Oxidation of Bridging Phosphanides

Reversible Transformation of Two Diphenylphosphanido Ligands into the Neutral Tetraphenyldiphosphane Ligand[**]

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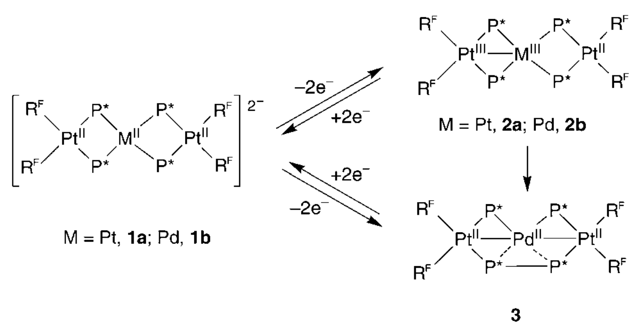
We have recently established that oxidation of the anionic trinuclear Pt^{II} complex $(NBu_4)_2[R^F_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}R^F_2]$ (**1a**; $R^F = C_6F_5$, Scheme 1) by Ag^+ ions yields the neutral Pt^{III} species $[R^F_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}R^F_2]$ (**2a**),[1], which contains a total of 46 valence electrons and hence a Pt–Pt bond. To our surprise, when the starting compound comprises at least one palladium center the analogous Pd^{III}-containing derivatives cannot be isolated from, or identified in, the reaction mixtures.[1]



Scheme 1. $R^F = C_6F_5$; $P^* = PPh_2$.

To understand the different response of the heteronuclear species towards oxidation by Ag^+ ions, and guide our experimental efforts towards identifying and finally isolating the reaction products, we searched the potential energy surface (PES) of a model reaction system with electronic structure calculation methods at the B3LYP level of theory[2,3] using the LANL2DZ basis set, as implemented in the Gaussian 03 series of programs.[4] To obtain a computationally convenient size we used a model reaction system where the phenyl groups of the phosphanide ligands are substituted by H atoms and the C_6F_5 ligands by CN ligands. The decision to substitute the C_6F_5 ligands by CN is based on electronic structure calculations of the coordinating ability (σ-donor and π-acceptor capacity) of the ligands and has been described previously.[5] The geometric and energetic profile of the oxidation reaction of **M1b**, along with the HOMO of all stationary points, computed at the B3LYP/LANL2DZ level of theory is depicted schematically in Figure 1.

One-electron oxidation of complex **M1b** yields the intermediate open-shell (doublet) anionic species **M1b1**, which is a symmetric (D_{2h} point group), trinuclear PtPdPt complex without any intermetallic interaction. This one-electron oxidation step requires about 49.3 $kcal\,mol^{-1}$ at the B3LYP/LANL2DZ level, which is provided by the reduction of the Ag^+ ions used as the oxidant (the electron affinity of the Ag^+ ions was predicted to be 178.7 $kcal\,mol^{-1}$). Interestingly, the one-electron oxidation involves a strong coordination of the Ag^+ ion to Pd and one terminal Pt atom to afford complex **M1bAg**, which adopts a chairlike structure (see Supporting Information) with a binding energy predicted to be 171.9 $kcal\,mol^{-1}$, thus illustrating that the $Pd\cdots Ag^+$ and $Pt\cdots Ag^+$ intermetallic bonds are relatively strong. These strong intermetallic interactions are also mirrored in the short $Pd\cdots Ag^+$ and $Pt\cdots Ag^+$ bond distances of 2.756 and 2.746 Å, respectively. Phosphanido Pt/Pd/Ag complexes of this type have recently been isolated by us.[6] It should be noted that the transfer of one electron is a favorable process because the LUMO of **M1bAg** is localized purely on the coordinated Ag^+ ion.

The salient feature of the structure of **M1b1** is the remarkable shortening of the $P\cdots P$ distance by about 0.29 Å with respect to the starting **M1b** species. The localization of the spin density on the P atoms of the bridging phosphanido ligands (Figure 1) is also noteworthy as it indicates that $P\cdots P$ interactions should start to evolve during the course of the oxidation process. Further one-electron oxidation of **M1b1** leads to a second-order saddle point (probably an effective monkey–saddle-type transition state[7] possessing a doubly degenerate zero eigenvalue of the Hessian) **M2b** at 170.5 $kcal\,mol^{-1}$, which is higher in energy than **M1b** and has two imaginary frequencies at 65 and 50 cm^{-1}. **M2b** adopts a symmetric structure with D_{2h} symmetry. All attempts to locate a true transition state, even by using larger basis sets, were unsuccessful, which suggests that the saddle point is probably on a quite shallow PES. Correcting the two imaginary frequencies and optimizing the new geometry afforded a local minimum at 5.5 $kcal\,mol^{-1}$. This is lower in

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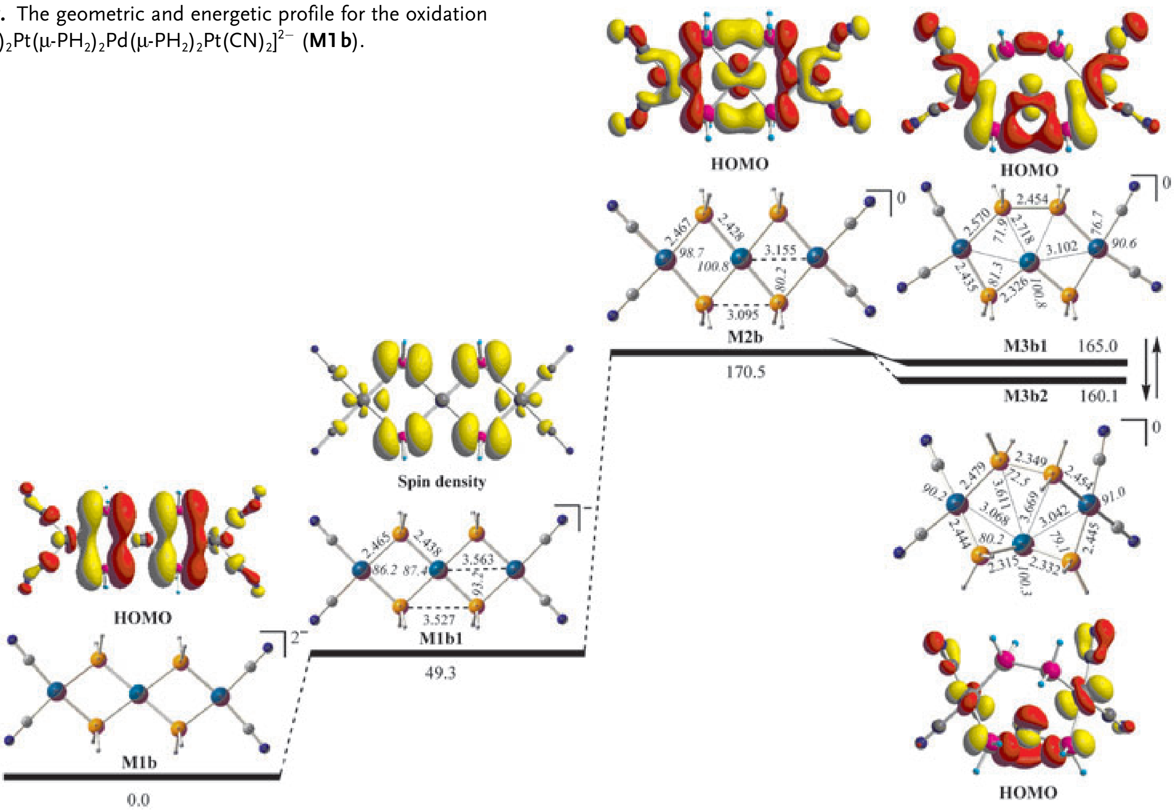
Figure 1. The geometric and energetic profile for the oxidation of $[(NC)_2Pt(\mu\text{-}PH_2)_2Pd(\mu\text{-}PH_2)_2Pt(CN)_2]^{2-}$ (**M1b**).



energy and corresponds to the planar complex **M3b1**, which contains a bridging diphosphane (H_2PPH_2) ligand.

Searching the PES further also allowed us to locate another minimum corresponding to the nonplanar complex **M3b2**, which is stabilized by 4.9 kcal mol^{-1} with respect to the planar conformer. The complexes **M3b1** and **M3b2** contain an angular Pt–Pd–Pt array with angles of 157.4° and 114.7°, respectively. Moreover, in **M3b2** the PPPP dihedral angle is 144.7°. It is important to note that the HOMO of **M2b** involves significant P···P orbital interactions that are responsible for the formation of the P–P bond in complexes **M3b1** and **M3b2**. Moreover, the nature of the HOMOs of **M3b1** and **M3b2** (Figure 1) strongly supports a fluxional behavior of the complexes that involves an easy interconversion of the P···P interactions in an almost barrierless process (activation barrier less than 10.4 kcal mol^{-1}) probably through a symmetric (D_{2h}) transition state similar to **M2b**. However, all attempts to locate the true transition state were unsuccessful.

In light of these theoretical predictions we studied the reaction of $[R^F_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}PPh_2)_2PtR^F_2]^{2-}$ (**1b**) with Ag^+ in greater detail and we were ultimately able to isolate $[R^F_2Pt(\mu\text{-}PPh_2)Pd(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PPPh_2)PtR^F_2]$ (**3**), a neutral platinum(II) and palladium(II) complex that contains a tetraphenyldiphosphane ligand. The process is reversible and the reduction of **3** with NBu_4BH_4 (1:2 molar ratio) yields **1b** (Scheme 1).

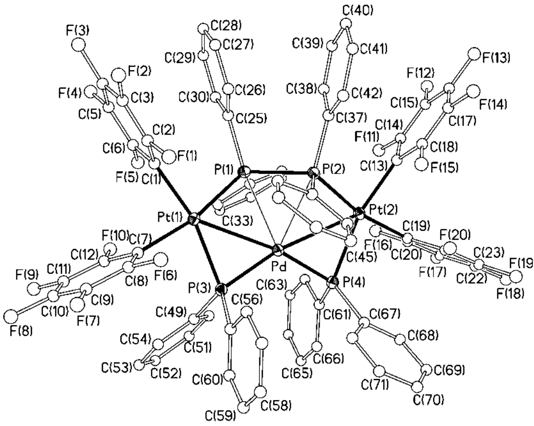


Figure 2. Molecular structure of complex **3**.

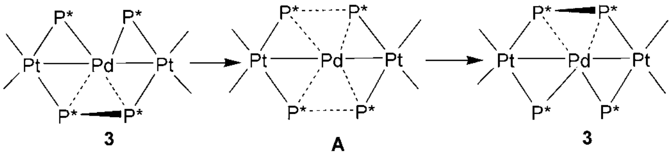
The structure of complex **3** is shown in Figure 2. The trinuclear complex contains an angular Pt–Pd–Pt array (137.23(2)°). The Pd atom is bonded to the platinum atoms through intermetallic bonds (Pt(1)–Pd 2.887(1) Å; Pt(2)–Pd 2.910(1) Å). In addition, there are two PPh_2 bridging ligands linking the Pd atom with each Pt center. All the metal atoms and the phosphanido P(3) and P(4) atoms lie in the same plane. A noteworthy structural feature is that the tetraphenyldiphosphane ligand formed bridges the two external atoms (Pt) of the array, in keeping with the theoretical predictions. P(1) and P(2) do not lie in the plane defined by the metal centers, although the midpoint of the P(1)–P(2) bond is included in this plane. The four Pt–P distances are very similar regardless of whether the P forms part of a phosphanide or the diphosphane ligand. The P(1)–P(2) distance is

2.261(1) Å, which is similar to the distance found in other complexes containing μ-Ph_2P-PPh_2,[8–11] while the distance between P(3) and P(4) is 3.730(1) Å, thereby excluding any P···P interaction. The Pd–P(3) and Pd–P(4) distances are 2.180(1) Å and 2.177(1) Å, respectively, and are the shortest Pd–P distances reported so far for bridging diphenylphosphanido ligands bonded to Pd. These short distances are probably related to the peculiar coordination sphere of the Pd center, which, apparently, apart from these Pd–P bonds, only establishes the intermetallic interactions and weak interactions,[12] if any, with the P atoms of the tetraphenyldiphosphane ligand (Pd–P(1) and Pd–P(2) are 2.656(1) Å and 2.675(1) Å, respectively). The Pd–P(diphosphane) distance in **M3b1** (2.718 Å) is very close to the experimental value for the "real" **3**. The coordination sphere of the platinum atoms is more conventional: each lies in the center of a square plane. The total valence-electron count in **3** is 44, in agreement with the presence of two M–M′ bonds.

The formation of free P_2R_4 has been observed from early transition metal and lanthanide complexes containing terminal phosphanido ligands,[13–16] and recently an interesting catalytic formation of free tetraphenyldiphosphane has been proposed to take place through an unusual Rh^V intermediate containing two *terminal* phosphanido ligands.[17] In the complex $[(ON)_2Fe(\mu\text{-}CH_2)(\mu\text{-}Ph_2PPPh_2)Fe(NO)_2]$ the η^2-*P,P′*-tetraphenyldiphosphane ligand is formed by coupling of a *bridging* phosphanido with a terminal secondary phosphane ligand.[18,19] Nevertheless, P–P bond formation from the oxidation of *two bridging* phosphanido ligands, as far as we know, has never been observed. However, the reverse process—the reaction of P_2R_4 with transition-metal complexes—is an easy entry into phosphanido complexes of transition metals.[20–23]

The formation of **3** could be regarded as a consequence of the oxidation of two metal centers in **1b** to afford **2b** (an intermediate that has not been observed or even theoretically predicted), analogous to the homotrinuclear complex **2a**, which evolves quickly through a reductive coupling of two bridging PPh_2 ligands to form tetraphenyldiphosphane and the M^{II} trinuclear derivative with 44 valence electrons. This result is in agreement with the greater lability of palladium derivatives than those of platinum and can be related to the faster reductive coupling between the PPh_2 and C_6F_5 groups observed in the palladium(III) intermediates than in the platinum(III) ones.[5]

The $^{31}P\{^1H\}$ NMR spectrum of **3** (CD_2Cl_2 solution) at 183 K shows two broad singlets at $\delta = 123.6$ and -80.0 ppm due to the phosphanido (P3, P4) and phosphane (P1, P2) ligands, respectively. The chemical shift of the equivalent PPh_2 phosphanido groups lies in the expected range for a single PPh_2 ligand bridging two metal centers that are joined by a metal–metal bond.[24–26] Both signals appear as broad singlets and, consequently, the couplings between the P atoms cannot be calculated. Each signal shows a pair of platinum satellites ($^1J_{Pt1,P3} = 1580$ Hz and $^1J_{Pt1,P1} = 1728$ Hz). Platinum satellites are also observed for the PPh_2 phosphanido signal due to $^2J_{Pt,P}$ coupling. However, these satellites are not well separated from the broad central signal and the $^2J_{Pt1,P4}$ value cannot be calculated accurately. This phosphorus–platinum coupling is in agreement with the presence of Pt–Pd bonds in an almost linear P–Pd–Pt arrangement. At 293 K only one very broad signal centered at about $\delta = 27$ ppm is observed, thus indicating that, at room temperature, a dynamic process renders the P atoms of the PPh_2 and P_2Ph_4 ligands equivalent. The ^{19}F NMR spectrum of **3** (CD_2Cl_2 solution) at 183 K shows four signals of equal intensity in the *o*-F region. At higher field two well-separated signals due to *p*-F atoms and overlapped signals due to *m*-F atoms are observed. This pattern indicates the presence of two inequivalent C_6F_5 rings and the inequivalence of both halves within each ring, and is in full agreement with the structure of **3** in the solid state. The spectrum at 293 K shows only three signals (2:1:2 intensity ratio) due to *o*-F, *p*-F, and *m*-F atoms respectively, i.e. all *o*-F atoms are equivalent, as are the *p*-F and *m*-F atoms. The dynamic process shown in Scheme 2, which follows from the NMR spectroscopic data, is in excellent agreement with the theoretically predicted fluxionality of the analogous **M3b** complexes.



Scheme 2. P* = PPh_2.

In summary, an unprecedented formation of tetraphenyldiphosphane from the coupling of two bridging phosphanido ligands, presumably via a Pd^{III} intermediate, has been predicted theoretically and achieved experimentally. Moreover, the behavior of **3** in solution at room temperature is very striking: the bridging diphosphane and two bridging phosphanido ligands become equivalent, thereby indicating that the Pd–P and P–P bonds are highly delocalized, in line with the electronic structure calculation results.

Experimental Section

3: $AgClO_4$ (0.110 g, 0.510 mmol) was added to an orange solution of **1b** (0.600 g, 0.251 mmol) in acetonitrile (20 mL). A dark-violet suspension and a silver mirror on the walls of the flask formed immediately. After stirring for 15 min at room temperature the mixture was filtered. The resultant dark-purple solid was washed with CH_2Cl_2 (40 mL) and filtered through Celite. The solution was evaporated to about 8 mL and **3** crystallized as an orange-red solid. This was filtered off and washed with 2 × 0.5 mL of cold CH_2Cl_2 (0.270 g, 58 % yield). ^{19}F NMR (282 MHz, CD_2Cl_2, 183 K, $CFCl_3$): $\delta = -113.5$ ($^3J_{Pt,F} = 342$ Hz, 2 × *o*-F), -115.4 ($^3J_{Pt,F} = 251$ Hz, 2 × *o*-F), -116.8 ($^3J_{Pt,F} = 364$ Hz, 2 × *o*-F), -121.0 ($^3J_{Pt,F} = 261$ Hz, 2 × *o*-F), -160.7 (2 × *p*-F), -161.3 (2 × *p*-F), -162.8 (2 × *m*-F), -163.6 (4 × *m*-F), -163.9 ppm (2 × *m*-F). ^{19}F NMR (282 MHz, CD_2Cl_2, 293 K, $CFCl_3$): $\delta = -116.5$ ($^3J_{Pt,F} = 304$ Hz, 8 × *o*-F), -161.7 (4 × *p*-F), -163.9 ppm (8 × *m*-F). C,H analysis for $C_{72}H_{40}F_{20}P_4PdPt_2$ (1905.6): calcd: C 45.38, H 2.11; found: C 45.18, H 1.99.

Reaction of **3** with NBu_4BH_4: A solution of NBu_4BH_4 (0.028 g, 0.110 mmol) in 2 mL of MeOH was added to a violet solution of **3** (0.100 g, 0.052 mmol) in $CHCl_3$ (8 mL). Yellow crystals of **1b** appeared immediately. After the mixture had been stirred for

15 min at room temperature, the resulting **1b** was filtered off and washed with MeOH (2 × 0.5 mL) (0.094 g, 75 % yield).

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