A Robust, Reactive, and Remarkably Simple to Prepare Sterically Encumbered *meta*-Terphenyl Ligand

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A cost-efficient, high yield and simple one-pot route to the sterically encumbered iodoterphenyl DcpI [Dcp = 2,6-(2,6-$Cl_2C_6H_3)_2C_6H_3$] is developed in which the necessary addition of external Grignard reagent is avoided. This material is employed as a convenient precursor to low-coordinate phosphorus compounds, such as DcpP=PDcp (**1**), DcpP=C(H)Ph (**4**), and DcpP=PMe_3. The resultant aryl is found to provide robust steric protection for **1** and **4** once in place, but reactive intermediates leading to insertion chemistry must be avoided in the course of their synthesis. A new bis(dibenzophosphole) **2** resulting from insertion of a phosphorus atom into vicinal C–Cl bonds was isolated and characterized. The single crystal X-ray structures of **1**, **2**, and **4** are presented.

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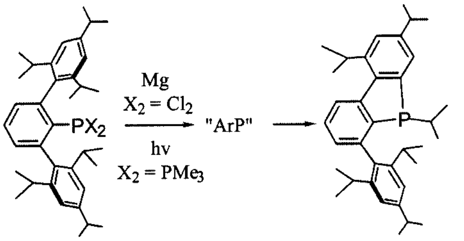
Sterically encumbered *meta*-terphenyl ligands represent an exciting class of protective groups. Recent reviews have detailed their widespread success for stabilizing new compounds having novel element−element multiple bonds, generating interesting molecular geometries and coordination environments, and synthesis of models for biological systems.[1] Yet despite their great success in stabilizing reactive functional groups, these types of ligands can be susceptible to intramolecular attack by high-energy intermediates. For example, it was recently noted that both reduction of 2,6-$Trip_2C_6H_3PCl_2$ with magnesium, and photolysis of $Trip_2C_6H_3P{=}PMe_3$, lead to the same phosphafluorene [Equation (1)].[2−4]



(1)

Presumably, the phosphinidene ("ArP"), generated from either process, inserts into an Ar−*i*Pr carbon−carbon bond to account for the final product. While phosphinidenes, the phosphorus analogues of carbenes, have been invoked in many reactions to justify a variety of products, direct evidence for such species is still quite limited.[5−7]

Our interest in examining the scope of this type of process and finding more convenient and economical variations of *meta*-terphenyl ligands led us to investigate systems based upon the 2,6-bis(2,6-dichlorophenyl)phenyl (Dcp) group. This terphenyl was first isolated in 22% yield by Kress from the black sludge that resulted from the thermal decomposition (exothermic) of 2,6-dichlorophenyllithium at temperatures above −45 °C (Scheme 1).[8] Hart subsequently found that the corresponding Grignard reagent was much more stable and could be used to prepare 2,6-bis(2,6-dichlorophenyl)benzene (DcpH) in moderate yields (44%).[9] This discovery led to the development of a convenient route to a range of terphenyls (2,6-$Ar_2C_6H_3E$, Scheme 1) using *meta*-dichlorobenzene and various Grignard reagents. The maximum steric screening provided by terphenyl ligands for reactive atoms and functional groups is largely defined by the *ortho* substituents on the outer aromatic rings. Hence, another particularly attractive facet of the Dcp terphenyl is its steric similarity to the widely used terphenyl 2,6-$Mes_2C_6H_3$ (Dmp). Because of the similar van der Waals radii for chlorine and methyl groups, one should be able to obtain the same steric coverage as the Dmp system at reduced cost and effort. We now report that the modification of the original Kress reaction and subsequent quenching with iodine leads to a high yield and convenient synthesis of DcpI, as well as its unusual stability and reactivity in low-coordinate phosphorus compounds.

The reaction first reported to yield DcpH was thus modified by not allowing the initial dichlorobenzene/butyllithium mixture to warm above −50 °C, and by the subsequent addition of I_2. A 65% yield of DcpI is achieved

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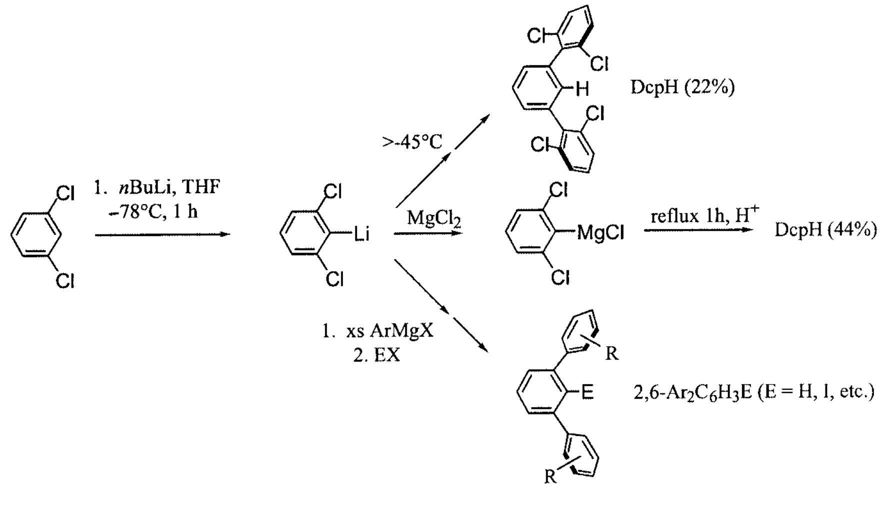
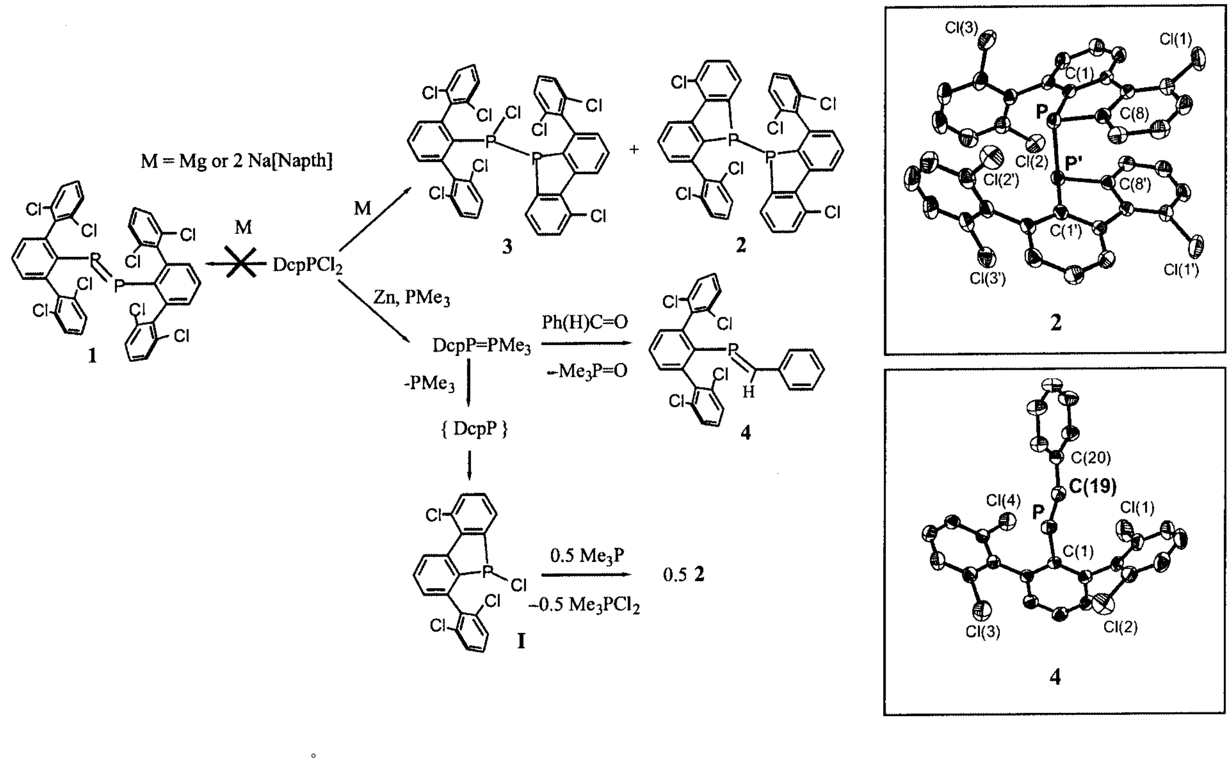


Scheme 1

after single recrystallization by an exceptionally convenient and simple procedure that provides better yields than many conventional iodoterphenyl syntheses (Scheme 1). With this pure material in hand, the synthesis of $DcpPCl_2$ was effected by standard methods (metallation of DcpI by *n*BuLi at −78 °C in THF, followed by addition of three equivalents of PCl_3 and warming to room temperature).

Synthesis of the diphosphene DcpP=PDcp (**1**) was then undertaken to assess the steric screening capabilities of the Dcp ligand. Attempts to prepare this material by reduction of $DcpPCl_2$ by proven and established methods[10] (by either ultrasound/magnesium or 2 equiv. Na[Napth]) surprisingly failed to provide any evidence of the desired diphosphene. Instead, two other major products (**2** and **3**) were observed in about equal amounts (Scheme 2, top). This result was puzzling, since the diphosphene bearing the nearly isosteric terphenyl Dmp ligand is quite robust and stable.[11] The identity (and perhaps the origins) of **2** became clearer when the synthesis of the phosphanylidene-σ^4-phosphorane $DcpP{=}PMe_3$ was undertaken (Scheme 2). Reduction of $DcpPCl_2$ by either Zn/PMe_3 or excess PMe_3 cleanly leads to $DcpP{=}PMe_3$ [^{31}P NMR (THF): δ = 6.7, −121.1 ppm, J_{PP} = 573 Hz] having NMR spectroscopic properties similar to its $DmpP{=}PMe_3$ analogue.[12] This material,



Scheme 2. Selected bond lengths [Å] and angles [°] for **2**: P−C(8) 1.810(2), P−C(1) 1.813(2), P−P′ 2.248(1), C(8)−P−C(1) 89.3(1), C(8)−P−P′ 101.69(8), C(1)−P−P′ 97.36(9); selected bond lengths [Å] and angles [°] for **4**: P−C(19) 1.634(3), P−C(1) 1.841(3), C(19)−P−C(1) 102.9(1), C(20)−C(19)−P 125.4(2)

however, quickly (10−15 min) and cleanly transforms to **2** [^{31}P NMR (THF): $\delta = -27.6$ ppm].

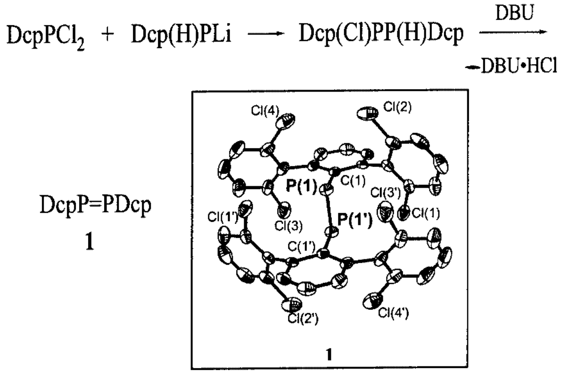
Interestingly, as the results of an X-ray diffraction study show (Scheme 2), two phosphorus atoms have inserted into the carbon−chlorine bonds of two terphenyl ligands and coupled to one another to provide bis(dibenzophosphole) **2**.[13] Despite the crowded nature about the P−P bond, a relatively normal P−P single bond length of 2.248(1) Å is found. The structure of **2** is remarkably similar to the disilane postulated to arise by insertion of a silylene into the carbon−carbon bonds of a Dmp terphenyl.[14]

The nature of **2** makes it tempting to speculate that the unstable phosphanylidene-σ^4-phosphorane loses PMe_3 in an initial step to generate a highly reactive phosphinidene (Scheme 2, bottom). This behavior would stand in contrast to the related phosphanylidene-σ^4-phosphoranes $ArP{=}PMe_3$ (Ar = Dmp, Mes*, 2,6-$Trip_2C_6H_3$) that are thermally stable at room temperature, but extrude PMe_3 upon photolysis.[3] The presumed product of phosphinidene insertion into the carbon−chlorine bond, chlorophosphafluorene **I**, has, however, proven to be much more difficult to detect than the analogous product derived from phosphinidene insertion into a carbon−carbon bond [Equation (1)]. It appears that the P−Cl bond in **I** must be more susceptible to further reduction than $DcpPCl_2$. For example, reactions of $DcpPCl_2$ and either 1 equiv. of Na[Napth] or 1/2 equiv. of Mg yield mixtures of **2** and unchanged $DcpPCl_2$. Likewise, the proposed intermediate **I** must also be very susceptible to trialkylphosphane-promoted dehalogenation and P−P coupling processes.[15]

The unstable $DcpP{=}PMe_3$ was trapped by excess benzaldehyde to give the new phosphaalkene DcpP=C(H)Ph [**4**, ^{31}P NMR ($CDCl_3$): $\delta = 233.0$] (> 95% by ^{31}P NMR, 62% isolated yield) by our version of a phospha-Wittig reaction (Scheme 2).[12,16] Scheme 2 also shows the results of a single-crystal X-ray diffraction study of **4**.[13] The main feature of interest, the P=C bond length of 1.634(3) Å, is at the shorter end of the spectrum of reported values for such compounds.[17−21] The phosphaalkene unit itself resides within the protective cleft of the large Dcp ligand.

The other major product produced by reduction of $DcpPCl_2$ by magnesium has been assigned as **3**, based on its ^{31}P NMR spectrum [$\delta = 96.3$ ppm (d, $J_{PP} = 305$ Hz), −5.0 (d, $J_{PP} = 305$ Hz)]. The identity of this product was more firmly established by its independent synthesis. Bis(dibenzophosphole) **2** was reductively cleaved by excess Na metal to a dibenzophospholide anion[22,23] [^{31}P NMR (THF): $\delta = 21.9$ ppm], which was treated with $DcpPCl_2$ to give **3** as the main product. Interestingly, this material does *not* appear to be an intermediate to **2** during the thermal decomposition of $DcpP{=}PMe_3$, as it does not react with Zn or PMe_3.

Though the Dcp ligand might be very susceptible to attack by phosphinidene (or other) intermediates, it is a very effective protective unit once in place. In fact, the diphosphene **1** is very stable and robust. Compound **1** was readily prepared by the stepwise process described in Scheme 3, which avoids potential generation of phosphinidenes. While **1** exhibits a typical ^{31}P NMR chemical shift value of $\delta = 500.3$ ppm, the compound has two notable features that distinguish it from the Dmp analogue. First, the presumed π-π* electronic transition of **1** is blue-shifted by approximately 19 nm compared to DmpP=Dmp (solid **1** is yellow, while DmpP=PDmp is orange). Secondly, the structure of **1** (Scheme 3) reveals a different orientation of the terphenyl groups.[13] Specifically, the two central rings of each terphenyl are nearly parallel to one another (and related by an inversion center). Similar orientations of the terphenyl groups of DmpPE=EDmp (E = As, Sb) are adopted in the solid state.[2]



Scheme 3. Selected bond lengths [Å] and angles [°] for **1**; (only one of two independent molecules shown); P(1)−C(1) 1.847(4), P(1)−P(1′) 2.039(2), C(1)−P(1)−P(1′) 98.46(15)

For the phosphorus species, it appears that the smaller central atom size and bond lengths disfavor this orientation due to steric clashes between Dmp groups across the P=P unit. Compound **1** lacks the *para* substituents present on the Dmp system, and thus interactions of the Dcp groups across the P=P unit are not as severe. Average P−P distances of 2.030 Å (two independent molecules in unit cell) and C−P−P bond angles spanning 98.5(2) to 98.9(1)° are otherwise unexceptional for **1**.

The facile self-destruction reactions of the Dcp ligand (as in **2** and **3**) bear some likeness to similar reactions of low-coordinate phosphorus compounds bearing the Mes* (Mes* = 2,4,6-$tBu_3C_6H_2$) group. In these materials the phosphorus atoms insert into the vicinal C−H bonds of the *tert*-butyl groups. For example, reduction of $Mes{*}PCl_2$ with activated magnesium gives rise to a phosphaindane.[4] In addition, photolysis of the diphosphene Mes*P=PMes* readily leads to such products, and therefore it was anticipated that under photolysis **1** would yield products such as **2** or **3**.[24] The remarkable stability of **1** is amply demonstrated by its complete inertness to continued photolysis (by either irradiation in a 254-nm photochemical reactor or by 355-nm laser light). In this regard, **1** behaves like the terphenyl-protected diphosphenes DmpP=PDmp[3] and ArP=PAr[25] (Ar = 2,6-Mes_2-4-MeC_6H_2).

We have thus shown that a relatively inexpensive and sterically encumbered *meta*-terphenyl ligand can rapidly be constructed for applications in low-coordinate phosphorus chemistry. Highly reactive phosphorus centers can insert into the carbon−chlorine bonds of the Dcp ligand and provide access to novel phosphafluorene-derived materials. If these high-energy intermediates can be avoided, then the resulting materials bearing the Dcp unit are very robust. This finding should also serve as another reminder for others searching for new compounds having multiply bonded elements, that the size of the ligand is not everything. In other applications, where an economically more desirable sterically demanding protecting group is required, the Dcp unit should also be useful.

Experimental Section

General: Air sensitive materials were handled in a dry box or using modified Schlenk line techniques under dry nitrogen. Solvents were obtained by distillation from Na-benzophenone ketyl under nitrogen. ^{1}H NMR and ^{31}P NMR spectra were acquired on a Varian Gemini 300 MHz spectrometer and are referenced to TMS and 85% H_3PO_4, respectively.

DcpI: 54.8 mL of *n*BuLi (2.5 M in hexanes, 138 mmol) was added dropwise to a solution of 1,3-dichlorobenzene (20.0 g, 136 mmol) in THF (250 mL) at −78 °C. The resulting white suspension was stirred for 1.5 h at −78 °C (dry ice/acetone bath), and then warmed to −50 °C (bath temperature) over a 30 min period. Elemental iodine (14.0 g, 55.2 mmol) was added under positive pressure of N_2 and the mixture was allowed to warm to room temperature over a 2 h period. Excess iodine was quenched with aqueous Na_2SO_3, and the organic products were extracted with diethyl ether. The combined organic layers were washed with water and then dried with Na_2SO_4. Removal of all volatiles under reduced pressure yielded a sticky light brown solid. Recrystallization from hot EtOH gave 14.9 g (65% yield) of pure white DcpI; m.p. 176−178 °C. ^{1}H NMR ($CDCl_3$): δ = 7.56 (t, J = 7.0 Hz, 2 H), 7.43 (d, J = 7.0 Hz, 4 H), 7.29 (t, J = 8.0 Hz, 1 H) 7.22 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 143.5, 141.9, 135.0, 129.6, 129.1, 128.6, 127.8, 104.8 ppm. HR-MS (FAB): calcd. for $C_{18}H_9Cl_4I$: 491.8503; found 491.8509 [M + H$^+$].

DcpPCl$_2$: Prepared in 52% yield using literature methods.[11] ^{1}H NMR (C_6D_6): δ = 7.09 (t, J = 8.0 Hz, 1 H), 6.97 (d, J = 8.0 Hz, 4 H), 6.81 (dd, $^3J_{H,H}$ = 8, $^4J_{PH}$ = 3 Hz, 2 H), 6.55 (d, J = 8.0 Hz, 2 H) ppm. ^{31}P NMR (C_6D_6): δ = 155.4 (s) ppm.

DcpPH$_2$: Prepared in 47% yield using literature methods.[11] ^{1}H NMR (C_6D_6): δ = 7.13 (t, J = 8.0 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 4 H), 6.96 (d, $J_{H,H}$ = 8, $^4J_{PH}$ = 2 Hz, 2 H), 6.57 (t, J = 8.0 Hz, 2 H), 3.23 (d, J_{PH} = 208 Hz) ppm. ^{31}P NMR (C_6D_6): δ = −148.1 (t, J_{PH} = 208 Hz) ppm.

2: To a stirred mixture of $DcpPCl_2$ (0.30 g, 0.60 mmol) and Zn dust (0.05 g, 0.76 mmol) in 10 mL of THF was added a solution of PMe_3 (0.19 g, 2.5 mmol) in 5 mL of THF. The solution immediately turned bright yellow, and a ^{31}P NMR spectrum of an aliquot, run after 5 min of reaction, indicated complete conversion into DcpP=PMe$_3$. After 20 min, the solvent was removed in vacuo, and the solids were extracted with hexanes. Removal of hexanes in vacuo yielded 0.16 g of **3** as a white solid (70% yield). Crystals suitable for X-ray structure determination were grown from hexanes/$CDCl_3$. ^{1}H NMR (C_6D_6): δ = 8.83 (d, J = 8.0 Hz, 2 H), 7.33 (t, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 4 H), 6.94 (d, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.0 Hz, 2 H), 6.63 (t, J = 8.0 Hz, 2 H), 6.34 (t, J = 8.0 Hz, 2 H), 6.00 (d, J = 8.0 Hz, 2 H) ppm. ^{31}P NMR (THF): δ = −27.6 ppm. HR-MS (FAB):calcd. for $C_{36}H_{19}Cl_6P_2$ 722.9093; found 722.9128 [M + H$^+$].

DcpP=C(H)Ph (4): To a stirred mixture of $DcpPCl_2$ (0.10 g, 0.21 mmol), zinc dust (0.02 g, 0.3 mmol), and benzaldehyde (0.090 g, 0.85 mmol) in 5 mL of THF in a 20-mL vial was added a solution of PMe_3 (0.10 g, 1.32 mmol) in 3 mL of THF. After 1 h of stirring, the solvent was removed in vacuo. The solid was extracted with hexanes, and the hexanes were evaporated to yield 0.060 g of **4** as a white powder (62%). Crystals suitable for X-ray structure determination were grown by slow concentration of a $CDCl_3$ solution. ^{1}H NMR ($CDCl_3$): δ = 9.08 (d, J = 24.0 Hz, 1 H), 7.49 (t, J = 7.0 Hz, 1 H), 7.27 (d, J = 7.0 Hz, 4 H), 7.20−7.08 (m, 10 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 233.0 ppm. HR-MS (FAB): calcd. for $C_{25}H_{16}Cl_4P$ 486.9743; found 486.9718 [M + H$^+$].

DcpP=PDcp (1): To a rapidly stirred solution of $DcpPCl_2$ (0.87 g, 1.9 mmol) in ether (50 mL), a suspension of DcpPH[Li·OEt$_2$] (0.90 g, 2.0 mmol) in 50 mL of diethyl ether was added dropwise over 30 min. After 1 h, a solution of DBU (0.26 g, 1.7 mmol) in 5 mL of diethyl ether was added and the mixture stirred for 2 h. The bright yellow mixture was then filtered and the solvent removed in vacuo to afford a crude yellow solid. The solid was taken up in THF/hexanes (4:1) and cooled to −35 °C to yield **1** as a yellow powder (0.31 g, 23%). ^{1}H NMR (C_6D_6): δ = 7.02 (t, J = 8.0 Hz, 1 H), 6.97 (d, J = 8.0 Hz, 4 H), 6.88 (d, J = 8.0 Hz, 2 H), 6.61 (t, J = 8.0 Hz, 2 H) ppm. ^{31}P NMR (C_6D_6): δ = 500.3. UV/Vis (THF): ε (448 nm) = 626 cm^{-1} M^{-1}; ε (352 nm) = 8551 cm^{-1} M^{-1}. $C_{36}H_{18}P_2Cl_8$: calcd. C 54.31, H 2.28; found C 53.91, H 2.53.

Acknowledgments

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[13] Crystal data of **1**: $C_{36}H_{18}Cl_8P_2$, M_r = 796.04, monoclinic, space group $P21/c$, a = 19.442(3), b = 12.083(2), c = 14.737(2) Å, β = 90.335(3)°, V = 3461.8(8) Å^3, Z = 4, $\rho_{calcd.}$ =1.527 g cm^{-3}, $2\theta_{max}$ = 50°, Mo-K_α radiation, λ = 0.71073 Å, μ = 0.771 mm^{-1}. Crystal data for **2**·n-C_6H_{14}: $C_{42}H_{18}Cl_6P_2$, M_r = 797.20, monoclinic, space group $C2/c$, a = 21.271(3), b =

12.587(2), c = 14.940(2) Å, β = 103.499(2)°, V = 3889.4(9) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.361 g cm^{-3}, $2\theta_{\max}$ = 50°, Mo-K_α radiation, λ = 0.71073 Å, μ = 0.554 mm^{-1}. Crystal data for **4**: $C_{25}H_{15}Cl_4P$, M_r = 488.14, monoclinic, space group $C2/c$, a = 30.200(7), b = 8.335(2), c = 18.698(4) Å, β = 91.947(4)°, V = 4704(2) Å^3, Z = 8, $\rho_{\text{calcd.}}$ = 1.379 g cm^{-3}, $2\theta_{\max}$ = 50°, Mo-K_α radiation, λ = 0.71073 Å, μ = 0.581 mm^{-1}. All data sets were collected with a Bruker SMART CCD diffractometer at 300(2) K. Lorentz polarization and empirical (SADABS) absorption corrections were applied. The structures were solved by direct methods and refined using SHELXTL. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and included as riding with U_{iso}(H) =1.3 U_{eq}(non-H). Of 17736 collected reflections for **1**, 6090 were unique (R_{int} = 0.0663). Final figures of merit for **1**: R = 0.0568 [$I > 2\sigma(I)$], Rw = 0.1142 (F^2, all data). Of 9341 collected reflections collected for **2**, 3360 were unique (R_{int} = 0.0326). Final figures of merit for **2**: R = 0.0425 [$I > 2\sigma(I)$], Rw = 0.1196 (F^2, all data). Of 11278 collected reflections for **4**, 4086 were unique (R_{int} = 0.0563). Final figures of merit for **4**: R = 0.0540 [$I > 2\sigma(I)$], Rw = 0.1161 (F^2, all data). The highest peaks in the final difference map were 0.609, 0.318 and 0.318 e Å^{-3} for **1**, **2** and **4**, respectively. CCDC-184750 (**1**), -184749 (**2**), and -184748 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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