

Phosphabenzenes as electron withdrawing phosphine ligands in catalysis

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The utility of phosphabenzenes as ligands in late transition metal catalysis is examined. Molecular orbital calculations indicate that phosphabenzenes possess a low lying LUMO permitting π -back bonding interactions. The resultant electron withdrawing nature of the phosphabenzenes is beneficial for reactions in which reductive elimination steps are rate-limiting. For example, phosphabenzenes were found to function well in nickel catalyzed [4 + 2] cycloadditions.

Introduction

Our interest in phosphabenzene derivatives (Fig. 1) as potential

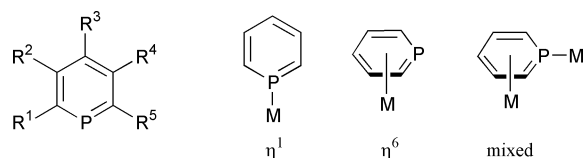


Fig. 1 Binding modes of phosphabenzene.

ligand candidates for transition metal catalyzed reactions was stimulated by several factors, including the novelty of such applications, the ease of preparation of ligand candidates, their stability, and the unique electronic properties of these systems.

Many complexes of phosphabenzenes with transition metals are known.¹ The coordination mode of phosphabenzenes may vary according to the metal to which they are bound. In general there are three conventional binding modes: η^1 , η^6 , and mixed (Fig. 1). The η^1 binding mode is typically observed with late transition metals in low oxidation states² while η^6 is favored by early transition metals in high oxidation states.³ Metals in the center of the transition series tend to exhibit mixed binding.⁴

Despite the prevalence of reported transition metal–phosphabenzene complexes, phosphabenzenes remain relatively unexplored as potential ligands in catalytic cycles. One important advancement in this area has been made by Breit *et al.* who demonstrated the utility of phosphabenzenes as ligands in the Rh-catalyzed hydroformylation of styrene. In this reaction 2,4,6-trisubstituted phosphabenzenes provided high activity and excellent regioselectivity for the branched aldehyde.⁵

Results and discussion

Phosphabenzene steric and electronic properties

A number of theoretical studies have been reported for phosphabenzenes^{6,7} which indicate that both high energy occupied and low energy unoccupied molecular orbitals have large coefficients at phosphorus.⁸ From B3LYP/6-31+G** calculations of the parent phosphabenzene,⁹ we generated the schematics¹⁰ of these orbitals as illustrated in Fig. 2. These representations indicate that phosphabenzene possesses a high lying orbital (HOMO^{2-}) suitable for σ -metal coordination which is close in energy to the π -bonding HOMO^{1-} and HOMO orbitals that

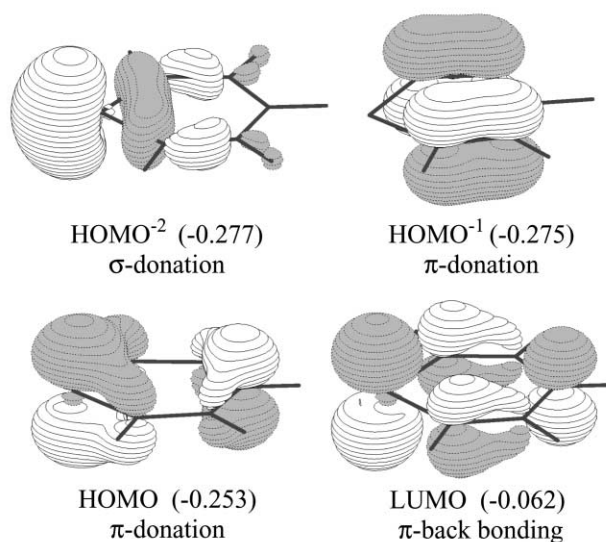


Fig. 2 B3LYP/6-31+G** molecular orbitals of phosphabenzene (orbital energies in eV are shown parenthetically).

would participate in η^6 -coordination. The fact that these orbitals are close in energy undoubtedly accounts for the range of coordination modes observed in various phosphabenzene metal complexes. The HOMO^{2-} donor orbital is complemented by the LUMO which enables phosphabenzene to act as a π -acceptor ligand when coordinated to a metal center through phosphorus. Based on these orbitals, phosphabenzenes in η^1 -metal complexes are expected to act as electron withdrawing ligands which can stabilize metals in lower oxidation states.

Tolman has introduced the parameters χ and θ to quantify the electronic and steric properties of ligands.¹¹ A large value of χ indicates that the ligand is a strong π -acceptor, while a small value of χ is indicative of strong σ -donation. The parameter θ provides a direct measure of ligand cone angle which is used as a measure of the volume around the metal occupied by the ligand.

In order to assess the steric properties of the phosphabenzenes, we calculated values of θ for 1–4 following a protocol similar to that employed by Tolman for unsymmetric trisubstituted phosphines. In this study, θ values were obtained by averaging the phosphabenzene occupancy angles (α and β) along two orthogonal planes (x and y) which are shown in

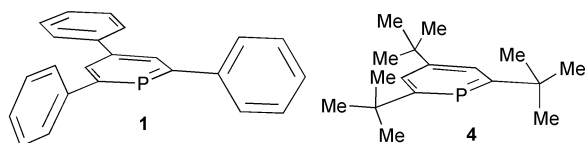
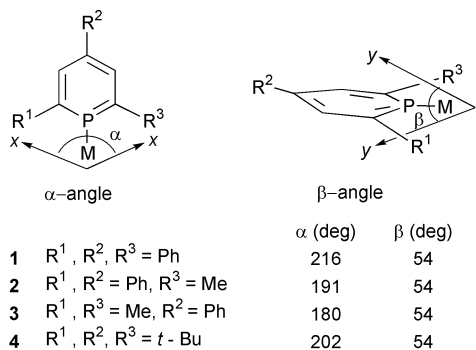
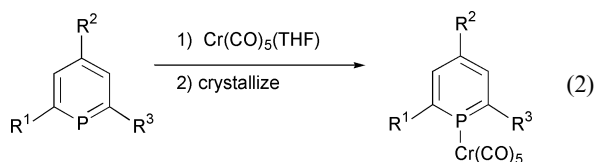
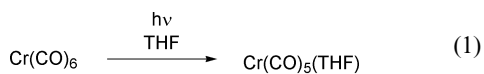


Fig. 3

Fig. 3. The occupancy angles, α and β , were measured from the geometries of the calculated structures.¹² In the conformations of **1–4** used in this analysis, the 2,6-substituents were oriented to minimize steric interactions with respect to phosphabenzene ring and a σ -bound metal; representative conformations used for **1** and **4** are illustrated in Fig. 3. While the steric demand is relatively small in the y plane (small β), the demand is very large in the x plane (large α). As such, the space occupied by phosphabenzene is better characterized as a flattened cone rather than a symmetric cone. While the average parameter θ (see Table 3 below) gives a general idea as to the steric demand of these compounds, consideration of α and/or β may be more appropriate depending on the coordination geometry of the metal and the rotational mobility about the phosphorus–metal bond. The latter may be partially fixed by π -backbonding interactions. In addition, the geometric arrangements of more than one phosphabenzene around a metal center are limited such that the steric factor θ may be underestimated in this analysis.

The χ parameter for **3** was estimated by Breit *et al.*^{5a} based upon the infrared CO stretching frequencies in the η^1 $\text{Cr}(\text{CO})_5$ complex with **1**^{13,14} (Eqn (1), and Eqn. (2)). In order to deter-



mine if this electronic parameter varies significantly upon substitution of the phosphabenzene ring with aryl or alkyl groups, we measured the stretching frequencies for the $\text{Cr}(\text{CO})_5$ complexes of **1–4** (Table 1). For the hindered phosphabenzene **4**, the $\text{Cr}(\text{CO})_5$ complex did not form indicating that the two *tert*-butyl groups *ortho* to the phosphorus sterically inhibit coordination. From measurements of the remaining complexes, it appears that the presence of aryl *vs.* alkyl groups on the phosphabenzene ring has a relatively small influence on the electron-withdrawing character of the phosphorus, and **1–3** are expected to have similar χ values between 23–24 which are comparable to those of phosphites (see Table 3 below).

These χ value estimates are consistent with charge calculations for **1–4** in which the phosphorus atoms have the partial

Table 1 Carbonyl IR shifts of $\text{Cr}(\text{CO})_5$ complexes of phosphabenzene (Eqn. (2))

Ligand	IR/ cm^{-1} pentane ^{a,b}	IR/ cm^{-1} CHCl_3 ^{a,c}
1	2066.9	2066.9 (2068.1)
	1994.1	1995.7
	1937.0	1937.7
2	2066.7	2066.8 (2068.1)
	1993.8	1994.3
	1933.2	1932.1
3	2066.0	2065.8 (2067.6)
	1992.5	1995.4
	1929.1	1926.8
4 ^d	—	—

^a Cast as a thin film on NaCl plates unless otherwise noted. ^b Mother liquor from pentane crystallization. ^c Crystals from pentane redissolved in CHCl_3 . Parenthetical entries are measurements of CHCl_3 solution. ^d Complex did not form.

Table 2 Calculated Mulliken and natural bond order charges for the phosphorus in **1–4**

Ligand	PM3 ^a Mulliken	HF/6-31 G* ^b		B3LYP/6-31G* ^b	
		Mulliken	NBO	Mulliken	NBO
	0.47	0.31	0.71	0.21	0.66
1	0.45	0.31	0.72	0.19	0.66
2	0.47	0.29	0.69	0.17	0.65
3	0.50	0.26	0.67	0.15	0.64
4	0.42	0.26	0.66	0.13	0.62

^a Calculated using SPARTAN. Mulliken and NBO charges were identical. ^b Calculated using Gaussian 98.

charges listed in Table 2.^{15,16} The B3LYP/6-31G* Mulliken charges obtained in this study for the parent phosphabenzene **1** are the same as those previously reported.¹⁷ The trends between the different derivatives are the same regardless of the method used; phosphabenzene containing alkyl groups tend to have smaller positive charges at phosphorus due to the donating nature of these groups. Overall, the charges are fairly similar between the different derivatives which should translate to similar χ values for these ligands (see Table 3 below). The phosphabenzene with more alkyl groups (**3**, **4**) have slightly greater electron density consistent with their slightly smaller χ values (more donating).

The χ and θ values measured in this study for **1–4** are collected in Table 3 together with the values for some common phosphorus ligands. From these values the phosphabenzene is expected to act as moderately electron withdrawing ligands with properties similar to phosphites. In addition, the steric size of these compounds can be adjusted by changing the 2,6-substituents without substantially altering the electronic properties.

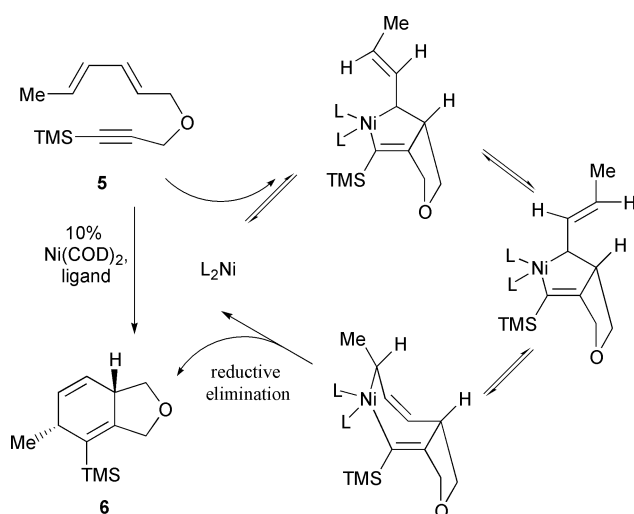
Phosphabenzene in nickel-catalyzed cycloisomerization

Based on the electronic properties described above, phosphabenzene is anticipated to affect the rate of a catalytic cycle through a strong electronic influence at the metal center. Therefore, a catalytic system was examined in which the rate determining step involves an increase in electron density at the metal center. The phosphabenzene ligands should stabilize the intermediates at this step and enhance the reaction. The formal [4 + 2] cycloadditions of dieneynes developed by Wender¹⁸ had the necessary prerequisites since the rate determining step is most likely reductive elimination of the product from the metal center (Scheme 1). The reported tetrahedral complex involving

Table 3 Steric and electronic parameters for representative phosphorus ligands

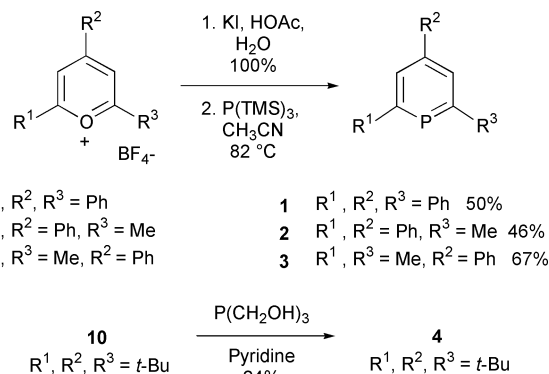
Entry	Ligand	χ^a	θ/deg^a
1	PPh ₃	12.9	145
2	PEt ₃	5.6	132
3	PCy ₃	0.3	170
4	P(OMe) ₃	23.3	107
5	P(OPh) ₃	29.1	128
6	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃	28.9	152
7	P(O- <i>i</i> -C ₃ HF ₆) ₃	51.3	130
8	1	24 ^b	135 ^c
9	2	24 ^c	123 ^c
10	3	23 ^c	117 ^c
11	4	~23 ^{c,d}	128 ^c

^a Data for entries 1–7 from Tolman *et al.* (Ref. 11). χ values obtained using the IR stretches of the Ni(CO)₄ complexes. ^b See Ref. 5a. ^c Estimated from L·Cr(CO)₅ IR stretches in this work (see text). ^d Since 4·Cr(CO)₅ did not form, χ could not be measured directly for **4**. The indicated value was estimated from **3**. ^e Determined from calculated structures in this work (see text).

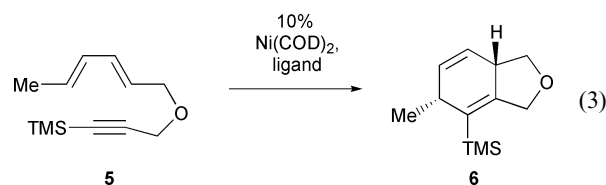
**Scheme 1** Mechanism of the nickel catalyzed [4 + 2] cycloaddition.

four phosphabenzene ligands bound to Ni(0) in an η^1 -mode, indicates that phosphabenzene ligands are suitable modifiers for the Ni(0) catalysts employed in this reaction.¹⁹

The phosphabenzene ligands examined in this study were chosen on the basis of ease of preparation, stability and symmetry. The series, **1–4**, with phenyl, methyl, and *tert*-butyl substituents permits a study of substituent steric and electronic effects on reactivity. In the series **1** to **3** the cone angle decreases as the *ortho*-phenyl groups are replaced with methyl groups while **4** (*ortho tert*-butyl groups) has a similar cone angle (but different electronic properties) compared to **1**. Although several methods have been reported for synthesis of phosphabenzene,²⁰ the unified protocols presented in Scheme 2 were found to be the most convenient for preparing these compounds. For phosphabenzene **1** was simplest, in which the pyrylium iodide salts are converted to the phosphabenzene upon treatment with tris(trimethylsilyl)phosphine. We found that exchange of the pyrylium tetrafluoroborates by treatment with KI in HOAc to the required pyrylium iodide salts was more convenient than direct preparation of the iodides.²² The tetrafluoroborate precursors **7**²³ and **8**²⁴ were synthesized following reported protocols while we prepared **9** by adapting a procedure used previously for the corresponding perchlorate salt.²⁵ For the tris(*tert*-butyl)-phosphabenzene **4**, these methods could not be employed and the alternate procedure with tris(hydroxymethyl)phosphine²⁶ as reported by Dimroth *et al.*²⁷ was used.

**Scheme 2** Synthesis of phosphabenzene.

The results of the phosphabenzene ligands in the nickel catalyzed cycloaddition (Eqn. 3) are shown in Table 4. Background



thermal reactions in both THF and cyclohexane (entries 1 and 2) indicated that the thermal process was slow and caused decomposition as well. All of the catalytic reactions afforded the product as a single diastereomer. As part of a control, the more hindered P(O-*o*-C₆H₄Ph)₃ phosphite ligand was found to be superior to P(OPh)₃ (entry 3 vs. 4). Use of 2,4,6-triphenylphosphabenzene (**1**) gave unexpectedly poor conversion (entry 8, 7% after 20 h) when the optimal conditions for the phosphite ligands were employed (30 mol% ligand, THF). Reasoning that the coordinating THF solvent may be interfering with coordination of the highly hindered **1**, the reaction was also examined in cyclohexane. Gratifyingly, this change resulted in much faster conversions (entry 9, 63% after 20 h).

Upon close analysis of the catalytic cycle (Scheme 1), only two phosphine ligands appear to be needed for coordination to nickel. Examination of the **1** : Ni(COD)₂ ratio revealed that a 2 : 1 ratio provided much better rates (92% after 20 h, entry 10) than a 3 : 1 or 1 : 1 ratio (63% and 25% conversion respectively; entries 9 and 12).

Since the use of the minimal amount of ligand and a non-coordinating solvent was found to be effective with the phosphabenzene ligands, these parameters were reexamined for the P(O-*o*-C₆H₄Ph)₃ case. Interestingly, the use of the non-coordinating solvent cyclohexane in place of THF led to poorer results (entry 6 vs. 4) in contrast to the observation for phosphabenzene **1**. To distinguish between a bulk solvent effect and a potential ligand role for the THF, the reaction was performed with the addition of 50 mol% THF to the conditions in entry 6 (entry 7). The reaction rate under these conditions was the same as when THF was the solvent, which further supports the hypothesis that THF coordinates to the nickel. In line with this hypothesis, an excess of P(O-*o*-C₆H₄Ph)₃ may be required to ensure a favorable equilibrium toward a 2 : 1 ligand : Ni complex when THF is present. Indeed, the minimal amount of phosphite (2 : 1 ligand : Ni) was less effective (entry 4 vs. 5) than when an excess was used (3 : 1 ligand : Ni), which again is the opposite of what was observed with **1**. Notably, the rates achieved under the optimal conditions with phosphabenzene **1** (entry 10) are superior to those for P(OPh)₃ and comparable to those for the more sterically congested P(O-*o*-C₆H₄Ph)₃. Since the phosphabenzene ligands are stable toward air and even chromatography, the use of such ligands may be advantageous in situations where the less stable phosphite ligands cannot be tolerated.

Table 4 Conversion vs. phosphine in the nickel-catalyzed isomerization (Eqn. 3)

Entry	Mol% ligand ^a	Ligand	Solvent ^b	% conversion ^c
1	—	—	THF	~4 ^d
2	—	—	Cyclohexane	10 ^{d,e}
3	30	P(OPh) ₃	THF	18
4	30	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃	THF	88
5	20	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃	THF	~40 ^d
6	30	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃	Cyclohexane	70
7	30	P(O- <i>o</i> -C ₆ H ₄ Ph) ₃	Cyclohexane ^f	89
8	30	1	THF	7
9	30	1	Cyclohexane	63
10	20	1	Cyclohexane	92
11	20	1	Cyclohexane ^g	89
12	10	1	Cyclohexane	25
13	20	2	Cyclohexane	81
14	20	3	Cyclohexane	66
15	10	4	Cyclohexane	19
16	20	4	Cyclohexane	31
17	30	4	Cyclohexane	22

^a 10 mol% Ni(COD)₂ used except for entries 1 and 2. ^b Reactions in THF were at 66 °C and in cyclohexane at 80 °C unless otherwise noted. ^c Conversions determined after 20 h by ¹H NMR. No substrate decomposition or by products observed unless indicated. ^d Significant decomposition observed. As such, the reported conversions represent an upper limit. ^e Isolated yield. 16% conversion by ¹H NMR. ^f 50 mol% THF. ^g Reaction run at 66 °C.

The phenyl groups (R¹, R³) adjacent to the phosphorus in the phosphabenzene play a key role. With derivative **2**, where one of these phenyl groups is replaced by Me, the reaction still proceeds well (entry 13). When only alkyl groups are present as in **3** (R¹, R³ = Me) or **4** (R¹, R³ = *t*-Bu), poor rates are observed (entries 14 and 16). Comparison of the cone angles to the yields for **1** (135°, 92%), **2** (123°, 81%), **3** (117°, 66%), and **4** (128°, 31%) indicates that the composition of the adjacent group (phenyl vs. alkyl) is as important as the steric size of the ligand. At least one *ortho*-phenyl group is needed to ensure high reactivity. This result is at first puzzling, since the orthogonal phenyl groups cannot engage in electron withdrawal through conjugative interaction with the phosphabenzene ring. However, the sp²-hybridized carbons of the *ortho*-phenyl groups in **1** and **2** are electron withdrawing compared to the sp³-hybridized carbons of the *ortho*-alkyl groups in **2**, **3**, and **4** which may be influencing the electronic character of the phosphabenzene ring.

Conclusion

The results obtained thus far indicate that the rate of this reaction is influenced by both the steric and electronic properties of the phosphabenzene ligands. As expected, the reaction is accelerated by a moderate increase in the steric demand of the ligand and a decrease in the electron density at nickel. Tuning of the electronic and steric properties of phosphabenzene can be accomplished by simple structural modifications allowing optimal combinations of χ and θ to be identified. While the exact role of solvent in the catalytic cycle of the nickel catalyzed cyclizations remains unclear, a significant rate enhancement is seen with phosphabenzene upon switching from a coordinating solvent to a non-coordinating solvent. This solvent effect is contrary to that observed for the phosphite cases, in which the maximum rate is obtained when another coordinating species is present. These results indicate that phosphabenzene would be useful ligands in applications which call for bulky, electron-deficient ligands that are stable to air and water.

Experimental

General

Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry nitrogen in glassware that had been either flame dried in a stream of nitrogen or dried in an

oven (90 °C) for at least six hours. When necessary, solvents and reagents were dried prior to use. Toluene, Et₂O, THF, and CH₂Cl₂ were de-oxygenated by purging with Ar and then dried by passing through activated alumina. Cyclohexane and THF for the Ni(0)-catalyzed reactions were distilled from Na-benzophenone ketyl and were further degassed in the reaction flask by bubbling N₂ through the solution. TMSCl, iPr₂NH, CH₃CN, pyridine, and HMPA were distilled from CaH₂. Anisole was distilled from Na. NaH was rinsed three times with hexanes (distilled from CaH₂) and dried under high vacuum prior to use. Ni(COD)₂ was purchased from Strem and was stored under an N₂ atmosphere in a dry box. Tris(trimethylsilyl)phosphine was purchased from Aldrich. Phosphabenzene **1**²¹ and **4**²⁷ were prepared following the published procedures.

Analytical thin layer chromatography (TLC) was performed on EM reagents 0.25 mm silica-gel 60-F plates. Visualization was accomplished with UV light. Chromatography on silica gel was performed using a forced flow of the indicated solvent system on EM reagents silica gel 60 (230–400 mesh).²⁸

¹H NMR spectra were recorded on Bruker AM-500 (500 MHz), AM-250 (250 MHz), or AM-200 (200 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or with the solvent resonance as the internal standard (CDCl₃ 7.26 ppm, DMSO-d₆ 2.49 ppm, D₂O 4.80 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Mass spectra were obtained on a low resolution Micromass Platform LC in electron spray mode. IR spectra were taken on a Perkin-Elmer FT-IR spectrometer using thin films or in a cell using CHCl₃ solution with CHCl₃ as background. Melting points were obtained on Thomas Scientific Unimelt apparatus and are uncorrected.

2,6-Dimethyl-4-phenylpyrylium tetrafluoroborate (**9**)

Compound **9** was synthesized by modification of a reported procedure for a related pyrylium.²⁹ 2,6-Dimethyl-4-pyrone (5.0 g, 0.04 mol) was dissolved in anisole (40 mL) with gentle heating. The solution was cooled to 5 °C and PhMgBr (0.04 mol) was added slowly as a 1 M solution in ether *via* cannula. The purple solution was then warmed to room temperature and poured over HBF₄ (6.7 mL of a 54% solution in ether, 0.048 mol). The red–orange precipitate was isolated by filtration and washed thoroughly with hot EtOH to yield **9** as a pink–orange solid (6.5 g) in 59% yield.

Synthesis of pyrylium iodides from pyrylium tetrafluoroborates 7–9

To a warm (40–50 °C) slurry of the pyrylium tetrafluoroborate (3.8 mmol) in acidified (2–4 drops HOAc) water (20 mL) was added KI (3.8 mmol). The solution was stirred until red (1–5 h) then cooled to room temperature. The iodide was collected by filtration and washed thoroughly with ether. Yields are quantitative.

6-Methyl-2,4-diphenylphosphabenzene (2) and 2,6-dimethyl-4-phenyl phosphabenzene (3)

Following the method that Märkl *et al.*²¹ employed for the synthesis of **1**, a solution of the pyrylium iodide precursor (2.5 mmol) in dry CH₃CN (15 mL) was purged with N₂. P-(TMS)₃ (2.8 mmol) was added *via* gas-tight syringe and the solution was heated at reflux for 20 h. After cooling, CH₃CN was removed *in vacuo* and the crude product was purified by flash chromatography on SiO₂ (0–5% EtOAc–hexanes) to yield the phosphabenzenes **2** and **3** as pale yellow powders in 46% yield and 67% yield respectively. **2**: mp 79–80 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.1 (d, *J* = 5.4 Hz, 1H), 7.9 (d, *J* = 7.0 Hz, 1H), 7.7 (d, *J* = 8.2 Hz, 2H), 7.6 (d, *J* = 9.3 Hz, 2H), 7.35 (m, 6H), 2.8 (d, *J* = 15.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.0 (d, *J* = 50 Hz), 169.0 (d, *J* = 50 Hz), 144.1 (d, *J* = 5 Hz), 144.0, 143.8, 133.4 (d, *J* = 12.5 Hz), 131.3 (d, *J* = 12.5 Hz), 129.3 (d, *J* = 10 Hz), 128.1, 127.9, 25.2 (d, *J* = 37.5 Hz); ³¹P NMR (250 MHz, CDCl₃) δ 188.76. **3**: mp 49–50 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 6.7 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.4 (t, *J* = 6.7 Hz, 1H), 2.73 (d, *J* = 15.1 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 168.8 (d, *J* = 49 Hz), 143.8, 142.8, 142.7, 132.5 (d, *J* = 13.7 Hz), 129.2, 128.04, 25.0 (d, *J* = 36.2 Hz); ³¹P NMR (250 MHz, CDCl₃) δ 193.3. Phosphabenzene **3** has previously been synthesized by a different method.³⁰

1-(3-Trimethylsilylprop-2-ynoxy)hexa-2,4-diene (5)

An LDA (0.88 mmol) solution was prepared by adding *i*Pr₂NH to BuLi at –78 °C. After stirring for 3 minutes, the LDA solution was cooled to –85 °C and (*E,E*)-1-(prop-2-ynoxy)hexa-2,4-diene³¹ (100 mg, 0.73 mmol) was slowly added as a solution in Et₂O (1.1 mL). After 3 min of stirring, TMSCl was added dropwise followed by the dropwise addition of HMPA as a solution in Et₂O. The reaction was allowed to warm slowly to room temperature with stirring for 30 min during which time the cloudy solution became a milky white suspension. The reaction was quenched with 3 M HCl and extracted with ether. The extracts were washed with saturated NaHCO₃ then brine, dried over MgSO₄ and concentrated. The crude product was purified by flash chromatography (5% Et₂O–pentane) to give **5** as a yellow liquid in 89% yield. ¹H NMR (200 MHz, CDCl₃) δ 6.3–5.95 (m, 2H), 5.85–5.55 (m, 2H), 4.12 (s, 2H), 4.05 (d, *J* = 6.5 Hz, 2H), 1.75 (d, *J* = 6.72 Hz, 3H), 0.17 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 134.5, 131.1, 130.6, 126.2, 102.0, 91.6, 70.3, 57.9, 18.4, 0.2.

Thermal control reactions

For purposes of comparison a sample of **6** was synthesized thermally from diene **5** (20 mg, 0.09 mmol) by heating in benzene (9.6 mL) at 80 °C in a resealable pressure tube. In addition, the thermal background reaction was determined in the solvent of choice for the phosphabenzene reactions (cyclohexane). Diene **5** (75 mg, 0.36 mmol) was dissolved in cyclohexane (36 mL) and set to reflux. Monitoring of the reaction progress was performed by ¹H NMR which indicated 16% conversion after 20 h with significant decomposition. Conversion was determined by comparing the relative integration for the peaks at δ 1.8, d{–CH₃(**5**)} and δ 1.19, d{–CH₃(**6**)}. Upon chromatography, a 10% isolated yield of **6** was obtained.

¹H NMR (CHCl₃, 500 MHz) δ 5.65 (s, 2H), 4.4 (d, *J* = 11.7 Hz, 1H), 4.2 (d, *J* = 11.7 Hz, 1H), 4.1 (t, *J* = 7.8 Hz, 1H), 3.25 (dd, *J* = 5, 11.3 Hz, 1H), 2.9 (m, 1H), 1.19 (d, *J* = 7.2 Hz, 3H), 0.17 (s, 9H).

General procedure for Ni(0)-catalyzed carbocyclization

Diene **5** (60 mg, 0.28 mmol) and **1** (28 mg, 0.086 mmol) were combined in an acid washed, base washed, flame dried Schlenk flask in an inert atmosphere glovebox and dissolved in distilled THF or cyclohexane (25 mL). A solution of Ni(COD)₂ (7.9 mg, 0.028 mmol) in distilled THF or cyclohexane (4 mL) was then added to the stirred solution, dropwise. The reaction flask was then removed from the glovebox and heated to reflux. Since there was no decomposition, the reaction progress could be monitored by ¹H NMR. Conversion was determined by comparing the relative integration for the peaks at δ 1.8 (d, CH₃, **5**) and δ 1.19 (d, CH₃, **6**).

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