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

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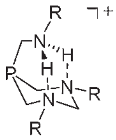
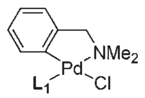
Rare examples of homodinuclear zwitterionic Pd^{II} and Pt^{II} complexes with bridging, two-coordinate P{*cyclo*-$CH_2N(R)CHN(R)CH_2$} ligands (R = 4-$FC_6H_4CH_2$, $C_6H_5CH_2$) have been characterized by single-crystal X-ray diffraction using synchrotron radiation. Short N−C distances and enlarged 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_2P^+)[1] or phosphido anions (R_2P^-)[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,[3] hydrocarbon,[4] and N,C-bonded β-diketiminato groups.[5] Burford and co-workers[6] have elegantly shown that phosphenium cations can be isolated upon coordination to tertiary phosphine ligands. Furthermore, phosphenium ions can readily be stabilized at transition-metal centers.[1] Phosphido ligands are known to bind in a terminal fashion[2] or, more commonly, bridge two metal centers.[2] While this bridging mode is common for phosphides, it is considerably more unusual for tertiary phosphines to function in this manner.[7]

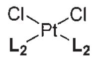
As part of continuing studies in our group investigating supramolecular interactions in (di)tertiary phosphines,[8] we recently reported easily accessible intramolecular hydrogen-bonded phosphine analogues of the cage ligand 1,3,5-triaza-7-phosphaadamantane (PTA).[8a] The recent surge in interest for PTA, and its analogues, can be traced to their ease of chemical modification,[9] diverse coordination, and cytotoxic and catalytic properties.[10] Herein we report the structural characterization of two peculiar homodinuclear zwitterionic Pd^{II} and Pt^{II} complexes of a partially delocalized six-membered P{*cyclo*-$CH_2N(R)CHN(R)CH_2$} (R = 4-$FC_6H_4CH_2$, $C_6H_5CH_2$) bridging phosphido ligand.



L_1 or L_2



1



2

The reaction of $[Pd(\kappa^2\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}Cl)]_2$ with 2 equiv of $\mathbf{L_1}$ (R = 4-$FC_6H_4CH_2$; X = Cl)[8a] in CH_2Cl_2 afforded the cyclometalated complex **1** in high yield (78%). Displacement of the labile acetonitrile ligands from $[PtCl_2(MeCN)_2]$ upon treatment with 2 equiv of $\mathbf{L_2}$ (R = $C_6H_5CH_2$; X = SbF_6)[8a] in CH_2Cl_2 afforded $PtCl_2(\mathbf{L_2})_2$ (**2**) in 82% isolated yield (see the Supporting Information for characterization 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 P(1) trans to N(4) of the cyclometalated ligand.[11] Around the coordination sphere of Pd(1), the Pd(1)−Cl(1), Pd(1)−P(1), Pd(1)−C(26), and

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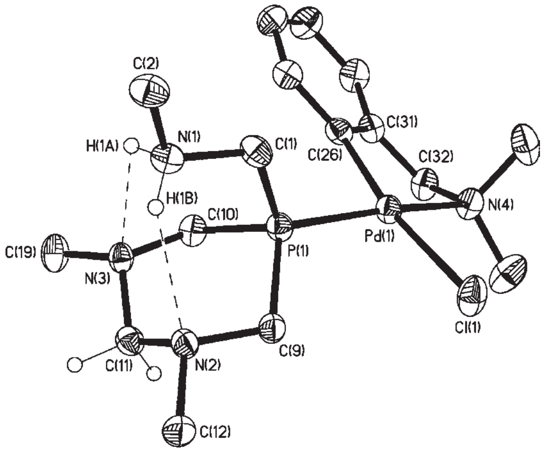
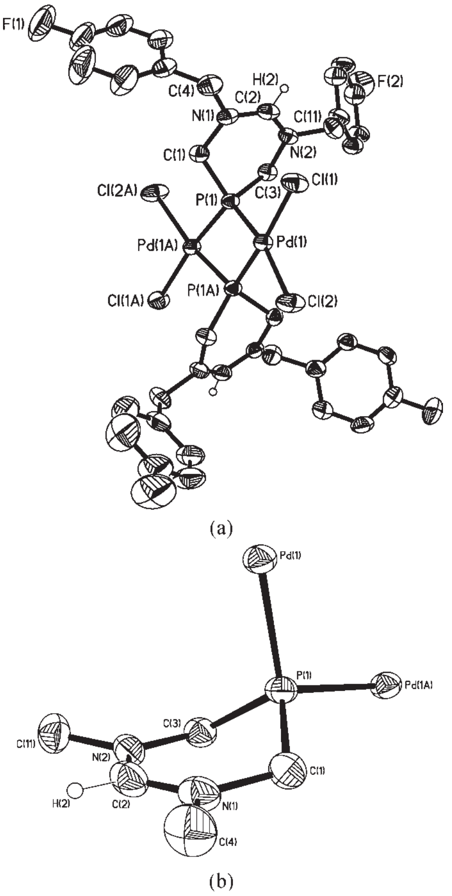


Figure 1. ORTEP of part of the cation in **1** showing the hydrogen-bonded ring conformation. Thermal ellipsoids are drawn at the 50% probability level. All C−H hydrogen atoms except those on N(1) and C(11) are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−P(1) 2.2247(6), Pd(1)−Cl(1) 2.3955(6), Pd(1)−N(4) 2.156(2), Pd(1)−C(26) 1.997(2), P(1)−C(1) 1.836(2), C(1)−N(1) 1.494(3); C(9)−P(1)−C(10) 100.70(11), P(1)−C(9)−N(2) 110.38(15), C(9)−N(2)−C(11) 110.79(18), C(11)−N(3)−C(10) 111.54(18), N(3)−C(10)−P(1) 110.83(15).

Pd(1)−N(4) distances are as anticipated.[11] One noticeable feature, and pertinent to the 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 accordance with formal single bonds. Furthermore, the N(2)−C(11)/C(11)−N(3) distances [1.468(3) and 1.457(3) Å] are consistent with single bonds, and the N(2)−C(11)−N(3) bond angle is 110.19(18)°. The $\sum$[N(2)/N(3)] angles are 330.5° and 332.6°, respectively, clearly indicating a distorted pyramidal geometry about each nitrogen 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(3) = 111.8(19)°; N(1)···N(2) = 2.944(3) Å, H(1B)···N(2) = 2.31(3) Å, and N(1)−H(1B)···N(2) = 137(2)°] conformationally locks the ligand structure through interactions between $-NH_2^+$ and both ternary nitrogen centers. The structural parameters for **1** are similar to those of the noncoordinated ligand $\mathbf{L_I}$.[8a]

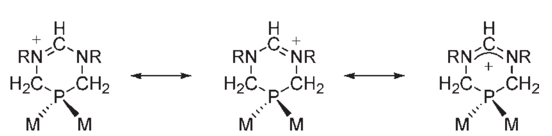
The X-ray crystal structures of **3** (Figure 2) and **4** (Supporting Information) have been determined and are unique.[12] In **3** and **4**, there is a central homodinuclear "$M_2Cl_4P_2$" arrangement (M = Pd, Pt) with the bridging μ^2-phosphido ligand perpendicular to this plane. Compound **3** lies on an inversion center about the midpoint defined by the Pd_2P_2 core. Along the P···P vector, the two 16-electron "MCl_2" 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 [2.2418(12) and 2.2350(12) Å for **3**; 2.2316(11), 2.2250(10), 2.2235(10), and 2.2314(11) Å for **4**], suggesting a near-symmetric bonding motif of the μ^2-bridging phosphide in both cases. Moreover, the Pd−P bond lengths in **3** are slightly longer than those found in **1**.



(a)

(b)

Figure 2. (a) ORTEP of **3**. Thermal ellipsoids are drawn at the 50% probability level. The disordered dimethyl sulfoxide solvent molecule, minor phenyl disordered component on N(2), and all C−H hydrogen atoms except those on C(2) are omitted for clarity. (b) ORTEP view showing the envelope ring conformation. Selected bond distances (Å) and angles (deg): Pd(1)−Cl(1) 2.3736(12), Pd(1)−Cl(2) 2.3842(13), P(1)−C(1) 1.825(5), C(1)−N(1) 1.469(6), N(2)−C(3) 1.475(6), C(3)−P(1) 1.835(4); Cl(1)−Pd(1)−P(1) 98.62(4), Cl(1)−Pd(1)−P(1A) 172.34(4), Cl(1)−Pd(1)−Cl(2) 94.00(5), P(1)−Pd(1)−P(1A) 73.84(5), P(1A)−Pd(1)−Cl(2) 93.60(4), P(1)−Pd(1)−Cl(2) 167.12(5), P(1)−C(1)−N(1) 112.6(3), C(1)−N(1)−C(2) 124.4(4), C(2)−N(2)−C(3) 123.2(4), N(2)−C(3)−P(1) 110.3(3).



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 phosphorus atom (or more likely the palladium metal center, thereby satisfying a 16-electron count).[13] Consequently, the central N−C−N carbon atom has undergone a change in hybridization from sp^3 (in **1**) to sp^2 (in **3** and **4**). Support for electron delocalization of the positive charge into the N−C−N backbone comes from the contracted

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[12] (a) CSD version 5.30 plus three updates. Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380−388. A CSD search revealed that the following complexes of the tertiary phosphine PhP{cyclo-$CH_2N(Ph)CH_2N(Ph)CH_2$} have been structurally determined: TECZAC, YUXKAD, YUXKEH, and YUXNEK. (b) The United Kingdom Chemical Database Service: Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746−749.

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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) and 127.6(4)° for **4**].[14] The $\sum$[N(2)/N(3)] angles for both structures are ca. 360°, respectively, clearly indicating that the nitrogen atoms adopt a planar configuration. Within each six-membered ring, the C−N−C−N−C atoms are essentially coplanar (±0.043 Å for **3**; ±0.061, ±0.054, ±0.043, and ±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) and 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 phosphorus ligand.[2] Finally, in **3**, the Pd(1)···Pd(2) separation is 3.556 Å, suggesting 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 the formation of **3** and **4** is unclear at present, one plausable pathway involves carbocation[15] formation via hydrogen abstraction/elimination from the central −(R)N−CH_2−N(R)− backbone. Elimination of "(R)NHCH_2−", possibly as $[(R)NH{=}CH_2]^+$, affords a highly reactive mononuclear terminal phosphido complex. Displacement of a tertiary phosphine **L₂** (for **2**) or adventious HCl protonation[16] of the cyclometalated κ^2-$C_6H_4CH_2NMe_2$ 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 the preparative routes to these highly unusual phosphido ligands and probe the mechanism for their transformation.

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Supporting Information Available: Synthetic details, characterization 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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