# Reactivity of a Cl-boratabenzene Pt(II) complex with Lewis bases: generation of the kinetically favoured Cl-boratabenzene anion

*Stephanie S. Barnes,[a] Marc-André Légaré,[a] Laurent Maron,[b] and Frédéric-Georges Fontaine*[a]*

[a] Département de Chimie and Centre de recherche sur la propriété des interfaces et de la catalyse (CERPIC), Université Laval, 1045 Avenue de la Médecine, Québec (Québec), Canada, G1V 0A6

[b] Université de Toulouse, INSA, UPS, LPCNO, CNRS, LPCNO, UMR, 5215 CNRS-UPS-INSA, 135 avenue de Rangueil, 31077, Toulouse, France

E-mail: frederic.fontaine@chm.ulaval.ca

***This is the peer reviewed version of the following article: [Reactivity of a Cl-boratabenzene Pt(II) complex with Lewis bases: generation of the kinetically favoured Cl-boratabenzene anion, Dalton Trans., 2011, 40, 12439–12442], which has been published in final form at [10.1039/c1dt11756d].***

# Reactivity of a Cl-boratabenzene Pt(II) complex with Lewis bases: generation of the kinetically favoured Cl-boratabenzene anion

**Stephanie S. Barnes,[a] Marc-André Légaré,[a] Laurent Maron,[b] and Frédéric-Georges Fontaine*[a]**

***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***
**DOI: 10.1039/b000000x**

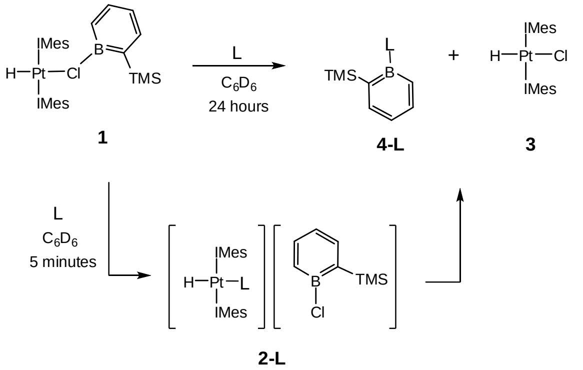
**Complex [(IMes)$_2$Pt(H)(ClBC$_5$H$_4$SiMe$_3$)] (IMes = 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene) reacts with Lewis bases (L = pyridine, trimethylphosphine, acetonitrile, *tert*-butylisocyanide) to generate the kinetically favoured ion pairs [(IMes)$_2$Pt(H)(L)][ClBC$_5$H$_4$SiMe$_3$]. Over time, the formation of the thermodynamically favoured borabenzene-L adducts is observed with L = pyridine and trimethylphosphine.**

Derivatives and metal complexes of borabenzene, and its anionic analogue boratabenzene, have a large range of applications,[1] notably as sources of chirality,[2] as catalysts for cyclotrimerization,[3] alkene polymerization[4] and C-H bond activation,[5] and for their optoelectronic properties.[6] A large variety of derivatives of borabenzene and boratabenzene have been synthesized,[7] but in order to form a thermally stable adduct,[8,9] a strong nucleophile needs to be present on boron, thus limiting the range of possible substituents. A class of boratabenzene species that would be of particular interest for further functionalization are haloboratabenzenes (X = Cl$^-$, Br$^-$, or I$^-$). Indeed, unlike most boratabenzene species reported with alkyl, amido, or phosphido substituents, the B-X bonds can undergo a large range of reactivities including transmetallation, oxydative cleavage, or reduction, which could lead to species unobtainable by other synthetic pathways. Although the most common precursors for borabenzene synthesis are chloroboracyclohexadienes, only one serendipitous report of a fluoroboratabenzene species exists,[10] resulting from an unusual rearrangement of an iridium metallabenzene.[11]

As part of our program aimed at the exploration of novel bonding modes for the borabenzene moiety - notably to generate novel Z-type interactions with transition metals[12] - we recently reported the synthesis of species [(IMes)$_2$Pt(H)(ClBC$_5$H$_4$SiMe$_3$)] (**1**),[13] one of the rare borabenzene metal complexes where the $\pi$ system of the heterocycle is not involved in binding the transition metal.[14] We wish to report that species **1** reacts unexpectedly with Lewis bases (L= pyridine (**Py**), trimethylphosphine (**PMe$_3$**), acetonitrile (**MeCN**), and *tert*-butylisocyanide (**2-BuNC**)) to generate the ionic pair [(IMes)$_2$Pt(H)(L)]$^+$[ClBC$_5$H$_4$SiMe$_3$]$^-$. Coordination isomers [(IMes)$_2$Pt(H)(Cl)] and 1-L-2-SiMe$_3$-borabenzene were calculated to be thermodynamically favoured compared to the ion pair, and were observed in presence of pyridine and PMe$_3$. It is the first report of the synthesis of borabenzene adducts from a boratabenzene precursor, and gives valuable insight on the stability of the chloroboratabenzene anion.

In our investigation on the Lewis acidity of the boron centre of **1**, we observed that the borabenzene fragment could be transferred to pyridine to generate a pyridine-borabenzene adduct (**4-Py**) 24 hours after the addition of 2 equivalents of pyridine in benzene-*d$_6$*.[13] However, close monitoring of the reaction mixture allowed the observation of a transient species, **2-Py** (Scheme 1). Using $^1$H NMR spectroscopy, we observed that the hydride of **2-Py** was upfield (δ -20.10) and that the $^1J_{\text{Pt-H}}$ was significantly lower (1348 Hz) than for **1** (δ -22.42, $^1J_{\text{Pt-H}}$ = 1915 Hz). In addition to the signals for the N-heterocyclic ligands, a new set of resonances was observed at δ = 8.05, 7.81, 7.03, and 6.85 with the H-H coupling constants expected for borabenzene species. Monitoring this reaction mixture over a 24 hour period did show that the resonances associated with **2-Py** disappeared at a similar rate to the formation of [(IMes)$_2$Pt(H)(Cl)] (**3**).

Scheme 1. Generation of **2-L** and **4-L** from **1**



Analogues of **2-Py** were observed in the presence of acetonitrile (**2-MeCN**), trimethylphosphine (**2-PMe$_3$**), and *tert*-butylisocyanide (**2-BuNC**). Although the resonances for the Pt-H shifted significantly for the three other complexes (δ -19.13, $^1J_{\text{Pt-H}}$ = 1551 Hz (**2- MeCN**); δ -5.65, $^1J_{\text{Pt-H}}$ = 1060 Hz (**2-PMe$_3$**); δ -7.79, $^1J_{\text{Pt-H}}$ = 1101 Hz (**2-BuNC**)), the $^1$H and $^{13}$C resonances associated to the borabenzene moiety were very similar from one compound to the next, although some small variations were observed.[15] The coordination of the phosphine in **2-PMe$_3$** was confirmed using $^{31}$P{$^1$H} and $^1$H NMR spectroscopy, where the $^1J_{\text{Pt-P}}$ and $^2J_{\text{H-P}}$ of 1060 and 187 Hz, respectively, are characteristic of phosphine coordination *trans* to a hydride. The $^{11}$B{$^1$H} NMR chemical shifts for all **2-L** were, within experimental error, at 38 ppm. It should be noted that species **2-PCy$_3$** was not observed when tricyclohexylphosphine was added to **1**.

We propose that **2-L** consists of the ion pair [(IMes)$_2$Pt(H)(L)][ClBC$_5$H$_4$SiMe$_3$]. To support this hypothesis, the generation of [(IMes)$_2$Pt(H)(L)]BF$_4$ was carried out by the addition of AgBF$_4$ to a solution of [(IMes)$_2$Pt(H)(Cl)] in benzene-*d$_6$* in presence of excess L (see ESI). With all L, the products displayed the same resonances associated to the cationic centre of species **2-L**, although solubility issues did not allow for clean isolation of the ionic species. ESI-MS or HRMS studies in benzene also gave probing evidences of the existence of **2-L** (see ESI). The ionic species [(IMes)$_2$Pt(H)(L)]$^+$ for **2-PMe$_3$** (m/z = 881.2), **2-Py** (m/z = 884.1), and **2-BuNC** (m/z = 887.1) were observed, although in all samples the principal ion corresponded to $[(IMes)_2Pt(H)]^+$ (m/z = 804.6). The chloroboratabenzene anion was also observed in the HRMS anionic mode at m/z = 183.0694.

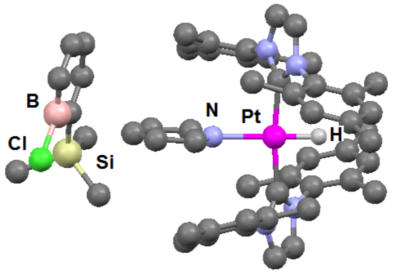


Figure 1. B3PW91/SDDALL(Pt,Cl,Si)/6-31g(d,p (N,C,H,B) optimized structure **2-Py**. Hydrogen atoms are omitted for clarity.

**Table 1**. Reaction coordinates minimized using DFT

| L | $\Delta E_{1\rightarrow 2L}$ (kcal.mol$^{-1}$) | $\Delta E_{2L\rightarrow 4L}$ (kcal.mol$^{-1}$) | $\Delta E_{2L\rightarrow 4l}^{C6D6}$ (kcal.mol$^{-1}$) | dist$_{Pt\text{-}H}$ (Å) |
|---|---|---|---|---|
| CN*t*Bu | -22.7 | -6.6 | -0.3 | 1.60 |
| PMe$_3$ | -5.6 | -8.4 | -3.2 | 1.59 |
| Py | -50.5 | -9.6 | -4.8 | 1.56 |
| MeCN | -12.2 | -1.1 | +3.7 | 1.56 |
| PCy$_3$ | 26.0 | -32.7 | -21.8 | N.A. |

It was possible to model these complexes using DFT (see ESI for computational details). The structure of **2-Py** is presented in Figure 1 and those of the other complexes are available in the ESI. The formation of the ion pair **2-L** from **1** was shown to be exothermic for all species, with the exception of **2-PCy$_3$** where the reaction is disfavoured by 26.0 kcal/mol (Table 1). All species have the platinum atom in a square planar environment, with the L ligand *trans* to the hydride. The biggest distortion from ideal geometry, in all cases, is being caused by steric repulsion between L and the IMes ligands. The 1-Cl-2-SiMe$_3$-boratabenzene anion is identical in all **2-L** complexes and does not have any significant interaction with the cation.

With time, species **2-L** degrades to generate **3**. However, in the case of the pyridine analogue, the generation of the adduct **4-Py** was observed.[13] Species **4-PMe$_3$** was also observed from **2-PMe$_3$**, based on a comparison with independently synthesized 1-PMe$_3$-2-SiMe$_3$-borabenzene, albeit in very low yield because of several side reactions. The transformation of **2-L** to **3** and **4-L** was also investigated using DFT (Table 1). In the gas phase, the neutral adducts were favoured thermodynamically over the ion pair, whereas the formation of **4-MeCN** was calculated to be endothermic in benzene. As can be expected from the experimental results, **4-Py** gives the most stable neutral system with reaction coordinates at -4.8 kcal.mol$^{-1}$ in benzene followed by **4-PMe$_3$** (-3.2 kcal.mol$^{-1}$). Although the formation of 1-PCy$_3$-2-SiMe$_3$-borabenzene is favoured, its absence in solution seems to indicate that the formation of **2-L** is a prerequisite for its generation.

To obtain more information on the mechanism of the transformation of **1** to **4-Py**, solutions with various equivalents of pyridine were monitored using $^1$H NMR spectroscopy. When one equivalent of pyridine was added to the solution, the complete generation of **2-Py** was observed within 30 minutes. Monitoring of the solution over a period of one week did not reveal the presence of a significant concentration of **4-Py**. However, when 5 equivalents of pyridine were added to **1**, it was possible to observe the gradual conversion of **2-Py** to **4-Py** over a period of few hours. These results suggest that an excess of pyridine is required to generate 1-pyridine-2-SiMe$_3$-borabenzene. More interestingly, thirty minutes after the addition of half an equivalent of pyridine, all of it was consumed and both **2-Py** and **1** were observed in solution. Whereas the resonances for the $[(IMes)_2Pt(H)(py)]^+$ were sharp, the $[ClBC_5H_4SiMe_3]^-$ resonances for **1** and **2-Py** were significantly broadened (see Figure S16). Variable temperature NMR spectroscopy did show that the peaks associated to both chloroboratabenzene species become sharper on cooling and coalesce into a single set of resonances upon warming. Such a phenomenon points towards a fluxional process where the chloroboratabenzene anion of **2-L** can undergo ligand exchange with the chloroboratabenzene of **1**, as seen in Figure 2. Modelling of the bandwidth of the TMS resonances with WINDNMR-Pr o[16] allowed the determination of the exchange rates and activation parameters ($\Delta H^\ddagger = 12.8 \pm 0.3$ kcal.mol$^{-1}$ and $\Delta S^\ddagger = -8 \pm 1$ cal.mol$^{-1}$.K$^{-1}$).

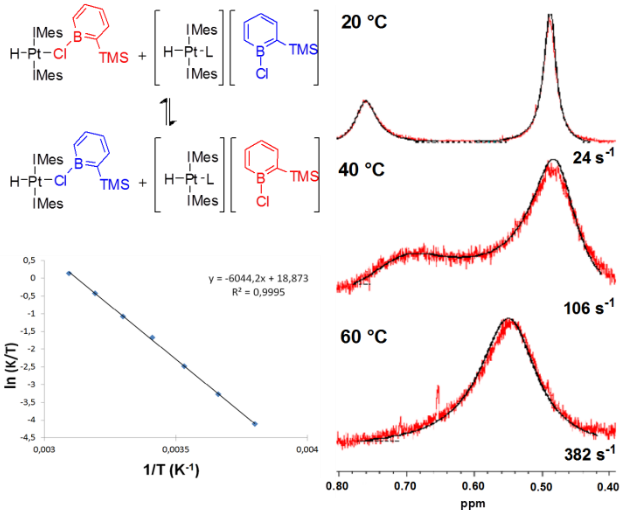
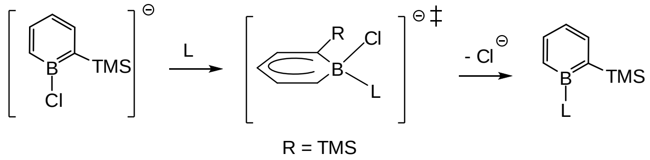


Figure 2. Experimental (red) and simulated (black) $^1$H NMR spectra of the –SiMe$_3$ region of **1** and **2-Py** at various temperatures with the associated rate constant. Eyring plot for the exchange of the 1-Cl-2-TMS-boratabenzene moieties in **1** and **2-Py.**

The first step of this transformation, the formation of **2-L**, is expected to occur by a mechanism similar to the $[ClBC_5H_4SiMe_3]^-$ exchange between **1** and **2-L**, where in this situation the chloroboratabenzene anion acts as the Lewis base. The negative value for the entropy of the transition state of -8 ± 1 cal.mol$^{-1}$.K$^{-1}$ suggests an associative pathway, but the relatively small values cannot discredit a dissociative pathway. Despite our efforts, no transition state associated with a concerted pathway could be optimized. However, the energy associated with the cleavage of the platinum chlorobotabenzene moiety (62.6 kcal.mol$^{-1}$) is overcome by the large electrostatic interaction (ion pairing in the range of 48.5 to 62.5 kcal.mol$^{-1}$) in **2-L.** Although the chloroboratabenzene moiety is formally a nucleophilic substrate because of the anionic charge, the boron atom in borabenzene is known to remain electrophilic.[17] If an excess of L ligand is available, it can undergo an associative substitution *via* the same intermediate speculated by Fu for the formation of R-boratabenzene adducts from 1-PMe$_3$-borabenzene in presence of organic nucleophiles.[18] The $\Delta E^{\ddagger}$ for the transition state observed in Scheme 2 was calculated to be 27 kcal.mol$^{-1}$ for L = **Py**. The chloride liberated by this substitution could then coordinate to the platinum centre, forming the strong Pt-Cl bond of **3**, calculated to be of 94.7 kcal.mol$^{-1}$.



Scheme 2. Associative mechanism for the dissociation of Cl$^{-}$ from **2-L** to generate **4-L**.

## Conclusions

In this report, the generation of the ionic pair **2-L** from an unusual platinum chloroboratabenzene species in presence of L = pyridine, $PMe_3$, MeCN and CN*t*Bu is reported. With $PMe_3$ and pyridine, an associative substitution at boron can occur since these Lewis bases are known to strongly stabilize borabenzene adducts. It exposes the difficulties associated with the generation of this interesting boratabenzene moiety using traditionnal nucleophilic substitution reactions on neutral borabenzenes. Indeed, the evidence show that it is a thermodynamically unstable species compared to the most common adducts. The rich and unusual chemistry of **1** with other substrates, and the coordination chemistry of the chloroboratabenzene anion are currently underway.

## Notes and references

[a] *Département de chimie & Centre de recherche sur les interfaces et la catalyse, Université Laval, 1045 avenue de la Médecine, Québec, QC, G1V 0A6, Canada. E-mail: frederic.fontaine@chm.ulaval.ca*

[b] *Université de Toulouse, INSA, UPS, LPCNO, CNRS, LPCNO, UMR 5215 CNRS-UPS-INSA, 135 avenue de Rangueil, 31077 Toulouse, France*

† We are grateful to NSERC (Canada), CFI (Canada), FQRNT (Québec) and CCVC (Québec) for financial support. M.-A. L. and S. S. B. would like to acknowledge CRSNG and FQRNT for scholarships. L.M. is a member of the Institut Universitaire de France and would like to acknowledge CalMIp and CINES for computing time. We acknowledge R. T. Baker and C. Diaz-Urrutia with their help with MS experiments. We acknowledge Prof. H. J. J. Reich for helpful comments. F.-G. F. would like to thank the CCRI for hosting him while writing this manuscript.

Electronic supplementary information (ESI) available: Synthetic procedures, NMR, MS, and DFT data for all products. For ESI see DOI: DOI: 10.1039/c0xx00000x.

[1] (a) G. C. Fu, *Adv. Organomet. Chem.*, 2001, **47**, 101–119; (b) G. E. Herberich and H. Ohst, *Adv. Organomet. Chem.*, 1986, **25**, 199–236; (c) A. J. Ashe III, S. Al-Ahmad and X. Fang, *J. Organomet. Chem.*, 1999, **581,** 92-97.

[2] (a) G. E. Herberich, B. Ganter and M. Pons, *Organometallics*, 1998, **17**, 1254-1256; (b) G. E. Herberich, U. Englert, B. Ganter and M. Pons, *Eur. J. Inorg. Chem.*, 2000, 979-986; (c) J. Tweddell, D. A. Hoic and G. C. Fu, *J. Org. Chem.*, 1997, **62**, 8286-8287.

[3] von H. Bönnemann, W. Brijoux, R. Brinkmann and W. Meurers, *Helv. Chem. Acta*, 1984, **67**, 1616-1624.

[4] (a) G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad and J. W. Kampf, *Organometallics*, 1997, **16**, 2492-2494; (b) A. J. Ashe III, S. Al-Ahmad, X. Fang and J. W. Kampf, *Organometallics*, 1998, **17**, 3883-3888; (c) J. S. Rogers, X. Bu and G. C. Bazan, *Organometallics*, 2000, **19**, 3948-3956; (d) Z. J. A. Komon, J. S. Rogers and G. C. Bazan, 2002, **21**, 3189-3195; (e) P. Cui, Y. Chen, X. Zeng, J. Sun, G. Li and W. Xia, *Organometallics*, 2007, **26**, 6519-6521; (f) J. S. Rogers, X. Bu and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 730-731; (g) J. S. Rogers, G. C. Bazan and C. K. Sperry, *J. Am. Chem. Soc.*, 1997, **119**, 9305-9306.

[5] D. H. Woodmansee, X. Bu and G. C. Bazan, *Chem. Commun.*, 2001, 619-620.

[6] (a) B. Y. Lee, S. Wang, M. Putzer, G. P. Bartholomew, X. Bu and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 3969-3970; (b) U. Behrens, T. Meyer-Friedrichsen and J. Heck, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1421-1430; (c) C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen and M. Parvez, *J. Am. Chem. Soc.*, 2006, **128**, 10885-10896; (d) T. K. Wood, W. E. Piers, B. A. Keay and M. Parvez, *Angew. Chem., Int. Ed.*, 2009, **48**, 4009-4012; (e) T. K. Wood, W. E. Piers, B. A. Keay and M. Parvez, *Chem. Eur. J.*, 2010, **16**, 12199-12206; (f) U. Hagenau, J. Heck, E. Hendrickx, A. Persoons, T. Schuld and H. Wong, *Inorg. Chem.*, 1996, **35**, 7863-7866; (g) D. J. H. Emslie, W. E. Piers and M . Parvez, 2003, **42**, 1252-1255.

[7] (a) Some leading articles: (a) G. Bélanger-Chabot, P. Rioux, L. Maron and F.-G. Fontaine, *Chem. Commun.*, 2010, **46**, 6816-6818; (b) Y. Yuan, Y. Chen, G. Li and W. Xia, *Organometallics*, 2010, **29**, 3722-3728; (c) D. A. Loginov, Z. A. Starivoka, E. A. Petrovskaya and A. R. Kudinov, *J. Organomet. Chem.*, 2009, **694**, 157-160; (d) N. Auvray, T. S. B. Baul, P. Braunstein, P. Croizat, U. Englert, G. E. Herberich and R. Welter, *Dalton Trans.*, 2006, 2950-2958; (e) X. Zheng and G. E. Herberich, *Eur. J. Inorg. Chem.*, 2003, 2175-2182.

[8] A $N_2$ adduct has been observed using IR at 10K in a nitrogen matrix: G. Maier, H. P. Reisenauer, J. Henkelmann and C. Kliche, *Angew. Chem., Int. Ed.*, 1988, **27**, 295-296.

[9] The coordination of the bora(ta)benzene moiety on a transition metal makes the boron more Lewis acidic and more prone to stabilize weaker donors: M. C. Amendola, K. E. Stockman, D. A. Hoic, W. M. Davis and G. C. Fu, *Angew. Chem., Int. Ed.*, 1997, **36**, 267-269.

[10] We did report the generation of the chloroboratobenzene anion by the addition of $[NBu_4]Cl$ as a proof of the existence of **1**, but the spectral properties and generality of the reaction was not reported. See reference 13.

[11] J. R. Bleeke, R. Behm, Y.-F. Xie, M. Y. Chiang, K. D. Robinson and A. M. Beatty, *Organometallics*, 1997, **16**, 606-623.

[12] (a) F.-G. Fontaine, J. Boudreau and M.-H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439–5454; (b) I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster and F. Breher, *Dalton Trans.* 2008, 5836–5865; (c) H. Braunschweig, R. D. Dewhurst and A. Schneider, *Chem. Rev.* 2010, **110**, 3924–3957; (d) G. Bouhadir, A. Amgoune and D. Bourissou, *Adv. Organomet. Chem.* 2010, **58**, 1–107; (e) A. Amgoune and D. Bourissou, D. *Chem. Commun.*, 2011, **47**, 859-871.

[13] A. Languérand, S. S. Barnes, G. Bélanger-Chabot, L. Maron, P. Berrouard, P. Audet and F.-G. Fontaine, *Angew. Chem., Int. Ed.*, 2009, **48**, 6695-6698.

[14] Phosphidoboratabenzene complexes are the exception: D. A. Hoic, W. M. Davis and G. C. Fu, *J. Am. Chem. Soc.*, 1996, **118**, 8176-8177.

[15] Although no significant close contact was observed between the ions in **2-L**, DFT gives an overall stabilization of over 40 kcal.mol$^{-1}$ for the ion pair when compared to the ions modeled independently. Because of the strong ion pairing, deviations in the chemical shifts can be expected for the borabenzene depending on the nature of L.

[16] H. J. J Reich *Chem. Educ. Software* 1996, **3D**, 2.

[17] H. Braunschweig, C.-W. Chiu, K. Radacki and T. Kupfer, *Angew. Chem., Int. Ed.*, 2010, **49**, 2041-2044.

[18] S. Qiao, D. A. Hoic and G. C. Fu, *J. Am. Chem. Soc.*, 1996, **118**, 6329-6330.