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Guilty as charged: non-innocent behavior by a pincer ligand featuring a central cationic phosphenium donor†

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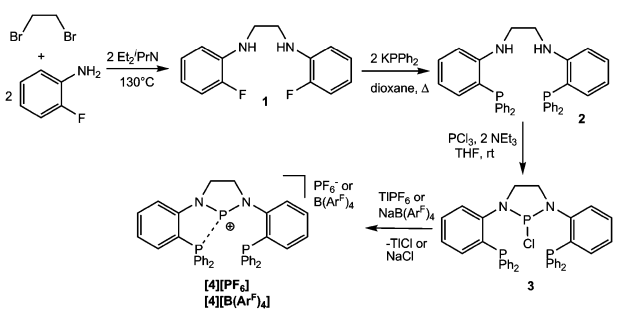
The synthesis of a new pincer ligand containing a central cationic *N*-heterocyclic phosphenium donor is described. The electrophilic nature of this cationic ligand renders it non-innocent, and coordination of this ligand to a $PtCl_2$ fragment leads to chloride migration from Pt to the cationic phosphorus center.

While *N*-heterocyclic carbene ligands (NHCs) have become ubiquitous in the field of transition metal and organocatalysis,[1–5] far less focus has been placed on the potential applications of their isovalent group 15 analogues, *N*-heterocyclic phosphenium cations (NHPs).[6–8] In contrast to the nucleophilic σ-donor nature of NHCs, the weak σ-donor and strong π-acceptor properties of NHPs lead to electrophilic character. Moreover, owing to their many possible resonance structures and the potential to adopt either planar or pyramidal geometries, Jones and coworkers have drawn a convincing analogy between NHPs and NO^+, highlighting the potential non-innocent character of these ligands.[9] Recent advancements in the chemistry of NHPs include new preparative methods[10–13] and new reactivity patterns,[9,10,14,15] but very few catalytic applications of these ligands have been reported to date.[16,17] This is surprising in light of the anticipated complementary reactivity of NHPs in comparison to their electronically opposite NHC relatives. However, this dearth of catalytic applications can likely be attributed to the susceptibility of NHPs to nucleophilic attack.[6–8]

A potential strategy for imparting stability in transition metal phosphenium complexes is the incorporation of these donors into chelating frameworks. Transition metal complexes of multidentate ligands featuring NHPs are noticeably absent from the literature, particularly in comparison to the growing number of NHC-containing chelating ligands.[18,19] In this report we have chosen to incorporate an *N*-heterocyclic phosphenium cation into the central position of a tridentate pincer ligand, motivated by: (1) the stability imparted by the rigid framework of pincer ligands,[20–22] (2) the placement of an open metal coordination site *trans* to the NHP moiety in these meridional-coordinating ligands, and (3) the ability to sterically modify the pendant donor functionalities to protect the phosphenium unit from nucleophilic attack. Incorporation of an NHP into a multidentate framework may allow stabilization of catalytically relevant transition metal complexes and more comprehensive comparisons with NHCs. Herein we report the synthesis and characterization of the first NHP-containing pincer ligand and its representative coordination chemistry with Pt^{II}.

Synthesis of the targeted ligand was not as straightforward as initially envisioned for several reasons including: (1) typical glyoxal condensation routes proved problematic with phosphine-substituted anilines,[23] and (2) lithiation of aryl bromides was complicated by the presence of acidic protons on the *ortho* anilido nitrogen atoms which appeared to undergo irreversible *N*-phosphination upon treatment with $^iPr_2PCl$ (see ESI†).[24] Nonetheless, phosphenium ligand $\mathbf{4}^+$ was synthesized successfully *via* the route shown in Scheme 1. Synthesis of the pincer ligand backbone was accomplished *via* alkylation of *o*-fluoroaniline with 1,2-dibromoethane to generate diamine **1**, followed by nucleophilic substitution of the aryl fluorides with $KPPh_2$ to generate the diphosphine **2** in modest yield (Scheme 1). Interestingly, no side reaction of the amine functionality with $KPPh_2$ was detected. Treatment of **2** with PCl_3 in the presence of two equivalents of NEt_3 leads to formation of the phosphine chloride **3**. Compound **3** has ^{31}P NMR shifts at −17.6 ppm and 147.9 ppm, characteristic of triarylphosphine and chlorodiaminophosphine moieties, respectively. Halide abstraction from **3** is accomplished using either $TlPF_6$ or $NaB(Ar^F)_4$ (Ar^F = 3,5-CF_3–C_6H_3) to obtain



Scheme 1 Synthesis of pincer ligand $\mathbf{4}^+$.

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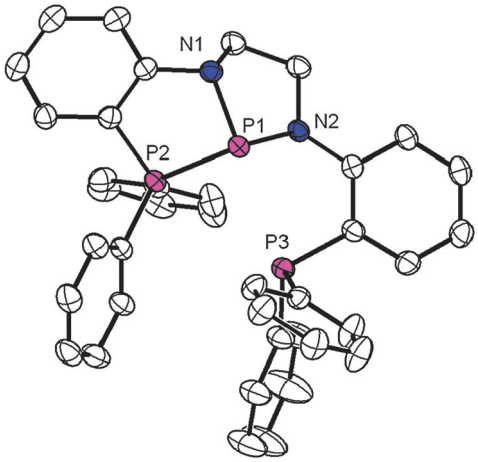
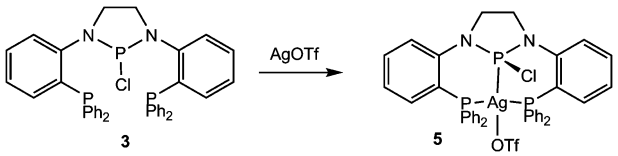


Fig. 1 Displacement ellipsoid representation of $\mathbf{4}^+$. PF_6^- counter-anion has been omitted for clarity. Relevant interatomic distances (Å): P1–P2, 2.2786(4); P1–P3, 2.858.

the phosphenium PP^+P pincer ligand **[4][PF$_6$]** or **[4][B(Ar^F)$_4$]** in 96.0% and 93.3% yields, respectively.

While the ^{31}P NMR shift of the PPh_2 moieties of $\mathbf{4}^+$ appears in the expected location (−11 ppm, doublet, J = 220 Hz), the ^{31}P resonance for the central phosphenium phosphorus atom is shifted remarkably upfield (~90 ppm, triplet, J = 220 Hz) in comparison to both **3** and other phosphenium cations reported in the literature.[6,7] An intramolecular phosphenium–phosphine Lewis acid/base interaction would account for this upfield shift. The solid state structure of **[4][PF$_6$]** shown in Fig. 1 indeed reveals a well-defined interaction between one of the triarylphosphine substituents and the central phosphenium cation with a P1–P2 distance of 2.2786(4) Å (*cf.* 2.858 Å for the unbound phosphine).‡ A similar P–P distance of 2.3065(9) Å was observed in the structure of the phosphenium–PMe_3 adduct reported by Baker *et al.*[13] While this asymmetry is apparent in the solid state, it is in stark contrast to the room temperature ^{31}P NMR spectrum, which implies equivalence of both phosphine arms on the NMR time scale at room temperature. Since the room temperature ^{31}P NMR signals are an average of rapidly exchanging P^+-bound and unbound phosphines, the actual $^1J_{P-P}$ can be determined by the following equation: $J_{obs} = \frac{1}{2}(^1J_{P-P} + {}^4J_{P-P})$. Assuming that $^4J_{P-P}$ is negligible, $^1J_{P-P}$ is calculated to be 440 Hz, consistent with Baker's phosphenium–PMe_3 adducts.[13] At low temperature the doublet at −11 ppm for the phosphine sidearms broadens and eventually coalesces at −65 °C, while the triplet at 88 ppm changes its shape as the temperature is lowered, presumably morphing into a doublet ($^1J_{P-P}$ = 440 Hz) as the central peak of the triplet coalesces into the baseline (see ESI†).

Interestingly, treatment of phosphine chloride **3** with AgOTf instead of $TlPF_6$ leads to formation of the silver coordination complex (PPClP)AgOTf (**5**) rather than halide abstraction (Scheme 2). The ^{31}P NMR resonances of the phosphine sidearms shift downfield upon metal coordination (−6.8 ppm), but the ^{31}P shift corresponding to the central phosphorus atom remains in the range for a halide-bound phosphorus (134 ppm). The phosphines show distinct coupling to $^{107/109}$Ag with $^1J_{Ag-P}$ = 590 Hz, while no coupling between the Ag center and the central phosphorus is observed. The



Scheme 2 Treatment of **3** with AgOTf.

solid state structure of **5** (Fig. 2) confirms that the P–Cl bond remains intact and reveals little or no interaction between the Ag center and the chloride-bound central phosphorus consistent with the lack of Ag–P coupling in solution.§ The complex adopts a distorted trigonal planar geometry around Ag and a clearly pyramidalized geometry about the central phosphorus donor. In addition to a long interatomic Ag–P2 distance (2.7230(13) Å), the Ag–P2–Cl (153.09(7)°) angle is significantly larger than that in reported transition metal chlorophosphine complexes (based on a 2010 CSD search), implying that there is negligible bonding between Ag and P2.

In an attempt to coordinate the chelating phosphenium cation to a metal, **[4][PF$_6$]** was treated with (COD)$PtCl_2$ (COD = 1,5-cyclooctadiene, Scheme 3). The ^{31}P NMR of the resulting product revealed a singlet at 2.9 ppm for the aryl phosphine sidearms and a singlet at 76.6 ppm for the central phosphorus atom. While both resonances feature ^{195}Pt satellites ($^1J_{Pt-P}$ = 2100 Hz (PR_3), $^1J_{Pt-P}$ = 4860 Hz (central P)) implying that both phosphorus-containing moieties are bound to the Pt center, the central phosphorus resonance is too far upfield to correspond to a metal-bound phosphenium unit.

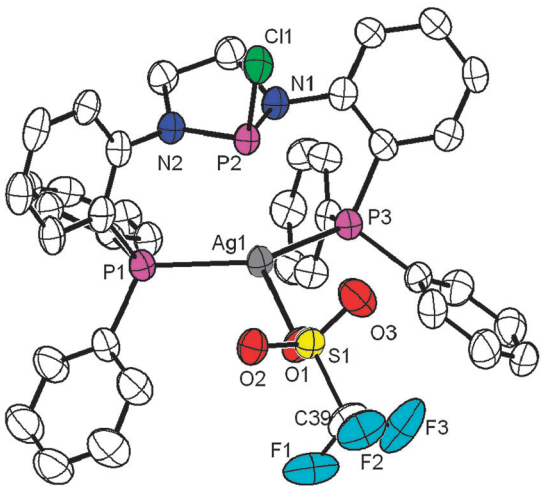
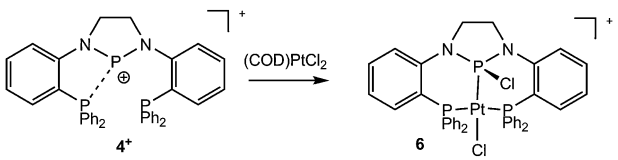


Fig. 2 Displacement ellipsoid diagram (50%) of **5**. Relevant interatomic distances (Å) and angles (°): Ag–P2, 2.7230(13); Ag–P1, 2.4457(13); Ag–P3, 2.4433(13); P2–Cl1, 2.1618(18); Ag–O1, 2.363(3); Cl1–P2–Ag, 153.09(7); P1–Ag–P3, 139.39(4); P3–Ag–O1, 107.85(11); P1–Ag–O1, 109.34(11).



Scheme 3 Treatment of $\mathbf{4}^+$ with (COD)$PtCl_2$.

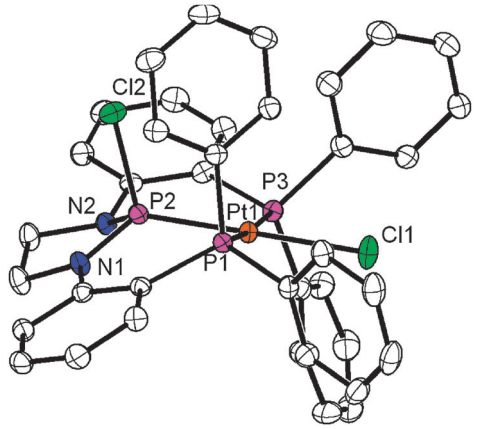


Fig. 3 Displacement ellipsoid diagram (50%) of **6**. PF_6^- counter-anion has been omitted for clarity. Relevant interatomic distances (Å) and angles (°): Pt–P1, 2.2980(5); Pt–P2, 2.1553(5); Pt–P3, 2.3018(5); Pt–Cl1, 2.3339(5); P2–Cl2, 2.0588(6); Pt–P2–Cl2, 110.06.

The X-ray structure of the product (Fig. 3), indeed, revealed that one of the Pt-bound Cl^- ligands had migrated to the central phosphenium unit, resulting in the cationic Pt complex [(PPClP)PtCl][PF_6] **6**.¶ Chloride attack on the electrophilic phosphenium unit is not particularly surprising, and similar halide and alkyl migration events have been previously reported.[13,25–27] In contrast to Ag complex **5**, the central chlorophosphine unit in **6** is bound tightly to Pt, with a P2–Pt distance (2.1553(5) Å) even shorter than that observed for the Pt-bound phosphines (Pt–P1: 2.2980(5) Å, Pt–P3: 2.3018(5) Å). Notably, this Pt–P2 distance is also remarkably similar to that in the Pt phosphenium complex reported by Baker and co-workers (2.116(3) Å).[15] This short interaction is likely due to extensive π-backbonding from Pt into the σ* orbital of the strongly acidic diamidochlorophosphine unit. Indeed, both the Pt–P distance and the $^1J_{Pt-P}$ coupling constant associated with the central phosphorus donor are in the range reported for Pt–$P(OMe)_3$ complexes.[28] Notably, no reaction was observed between **6** and $TlPF_6$, implying that chloride ion abstraction is not feasible once coordinated to a metal center.

In conclusion, a new pincer ligand containing a central *N*-heterocyclic phosphenium cation has been synthesized. Preliminary investigations into the coordination chemistry of this ligand with the $PtCl_2$ fragment suggest that the electrophilic nature of the central phosphenium donor facilitates halide migration from Pt to P. Further modification of the ligand framework with more sterically encumbering substituents may prevent this intramolecular halide transfer. Additional investigations into the coordination chemistry of $\mathbf{4}^+$ with a variety of other transition metals are currently underway and will be reported in subsequent publications.

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Notes and references

‡ Crystal data for **[4][PF_6]**: $C_{38}H_{32}F_6N_2P_4$, M = 754.57, monoclinic, a = 20.0011(5) Å, b = 24.3395(6) Å, c = 16.1163(4) Å, α = 90°, β = 115.9030(10)°, γ = 90°, V = 7057.5(3) Å^3, T = 120 K, space group $C12/c1$, Z = 8, R_{int} = 0.040. The final R_1 values were 0.0449 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1038 ($I > 2\sigma(I)$).
§ Crystal data for **5**: $C_{47}H_{48}Ag_1Cl_1F_3N_2O_5P_3S_1$, M = 1046.21, orthorhombic, a = 11.9962(5) Å, b = 15.9208(7) Å, c = 25.0428(10) Å, α = 90°, β = 90°, γ = 90°, V = 4782.9(3) Å^3, T = 120 K, space group $P2_12_12_1$, Z = 4, R_{int} = 0.062. The final R_1 values were 0.0420 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0968 ($I > 2\sigma(I)$).
¶ Crystal data for **6**: $C_{38}H_{32}Cl_2N_2P_3Pt{\cdot}F_6P$, M = 1020.56, monoclinic, a = 12.5297(7) Å, b = 13.4232(7) Å, c = 22.7095(13) Å, α = 90°, β = 96.303(2)°, γ = 90°, V = 3796.4(4) Å^3, T = 120 K, space group $P12_1/n1$, Z = 4, R_{int} = 0.028. The final R_1 values were 0.0182 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0435 ($I > 2\sigma(I)$).

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