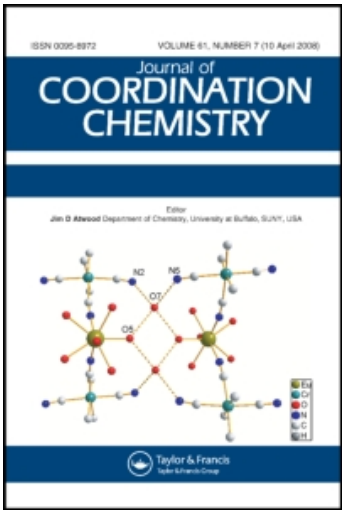

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SYNTHESIS AND SOLUTION NMR-STUDIES OF THE TRIS(3,5-DIMETHYLPYRAZOL-1-YL) HYDROBORATOPALLADIUM(II) COMPLEX, Pd{(pz*)$_3$BH}(PPh$_3$)CI

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SYNTHESIS AND SOLUTION NMR-STUDIES OF THE TRIS(3,5-DIMETHYLPYRAZOL-1-YL) HYDROBORATOPALLADIUM(II) COMPLEX, Pd{(pz*)$_3$BH}(PPh$_3$)Cl

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The sterically hindered tris(3,5-dimethylpyrazol-1-yl)hydroborate complex of palladium, Pd{(pz*)$_3$BH}(PPh$_3$)Cl (**1**) has been prepared by the stepwise reaction of $(CH_3CN)_2PdCl_2$ with K{(pz*)$_3$BH}, and then PPh$_3$. The complex **1** has been fully characterized by microanalysis and various spectroscopic methods. A solution NMR study of **1** revealed that two pz* groups of the {(pz*)$_3$BH} ligand coordinate to palladium in *cis* positions, while the remaining group is not coordinated. VT NMR experiments have been performed to determine that signal broadening of the phenyl proton resonances in the ^{1}H-NMR spectrum is likely attributed to restricted rotation of the coordinated PPh$_3$ within the congested complex on the NMR time scale. Complex **1** was metastable in solution towards reaction with water to decompose into several uncharacterized species, in which a facile hydrolytic cleavage of the B–H bond proceeded as judged by IR and ^{1}H-NMR spectra of the products. Reaction of **1** with PPh$_3$ in $CDCl_3$ exclusively yielded *cis*-$PdCl_2(PPh_3)_2$, implicating a chlorine abstraction from the solvent.

Keywords: Tris(3,5-dimethylpyrazol-1-yl)hydroborate palladium; Solution NMR-studies; Chlorine abstraction; Catalytic hydrogenation; Oxidative dehydrogenation

INTRODUCTION

Poly(pyrazolyl)borate complexes of the group 10 metals, nickel triad, are of interest not only because of their stereochemical features in coordination

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chemistry but because of relevance to catalysis in hydrogenation and oxidative dehydrogenation reactions [1–3]. Thus, a few examples of such complexes have recently been reported by several research groups [3–6]. The stereochemistry and coordination behavior of poly(pyrazolyl)borate derivatives with these metals vary depending not only on the ligand features but also on the oxidation states of the metal. Recently, a series of four-coordinate nickel(II) and palladium(II) complexes having the bulky bis- and tris-(3-tert-butylpyrazolyl)borate ligands were reported, in which the ligands adapt only one coordination site [5]. It is noted, however, that the bis- and tris-(pyrazolyl)borates bearing less bulky groups complex with divalent palladium and platinum in a bidentate mode [6]. Recently diorganopalladium(II) and platinum(II) complexes having the tris(pyrazolyl)borate ligand were reported to undergo oxidative addition reactions to generate stable tetravalent metal hydride complexes [3]. In these oxidized derivatives, all pyrazolyl groups of tris(pyrazolyl)borate occupy three sites of the metal coordination sphere as a tripodal ligand, resulting in the formation of octahedral geometry. Indeed, such complexes are considered as intermediates in catalytic hydrogenation of unsaturated substrates, particularly involving organopalladium species. Of relevance to the significant roles of palladium species in many catalytic reactions, we report a novel palladium(II) complex containing tris(3,5-dimethylpyrazol-1-yl)hydroborate, $\{(pz^*)_3BH\}^-$, in which two pz* groups coordinate to palladium in *cis* positions, while the remaining group is not coordinated.

EXPERIMENTAL

All preparations of air sensitive compounds were carried out on a standard Schlenk line or in an inert atmosphere glove box under argon. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen, and then stored over molecular sieves. *n*-Hexane was distilled from sodium/benzophenone ketyl with tetraglyme (tetraethylene glycol dimethyl ether). CH_2Cl_2 was dried by refluxing over sodium hydride under nitrogen. The compounds $K\{(pz^*)_3BH\}$ and $(CH_3CN)_2PdCl_2$ were prepared according to literature methods [7]. All other reagents were from various commercial companies and used as supplied.

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets. ^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$- and $^{11}B\{^1H\}$-NMR spectra were measured on a Varian Gemini 2000 spectrometer equipped with a temperature controller, using the deuterium signal of the solvent as

an internal lock frequency. Chemical shifts for ^1H and $^{13}C\{^1H\}$-NMR are reported in ppm (δ) relative to TMS. Chemical shifts for $^{31}P\{^1H\}$- and $^{11}B\{^1H\}$-NMR were measured in ppm relative to external 85% H_3PO_4 and $BF_3 \cdot OEt_2$ (sealed capillary), respectively. In the VT NMR experiments, temperature calibrations have been performed using methanol and ethyleneglycol at low and high temperatures, respectively. Elemental analysis was performed at the Korea Basic Science Institute in Seoul, Korea.

Preparation of Tris(3,5-dimethylpyrazol-1-yl)hydroboratopalladium(II) Complex, Pd{(pz*)$_3$BH}(PPh$_3$)Cl

A mixture of $(CH_3CN)_2PdCl_2$ (100 mg, 0.385 mmol) and K{(pz*)$_3$BH} (130 mg, 0.385 mmol) was stirred in CH_2Cl_2 (20 mL) for 6 h. The color of the suspension gradually changed from orange to brownish-orange. To the resulting brownish suspension was added a dichloromethane solution of PPh_3 (101 mg, 0.385 mmol) dropwise. The reaction mixture was stirred for an additional 12 h, resulting in a tan solution. The solution was filtered to remove a small amount of black solid formed during the course of the reaction. The solution volume was reduced to ca. 3 mL. Addition of *n*-hexane to the concentrated solution gave tan precipitates, which were isolated by filtration. The $^{31}P\{^1H\}$-NMR spectrum of this crude product revealed that Pd{(pz*)$_3$BH}(PPh$_3$)Cl was formed as a major product (ca. 86%) along with a minor product of *cis*-$Pd(PPh_3)_2Cl_2$ (ca. 14%). The analytically pure compound Pd{(pz*)$_3$BH}(PPh$_3$)Cl was isolated from CH_2Cl_2/*n*-hexane by fractional recrystallization; Pd{(pz*)$_3$BH}(PPh$_3$)Cl is much more soluble than *cis*-$Pd(PPh_3)_2Cl_2$ in CH_2Cl_2. Yield 147 mg (54%). IR: ν(BH) = 2502 cm^{-1} (w, br). ^1H-NMR ($CDCl_3$): δ1.51 *s* (3H, CH_3), δ 1.85 *s* (3H, CH_3), δ 2.01 *s* (3H, CH_3), δ 2.30 *s* (3H, CH_3), δ 2.52 *s* (3H, CH_3), δ 2.67 *s* (3H, CH_3), δ 5.63 *s* (1H, CH(Tp*)), δ 5.72 *s* (1H, CH(Tp*)), δ 5.86 *d* (1H, CH(Tp*); ^5J(PH) = 1.40 Hz), δ 6.9–7.5 *m* (15H, phenyl), δ 15.6 br (1H, BH). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 21.9 *s*. $^{11}B\{^1H\}$-NMR ($CDCl_3$): δ −5.91 *s*. $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 11.1 (CH_3), δ 11.8 (CH_3), δ 13.1 (CH_3), δ 15.0 (CH_3), δ 107.9 (pz*), δ 108.4 (pz*), δ 109.7 (pz*), δ 128, 135 br (Ph). Anal. Calcd. for $C_{33}H_{37}BClN_6PPd$(%): C, 56.51; H, 5.32; N, 11.98. Found: C, 56.14; H, 5.10; N, 12.06.

Reaction of Pd{(pz*)$_3$BH}(PPh$_3$)Cl with PPh$_3$ in $CDCl_3$ to Give *cis*-Pd(PPh$_3$)$_2$Cl$_2$

To a $CDCl_3$ solution of Pd{(pz*)$_3$BH}(PPh$_3$)Cl was added an excess of PPh_3. *cis*-$Pd(PPh_3)_2Cl_2$ was slowly formed in solution as evidenced by

^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. After 48 h, Pd{(pz*)$_3$BH}(PPh$_3$)Cl completely disappeared to give *cis*-Pd(PPh$_3$)$_2$Cl$_2$, exclusively. For *cis*-Pd(PPh$_3$)$_2$Cl$_2$, ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 23.7 *s*.

RESULTS AND DISCUSSION

A stepwise addition of K{(pz*)$_3$BH} and then PPh$_3$ into a CH_2Cl_2 solution of $(CH_3CN)_2PdCl_2$ afforded Pd{(pz*)$_3$BH}(PPh$_3$)Cl (**1**) (Scheme 1). Our initial attempt at preparation of a palladium tris(3,5-dimethylpyrazolyl)borate complex from the reaction of a stoichiometric mixture of $(CH_3CN)_2PdCl_2$ and K{(pz*)$_3$BH} was unsuccessful, resulting in the formation of several uncharacterized species. Thus, we employed an equimolar amount of triphenylphosphine as a supporting ligand. When a stoichiometric mixture of $(CH_3CN)_2PdCl_2$ and K{(pz*)$_3$BH} was stirred in CH_2Cl_2, an orange suspension was gradually, though very slowly, changed to a brownish-orange solution. After 6 h, slow addition of an equimolar amount of PPh$_3$ in CH_2Cl_2 into this solution afforded the tris(3,5-dimethylpyrazol-1-yl)hydroborate complex of palladium(II), Pd{(pz*)$_3$BH}(PPh$_3$)Cl (**1**), along with a minor amount of *cis*-Pd(PPh$_3$)$_2$Cl$_2$ (see Experimental). The reaction afforded only two products as evidenced by ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. We found that the rapid addition of PPh$_3$ afforded *cis*-Pd(PPh$_3$)$_2$Cl$_2$ as a predominant product. Reacting a mixture of $(CH_3CN)_2PdCl_2$, K{(pz*)$_3$BH} and PPh$_3$ at the same time also produced mainly *cis*-Pd(PPh$_3$)$_2$Cl$_2$. The analytically pure compound Pd{(pz*)$_3$BH}(PPh$_3$)Cl in 54% overall yield was obtained by fractional recrystallization of the two products from CH_2Cl_2/*n*-hexane. Column chromatographic separation of the crude products was unsuccessful due to decomposition of Pd{(pz*)$_3$BH}(PPh$_3$)Cl on silica gel (*vide infra*).

The complex Pd{(pz*)$_3$BH}(PPh$_3$)Cl (**1**) has been fully characterized by microanalysis and various spectroscopic methods. In the ^{1}H-NMR spectrum (Fig. 2), the BH resonance was observed far downfield at δ 15.6 as a broad signal (IR: ν(BH) = 2502 cm^{-1} (w, br)). This observed large downfield shift is likely due to inductive effects of the 3,5-dimethylpyrazolyl groups attached to boron as well as due to a ring-shift effect upon chelation

$$Pd(CH_3CN)_2Cl_2 + K\{(pz^*)_3BH\} \xrightarrow[CH_2Cl_2]{-KCl} \xrightarrow{PPh_3} Pd\{(pz^*)_3BH\}(PPh_3)Cl$$

SCHEME 1

on palladium [8]. The six methyl groups attached to the 3,5-positions of the pyrazolyl rings are all magnetically inequivalent, exhibiting six singlet-resonances at δ 1.51, δ 1.85, δ 2.01, δ 2.30, δ 2.52 and δ 2.67, respectively. This observation implies that all three 3,5-dimethylpyrazolyl groups are in different geometric environments around the coordination sphere. This stereochemical feature can be supported by the observation of three inequivalent 4-H resonances of the 3,5-dimethylpyrazolyl rings, which appeared at δ 5.63, δ 5.72 and δ 5.86, respectively. Two at δ 5.63 and δ 5.72 appeared as singlets, while the other signal at δ 5.86 appeared as a doublet with a very small $^5J(\mathrm{PH}) = 1.40\,\mathrm{Hz}$ [9]. The 3,5-dimethylpyrazolyl group corresponding to this doublet 4-H resonance can be assigned as being coordinated on palladium *trans* to the PPh_3 ligand, while another group is *trans* to the chloro ligand and the other one is uncoordinated; for the methyl resonances mentioned above, the two resonances observed at δ 2.01 and δ 2.67 are relatively broad ($\Delta\nu_{1/2} \cong 4.0-5.3\,\mathrm{Hz}$) compared to the others ($\Delta\nu_{1/2} \cong 1.4-1.9\,\mathrm{Hz}$), thus being assignable to the uncoordinated 3,5-dimethylpyrazolyl group (Figs. 1 and 2). The $^{11}B\{^1H\}$-NMR spectrum of **1** shows single resonance at $\delta - 5.91$. Recent study for tris(3,5-dimethylpyrazolyl)borate (Tp*) complexes have demonstrated that both the ^{11}B-NMR chemical shift and the ν(BH) can be used to assign the hapticity

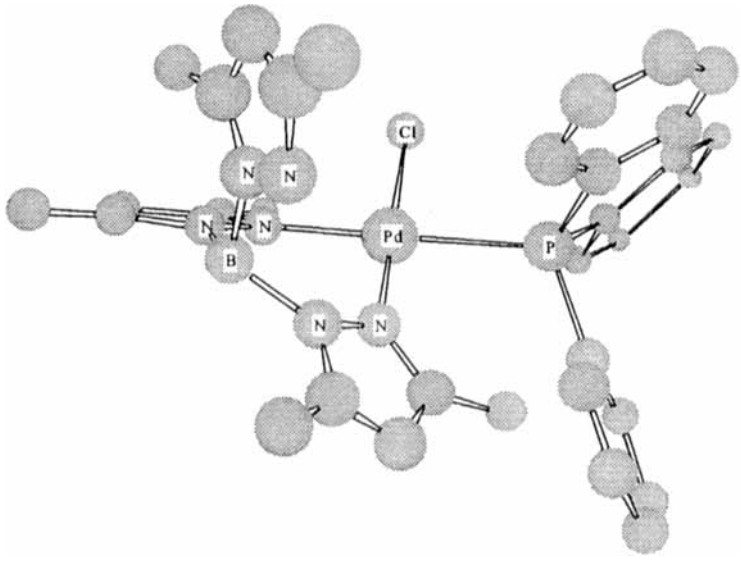


FIGURE 1 3-D Molecular structure of $Pd\{(pz^*)_3BH\}(PPh_3)Cl$ (1) optimized using a CS Chem3D molecular modeling program.

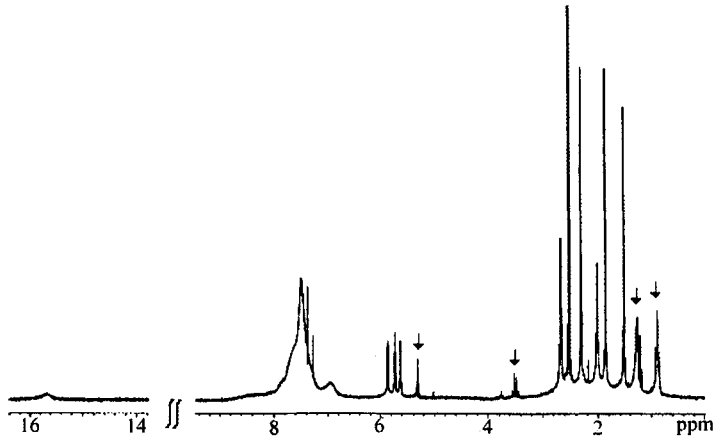


FIGURE 2 ^{1}H-NMR spectrum of Pd{(pz*)$_3$BH}(PPh$_3$)Cl (**1**) in $CDCl_3$ at ambient temperature. The arrows denote solvents peaks of CH_2Cl_2, diethyl ether and *n*-hexane.

of Tp* ligands [10]. In the study, η^2-Tp* complexes show ^{11}B-NMR resonances between $\delta -5.9$ and -7.0, while resonances for complexes having η^3-Tp* ligands appear between $\delta -8.4$ and -9.8. Thus the ^{11}B-NMR resonance at $\delta -5.91$ for the present complex **1** is consistent with η^2-coordination of the Tp* ligand as previously observed by Jones. The B–H stretching frequency of **1** is 2502 cm^{-1} (in KBr), which is in the borderline between 2476 cm^{-1} (the upper limit value for η^2-Tp* complexes) and 2521 cm^{-1} (the lower limit value for η^3-Tp* complexes) [10]. This high-energy shift of the ν(BH) for the complex **1** can be ascribed to the electron rich palladium center. Recent X-ray crystal structures for bidentate tris(pyrazolyl)borate complexes of palladium(II) revealed that the uncoordinated pyrazolyl group lies above the coordination plane [6b].

All the phenyl protons of the coordinated PPh$_3$ in the ^{1}H-NMR spectrum of **1** were observed as very broad signals ($\Delta\nu_{1/2} \cong 28-33$ Hz) in the range of δ 6.9–7.5 (Fig. 2). A notable phenomenon observed for the prominent signal broadening of the phenyl protons, while all proton signals of the 3,5-dimethylpyrazolyl groups were relatively sharp, implicates that the palladium complex is structurally non-rigid in solution. This prominent signal broadening is presumably due to restricted free rotation of the coordinated PPh$_3$ within the congested complex, which occurs moderately faster than the NMR time scale at ambient temperature [11]. We think that this feature is not attributable to a strong interaction of the free 3,5-dimethylpyrazolyl group (the uncoordinated one) with palladium, thereby altering the stereochemical environment of the coordination sphere because

the $^{31}P\{^1H\}$-NMR resonance of the complex displayed a relatively sharp single peak at δ 21.9 ($\Delta\nu_{1/2} \cong 9$ Hz). In the $^{13}C\{^1H\}$-NMR spectrum of **1**, all the phenyl carbons also appeared as broad resonances at δ 128 and δ 135 ($\Delta\nu_{1/2} \cong 46-84$ Hz), while the carbon-signals of the 3,5-dimethylpyrazolyl groups are relatively sharp ($\Delta\nu_{1/2} \cong 10-13$ Hz).

In order to investigate the dynamic processes of **1** in solution, VT-NMR experiments were performed. At temperatures up to 70°C, no signal change of **1** in the ^1H-NMR spectrum in $CDCl_3$ was observed. However, at low temperatures, the broad signals in the phenyl region started to resolve around 0°C, and cleanly resolved into several multiplets at -10°C as shown in Figure 3.

Complex **1** was metastable in solution to react with water to decompose into several species, displaying a couple of signals around δ 21.5 in the $^{31}P\{^1H\}$-NMR spectrum. Although these species were not fully characterized, a facile hydrolytic cleavage of the B–H bond was likely involved in the reaction as judged by the observation of no characteristic B–H peaks in the IR and ^1H-NMR spectra of the products. When we attempted the synthesis of **1** in acetone instead of using dry CH_2Cl_2 as a solvent, we obtained similar decomposed species as evidenced by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy. It is also worth noting that attempts at column chromatographic separation

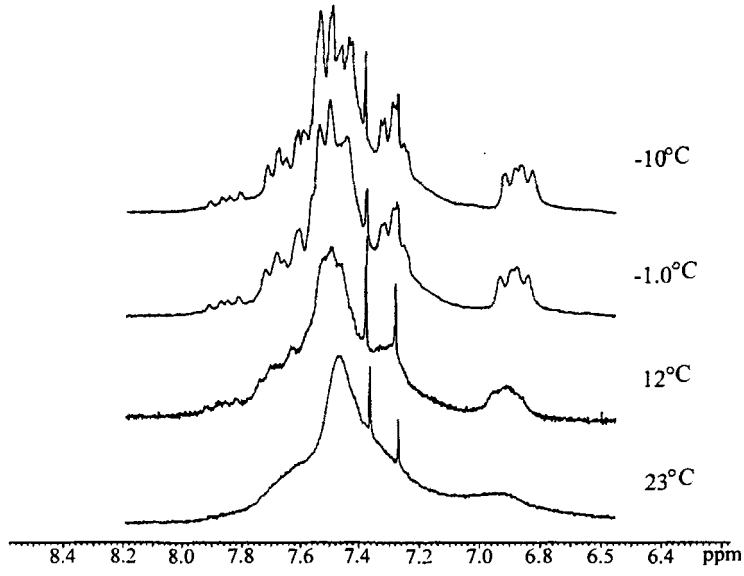
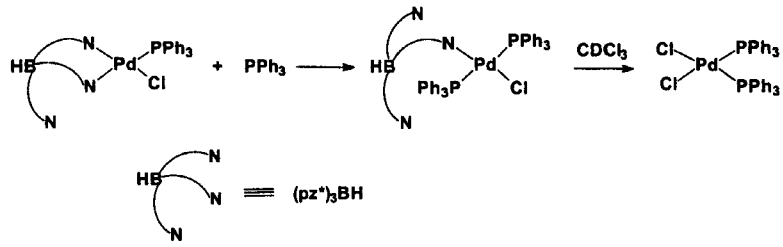


FIGURE 3 VT ^1H-NMR spectra of $Pd\{(pz^*)_3BH\}(PPh_3)Cl$ (**1**) in $CDCl_3$ shown in the phenyl protons region.



SCHEME 2 A plausible reaction pathway for the formation of *cis*-$Pd(PPh_3)_2Cl_2$ from the reaction of **1** and PPh_3 in $CDCl_3$.

of the crude products obtained from the preparation of **1** in dry CH_2Cl_2 resulted in comparable decomposition species (*vide supra*).

Reaction of **1** with PPh_3 in $CDCl_3$ yielded *cis*-$PdCl_2(PPh_3)_2$, exclusively. The formation of *cis*-$PdCl_2(PPh_3)_2$ has been confirmed by its independent synthesis from the reaction of $(CH_3CN)_2PdCl_2$ with two equivalents of PPh_3, exhibiting a single resonance at δ 23.7 in the $^{31}P\{^1H\}$-NMR spectrum. No decomposed palladium species has been observed in the solution, indicating that chlorine abstraction from $CDCl_3$ was involved in the reaction [12]. Similar results have been obtained in other chlorinated solvents such as CCl_4 and CD_2Cl_2. The observed rate for the formation of the palladium dichloride was in the order of $CCl_4 > CDCl_3 > CD_2Cl_2$. The percentage of the product formed from the reaction of **1** with PPh_3 (ca. two equivalents) for 22 hours in the above ordered chlorinated solvent was 71%, 27% and 7%, respectively. When we performed this reaction in d_6-benzene solution, we observed only a small amount of *cis*-$PdCl_2(PPh_3)_2$ but mostly decomposed palladium metal as black solid. Thus, the formation of *cis*-$PdCl_2(PPh_3)_2$ is a consequence of substitutional replacement of one of the coordinated 3,5-dimethylpyrazolyl groups by PPh_3 leading to a bis-triphenylphosphine palladium species bearing a monodentate tris(3,5-dimethylpyrazolyl)hydroborate ligand, which then subsequently reacts with $CDCl_3$ to produce the palladium dichloride (Scheme 2). Although a monohapto species was not detected from the reaction of **1** with PPh_3 (either of an equivalent or an excess amount), the sterically hindered palladium complex $Pd\{(3\text{-}t\text{-butylpyrazolyl})_3BH\}(PMe_3)_2(Ph)$ containing a monohapto borate ligand has been previously reported [5].

Acknowledgments

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References

[1] (a) S. Trofimenko, *Chem. Rev.* **93**, 943 (1993); (b) S. Trofimenko, *Chem. Rev.* **72**, 497 (1972); (c) S. Trofimenko, *Prog. Inorg. Chem.* **34**, 115 (1986).

[2] (a) C. Vicente, G. B. Shul'pin, B. Moreno, S. Sabo-Etienne and B. Chaudret, *J. Mol. Catal. A: Chemical* **98**, L5 (1995); (b) B. Moreno, S. Sabo-Etienne, B. Chaudret, A. Rodriguez, F. Jalon and S. Trofimenko, *J. Am. Chem. Soc.* **117**, 7441 (1995); (c) W.-C. Chan, C.-P. Lau, Y.-Z. Chen, Y.-Q. Fang and S.-M. Ng, *Organometallics* **16**, 34 (1997); (d) Y.-Z. Chen, W.-C. Chan, C.-P. Lau, H. S. Chu and H. L. Lee, *Organometallics* **16**, 1241 (1997); (e) C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid and K. Kirchner, *Organometallics* **15**, 3998 (1996); (f) A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics* **17**, 3152 (1998).

[3] (a) A. J. Canty, H. Jin, A. S. Roberts, B. W. Skelton, P. R. Traill and A. H. White, *Organometallics* **14**, 199 (1995); (b) A. J. Canty, A. Dedieu, H. Jin, A. Milet and M. K. Richmond, *Organometallics* **15**, 2845 (1996); (c) A. J. Canty, H. Jin, A. S. Andrew, B. W. Skelton and A. H. White, *Organometallics* **15**, 5713 (1996); (d) S. A. O'Reilly, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.* **118**, 5684 (1996); (e) D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.* **119**, 10235 (1997).

[4] (a) M. Onishi, K. Hiraki, M. Shironita, Y. Yamaguchi and S. Nakagawa, *Bull. Chem. Soc. Japan* **53**, 961 (1980); (b) M. K. Das, K. Niedenzu and S. Roy, *Inorg. Chim. Acta* **150**, 47 (1988); (c) A. L. Rheingold, C. B. White and S. Trofimenko, *Inorg. Chem.* **32**, 3471 (1993); (d) E. Gutierrez, M. C. Nicasio, M. Paneque, C. Ruiz and V. Salazar, *J. Organomet. Chem.* **549**, 167 (1997).

[5] E. Gutierrez, S. A. Hudson, A. Monge, M. C. Nicasio, M. Paneque and E. Carmona, *J. Chem. Soc. Dalton Trans.* **17**, 2651 (1992).

[6] (a) M. Onishi and K. Hiraki, *Inorg. Chim. Acta* **224**, 131 (1994); (b) A. J. Canty, H. Jin, A. S. Roberts, P. R. Traill, B. W. Skelton and A. H. White, *J. Organomet. Chem.* **489**, 153 (1995).

[7] (a) S. Trofimenko, *J. Am. Chem. Soc.* **89**, 6288 (1967); (b) M. A. Andrews, T. C. Chang, C. F. Chen, T. J. Emge, K. P. Kelly and T. F. Koetzle, *J. Am. Chem. Soc.* **106**, 5913 (1984).

[8] P. E. Garrou, *Chem. Rev.* **81**, 229 (1981).

[9] J. G. Verkade and L. D. Quin (Eds.), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis-Organic Compounds and Metal Complexes.* (VCH Publishers, Inc., 1987), p. 365.

[10] T. O. Northcutt, R. J. Lachicotte and W. D. Jones, *Organometallics* **17**, 5148 (1998).

[11] It is obscure that whether the free rotation is associated with the Pd–P bond or the P–C(ipso) bond. However previous studies for similar dynamic properties of the PPh_3 ligand in $(\eta^5\text{-Cp})Fe(CO)(PPh_3)(COCH_3)$ has revealed that rotation of the phenyl ring about the P–C(ipso) bond is considerably lower energy process than the phosphine rotation about the Fe–P bond, failing to observe arrest of the phenyl ring rotation down to $-90°C$ in the VT ^{1}H-NMR: see S. G. Davies, A. E. Derome and J. P. McNally, *J. Am. Chem. Soc.* **113**, 2854 (1991).

[12] A chlorine abstraction from a chlorinated solvent by palladium(II) complexes has been recently observed: (a) S. Y. Ryu, W. Yang, H. S. Kim and S. Park, *Bull. Korean Chem. Soc.* **18**, 1183 (1997); (b) S. Y. Ryu, H. Kim, H. S. Kim and S. Park, *J. Organomet. Chem.* **592**, 194 (1999).