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Unusual Metal-Coordinated Zwitterionic P–C–N–C–N–C Phosphido Adducts

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Rare examples of homodinuclear zwitterionic Pd\textsuperscript{II} and Pt\textsuperscript{II} complexes with bridging, two-coordinate P(cyclo-CH\textsubscript{2}N(R)CHN(R)CH\textsubscript{2}) ligands (R = 4-FC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}, C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}) have been characterized by single crystal X-ray diffraction using synchrotron radiation. Short N–C distances and enlarged N–C–N bond angles support electron delocalization in the central N–C–N backbone.

Two-coordinate phosphorus ligands attract considerable interest for their diverse transition metal chemistry. Phosphenium cations (R\textsubscript{2}P\textsuperscript{+})\textsuperscript{1} or phosphido anions (R\textsubscript{2}P\textsuperscript{−})\textsuperscript{2} are important classes of two-coordinate phosphorus ligands. Phosphenium ions have been widely studied and stabilized by various donor substituents e.g. aryl/alkylamino\textsuperscript{3}, hydrocarbon\textsuperscript{4} and N,C-bonded β-diketiminato groups.\textsuperscript{5} Burford and co-workers\textsuperscript{6} have elegantly shown phosphenium cations can be isolated upon coordination to tertiary phosphine ligands. Furthermore, phosphenium ions can readily be stabilized at transition metal centers.\textsuperscript{1} Phosphido ligands are known to bind in a terminal fashion\textsuperscript{2} or, more commonly, bridge two metal centers.\textsuperscript{2} Whilst this bridging mode is common for phosphides, it is considerably more unusual for tertiary phosphines to function in this manner.\textsuperscript{7}

As part of continuing studies in our group investigating supramolecular interactions in (di)tertiary phosphines,\textsuperscript{8} we recently reported easily accessible intramolecular H-bonded phosphine analogues of the cage ligand PTA (PTA = 1,3,5-triaza-7-phosphaadamantane).\textsuperscript{8a} The recent surge in interest with PTA, and its analogues, can be traced to the ease of chemical modification\textsuperscript{9} and diverse coordination, cytotoxic and catalytic properties.\textsuperscript{10} Herein we report the structural characterization of two peculiar homodinuclear zwitterionic Pd\textsuperscript{II} and Pt\textsuperscript{II} complexes of a partially delocalized six-membered P{cyclo-CH\textsubscript{2}N(R)CHN(R)CH\textsubscript{2}} (R = 4-FC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}, C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}) bridging phosphido ligand.

Reaction of [Pd(κ\textsubscript{2}-C\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}NMe\textsubscript{2})(μ-Cl)]\textsubscript{2} with two equiv. of L\textsubscript{1} (R = 4-FC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}; X = Cl)\textsuperscript{8a} in CH\textsubscript{2}Cl\textsubscript{2} afforded the cyclometallated complex 1 in high yield (78%). Displacement of the labile acetonitrile ligands from [PtCl\textsubscript{2}(MeCN)\textsubscript{2}] upon treatment with two equiv. of L\textsubscript{2} (R = C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}; X = SbF\textsubscript{6})\textsuperscript{8a} in CH\textsubscript{2}Cl\textsubscript{2} afforded PtCl\textsubscript{2}(L\textsubscript{2})\textsubscript{2} in 82% isolated yield (see Supporting Information for characterizing data for 1 and 2).

The molecular structure of 1 has been confirmed by X-ray crystallography (Figure 1) and shows an approximate square-planar geometry about Pd(1) with Pd(1) trans to N(4) of the cyclometallated ligand.\textsuperscript{11} Around the coordination sphere of Pd(1), the Pd(1)–Cl(1), Pd(1)–P(1), Pd(1)–C(26) and Pd(1)–N(4) distances are as anticipated.\textsuperscript{11} One noticeable feature, and pertinent to structural discussions of 3 and 4 (vide infra), are the key metric parameters within the saturated P(1)–C(9)–N(2)–C(11)–N(3)–C(10) ring. The P(1)–C(9)/P(1)–C(10) [1.826(2) and 1.836(2) Å] and C(9)–N(2)/C(10)–N(3) bond lengths [1.470(3) and 1.458(3) Å] are all in accord with formal single bonds.
Furthermore, the N(2)−C(11)/C(11)−N(3) distances [1.468(3) Å, 1.457(3) Å] are consistent with single bonds and the N(2)−C(11)−N(3) bond angle is 110.19(18)°. The Σ[N(2)/N(3) angles] are 330.5° and 332.6° respectively, clearly indicating a distorted pyramidal geometry about each N atom. Finally, intramolecular N−H···N hydrogen bonding [N(1)···N(3) 2.895(3) Å, H(1A)···N(3) 2.43(3) Å, N(1)−H(1A)···N(2) 111.8(19)°, N(1)···N(2) 2.944(3) Å, H(1B)···N(2) 2.31(3) Å, Å, N(1)−H(1B)···N(2) 330.5 º] are consistent with single bonds. Furthermore, the N(2)−C(1)/C(1)−N(3) bond angles are 127.1(4)° for 3, 126.1(4), 127.6(4) for 4, 127.6° for 3 and 4, suggesting a near symmetric bonding motif of the μ²-bridging phosphido ligand perpendicular to this plane. Compound 3 lies on an inversion center about the midpoint defined by the PdP2 core. Along the P···P vector, the two 16-electron “MCl2” metal fragments are slightly distorted, from planarity, by 13.0° (for 3) and 2.1° (for both independent molecules in 4). The M−P distances are essentially equivalent [2.2448(12), 2.2350(12) Å for 3; 2.2316(11), 2.2250(10) and 2.2235(10), 2.2314(11) Å for 4] suggesting a nearly symmetric bonding motif of the μ²-bridging phosphido in both cases. Moreover, the Pd−P bond lengths in 3 are slightly longer than those found in 1.

The coordinated ligand, in 3 and 4, can be regarded as zwitterionic whereby the positive charge is located on the central N−C−N backbone and the negative charge (not shown) on the P atom (or more likely the Pd metal center thereby satisfying a 16-electron count). Consequently the central N−C−N carbon atom has undergone a change in hybridization from sp² (in 1) to sp³ (in 3 and 4). Support for electron delocalization of the positive charge into the N−C−N backbone comes from the contracted N−C bond lengths [N(1)−C(2) 1.311(6) Å and C(2)−N(2) 1.320(6) Å for 3; N(1)−C(2) 1.302(5) [1.306(5)] Å and C(2)−N(2) 1.303(5) [1.312(5)] Å for 4] and expanded N−C−N angles [127.1(4)° for 3; 126.1(4), 127.6(4) for 4]. The Σ[N(2)/N(3) angles] for both structures are ca. 360° respectively clearly indicating the N atoms adopt a planar configuration. Within each six-membered ring, the C−N−C−N−C−N atoms are essentially co-planar (±0.043 Å for 3; ±0.061, 0.054, 0.043, 0.031 Å for 4). Furthermore, in 3 the P(1) atom lies out of this plane by 0.866 Å (hinge angle between mean planes C(1)/N(1)/C(2)/N(2)/C(3) vs. C(1)/P(1)/C(3) = 45.4°) while in 4, the equivalent hinge angles lie in the range 44.2−46.6°. The metric parameters for 3 and 4 clearly support a two-coordinate P-ligand. Finally, in 3 the Pd(1)···Pd(2) separation is 3.556 Å.
ting the absence of any single metal–metal bonding and similarly seen for 4 [Pt(1)···Pt(2)/Pt(3)···Pt(4) 3.520/3.521 Å].

Although the mechanism for formation of 3 and 4 is unclear at present, one plausible pathway involves carboxylation formation via hydrogen abstraction/H₂ elimination from the central –(R)N–CH₂–N(R)– backbone. Elimination of “(R)NCH₂”–, possibly as [(R)NH–CH₃]⁺, affords a highly reactive mononuclear terminal phosphido complex. Displacement of a tertiary phosphine L₃ (for 2) or adventitious HCl protonation of the cyclometallated C,N-ligand (for 1), followed by dimerization, may account for the formation of the observed homodinuclear complexes.

In summary, homodinuclear late-transition metal centers can be used to stabilize unexpected zwitterionic, two-coordinate phosphorus ligands in a bridging ligation mode. Further studies are currently underway to investigate preparative routes to these highly unusual phosphido ligands and probe the mechanism for their transformation.

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Supporting Information Available: Synthetic details, characterizing data and X-ray data for 1, 3 and 4 in CIF format and additional figures and details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Single crystal X-ray crystallography has been used to elucidate the solid state structures of an unusual pair of homodinuclear zwitterionic complexes $\text{M}_2\text{Cl}_4[\mu^2-\text{P}\{\text{cyclo-CH}_2\text{N(R)CHN(R)CH}_2\}]_2$ ($\text{M} = \text{Pd}, \text{R} = 4$-FC$_6$H$_4$CH$_2$ (shown below); $\text{M} = \text{Pt}, \text{R} = \text{C}_6\text{H}_5\text{CH}_2$).