

Novel cofacial oxidative coupling reaction of phosphinine in the presence of Cu(I) and ClO₄⁻†

Takahiko Kojima,* Yoshitaka Ishioka and Yoshihisa Matsuda*

Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Higashi-Ku, Fukuoka 812-8581, Japan. E-mail: cosyscc@mbox.nc.kyushu-u.ac.jp (T. K.); Fax: 81 92 642 2570; Tel: 81 92 642 4179

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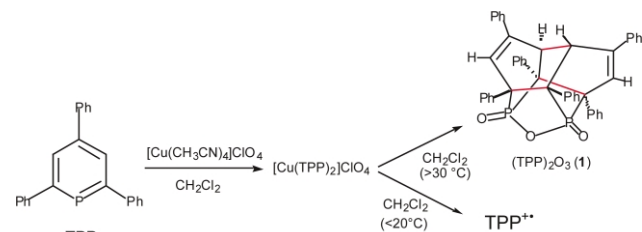
2,4,6-Triphenylphosphinine (TPP) underwent unprecedented cofacial oxidative coupling to form a novel C₂-symmetric cage compound, having extremely long C–C bonds.

Phosphinine is a heteroaromatic compound containing a phosphorus atom, which was first synthesized by Märkl.¹ Its chemistry has been strongly extended by the synthesis of a variety of phosphinine families,² including the preparation of their organometallic complexes³ by Le Floch and Mathey. A remarkable property of phosphinines is that they have a low-lying π* orbital as the LUMO which has a large coefficient at the phosphorus atom. This property renders the phosphinine a strong π-acceptor to undergo π-back bonding from a metal centre. Recently, Rh(I)-phosphinine complexes have been applied to catalytic hydroformylation of olefins.⁴ Thus, the chemistry of phosphinine is now developing in several directions, allowing us to access a new frontier of organometallic chemistry and catalysis. In order to consider the reactivity and properties of phosphinine–metal complexes, it is necessary to gain more insights into the reactions of phosphinines with metal ions.

The first phosphinine synthesized was 2,4,6-triphenylphosphinine (TPP)¹ and its transition metal complexes have been reported. A variety of metal ions form η¹-,⁵ η⁶-,⁶ and μ₂-TPP⁷ complexes, including Cu(I).⁸ TPP has been known to undergo one-electron oxidation to form a phosphinine cation radical, which is stable at room temperature.⁹ Also, TPP can be reduced to form an anion radical.¹⁰ Here, we present the first report of a novel oxidative coupling of two phosphinines in the presence of Cu(I) and ClO₄⁻ to form a stable phosphorus-containing cage compound of a dialkylphosphoric anhydride with extremely long C–C single bonds.

The reaction of TPP with [Cu(CH₃CN)₄]ClO₄ in CH₂Cl₂ at room temperature under N₂ gave the bis-TPP complex, [Cu(TPP)₂]ClO₄, in good yield. Recrystallization from CH₂Cl₂–hexane under air at room temperature (>25 °C) gave yellow block crystals of **1**, suitable for X-ray crystallography.† Compound **1** also can be obtained in good yield by refluxing [Cu(TPP)₂]ClO₄ in CH₂Cl₂ under air. The reactions are summarized in Scheme 1. The crystal structure of **1** was determined by X-ray crystallography and it revealed that a pair of enantiomers exists in an asymmetric unit (Fig. S1†). An ORTEP drawing of the *R*-isomer and its core structure are depicted in Fig. 1 and selected bond lengths and angles are listed in the figure caption.

Two TPP molecules are coupled together at the two 2- and 6-positions (2–2 and 6–6) and between the 3 and 5 positions



† Electronic supplementary information (ESI) available: Synthetic route to **1**, NMR data of **1**, ORTEP drawing of the asymmetric unit. See <http://www.rsc.org/suppdata/cc/b3/b308892h/>

obliquely (3–5). The two phosphorus atoms are oxidized and connected together with a μ-oxo linkage. The molecule has a C₂ axis, which penetrates the bridging oxygen (O2) and the middle of the C2–C25 bond. Interestingly, all the eight coupled positions (P1, P2, C1, C2, C5, C24, C25 and C28) are stereogenic. All the stereogenic centres in one molecule are in the *R* configuration and are in the *S* configuration in the other molecule, indicating the coupling process proceeds with complete stereoselectivity. The bond lengths of newly formed C–C bonds are 1.611(5) Å for C1–C28, 1.650(5) Å for C5–C24 and 1.545(5) Å for C2–C25. The first of these two bonds are extremely long for C–C single bonds and are comparable to those of highly distorted prismane-like compounds having C–C bonds longer than 1.60 Å.¹¹

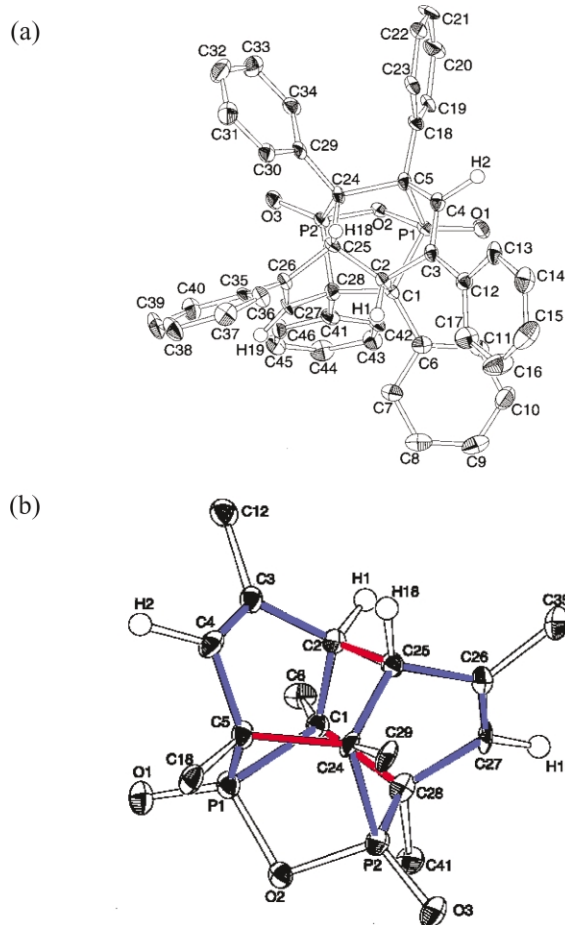


Fig. 1 (a) An ORTEP drawing of the *R*-isomer of **1** (*R*-**1**) with 50% probability thermal ellipsoids. (b) The core structure of *R*-**1**. The blue-lined scaffold represents the original TPP moiety and the newly formed C–C bonds are shown as red lines. Selected bond lengths (Å) and angles (°): P1–O1 1.464(3), P1–O2 1.630(3), P1–C1 1.895(4), P1–C5 1.841(4), P2–O2 1.621(3), P2–O3 1.465(3), P2–C24 1.884(4), P2–C28 1.824(4), C1–C28 1.611(5), C5–C24 1.650(5), C2–C25 1.545(5), C3–C4 1.328(6), C26–C27 1.339(5); O1–P1–O2 114.2(2), O2–P2–O3 113.6(2), P1–O1–P2, 103.7(1).

In the ^1H NMR spectrum of **1** in CDCl_3 (see Fig. S2 †), a characteristic AMX quartet was observed at 3.35 ppm ($^3J_{\text{HH}} = 15$ Hz and $^3J_{\text{PH}} = 11$ Hz), which was assigned to the 3(5)-H at the linked position.¹²

The formation of **1** was governed by Cu(I) and ClO_4^- and moderate temperature. The requirement for perchlorate anion was confirmed by observing no reaction in the case of $[\text{Cu}(\text{TPP})_2]\text{X}$ ($\text{X} = \text{BF}_4, \text{PF}_6$). The requirement for Cu(I) was also indicated because TPP remained intact in the absence of Cu(I) and in the presence of ClO_4^- ($n\text{-Bu}_4\text{NClO}_4$) without Cu(I). In addition, the reaction temperature was revealed to be critical for the formation of **1**. In CH_2Cl_2 , $[\text{Cu}(\text{TPP})_2]\text{ClO}_4$ decomposed to form free $\text{TPP}^{+\cdot}$ at lower temperatures (< 20 °C), which was detected by ESR to show a doublet ($A_{\text{P}} = 23$ G at $g = 2.0020$), consistent with observations reported by Dimroth *et al.*^{9b} We estimate the spin density at the phosphorus atom to be 11.7% based on the hyperfine coupling constant. In contrast, refluxing a CH_2Cl_2 solution of $[\text{Cu}(\text{TPP})_2]\text{ClO}_4$ gave **1** in moderate yield. This clearly indicates that the oxidation of Cu(I)-coordinated TPP by ClO_4^- is the first step to form $\text{TPP}^{+\cdot}$ followed by the rate-limiting coupling reaction. The stoichiometry of coupling is controlled by the number of TPP ligands coordinated to the Cu(I) centre, therefore, no other coupling products are observed. This also suggests that the coupling reaction takes place in an intramolecular manner, and not in an intermolecular manner.

It has been reported that TPP undergoes [4+2] cycloaddition with hexafluoro-2-butyne to form a 1,4-addition product.¹³ Actually, DFT calculations for TPP indicated that HOMO mainly populates at the phosphorus and the 4-position.¹⁴ However, in the present case, no 1,4-addition product was observed and the phosphorus atom was oxygenated instead. Our observation of radical formation from the Cu(I)-precursor complex suggests that coordinated TPP can be oxidized more easily than the free form due to π -back donation from the Cu(I) centre, which renders the TPP more electron-rich. This argument is supported by the large negative shift of oxidation potentials of TPP (0.88 V *vs.* Ag/AgNO_3) compared to that of $[\text{Cu}(\text{TPP})_2]\text{ClO}_4$ (0.66 V),¹⁵ and a large upfield coordination shift from 183.0 ppm for TPP to 144.4 ppm for $[\text{Cu}(\text{TPP})_2]\text{ClO}_4$ ($\Delta\delta = -38.6$ ppm).¹⁶ In addition to the π -back donation, the role of Cu(I) is assumed to converge the reactants at a close distance to facilitate the two TPP molecules to react with each other. The oxidation reduces the HOMO–LUMO gap between TPP and $\text{TPP}^{+\cdot}$ to couple together. Recently, Mathey and coworkers have reported radical coupling reactions to give P–P coupled products of a macrocyclic phosphinine *via* the formation of an anion radical.¹⁷ However, in our case, such P–P coupling was not observed and such reactions should be prevented by the coordination to Cu(I) through the phosphorus atoms and also by the steric hindrance of two 2- and 6-phenyl groups. We note the report of an intramolecular and ionic $5s + 5s$ [6+4] cycloaddition to form a similar scaffold by the reaction of phosphinine derivatives with diazoalkanes without oxidation of phosphorus centres.¹⁸ In sharp contrast to **1**, the compounds referred to as diphosphachiropteradienes¹⁹ undergo decomposition to give the corresponding phosphinines and more complicated coupling products.¹⁸ The two phosphorus atoms in **1** are irreversibly oxidized to form the phosphoric anhydride linkage, which can contribute to the stabilization of **1**. The participation of Cu(I) ion and ClO_4^- , and the stability of **1**, however, make the reaction described here different from those reported by Märkl and coworkers. Further investigation on the reaction mechanism is underway.

In conclusion, we have succeeded in synthesizing and isolating an unprecedented Cu(I)-assisted oxidative coupling product of

phosphinines and have established its structure unambiguously by X-ray crystallography. Our results described here represent the discovery of a new reactivity of phosphinines and pave the way for other novel phosphorus-containing cage compounds to be synthesized and discovered.

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Notes and references

‡ Crystal data: **1**, $\text{C}_{92}\text{H}_{68}\text{O}_6\text{P}_4$, $M = 1393.44$, $T = -160(1)$ °C, monoclinic, space group $P2_1/n$, $a = 23.4513(5)$, $b = 13.4607(2)$, $c = 24.5485(5)$ Å, $\beta = 116.1286(4)^\circ$, $V = 6957.3(2)$ Å³, $Z = 4$, $R_1 = 0.072$ ($I > 2\sigma(I)$), $R_w = 0.185$ (all data), GOF = 1.02. CCDC 207184. See <http://www.rsc.org/suppdata/cc/b3/b308892h/> for crystallographic data in CIF or other electronic format.

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- Cyclic voltammograms were recorded in CH_2Cl_2 (0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4$) under N_2 at room temperature. The oxidation waves were irreversible at a scan rate of 50–500 mV s^{-1} .
- $^{31}\text{P}\{^1\text{H}\}$ NMR data (δ/ppm in CDCl_3): 145.7 (s) ($[\text{Cu}(\text{TPP})_2]\text{PF}_6$) and 144.4 (s) ($[\text{Cu}(\text{TPP})_2]\text{ClO}_4$).
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- The compound reported in ref. 18, in sharp contrast to **1**, exhibits normal C–C bond lengths of 2–2 and 6–6 bondings (1.567 Å), but a longer C–C bond length (1.627 Å) for the 3–5 linkage. These data were obtained from a Chem 3D model based on the CSD data (CSD-52330).