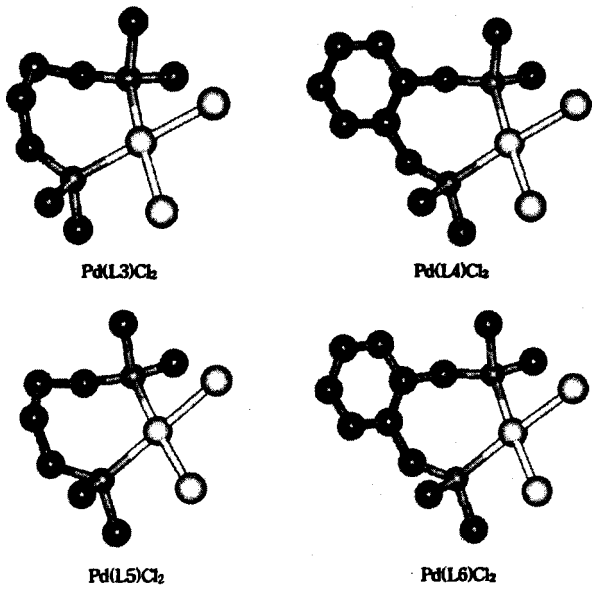


Figure 1. Optimized structures of $Pd(L)Cl_2$ complexes.

shift may be more effective in the $Pd(L1)Cl_2$ complex compared to $Pd(L2)Cl_2$, resulting higher up-field shift. This result indicates that the more basic N lone pairs of L1 (sp^3 hybrid) make the phosphrous atom a better donor on the coplanar phosphrous atom than L2 (sp^2 hybrid).

Optimized Geometries. When 7-membered chelate ligand is coordinated to metal, the molecular models for *cis*-$Pd(L)Cl_2$ complexes indicate that chelate ring can exist in four different conformations.[15] The most stable conformer of all palladium complexes $Pd(L)Cl_2$ are depicted in Figure 1. The optimized molecular model in ground state is pseudo-boat (C_s) type conformer on the $Pd(L3)Cl_2$ and $Pd(L5)Cl_2$ complexes. But, the molecular model of $Pd(L4)Cl_2$ and Pd (L6)Cl_2 show that the more stable conformer is one where Pd, P and N-atom(L4) (or C-atom(L6)) of chelated group are nearly coplanar, while the benzene ring are bent from this plane. These results are good agreement with EHMO calculation results[10c] and the X-ray structure of well known $Rh(Ph_2PNHCH(C_4H_8)CHNHPR_2)(COD)PF_6$ and $Pt(L6)(C_2H_4)X_2$.[16]

The optimized geometrical parameters for the palladium (II) complexes, $Pd(L)Cl_2$ (L is $R_2PNH(CH_2)_2NHPR_2$ (L3), $R_2PNHC_6H_4NHPR_2$ (L4)) are shown in Figure 2. For comparison, the results of $R_2P(CH_2)_4PR_2$ (L5) and $R_2PCH_2(C_6H_4)CH_2PR_2$ (L6) analogs have also shown in the figure.

As shown in Figure 2, the P-Pd-P bond angles of chelating diphosphine ligands are 99.28° (H) and 99.23° (CH_3) for L3, 99.84° (H) and 99.27° (CH_3) for L4, 100.52° (H) and 100.58° (CH_3) for L5, 100.68° (H) and 100.39° (CH_3) for L6, respectively. These optimized bite angles are similar to those of L6 coordinated Pt complexes,[16] $[Pt(L6)(C_2H_4)]^{2+}$. Whereas the Cl-Pd-Cl chelation angle is just over 90° in all $Pd(L)Cl_2$.

The Pd-P distances are 2.25 Å (H) and 2.26 Å (CH_3) for L3, 2.24 Å (H) and 2.27 Å (CH_3) for L4, 2.25 Å (H) and 2.28 Å (CH_3) for L5, 2.27 Å (H) and 2.29 Å (CH_3) for L6, respectively. These values are quite close to experimental average values (exemplified by 2.2 Å for $Pd(L)Cl_2$, L is dpe, dpp[17]). The Pd-P bond distances of 2.23-2.28 Å are in the

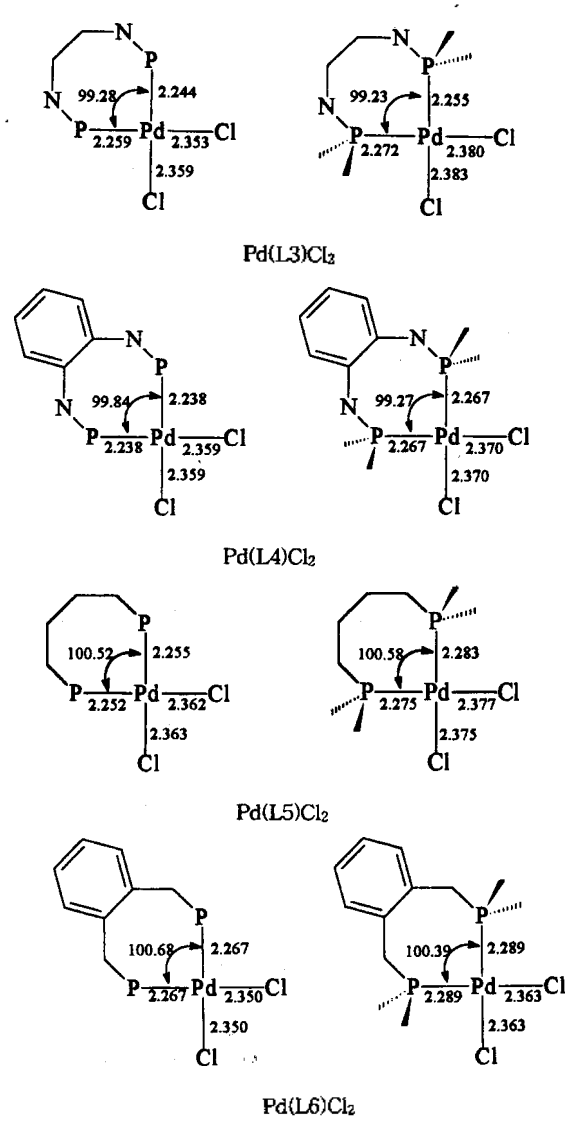


Figure 2. Optimized geometries of $Pd(L)Cl_2$ systems at the HF/ECP level. Geometrical parameters are given in angstroms and degrees.

normal range for *cis*-chelated phosphorus.

When the aminophosphine coordinated to palladium(II) atom, the Pd-Cl distances are 2.35-2.38 Å in $Pd(L3)Cl_2$ and 2.37 Å in $Pd(L4)Cl_2$, respectively, whereas in Pd (diphosphine)Cl_2 these distances are 2.35-2.37 Å. The Pd-Cl bond is obviously sensitive to the nature of the *trans* atom as seen in the Figure 2. The Pd-Cl bond is longer when aminophosphines is trans coordinated than diphosphines coordinated complexes.

According to the aminophosphine (L3 and L4) complex change to diphosphine (L5 and L6) complex, we can see that the average value of Pd-P distance increases from 2.24 Å (H), 2.26 Å (CH_3) to 2.26 Å (H), 2.28 Å (CH_3), while the Pd-Cl distance decreases from 2.36 Å (H), 2.38 Å (CH_3) to 2.35 Å (H), 2.37 Å (CH_3). The longer Pd-Cl bond in aminophosphine complexes is *trans* to the shorter Pd-P bond which is in agreement with a trans effect.

These results suggest that the basic nitrogen lone pairs make the phosphorous atom better donor on the coplanar

Table 2. The Energies (in Hartrees) and Mulliken Charges for $[Pd(L)Cl_2]$ Systems

$Pd(L)Cl_2$		Energy	net charge				
			Pd	P	P	Cl	Cl
L3	H (C_s)	−1811.4579	0.581	0.445	0.419	−0.558	−0.559
$R_2PNH(CH_2)_2NHPR_2$	CH_3 (C_s)	−1966.8123	0.530	0.986	0.978	0.565	0.569
L4	H (C_2)	−1961.9736	0.593	0.439	0.439	−0.559	−0.559
$R_2PNH(C_6H_4)NHPR_2$	CH_3 (C_2)	−2117.3294	0.535	1.032	1.032	−0.585	−0.585
L5	H (Cs)	−1779.6308	0.625	0.215	0.225	−0.527	−0.524
$R_2P(CH_2)_4PR_2$	CH_3 (Cs)	−1934.9796	0.602	0.788	0.791	−0.552	0.557
L6	H (C_2)	−1930.1463	0.624	0.282	0.282	−0.546	−0.546
$R_2PCH_2(C_6H_4)CH_2PR_2$	CH_3 (C_2)	−2085.4952	0.587	0.857	0.857	−0.572	−0.572

phosphorus atom and the formation of π-bond by back bonding form the metal.

Atomic Charges. The electronic distribution of substituted methyl group bound to a phosphorus atom shows to be very sensitive to changes in the ligating atoms coordinated to phosphorus. This sensitivity should reflect the atomic charges of the trans coordinated chlorine atoms. An accurate calculation of these charges, therefore, seems to be necessary. The electronic effects on the experimental systems have been evaluated through *ab initio* MO calculations on the $Pd(L)Cl_2$ system. As shown in Table 2, in the $Pd(L)Cl_2$ systems, Mulliken atomic charges of constituent atoms (Pd, P and Cl) are different when coordinated ligands are aminophosphine and diphosphines. As expected, in all the systems considered, when aminophosphine coordinated to Pd atom, atomic charges on Pd atom are lower than diphosphine complexes. The atomic charges on Cl atom are more negative than those of diphosphine complexes. These results indicate that the electronic density for diphosphine complexes ($[Pd(L5)Cl_2]$ and $[Pd(L6)Cl_2]$) are more concentrated on Pd atom than aminophosphine coordinated complexes ($[Pd(L3)Cl_2]$ and $[Pd(L4)Cl_2]$). The tendency of decreasing in these values is in good agreement with EHMO results.[10c] These differences in the elctronic density are probably due to the fact that the basic N lone pairs make the phosphorus a better donor on the coplanar phosphorus atom.

The peculiar behavior of the complexes with diphosphines ligands seems to be associated with their relatively large bite angles observed for the $Pd(L)Cl_2$ complexes with dppb, diop and dpmb ligands. Optimal bite angles determined (around 100°) of the present complexes are clearly different from that around 80° computed for Pd(dppe)Cl_2 complex with smaller chelate. From these results, we concluded that aminophosphine ligand exerts a stronger *trans* influence than the dppb ligand, and therefore, $Pd(L)Cl_2$ complexes may be used as catalyst in various organic syntheses such as the co-polymerization of olefin and CO.

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References

1. (a) van Leeuwen, P. W. N. M.; Roobeek, C. F.; van der Heijden, H. *J. Am. Chem. Soc.* **1994**, *116*, 12117. (b) Mandai, T.; Matsumoto, T.; Tsujiguchi, Y.; Matsuoka, S.; Tsuji, J. *J. Organomet. Chem.* **1994**, *473*, 343. (c) Mandai, T.; Tsufiguchi, Y.; Tsuji, J.; Saito, S. *J. Am. Chem. Soc.* **1993**, *115*, 5865. (d) Mandai, T.; Suzuki, S.; Ikawa, A.; Murakami, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1991**, *32*, 7687. (e) Tolman, C. A. *Chem. Rev.* **1975**, *77*, 313.
2. (a) Collman, J. P.; Roper, W. R. *J. Organomet. Chem.* **1968**, *7*, 54. (b) Fitton, P.; Johnson, M. P.; Mckeon, J. E. *Chem. Commun.* **1969**, 6. (c) Malatesta, L.; Cenini, S. *Zerovalent Compounds of Metals*; Academic Press: New York, U. S. A., 1974.
3. (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. (c) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (d) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030. (e) van Asselt, R.; Elsevier, C. J. *Organometallics* **1994**, *13*, 1972.
4. (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, U. S. A., 1985. (b) Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 327. (c) Schoenberg, A.; Bartolrtti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (d) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761.
5. (a) Milani, B.; Vicentini, L.; Sommazzi, A.; Garbassi, F.; Chiarparin, E.; Zangrando, E.; Mestroni, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3139. (b) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.
6. (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436; *ibid.* *118*, 4748 ref. cit. therein. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) van Asselt, R.; Gielens, E. C. G.; Rulke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977. (d) Rulke, R. E.; Kaasjager, V. E.; Elsevier, C. J.; van Leeuwen, P. W. E. N. M.; Vrieze, K. *Organometallics* **1996**, *15*, 668.
7. Scrivanti, A.; Botteghi, C.; Toniolo, L.; Berton, A. *J. Organomet. Chem.* **1988**, *344*, 261, & ref. cit. therein.
8. (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432. (b) Palenik, G. J.; Mathew, M.; Steffen, W. L.; Beran, G. *J. Am. Chem. Soc.* **1975**, *97*, 1059. (c) Carrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
9. (a) Doh, M. K.; Kim, B. G. *J. Korean Chem. Soc.* **1983**, *27*, 255. (b) Doh, M. K.; Kim, B. G. *Bull. Korean Chem. Soc.* **1988**, *9*, 198.
10. (a) Doh, M. K.; Kim, B. G.; Jung, M. J.; Song, Y. D.;

Park, B. K. *J. Korean Chem. Soc.* **1993**, *37*, 431. (b) Doh, M. K.; Kim, B. G.; Jung, M. J.; Song, Y. D.; Park, B. K. *J. Korean Chem. Soc.* **1993**, *37*, 903. (c) Kim, B. G.; Yang, K.; Jung, M. J.; Doh, M. K. *J. Korean Chem. Soc.* **1994**, *38*, 456.
11. Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-sensitive Compounds*; John Wiley & Sons: U. S. A., 1986.
12. Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.
13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Comperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Gaussian Inc.; Pittsburgh, PA, 1995.
14. (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
15. Hanack, M. *Conformational Theory*; Academic Press: U. S. A. 1965; pp 158-162.
16. Camalli, M.; Caruso, F.; Chaloupka, S.; Leber, E. M.; Rimml, H.; Venanzi, L. M. *Helv. Chim. Acta* **1990**, *73*, 2263.
17. (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *10*, 2432. (b) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, *14*, 1110. (c) Onuma, K.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 761.

A New Functional Model of Catechol Dioxygenases: Properties and Reactivity of [Fe(BLPA)DBC]BPh_4

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[Fe^{III}(BLPA)DBC]BPh_4, a new functional model for the catechol dioxygenases, has been synthesized, where BLPA is bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine and DBC is 3,5-di-*tert*-butylcatecholate dianion. The BLPA complex has a structural feature that iron center has a six-coordinate geometry with N_4O_2 donor set. It exhibits EPR signals at g=5.5 and 8.0 which are typical values for the high-spin Fe^{III} (S=5/2) complex with axial symmetry. The BLPA complex reacts with O_2 within a few hours to afford intradiol cleavage (75%) and extradiol cleavage (15%) products which is very unique result of all [Fe(L)DBC] complexes studied. The iron-catecholate interaction of BLPA complex is significantly stronger, resulting in the enhanced covalency of the metal-catecholate bonds and low energy catecholate to Fe^{III} charge transfer bands at 583 and 962 nm in CH_3CN. The enhanced covalency is also reflected by the isotropic shifts exhibited by the DBC protons, which indicate increased semiquinone character. The greater semiquinone character in the BLPA complex correlates well with its high reactivity towards O_2. Kinetic studies of the reaction of the BLPA complex with 1 atm O_2 in CH_3OH and CH_2Cl_2 under pseudo-first order conditions show that the BLPA complex reacts with O_2 much slower than the TPA complex, where TPA is tris(2-pyridylmethyl)amine. It is presumably due to the steric effect of the methyl substituent on the pyridine ring. Nevertheless, both the high specificity and the fast kinetics can be rationalized on the basis of its low energy catecholate to Fe^{III} charge transfer bands and large isotropic NMR shifts for the BLPA protons. These results provide insight into the nature of the oxygenation mechanism of the catechol dioxygenases.

Introduction

The catechol dioxygenases are non-heme iron enzymes that catalyze the oxidative cleavage of catechols and serve as part of nature's strategy for degrading aromatic molecules in the environment.[1] They are found in soil bacteria with two different types: one is intradiol-cleaving enzymes utilize Fe(III), and the other is extradiol-cleaving enzymes utilize Fe(II) and Mn(II). Significant progress[2-7] has been made in understanding the active site of the intradiol cleaving enzymes and is highlighted by the recent solution of the crystal structure of native protocatechuate 3,4-dioxygenase(3,4-PCD) showing that the iron(III) center of the active site of 3,4-PCD enzyme has five-coordinate geometry.[8] Furthermore, many spectroscopic studies suggested that the iron(III) center remains as a five-coordinate system even after binding with substrate catechol.[9,10] Model systems that mimic enzyme reactions are important mechanistic tools, because the flexibility in ligand design allows a systematic investigation of the important factors affecting reactivity as well as reac-