P Ligands

Molecular and Electronic Structure of Platinum Bis(*N*-arylamino)phosphenium Complexes including [Pt(phosphane)(phosphenium)-(N-heterocyclic carbene)]**

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*Dedicated to Professor M. Frederick Hawthorne
on the occasion of his 75th birthday*

The application of electrophilic late-transition-metal complexes in catalysis has enjoyed widespread success in recent years.[1–6] We have been investigating electrophilic platinum complexes for catalysis and hydrocarbon C–H bond activation[7,8] and recently reported a simple strategy for obtaining unsaturated electrophilic metal centers by addition of bulky bis(*N*-arylamino)phosphenium cations, easily derived from bis(*N*-aryl)diimines.[9] Detailed theoretical investigations[10] of

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[**] The authors thank the US Department of Energy's Laboratory-Directed R&D program at Los Alamos for support of this project and partial support of T.M.G.'s summer sabbatical at Los Alamos. We are also grateful to the referees for a number of helpful comments.

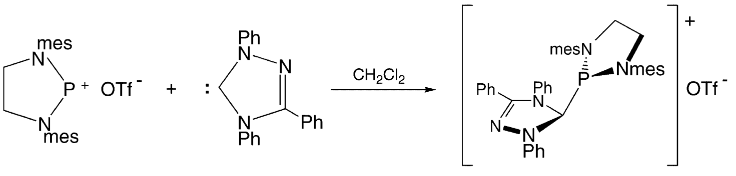
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352326

the electronic structure of these phosphenium cations, their donor–acceptor adducts, and transition-metal complexes showed them to be excellent π acceptors, but poor σ donors[11] and thus complementary to N-heterocyclic carbenes (NHCs, which are good σ donors, poor π acceptors).[12]

Herein we report the synthesis, characterization, and electronic structure of an N-heterocyclic carbene adduct (CN_2) of the bis(*N*-mesitylamino)phosphenium cation [PN_2^+, Eq. (1); mes = 2,4,6-$Me_3C_6H_2$, Tf = SO_2CF_3]. In the reaction of this adduct with [$Pt(PPh_3)_3$] to form the [$Pt(PPh_3)(PN_2)(CN_2)$]$^+$ ion, we demonstrate that NHC-phosphenium adducts are particularly well suited for preparing the first platinum phosphenium complexes, supplying both excellent σ-donor and π-acceptor ligands from the same reagent.

Phosphenium cations[13] have experienced a resurgence as ligands for transition metals[9,14] and main-group elements,[15] and as π-acceptor ligands for homogeneous catalysis.[16] We are interested in cyclic bis(*N*-arylamino)phosphenium cations as "bulky CO" ligands that create electrophilic metal centers and also offer a Lewis acid function in the metal's coordination sphere for bifunctional catalysis.[17] Given the poor σ-donor ability of phosphenium cations,[10b] stable donor–acceptor adducts (L→PN_2)$^+$ could serve as useful reagents by supplying both donor and acceptor ligands to the metal. As our previously reported PMe_3 adducts were formed reversibly,[9] we investigated the stronger donor NHC ligand **2**.[18]



1, (PN_2)OTf **2**, CN_2 **3**

(1)

Reaction of [PN(mes)CH_2CH_2N(mes)]OTf (**1**) with NHC (**2**; CN_2)[19] afforded the donor–acceptor adduct [N_2C:→PN_2]OTf (**3**) as a colorless solid in good yield.[20] Adduct **3** was characterized by NMR spectroscopy and its electronic structure determined using density functional theory (DFT). The ^{31}P chemical shift of **3** ($\delta = 113.7$ ppm) is significantly upfield from that of **1** ($\delta = 188.6$ ppm) whereas the carbene carbon resonance shifts from $\delta = 214.4$ ppm in CN_2 to $\delta = 165.7$ ppm in **3** and exhibits a large one-bond C–P coupling constant (199 Hz). Similar NHC–phosphinidene complexes, albeit with two-coordinate phosphorus centers, feature $J_{\text{C-P}}$ coupling constants of approximately 100 Hz.[21] In contrast to the PMe_3 adduct,[9] variable temperature ^{31}P and ^{13}C NMR spectra of **3** showed no shifting of the resonance signals (as would be expected for reversible adduct formation) but only a gradual sharpening as the temperature was lowered. Hindered rotation about the N−C_{mes} bond leads to very broad resonances in the proton NMR spectrum at 25 °C, as observed previously for PN_2Cl[9] and confirmed for **3** by observation of six different mesityl methyl signals at −56 °C in the ^{13}C NMR.[22] We have studied the model adduct [(MeNN=CMeNMe)C→P(NMeCH_2CH_2NMe)]$^+$ (Figure 1) with hybrid DFT (B3LYP and the 6-31G* basis set).[23] The calculation finds a P−C bond length of 1.91 Å and an angle between the vector which bisects the PN_2 angle and the P–C vector of only 103°, indicative of partial rehybridization at the phosphorus center. These parameters can be contrasted with the other reported NHC-phosphenium cation adduct,[18] [carb:→PPh_2]$AlCl_4$ (**4**, carb = 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) in which our calculated P−C bond length is 1.87 Å (experimentally determined: 1.813(7) Å) and the analogous angle involving the PPh_2 unit is 113°(experimentally determined: 112.7°). The NHC adduct of the more electrophilic [PPh_2]$^+$ ion may thus be better represented as an imidazolatophosphane with a lone pair at phosphorus, whereas the N donors in **3** stabilize the localized positive charge on the phosphorus center. Adduct **3** is also distinguished from adducts of diaminophosphenium cations with electrophilic carbenes, such as [$(Me_3Si)_2C$=P(N*i*$Pr_2)_2$]$^+$ which has $\delta(^{13}\text{C}) = 76.51$ ppm ($J_{\text{C-P}} = 87.6$ Hz) and $d_{\text{P-C}} = 1.620(3)$ Å.[24]

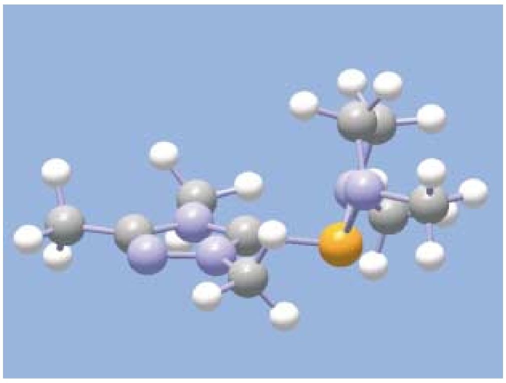
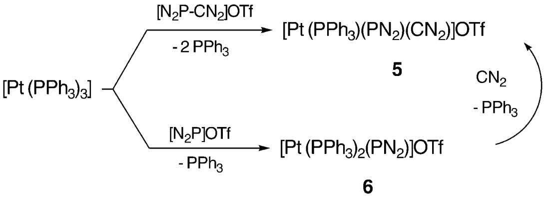


Figure 1. Optimized structure (DFT) of model NHC–phosphenium cation adduct. Orange = P, lilac = N, gray = C, white = H.

Reaction of adduct **3** with [$Pt(PPh_3)_3$] displaces two phosphane ligands to give three-coordinate [Pt(phosphane)(phosphenium)(carbene)]OTf [**5**, Eq. (2)].[25] While platinum(0) phosphane complexes participate readily in oxidative addition reactions, cleavage of the P−C bond in **3** affords a zerovalent product and may therefore be considered a "non-oxidative addition" reaction similar to those of tetraaminoethylene derivatives that afford bis(diaminocarbene) metal complexes.[26] Complex **5** may also be obtained from stepwise reactions of the phosphenium cation with [$Pt(PPh_3)_3$] to yield PPh_3 and [$Pt(PPh_3)_2$(phosphenium)][OTf], (**6**)[27] followed by



(2)

treatment with NHC **2** to liberate another PPh_3 and afford **5** [Eq. (2)]; in contrast, $[Pt(PPh_3)_3]$ did not react readily with the NHC ligand.

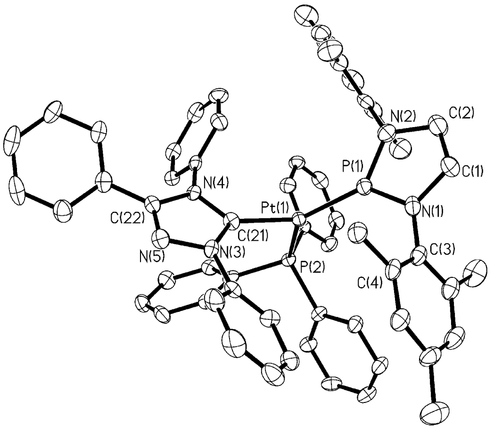


Figure 2. Molecular structure of **5**, thermal ellipsoids are set at 30% probability. Hydrogen atoms and triflate counteranion are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Pt(1)-C(21) 2.037(10), Pt(1)-P(1) 2.116(3), Pt(1)-P(2) 2.316(3), P(1)-N(1) 1.622(10), P(1)-N(2) 1.638(11); C(21)-Pt(1)-P(1) 132.9(3), C(21)-Pt(1)-P(2) 101.9(3), P(1)-Pt(1)-P(2) 125.25(11).

Complexes **5** and **6** were characterized by elemental analysis and NMR spectroscopy and the molecular and electronic structure of **5** were determined by X-ray diffraction (Figure 2)[28] and DFT calculations. The Pt-P coupling constants for the phosphenium ligands in **5** (7354 Hz) and **6** (6498 Hz) were significantly larger than those for the phosphane ligands (3795 and 4237 Hz, respectively). These large coupling constants correlate with short Pt−P bond lengths; that in **5** is the shortest reported to date[29] (2.116(3) Å) and is approximately 7% shorter than the average bond length found in tricoordinate $[Pt(PPh_3)_3]$ (ca. 2.266 Å).[30] While the structure of the NHC ligand in **5** (C_2 axis bisecting C(22) and N(4) and passing through the N(3)–C(Ar) vector) allows hypothetically for binding through the carbene carbon atom or the nitrogen atom of the central ring, platinum coordination by the carbene carbon atom was confirmed by ^{13}C NMR spectroscopy ($\delta = 194.5$ ppm with $J_{\text{Pt-C}} = 1614$ and $^2J_{\text{P-C}} = 84.5$ Hz). The PN_2 and CN_2 planes of the phosphenium and carbene ligands are nearly perpendicular (87.8 and 79.2°) to the distorted PtP_2C trigonal plane, as predicted by DFT calculations. The perpendicular orientation of the PN_2 and CN_2 planes in **5** is also apparent in DFT studies of the model complex in which all eight aryl substituents in **5** are replaced with methyl groups. This preference can be understood in terms of Pt(dπ)–P(pπ) back bonding. The ligand field arising from the three ligand lone-pair orbitals constitutes a pseudo D_{3h} environment about the platinum center. In such a situation, the two energetically highest d orbitals are $d_{x^2-y^2}$ and d_{xy} in character, where the z axis is chosen perpendicular to the plane and the x direction is chosen to lie along the $Pt–P_{\text{phosphane}}$ axis. Both orbitals are filled in the nominally d^{10} complex, but note that while the d_{xy}–PN_2 σ interaction is repulsive, the $d_{x^2-y^2}$ orbital has the correct symmetry to interact with the PN_2 empty P(pπ) orbital as observed in the HOMO of the model complex (see Supporting Information Figure S4). A similar argument holds for the CN_2 ligand, but it is a significantly poorer π acid than the PN_2^+ ligand.[31]

In conclusion, we have prepared a cationic NHC-phosphenium adduct from its constituents and shown that it can replace two phosphane ligands of $[Pt(PPh_3)_3]$ with strong σ-donor NHC and effective π-acceptor phosphenium ligands. These first examples of platinum phosphenium complexes are characterized by short Pt−P bonds and large Pt–P coupling constants. We are currently conducting further additions of NHC-phosphenium adducts to transition metals and investigating the reactivity and catalytic activity of the resulting complexes.

Received: July 7, 2003
Revised: December 6, 2003 [Z52326]

Keywords: heterocycles · N-heterocyclic carbenes · P ligands · platinum

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[18] One other phosphenium–NHC adduct (**4**) was prepared previously by reaction of $[PPh_2(NHC)]Cl$ with $AlCl_3$ (^{31}P NMR: $\delta = -27$ ppm; carbene carbon atom not detected in ^{13}C NMR spectrum): N. Kuhn, J. Fahl, R. Boese, D. Blaeser, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729.

[19] IUPAC name for **2** is 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene.

[20] **3**: Solid $(PN_2)OTf$ (**1**; 0.945 g, 2 mmol) was added slowly over 30 min to a solution of NHC **2** (594 mg, 2 mmol) in cold (0 °C) CH_2Cl_2 (15 mL). The solution was allowed to stir overnight and volatiles were removed in vacuo, yield 1.26 g, 82 %. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 2.29$ (vbr, 18 H, *o*,*p*-Me of *N*-mes), 3.67 (vbr, 4 H, PN_2CH_2), 6.90 (vbr, 4 H, *m*-H of *N*-mes), 7.25–7.70 ppm (ov m, 15 H, *N*-Ph and *C*-Ph); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) 20.07, 20.65, 21.21 ($C_6H_2(CH_3)_3$), 54.00 (PN_2CH_2), 123.46, 128.99, 129.88, 129.94, 130.29, 130.63, 130.93, 131.10, 131.21, 131.40, 132.03, 137.09, 138.20, 165.70 ppm (d, ipso carbene C, $J_{P\text{-}C}$ 199.4 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) $\delta = 113.7$ ppm (br).

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[22] As noted by a referee, in the absence of a more detailed study we cannot rule out hindered rotation about the P–C bond as well.

[23] DFT calculations employed the B3LYP functional and the LANL2DZ and relativistic-effective core potential and associated basis for Pt, except that the Pt basis set was completely uncontracted. This approach yields two p functions with nearly identical exponents (0.6048 and 0.5982); only the former was retained. The 6-31G* basis set was utilized for the ligands.

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[25] **5**: Two different procedures involved adding either a) **2** to **6** or b) **3** to a solution of $[Pt(PPh_3)_3]$. Both reactions were carried out on a 1-mmol scale at −10 °C in CH_2Cl_2 (20 mL) and were allowed to warm to room temperature over 3 h, whereupon volatiles were removed in vacuo. The resulting yellow powder was purified by washing with warm (50 °C) toluene (2 × 50 mL) and collecting the slightly yellow solid. Yield a) 0.58 g (44 %), b) 0.54 g (41 %). Crystals suitable for X-ray diffraction studies were grown from a saturated CH_2Cl_2 solution layered with toluene. ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 1.85$, 2.27 (6 H, *o*-Me of *N*-mes), 2.46 (6 H, *p*-Me of *N*-mes), 3.78 (4 H, PN_2CH_2), 6.39, 6.67, 6.86, 6.97, 7.17, 7.29, 7.37, 7.74 ppm (m, *m*-H of *N*-mes, Ph); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) $\delta = 18.13$, 18.60 (*o*-Me of *N*-mes), 21.45 (*p*-Me of *N*-mes), 51.67 (PN_2CH_2), 121.18, 126.00, 128.42, 129.01, 129.12, 129.29, 129.67, 129.84, 130.60, 131.53, 133.54, 133.66, 136.96, 137.42, 138.98, 194.48 ppm (ipso-carbene *C*, $^1J_{Pt\text{-}C}$ 1614.3 Hz, $^2J_{C\text{-}P}$ 84.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) $\delta = 36.7$ (dd, $^1J_{Pt\text{-}P} = 3795$ Hz, $^2J_{P\text{-}P} = 240$ Hz, PPh_3), 271.8 ppm (dd, $^1J_{Pt\text{-}P} = 7354$ Hz, $^2J_{P\text{-}P} = 240$ Hz, PN_2).

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[27] **6**: Solid PN_2OTf (0.472 g, 1.0 mmol) was added slowly over 1 h to a cold (0 °C) solution of $[Pt(PPh_3)_3]$ (1.07 g, 1.0 mmol) in CH_2Cl_2 (20 mL). The solution was warmed to ambient temperature and stirred for 3 h. Solvent was removed in vacuo and the subsequent pale yellow powder was dissolved in warm toluene (60 °C; 30 mL). The toluene solution was allowed to sit in the freezer overnight upon which a pale yellow oil formed at the bottom of the flask. The toluene was decanted off and the oil pumped on for 5 h to yield a yellow powder. Yield 0.64 g, 49.8 %. ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 2.06$ (12 H, *o*-Me of *N*-mes), 2.36 (6 H, *p*-Me of *N*-mes), 3.99 (4 H, PN_2CH_2), 6.91, 7.15, 7.35 ppm (ov m, 34 H, *m*-H of *N*-mes, Ph); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) 18.27 (*o*-Me of *N*-mes), 21.40 (*p*-Me of *N*-mes), 51.99 (PN_2CH_2), 129.16, 130.46, 131.15, 133.86, 134.19, 134.37, 136.77, 139.35 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) 43.9 (dd, $^1J_{Pt\text{-}P} = 4237$ Hz, $^2J_{P\text{-}P} = 232$ Hz, PPh_3), 289.0 ppm (dtr, $^1J_{Pt\text{-}P} = 6498$ Hz, $^2J_{P\text{-}P} = 232$ Hz, PN_2).

[28] X-ray diffraction data for $[Pt(PPh_3)(PN_2)(CN_2)]OTf$ (**5**) were collected on a Bruker P4/CCD diffractometer (Bruker AXS) using graphite monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at $T = 183$ K. A pale yellow block of the dichloromethane solvate $C_{58}H_{56}F_3N_5O_3P_2PtS{\cdot}CH_2Cl_2$ measuring $0.2 \times 0.1 \times 0.1$ mm^3 was covered with paratone oil in an inert atmosphere and mounted on a glass fiber. Monoclinic, $P2_1/c$ with $a = 16.653(6)$, $b = 18.830(6)$ $c = 19.924(7)$ Å, $\alpha = 90$, $\beta = 112.614(5)$, $\gamma = 90°$, $V = 5767(3)$ Å^3, $Z = 4$. ρ_{calcd} 1.513 mg m^{-3}. 30393 reflections collected of which 8057 independent reflections with $I > 2\sigma$. All non-hydrogen atoms were refined anisotropically with final $R1 = 0.0773$, $wR2 = 0.1382$ for $I > 2\sigma$. CCDC-212747 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[29] A Cambridge CSD search revealed one shorter bond of 2.114 Å. However, this is one of two chemically identical but crystallographically independent molecules in the unit cell. This molecule features two Pt centers bridged by hydrido and phosphido units. The shortness of the Pt–P bond is thus likely to be due to the compensation of the short Pt–H bond. Regardless, the bond length must be reported as an average of the two distances in the cell and is reported in the paper as 2.162(8) Å. Cf. J. Jans, R. Naegeli, L. M. Venanzi, A. Albinati, *J. Organomet. Chem.* **1983**, *247*, C37.

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