Stabilizing $P\equiv P$: P_2^{2-} , $P_2^{\bullet-}$ and P_2^0 as bridging Ligands

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SUMMARY

In contrast to its lighter congener N_2 , neutral diphosphorus with a $P\equiv P$ triple bond is a highly reactive species observable only in the gas phase and by matrix isolation. Previous efforts for stabilization with Lewis-bases (e.g., carbenes) or by transition metal coordination led to charge transfer to highly electrophilic P_2 and therefore significant reduction of the bond order. We here report the crystallographic, spectroscopic and quantum chemical characterization of the redox series $[(\mu^2, \eta^1: \eta^1-P_2)\{Pt(PNP)\}_2]$ ($PNP = N(CHCHP^tBu_2)_2$), which features $(P_2)^{2-}$, $(P_2)^{\bullet-}$, and $(P_2)^0$ as bridging ligands. While common for N_2 , the stabilization as a neutral, triply bonded $P\equiv P$ ligand is unprecedented for the heavier homologue. It was enabled by coordination of the dipnictogen to redox inactive Lewis acidic metal fragments and gives rise to controlled release of P_2 in condensed phase.

INTRODUCTION

The distinct chemical differences between the 2p elements and their heavier homologs are an intriguing feature of the periodic table. For example, the classical double-bond rule implies a fundamental instability of compounds with π bonded p-block elements beyond the second period.^{1,2,3,4,5,6,7,8,9} This observation is a manifestation of fundamental differences in chemical bonding attributable to the relative sizes of valence s and p atomic orbitals (AOs).^{10,11,12,13} The absence of radial nodes renders the lowest orbital of a given angular momentum, i.e. the ‘primogenic’ 1s, 2p, 3d, 4f orbitals, exceptionally compact.¹² The similar size of 2s and 2p orbitals facilitates $p\pi-p\pi$ bonding and weakens single bonding to N, O, and F owing to lone-pair repulsion. The presence of radial nodes leads to significant size expansion of np AOs for the heavier elements and the resulting valence s/p size mismatch causes hybridization defects.^{10,11} This leads to stronger σ bonds and weaker π bonds for p-block elements beyond the second period.^{14,15}

Jerabek and Frenking put forth a detailed assessment of these relations pertinent to the disparate stabilities of the homolog N_2/N_4 and P_2/P_4 pairs.^{16,17} The high stability of N_2 contrasts with the highly endothermic nature of diatomic $P\equiv P$ ($\Delta_f H^\circ_{\text{gas}} = 33.4 \text{ kcal}\cdot\text{mol}^{-1}$) vs. singly bonded allotropic modifications such as white P_4 ($\Delta_f H^\circ_{\text{gas}} = 14.1 \text{ kcal}\cdot\text{mol}^{-1}$) or polymeric black phosphorus.¹⁸ This thermochemical challenge has spurred the development of strategies for *in situ* synthesis of P_2 either by pyrolysis or photolysis of white phosphorus,^{19,20} or of organic or organometallic precursors.^{21,22}

In search of stabilizing P_2 , Lewis base coordination was exploited as a conceptual route in recent years. Starting from P_4 or the coupling of P_1 -synthons, P_2 adducts with strong carbene, boryl, vinyl or silylene donors could be isolated (Figure 1).^{23,24,25,26,27,28,29,30,31} However, Lewis base coordination injects electron density into π^* MOs, thereby reducing the $P\equiv P$ bond order and resulting in products with diphosphene or even diphosphane character.^{32,33} Triply bonded diphosphorus might alternatively be stabilized by coordination of Lewis acids to the non-bonding terminal lone pairs: Isolable P_2 transition metal complexes were obtained by P_4 activation with low-valent transition metal complexes,^{34,35,36,37} or decarbonylative coupling of phosphaketene complexes (Figure 1).^{38,39,40,41} However, the electron affinity of P_2 (0.63 eV),⁴² which exceeds that of O_2 (0.45 eV),⁴³ induces considerable charge transfer and the reported complexes contain ligands with $(P=P)^{2-}$ or $(P=P)^{\bullet-}$ character. While formally neutral, linearly

The Bigger Picture

Chemical synthesis relies on strategies to stabilize well-defined molecular building blocks, yet retaining their fundamental reactivity. This is illustrated by the classic pnictogen dichotomy: In contrast to highly stable N_2 , the higher homologues Pn_2 evade isolation – and thus synthetic use – due to the preference of heavier p-block elements for σ -bonded structures. Previous strategies to stabilize P_2 and related π -bonded compounds utilized coordination to electron donors, yet with significant alteration of bonding and reactivity. We here demonstrate the coordination of redox inactive transition metal fragments as a strategy to stabilize P_2 at ambient conditions. The $P\equiv P$ triple bond character is retained, as in free P_2 , and controlled release of the Lewis acidic capping agents offers P_2 transfer reactivity to molecular products.

bridging N_2 ligands ($EA(N_2) = -1.9$ eV)⁴⁴ are most common,⁴⁵ and the analogous $P\equiv N$ ligand was recently reported,⁴⁶ *bona fide* $(P_2)^0$ complexes with triply bonded $P\equiv P$ ligands remain unknown as of today.

Figure 1. Synthetic approaches and selected examples for the stabilization of P_2 -fragments.

Previous synthetic strategies that utilize the high electrophilicity, such as the coordination of Lewis bases (LB), Lewis acid (LA) and base push-pull interaction or of reducing metal ions decrease the P–P bond order. The $P\equiv P$ triple bond is retained by coordination of Lewis acids, such as redox innocent metal ions.

In the recent past, we examined the coupling of terminal pnictogen ligands,^{47,48,49} leading to a rhenium pincer complex with a $(P=P)^0$ ligand stabilized by Lewis base and acid push-pull interaction (Figure 1).⁴¹ We have further utilized a related platinum pincer platform to synthesize the metallonitrene complex $[Pt(N)(PNP)]$ ($PNP = N(CHCHP^tBu_2)_2$) with singly bound N^- biradical.⁵⁰ The presence of the subvalent atomic nitrogen ligand relies on negligible back-bonding by the $\{Pt^I(PNP)\}$ fragment. This observation sparked our interest to evaluate this platform for the stabilization of a $(P_2)^0$ ligand without substantial charge transfer. We here report the redox series $[(P_2)\{Pt(PNP)\}]^{n+}$ ($n = 0-2$) with end-on bridging $(P_2)^{2-}$, $(P_2)^{-}$ and, for the first time, triply bonded $(P\equiv P)^0$ ligands.

RESULTS AND DISCUSSION

Preparation of the Diphosphene Complex $[(\mu-P_2)\{Pt(PNP)\}_2]$ (**2**)

Figure 2. Synthesis and key spectroscopic and computational data of the $(P_2)^{n-}$ complexes 2-4 ($n = 2-0$)

(A) $^{31}P\{^1H\}$ NMR signal of the $(P_2)^{2-}$ bridge of complex **2**.

(B) Q-band EPR spectrum of complex **3** in PhCl at 147 K (black; 34.2452 GHz) and simulated spectrum (red).

(C) Spin-density plot of complex **3** (isosurface at $\pm 0.005 a_0^{-3}$; methyl groups and hydrogen atoms omitted for clarity).

(D) $^{31}P\{^1H\}$ NMR signal of the $(P_2)^0$ bridge of complex **4**.

(E) 2D plot of ∇^2 (see the ESI for more details) and NLMOs representing the $P\equiv P$ triple bond of **4** (orbital isosurfaces at $\pm 0.05 a_0^{-3/2}$).

The platinum(II) phosphaketene complex $[Pt(OCO)(PNP)]$ (**1**, Supplemental Experimental Procedures) was synthesized by salt-metathesis from the previously reported triflate complex⁵⁰ and $Na(dioxane)_x(OCP)$. The structural assignment was confirmed by single crystal X-ray diffraction (Figure S75). The $^{31}P\{^1H\}$ NMR shift ($\delta_P = -374 \text{ ppm}$) and stretching mode ($\nu = 1869 \text{ cm}^{-1}$) of the phosphaketene group are in the typical range of late transition metal η^1 -

PCO complexes.³⁹ In analogy to other group 9 and 10 PCO complexes,^{38,39} the photolysis of **1** in benzene at room temperature (LED, $\lambda_{\text{exc}} = 456 \text{ nm}$) led to decarbonylative P–P coupling and isolation of diphosphene complex $[(\mu\text{-P}_2)\{\text{Pt}(\text{PNP})\}_2]$ (**2**) in over 90% yield (Figure 2). The phosphide (or metallophosphinidene) species $[\text{Pt}(\text{P})(\text{PNP})]$ is a likely transient intermediate but could not be characterized, e.g. by photocrystallography like the analogous metallonitrene $[\text{PtN}(\text{PNP})]$,⁵⁰ due to insufficient conversion upon single crystal photolysis. Notably, N–N coupling of the related nitridyl complex $[\text{Ir}(\text{N})(\text{PNP})]$ was previously reported.⁴⁷

The molecular structure of **2** in the solid state (Figure 3) features a strongly bent Pt–P–Pt core with a typical P=P double bond distance (Table 1) as in the diphosphene $\text{Mes}^*\text{P}=\text{PMes}^*$ ($2.034(2) \text{ \AA}$).⁵¹ Notably, the two $\{\text{Pt}(\text{PNP})\}$ fragments are oriented almost perpendicular with respect to each other (80.8°), resulting in idealized C_s symmetry. The single $^{31}\text{P}\{^1\text{H}\}$ NMR signal for the pincer ligands ($\delta_{\text{P}}(\text{C}_6\text{D}_6) = +57.3 \text{ ppm}$) and one at low field for the P_2 -bridge ($\delta_{\text{P}}(\text{C}_6\text{D}_6) = +707 \text{ ppm}$) indicate fluxional behavior on the NMR time-scale, which could not be frozen at temperatures down to -60°C . The ^{31}P chemical shift supports P=P double bonding as in Grützmacher's diiridium complex ($\delta_{\text{P}} = +683 \text{ ppm}$) or Bertrand's phosphonium stabilized diphosphene ($\delta_{\text{P}} = +675 \text{ ppm}$).^{39,52} $^{195}\text{Pt}\text{-}^{31}\text{P}$ J -coupling of the P_2 bridge ($J_{\text{PtP}} = 326 \text{ Hz}$, Figure 2A) is about an order of magnitude smaller compared with the pincer ligand ($J_{\text{PtP}} = 2976 \text{ Hz}$), which is in line with high phosphorus $3p$ -character of diphosphenediide bonding with the metal ions.⁵³ Accordingly, natural bond orbital (NBO) analysis reveals a Pt–P natural localized molecular orbital (NLMO) with 83% p -character of the P atom contribution (averaged 62% for the pincer P atoms). The UV/vis spectrum of **2** features a weak transition at 686 nm ($\epsilon = 90 \text{ M}^{-1}\text{cm}^{-1}$), which can be assigned to the formally dipole forbidden $\pi^*(\text{P}_2) \rightarrow \pi^*(\text{P}_2)$ HOMO/LUMO transition within the $(\text{P}_2)^{2-}$ core as confirmed by TD-DFT (Figure S85). In the Raman spectrum ($\lambda_{\text{exc}} = 514.5 \text{ nm}$, THF, Figure S30), the P=P stretching vibration is tentatively assigned to a band around 582 cm^{-1} (calc: 654 cm^{-1} , unscaled), which is close to the range found for organic diphosphenes ($610\text{--}624 \text{ cm}^{-1}$).^{54,55}

Figure 3. Molecular structures of **2 and the cations of **3** and **4** in the crystal.**

Thermal ellipsoids drawn at 50% probability. Hydrogen atoms, solvent molecules and counter-anions are omitted for clarity. Selected bond parameters are given in Table 1.

Table 1. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) of complexes **2–**4****

	Pt–N	Pt–P _{PNP}	Pt–P _{P2}	P–P	Pt–P–P
2	2.099(4) 2.097(4)	2.3190(14) to 2.3292(14)	2.3077(14) 2.3260(16)	2.037(2)	108.30(8) 119.22(9)
3^a	2.057(9) 2.068(9)	2.329(3) to 2.335(3)	2.261(3) 2.251(3)	1.984(5)	121.75(18) 133.87(18)
4	2.017(2)	2.3535(7) to 2.3575(8)	2.2003(9)	1.8649(17)	162.67(6)

^aValues from one of two independent molecules in the asymmetric unit.

The notion of two platinum(II) pincer fragments that are bridged by a singlet diphosphenediide ligand is corroborated by quantum chemical assessment of the electronic structure (further details are provided as ESI). NBO/NLMO analysis supports a P=P double bond for the bridging (P_2)²⁻ ligand and a lone pair localized on each of the two phosphorus atoms (Figure S81), resembling bonding in parent diphosphene HP=PH. This is in line with a topological analysis of the computed electron density within Bader's quantum theory of atoms in molecules (QTAIM): all relevant bond classification criteria, including a significant bond ellipticity and a delocalization index close to two,^{56,57} bear strong resemblance to P_2H_2 (Figure S84).

Stepwise Oxidation of the P_2^{2-} bridge

The low-energy electronic $\pi^*(P_2) \rightarrow \pi^*(P_2)$ HOMO/LUMO transition is suggestive of P_2 centered redox chemistry. Diphosphenyl radical cations, {RPPR}^{•+}, are generally reactive species and could be stabilized with substituents that allow for spin delocalization (R = carbene)^{26,58,59,60} and coordination to chromium.⁶¹ The cyclic voltammogram of **2** in PhF shows two reversible oxidation waves at $E_1^\circ = -0.91$ V and $E_2^\circ = 0.01$ V (versus $FeCp_2^{+/0}$, Figure S28), respectively.⁶² Reversibility of E_2 requires the use of inert electrolytes, like PhF/[NBu₄][BARF₄], indicating high electrophilicity after two-electron oxidation. Chemical oxidation with 1 eq. [Cp^*Fe][BARF₄] gave [$(\mu-P_2)\{Pt(PNP)\}_2$][BARF₄] (**3**) in 84% isolated yield (Figure 2). The radical cation resembles the conformation of parent **2** (Figure 3), yet with a slightly relaxed zig-zag-shaped Pt–P–Pt core, as expressed by the Pt–P–P angles (Table 1). Furthermore, the Pt– P_2 ($\Delta d_{av} = -0.06$ Å) and P–P ($\Delta d = -0.05$ Å) bonds are shortened. These structural features are in line with the removal of an electron from an antibonding $\pi^*(P_2)$ MO. Accordingly, a band at 626 cm⁻¹ in the Raman spectrum (Figure S31) is assigned to the P–P stretching vibration. The hypsochromic shift with respect to parent **2** ($\Delta\nu = 44$ cm⁻¹), is in excellent agreement with DFT ($\Delta\nu = 49$ cm⁻¹ at the $\omega B97X-D/def2-TZVP$ level), as well as the shortening of the P–P bond ($\Delta d_{DFT} = -0.05$ Å). The $\pi^*(P_2) \rightarrow \pi^*(P_2)$ transition is further moved into the NIR region as a broad line at 846 nm ($\epsilon = 890$ M⁻¹·cm⁻¹).

Magnetic characterization of **3** by SQUID magnetometry (Figure S38) features simple Curie-type paramagnetism of the doublet ($S = 1/2$) ground state. The Q-band EPR spectrum in frozen chlorobenzene at 147 K shows a rhombic signal (Figure 2B). Notably, the g -anisotropy ($g = [2.042, 1.994, 1.887]$) is far below that of typical platinum(III) compounds.⁶³ Besides hyperfine interaction (HFI) with the two platinum nuclei ($A_{iso}(^{195}Pt) = 669$ and 567 MHz), large HFI with the P_2 bridge is resolved ($A_{iso}(^{31}P) = 441$ and 267 MHz), which considerably exceeds that of carbene and vinyl stabilized diphosphenyl radical cations (34–150 MHz).^{26,58,59,60} This observation is in line with predominantly diphosphenediide-centered oxidation of **2** and an unsymmetric spin density distribution of radical cation **3**.⁶⁴ DFT calculations confirm this picture and locate the spin density of **3** mainly on the P_2 fragment (Figure 2C) as a result of depopulation of the $\pi^*(P_2)$ HOMO of parent **2**. Accordingly, the P–P bond order increases upon oxidation, as reflected by the Wiberg bond orders and the QTAIM delocalization indices (WBI; **2**: 1.86, **3**: 2.09, and DI(P,P); **2**: 1.81, **3**: 1.95; Figure S81–S82). Despite very small spin densities at the Pt atoms, the large isotropic ¹⁹⁵Pt HFI of **3** results from significant s orbital contribution (~30%), as judged from the isotropic hyperfine coupling constant of ¹⁹⁵Pt⁰ ($a_0 \approx 12000$ G) and comparison with the ³¹P nuclei of the P_2 bridge (~9% s character, $a_0 \approx 4700$ G).⁶⁵ Notably, spin-orbit contributions are insignificant, which supports a phosphorus-centered π -radical (cf. ESI for computed EPR results).⁶⁶

Oxidation of **2** with slightly more than 2 eq. AgBARF₄ in PhF enabled the isolation of the light-sensitive dicationic complex [$(\mu-P_2)\{Pt(PNP)\}_2$][BARF₄]₂ (**4**) in 54% yield. In the crystal (Figure 3), the overall configuration of the cation residue is retained with little structural variation of the {Pt(PNP)} fragments. However, the P–P bond (1.8649(17) Å) is further shortened (Table 1), even below the bond distance of free, triply bonded P_2 in the gas phase (1.8934 Å).^{44,67} Furthermore, the Pt–P–Pt core is much closer to linearity (Pt–P–P: 162.67(6)°). These structural changes are reflected by the NMR data: In comparison to parent **2** ($\delta_P = +707$ ppm), the ³¹P{¹H} NMR signal of the P_2 bridge ($\delta_P(CD_2Cl_2) = +248$ ppm) is distinctly high-field shifted, which is in line with a higher lying excited state due to the vacant $\pi^*(P_2)$ MO. Note, that the side-on bound (P_2)⁴⁻ ligand in Mezailles' complex [$(\mu^2, \eta^2-\eta^2-$

$P_2\{Pt(dppp)_2\}$ was found at even higher field ($\delta_P = +49.3$ ppm).⁶⁸ Accordingly, the low-energy $\pi^*(P_2) \rightarrow \pi^*(P_2)$ electronic transition observed for **2** and **3** is absent for **4**. Mutual coupling of $^1J_{PP'} = 300$ Hz was obtained for the magnetically inequivalent nuclei of the P_2 bridge of **4**, which compares well with the computational estimate for free $P \equiv P$ ($|^1J_{iso}| = 498$ Hz) by Wasylshen and co-workers.⁶⁹ Importantly, the $^{195}Pt-^{31}P$ J -coupling of the metal with the bridge ($^1J_{PtP} = 2877$ Hz, Figure 2D) is about an order of magnitude higher compared with the P_2^{2-} ligand of **2** (326 Hz, Figure 2A). This large $^1J_{PtP}$ coupling can be rationalized with a distinct increase of phosphorus 3s character for bonding with the metal,⁵³ as expected for a linearly bridging, neutral $P \equiv P$ ligand.

Structural and spectroscopic parameters of the 2-electron oxidized product **4** are thus consistent with a Pt^{II}/Pt^{II} complex bridged by a neutral $P \equiv P$ ligand, with little effective charge transfer upon coordination. This coordination mode is commonly observed for the lighter analogue N_2 , yet unprecedented for P_2 . Further support for an increased bond order comes from computed vibrational data: While the $P \equiv P$ stretching mode of **4** could not be found by Raman spectroscopy due to its intense color, DFT calculations predict 914 cm^{-1} for the vibration, which is further blue shifted with respect to **2** (654 cm^{-1}) and **3** (703 cm^{-1}), respectively, and even beyond the value of 850 cm^{-1} computed for free P_2 (Figure S84).

NBO analysis of **4** confirms $P \equiv P$ bonding comprising a σ and two π bonds (Figure 2E) and reveals a $Pt-P$ NLMO composition with higher s character at P (62% s and 38% p) than present in parent **2** (16% s and 83% p), which is fully in line with our NMR data interpretation. The WBI of the P_2 fragment (2.48) is significantly larger than that in monocationic complex **3** (2.09) and a positive NPA charge of 0.29 is computed for the P_2 bridge in **4** (**3**: -0.13 ; **2**: -0.59). The QTAIM topological signatures closely resemble those computed for free P_2 : a negligible bond ellipticity ($\epsilon = 0.03$) and a further increased delocalization index ($DI(P,P) = 2.31$) as compared to **3** (results for free P_2 : $\epsilon = 0.00$; $DI(P,P) = 3.04$). A $P \equiv P$ bond order somewhat below three indicates π -backdonation of the $\{Pt(PNP)\}$ fragments. Accordingly, energy decomposition analysis (EDA-NOCV, cf. ESI) reveals marked π -donation from the $Pt(PNP)$ fragments into both $\pi^*(P_2)$ orbitals, which slightly exceeds the amount of σ -donation from P_2 to Pt (Figure S91b) and is clearly more pronounced than in **2**. Furthermore, $P \rightarrow Pt$ donation in **4** is dominated by the σ -type lone pairs of the P_2 fragment, while the donor interaction in **2** involves the doubly occupied $\pi^*(P_2)$ orbital. These differing bonding motifs give rise to the *zig-zag* structure of **2** and the nearly linear arrangement of the $Pt-P-Pt$ core in **4**, respectively.

Reactivity of the $(P \equiv P)^0$ complex **4**

The scarcity of platinum dinitrogen complexes contrasts with the remarkable thermal stability of **4** in inert solvents. While platinum dinitrogen complexes could only be characterized by matrix isolation and gas phase techniques,⁷⁰ heating of **4** in PhF to 70°C overnight showed no signs of P_2 release even in the presence of the potential trapping agent 1,3-cyclohexadiene (1,3-CHD).^{21,22} However, P_2 release from **4** can be triggered by isonitrile or CO addition. With CN^tBu , $[Pt(CN^tBu)(PNP)]^+$ (**5a**) is formed at low temperature as main Pt product (87%). In addition, P_4 ($\delta_P = -524$ ppm) is observed in up to 27% yield. NMR-silent polymeric elemental P_n is presumably the prevalent phosphorous product from P_2 oligomerization.^{21,22} We note in passing that P_2 oligomerization predominantly yields red phosphorous,⁷¹ while the symmetry-forbidden dimerization is associated with a significant kinetic barrier.^{19,72,73}

Figure 4. Experimental and computational results for P_2 transfer reactivity from complex **4**

(A) P_2 release from complex **4** upon reaction with *tert*-butylisocyanide and CO and trapping with 1,3 cyclohexadiene (1,3-CHD).

(B) Computed reaction sequence for P_2 release from **4** with CO.

(C) End-on/side-on isomerization of P_2 as a terminal ligand and dimerization to complex **7** (cf. ESI for further details).

Relative free energies are given in parentheses (ΔG^{298} in kcal·mol⁻¹), transition state imaginary frequencies in cm⁻¹; methyl groups and hydrogen atoms omitted for clarity.

In the presence of 1,3-CHD, two products could be identified by ESI-MS (Figure S60) and NMR spectroscopy (Figures S53 and S55) in a ratio close to 1:1, i.e., **5a** and **6** (Figure 4A) as the product from Diels-Alder trapping of P_2 with 2 eq. 1,3-CHD. The spectroscopic signature of the $P_2(C_6H_8)_2$ ligand resembles that of a tungsten complex obtained by Cummins' group.²² Analogous results were observed with CO/1,3-CHD (Scheme 4A). However, in the absence of 1,3-CHD, $[Pt(CO)(PNP)]^+$ (**5b**) was obtained in only 52% yield and no free P_4 was formed. Furthermore, a new complex (**7**) is observed with a broad ^{31}P signal ($\delta_P = -240$ ppm, Figure S46) that integrates equally with the pincer ^{31}P signal. The distinct high-field signal resembles the side-on bound P_4 ligand of $[Rh(\eta^2-P_4)Cl(PPh_3)_2]$ (coordinated P: $\delta_P = -279$ ppm; non-coordinated P: $\delta_P = -284$ ppm).^{74,75} Complex **7** does not react with CO or 1,3-CHD, but the addition of CN*t*Bu immediately gives **5a** and free P_4 (ca. 3:1, Figure S51).⁷⁶ While **7** could not be isolated so far, these results support the assignment of the P_4 complex $[(P_4)\{Pt(PNP)\}_2]^{2+}$. The absence of ^{195}Pt satellites is attributed to fluxional P_4 coordination,⁷⁵ which could not be frozen even at low temperatures ($\delta_P^{203K} = -224$ ppm, Figure S47).

Quantum chemical assessment⁷⁷ of the reaction of **4** with CO (Figure 4B) supports initial attack of CO to give **5b** and $[Pt(P_2)PNP]^+$ (**I1**) with an end-on coordinated P_2 ligand. The side-on isomer of **I2** is less stable by only 4 kcal·mol⁻¹ (Figure 4C). The concerted substitution step via **TS1** exhibits an appreciable activation barrier of $\Delta^\ddagger G = 23$ kcal·mol⁻¹, which is in line with the slow experimental rate. Notably, subsequent associative P_2 liberation from **I1** is kinetically even more challenging (**TS2**; $\Delta^\ddagger G = 25$ kcal·mol⁻¹), as confirmed by high-level coupled cluster calculations for a molecular model (see ESI). The difference of barriers $\Delta\Delta^\ddagger G$ suggests a sizable lifetime of **I1** under CO. However, a plausible path for the dimerization of **I1** to the P_4 complex assigned to **7** was found, which is strongly exergonic and connected with a moderate overall activation barrier ($\Delta^\ddagger G = 22$ kcal·mol⁻¹, Figure 4C). Hence, the selectivity in white vs. polymeric phosphorus scales with the relative rates for dimerization of coordinated P_2 vs. release of free P_2 . In agreement with findings of Cummins and co-workers,²² our results exemplify that P_2 complexes like **I1** seem to be the key intermediates

for the selective formation of molecular phosphorous products from P_2 in the condensed phase.

Conclusion

Photolytic phosphide coupling gave access to the P_2 -bridged redox series **2-4**. The sequential redox steps are predominantly P_2 -centered as expressed, e.g., by increasing linearization of the Pt–P–Pt core along the redox series, the large ^{31}P HFI of radical cation **3** and significantly increased $^1J_{PtP}$ coupling in **4** vs. **2**. NBO and QAIM analyses support the assignment of bridging $(P=P)^{2-}$ diphosphenediide (**2**), $(P_2)^{\bullet-}$ diphosphenide radical (**3**), and ultimately the neutral a $(P\equiv P)^0$ diphosphorous ligands (**4**) with an electronic structure comparable to free P_2 . While the lower homologue N_2 is commonly found as a neutral, linearly bridging ligand, compound **4** represents the first molecular-level example in condensed phase to mimic the bonding situation of neutral, free diphosphorus at ambient conditions. Preservation of the $(P\equiv P)$ triple bonding character relies on the coordination to redox-inactive, Lewis-acidic platinum pincer fragments that exhibit minimal charge transfer to the highly electrophilic P_2 unit. In contrast to the predicted preference for side-on binding of neutral heavier dipnictogen $(Pn_2)^0$,⁷⁸ our approach enables the exploration of diverse multiple-bonding situations of end-on bound heavier dipnictogen. It complements the popular strategy to stabilize multiply bonded, heavy p-block fragments by Lewis-bases, yet without accompanying reduction of the bond order. At the same time, controlled dissociation of one capping Lewis-acid fragment enables the use as P_2 transfer reagent for the synthesis of molecular organic and inorganic products.

EXPERIMENTAL PROCEDURES

The experimental details of chemical synthesis, spectroscopic, magnetic and crystallographic characterization and quantum mechanical calculations are provided in the Supplemental Information.

Resource Availability

Lead Contact

Further information and requests for resources should be directed to and will be fulfilled by Sven Schneider (sven.schneider@chemie.uni-goettingen.de).

Data and Code Availability

Crystallographic data of **1-4**, **5a-OTf** have been deposited in the Cambridge Crystallographic Data Center under accession numbers CCDC: 2068022-2068026. This data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, Figures S1-S95, Tables S1-S21 and 5 data files and can be found with this article online at XXX.

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AUTHOR CONTRIBUTIONS

S.Sch. and M.C.H. designed the project. S.Sch. supervised the experimental work and M.C.H. the quantum chemical study. J.S. carried out synthetic and spectroscopic work and H.V., J.I.S. and M.D. the quantum chemical calculations. C.W. and M.O. performed the crystallographic, S.D. the magnetic and I.T. the EPR spectroscopic characterization. C.H. carried out the Raman experiments supervised by C.L. The manuscript was jointly written by J.S, H.V., M.C.H. and S.Sch. and all authors discussed the results in detail and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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