1,3-Butadiene Analogues

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Tl$_2$[Aryl$_2$P$_4$]: A Thallium Complexed Diaryltetraphosphabutadienediide and its Two-Electron Oxidation to a Diaryltetraphosphabicyclobutane, Aryl$_2$P$_4$**

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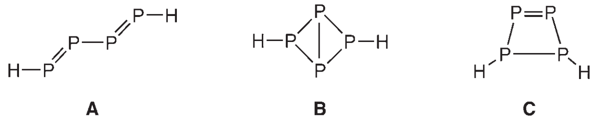
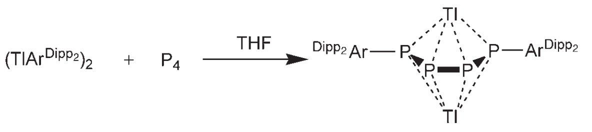
The synthesis and characterization of multiply bonded heavier main group element compounds is a major area of interest in organometallic chemistry.[1] A primary focus of this work has been the stabilization of homonuclear multiply bonded dimeric species of the heavier group 13, 14, and 15 elements and the study of their reactivity.[2] More recently this has led to the stabilization of multinuclear conjugated heavier element arrays containing more than two multiply bonded heavier elements.[3] For example, Weidenbruch and co-workers have prepared silicon[3a] and germanium[3b] analogues of 1,3-butadiene with the use of bulky triisopropylphenyl substituents and have been shown by spectroscopy that they display conjugation. However, the corresponding tetraphosphabutadienes (P$_4$R$_2$) and heavier group 15 congeners have not been isolated.[4] Calculations on three parent P$_4$H$_2$ isomers (**A**–**C**, Scheme 1) revealed that the tetraphosphabutadiene (**A**) is ca. 20 kcal mol^{-1} less stable than the tetraphosphacyclobutane isomer **B**, while the tetraphosphacyclobutene isomer **C** is 10.7 kcal mol^{-1} less stable than **B**.[5]

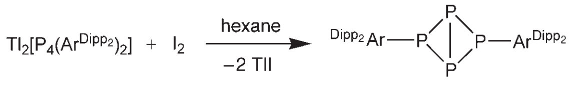


Scheme 1.

The prediction that **A** is the least stable isomer suggests that the preparation of substituted analogues of **A** is a formidable challenge. We were led to consider the existence of stable species with structural frameworks related to **A** during the investigations of reactions of the recently reported "dithallene"[2a] (TlAr$^{\text{Dipp}_2}$)$_2$ (Ar$^{\text{Dipp}_2}$ = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,6-iPr$_2$)$_2$) with white phosphorus.[6] We now report that the reaction of the weakly dimerized "dithallene" (TlAr$^{\text{Dipp}_2}$)$_2$ with P$_4$ results in aryl group transfer to phosphorus to afford Tl$_2$[P$_4$(Ar$^{\text{Dipp}_2}$)$_2$] (**1**), a thallium salt of the diaryltetraphosphabutadienediide, which is a doubly reduced analogue of **A** [Eq. (1)]. Furthermore, we describe the facile two-electron oxidation of **1** by I$_2$ to yield the neutral diaryltetraphosphabicyclobutane, P$_4$(Ar$^{\text{Dipp}_2}$)$_2$ (**2**), a substituted analogue of **B** [Eq. (2)].



1   (1)



2   (2)

Reaction of (TlAr$^{\text{Dipp}_2}$)$_2$ with P$_4$ in THF and subsequent recrystallization from hexane yielded **1** as burgundy crystals in 40 % yield. Complex **1** was characterized by ^{1}H, ^{13}C, ^{31}P, and $^{203/205}$Tl NMR spectroscopy, UV/Vis spectroscopy, and single-crystal X-ray crystallography. The structure[7a] of **1** (Figure 1) revealed a planar C(1)-P(1)-P(2)-P(2A)-P(1A)-C(1A) dianionic core with a *cis* conformation which is complexed to Tl(1) and Tl(1A) ions disposed equidistant above and below the P$_4$C$_2$ array (Tl–P distances 3.032(3)–3.168(3) Å). The Tl$^{\text{I}}$ centers also interact with the flanking Dipp substituents of Ar$^{\text{Dipp}_2}$ (Tl–centroid distances are 3.290(3) and 3.204(3) Å).

The Tl–centroid distances in **1** are greater than those in [(Mes)$_6$Tl$_4$(GaBr$_4$)$_4$][8a] (2.94–3.03 Å), TlN(Me)Ar$^{\text{Mes}_2}$[8b] (3.03 Å), and [Tl{N[C(C$_3$F$_7$)N(Ar)]$_2$}][8c] (ca. 3.0 Å; Ar = Mes or Dipp) and are substantially greater than the Tl–centroid distances (2.49 Å) observed in the dimer [C$_5$(CH$_2$Ph)$_5$Tl]$_2$.[2b] Calculated Tl–arene interaction energies vary from very weak (ca. 3 kcal mol^{-1})[8b] to relatively strong (ca. 20 kcal mol^{-1})[8c] depending on the model.[9] The Tl–arene interaction energies in **1** are probably weak, however, they may be responsible for the *cis* conformation. The P–P distances in **1** are almost identical (P(1)–P(2) 2.136(4); P(2)–P(2A) 2.143(6) Å) and lie between those observed in doubly-bonded diphosphenes[10] (1.98–2.05 Å) and typical P–P single bonds[11] (ca. 2.21 Å).

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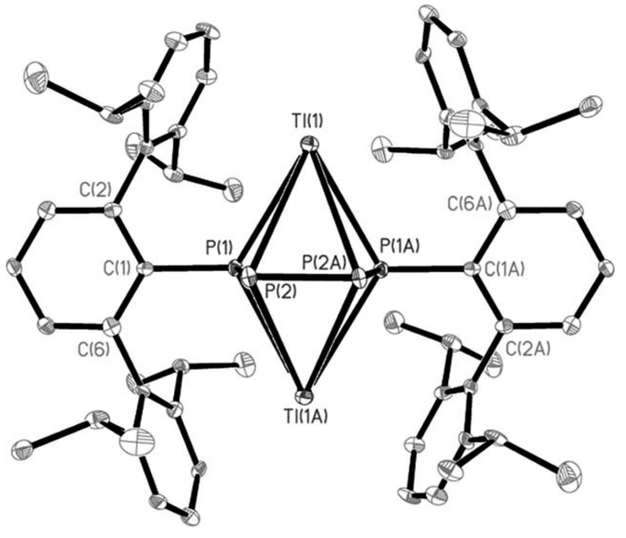


Figure 1. Thermal ellipsoid (30%) plot of **1**. H atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: P(1)–C(1) 1.868(11), P(1)–P(2) 2.136(4), P(2)–P(2A) 2.143(6), Tl(1)–P(1) 3.066(3), Tl(1)–P(1A) 3.032(3), Tl(1)–P(2) 3.168(3), Tl(1)–P(2A) 3.144(3); C(1)-P(1)-P(2) 100.7(3), P(1)-P(2)-P(2A) 101.75(10), C(1)-P(1)-Tl(1) 120.9(3), C(1)-P(1)-Tl(1A) 117.8(3).

The ^{205}Tl NMR spectrum of **1** consisted of a broad signal (1750 Hz at half height) at ca. 2730 ppm, which is within the range observed for Tl^{I} compounds.[12] There is a pair of satellite signals ($^{2}J_{^{205}\mathrm{Tl},^{203}\mathrm{Tl}} \approx$ 12000 Hz) arising from coupling to the ^{203}Tl isotope (Figure 2). A pseudo-quintet pattern is superimposed on the three broad signals, which presumably results from the similar $^{1}J_{^{205}\mathrm{Tl},\mathrm{P}(1)}$ and $^{1}J_{^{205}\mathrm{Tl},\mathrm{P}(2)}$ coupling constants of ca. 500 Hz. The ^{203}Tl NMR spectrum consists of the same pseudo-quintet pattern, with a pair of ^{205}Tl satellite signals ($^{2}J_{^{203}\mathrm{Tl},^{205}\mathrm{Tl}} \approx$ 12000 Hz). However, because of the greater abundance of the ^{205}Tl isotope (^{203}Tl 29.5%, ^{205}Tl 70.5%), the ^{205}Tl satellite signals are larger. The large size of the $^{2}J_{^{205}\mathrm{Tl},^{203}\mathrm{Tl}}$ coupling constant (ca. 12000 Hz) in both spectra is noteworthy.[13] The pseudo quintet displayed in the Tl NMR spectra indicates that the association of the thallium ions and the P_4 array is preserved in solution.

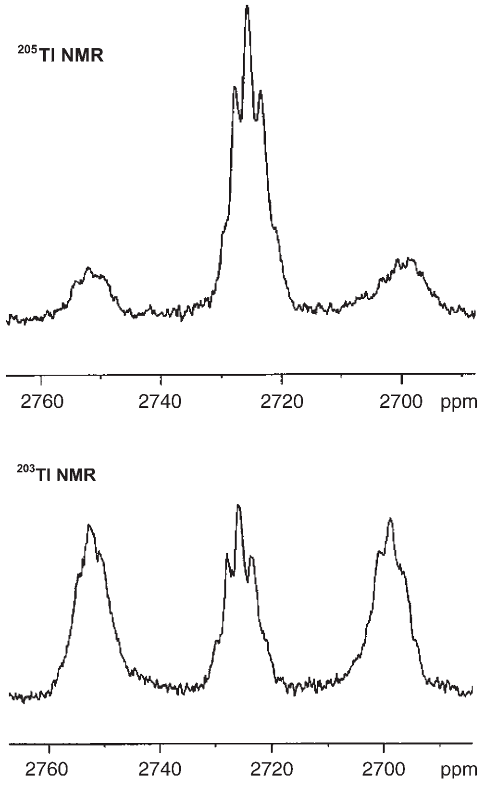
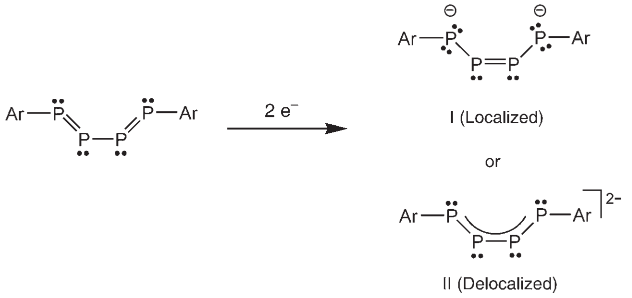


Figure 2. ^{205}Tl and ^{203}Tl NMR spectra of **1**.

The ^{31}P NMR spectrum revealed two broad multiplets (width at half height ca. 850 Hz) at 280 and 185 ppm, likely due to $^{1}J_{\mathrm{P,P}}$, $^{1}J_{^{205}\mathrm{Tl},\mathrm{P}}$, and $^{1}J_{^{203}\mathrm{Tl},\mathrm{P}}$ coupling. Variable-temperature spectroscopy in the range −90 to 60°C did not allow for extraction of specific coupling constants. The UV/Vis spectrum displayed three intense absorptions at 322, 432, and 546 nm ($\varepsilon = 1000$–$13000\,\mathrm{mol^{-1}\,L\,cm^{-1}}$), where the longer-wavelength absorptions are probably due to the orbitally allowed $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions.

Compound **1** is a thallium complexed diaryltetraphosphabutadienediide and can formally be derived from the two-electron reduction of the neutral diaryltetraphosphabutadiene. This affords a 6π system where two bonding forms are possible: the negative charge can be localized on the terminal phosphorus atoms (**I**) or the negative charge can be delocalized over the entire P_4 unit (**II**) (Scheme 2).



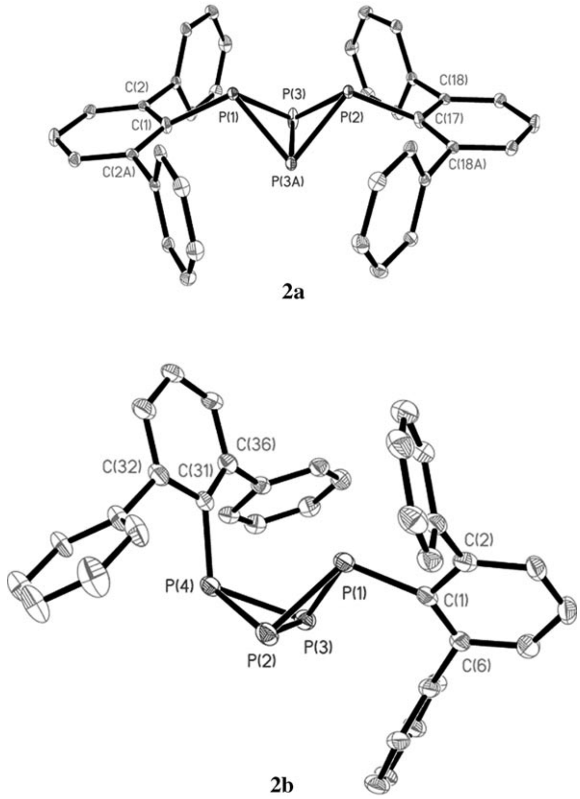
Scheme 2.

The isolated dianions of substituted 1,3-butadiene[14] and 1,2-bis(diphosphinyl)ethenes,[15] which are isoelectronic to **1**, display a localized bonding pattern analogous to structure **I**, where minimization of the Coulombic repulsion between the two negative charges is achieved. However, the P–P distances in **1** are nearly identical suggesting that a more delocalized bonding scheme (structure **II**) is present, which gives a formal P–P bond order of 1.33.[16] The Tl–P interactions may be responsible for decreasing intrachain electronic repulsion in **1**.

The synthesis of a neutral diaryltetraphosphabutadiene derivative analogous to **A** was attempted by oxidation of **1**. However, reaction of **1** with I_2 gave $P_4(\mathrm{Ar^{Dipp_2}})_2$ as the diaryltetraphosphabicyclobutane isomer.[7c,17] It seems likely that a species with a structure analogous to **A** is generated initially but that this isomerizes to **2**.[18] The isomerization is reminiscent to that of 1,3-butadiene to bicyclobutane which has been well explored in the classic work of Woodward and Hoffmann.[19]

The ^{31}P NMR spectrum of **2** gave two triplet resonances centered at $\delta = -331.8$ (bridgehead P atoms) and $\delta = -163.0$ ppm ($^{1}J_{P,P} = 189$ Hz), consistent with either a rigid *trans*,*trans*-diaryltetraphosphabicyclobutane, or a fluxional structure with C_{2v} symmetry. Previously reported disubstituted tetraphosphabicyclobutanes, R_2P_4 (R = 2,4,6-tBu$_3$C$_6$H$_2$ (**3**),[17a] (Me$_3$Si)$_2$N (**4**),[17b] [(Me$_3$Si)$_2$N]$_2$P (**5**),[17c]) crystallized in the *trans*,*trans* configuration. However, unlike **2**, the ^{31}P NMR spectra of **4** and **5** showed evidence for both the C_s-symmetric *cis*,*trans* conformer and *trans*,*trans* conformer in solution. In contrast, the ^{31}P NMR spectrum of the Mes* substituted **3** afforded only two resonances ($\delta = -272$ and -130 ppm) with chemical shift values similar to **2**.

The crystal structure (**2a**; from benzene)[7b] revealed a *trans,trans* structure (Figure 3), which is similar to a range of previously structurally characterized tetraphosphabicyclobutanes and is consistent with the ^{31}P NMR spectrum of **2** in solution ([D$_8$]THF, −90 to 60 °C). However, crystals of **2** grown from hexane[7c] displayed a *cis,trans* structure (**2b**), an isomeric form that has not been observed in the solid state. The P–P distances, including the bridgehead P–P bonds, of **2a** (2.203(1)–2.207(2) Å) and **2b** (2.205(2)–2.243(2) Å) are similar and consistent with P–P single bonding. The bridgehead P–P bonds (**2a**, 2.203(2); **2b**, 2.219(2) Å) are ca. 0.10 Å longer than in **4** and ca. 0.05 Å longer than in **3** and **5**. The P$_4$ fold angle of **2a** is 92.9° and falls only slightly outside of the known range (95.2–95.6°) for **3**–**5**. However, the P$_4$ fold angle of 71.9° in **2b** is accompanied by a widening of the P(1)-P(2)-P(4) (89.33(7)°) and P(1)-P(3)-P(4) (88.66(7)°) angles resulting from alleviation of the steric interactions between the two Ar$^{\mathrm{Dipp}_2}$ substituents. Calculations regarding the relative stability of the *trans*,*trans* and *cis*,*trans* conformations of P$_4$H$_2$ indicate that the *trans*,*trans* isomer is more stable, but only by 1.2 kcal mol^{-1}.[20] Since both isomers are obtainable in the solid state, crystal packing effects probably dictate the solid state conformation.



2a

2b

Figure 3. Thermal ellipsoid (30%) plots of **2a** and **2b**. H atoms and isopropyl groups on Ar$^{\mathrm{Dipp}_2}$ are not shown for clarity. Selected bond lengths [Å] and angles [deg]: **2a**: P(1)–C(1) 1.866(3), P(2)–C(17) 1.887(3), P(1)–P(3) 2.207(1), P(2)–P(3) 2.201(1), P(3)–P(3A) 2.203(2); P(1)-P(3)-P(2) 77.81(4); the P$_4$ fold angle, defined as the dihedral angle between the P(1)-P(3)-P(3A) and P(2)-P(3)-P(3A) planes, is 92.9. **2b**: P(1)–C(1) 1.874(6), P(1)–P(2) 2.205(2), P(1)–P(3) 2.243(2), P(2)–P(4) 2.216(2), P(2)–P(3) 2.219(2), P(3)–P(4) 2.205(2), P(4)–C(31) 1.821(6); P(1)-P(2)-P(4) 89.33(7), P(1)-P(3)-P(4) 88.66(7); the P$_4$ fold angle, defined as the dihedral angle between the P(1)-P(2)-P(4) and P(4)-P(3)-P(2) planes, is 71.9°.

In conclusion, the thallium complexed diaryltetraphosphabutadienediide (**1**) has been synthesized from the reaction of (Ar$^{\mathrm{Dipp}_2}$Tl)$_2$ and white phosphorus. The negative charge is delocalized over the P$_4$ array, as suggested by the essentially equal P–P distances and planar P$_4$C$_2$ core, to afford an average P–P bond order of approximately 1.33. Reaction of **1** with I$_2$ afforded the diaryltetraphosphabicyclobutane **2** which depending on the solvent of crystallization can be obtained as either the *trans*,*trans* (**2a**) or the *cis*,*trans* isomer (**2b**). Future work will focus on evaluating the ability of **1** as a [P$_4$Aryl$_2$]$^{2-}$ transfer agent, and exploring the reduction chemistry of **2**.

Experimental Section

All manipulations were carried out under anhydrous and anaerobic conditions.

1: An aluminum foil-wrapped 100-mL Schlenk flask was charged with equimolar portions of (Ar$^{\mathrm{Dipp}_2}$Tl)$_2$ (0.916 g, 0.761 mmol) and freshly distilled white P$_4$ (0.094 g, 0.76 mmol). This mixture was placed in a water–ice bath and, with vigorous magnetic stirring, THF (ca. 60 mL) that had been pre-cooled to 0 °C was added. The resulting deep red solution was stirred for 12 h, whereupon it was filtered from some precipitate (presumably Tl metal) using a glass-fiber tipped cannula. The solvent was removed under a dynamic vacuum and the residue was washed with ca. 15 mL of cold hexane. The product was obtained as a burgundy microcrystalline solid that is sparingly soluble in hydrocarbon solvents and does not display any detectable light sensitivity. Redissolving with warm hexane (ca. 35 mL) followed by overnight cooling to ca. −15 °C afforded X-ray quality crystals of **1**. Yield: 0.205 g, 40%; Mp: darkens at 130 °C, 226 °C (dec.) ^{1}H NMR (300.1 MHz, [D$_8$]THF, 25 °C): $\delta = 0.96$ (d, 24 H, CH(CH_3)$_2$, $^{3}J_{H,H} = 6.9$ Hz), 1.33 (d, 24 H, CH(CH_3)$_2$, $^{3}J_{H,H} = 6.9$ Hz), 2.70 (sept, 8 H, CH(CH$_3$)$_2$, $^{3}J_{H,H} = 6.9$ Hz), 6.88 (d, 4 H, m-C$_6$H$_3$, $^{3}J_{H,H} = 7.5$ Hz), 6.99 (t, 4 H, p-dipp, $^{3}J_{H,H} = 7.7$ Hz), 7.11–7.16 (t, partially buried, p-C$_6$H$_3$), 7.11 ppm (d, 8 H, m-dipp, $^{3}J_{H,H} = 8.1$ Hz); ^{13}C{^{1}H} NMR: (75.5 MHz, [D$_8$]THF, 25 °C): $\delta = 24.1$ (o-CH(CH$_3$)$_2$), 26.0 (o-CH(CH$_3$)$_2$), 31.8 (o-CH(CH$_3$)$_2$), 124.4 (p-C$_6$H$_3$), 126.5 (p-dipp), 129.4 (i-C$_6$H$_3$), 130.8 (m-C$_6$H$_3$), 142.6 (o-C$_6$H$_3$), 144.5 (i-dipp), 147.5 (o-dipp), 148.1 ppm (m-dipp); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF, 50 °C, referenced externally to 85% H$_3$PO$_4$): $\delta = 185$ (m), 280 ppm (m); ^{205}Tl NMR (230.71 MHz, [D$_8$]THF, 25 °C, referenced externally to TlNO$_3$(aq)): $\delta = 2730$ ppm (m, $^{2}J_{^{205}\mathrm{Tl},^{203}\mathrm{Tl}} \approx 12000$ Hz); ^{203}Tl NMR (228.47 MHz, [D$_8$]THF, 25 °C, referenced externally to TlNO$_3$(aq)): $\delta = 2730$ ppm (m, $^{2}J_{^{205}\mathrm{Tl},^{203}\mathrm{Tl}} = 12000$ Hz); UV/Vis (hexanes) λ_{max} [nm] (ε in mol^{-1} L cm^{-1}): 222 (45000), 322 (13000), 432 (990), 546 (2400).

2: I_2 (0.068 g, 0.270 mmol) was dissolved in hexane (80 mL). This solution was added dropwise to **1** (0.355 g, 0.267 mmol) dissolved in hexane (20 mL). Upon complete addition the color of the solution had changed from deep red to colorless. The slurry was stirred for 2 h and the precipitate (TlI) was removed by filtration through a Celite-padded frit. The solution was concentrated to ca. 10 mL and storage at ca. −20 °C overnight afforded colorless X-ray quality crystals of **2b**. Yield: 0.130 g, 53 %; Mp > 320 °C. ^{1}H NMR (300.1 MHz, [D$_8$]THF, 25 °C): $\delta = 0.93$ (d, 24 H, CH(C*H*$_3$)$_2$, $^3J_{H,H} = 6.6$ Hz), 1.13 (d, 24 H, CH(C*H*$_3$)$_2$, $^3J_{H,H} = 6.9$ Hz), 2.31 (sept, 8 H, C*H*(CH$_3$)$_2$, $^3J_{H,H} = 6.6$ Hz), 6.94 (d, 4 H, *m*-C$_6$H$_3$, $J_{HH} = 7.5$ Hz), 7.14 (d, 8 H, *m*-dipp, $J_{H,H} = 7.8$ Hz), 7.20 (t, 4 H, *p*-C$_6$H$_3$, $J_{H,H} = 7.8$ Hz), 7.37 ppm (t, 4 H, *p*-dipp, $J_{H,H} = 7.8$ Hz); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF, 25 °C): $\delta = 22.9$ (CH(*C*H$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 30.8 (*C*H(CH$_3$)$_2$), 123.1 (*m*-dipp), 127.0 (*p*-C$_6$H$_3$), 129.0 (*m*-C$_6$H$_3$), 129.3 (*p*-dipp), 135.5 (m, *i*-C$_6$H$_3$), 138.7 (*o*-C$_6$H$_3$), 145.4 (m, *i*-dipp), 146.5 ppm (*o*-dipp); ^{31}P NMR (121.5 MHz, [D$_8$]THF, 25 °C): $\delta = -331.8$ (t, 2 P, bridgehead, $^1J_{P,P} = 189.2$ Hz), −163.0 ppm (t, 2 P, terminal, $^1J_{P,P} = 189.2$ Hz). X-ray quality crystals of **2a** were obtained by dissolving **2b** in C$_6$D$_6$ followed by slow cooling to 7 °C. The spectroscopic properties of **2a** (in [D$_8$]THF) were identical to those of **2b** (in [D$_8$]THF).

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[7] Crystallographic data for **1**, **2a**, **2b**: Recorded at 90 K with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å): **1** $a = 18.690(4)$, $b = 18.690(4)$, $c = 16.783(9)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, trigonal, space group $P3_221$, $Z = 3$, $R1 = 0.0418$ for 5243 ($I > 2\sigma(I)$) data, w$R2$ (all data) = 0.1418; **2a** $a = 15.990(3)$, $b = 26.291(5)$, $c = 16.876(3)$ Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, space group *Pnma*, $Z = 4$, $R1 = 0.0402$ for 4674 ($I > 2\sigma(I)$) data, w$R2$ (all data) = 0.1018; **2b** $a = 13.600(3)$, $b = 22.500(4)$, $c = 19.418(7)$ Å, $\alpha = 90°$, $\beta = 117.57(2)°$, $\gamma = 90°$, monoclinic, $P2_1/c$, $Z = 4$, $R1 = 0.0882$ for 4381 ($I > 2\sigma(I)$) data, w$R2$ (all data) = 0.2275. CCDC-279795 (**1**), CCDC-279797 (**2a**), CCDC-279796 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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