

Benzene C–H activation by platinum(II) complexes of bis(2-diphenylphosphinophenyl)amide†

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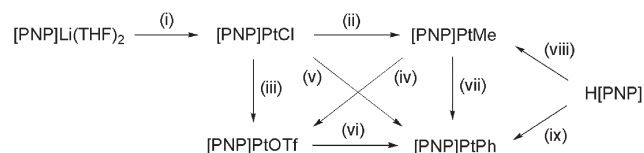
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The amido diphosphine complexes [PNP]PtMe and [PNP]PtOTf, where [PNP][−] is bis(2-diphenylphosphinophenyl)amide, effectively activate the benzene C–H bond in the presence of an appropriate Lewis acid or base, leading to the formation of [PNP]PtPh quantitatively.

The search for appropriate methods to facilitate intermolecular C–H bond activation of hydrocarbons continues to constitute an active area of exploratory research.¹ Much recent attention has been paid to systems involving platinum, due largely to the pioneering work of Shilov and co-workers who successfully demonstrated selective alkane oxidation by aqueous solutions of chloroplatinate salts.² In this regard, multidentate chelating ligands incorporating exclusively nitrogen donor atoms have been examined extensively.³ In contrast, studies involving platinum complexes supported by phosphine-derived chelating ligands remain relatively undeveloped.⁴ This is somewhat surprising in view of the facile accessibility of ³¹P NMR handle to the investigation of mechanistic C–H activation processes. We have recently prepared a series of *o*-phenylene derived amido phosphine ligands and demonstrated the versatility of these hybrid compounds in reactivity involving a variety of metals.⁵ For instance, nickel and palladium complexes of bis(2-diphenylphosphinophenyl)amide ([PNP][−])^{6,7} are found to be markedly thermally stable, even at elevated temperatures, therefore leading to differing reaction chemistry relative to the closely related [N(SiMe₂CH₂PR₂)₂][−] system.⁸ In this contribution, we describe the preparation and characterization of divalent platinum complexes of [PNP][−], and their reactivity with respect to intermolecular benzene C–H bond activation.

The reaction of [PNP]Li(THF)₂⁶ with PtCl₂(SMe₂)₂ in THF at −35 °C produced [PNP]PtCl quantitatively (Scheme 1).



Scheme 1 Synthesis of platinum complexes supported by the [PNP][−] ligand. *Reagents and conditions:* i, PtCl₂(SMe₂)₂, THF, −35 °C; ii, MeMgCl, THF, −35 °C; iii, AgOTf, C₆H₆, RT; iv, HOTf, C₆H₆, RT; v, PhMgCl, THF, −35 °C; vi, NEt₃ or MeNCy₂ or DABCO, C₆H₆, 110 or 150 °C; vii, B(C₆F₅)₃, C₆H₆, RT; viii, 0.5 equiv. of [PtMe₂(μ-SMe₂)₂], THF–Et₂O, −35 °C; ix, *cis*-PtPh₂(SMe₂)₂, THF, −35 °C.

† Electronic supplementary information (ESI) available: preparation and characterization of compounds. See <http://www.rsc.org/suppdata/cc/b5/01520k/>

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Subsequent methylation of [PNP]PtCl with MeMgCl afforded [PNP]PtMe cleanly. The methyl complex may be alternatively prepared by addition of H[PNP]⁶ to an ethereal solution of [PtMe₂(μ-SMe₂)₂] at −35 °C. Similarly to their nickel and palladium analogues,^{6,7} both [PNP]PtCl and [PNP]PtMe are thermally stable at high temperatures. For instance, no decomposition was observed when [PNP]PtCl (13.0 mM in benzene) or [PNP]PtMe (12.7 mM in benzene) was heated to 150 °C under aerobic conditions for three days as indicated by ³¹P{¹H} NMR spectroscopy.

The solution NMR data of [PNP]PtCl and [PNP]PtMe are consistent with a square-planar geometry for these molecules, reminiscent of the corresponding nickel and palladium chemistry.^{6,7} The [PNP][−] ligand is in a meridional coordination mode, as evidenced by the presence of diagnostic virtual triplet⁹ resonances observed for the *o*-phenylene carbon atoms in the ¹³C{¹H} NMR spectrum. The phosphorus donors exhibit only one singlet resonance flanked by ¹⁹⁵Pt satellite signals with ¹J_{PtP} of 2751 and 2983 Hz for [PNP]PtCl and [PNP]PtMe, respectively (Table 1). The methyl ligand in [PNP]PtMe is unambiguously observed as a triplet resonance at 1.37 ppm with ³J_{HP} of 5.5 Hz in the ¹H NMR spectrum and a triplet at −22.71 ppm with ²J_{CP} of 5.7 Hz in the ¹³C{¹H} NMR spectrum.

Single crystals of [PNP]PtCl and [PNP]PtMe suitable for X-ray diffraction studies were grown by slow evaporation of a concentrated benzene solution at room temperature. The X-ray structures of [PNP]PtCl‡ and [PNP]PtMe‡, as illustrated in Figs. 1 and 2, respectively, are in good agreement with the solution structures determined by NMR spectroscopy. The platinum center in both molecules lies perfectly on the square plane defined by the four donor atoms with the chloride or methyl ligand being *trans* to the amido nitrogen atom. Similarly to that found in [PNP]PdCl,⁷ the two *o*-phenylene rings in [PNP]PtCl and [PNP]PtMe are tilted with respect to the coordination plane due to the steric repulsion between the two CH groups ortho to the amido nitrogen atom. The remaining parameters are unexceptional.

Alkyl abstraction mediated by Lewis acidic B(C₆F₅)₃ from transition metal complexes has been well-documented.¹⁰

Table 1 ³¹P NMR data for [PNP]PtX^a

X	δ _P	¹ J _{PtP}
Cl	25.43	2751
Me	30.57	2983
OTf	27.76	2809
Ph	27.90	2967

^a All spectra were recorded in C₆D₆; chemical shifts in ppm, coupling constants in Hz.

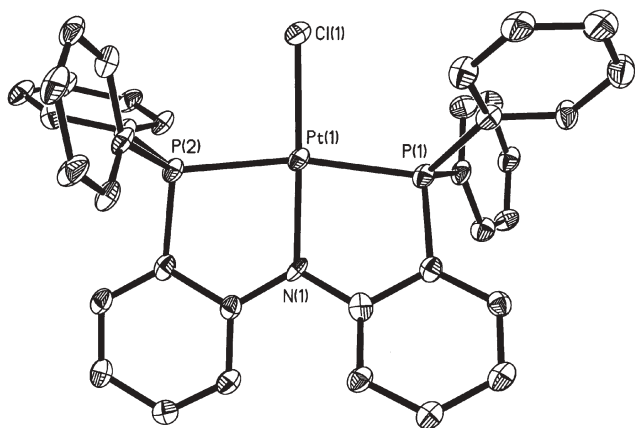


Fig. 1 Molecular structure of [PNP]PtCl with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains five unbound benzene molecules, which are omitted for clarity. Selected bond distances (Å) and angles (°): Pt(1)–N(1) 2.024(6), Pt(1)–P(2) 2.270(2), Pt(1)–P(1) 2.284(2), Pt(1)–Cl(1) 2.318(2); N(1)–Pt(1)–P(2) 83.72(19), N(1)–Pt(1)–P(1) 83.60(19), P(2)–Pt(1)–P(1) 167.30(8), N(1)–Pt(1)–Cl(1) 177.51(19), P(2)–Pt(1)–Cl(1) 94.52(8), P(1)–Pt(1)–Cl(1) 98.18(8).

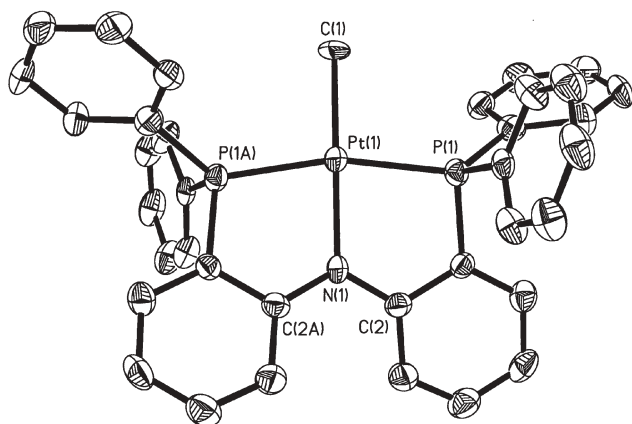


Fig. 2 Molecular structure of [PNP]PtMe with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (°): Pt(1)–N(1) 2.09(2), Pt(1)–C(1) 2.11(3), Pt(1)–P(1A) 2.2737(18), Pt(1)–P(1) 2.2737(18); N(1)–Pt(1)–C(1) 180.0, N(1)–Pt(1)–P(1A) 82.31(7), C(1)–Pt(1)–P(1A) 97.69(7), N(1)–Pt(1)–P(1) 82.31(7), C(1)–Pt(1)–P(1) 97.69(7), P(1A)–Pt(1)–P(1) 164.63(13).

Interestingly, treatment of a benzene solution of [PNP]PtMe with a stoichiometric amount of $B(C_6F_5)_3$ at room temperature led to the formation of [PNP]PtPh in quantitative yield, a consequence that arises from the cleavage of a benzene C–H bond. This reaction is complete in 31 h as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. The identity of [PNP]PtPh was further confirmed by independent preparation of this molecule from the reactions of either *cis*-PtPh₂(SMe₂)₂ with H[PNP]⁶ or [PNP]PtCl with PhMgCl in ethereal solutions (Scheme 1). Controlled experiments reveal that the conversion of [PNP]PtMe to [PNP]PtPh is proportional to the substoichiometry of $B(C_6F_5)_3$ employed, indicating a non-catalytic process for this reaction.

Addition of one equiv. of triflic acid to a benzene solution of [PNP]PtMe at room temperature afforded [PNP]PtOTf in 61% isolated yield. The triflate complex can also be prepared from the

reaction of [PNP]PtCl with AgOTf quantitatively on the basis of $^{31}P\{^1H\}$ NMR investigation. The lability of the triflate ligand in [PNP]PtOTf is demonstrated by its facile displacement by pyridine (py) and acetonitrile.¹¹ Fig. 3 depicts the X-ray structure of {[PNP]Pt(py)}OTf,‡ in which the fourth coordination site of the square-planar platinum center is occupied by a pyridine ligand. Nevertheless, the triflate complex [PNP]PtOTf is thermally stable in benzene (6.8 mM) at 150 °C for 20 h as indicated by $^{31}P\{^1H\}$ NMR spectroscopy, as is its pyridine adduct {[PNP]Pt(py)}OTf (8.4 mM).

Interestingly, heating a benzene solution of [PNP]PtOTf to 110 °C or above in the presence of a variety of aliphatic amines such as triethylamine, *N*-methyl-dicyclohexylamine (MeNCy₂), or 1,4-diazabicyclo[2.2.2]octane (DABCO) yielded [PNP]PtPh quantitatively. This reaction is complete in 2.5 h at 150 °C as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. Attempts to employ an excess amount of amines did not increase the rate of formation of [PNP]PtPh. In contrast, no reaction was found for [PNP]PtCl under similar conditions, suggesting that prior dissociation or displacement of the labile triflate ligand in [PNP]PtOTf is essential for intermolecular benzene C–H bond activation in this process. A similar phenomenon was also reported recently for platinum complexes supported by a bis(8-quinolinyl)amide ligand.¹²

In summary, we have prepared a series of platinum complexes supported by the tridentate [PNP][−] ligand and demonstrated intermolecular benzene C–H bond activation promoted by these molecules in the presence of an appropriate Lewis acid or base. Studies directed to define the reaction mechanism and scope of applicable hydrocarbon substrates are currently under way.

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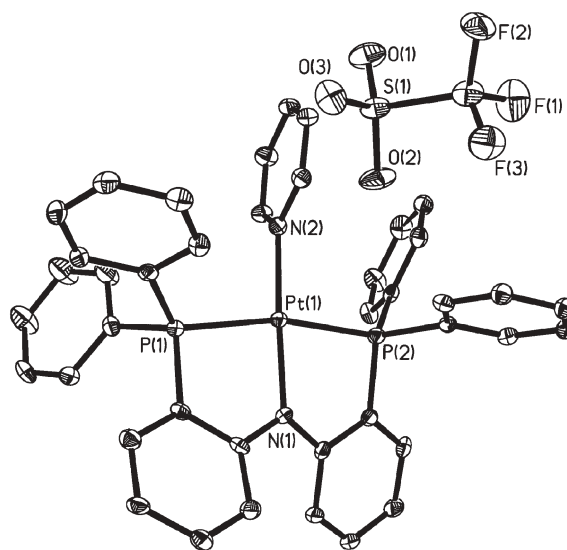


Fig. 3 Molecular structure of {[PNP]Pt(py)}OTf with thermal ellipsoids drawn at the 35% probability level. One toluene molecule found in the asymmetric unit cell is omitted for clarity. Selected bond distances (Å) and angles (°): Pt(1)–N(1) 2.025(5), Pt(1)–N(2) 2.056(5), Pt(1)–P(2) 2.2735(17), Pt(1)–P(1) 2.2941(17); N(1)–Pt(1)–N(2) 175.6(2), N(1)–Pt(1)–P(2) 82.68(16), N(2)–Pt(1)–P(2) 93.60(16), N(1)–Pt(1)–P(1) 84.00(16), N(2)–Pt(1)–P(1) 99.65(15), P(2)–Pt(1)–P(1) 166.60(6).

Notes and references

‡ Crystal data: for {[PNP]PtCl·5C₆H₆: C₆₆H₅₈ClNP₂Pt, *M* = 1157.61, monoclinic, space group *P*₂₁/*n*, *a* = 17.3780(5), *b* = 12.7050(4), *c* = 25.5550(7) Å, β = 104.5820(10)°, *V* = 5460.5(3) Å³, *T* = 100(2) K, *Z* = 4, μ(Mo-Kα) = 2.719 mm⁻¹, 21551 reflections measured, 9430 unique (*R*_{int} = 0.1316) which were used in all calculations. Final *R*₁ [*I* > 2σ(*I*)] = 0.0781, *wR*₂ [*I* > 2σ(*I*)] = 0.2004, *R*₁ (all data) = 0.0914, *wR*₂ (all data) = 0.2174, GOF (on *F*²) = 1.032, CCDC 261444. For [PNP]PtMe: C₃₇H₃₁NP₂Pt, *M* = 746.66, orthorhombic, space group *F*2*dd*, *a* = 9.9610(2), *b* = 18.6010(4), *c* = 32.7250(9) Å, *V* = 6063.4(2) Å³, *T* = 293(2) K, *Z* = 8, μ(Mo-Kα) = 4.761 mm⁻¹, 7661 reflections measured, 2559 unique (*R*_{int} = 0.0536) which were used in all calculations. Final *R*₁ [*I* > 2σ(*I*)] = 0.0355, *wR*₂ [*I* > 2σ(*I*)] = 0.0990, *R*₁ (all data) = 0.0438, *wR*₂ (all data) = 0.1123, GOF (on *F*²) = 0.975, CCDC 261443. For {[PNP]Pt(py)}OTf·PhMe: C₄₉H₄₁F₃N₂O₃P₂PtS, *M* = 1051.93, monoclinic, space group *P*₂₁/*n*, *a* = 15.1140(2), *b* = 17.6950(3), *c* = 16.9010(3) Å, β = 105.9800(10)°, *V* = 4345.38(12) Å³, *T* = 100(2) K, *Z* = 4, μ(Mo-Kα) = 3.409 mm⁻¹, 32860 reflections measured, 7654 unique (*R*_{int} = 0.0676) which were used in all calculations. Final *R*₁ [*I* > 2σ(*I*)] = 0.0422, *wR*₂ [*I* > 2σ(*I*)] = 0.1023, *R*₁ (all data) = 0.0609, *wR*₂ (all data) = 0.1399, GOF (on *F*²) = 1.181, CCDC 261442. The hydrogen atoms in the methyl group of [PNP]PtMe and the toluene methyl group of {[PNP]Pt(py)}OTf·PhMe can not be located experimentally. See <http://www.rsc.org/suppdata/cc/b5/b501520k/> for crystallographic data in CIF or other electronic format.

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