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CLUSTER ISSUE

η^2-Coordination of a Phosphaalkyne to an Amino Olefin Nickel Complex and Regioselective Catalyzed Cyclooligomerization to Dewar 1,3,5-Triphosphabenzene

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We report herein an efficient synthesis of a Dewar-triphosphabenzene derived from [2+2+2] cycloaddition of three phosphaalkyne molecules promoted by an amino olefin Ni^0 complex as the catalyst. Amino diolefin Ni^I complex **1** serves as a precursor complex that reacts with triphenylmethylphosphaethyne under reducing conditions at low temperature to give Ni^0 complex **3** with a coordinated phosphaalkyne in a η^2-mode. The structure of **3** was determined by X-ray diffraction methods and suggests a bonding situation for the phosphaalkyne that is between a side-on coordinated C≡P molecule and a metallaphosphacyclopropene structure. The reaction of **3** with a 10-fold excess of phosphaethylene under reducing conditions at room temperature resulted in the formation of 2,4,6-tris(triphenylmethyl)-Dewar-1,3,5-triphosphabenzene (**4**) in good yield.

Introduction

Innovative materials with interesting reactivities and properties that diverge from carbon-based chemistry can be expected from studies of heteroatom-based π systems, in which phosphorus centers with a low coordination number substitute the CR groups. In comparison to the chemistry of benzene, the chemistry of analogous aromatic phosphorus heterocycles is still poorly developed. This is especially true for heterocycles with more than one phosphorus atom within the ring skeleton.[1] Several phospha-[2] and diphosphabenzene derivatives,[3] a few 1,3,5-triphosphabenzene valence isomers,[4] and hexaphosphabenzene are known.[5]

The synthesis of sterically stabilized phosphaalkynes has been developed over the past decades, and these molecules show a remarkable versatility as useful building blocks in organophosphorus chemistry. Frequently, they react like their organic counterparts, alkynes, and undergo a wide range of cycloadditions, but they may show dual behavior in the coordination sphere of metals, because the phosphorus lone pair of electrons or the C≡P unit may be engaged in bonding to the metal centers. Note that the number of isolated examples of side-on coordination complexes is rather limited owing to the tendency of phosphaalkynes to oligomerize in the coordination sphere of a metal center.[6,14] It has been proposed that species with η^2-coordinated C≡P units are key intermediates in the formation of phosphaheterocycles.[7,8] In the coordination sphere of electron-rich transition metals (M = Ni, Co, Rh, Fe), phosphaalkynes have shown the tendency to cyclodimerize to 1,3-diphosphete ligands.[7a,7b,7h,9] By analogy to alkynes, which readily cyclotrimerize to benzene derivatives in a large number of transition-metal-catalyzed processes,[10] it is expected that phosphaalkynes readily form 1,3,5-triphosphabenzene derivatives or isomers thereof. This, however, has been observed only in some cases. Scheme 1 displays valence isomers of triphosphabenzene systems coordinated to Hf[7f] and V[11] and an earlier example of a partially characterized Mo^0 complex derived from a triolefin metal precursor.[4a] The suggested structure of the latter species could not be confirmed by independent studies.[12] A significant example of cyclotrimerization to form the complexed Dewar 1,3,5-benzene, which was fully characterized by single-crystal X-ray diffraction, is depicted in Scheme 1. This report was followed by the only metal-promoted cyclotrimerization of phosphaalkynes to give metal-free phosphaheterocycles under stoichiometric conditions.[4b]

The Hf complex with a Dewar triphosphabenzene ligand reacts readily with hexachloroethane and subsequent thermal treatment to afford the two isomeric structures shown

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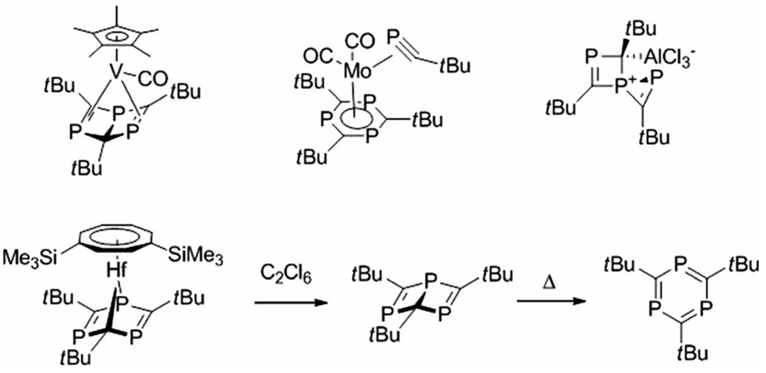


Scheme 1. Known examples of triphosphaheterocycles derived from RCP oligomerization: 1,3,5-triphosphabenzene, Dewar benzene (two coordination modes known), and spirocyclic betaine.

in Scheme 1.[7f,7j] The trimerization of phosphaalkynes promoted by $AlCl_3$ has been reported by Regitz et al. In this reaction, the Lewis acid is incorporated in the phosphaheterocycle to afford a cyclotetramer after an oxidative process in which the not-isolated Dewar benzene is an intermediate.[13] To the best of our knowledge, a catalytic cyclotrimerization of phosphaalkynes to give metal-free products has not been reported. Moreover, although Dewar triphosphabenzene species have been fully characterized by NMR spectroscopy experiments,[7f] a detailed experimental structure determination of a non-coordinated molecule by X-ray crystallography is lacking.

Results and Discussion

We synthesized the stable Ph_3C–CP phosphaalkyne from Ph_3C–CH_2–PCl_2 through a simple elimination reaction and investigated its coordination chemistry to group 8 transition-metal centers. The very robust η^1-complexes $[MH(dppe)_2(Ph_3CCP)]OTf$ [M = Fe or Ru, dppe = 1,2-bis(diphenylphosphino)ethane][14] are easily obtained. Strong protic acids promote intramolecular electrophilic aromatic substitution in coordinated Ph_3C–CP, which leads to benzophosphole compounds.[15] It is well established that Ni^0 complexes catalyze the [2+2+2] cycloaddition of alkynes to give arene compounds.[10a,16] In this paper, we report an analogous reaction by using the stabilized Ph_3C–CP phosphaalkyne that proceeds under reducing conditions to give a Dewar triphosphabenzene. A Ni^I complex coordinated by a tridentate ligand containing two potentially hemilabile olefin ligands was used as the catalyst precursor.

The Ni^I complex $[Ni(trop_2NMe)(O_2CCF_3)]$ (**1**)[17] was prepared by the addition of the tridentate ligand $trop_2NMe$ (trop = 5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl) to $Ni^{II}(O_2CCF_3)_2$ by using Zn powder as a reducing agent. The coordination sphere of this 19-valence-electron-configured Ni^I center consists of the $trop_2NMe$ ligand, which has a preorganized concavely shaped binding site for transition-metal centers, and a non-symmetrically κ^2-binding trifluoroacetate (see Figure 1 for a structure plot). The reaction of Ni^I complex **1** under reducing conditions with the use of phosphaalkyne **2** as the ligand furnished complex **3** (Scheme 2). After cooling the reaction mixture to –30 °C for 12 h, complex **3** was isolated as orange crystals in 60% yield. A suitable single crystal was used for X-ray diffraction analysis to elucidate the structure.

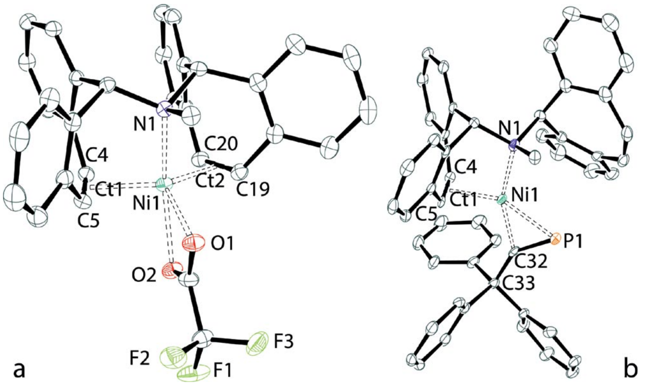
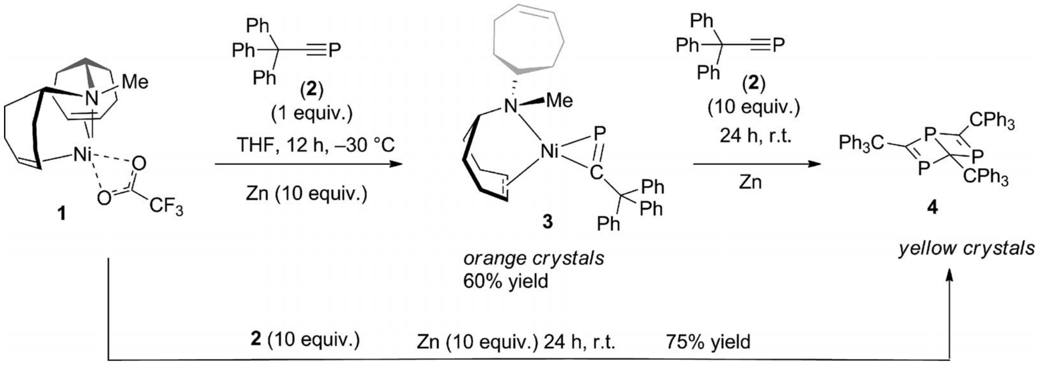


Figure 1. (a) ORTEP diagram of complex **1** with 50% ellipsoid probability. The second crystallographically independent molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°] with data for second molecule in brackets: Ni1–N1 207.31(15) [205.87(15)], Ni1–Ct1 200.5 (201.2), Ni1–Ct2 198.4 (198.7), C4–C5 138.9(3) [138.9(3)], C19–C20 139.1(3) [139.5(3)], Ni1–O1 214.07(13) [207.98(13)], Ni1–O2 224.64(13) [240.80(14)]. (b) ORTEP diagram of complex **3** with 50% ellipsoid probability. Hydrogen atoms and two solvent molecules are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ni1–P1 221.88(13), Ni1–N1 208.5(4), Ni1–Ct1 193.3, Ni1–C32 188.7(4), P1–C32 163.5(4), C4–C5 140.2(6), N1–Ni1–P1 107.09(10), P1–C32–C33 145.29(10), N1–Ni1–C4 93.60(15).

Figure 1 (a, b) shows ORTEP plots of the structures of complexes **1** and **3**. Ni^I complex **1** (Figure 1, a) has a structure that is very similar to its NH analogue $[Ni(trop_2NH)(O_2CCF_3)]$.[17] Notably, the coordinated olefinic units, $C{=}C_{trop}$, have a rather short interatomic distance (about 139 pm); this is indicative of rather weak metal-to-ligand backbonding, which supports the assumption that the $trop_2NMe$ ligand may behave as a hemilabile ligand in **1**. Ni^0 complex **3** adopts a planar geometry (see Figure 1) with N1, the centroid of the $C{=}C_{trop}$ unit (ct1), P1, and C32 approximately in the same plane.

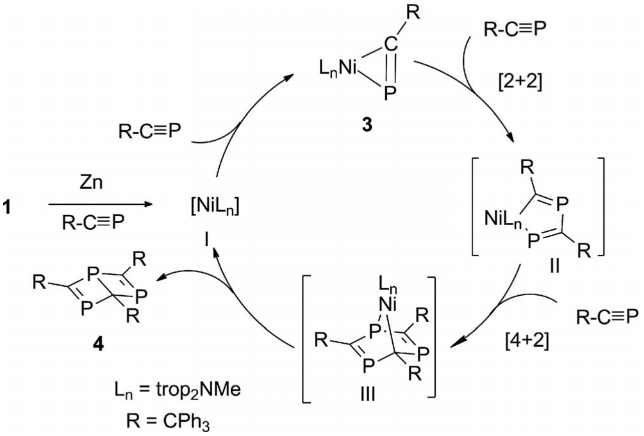
The $trop_2NMe$ ligand binds through the NMe moiety and only one η^2-olefin unit in a bidentate fashion. The Ni–



Scheme 2. η^2-Coordination of TrCP to Ni at low temperature and catalyzed regioselective oligomerization.

N bond in Ni^0 complex **3** has the same length as that in Ni^I complex **1** within experimental error, 208 vs. 207 pm. Likely because of the lower coordination number of the 16 valence-electron-configured Ni^0 center, the Ni–ct1 (ct1 = centroid of the C4–C5 bond) distance (193 pm) is substantially shorter than that in the monovalent diolefin Ni^I complex (Ni–ct1 210 pm, Ni–ct2 212 pm). The length of the coordinated $C{=}C_{trop}$ bond (C4–C5, 140 pm) is only slightly longer than that in complex **1** (C4–C5 139 pm, C19–C20 139 pm) and indicates, likewise, a comparatively low degree of metal-to-ligand backbonding from filled d orbitals at the metal center into the π* orbital of the $C{=}C_{trop}$ unit. The C≡P unit is coordinated to the Ni center in a side-on mode. Here, the back donation of Ni^0 of the $Ni(trop_2NMe)$ fragment into the π* orbitals of the C≡P bond induces a substantial elongation of the interatomic distance (163 pm) compared to that of free $Ph_3C{\equiv}P$ (153 pm).[5] The degree of sp^2 hybridization at C32 is also reflected in the considerable bending of the P–C32–C33 bond angle (145°) versus the almost-linear disposition of the phosphaalkyne (178°). This type of bonding is similar to that in previously reported structures of η^2-ligated phosphaalkynes [RC≡P, R = *t*Bu or adamantyl (Ad)] and indicates an intermediate bonding situation that lies between a side-on coordinated C≡P bond and a metallaphosphacyclopropene structure.[6d,18] Furthermore, in the ^{31}P NMR spectrum, the resonance (δ = 194 ppm) is considerably shifted to higher frequencies with respect to uncoordinated $Ph_3CC{\equiv}P$ (δ = –64 ppm), typically observed for a η^2-bonding mode.[19] In the ^{13}C NMR spectrum, the resonance for C32 (δ = 234.3 ppm) is considerably shifted to a lower field relative to the same resonance of the starting material (δ = 177.6 ppm).

The $^{31}P\{^1H\}$ NMR spectroscopic data acquired for the mother liquor from the crystallization indicate the presence of phosphorus-containing product **4**, which exhibits two coupled resonances at δ = +346 ppm for two phosphorus nuclei in chemically identical environments (d, $^3J_{PP}$ = 36 Hz) and at δ = 86 ppm (t, $^3J_{PP}$ = 36 Hz) for one nucleus coupled to two ^{31}P nuclei with identical coupling constants, which give rise to a triplet. An early example of *tert*-butyl-substituted Dewar 1,3,5-triphosphabenzene was isolated and characterized spectroscopically by Binger et al.,[7f] and it shows an almost-identical $^{31}P\{^1H\}$ NMR spectrum. If either complex **1** or **3** was stirred in THF in the presence of a 10-fold excess of the tritylphosphaalkyne and an excess amount of Zn powder for about 24 h at room temperature, the reaction gave **4** as the major product with the minimal presence of complex **3**, as assayed by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 3). Compound **4** was obtained in good yield (70–75%) in this catalytic reaction.



Scheme 3. Mechanistic hypothesis for Ni-catalyzed R–C≡P oligomerization.

The structure of **4** was investigated by single-crystal X-ray diffraction analysis, which confirmed a Dewar 1,3,5-triphosphabenzene (Figure 2). The $P{=}C_{sp^2}$ distances in the bicyclic structure show the archetypal interatomic distances (168 pm) also observed in phosphetes.[19] Species **4** is remarkably stable for prolonged periods of time. We would like to stress that trityl-substituted Dewar benzene does not thermally rearrange to the benzenoid isomer upon heating at 90 °C for 5 h, as was previously observed for the former *tert*-butyl-substituted compound, whereas photochemical conditions provoke the formation of multiple uncharacterized products. This aspect is currently under further investigation.

By monitoring the reaction of complex **3** with **2** by ^{31}P NMR spectroscopy, no intermediates were observed. However, a plausible mechanism for the cyclotrimerization of phosphaalkynes to a Dewar triphosphabenzene can be proposed (Scheme 3). On the basis of the established mecha-

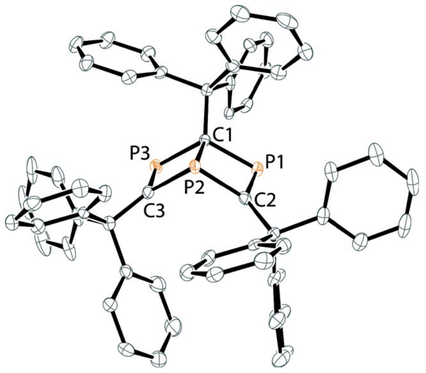


Figure 2. ORTEP diagram of **4** with 50% ellipsoid probability. Hydrogen atoms and one solvent molecule are omitted for clarity. Selected bond lengths [pm] and angles [°]: P1–P2 262.71(14), P2–P3 265.14(15), P1–C1 186.3(4), P1–C2 168.7(4), P2–C1 186.6(4), P2–C2 182.6(4), P2–C3 184.6(4), P3–C1 187.6(4), P3–C3 168.8(4), C1–P1–C2 88.42(18), C1–P3–C3 88.38(17), ΣC2 358.7(8), ΣC3 359.7(8).

nism for the trimerization of alkynes promoted by Ni^0 complexes,[10] the initial step could involve the coordination of a second molecule of Ph_3C–CP (eventually under displacement of the last coordinated $C{=}C_{trop}$ unit in **3**) followed by oxidative coupling of both coordinated phosphaalkyne molecules to give metallocyclodiphosphapentadiene complex **II** as an intermediate. A third equivalent of Ph_3C–CP can then add (either directly or after previous coordination to the Ni^{II} center in **II**) in a [4+2] cycloaddition process to afford metallobicyclotriphosphadiene complex **III**. Reductive elimination would finally afford product **4**. It is likely that the aminobisolefin $trop_2NMe$ ligand plays the role of a hemilabile ligand in this catalytic process. We believe that the $C{=}C_{trop}$ units help to stabilize the reduced nickel species. However, it remains unclear how Zn as a reducing agent intervenes in the reaction. Note that Ni^0 complex **3** does not promote the trimerization to **4** in the absence of Zn. Likewise, a reaction with the use of Zn alone in the absence of nickel complex **1** or **3** does not give any product.

We assume that the steric bulk of the trityl group on the phosphaalkyne and its interaction with the coordination sphere of the Ni complex are responsible for the regioselective formation of non-planar compound **4** resulting from head-to-tail couplings of Ph_3C–CP units.

Conclusions

In this paper we have shown that side-on coordinated phosphaalkyne 16e Ni^0 complex **3** is easily obtained under reducing conditions from a 19e Ni^I precursor complex. Complex **3** promotes the cyclotrimerization of a phosphaalkyne under reducing conditions, which allows the successful synthesis of free Dewar 1,3,5-triphosphabenzene **4**. In this catalytic reaction, we obtained, for the first time, an indication that trop-type molecules may behave as hemilabile ligands. We hope that this catalytic approach opens the possibility for the related synthesis of new phosphaheterocycles including those that carry diverse functional groups (R = FG). Such molecules are relevant for the development of new materials based on phosphorus-containing building blocks.

Experimental Section

General: All experiments were performed by using standard Schlenk and vacuum-line techniques or were performed in a Braun glove box under an inert atmosphere of Ar. All reagents were used as received from commercial suppliers unless otherwise noted. All solvents were distilled under an atmosphere of Ar from the appropriate drying agent and stored over 4 Å molecular sieves prior to use. All NMR spectra were recorded with Bruker Avance 250, 300, and 400 MHz spectrometers. Coupling constants *J* are given as absolute values. IR spectra were recorded with a Perkin–Elmer-Spectrum 2000 FTIR Raman spectrometer with KBr beam splitter (range 500–4000 cm^{-1}). Mass spectra were recorded with a Waters Micromass AutoSpec Ultima MassLynx 4.0 EI, a Bruker Daltonics maxis ESI-QTOF, and a Varian HiResMALDI by ETH Zürich D-CHAB/LOC MS Service. Melting points were determined with a Büchi melting point apparatus. The compounds Ph_3CCH_2Cl, $Ph_3CCH_2PCl_2$, and Ph_3CCP were synthesized according to previously reported procedures.[15]

$[Ni(trop_2NMe)(O_2CCF_3)]$ (1): A 20 mL Schlenk tube was charged with ($trop_2NMe$) (200 mg, 0.48 mmol, 1.0 equiv.). The solid was suspended in THF (3 mL) and $[Ni(tfa)_2]$ (138 mg, 0.48 mmol, 1.0 equiv.) was subsequently added. Zinc powder (327 mg, 5.00 mmol, 10 equiv.) was added to the pale-greenish solution. The mixture was allowed to stir overnight. The zinc powder was filtered off the dark-green solution through a plug of Celite. Subsequently, iPr_2O (2 mL) was added to the filtrate. Layering the solution with *n*-hexane (3 mL) resulted in the formation of colorless crystals after 12 h at –30 °C. The deep-green supernatant solution was decanted from the colorless byproduct and layered with *n*-hexane (2 mL). Large deep-green needles grew within 24 h at room temperature (also suitable for single-crystal X-ray diffraction analysis). The mother liquor was decanted, and the crystals were washed with cold iPr_2O (3 × 1 mL). The obtained air-sensitive crystals were dried in a stream of argon (200 mg, 71% yield), m.p. 155–158 °C. HRMS (ESI): calcd. for $C_{31}H_{25}NNi$ $[Ni(trop_2NMe)]^+$ 469.1340; found 469.1336. IR (ATR): $\tilde{\nu}$ = 1642 (s), 1483 (w), 1457 (w), 1276 (w), 1189 (s), 1134 (s), 1037 (w), 981 (w), 901 (w), 912 (w), 875 (w), 846 (m), 704 (w), 767 (w), 741 (m), 726 (s) cm^{-1}.

$[Ni(trop_2NMe)(\eta^2\text{-}TrCP)]\cdot 2DME$ (3): A 20 mL vial was charged with $Ph_3C{-}C{\equiv}P$ (**2**; 23 mg, 0.08 mmol, 1.0 equiv.) and THF (3 mL). $[Ni(trop_2NMe)(O_2CCF_3)]$ (61 mg, 0.08 mmol, 1.0 equiv.) was added, and the mixture was stirred until a clear dark-green solution formed. Zinc powder (52 mg, 0.80 mmol, 10 equiv.) was added to the solution, and the mixture was stirred vigorously for 1 h at room temperature. The reaction mixture was cooled down to –30 °C for 12 h. The color of the solution turned to red. The remaining zinc powder was filtered off by using syringe filters and dimethoxyethane (2 mL) was added to the filtrate. The mixture was layered with *n*-hexane (3 mL). The product was allowed to crystallize for 24 h at –30 °C. The supernatant solution was decanted, and the orange crystals were washed with *n*-hexane (1 mL) and dried under vacuum (45 mg, 60% yield), m.p. 210–212 °C (decomp.). ^1H NMR (400.13 MHz, $[D_8]THF$): δ = 7.90–7.88 (m, 3 H, CH_{ar}), 7.57–7.40 (m, 5 H, CH_{ar}), 7.38–6.39 (m, 23 H, CH_{ar}), 5.40 (d, $^3J_{HH}$ = 9.4 Hz, 1 H, CH_{olef}), 5.12 (d, $^3J_{HH}$ = 9.9 Hz, 1 H, CH_{olef}), 4.92 (d, $^3J_{HH}$ = 9.7 Hz, 1 H, CH_{olef}), 4.82 (d, $^3J_{HH}$ = 9.4 Hz, 1 H, CH_{olef}), 3.84 (s, 1 H, CH_{bzl}), 3.76 (s, 1 H, CH_{bzl}), 1.78

(br. s, 3 H, NCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_8$]THF): δ = 234.3 (*C*P confirmed by correlation with CH_3 in $^1H^{13}C$ HMBC, *J* = 22.9 Hz), 151.2 (C_{quart}) 138.2 (C_{quart}), 137.9 (C_{quart}), 137.6 (C_{quart}), 137.3 (C_{quart}), 136.8 (CH_{ar}), 136.5 (CH_{ar}), 136.3 (CH_{ar}), 135.8 (CH_{ar}), 135.7 (CH_{ar}), 135.4 (CH_{ar}), 135.1 (CH_{ar}), 134.8 (CH_{ar}), 134.6, (CH_{ar}), 133.4 (CH_{ar}), 130.8 (CH_{ar}), 129.9 (CH_{ar}), 129.5 (CH_{ar}), 129.2 (CH_{ar}), 128.9 (CH_{ar}), 128.5 (CH_{ar}), 128.1 (CH_{ar}), 127.5 (CH_{ar}), 127.1 (CH_{ar}), 126.9 (CH_{ar}),125.3 (CH_{ar}), 124.7 (CH_{ar}), 92.8 (CH_{olef}), 82.1 (CH_{olef}), 79.6 (CH_{bnzl}), 74.5 (CH_{olef}), 72.3 (CH_{olef}), 52.4 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, [D$_8$]THF): δ = 194.3 ppm. IR (ATR): $\tilde{\nu}$ = 2774 (w), 2463 (w), 2358 (w), 2168 (w), 1597 (w), 1478 (s), 1456 (w), 1423 (w), 1360 (w), 1304 (w), 1273 (w), 1260 (w), 1187 (w), 1163 (w), 1136 (w), 1102 (w), 1044 (m), 957 (w), 948 (w), 914 (w), 878 (w), 819 (w), 776 (w), 740 (m), 725 (m), 654 (w) cm^{-1}. HRMS (MALDI-TOF): calcd. for $C_{51}H_{40}NNiP$ 755.2252; found 755.2261.

2,4,6-Tris(trityl)-Dewar-1,3,5-triphosphabenzene (4)

Method A: $Ph_3CC{\equiv}P$ (**2**; 29 mg, 0.1 mmol, 10.0 equiv.) was added to a solution of complex **3** (7.5 mg, 0.01 mmol, 1.0 equiv.) in THF (3 mL). Zn powder (6.5 mg, 0.1 mmol, 10.0 equiv.) was added to the red solution, and the mixture was vigorously stirred at room temperature in a glove box for 24 h. The excess of zinc powder was filtered off by using syringe filters. The volatile materials were removed under reduced pressure to afford an orange residue. Analysis of the residue by ^{31}P NMR spectroscopy denoted the presence of **4** as the main phosphorus-containing compound. The residue was extracted in toluene (5 mL) and filtered through a pad of Celite. The solution was layered with *n*-hexane and cooled to –30 °C for 48 h to afford pale-yellow crystals (20 mg, 69 %).

Method B: $Ph_3CC{\equiv}P$ (**2**; 29 mg, 0.1 mmol, 10.0 equiv.) was added to a solution of complex **1** (5.7 mg, 0.01 mmol, 1.0 equiv.) in THF (3 mL). Zn powder (6.5 mg, 0.1 mmol, 10.0 equiv.) was added to the green solution, and the mixture was vigorously stirred at room temperature in a glove box for 24 h. The excess of zinc powder was filtered off by using syringe filters. The volatile materials were removed under reduced pressure to afford a reddish residue. The same protocol as that in method A was followed to afford pale-yellow crystals (21.5 mg, 75 %), m.p. 180–182 °C. ^1H NMR (400.13 MHz, C_6D_6): δ = 7.71 (br. s, 3 H, CH_{ar}), 7.26–7.20 (m, 5 H, CH_{ar}), 7.12–7.10 (m, 2 H, CH_{ar}), 7.04–6.97 (m, 5 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 262.1 (P–*C*=P), 147.4 (C_{quart}), 137.7 (C_{quart}), 129.8 (CH_{ar}), 129.1 (CH_{ar}), 128.2 (CH_{ar}), 127.8 (CH_{ar}), 127.6 (CH_{ar}), 126.5 (CH_{ar}), 72.1 (CP_3), 61.0 (CPh_3), 57.6 (CPh_3) ppm. Note: Owing to the low relative intensity of the quaternary carbon atoms attached to P, the following acquisition parameters were used to record the ^{13}C NMR spectrum: d1 = 30 s and p1 = 0.2 µs and processing parameter lb = 10 Hz; nonetheless the multiplicity of these signals were not resolved. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ = 346.2 (d, $^3J_{PP}$ = 36.0 Hz, 2 P), 86.5 (t, $^3J_{PP}$ = 36.0 Hz, 1 P) ppm. IR (ATR): $\tilde{\nu}$ = 3058 (w), 2964 (w), 1490 (m), 1445 (s), 1263 (s), 1076 (s), 1023 (s), 798 (s), 760 (s), 747 (s), 699 (s) cm^{-1}. HRMS (EI): calcd. for $C_{60}H_{45}P_3$ 858.2734, found 858.2769. $C_{60}H_{45}P_3$ (858.92): calcd. C 83.90, H 5.28; found C 82.95, H 5.75.

Crystallographic Analysis: The crystals were measured with a Bruker APEX' platform diffractometer with CCD area detector; Mo-K_α radiation (0.71073 Å). The refinement against full-matrix (vs. F^2) was done with SHELXTL (ver. 6.12) and SHELXL-97. Empirical absorption correction was done with SADABS (ver. 2.03). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement by using a riding model. For details see the crystallographic data for each compound below.

CCDC-958684 (for **1**), -954392 (for **3**), and -954394 (for **4**) 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.

Crystal Data for 1: Triclinic $P\bar{1}$, unit cell *a* = 1319.51(12) pm, *b* = 1446.68(12) pm, *c* = 1471.19(12) pm, α = 96.027(2)°, β = 91.983(2)°, γ = 111.330(2)°, volume 2.5935(4) nm^3, *Z* = 4, density (calculated) = 1.494 g cm^{-3}, absorption coefficient = 0.803 mm^{-1}, coefficient *F*(000) = 1204, crystal size 0.23 × 0.12 × 0.09 mm^3, Θ range for data collection 1.52 to 28.33°, index ranges $-17 \le h \le 17$, $-19 \le k \le 19$, $-19 \le l \le 19$, reflections collected 27093, independent reflections 12789 [*R*(int) = 0.0257], completeness to Θ (28.33°) = 99.0 %, absorption correction empirical, refinement method full-matrix least-squares on F^2, data/restraints/parameters 12789/0/723, goodness-of-fit on F^2 1.053, final *R* indices [$I > 2\sigma(I)$] *R*1 = 0.0403, *wR*2 = 0.1003, *R* indices (all data) *R*1 = 0.0487, *wR*2 = 0.1052, largest diff. peak and hole 1.119 and –0.328 e Å^{-3}.

Crystal Data for 3: Triclinic $P\bar{1}$, unit cell *a* = 1314.6(2) pm, *b* = 1339.3(2) pm, *c* = 1286.5(3) pm, α = 83.456(4)°, β = 76.260(4)°, γ = 70.568(4)°, volume = 2.2346(7) nm^3, *Z* = 2, density (calculated) = 1.325 g cm^{-3}, absorption coefficient = 0.518 mm^{-1}, coefficient *F*(000) = 942, crystal size 0.25 × 0.21 × 0.20 mm^3, Θ range for data collection 1.61 to 26.37°, index ranges $-16 \le h \le 16$, $-16 \le k \le 16$, $-17 \le l \le 17$, reflections collected 19791, independent reflections 9079 [*R*(int) = 0.0524], completeness to Θ (26.37°) = 0.993, absorption correction empirical, absorption correction *T* min and max 0.8814 and 0.90, 35 refinement method full-matrix least-squares on F^2, data/restraints/parameters 9079/0/572, goodness-of-fit on F^2 1.083, final *R* indices [$I > 2\sigma(I)$] *R*1 = 0.0778, *wR*2 = 0.1849, *R* indices (all data) *R*1 = 0.1032, *wR*2 = 0.1974, largest diff. peak and hole 1.360 and –1.010 e Å^{-3}.

Crystal Data for 4: Monoclinic *P*21/*c*, unit cell *a* = 962.16(17) pm, *b* = 1833.2(3) pm, *c* = 2842.7(5) pm, β = 94.057(3)°, volume = 5001.6(15) nm^3, *Z* = 4, density (calculated) = 1.263 g cm^{-3}, absorption coefficient = 0.163 mm^{-1}, coefficient *F*(000) = 2000, crystal size 0.74 × 0.04 × 0.02 mm^3, Θ range for data collection 1.32 to 25.06°, index ranges $-11 \le h \le 11$, $-21 \le k \le 21$, $-33 \le l \le 33$, reflections collected 39775, independent reflections 8851 [*R*(int) = 0.1520], completeness to Θ (25.06°) = 0.997, absorption correction empirical, absorption correction *T* min and max 0.7496 and 0.9280, refinement method full-matrix least-squares on F^2, data/restraints/parameters 8851/0/632, goodness-of-fit on F^2 1.012, final *R* indices [$I > 2\sigma(I)$] *R*1 = 0.0672, *wR*2 = 0.1335, *R* indices (all data) *R*1 = 0.1280, *wR*2 = 0.1581, largest diff. peak and hole 0.629 and –0.403 e Å^{-3}.

Supporting Information (see footnote on the first page of this article): Selected NMR spectra for **3** and **4**.

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