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Benzene C−H Activation at a Charge Neutral Zwitterionic Platinum(II) Complex

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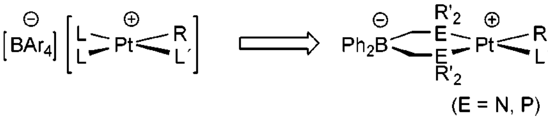
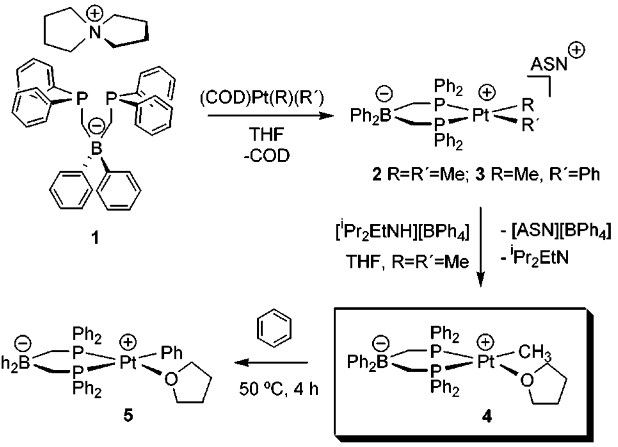
Cationic, coordinatively unsaturated metal centers exhibit a wide range of both stoichiometric and catalytic transformations.[1] Such species are frequently generated by methide abstraction with a strong Lewis acid,[2] or alternatively by protonation with an acid whose conjugate base is noncoordinating or weakly coordinating.[3] We are targeting charge neutral, zwitterionic complexes that display reaction chemistry reminiscent of these reactive metal centers. Of particular interest is the development of species that exhibit transformations at X−H bonds, where an X−H bond refers generally to a C−H or other robust σ bond. A conceptual diagram illustrating this strategy is shown in Scheme 1.

Scheme 1



Herein we describe a neutral platinum(II) alkyl complex supported by the novel, anionic bidentate phosphine ligand $[Ph_2B(CH_2PPh_2)_2]$.[4] This platinum system was examined for several reasons. First, C−H activation at Pt(II) metal centers is now well-established, particularly for systems with N-donor ligands.[2a,3,5] In contrast, there are limited examples of intermolecular C−H bond activation at platinum(II) centers supported by phosphine donor ligands: these phosphine-supported systems require relatively high temperatures (125−150 °C).[6] We envisioned that zwitterionic, bis(phosphino)borate platinum complexes would promote transformations at C−H bonds. Furthermore, it was hoped that such complexes would be soluble in relatively nonpolar media, contrasting their discrete salt relatives. Systems thus designed should be amenable to mechanistic study due to the presence of a useful spectroscopic ^{31}P NMR handle. In addition, designing systems that attenuate or eliminate counteranion effects may provide an important mechanistic simplification. We describe below the synthesis of $[Ph_2B(CH_2PPh_2)_2][ASN]$ (**1**) (ASN = 5-azonia-spiro[4.4]nonane) and examine its ability to promote C−H bond activation chemistry at a platinum(II) center.

Scheme 2



Synthesis of **1** was readily achieved by low-temperature addition of a toluene solution of diphenylchloroborane to a diethyl ether solution of $Ph_2PCH_2Li(TMEDA)$ (TMEDA = *N,N,N′,N′*-tetramethylethylene-1,2-diamine). This generates $[Ph_2B(CH_2PPh_2)_2][Li(TMEDA)_2]$, whose structure is shown in Figure 1.[7] Cation exchange provides the ASN salt, **1**, in high yield.

Reaction of **1** with either $(COD)Pt(Me)_2$ or (COD)Pt(Me)(Ph) in THF forms the expected anionic platinum(II) products $[\{Ph_2B(CH_2PPh_2)_2\}Pt(Me)_2][ASN]$ (**2**) and $[\{Ph_2B(CH_2PPh_2)_2\}Pt(Me)(Ph)][ASN]$ (**3**) in high yield (Scheme 2). To generate the key neutral platinum complex, $\{Ph_2B(CH_2PPh_2)_2\}Pt(Me)(L)$, several strategies were surveyed including protonolysis by acid and methide abstraction by $B(C_6F_5)_3$. All of these strategies effected the removal of one methyl group from **2**, as determined by ^{31}P NMR spectroscopy; however, most routes did not enable the clean isolation of a $\{Ph_2B(CH_2PPh_2)_2\}Pt(Me)(L)$ complex. We were fortunate to find that protonation of **2** in THF with the bulky ammonium salt $[^iPr_2EtNH][BPh_4]$ did enable both the clean generation of $\{Ph_2B(CH_2PPh_2)_2\}Pt(Me)(THF)$ (**4**) and its isolation. The salt byproduct, $[ASN][BPh_4]$, precipitates from THF and is readily removed. Solid **4** can be subsequently isolated by rapid precipitation from THF with pentane, a procedure that also removes the neutral amine byproduct, $^iPr_2EtN$. It is noteworthy that the protonation of **2** directly contrasts with the reactivity of a related compound, $(dppp)PtMe_2$ (dppp = 1,3-bis(diphenylphosphino)propane), which did not exhibit reactivity with $[^iPr_2EtNH][BPh_4]$ at 50 °C in THF solution over 24 h.

An X-ray diffraction study on single crystals of **4** confirmed its structural assignment (Figure 2).[8] To date, this represents the third crystallographically characterized example of a platinum-THF adduct and is the only charge neutral species thus characterized for divalent platinum.[9] Importantly, the coordinated THF molecule in **4** is weakly bound: it is readily substituted by a variety of neutral ligands (CO, pyridine, H_2O, acetone, Et_3N) and

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[3] (a) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (b) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831−10845.

[4] A lithium adduct of an anionic, bis(phosphino)aluminate species has been previously reported. See: Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1985**, *4*, 231−238.

[5] Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848−849.

[6] (a) Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379−2386. (b) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843−2853. (c) Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493−4499.

[7] $[Ph_2B(CH_2PPh_2)_2][Li(TMEDA)_2]$ ($C_{50}H_{65}BLiN_4P_2$), MW = 801.75, colorless prism, collection temperature = 98 K, monoclinic, space group = $P2_1/c$, $a = 11.7922(6)$ Å, $b = 11.7081(6)$ Å, $c = 33.1336(18)$ Å, $\alpha = 90°$, $\beta = 94.0620(10)°$, $\gamma = 90°$, $V = 4563.1(4)$ Å^3, $Z = 4$, $R_1 = 0.061$ $[I > 2\sigma(I)]$, GOF = 1.952.

[8] **4**·2(THF) ($C_{43}H_{45}BOP_2Pt\cdot 2(C_4H_8O)$), MW = 845.67 × 2(72.10), colorless block, collection temperature = 98 K, triclinic, space group = $P1$, $a = 12.210(4)$ Å, $b = 12.803(4)$ Å, $c = 16.205(5)$ Å, $\alpha = 109.614(5)°$, $\beta = 104.361(5)°$, $\gamma = 96.489(5)°$, $V = 2257.6(12)$ Å^3, $Z = 2$, $R_1 = 0.043$ $[I > 2\sigma(I)]$, GOF = 1.404.

[9] (a) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831−11843. (b) Schlect, S.; Magull, J.; Fenske, D.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1994−1995.

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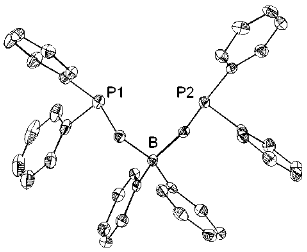

Figure 1. 50% displacement ellipsoid representation of [$Ph_2B(CH_2PPh_2)_2$]. Hydrogen atoms and the $Li(TMEDA)_2$ countercation are omitted for clarity.

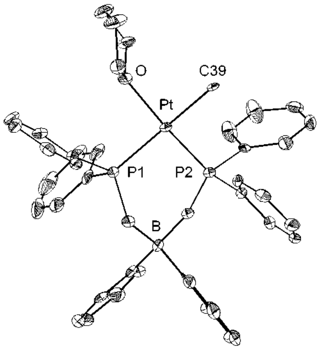

Figure 2. 50% displacement ellipsoid representation of {$Ph_2B(CH_2PPh_2)_2$}Pt(Me)(THF)·2THF (**4**). Hydrogen atoms and THF molecules are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Pt−P1, 2.313(2); Pt−P2, 2.193(2); Pt−O, 2.170(4); Pt−C39, 2.087(6); P1−Pt−P2, 91.93(6); P1−Pt−O, 91.2(1); O−Pt−C39, 87.4(2); C39−Pt−P2, 89.9(2); P1−Pt−C39, 174.9(2); P2−Pt−O, 174.4(1).

is very unstable under reduced pressure (placing **4** under vacuum leads to a single new product whose identity has yet to be determined). It should also be noted that **4** slowly degrades in THF solution at ambient temperature.

With target complex **4** in hand, its ability to engage the aryl C−H bonds of benzene was examined. When a solid sample of **4** is dissolved and gently warmed in benzene, a solvent in which it is appreciably soluble, formation of one major product is observed. At 50 °C, the reaction is complete after 4 h. The major product (≈80%) formed is {$Ph_2B(CH_2PPh_2)_2$}Pt(Ph)(THF) (**5**) based upon spectroscopic data. To confirm its assignment, **5** was independently generated by methide abstraction from **3** with $B(Ar)_3$ in THF. It is noted that addition of several molar equivalents of THF to a benzene solution of **4** slows the rate of benzene activation.[10]

Analogous to its reactivity with benzene, **4** reacts with toluene preferentially at the C−H bonds of the aryl ring. There is no evidence for competitive benzylic C−H activation. Spectroscopic evidence suggests that the predominant isomer formed is the *p*-tolyl platinum complex and we tentatively assign the product ratio as 3:1:1 for the para:meta:ortho isomers, respectively.

We have begun to examine the potential of **4** to activate alkyl C−H bonds and have not, as yet, conclusively observed such a reaction. Incubation of a THF solution of **4** under an atmosphere of $^{13}CH_4$ at 75 °C for 10 h afforded no detectable incorporation (^{13}C NMR) of an isotopically enriched methyl group. This contrasts results reported for complexes with amine and imine donor ligands, where $^{13}CH_4$ has been demonstrated to reversibly react with the compounds $[(TMEDA)Pt(CH_3)(NC_5F_5)]^+$ in pentafluoropyridine and $[(ArN{=}C{-}C{=}NAr)Pt(CH_3)(H_2O)]^+$ in dichloromethane.[3,5] Additionally, no reaction occurred upon dissolution of **4** in a 1:1 THF:cyclohexane mixture at 75 °C over a period of 12 h. A possible reaction between **4** and the C−H bonds of methane or cyclohexane is likely inhibited by the presence of a large excess of tetrahydrofuran. Complex **4**, while soluble in aromatic hydrocarbons, reacts rapidly with them relative to other, nonaromatic solvent molecules; however, **4** is not appreciably soluble in simpler hydrocarbons such as pentane and cyclohexane, and hence its reactivity in the absence of solubilizing THF equivalents has yet to be determined. Efforts to prepare more lipophilic derivatives of **4** with new bis(phosphino)borate ligands are currently underway.

In conclusion, a monoanionic bidentate bis(phosphino)borate ligand has been developed,[11] and its influence on platinum(II) C−H bond activation processes has been explored. Notably, the neutral, zwitterionic platinum(II) complex **4** has been cleanly generated and reacts preferentially with aryl C−H bonds at 50 °C. We anticipate that the reactive complex **4** and related Group 10 complexes will exhibit a rich reaction chemistry.

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Supporting Information Available: Detailed experimental procedures for the preparation and characterization of compounds **1**−**5** and tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for [$Ph_2B(CH_2PPh_2)_2$][$Li(TMEDA)_2$] and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] The conversion of **4** to **5** occurs in greater yield in the presence of several molar equivalents of THF, albeit more slowly. Notably, H_2O has been observed to inhibit C−H activation in related systems by Tilset and co-workers (see ref 3b).

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