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$[Pd_2(\eta^4\text{-}P_7)_2]^{4-}$: a Pd_2 sandwiched by two anionic nortricyclane-type polyphosphides

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By introducing $[Pd(PPh_3)_4]$ into a P_7^{3-} solution, we have successfully synthesized and crystallized $[Pd_2(\eta^4\text{-}P_7)_2]^{4-}$ (1a) in $[Na(crypt\text{-}222)]_4$1a. As a phosphide congener of the reported $[Pd_2As_{14}]^{4-}$, 1a can be viewed as a Pd_2 sandwiched by two $(\eta^4\text{-}P_7)$ units, representing the first organic-ligand–free Pd–P cluster. In addition, 1a provides a platform for investigating Pd–P alloys on the molecular level.

As an important phosphorus precursor in industry, white phosphorus (P_4; Fig. 1a, left) has attracted great interest and has yielded tremendous applications in the fields of organo- and organometallic phosphorus chemistry.[1–4] Conversely, its toxicity and metastable nature—being sensitive to temperature, air and light—make it difficult to handle during synthesis and often lead to the formation of P_n^q species with varied nuclearities ($n \neq 4$).[5] As an alternative, the anionic nortricyclane-type polyphosphide P_7^{3-} (light and temperature stable) serves as a closely related cage (Fig. 1a, right), but its chemistry remains largely underinvestigated.[6–8] P_7^{3-}, consisting of one basal three-membered ring, three bridging P atoms and one apical atom, can formally be regarded as adjacent P–P bonds of a P_4 being inserted by three P^-.[5]

Upon bonding with s-/d-/f-p-block (semi)metal atom(s),[9] P_7^{3-} may remain intact and in the first situation: each of the two or three bridging P atoms serves as a two-electron (2-e) donor (η^1; Fig. 1b), such as in the protonated $[M_2(\eta^1\text{-}:\eta^1\text{-}HP_7)_2]^{2-}$ (M = Ag, Au) and the neutral $\{[M^1]_3(\eta^1\text{-}:\eta^1\text{-}:\eta^1\text{-}P_7)\}$ ($[M^1]$ = $TtMe_3$, Tt = Ge, Sn, Pb; $FeCp(CO)_2$, $AuNHC^{Dipp}$),[10–13] or in the second situation: act as a four-electron (4-e) donor (η^2; Fig. 1c), such as in $[(PPh_3)HPt(\eta^2\text{-}P_7)]^{2-}$, $[M(\eta^2\text{-}P_7)_2]^{3-}$ (M = Zn, Cd) and $\{[M^2]_3(\eta^2\text{-}:\eta^2\text{-}:\eta^2\text{-}P_7)\}$ ($[M^2]$ = $RE(NN^{fc})(THF)_n$, NN^{fc} = 1,1-fc(NSi^tBuMe_2)$_2$, fc = ferrocenylene, RE/n = Sc/0, Y/1, La/1, Lu/1; Li(tmeda), $Li(THF)_2$).[14–20] On breaking one of the basal P–P bonds, two of the basal P atoms and two of the bridging P atoms together bond to one metal in a six-electron (6-e) donor η^4 fashion (Fig. 1d), such as for $[(\eta^4\text{-}P_7)Fe(\eta^4\text{-}P_4)]^{3-}$, $[Fe(\eta^4\text{-}HP_7)_2]^{2-}$, $[(C_5Me_5)Fe(\eta^4\text{-}P_7)]^{2-}$, $[(\eta^4\text{-}P_7)Ni(CO)]^{3-}$ and $[(\eta^4\text{-}P_7)M(CO)_3]^{3-}$ (M = Cr, Mo, W).[19,21–25] Although the original $\{P_7\}$ unit tends to maintain its nortricyclane-type structure under various interactions, P_7^{3-} does undergo fragmentations and rearrangements in certain situations, for example during chemical activation of P_7^{3-} with $[Co(PEt_2Ph)_2(Mes)_2]$ yields $[(\eta^5\text{-}P_5)Co\{\eta^2\text{-}P_2H(Mes)\}]^{2-}$ containing a planar *cyclo*-$\{P_5\}$.[26] Very recently, a series of hybrid sandwich complexes with early transition metals at their centers ($[(\eta^5\text{-}P_5)VCp]^{1-/2-}$, $[(\eta^5\text{-}P_5)CrCp]^-$ and $[(\eta^5\text{-}P_5)Mn(C_5Me_5)]^-$; Fig. 1e) have been isolated by reacting P_7^{3-} with the corresponding $[MCp_2]$ (M = V, Cr) and $[Mn(C_5Me_5)_2]$, respectively,[27] representing another breakthrough as pioneered by the sandwich-type $[(\eta^5\text{-}P_5)Fe(C_5Me_5)]$.[28]

Besides planar *cyclo*-P_5, the aforementioned η^4-type $\{P_7\}$ unit has proven to be another important candidate for constructing phosphorus-based sandwich compounds. In previously reported works,[19,21–25] on cutting off one of the basal P–P bonds, the $\{P_7\}$ unit donates six electrons and forms σ-type delocalized interactions with the central metal atom (**5c–2e** bond). The $\{P_7\}$ unit shows a bonding nature isolobal with rectangularly distorted cyclobutadiene complexes–and, due to its flexibility, can accommodate metal ion(s). However, in the CCDC database (until Oct. 2025), examples of central metal atom(s) sandwiched by ligands that are 6-e donors $\{\eta^4\text{-}P_7\}$ are remarkably rare.[19,21–25]

In this work, we report the synthesis, crystallization and characterization of salt compound **1**–made up of a Pd_2 centered anion $[Pd_2(\eta^4\text{-}P_7)_2]^{4-}$ (**1a**) and the cation $[Na(crypt\text{-}222)]^+$ (crypt-222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)–denoted as $[Na(crypt\text{-}222)]_4$**1a** (**1**). **1** was synthesized by reacting Na_3P_7[29] with $[Pd(PPh_3)_4]$/crypt-222 in DMF (Scheme 1). This reaction mixture was stirred at room temperature (r.t.) for 3 hours, and the resulting dark brown solution was filtered and layered with THF. After 7 days crystallization

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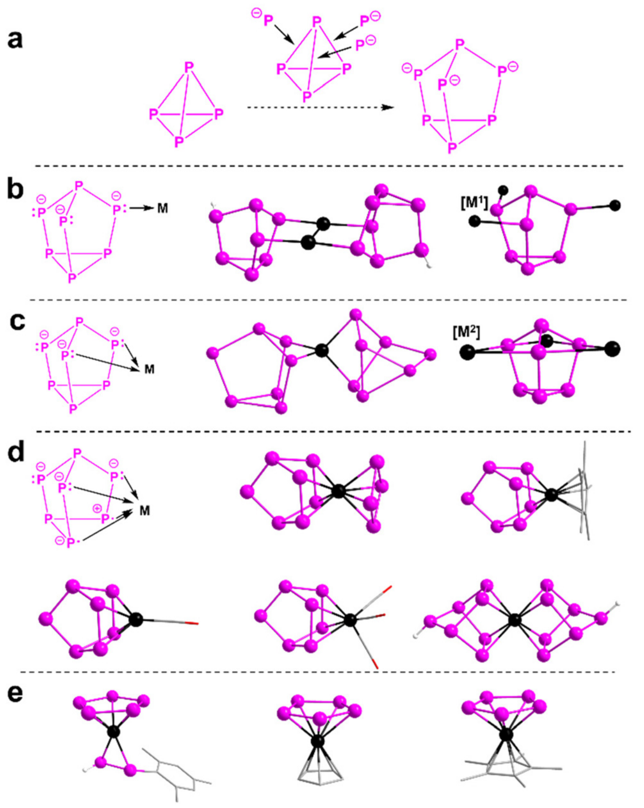
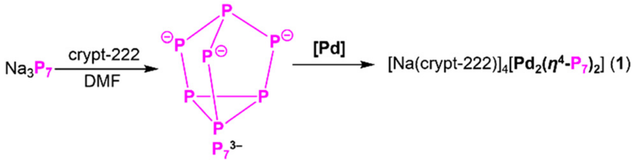


Fig. 1 (a) Comparison of P_4 (left) and P_7^{3-} (right) structures; (b) 2-e– donor (η^1-P_7) unit on its own and in example compounds $[M_2(\eta^1\text{-}:\eta^1\text{-}HP_7)_2]^{2-}$ (M = Ag, Au) and the neutral $\{[M^1]_3(\eta^1\text{-}:\eta^1\text{-}:\eta^1\text{-}P_7)\}$ ($[M^1]$ = $TtMe_3$, Tt = Ge, Sn, Pb; $FeCp(CO)_2$, $AuNHC^{dipp}$);[10–13] (c) 4-e–donor (η^2-P_7) unit and example compounds $[M(\eta^2\text{-}P_7)_2]^{3-}$ (M = Zn, Cd) and $\{[M^2]_3(\eta^2\text{-}:\eta^2\text{-}:\eta^2\text{-}P_7)\}$ ($[M^2]$ = $RE(NN^{fc})(THF)_n$, NN^{fc} = 1,1-fc$(NSi^tBuMe_2)_2$, fc = ferrocenylene, RE/*n* = Sc/0, Y/1, La/1, Lu/1; Li(tmeda), $Li(THF)_2$);[14–20] (d) 6-e– donor (η^4-P_7) unit and example compounds $[(\eta^4\text{-}P_7)Fe(\eta^4\text{-}P_4)]^{3-}$, $[(C_5Me_5)Fe(\eta^4\text{-}P_7)]^{2-}$, $[(\eta^4\text{-}P_7)Ni(CO)]^{3-}$, $[(\eta^4\text{-}P_7)M(CO)_3]^{3-}$ (M = Cr, Mo, W) and $[Fe(\eta^4\text{-}HP_7)_2]$;[2–19,21–25] and (e) example compounds resulting from fragmentations and rearrangements of P_7^{3-}: $[(\eta^5\text{-}P_5)Co\{\eta^2\text{-}P_2H(Mes)\}]^{2-}$, $[(\eta^5\text{-}P_5)VCp]^{1-/2-}$, $[(\eta^5\text{-}P_5)CrCp]^-$ and $[(\eta^5\text{-}P_5)Mn(C_5Me_5)]^-$.[26,27]



Scheme 1 Illustration of the procedure used to synthesize compound **1**. **[Pd]** = $[Pd(PPh_3)_4]$.

time at r.t., dark red block-shaped crystals were isolated from the wall and bottom of the vial in a yield of ~10% based on Na_3P_7. The obtained complex was characterized by carrying out single-crystal X-ray diffraction (SCXRD) and energy-dispersive X-ray spectroscopy (EDS) analyses. The detailed synthesis and structural characterization of **1** are provided in SI (Fig. S1–S3, Tables S1 and S2).

X-ray diffraction shows that compound **1** crystallizes in the triclinic space group $P\bar{1}$ with half a positionally ordered **1a** anion and two $[Na(crypt\text{-}222)]^+$ counter cations in the asymmetric unit. As shown in Fig. 2a, cluster **1a** is best described as a Pd_2 sandwiched by two anionic nortricyclane-type polyphosphides (η^4-P_7) with an overall length of close to 1 nm (9.81 Å). One of the basal $\{P_3\}$ triangle P–P bonds in the P_7^{3-} precursor, namely that showing a bond length of 2.28 Å (Fig. 2b, top),[30] is broken in **1a**, resulting in elongated P1/3⋯P2/4 distances (2.897/2.880 Å, calculated; Fig. 2b, bottom), each of which is far greater than the sum of the covalent single-bond radii for P_2 (2.22 Å).[31] The rest of the P–P bonds in the precursor show lengths in **1a** within the normal range for unbroken bonds (2.1430(5)–2.2199(5) Å) and comparable with the reported ones.[32–36] The distance between the bridging P atoms of the P_7^{3-} precursor is 3.38 Å, and thus an obvious structural rearrangement occurs in order for these atoms to coordinate the central Pd_2. The **1a** represents, to the best of our knowledge, the first reported organic-ligand-free Pd-P compound. Note that the reported $[(P_2)\{Pd(PNP)\}_2]$ (2.33 Å; PNP = $N(CHCHP^tBu_2)_2$),[37] $[(\eta^2\text{-}L_CP = PL_C)M(PPh_3)_2]^{2+}$ (2.35–2.40 Å; L_C = 4,5-dimethyl-1,3-diisopropyl-imidazol-2-yl),[38] $[CH_3N(CH_2CH_2NP^iPr_2)_2U(I)(\mu\text{-}Pd)(\mu\text{-}I)]_2$ (2.33 Å)[39] and $[L_6Al_6Pd_3K_2]$ (2.33 Å; L = $[(CH_3)_2N(CH_2)_2NP^iPr_2]^-$)[40] contain Pd–P bond lengths similar to those in **1a** (2.3778(4)–2.4006(4) Å).

Organometallic complexes of sandwich-type dipalladium are not uncommon. The first structurally well-defined such compound with unsaturated hydrocarbon ligands was reported in 1965 ($[LPd(C_6H_6)]$, L = $(Al_2Cl_7)^-$; Fig. 3a)[41,42] and then extended to monolayer palladium sheets, as for $[Tr_2Pd_3Cl_3]^-$ (Tr = C_7H_7; Fig. 3b).[43] The metallic sandwich-type clusters $\{(Ge_9)_2[\eta^6\text{-}Ge(PdPPh_3)_3]\}^{4-}$ containing planar $\{Ge@Pd_3\}$

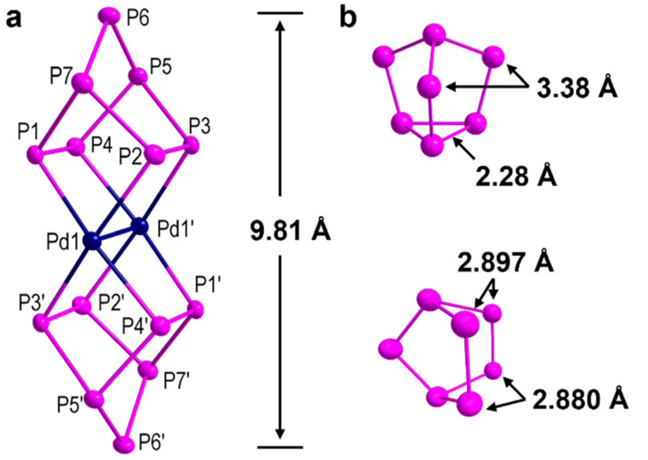


Fig. 2 (a) Molecular structures of the anion $[Pd_2(\eta^4\text{-}P_7)_2]^{4-}$ (**1a**) with thermal ellipsoids drawn at 50% probability (′: $-X$, $2-Y$, $2-Z$). Selected interatomic distances [Å] and angles [°] in **1a**: Pd1–Pd1′ 2.69687(19), Pd1–P1/2/3/4 2.3778(4)–2.4006(4), P1–P4/7 2.1961(5)/2.2199(5), P2–P3/7 2.2123(5)/2.2054(5), P3/4/6–P5 2.1430(5)–2.2100(5), P6–P7 2.1432(5); P1/2–Pd1–P4′/3′ 168.002(12)/168.293(13), P1–Pd1–P2 74.227(12), P2–Pd1–Pd1′ 82.247(10); and (b) structural difference between the original P_7^{3-} precursor (top) and the (η^4-P_7) unit (bottom) derived from **1a**.

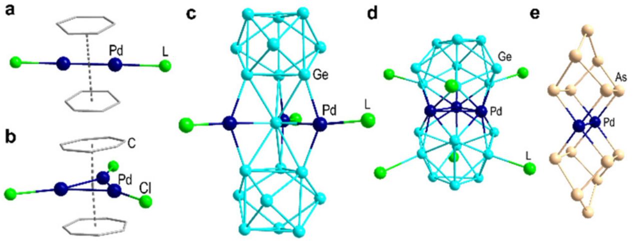
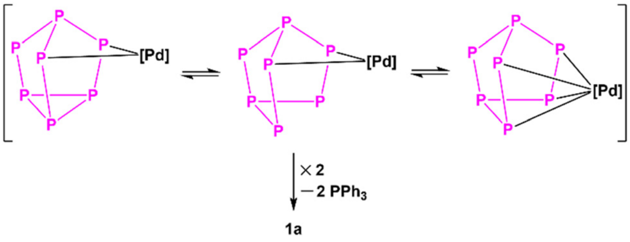


Fig. 3 Examples of sandwich-type organometallic and inorganic complexes containing multinuclear palladium: (a) $[LPd(C_6H_6)]$, L = $(Al_2Cl_7)^-$;[41,42] (b) $[Tr_2Pd_3Cl_3]^-$ (Tr = C_7H_7);[43] (c) $\{(Ge_9)_2[\eta^6\text{-}Ge(PdPPh_3)_3]\}$;$^{4-}$[44] (d) $[Ge_{18}Pd_3(Tt^iPr_3)_6]^{2-}$ (Tt = Si, Sn);[45,46] (e) $[Pd_2As_{14}]$.$^{4-}$[47]

flanked by nonagermanide caps (Fig. 3c)[44] and $[Ge_{18}Pd_3(Tt^iPr_3)_6]^{2-}$ (Tt = Si, Sn; Fig. 3d) containing a central Pd_3 triangle[45,46] have also been reported. Dipalladium sandwiched by inorganic ligands, however, has only been previously observed in $[Pd_2As_{14}]^{4-}$ (Fig. 3e),[47] featuring here a Pd–Pd bond length (2.714 Å) slightly longer than that in **1a** (2.69687(19) Å). Thus, to the best of our knowledge, **1a** represents the first organic-ligand–free Pd–P cluster and only the second example of a sandwich-type dipalladium inorganic compound. Recently, a few related reports containing $\{As_n\}$ units such as $[MM'As_{16}]^{4-}$ (M = Nb or Ta, M′ = Cu or Ag) and $[Fe_3(As_3)_3(As_4)]^{3-}$ have also been reported.[48,49]

The reported $[Pd_2As_{14}]^{4-}$ was obtained *via* the reaction between As_7^{3-} and $[Pd(PCy_3)_2]$ (Cy = cyclohexyl) in ethylenediamine (en)—with en serving not only as solvent, but also as hydrogenation agent taking part in the redox process. "$[As_7PdH(PCy_3)]^{2-}$" was proposed as an intermediate towards the formation of $[Pd_2As_{14}]^{4-}$. We also tried to react P_7^{3-} with $[Pd(PPh_3)_4]$ in en but failed, indicative of the aprotic DMF as pure solvent being crucial for forming **1a**, and of the $[Pd(PPh_3)_4]$ precursor not proceeding through the hydrogenation pathway—and hence indicative of the mechanism of formation of **1a** differing obviously from that of $[Pd_2As_{14}]^{4-}$. Actually, one recent work described in a manuscript titled "Dynamic Behavior of the P_7^{3-} Cluster and Its Derivatives with Main-Group and Transition Metal Fragments",[50] in combination with the aforementioned examples (*e.g.* $[(\eta^4\text{-}P_7)Ni(CO)]^{3-}$ and $[(PPh_3)HPt(\eta^2\text{-}P_7)]^{2-}$)[19] may provide convincing ideas regarding the formation of **1a**: the coordination type of $\{P_7\}$ in the intermediate Pd–P cluster is neither exactly η^4- nor η^2-, but rather in an equilibrium state in between, and the coupling of two such transition-state fragments form **1a** (Scheme 2).



Scheme 2 Proposed reaction pathway to form **1a**. **[Pd]** = $[Pd(PPh_3)]$.

Conclusions

In conclusion, by introducing $[Pd(PPh_3)_4]$ into P_7^{3-} solution, we have successfully synthesized $[Pd_2(\eta^4\text{-}P_7)_2]^{4-}$ (**1a**) in $[Na(crypt\text{-}222)]_4$**1a**, representing the first organic-ligand–free Pd–P cluster and the second example of a sandwich-type dipalladium inorganic compound. **1a** can be viewed as a Pd_2 sandwiched by two $(\eta^4\text{-}P_7)$ units—with each such unit resulting from breaking one of the basal P–P bonds of the P_7^{3-} precursor in combination with a geometrical rearrangement upon coordinating with the Pd_2. Our results prove that anionic nortricyclane-type polyphosphide can be used in the construction of sandwich-type clusters and provide a platform for investigating Pd–P alloys on the molecular level, and can finally be applied in catalytic or other fields.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data generated or analyzed during this study are included in this published article and its supplementary information (SI). Supplementary information: additional detailed synthesis, crystal photographs, X-ray diffraction analyses, EDS measurements. See DOI: https://doi.org/10.1039/d5dt02437d.

CCDC 2493250 ($[Na(crypt\text{-}222)_4]$**1a**) contains the supplementary crystallographic data for this paper.[51]

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