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Electron-Rich Trialkyl-Type Dihydro-KITPHOS Monophosphines: Efficient Ligands for Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling. Comparison with Their Biaryl-Like KITPHOS Monophosphine Counterparts

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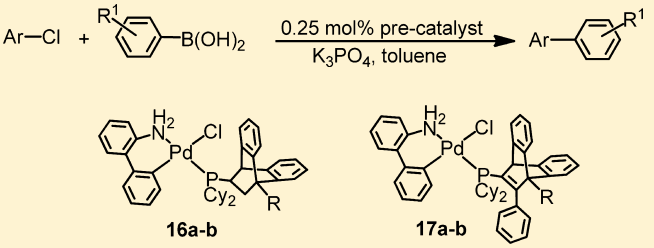
Supporting Information

ABSTRACT: The Diels–Alder cycloaddition between dicyclohexylvinylphosphine oxide and anthracene or 9-methylanthracene affords the bulky electron-rich trialkyl-type dihydro-KITPHOS monophosphines 11-(dicyclohexylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene and 11-(dicyclohexylphosphinoyl)-9-methyl-12-phenyl-9,10-dihydro-9,10-ethenoanthracene, respectively, after reduction of the corresponding oxide. Both phosphines are highly air-sensitive and rapidly oxidize on silica gel during purification but have been isolated as air-stable cyclometalated palladium precatalysts of the type [Pd{$\kappa^2N2',C1$-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl(L)]. Both palladium precatalysts form highly active systems for the Suzuki–Miyaura cross-coupling of a range of aryl chlorides with aryl boronic acids, giving the desired products in good to excellent yield under mild conditions and a catalyst loading of 0.25 mol %. A comparison of the performance of catalysts based on dihydro-KITPHOS monophosphines against their first-generation biaryl-like KITPHOS counterparts revealed that the latter are consistently more efficient for the vast majority of substrate combinations examined, albeit by only a relatively small margin in some cases. This, together with the greater air stability and ease of handling of biaryl-like KITPHOS monophosphines, renders them more practical ligands for palladium-based cross-coupling. The steric parameters of both classes of KITPHOS monophosphine and a selection of electron-rich biaryl monophosphines have been quantified using a combination of Solid-G to determine the percentage of the metal coordination sphere shielded by the phosphine (the *G* parameter), and Salerno molecular buried volume calculations (Samb*V*ca) to determine the percent buried volume (%V_{bur}); the corresponding Tolman cone angles have also been determined from correlations and the relative merits of the two approaches discussed. The electronic properties of these phosphines have also been investigated using DFT to calculate the A_1 ν(CO) frequency in $LNi(CO)_3$ (B3LYP/6-31G(2d,p)[LanL2DZ on Ni]), and the resulting computed electronic parameters (CEP) were used to estimate the corresponding experimental Tolman electronic parameters (TEP).



INTRODUCTION

Since the late 1990s, bulky electron-rich monodentate phosphines[1] have evolved into a highly powerful class of ligand for a host of palladium-catalyzed transformations; examples include Suzuki–Miyaura,[2] Negishi,[3] Kumada,[4] Stille.[5] and Hiyama[6] cross-couplings, Buchwald–Hartwig amination,[7] borylation,[8] silylation,[9] etherification,[10] α-arylation,[11] direct arylation,[12] and carbonylation.[13] Two distinct classes of monophosphines can be identified: the first of these are the trialkyl-based phosphines such as P(*t*-Bu)$_3$,[14] PCy_3,[14] and PAd_2R (Ad = 1-adamantyl, R = CH_2Ph, *n*-Bu, *t*-Bu)[15] and most recently 9-fluorenylphosphines[16] (Figure 1, **1**–**4**); the last species were introduced as architecturally modular trialkylphosphines to overcome the limited structural versatility associated with this class of ligand. The efficiency of trialkylphosphines appears to be due to a combination of their steric bulk and high basicity, favoring formation of an active low-coordinate complex,[17] provided the steric bulk of the substrate and phosphine are matched, as too much bulk has been shown to be detrimental for selected cross-coupling reactions.[18] The second class are biaryl-based monophosphines such as **5**–**7**, first introduced by Buchwald in 1998, characterized by their steric bulk, high basicity, and a proximal non-phosphine-containing aryl ring and assembled via an elegant modular and versatile one-pot procedure.[19] The efficacy of these phosphines has been attributed to a number of factors: (i) their electron-rich character which facilitates oxidative addition of unreactive aryl chlorides,[20] (ii) their bulk which promotes formation of the active monophosphine complex L_1Pd^0,[17] (iii) increased catalyst lifetime due to stabilization of intermediate complexes through either a Pd–arene interaction with the *ipso* carbon atom or a Pd–O interaction with an oxygen atom of the methoxy group on the non-phosphine-containing aromatic ring,[2f,21] and (iv)

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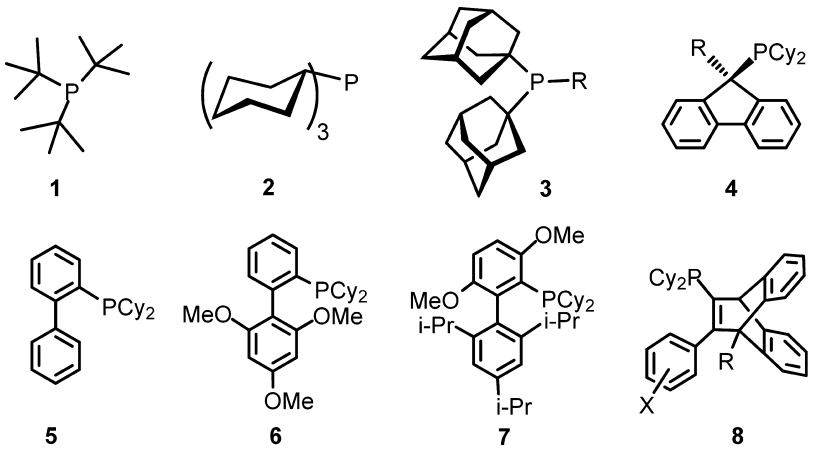

Figure 1. Bulky electron-rich monodentate phosphines **1**−**8**.

the substitution pattern of both the non-phosphine-containing aryl ring and the upper arene;[22] in particular, bulky biaryl monophosphines 3,6-substituted on the upper arene are uniquely effective ligands for certain classes of challenging palladium-catalyzed carbon−heteroatom coupling reactions.[23]

As the biaryl framework is integral to the success of these ligands, it has been used as the lead motif for developing alternative systems based on biaryl-like units such as *N*-phenylpyrrole,[24] 2-phenylindole,[25] arylpyrazole, and bipyrazole,[26] as well as the 2,3-dihydrobenzo[*d*][1,3]oxaphosphole framework.[27] We have also embraced this design concept and recently introduced a new class of biaryl-like monophosphines **8**,[28] KITPHOS, the basic architecture of which closely resembles Buchwald's biaryl monophosphines in that a bulky electron-rich PR_2 group is connected to a carbon−carbon double bond, albeit as part of an anthracene-derived bicyclic framework, with a proximal non-phosphine-containing aryl ring that can be systematically modified. In addition to their being architectural analogues, we have been exploring whether electron-rich KITPHOS monophosphines could be surrogates for their biaryl-based counterparts. Encouragingly, preliminary studies have revealed that these ligands either rival or outperform their biaryl-based counterparts across a wide range of palladium-catalyzed Suzuki−Miyaura and Buchwald−Hartwig cross-couplings[29a−c] as well as gold(I)-catalyzed intramolecular cycloisomerizations[29d,e] and most recently the ruthenium-catalyzed direct ortho arylation of 2-phenylpyridine and *N*-phenylpyrazole.[30] Key features of KITPHOS monophosphines include their operationally straightforward synthesis via [4 + 2] cycloaddition between a 1-alkynylphosphine oxide and anthracene in moderate to reasonable yield from relatively inexpensive starting materials, as well as their highly modular construction, which allows the substitution pattern of the 1-alkynylphosphine oxide aryl group to be systematically varied, the steric bulk and the basicity of the phosphino group to be fine-tuned, and the biaryl-like fragment to be modified by performing the cycloaddition with a substituted anthracene or its equivalent. For comparison, electron-rich biaryl monophosphines are typically prepared in an elegant, modular one-pot protocol that involves addition of an aryl Grignard to an in situ generated benzyne followed by trapping of the resulting biaryl−metal intermediate with an appropriate chlorophosphine.[31]

Having demonstrated the validity of the biaryl-like analogy, we became interested in extending the same methodology to the Diels−Alder cycloaddition between a vinylphosphine oxide and anthracene to afford the dihydro-KITPHOS class of monophosphine (Figure 2) and exploring the extent to which

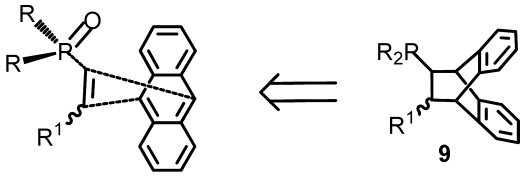

Figure 2. Retrosynthesis of dihydro-KITPHOS monophosphines.

these phosphines resemble or mimic bulky electron-rich trialkyl-type systems such as **1**−**4**. Moreover, this approach would not be constrained by the limited structural flexibility/versatility associated with conventional trialkylphosphines, since the modular construction of dihydro-KITPHOS monophosphines will enable their steric bulk and basicity to be modified through the phosphino group as well as the substituents attached to the vinyl-derived two-carbon bridge and the anthracene unit. Herein, we report the synthesis of two trialkyl-type dihydro-KITPHOS monophosphines, isolation of their borane adducts and phosphonium salts, the synthesis of palladium precatalysts, an evaluation of their efficiency as ligands in the palladium-catalyzed Suzuki−Miyaura cross-coupling of aryl chlorides, a comparison of their performance against the corresponding biaryl-like KITPHOS monophosphine-based systems, and an initial quantification of their steric and electronic parameters.

RESULTS AND DISCUSSION

Synthesis of KITPHOS-Based Phosphines, Their Borane Adducts, and Phosphonium Salts. Our interest in dihydro-KITPHOS monophosphines **9a**,**b** began after recognizing their trialkyl-type character and the close similarity of their steric and electronic properties to those of tricyclohexylphosphine and tri-*tert*-butylphosphine. Monophosphines **9a**,**b** were prepared in good yield following the procedure outlined in Scheme 1, which involves the Diels−Alder cycloaddition between dicyclohexylvinylphosphine oxide (**10**) and either anthracene or 9-methylanthracene followed by reduction of the resulting monoxides **11a**,**b** by heating the oxide in a mixture of chlorosilane, toluene, and triethylamine at 110 °C for 48 h in a sealed vessel. The dicyclohexylvinylphosphine oxide required

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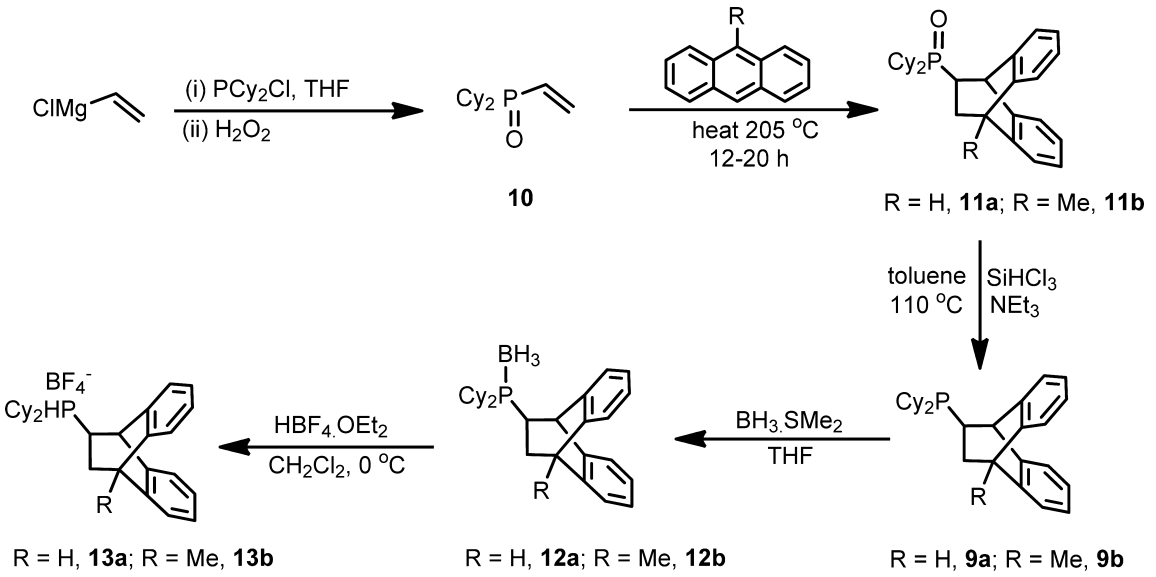
Scheme 1



for the Diels–Alder cycloaddition was prepared in near-quantitative yield by reaction of vinylmagnesium chloride with chlorodicyclohexylphosphine,[32] followed by oxidation immediately prior to workup; the product can typically be used for the subsequent step without further purification. The Diels–Alder reactions were most conveniently carried out by heating the reactants in sealed 20 mL Wheaton V-20 reaction vials using an Asynt DrySyn multiposition heating block and the progress monitored using ^{31}P NMR spectroscopy to analyze samples of the reaction mixture at regular time intervals.

Unfortunately, attempts to purify **9a,b** by flash chromatography resulted in rapid oxidation, and the corresponding oxide was the sole product to elute from the column, which is perhaps not surprising considering their trialkyl-type nature. However, spectroscopically pure samples were isolated by conducting the base hydrolysis and aqueous workup of the reduction mixture under a nitrogen atmosphere and analytically pure samples were obtained by careful crystallization. The Diels–Alder reaction between 9-methylanthracene and **10** occurs with high regioselectivity to afford a single adduct, presumably that with the bulky methyl-substituted bridgehead atom attached to the least substituted carbon atom of the vinylphosphine oxide derived two-carbon bridge, in much the same manner as previously reported for the corresponding double Diels–Alder cycloaddition with 1,4-bis-(diphenylphosphinoyl)buta-1,3-diyne.[33] The regioselectivity of addition is supported by a comparison of the ^{1}H and ^{13}C NMR spectra of **9a,b**; specifically the bridgehead hydrogen atoms of **9a** appear as a doublet and broad singlet at δ 4.37 and 4.29, respectively. The coupling constant of 5.9 Hz in the former is consistent with a three-bond phosphorus–hydrogen coupling and is similar to that of 4.9 Hz for the doublet at δ 4.31 associated with the sole bridgehead hydrogen atom of **9b**. The bridgehead carbon atoms of **9a,b** show a similar distinctive pattern of P–C coupling; in both cases one bridgehead carbon atom appears as a doublet (J_{PC} = ca. 16 Hz) and the other as a singlet; the doublet associated with **9b** has been unequivocally assigned to the bridgehead CH using the DEPT NMR sequence: the magnitude of this coupling is entirely consistent with a two-bond coupling in the proposed regioisomer. The high regioselectivity can be accounted for by considering the possible steric interactions between the 9-methyl substituent and the dicyclohexylphosphinoyl group in the transition state for cycloaddition. The rapid oxidation of **9a,b** is in stark contrast to their biaryl-like counterparts **8**, which can be purified by column chromatography and are air-stable solids that can be stored for several months with no evidence of oxidation.[28a]

As **9a,b** are highly air-sensitive, they were immediately transformed into their borane adducts by reaction with $BH_3{\cdot}SMe_2$ in THF; workup and purification by column chromatography gave **12a,b**, both as air-stable white solids, in near-quantitative yield. The ^{31}P NMR spectrum of **12a** contains a doublet at δ 33.7 (J = 69.2 Hz), and the corresponding signal for **12b** appears at δ 32.8 (J = 65.3 Hz); as expected, both are shifted downfield relative to the corresponding phosphine. The ^{11}B NMR spectra of **12a,b** contain characteristically broad resonances at δ −43.4 and −43.5, respectively. The ^{1}H NMR spectra of **12a,b** both contain a high-field broad multiplet associated with the BH_3 group, while the protons attached to the bridgehead carbon atoms of **12a** appear as a doublet and a broad triplet at δ 4.74 (J_{PC} = 5.4 Hz) and 4.36 (J_{PC} = 2.1 Hz), respectively; the sole bridgehead proton of **12b** appears as a doublet at δ 4.72 (J_{PC} = 4.6 Hz). As **12a,b** are the first examples of dihydro-KITPHOS monophosphines, a single-crystal X-ray study of **12a** was undertaken to compare the key structural features with those of other trialkyl monophosphine–borane adducts; a perspective view of the molecular structure is shown in Figure S2 of the Supporting Information together with a brief discussion. Deprotection of **12a,b** using the catalyst-free alcoholysis procedure recently developed by Van der Eycken was attempted, as this generates volatile byproducts that can be easily removed and avoids the need for further purification.[34] Unfortunately, there was no evidence for liberation of the phosphine even after heating ethanol solutions of **12a,b** at reflux for 48 h and near-quantitative amounts of the borane adducts were recovered.

Taking a lead from the pioneering work of Fu,[35] **9a,b** were expected to be stable for long periods of time as their phosphonium salts, with the advantage that they could ultimately be used as replacements for the corresponding phosphine, since deprotonation by a Brønsted base under the

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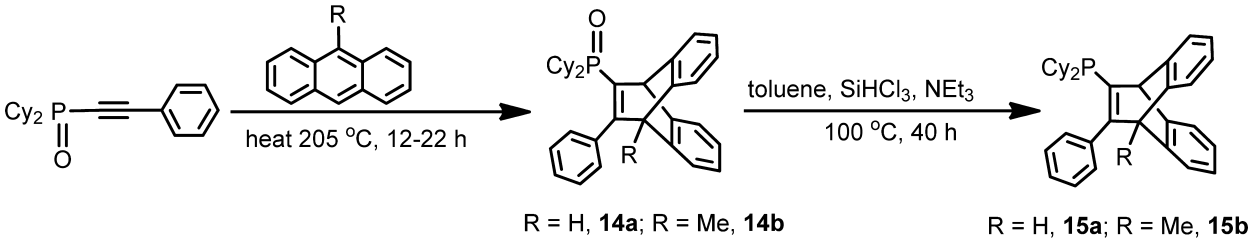
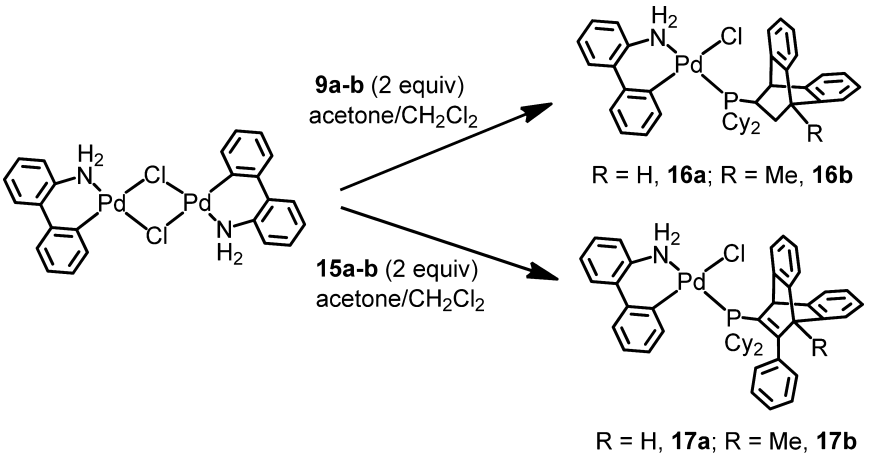
Scheme 2



Scheme 3



reaction conditions typically used for palladium-catalyzed cross-coupling would liberate the trialkylphosphine. Following a procedure developed by Denmark to transform air-stable phosphine–borane adducts directly into phosphonium tetrafluoroborate salts,[36a] treatment of **12a,b** with $HBF_4{\cdot}OEt_2$ in dichloromethane at 0 °C followed by an aqueous fluoroboric acid wash gave **13a,b** as spectroscopically and analytically pure white crystalline solids in high yield.[36] The proton-coupled ^{31}P NMR spectra of **13a,b** contain doublets at δ 33.7 and 31.9, respectively, with characteristically large one-bond phosphorus–hydrogen coupling constants of 477 and 475 Hz, respectively; similar values of $^1J_{PH}$ have been reported for $[Cy_2(t\text{-Bu})PH][BF_4]$,[36] $[Cy_2EtPH][BF_4]$,[37] and $[Cy_3PH][BF_4]$.[38] The corresponding phosphonium protons appear as doublets at δ 5.91 and 5.90 in the ^1H NMR spectra of **13a,b**, respectively; a doublet at δ 4.95 (J_{PC} = 6.1 Hz) and a singlet at δ 4.50 belong to the protons attached to the two bridgehead carbon atoms of **13a**, and a doublet at δ 4.93 (J = 6.4 Hz) corresponds to the sole bridgehead proton of **13b**.

With the intention of undertaking a systematic comparison between the performance of dihydro-KITPHOS monophosphines and that of their corresponding biaryl-like counterparts as ligands for palladium-catalyzed Suzuki–Miyaura cross-coupling, it was also necessary to prepare **15b**; this was achieved in good yield by following the procedure reported for **15a**,[28a] which involved a Diels–Alder reaction between (dicyclohexylphosphinoylethynyl)benzene and 9-methylanthracene followed by reduction of the resulting KITPHOS monoxide **14a,b** with chlorosilane/triethylamine in toluene at 110 °C (Scheme 2). KITPHOS monophosphine **15b** was isolated as an air-stable off-white crystalline solid after purification by column chromatography; the identity and purity were unequivocally established using conventional spectroscopic and analytical techniques.

Synthesis of Palladium Precatalysts. With the intention of comparing the performance of dihydro-KITPHOS monophosphines and that of their associated biaryl-like counterparts as ligands for palladium-catalyzed Suzuki–Miyaura cross-coupling, precatalysts **16a,b** and **17a,b** were prepared by reaction of the corresponding phosphine with the chloride-bridged dimer $[Pd\{\kappa^2N2',C1\text{-}2\text{-}(2'\text{-}NH_2C_6H_4)C_6H_4\}(\mu\text{-}Cl)]_2$,[49] in a 1/1 mixture of dichloromethane and acetone at room temperature (Scheme 3). Precatalysts of this type have recently been introduced by Buchwald and co-workers as air- and moisture-stable complexes that can be "activated" under standard conditions by elimination of HCl and 9*H*-carbazole to afford the active monocoordinated species L_1Pd^0.[40] The use of this new class of one-component precatalysts is markedly more efficient than generating the catalyst from a source of Pd(0) such as $Pd_2(dba)_3$, as competitive coordination of dba retards formation of the catalyst and/or diminishes reactivity, or from $Pd(OAc)_2$, which must be reduced in situ and generally requires more than 2 equiv of phosphine. Precatalysts **16a,b** and **17a,b** were all purified by column chromatography, isolated as air-stable off-white solids, and crystallized by slow diffusion techniques.

Interestingly, the room-temperature ^{31}P NMR spectra of **16a,b** each contain two broad signals, while those of **17a,b** contain only one broad resonance. Buchwald[40] and Krska[41] have both reported that the ^{31}P NMR spectra of the corresponding precatalysts based on SPHOS and a trioxa-6-phosphaadamantane ligand, respectively, also contain two broad signals; in both cases the line broadening was unspecifically attributed to the presence of rotamers in exchange. In the present work, the origin of this line broadening was investigated further by conducting a variable-temperature ^{31}P NMR study on **17a** in d_2-DCM, the result of which is shown in Figure 3. At room temperature the spectrum

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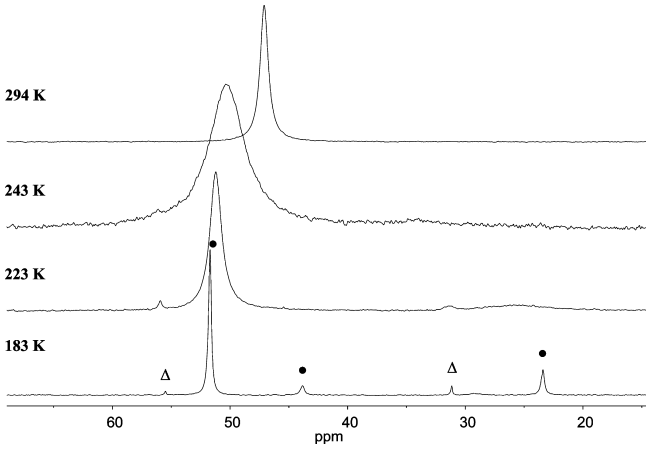

Figure 3. Selected variable-temperature $^{31}P\{^{1}H\}$ NMR spectra of [Pd{$\kappa^2N2',C1$-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl{11-(dicyclohexylphosphino)-9-methyl-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}] (**17a**): (●) major rotamer; (△) minor rotamer.

consists of a single peak at 47.1 ppm with a half-height line width of 156 Hz. As the temperature is lowered, the peak broadens and at 243 K has a half-height line width of 700 Hz. Below this temperature two distinct sets of signals begin to evolve; one of these appears as two resonances at 55.5 and 31.2 ppm (△) that sharpen rapidly as the temperature is lowered. However, these comprise only a very minor component of the exchanging system and will be disregarded in the following discussion. The major components (●) appear as a set of three signals at 51.7 (**A**), 43.8 (**B**), and 23.4 ppm (**C**) which sharpen more slowly over a wider reduced temperature range and have relative proportions of 79.8, 5.5, and 14.7%, respectively, at 183 K.

More detailed information concerning the exchange process was obtained from a magnetization transfer experiment (EXSY). The low-temperature ^{31}P EXSY spectrum of **17a** (see Figure S3 in the Supporting Information) clearly shows that the signals at 51.7, 43.8, and 23.4 ppm are in mutual chemical exchange, whereas the minor signals at 55.5 and 31.2 ppm are involved in a separate process where the exchange is much slower. These observations are consistent with the major components comprising a system of three interchanging conformers, and line-shape analysis using the program gNMR was undertaken of the ^{31}P NMR spectra across the overlapping temperature ranges 183−313 K (dichloromethane-d_2) and 295−373 K (toluene-d_8). Apparently satisfactory fits using a single exchange rate were obtained between 223 and 373 K, but this is clearly an oversimplification, and from 183 to 213 K it was necessary to use three separate rates to achieve an acceptable simulation. The application of the Boltzmann and Eyring equations to this rather limited data set was used to determine the relative ground-state energies and barrier heights shown in Table 1; the results are also presented schematically in Figure 4 for the three-conformer system. It is noteworthy that the most stable conformer (**A**) is associated with the lowest barriers to interconversion, while the least stable conformer (**B**) is associated with lower barriers than intermediate **C**. The foregoing behavior can be attributed most reasonably to restricted rotation about either the Pd−P bond or the P−"anthracyl" bond of **17a** (but probably not both, since this would lead to more complex spectra). To test this, low-temperature ^{31}P NMR spectra were obtained for **9a** and its

Table 1. Approximate Relative Energies of Conformers A−C of 17a and the Barriers to Conversion

conformer or barrier	rel energy/kJ mol^{-1}
A	0
A/B	25.1
B	4.2
B/C	41.2
C	2.5
C/A	31.1

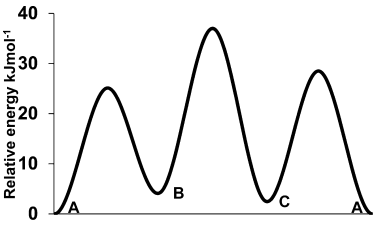

Figure 4. Approximate energies involved in the interconversion among conformers **A**−**C** of **17a**.

sulfide and in neither case were any significant changes in the spectra observed at temperatures down to 183 K, thus suggesting that rotation about the P −anthracyl bond in **17a** would also be relatively free. On the basis that hindrance to rotation about the Pd−P bond is responsible for the NMR line broadening, the three idealized conformers **17a**$_i$, **17a**$_{ii}$, and **17a**$_{iii}$ may be considered; these are shown in Figure 5 as

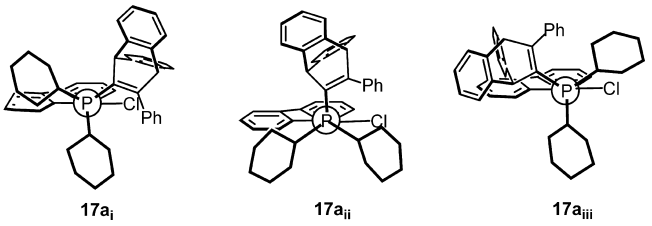

Figure 5. Newman projections of the three possible solution-state conformations of **17a**.

Newman projections down the P−Pd bond. Of the three possible solution-state conformations **17a**$_{ii}$ corresponds most closely to the situation in the crystal structure and is therefore probably the most stable (**A**).

Even though the spectroscopic properties and analytic data for **16a**,**b** and **17a**,**b** are all fully consistent with the proposed formulation, the exchange broadening in the ^{31}P and ^{1}H NMR spectra prompted us to undertake single-crystal X-ray analyses of **16a** and **17a**,**b** to compare their key structural features with those for closely related complexes of electron-rich biaryl monophosphines. Perspective views of the molecular structures of **16a** and **17a**,**b** are given in Figures 6−8, respectively. In each precatalyst, the phosphine occupies the coordination site *trans* to the amin,e since it has a much lower *trans* influence than the strongly σ-donating metalated aromatic ring. The Pd−P(1) distances of 2.2737(11) Å (**16a**), 2.2699(7) Å (**17a**), and 2.2641(13) Å (**17b**) are similar to those of 2.270(1) and 2.2786(9) Å in [Pd{$\kappa^2N2',C1$-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl-(XPHOS)][42] and [Pd(κ^2C,N-$C_6H_4CH_2CH_2NH_2$-2)Cl-(SPHOS)],[40a] respectively, as are the Pd−C(1) bond lengths of 2.029(5) Å (**16a**), 2.005(3) Å (**17a**), and 2.005(5) Å (**17b**); the corresponding distances in [Pd{$\kappa^2N2',C1$-2-(2′-$NH_2C_6H_4$)-

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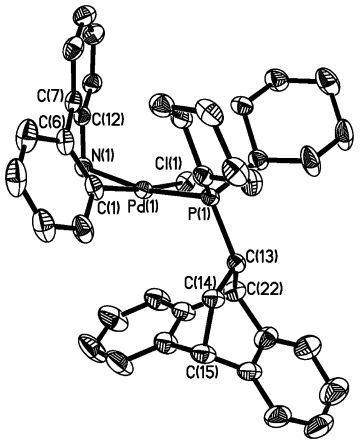

Figure 6. Molecular structure of [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)-C_6H_4}Cl{11-(dicyclohexylphosphino)-9,10-dihydro-9,10-ethanoanthracene}] (**16a**). Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 40% probability level.

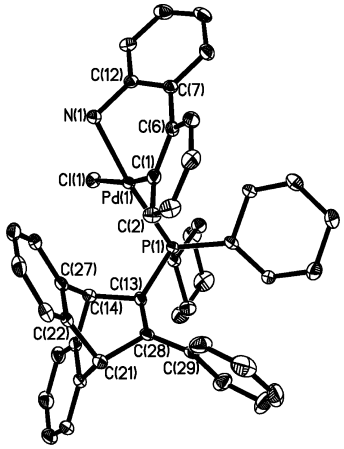

Figure 7. Molecular structure of [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)-C_6H_4}Cl{11-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}] (**17a**). Hydrogen atoms and the dichloromethane and hexane molecules of crystallization have been omitted for clarity. Ellipsoids are at the 40% probability level.

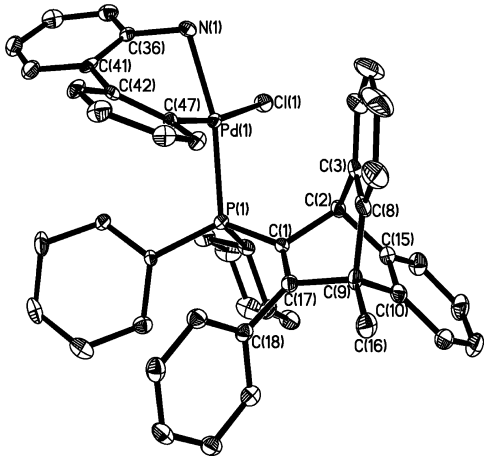

Figure 8. Molecular structure of [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)-C_6H_4}Cl{11-(dicyclohexylphosphino)-9-methyl-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}] (**17b**). Hydrogen atoms and the dichloromethane molecule of crystallization have been omitted for clarity. Ellipsoids are at the 40% probability level.

C_6H_4}Cl(XPHOS)][42] and [Pd(κ^2-*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)-Cl(SPHOS)][40a] are 2.022(4) and 2.004(4) Å, respectively. The P(1)−Pd−Cl(1) angles of 97.08(4)° (**16a**), 96.99(2)° (**17a**), and 97.95(4)° (**17b**) lie within a fairly narrow range, as do the P(1)−Pd−C(1) angles of 93.52(12)° (**16a**), 91.83(8)° (**17a**), and 91.67(14)° (**17b**); all are greater than the ideal value of 90° and close to the corresponding angles in [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl(SPHOS)][45] and [Pd(κ^2-*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)Cl(SPHOS)].[40a]

Steric and Electronic Properties of KITPHOS-Based Monophosphines: Comparison with Biaryl Monophosphines. The steric properties of electron-rich trialkyl- and biaryl-based monophosphines are integral to their efficacy in palladium-catalyzed C−C and C−N bond formation. Experimental and computational studies have suggested this to be associated with promoting the formation and stabilization of a monocoordinate complex and, in the case of biaryl monophosphines, to the longevity of the catalyst due to additional stabilization of intermediates by interaction of the non-phosphine-containing aromatic π system with the palladium center. Surprisingly, until recently, there have been no attempts to quantify the steric properties of this highly versatile class of ligand. As calculations using the Tolman model[43] have often proven difficult for elaborate phosphines and N-heterocyclic carbenes (NHC), Nolan and Cavello recently proposed an alternative model to measure steric bulk,[44] the percent buried volume (%V_{bur}), defined as the percent of the total volume of a sphere occupied by a ligand; the volume of this sphere represents the potential coordination sphere space around the metal occupied by a ligand and is calculated using the Samb*V*ca software.[45] Gold(I) complexes were shown to be a suitable model for quantifying the steric parameters of phosphines, as there was an excellent correlation between the %V_{bur} value in [Au(PR_3)Cl] and the Tolman cone angle (θ). Since crystallographic data are available for several gold(I) complexes of KITPHOS and dihydro-KITPHOS monophosphines, their percent buried volumes have been determined and compared with the corresponding values for selected gold(I) complexes of biaryl monophosphines, full details of which are presented in Table 2. The %V_{bur} values of 43.8 and 45.0 for KITPHOS monophosphine **15a** coordinated to $AuNTf_2$ and Au(tht), respectively, are similar, which suggests that buried volume calculations carried out with Au(I) complexes provide a reliable and accurate measure of the steric properties of the monophosphine (entries 1 and 2); this is reinforced by values of 45.5 and 46.0 determined for the corresponding gold(I) complexes of 2-MeOKITPHOS (entries 5 and 6).

Surprisingly, the %V_{bur} value of 44.4 calculated for dihydro-KITPHOS monophosphine **9a** in [LAuCl] is similar to those of 43.8 and 45.8 for biaryl-like KITPHOS monophosphines **15a**,**b**, respectively, in the same complexes and close to that of 45.0 in the corresponding tetrahydrothiophene adduct (entries 1−4). As **9a** lacks a proximal phenyl ring, its larger than expected %V_{bur} may suggest that this fragment does not contribute significantly to the steric profile, although the different geometrical constraints imposed by the sp^3 nature of the two-carbon bridge of the bicyclic framework in **9a** in comparison with the planar double bond in **15a**,**b** might be responsible for the unexpected similarity in their steric parameters. It will be necessary to analyze a much larger cohort of "substituted" KITPHOS-based monophosphines in order to understand what factors control the steric profile of these ligands. This is in stark contrast to the corresponding comparison between PCy_2Ph and

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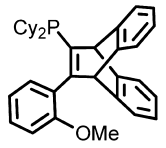
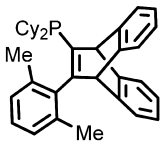
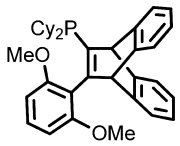
Table 2. $\%V_{bur}$ Values Calculated for KITPHOS Monophosphines and Biaryl Monophosphines in [(L)Au(I)] and [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl(L)] Complexes



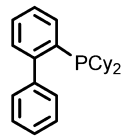
2-MeOKITPHOS



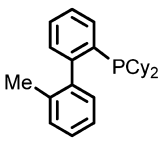
2,6-MeKITPHOS



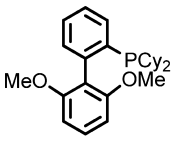
2,6-MeOKITPHOS



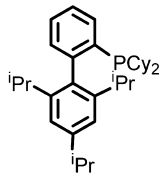
Cy-JohnPhos



MePHOS



SPHOS



XPHOS

entry	complex	$\%V_{bur}$[a]	cone angle θ/deg[b]
1	**15a**·AuNTf$_2$[29d]	43.8	206
2	**15a**·Au(tht)[29c]	45.0	209
3	**9a**·AuCl	44.2	206
4	**15b**·AuCl	45.8	212
5	2-MeOKITPHOS·AuCl[29d]	45.5	211
6	2-MeOKITPHOS·AuNTf$_2$[29d]	46.0	213
7	2,6-MeKITPHOS·AuNTf$_2$[29e]	45.7	212
8	2,6-MeOKITPHOS·AuNTf$_2$[29e]	46.0	213
9	PCy_2Ph·AuCl[46]	32.7	159
10	Cy-JohnPhos·AuCl[47]	46.7	226
11	MePHOS·AuCl[48]	49.3	238
12	SPHOS·AuCl[47]	49.7	240
13	XPHOS·AuCl[48]	53.1	256
14	(*t*-Bu)$_3$P·AuCl[49]	38.1	182
15	precatalyst **16a**	39.9	189
16	precatalyst **17a**	36.5	176
17	precatalyst **17b**	35.7	173
18	precatalyst **18**	30.5	152

[a]$\%V_{bur}$ for Au−P bond length at 2.28 A. [b]Calculated by linear regression.

Cy-JohnPhos in [LAuCl], which has been used to evaluate the steric influence of the proximal phenyl ring; the $\%V_{bur}$ values of 32.7 and 46.7, respectively, clearly show that the biaryl phenyl ring has a marked influence and increases the buried volume by 14% (entries 9 and 10). Moreover, the buried volume of biaryl monophosphines increases quite dramatically as a function of the biaryl substitution, reaching a value of 53.1 for XPHOS, which corresponds to a $\Delta\%V_{bur}$ value of 6.4 from Cy-JohnPhos (entries 11−13). In contrast, substitution of the aryl ring in biaryl-like KITPHOS monophosphines does not appear to affect steric bulk either to the same extent or in the same manner, as the buried volumes for **15a** and its 2-OMe-, 2,6-OMe_2-, and 2,6-Me_2-substituted counterparts in LAuX all lie within in a narrow range between 43.8 and 46.0, corresponding to a $\Delta\%V_{bur}$ value of 2.2% (entries 5−8).

The gold(I) chloride complexes of **9a** and P^tBu_3 have been used to evaluate and compare their steric properties, and the $\%V_{bur}$ values of 44.2 and 38.1, respectively, clearly lend some validity to our description of dihydro-KITPHOS monophosphines as bulky trialkyl-type monophosphines. Moreover, since P^tBu_3 is an effective ligand for a range of palladium-catalyzed transformations, the additional steric bulk associated with dihydro-KITPHOS monophosphines may well manifest itself in catalyst performance. As $\%V_{bur}$ calculations have shown that the steric bulk of P^tBu_3 depends on the number and size of additional ligands coordinated directly to the metal center, with an interest in further developing the use of KITPHOS-based monophosphines in palladium catalysis, the buried volumes for **9a** and **15a,b** in their precatalysts [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}(Cl)L] (**16a**, **17a,b**) have also been calculated, the results of which are given in Table 2 (entries 15−17). For each KITPHOS monophosphine, the $\%V_{bur}$ value is markedly smaller than the corresponding value for its LAuX complex; the average value of 37.4 represents a 16% decrease in $\%V_{bur}$. Considering PCy_2Ph as the reference for biaryl monophosphines, precatalyst [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)-C_6H_4}Cl(PCy_2Ph)] was also prepared and its crystal structure determined; a perspective view of the molecular structure is shown in Figure S2 of the Supporting Information. As for KITPHOS monophosphines, the buried volume of 30.5% for PCy_2Ph in this precatalyst is also smaller than the corresponding value of 32.7 in (PCy_2Ph)AuCl, though this reduction is much less pronounced.

Interestingly, dihydro-KITPHOS monophosphine **9a** has the largest steric bulk in its precatalyst with a $\%V_{bur}$ of 39.5 and a cone angle of 189°, while **15a,b** are decidedly smaller with $\%V_{bur}$ values of 36.5 and 35.7, respectively. On the basis of this limited comparison, KITPHOS monophosphines appear to be sterically malleable and capable of adjusting their bulk according to the immediate surroundings/environment: i.e., the space available around the metal center. Thus, there appear to be subtle differences in the factors that influence the steric bulk of KITPHOS monophosphines in comparison with their biaryl counterparts, as gauged by the trends and absolute values of $\%V_{bur}$ in Table 2; however, more data will clearly be required to lend credibility and validity to this interpretation.

The steric parameters of selected KITPHOS-based and biaryl monophosphines have also been determined using Solid-G calculations (Table 3), as this method provides a measure of steric congestion in terms of percentage of the metal coordination sphere shielded by the ligand; the *G* parameter essentially measures the probability of an incoming reagent not

Table 3. *G* Parameters for KITPHOS and Biaryl Monophosphines Calculated from the Solid Angle Data[a]

entry	phosphine	*G* param[a]	cone angle θ/deg[b]
1	**9a**	49.7	179
2	**9b**	50.57	181
3	**15a**	53.5	188
4	**15b**	52.5	186
5	2-MeOKITPHOS	55.0	192
6	2,6-MeKITPHOS	56.9	196
7	2,6-MeOKITPHOS	58.0	198
8	PCy_2Ph	33.9	142
9	Cy-JohnPhos	52.9	187
10	MePHOS	54.5	190
11	SPHOS	61.0	205
12	XPHOS	73.1	234
13	(*t*-Bu)$_3$P	37.6	151

[a]Calculated using Solid-G.[53] [b]Equivalent cone angle calculated from the on-linear relationship $\Omega = 100[1 - \cos(\theta/2)]$, where $G = 100(\Omega/(4\pi))$.

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accessing the metal center.[50] The *G* parameter is calculated from the solid angle, Ω, which corresponds, at least visually, to the area of the ligand projection shadow (*A*) formed by a light source originating from the central metal of the organometallic complex and located at the center of a sphere of radius 13 Å. Qualitatively, the *G* parameters calculated for KITPHOS monophosphines show a trend similar to that for the $\%V_{bur}$ values in that **9a** and **15a,b** are all only marginally smaller than their aryl ring substituted counterparts and, regardless of the extent of substitution, all the *G* parameters lie within a narrow range between 49.7 and 58.0 corresponding to cone angles of 179 and 198°, respectively (entries 1−7). For comparison, the *G* parameters for the biaryl monophosphines show that steric congestion at the metal center increases rapidly with increasing substitution of the lower aryl ring (entries 8−12); however, the *G* values of 52.9 and 54.5 for JohnPhos and MePHOS, respectively, are slightly smaller than anticipated on the basis of the trend in buried volumes and present steric congestion similar to that of unsubstituted or 2-OMe-substituted KITPHOS monophosphines, which have *G* parameters of 53.5 and 55.0, respectively.

As the donor properties of monophosphines also play an integral role in achieving efficient catalysis by influencing either the oxidative addition and/or transmetalation step, it is surprising that there are so few reports that provide details on the electronic properties of commonly used bulky electron-rich monodentate phosphines. Thus, we have undertaken a comparative study and computed the ligand electronic parameters for selected KITPHOS-based monophosphines and their corresponding biaryl-based counterparts. Initially a correlation between the computed electronic parameter (CEP) and the experimentally measured Tolman electronic parameter (TEP) was determined for a range of phosphines, as previously described by Clot and co-workers.[51] DFT (B3LYP) calculations were conducted on $LNi(CO)_3$, and a frequency calculation on the fully optimized structure provided the A_1 ν(CO) vibrational frequency and comparison with the corresponding experimental IR stretching frequencies gave a correlation coefficient of 0.984. Regression analysis gave the following equation relating the computed electronic parameter (cm^{-1}) to the experimentally measured TEP (cm^{-1}):

$$TEP = 0.9473(CEP) + 35.638$$

This function has been used to estimate the TEPs for KITPHOS monophosphines **9a,b**, **15a,b**, and 2,6-MeOKITPHOS together with a range of related biaryl monophosphines; values are given in Table 4. The estimated TEPs provide a measure of the net donor power of KITPHOS monophosphines, which decreases in the order 2,6-MeOKITPHOS > **9b** > **9a** > **15b** > **15a**; this series is supported by the J_{PSe} values, which increase in the order 2,6-MeOKITPHOS (684 Hz), **9b** (694 Hz), **9a** (696 Hz), **15b** (702 Hz), and **15a** (702 Hz). The magnitude of this parameter is inversely correlated with the σ-donor strength of PR_3.[52] The estimated TEPs for the biaryl monophosphines show a similar trend, with the donor strength decreasing in the order SPHOS > XPHOS > MePHOS > Cy-JohnPhos. A comparison of the estimated TEPs shows the net donor power of **9a,b** and **15a,b** to be similar to that of MePHOS and Cy-JohnPhos, while 2,6-OMeKITPHOS more closely resembles SPHOS.

Palladium-Catalyzed Suzuki−Miyaura Coupling of Aryl Chlorides. Having previously shown that biaryl-like KITPHOS monophosphines combine with $Pd(OAc)_2$ to form highly efficient catalysts for the Suzuki−Miyaura coupling[29a,b] and because bulky electron-rich trialkylphosphines also generally form effective catalysts for this reaction, we chose to use this transformation to investigate the efficacy of trialkyl-type dihydro-KITPHOS monophosphines against their biaryl-like counterparts and to explore the effect on catalyst performance of removing the proximal aryl ring and the double bond in the anthracene-derived bicyclic framework. Precursors **16a,b** and **17a,b** were used for the catalyst evaluation, as they are easy to prepare, air-stable, a convenient source of the active monocoordinated complex L_1Pd^0, and cost-effective, since only 1 equiv of phosphine is required per palladium atom; compare this with catalysts generated from palladium acetate, which typically require 2.5 equiv of the phosphine to achieve optimum performance. Our preliminary comparison and optimization focused on the benchmark coupling between 4-chloroacetophenone and benzeneboronic acid using 0.25 mol % precatalyst in toluene at 50 °C with K_3PO_4 as base; for brevity and clarity selected results are presented in Table 5 and full details of the optimization study are provided in Table S1 of the Supporting Information. Under these conditions precatalysts **17a,b** were marginally more efficient than **16a,b**; the former gave conversions of 91% (**17a**) and 87% (**17b**) after 30 min in comparison with 81% (**16a**) and 79% (**16b**) for the latter, in the same time (entries 1−2). Excellent conversions were also obtained in THF, under otherwise identical conditions; however, the presence of added water resulted in slightly lower conversions.[53] As previously reported, the correct combination of base and solvent is crucial to achieving good conversions; K_3PO_4 was most effective for reactions conducted in toluene, while KF and K_3PO_4 were both highly effective for reactions in THF, the combination of toluene and KF was slightly less efficient, K_2CO_3 was more effective in toluene than THF, and other bases, such as alkali-metal acetates and sodium *tert*-butoxide, were markedly less effective in both solvents. Although **9a,b** are highly air-sensitive, following a protocol popularized by Fu and co-workers,[54] catalyst mixtures generated from $Pd(OAc)_2$ (0.5 mol %), 2.5 equiv of the corresponding phosphonium salt, **13a** or **13b**, and K_3PO_4 in THF gave conversion of 73% and 84%, respectively, for the cross-coupling between 4-chloroacetophenone and benzene-

Table 4. CEP (cm^{-1}) and TEP (cm^{-1}) for Selected Monophosphines

ligand	TEP	CEP
P(*t*-Bu)$_3$	2056.1	2132.5
P(*i*-Pr)$_3$	2059.2	2138.0
P(*o*-tolyl)$_3$	2066.6	2142.6
PPh_2Me	2067.0	2144.7
PPh_2OMe	2072.0	2148.4
P(OEt)$_3$	2076.3	2155.1
P(OMe)$_3$	2079.5	2157.6
$PCy_2{}^iPr$	2057.9	2134.8
Cy-JohnPhos	2059.4	2136.3
MePHOS	2058.7	2135.6
SPHOS	2052.6	2129.1
XPHOS	2056.0	2132.7
9a	2057.0	2133.8
9b	2056.6	2133.4
15a	2058.1	2135.0
15b	2057.6	2134.4
2,6-MeOKITPHOS	2050.9	2127.4

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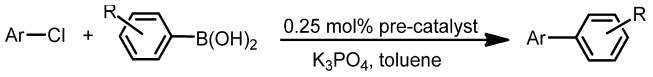
Table 5. Palladium-Catalyzed Suzuki–Miyaura Coupling of Aryl and Heteroaryl Chlorides Using Precatalysts 16a,b and 17a,b[a]



entry	Ar	R	precatalyst	temp (°C)	time (h)	conversn (%)[b]
1	C_6H_5	H	**16a,b**	50	0.5	81, 79
2	C_6H_5	H	**17a,b**	50	0.5	91, 87
3	4-CN	H	**16a,b**	50	0.5	59, 57
4	4-CN	H	**17a,b**	50	0.5	86, 88
5	2-CN	H	**16a,b**	60	1	81, 83
6	2-CN	H	**17a,b**	60	1	97, 88
7	4-CHO	H	**16a,b**	50	1	51, 56
8	4-CHO	H	**17a,b**	50	1	72, 80
9	2-CHO	H	**16a,b**	60	1	55, 59
10	2-CHO	H	**17a,b**	60	1	84, 90
11	2-C(O)Me	H	**16a,b**	70	4	88, 86
12	2-C(O)Me	H	**17a,b**	70	4	89, 92
13	3-py	H	**16a,b**	50	1	84, 82
14	3-py	H	**17a,b**	50	1	95, 85
15	2-py	H	**16a,b**	60	1	70, 71
16	2-py	H	**17a,b**	60	1	88, 78
17	4-OMe	H	**16a,b**	70	3	38, 44
18	4-OMe	H	**17a,b**	70	3	71, 69
19	4-Me	H	**16a,b**	80	3	74, 69
20	4-Me	H	**17a,b**	80	3	87, 75
21	$4\text{-}NH_2$	H	**16a,b**	80	6	83, 79
22	$4\text{-}NH_2$	H	**17a,b**	80	6	92, 93
23	$2,6\text{-}Me_2$	H	**16a,b**	80	6	81, 76
24	$2,6\text{-}Me_2$	H	**17a,b**	80	6	96, 89
25	$2,6\text{-}Me_2$	2-Me	**16a,b**	70	7	95, 89
26	$2,6\text{-}Me_2$	2-Me	**17a,b**	70	7	41, 46
27	$2,6\text{-}Me_2$	2-Me	**16a,b**	70	14	76, 74

[a]Reaction conditions: 1 mmol of Ar-Cl, 1.5 mmol of $ArB(OH)_2$, 2.0 mmol of K_3PO_4, 2.5 μmol (0.25 mol %) of **16a,b** and **17a,b,** 2 mL of toluene. [b]Conversions determined by GC analysis of the reaction mixture using decane as internal standard and based on aryl chloride. Average of three runs.

boronic acid. While these conversions were comparable to those of 84% and 92% obtained with **16a,b**, respectively, the need for a higher catalyst loading together with 2.5 equiv of the phosphonium salt further underpins the cost effectiveness and efficacy of the palladium precatalysts. Good conversions could also be obtained in toluene with a catalyst loading as low as 0.02 mol %, although significantly longer reaction times were required to reach acceptable conversions.

Having identified a set of optimum conditions and obtained encouraging conversions, catalyst testing was extended to the coupling of a range of aryl and heteroaryl chlorides with arylboronic acids. Gratifyingly, **16a,b** and **17a,b** formed effective catalysts for the Suzuki–Miyaura coupling of a range of activated aryl and heteroaryl chlorides with arylboronic acids as well as unactivated and sterically challenging substrate combinations; full details are presented in Tables 5. Each of the precatalysts **16a,b** and **17a,b** gave good conversion for activated aryl chlorides under mild conditions; however, catalysts based on biaryl-like KITPHOS monophosphines **17a,b** consistently outperformed their dihydro-KITPHOS counterparts, albeit by only a small margin in some cases. For example, disparate conversions were obtained for the cross coupling between 4-chlorobenzonitrile and benzeneboronic acid; 0.25 mol % of **17a,b** gave conversions of 86% and 88%, respectively, after 0.5 h while **16a,b** only reached 59% and 57% conversion, respectively, in the same time, whereas, comparable conversions of 88/86% and 89/92% were obtained with **16a,b** and **17a,b**, respectively, for the reaction between 2-chloroacetophenone and benzeneboronic acid. Precatalysts **16a,b** and **17a,b** also efficiently promoted the cross-coupling of 2- and 3-chloropyridine with benzeneboronic acid, giving good conversions to the corresponding heterobiaryl under mild conditions in short reaction times. However, for these substrate combinations the difference in catalyst performance between **16a,b** and **17a,b** was less pronounced than for the aryl chlorides.

Electron-rich and sterically hindered coupling partners typically required longer reaction times and/or higher temperatures to reach good conversions. For example, **17a,b** formed highly efficient catalysts for the reaction between 4-chloroanisole and benzeneboronic acid; the conversions of 71% and 69%, respectively, after 3 h at 70 °C were markedly higher than those of 38% and 44% obtained with catalysts generated from **16a,b**, respectively. Similarly, **17a,b** both outperformed their dihydro-KITPHOS-based counterparts for the coupling of 4-chlorotoluene and benzeneboronic acid, although the difference in performance was less marked than for 4-chloroanisole. Interestingly, precatalysts **16a,b** gave conversions of 95% and 89%, respectively, for the sterically challenging substrate combination of 1-chloro-2,6-dimethylbenzene and 2-methylbenzeneboronic acid after 7 h at 70 °C, which is a marked improvement on the conversions of 41% and 46% obtained with **17a,b**, respectively, after the same time; however, conversions of 76% and 74%, respectively, were obtained after a reaction time of 14 h. Similarly, **16a,b** and **17a,b** also form efficient catalysts for the Suzuki–Miyaura coupling between aryl chlorides and 2,6-dimethoxybenzeneboronic acid, with **17a,b** giving slightly better conversions than **16a,b** across the limited range of substrates examined. Even though catalysts based on dihydro-KITPHOS monophosphines appear to be less efficient than their biaryl-like counterparts, good conversions have been obtained at relatively low catalyst loadings. However, more exhaustive catalyst testing will be required in order to establish the relative merits of these phosphines and to begin developing a structure–efficiency relationship. In this regard, we also note that while dihydro-KITPHOS monophosphines lack the proximal phenyl ring characteristic of biaryl-like KITPHOS monophosphines and Buchwald biaryl monophosphines, the aromatic rings of the anthracene-derived bicyclic architecture may be in an appropriate spatial arrangement with respect to the phosphorus donor to form a weak interaction to the palladium center and thereby stabilize Pd(0) intermediates; i.e. dihydro-KITPHOS monophosphines may combine features of electron-rich trialkyl and biaryl monophosphines. In this regard, a hybrid phosphine based on three tertiary alkyl groups, one of which contains a phenyl ring which adopts a spatial arrangement with respect to phosphorus that resembles a biaryl monophosphine, has recently been designed and shown to be an effective ligand for the palladium-catalyzed amination of aryl chlorides.[55]

CONCLUSIONS

Bulky electron-rich trialkyl-type dihydro-KITPHOS monophosphines have been prepared via Diels–Alder cycloaddition between an anthracene and dicyclohexylvinylphosphine oxide; these phosphines lack the "proximal" phenyl ring and adjacent

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alkyne-derived double bond of their biaryl-like KITPHOS counterparts. They are highly air-sensitive and are rapidly oxidized on silica gel during purification, which is entirely consistent with their trialkyl-type character. However, air-stable phosphonium salts and borane adducts have been prepared as well as cyclometalated palladium precatalysts of the type [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl(L)]. Most importantly, this study has revealed that biaryl-like KITPHOS monophosphines are more practical ligands for palladium-catalyzed Suzuki−Miyaura cross-coupling than their trialkyl-type counterparts, since they gave higher conversions across the majority of substrate combinations tested, albeit in some cases by a relatively small margin, and are also air-stable, easy to handle, available in higher overall yield, and markedly more cost effective. This study has also reinforced recent reports that the use of precatalysts is a more practical, efficient, and cost-effective approach than generating catalysts in situ from either the phosphine or phosphonium salt and a source of Pd(II) or Pd(0), since catalyst loadings can be reduced quite significantly, to achieve comparable conversions under similar conditions, and only 1 equiv of phosphine is required; both factors could translate into a significant cost savings. While dihydro-KITPHOS monophosphines lack the proximal biaryl-like phenyl ring of KITPHOS monophosphines, the aromatic rings of the anthracene-derived bicyclic architecture may be able to form a weak interaction to the palladium center and thereby stabilize Pd(0) intermediates; i.e. dihydro-KITPHOS monophosphines may combine features of electron-rich trialkyl and biaryl monophosphines. The steric parameters of both classes of KITPHOS monophosphine and a selection of biaryl monophosphines have been quantified using a combination of Solid-G and Salerno molecular buried volume calculations (Samb*V*ca) and the corresponding Tolman cone angles determined from correlations. Interestingly both methods show that the steric properties of KITPHOS monophosphines lie within a relatively narrow range, regardless of the substitution pattern of the aryl ring, whereas the buried volumes of their biaryl counterparts increase quite dramatically as a function of the biaryl substitution. Synthetic, spectroscopic, and computational studies are now underway to (i) further modify the KITPHOS framework in order to determine what features are key to improving catalyst performance, with an emphasis on understanding steric effects, (ii) explore whether the anthracene-based π system can interact with the palladium center and stabilize the active species, and (iii) identify the precise form of the rotamers responsible for the line broadening in the ^{31}P NMR spectra of the precatalysts.

EXPERIMENTAL SECTION

General Comments. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Dichloromethane and chloroform were distilled from calcium hydride, THF and toluene from sodium, and hexane and diethyl ether from Na/K alloy, under an atmosphere of nitrogen. Vinylmagnesium chloride, chlorodicyclohexylphosphine, dicyclohexylphenylphosphine, hydrogen peroxide, trichlorosilane, anthracene, and 9-methylanthracene were purchased from commercial suppliers and used without further purification. KITPHOS monophosphine **15a**,[28a] dicyclohexylphosphinoylethynyl)benzene,[32] and [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}(μ-Cl)]$_2$[39] were prepared as previously described. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on JEOL LAMBDA-500 and ECS-400 instruments. Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60F 254, and column chromatography was performed using Merck Kieselgel 60. Gas chromatography−mass spectrometry was performed on a Saturn 2220 GC-MS system using a factorFour VF-5 ms capillary column (30 m, 0.25 mm, 0.25 μm), and high-resolution mass spectrometry was conducted on a Waters Micromass LCT Premier mass spectrometer.

Synthesis of Dicyclohexylvinylphosphine Oxide (10). An oven-dried Schlenk flask was cooled to room temperature under vacuum, back-filled with nitrogen, charged with THF (20 mL) and vinylmagnesium bromide (1.0 M in THF, 6.45 mL, 6.45 mmol), and then cooled to −78 °C in a dry ice/acetone bath. Another flame-dried Schlenk flask was charged with THF (5 mL) and chlorodicyclohexylphosphine (1.45 g, 6.25 mmol), and the resulting solution was added dropwise to the solution of vinylmagnesium bromide via cannula transfer. The reaction mixture was warmed to room temperature and stirred for a further 2 h. The clear colorless solution was then cooled to 0 °C and H_2O_2 (35% aqueous solution, 1.76 mL, 20.0 mmol) added dropwise. After it was stirred for 30 min, the solution was diluted with diethyl ether (50 mL) and washed with water (50 mL) and the aqueous layer extracted with diethyl ether (2 × 50 mL). The organic phases were combined, dried over magnesium sulfate, and filtered, and the solvent was removed under vacuum to give the desired product as a highly viscous colorless liquid in 83% yield (1.24 g). ^{31}P{^{1}H} NMR (161.83 MHz, $CDCl_3$, δ): 46.1. ^{1}H NMR (500.16 MHz, $CDCl_3$, δ): 6.31 (m, 2H, C*H*═C*H*$_a$H$_b$), 6.01 (dddd, *J* = 23.5, 15.8, 11.9, 4.1 Hz, 1H, C*H*═CH$_a$*H*$_b$), 1.9 (m, 2H, Cy-*H*) 1.84−1.55 (m, 8H, Cy-*H*), 1.39−1.12 (m, 12H, Cy-*H*). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ): 136.5 (CH═CH_2), 127.0 (d, ^1J = 83.0 Hz, PCH═CH_2), 34.7 (d, *J* = 69.2 Hz, Cy), 26.5 (d, *J* = 12.5 Hz, Cy), 26.3 (d, *J* = 12.4 Hz, Cy), 25.9 (Cy), 25.6 (Cy), 24.4 (d, *J* = 3.9 Hz, Cy). LRMS (ESI$^+$): *m*/*z* 241 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{14}H_{25}PO$ [M + H]$^+$ *m*/*z* 241.1721, found *m*/*z* 241.1725.

Synthesis of 11-(Dicyclohexylphosphinoyl)-9,10-dihydro-9,10-ethanoanthracene (11a). Four 25 mL Wheaton V vials were each charged with dicyclohexylvinylphosphine oxide (0.400 g, 1.67 mmol) and anthracene (0.891 g, 5.01 mmol). The vials were sealed and gradually heated to 220 °C. After 20 min the temperature was lowered to 210 °C and the mixture heated for a further 12−16 h. The resulting dark brown residue was dissolved in the minimum amount of dichloromethane, placed on top of a silica gel column, and eluted with dichloromethane to remove unreacted anthracene before eluting with CH_2Cl_2/MeOH (95/5) to afford **11a** as a beige solid in 76% yield (2.12 g). Mp: 177−181 °C. ^{31}P{^{1}H} NMR (161.83 MHz, $CDCl_3$, δ): 52.8. ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 7.40 (m, 1H, C_6H_4) 7.31−7.24 (m, 3H, C_6H_4), 7.12−7.06 (m, 4H, C_6H_4), 4.71 (dd, *J* = 4.7, 1.4 Hz, 1H, bridgehead C*H*), 4.36 (br, 1H, bridgehead C*H*), 2.30 (m, 1H, Cy-*H*), 2.0−0.85 (m, 24H, Cy-*H* + PC*H*C*H*$_2$). ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$, δ): 144.9 (C_6H_4Q), 144.3 (C_6H_4Q), 142.9 (C_6H_4Q), 140.7 (C_6H_4Q), 126.3 (C_6H_4), 126.2 (C_6H_4), 125.9 (C_6H_4), 125.7 (C_6H_4), 123.9 (C_6H_4), 123.2 (C_6H_4), 122.9 (C_6H_4), 120.4 (C_6H_4), 44.1 (d, *J* = 3.7 Hz, bridgehead *C*H), 43.4 (bridgehead *C*H), 36.3 (d, *J* = 57.0 Hz, *C*H), 36.2 (d, *J* = 60.1 Hz, *C*H), 35.7 (d, *J* = 59.1 Hz, *C*H), 28.8 (CH_2), 27.6 (d, *J* = 1.9 Hz, CH_2), 27.9 (d, *J* = 11.2 Hz, CH_2), 27.8 (d, *J* = 9.5 Hz, CH_2), 27.6 (d, *J* = 5.2 Hz, CH_2), 26.7 (d, *J* = 7.9 Hz, CH_2), 26.2 (d, *J* = 3.2 Hz, CH_2), 26.1 (d, *J* = 3.1 Hz, CH_2), 26.0 (2 × CH_2), 25.8 (d, *J* = 2.7 Hz, CH_2). LRMS (ESI$^+$): *m*/*z* 419 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{28}H_{36}OP$ [M + H]$^+$ *m*/*z* 419.2504, found *m*/*z* 419.2505. Anal. Calcd for $C_{28}H_{35}OP$: C, 80.35; H, 8.43. Found: C, 80.66; H, 8.79.

Synthesis of 11-(Dicyclohexylphosphinoyl)-9-methyl-9,10-dihydro-9,10-ethanoanthracene (11b). Compound **11b** was prepared according to the procedure described above for **11a** on the same scale (4 × 1.67 mmol) and isolated as an analytically pure pale brown solid in 79% yield (2.29 g, 5.27 mmol) after purification by column chromatography. Mp: 173−175 °C. ^{31}P{^{1}H} NMR (161.83 MHz, $CDCl_3$, δ): 52.1. ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 7.40 (d, *J* = 8.1 Hz, 1H, C_6H_4), 7.27 (d, *J* = 7.9 Hz, 1H, C_6H_4), 7.23 (d, *J* = 8.1 Hz, 1H, C_6H_4), 7.11 (m, 4H, C_6H_4), 4.70 (d, *J* = 3.9 Hz, 1H, bridgehead C*H*), 2.35 (m, 1H, Cy-*H*) 1.95 (s, 3H, C*H*$_3$) 1.90−0.82 (m, 24H, Cy-*H* + PC*H*C*H*$_2$). ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$,

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δ); 146.4 (C_6H_4Q), 145.3 (C_6H_4Q), 145.2 (d, J = 11.4 Hz, C_6H_4Q), 141.1 (C_6H_4Q), 126.2 (C_6H_4), 126.0 (C_6H_4), 125.9 (C_6H_4), 125.8 (C_6H_4), 125.4 (C_6H_4), 122.6 (C_6H_4), 121.3 (C_6H_4), 120.4 (C_6H_4), 43.7 (bridgehead *C*H), 42.4 (d, J = 5.0 Hz, bridgehead *C*Me), 37.7 (d, J = 57.2 Hz, *C*H), 36.3 (d, J = 60.1 Hz, *C*H), 36.1 (CH_2), 35.7 (d, J = 60.1 Hz, *C*H), 27.6 (d, J = 1.9 Hz, CH_2), 27.0 (d, J = 12.4 Hz, CH_2), 26.9 (d, J = 9.4 Hz, CH_2), 26.5 (CH_2), 26.6 (d, J = 4.5 Hz, CH_2), 26.3 (d, J = 3.1 Hz, CH_2), 26.1 (d, J = 3.1 Hz, CH_2), 26.0 (s, 2 × CH_2), 25.7 (d, J = 3.0 Hz, CH_2), 17.9 (CH_3). LRMS (ESI$^+$): m/z 433 $[M + H]^+$. HRMS (ESI$^+$): exact mass calcd for $C_{29}H_{38}OP$ $[M+H]^+$ m/z 433.2660, found m/z 433.2664. Anal. Calcd for $C_{29}H_{37}OP$: C, 80.52; H, 8.62. Found: C, 80.64; H, 8.77.

Reduction of 11-(Dicyclohexylphosphinoyl)-9,10-dihydro-9,10-ethanoanthracene (11a). A flame-dried Schlenk flask was charged with **11a** (2.128 g, 5.09 mmol), toluene (75 mL), and triethylamine (34.1 mL, 245 mmol). Trichlorosilane (7.5 mL 74.5 mmol) was added slowly, the flask was sealed, and the mixture was heated at 110 °C for 72 h. The reaction mixture was diluted with diethyl ether (40 mL) and added slowly to a mixture of ice (10 g) and 20% aqueous sodium hydroxide (20 mL). After the mixture was stirred vigorously for 30 min, the organic layer was removed and the aqueous phase extracted with diethyl ether (3 × 30 mL). The organic fractions were combined, washed with $NaHCO_3$ (2 × 30 mL), water (2 × 20 mL), and brine (2 × 20 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum to afford **9a** as a spectroscopically pure beige solid in 83% yield (1.69 g). Mp: 116−118 °C dec. $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, δ): 11.4. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.31−7.24 (m, 4H, C_6H_4), 7.13−7.10 (m, 4H, C_6H_4), 4.37 (br, 1H, bridgehead *C*H), 4.29 (d, J = 5.9 Hz, bridgehead *C*H), 2.19 (m, 1H, Cy-*H*), 2.00−1.01 (m, 24H, Cy-*H* + PC*H*C*H*$_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 145.2 (d, J = 6.7 Hz, C_6H_4Q), 144.1 (C_6H_4Q), 143.2 (C_6H_4Q), 140.8 (C_6H_4Q), 126.1 (C_6H_4), 125.7 (2 × C_6H_4), 125.6 (C_6H_4), 125.1 (C_6H_4), 123.7 (C_6H_4), 122.9 (C_6H_4), 122.7 (C_6H_4), 47.6 (d, J = 16.1 Hz, bridgehead *C*H), 44.5 (bridgehead *C*H), 33.5 (d, J = 18.1 Hz, *C*H), 32.9 (d, J = 18.1 Hz, *C*H), 32.8 (d, J = 15.3 Hz, CH_2), 31.8 (d, J = 20.0 Hz, *C*H), 31.6 (d, J = 4.7 Hz, CH_2), 31.5 (d, J = 7.6 Hz, CH_2), 31.4 (d, J = 6.4 Hz, CH_2), 30.9 (d, J = 7.6 Hz, CH_2), 28.1 (d, J = 9.5 Hz, CH_2), 28.0 (d, J = 7.3 Hz, CH_2), 27.8 (d, J = 9.7 Hz, CH_2), 27.8 (d, J = 8.3 Hz, CH_2), 26.7 (CH_2), 26.6 (CH_2). LRMS (ESI$^+$): m/z 403 $[M + H]^+$. HRMS (ESI$^+$): exact mass calcd for $C_{28}H_{36}P$ $[M + H]^+$ m/z 403.2555, found m/z 403.2564. Anal. Calcd for $C_{28}H_{35}P$: C, 83.54; H, 8.76. Found: C, 83.77; H, 9.03.

Reduction of 11-(Dicyclohexylphosphinoyl)-9-methyl-9,10-dihydro-9,10-ethanoanthracene (11b). Compound **11b** was reduced according to the procedure described above for **11a** on the same scale to give **9b** as a spectroscopically pure off-white solid in 79% yield (1.63 g). An analytically and spectroscopically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. Mp: 119−123 °C dec. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, δ): 11.7. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.31−7.24 (m, 4H, C_6H_4), 7.16−7.13 (m, 4H, C_6H_4), 4.29 (d, J = 4.9 Hz, 1H, bridgehead *C*H), 2.30 (m, 1H, Cy-*H*), 1.98 (s, 3H, CH_3), 1.93−1.10 (m, 24H, Cy-*H* + PC*H*C*H*$_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 146.1 (C_6H_4Q), 145.6 (d, J = 7.6 Hz, C_6H_4Q), 145.1 (C_6H_4Q), 141.2 (d, J = 1.9 Hz, C_6H_4Q), 125.9 (C_6H_4), 125.6 (C_6H_4), 125.5 (C_6H_4), 125.4 (C_6H_4), 125.1 (C_6H_4), 122.6 (C_6H_4), 121.1 (C_6H_4), 120.2 (C_6H_4), 47.9 (d, J = 15.9, bridgehead *C*H), 42.6 (bridgehead *C*Me), 40.3 (d, J = 13.4 Hz, CH_2), 33.5 (d, J = 18.1 Hz, *C*H), 33.2 (d, J = 19.0 Hz, *C*H), 32.9 (d, J = 18.1 Hz, *C*H), 31.6 (CH_2), 31.5 (CH_2), 31.5 (d, J = 10.4 Hz, CH_2), 30.9 (d, J = 8.6 Hz, CH_2), 28.2 (d, J = 9.5 Hz, CH_2), 28.1 (d, J = 6.1 Hz, CH_2), 27.9 (d, J = 9.5 Hz, CH_2), 27.7 (d, J = 6.7 Hz, CH_2), 26.8 (CH_2), 26.6 (CH_2), 18.0 (CH_3). LRMS (ESI$^+$): m/z 417 $[M + H]^+$. HRMS (ESI$^+$): exact mass calcd for $C_{29}H_{39}P$ $[M + H]^+$ m/z 417.2711, found m/z 417.2705. Anal. Calcd for $C_{29}H_{38}P$: C, 83.61; H, 8.95. Found: C, 83.82; H, 9.17.

Synthesis of 11-(Dicyclohexylphosphino)-9,10-dihydro-9,10-ethanoanthracene−Trihydroborane (12a). A Schlenk flask containing **9a** (0.300 g, 0.744 mmol) in THF (20 mL) was treated dropwise with $BH_3{\cdot}SMe_2$ (1.0 M, 2.32 mL, 2.23 mmol) and the resulting solution stirred for 2−3 h, after which time saturated aqueous NH_4Cl (5 mL) was slowly added. The mixture was stirred for 1 h and then poured into water (50 mL) and extracted with dichloromethane (3 × 50 mL). The organic phases were combined, washed with saturated $NaHCO_3$ (50 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum. The product was purified by column chromatography, with hexane/ethyl acetate (98/2) as eluent, to afford **12a** as a spectroscopically pure white solid in 93% yield (0.29 g). Crystals suitable for X-ray structure determination were grown by slow diffusion of hexane into a dichloromethane solution at room temperature. Mp: 144−146 °C dec. $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, δ): 33.7 (q, J = 39.2 Hz). $^{11}B\{^1H\}$ NMR (128.27 MHz, $CDCl_3$, δ): −43.4 (d, J = 39.2 Hz). ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.40 (m, 1H, C_6H_4), 7.31−7.24 (m, 3H, C_6H_4), 7.15−7.07 (m, 4H, C_6H_4), 4.74 (d, J = 5.4 Hz, 1H, bridgehead *C*H), 4.36 (br t, J = 2.1 Hz, 1H, bridgehead *C*H), 2.18 (m, 1H, Cy-*H*), 2.05 (m, 1H, Cy-*H*), 1.95−0.85 (m, 23H, Cy-*H* + PC*H*C*H*$_2$), 0.4 (d, J = 98 Hz, 3H, BH_3). $^{13}C\{^1H\}$ NMR (100.52 MHz, $CDCl_3$, δ): 145.0 (d, J = 11.4 Hz, C_6H_4Q), 144.4 (C_6H_4Q), 142.6 (C_6H_4Q), 140.4 (C_6H_4Q), 126.2 (C_6H_4), 125.4 (4 × C_6H_4), 123.7 (C_6H_4), 123.1 (C_6H_4), 122.6 (C_6H_4), 44.7 (bridgehead *C*H), 44.0 (d, J = 2.9 bridgehead *C*H), 32.3 (d, J = 24.6 Hz, *C*H), 31.0 (d, J = 30.6 Hz, CH), 30.7 (d, J = 28.1 Hz, *C*H), 29.8 (CH_2), 27.9 (d, J = 3.0 Hz, CH_2), 27.9 (CH_2), 27.6 (CH_2), 27.2 (d, J = 11.5 Hz, CH_2), 27.1 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 26.7 (d, J = 11.4 Hz, CH_2), 25.8 (CH_2), 25.7 (CH_2); Anal. Calcd for $C_{28}H_{38}BP$: C, 80.77; H, 9.20. Found: C, 81.08; H, 9.39.

Synthesis of 11-(Dicyclohexylphosphino)-9-methyl-9,10-dihydro-9,10-ethanoanthracene−Trihydroborane (12b). Compound **12b** was prepared according to the procedure described above for **12a** on the same scale and isolated as a spectroscopically and analytically pure white solid in 89% yield (0.28 g), after purification by column chromatography, with hexane/ethyl acetate (98/2) as eluent. Mp: 149−153 °C dec. $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, δ): 32.8 (q, J = 36.8 Hz). $^{11}B\{^1H\}$ NMR (128.66 MHz, $CDCl_3$, δ): −43.5 (d, J = 36.8 Hz). ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.40 (dd, J = 6.9, 1.5 Hz, 1H, C_6H_4), 7.32−7.24 (m, 3H, C_6H_4), 7.18−7.10 (m, 4H, C_6H_4), 4.72 (d, 1H, J = 4.6 Hz, bridgehead *C*H), 2.27 (m, 1H, Cy-*H*), 1.96 (s, 3H, CH_3), 1.85−0.85 (m, 24H, Cy-*H* + PC*H*C*H*$_2$), 0.4 (br d, J = 111 Hz, 3H, BH_3). $^{13}C\{^1H\}$ NMR (100.52 MHz, $CDCl_3$, δ); 146.6 (C_6H_4Q), 145.5 (C_6H_4Q), 144.9 (d, J = 11.1 Hz, C_6H_4Q), 141.0 (C_6H_4Q), 126.3 (C_6H_4) 126.0 (C_6H_4), 125.9 (C_6H_4), 125.8 (C_6H_4), 125.8 (C_6H_4), 122.6 (C_6H_4), 121.3 (C_6H_4), 120.5 (C_6H_4), 45.2 (bridgehead *C*H), 42.5 (d, J = 2.8 Hz, bridgehead *C*Me), 37.3 (CH_2), 33.9 (d, J = 25.8 Hz, *C*H), 31.2 (d, J = 29.6 Hz, *C*H), 30.8 (d, J = 28.6 Hz, *C*H), 28.2 (2 × CH_2), 27.8 (CH_2), 27.4 (d, J = 11.4 Hz, CH_2), 27.3 (CH_2), 27.1 (CH_2), 27.0 (CH_2), 26.8 (d, J = 11.5 Hz, CH_2), 26.1 (CH_2), 26.0 (CH_2), 17.9 (CH_3). Anal. Calcd for $C_{29}H_{40}BP$: C, 80.92; H, 9.37. Found: C, 81.11; H, 9.52.

Synthesis of 9,10-Dihydro-9,10-ethanoanthracenyl-11-(dicyclohexylphosphonium) Tetrafluoroborate (13a). A flame-dried Schlenk flask was cooled under vacuum, back-filled with nitrogen, charged with phosphine−borane adduct **12a** (0.300 g, 0.721 mmol), and evacuated and filled with nitrogen. Dichloromethane (15 mL) was added, the resulting solution was cooled to 0 °C, and $HBF_4{\cdot}OEt_2$ (54 wt %, 1.46 mL, 10.8 mmol) was added dropwise by syringe. The mixture was stirred for 30 min at 0 °C and then warmed to room temperature (ca. 22 °C) and stirred for a further 30 min before HBF_4(aq) (48 wt %, 10 mL, 76 mmol) was added. The resulting biphasic mixture was stirred vigorously for 20 min and diluted with CH_2Cl_2 (15 mL), and the aqueous phase was separated and extracted with CH_2Cl_2 (2 × 10 mL). The organic phases were combined, dried, filtered, and concentrated to a thick syrup, which was added dropwise to a conical flask containing rapidly stirred diethyl ether (60 mL). The resulting solid was filtered, washed with diethyl ether, and dried under vacuum to afford **13a** as a spectroscopically pure white solid in 68% yield (0.24 g). Mp: 178−183 °C. $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, δ): 33.7. ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.55 (d, J = 7.1 Hz, 1H, C_6H_4), 7.46 (dd, J = 5.2, 3.4 Hz, 1H, C_6H_4), 7.36 (d, J = 7.2 Hz, 1H, C_6H_4), 7.29 (dd, J = 5.3, 3.4 Hz, 1H, C_6H_4), 7.24−7.12 (m, 4H, C_6H_4), 5.91 (d, J = 477 Hz, 1H, P*H*), 4.95 (d, J = 6.1 Hz, 1H, bridgehead *C*H), 4.50 (s, 1H, bridgehead *C*H),

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2.78 (br m, 1H, Cy-*H*), 2.45 (br m, 1H, Cy-*H*), 2.25 (br m, 1H, Cy-*H*), 1.91−1.09 (m, 22H, Cy-*H* + PC*HCH*$_2$). ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$, δ); 143.4 (C_6H_4Q), 143.7 (d, J = 14.1 Hz, C_6H_4Q), 141.5 (C_6H_4Q), 138.7 (C_6H_4Q), 127.7 (C_6H_4), 127.0 (C_6H_4), 126.9 (C_6H_4), 126.8 (C_6H_4), 125.2 (C_6H_4), 124.2 (C_6H_4), 124.0 (C_6H_4), 123.8 (C_6H_4), 45.1 (bridgehead *C*H), 42.3 (d, J = 2.9 Hz, bridgehead *C*H), 29.6 (d, J = 12.4 Hz, CH_2), 29.4 (d, J = 15.3 Hz, CH_2), 29.3 (d, J = 38.1 Hz, *C*H), 28.7 (d, J = 37.2 Hz, *C*H), 28.3 (d, J = 39.1 Hz, *C*H), 28.0 (d, J = 2.9 Hz, CH_2), 27.7 (d, J = 3.8 Hz, CH_2), 27.0 (d, J = 3.9 Hz, CH_2), 26.3 (d, J = 13.3 Hz, CH_2), 26.1 (CH_2), 25.9 (d, J = 13.4 Hz, CH_2), 25.9 (CH_2), 24.8 (CH_2), 24.7 (CH_2). LRMS (ESI$^+$): m/z 403 [M]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{28}H_{36}P$ [M]$^+$ m/z 403.2555, found m/z 403.2546. Anal. Calcd for $C_{28}H_{36}BF_4P$: C, 68.58; H, 7.40. Found: C, 68.91; H, 7.68.

Synthesis of 9-Methyl-9,10-dihydro-9,10-ethanoanthracen-yl-11-(dicyclohexylphosphonium) Tetrafluoroborate (13b). Compound **13b** was prepared according to the procedure described above for **13a**, on the same scale, and isolated as a spectroscopically and analytically pure white solid in 72% yield (0.26 g). Mp: 174−178 °C. ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$, δ): 31.9. ^{1}H NMR (500.16 MHz, $CDCl_3$, δ): 7.55 (d, J = 7.4, Hz, 1H, C_6H_4), 7.48 (d, J = 7.4 Hz, 1H, C_6H_4), 7.35 (d, J = 7.4 Hz, 1H, C_6H_4), 7.30−7.26 (m, 2H, C_6H_4), 7.22−7.14 (m, 3H, C_6H_4), 6.39 (d, J = 475 Hz, 1H, P-*H*), 5.90 (d, J = 475 Hz, 1H, P-*H*), 4.93 (d, J = 6.4 Hz, 1H, bridgehead *C*H), 2.87 (m, 1H, Cy-*H*), 2.42 (m, 1H, Cy-*H*), 2.01 (s, 3H, CH_3), 1.91−0.92 (m, 3H, Cy-*H* + PC*HCH*$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ): 145.7 (C_6H_4Q), 143.8 (C_6H_4Q), 142.0 (d, J = 13.4 Hz, C_6H_4Q), 139.0 (C_6H_4Q), 127.7 (C_6H_4), 127.0 (C_6H_4), 126.9 (C_6H_4), 126.7 (C_6H_4), 125.2 (C_6H_4), 124.2 (C_6H_4), 121.4 (C_6H_4), 121.3 (C_6H_4), 45.3 (bridgehead *C*H), 42.3 (d, J = 2.9 Hz, bridgehead *C*Me), 36.7 (CH_2), 29.6 (d, J = 41.0 Hz, *C*H), 29.4 (d, J = 7.6 Hz, CH_2), 29.2 (d, J = 38.3 Hz, *C*H), 28.8 (d, J = 38.1 Hz, *C*H), 28.1 (d, J = 2.9 Hz, CH_2), 27.9 (d, J = 3.8 Hz, CH_2), 27.8 (d, J = 3.2 Hz, CH_2), 26.4 (d, J = 13.4 Hz, CH_2), 26.2 (CH_2), 26.1 (d, J = 12.2 Hz, CH_2), 26.0 (CH_2), 25.0 (CH_2), 24.9 (CH_2), 17.6 (CH_3). LRMS (ESI$^+$): m/z 417 [M]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{29}H_{38}P$ [M]$^+$ m/z 417.2711, found m/z 417.2705. Anal. Calcd for $C_{29}H_{38}BF_4P$: C, 69.06; H, 7.59. Found: C, 69.29; H, 7.79.

Synthesis of 11-(Dicyclohexylphosphinoyl)-9-methyl-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (14b). Four 25 mL Wheaton V vials were each charged with (dicyclohexylphosphinoylethynyl)benzene (0.500 g, 1.60 mmol) and 9-methylanthracene (0.917 g, 4.78 mmol). The vials were sealed and gradually heated to 220 °C, and then after 20 min the temperature was lowered to 210 °C and the mixture was heated for a further 16 h. The resulting dark solid residue was purified by column chromatography, with CH_2Cl_2 as eluent to remove the unreacted 9-methylanthracene and then CH_2Cl_2/ethyl acetate (3/2), to afford **14b** as an off-white solid in 77% yield (2.49 g). ^{31}P{^{1}H} NMR (161.83 MHz, $CDCl_3$, δ): 49.0. ^{1}H NMR (500.0 MHz, $CDCl_3$, δ): 7.41 (d, J = 6.1 Hz, 2H, Ar-*H*), 7.30−7.23 (m, 5H, Ar-*H*, 7.05−7.01 (m, 4H, Ar-*H*), 6.71 (dd, J = 9.6, 3.8 Hz, Ar-*H*), 5.6 (d, J = 7.01 Hz, 1H, bridgehead C*H*), 5.23 (d, J = 2.3 Hz, 1H, bridgehead *C*H), 1.72 (s, 3H, CH_3), 1.70−0.90 (m, 22H, Cy-*H*). ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$, δ): 164.6 (d, J = 5.1 Hz, *C*═CP), 146.8 (C_6H_4Q), 146.0 (C_6H_4 Q), 139.8 (d, J = 79.7 Hz, C═*C*P), 137.1 (d, J = 3.5 Hz, C_6H_5Q), 127.6 (C_6H_5 *p*-C), 127.4 (C_6H_5 *o*-C), 127.3 (C_6H_5 *m*-C), 124.7 (C_6H_4), 124.6 (C_6H_4), 123.4 (C_6H_4), 120.6 (C_6H_4), 54.6 (d, J = 8.6 Hz, bridgehead *C*Me), 51.5 (d, J = 7.6 Hz, bridgehead *C*H), 37.2 (d, J = 67.1 Hz, Cy), 26.4 (d, J = 2.9 Hz, Cy), 26.3 (d, J = 3.8 Hz, Cy), 25.7 (d, J = 2.9 Hz, Cy), 25.6 (Cy), 25.3 (d, J = 2.9 Hz, Cy). LRMS (ESI$^+$): m/z 507 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{35}H_{40}OP$ [M + H]$^+$ m/z 507.2817, found m/z 507.2811. Anal. Calcd for $C_{35}H_{39}OP$: C, 82.97; H, 7.76. Found: C, 83.19; H, 8.03.

Reduction of 11-(Dicyclohexylphosphinoyl)-9-methyl-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (14b). A flame-dried Schlenk flask was charged with **14b** (0.70 g, 1.38 mmol), toluene (25 mL), and triethylamine (7.5 mL, 53.6 mmol). Trichlorosilane (1.35 mL, 13.4 mmol) was added slowly and the mixture heated at 110 °C for 72 h. The reaction mixture was diluted with diethyl ether (20 mL) and added slowly to a mixture of ice (10 g) and 20% aqueous NaOH (20 mL). After the mixture was stirred vigorously at room temperature for 30 min, the organic layer was removed and the aqueous phase extracted with diethyl ether (3 × 30 mL). The organic fractions were combined, washed with saturated $NaHCO_3$ (2 × 20 mL), water (2 × 20 mL), and brine (2 × 20 mL), dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The product was purified by column chromatography, with hexane/ethyl acetate (9/1) as eluent, to afford **15b** as a spectroscopically pure white solid in 76% yield (0.51 g). An analytically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. Mp: 148−151 °C. ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$, δ): −12.1. ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 7.47−7.34 (m, 2H, Ar-*H*), 7.28−7.24 (m, 5H, Ar-*H*), 7.05−6.99 (m, 4H, Ar-*H*), 6.72−6.68 (m, 2H, Ar-*H*), 5.40 (br, 1H, bridgehead C*H*), 2.01 (br m, 2H, Cy-*H*), 1.75−1.55 (m, 48, Cy-*H*), 1.40−0.90 (m, 10H, Cy-*H*). ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$, δ): 165.9 (d, J = 22.9 Hz, *C*═CP), 147.7 (C_6H_4Q), 147.2 (C_6H_4Q), 144.6 (d, J = 21.4 Hz, C═*C*P), 138.7 (d, J = 6.1 Hz, C_6H_5Q), 128.9 (C_6H_5 *o*-*C*), 127.6 (C_6H_5 *m*-*C*), 126.9 (C_6H_5 *p*-*C*), 124.4 (C_6H_4), 124.3 (C_6H_4), 122.9 (C_6H_4), 120.3 (C_6H_4), 53.8 (d, J = 5.3 Hz, bridgehead *C*Me), 53.7 (d, J = 4.5 Hz, bridgehead *C*H), 34.2 (d, J = 9.9 Hz, Cy), 30.6 (d, J = 12.2 Hz, Cy), 30.3 (d, J = 7.6 Hz, Cy), 27.4 (d, J = 6.9 Hz, Cy), 26.5 (Cy), 26.3 (Cy), 15.2 (CH_3). LRMS (ESI$^+$): m/z 491 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{35}H_{40}P$ [M + H]$^+$ m/z 491.2868, found m/z 491.2870. Anal. Calcd for $C_{35}H_{39}P$: C, 85.68; H, 8.01. Found: C, 85.87; H, 8.21.

[Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl{11-(dicyclohexylphosphino)-9,10-dihydro-9,10-ethanoanthracene}] (16a). To a solution of [Pd{κ^2*N*2′,*C*1-2-(2′-$NH_2C_6H_4$)C_6H_4}(μ-Cl)]$_2$ (0.25 g, 0.405 mmol) in acetone (8−10 mL) was added a solution of **9a** (0.326 g, 0.81 mmol) in dichloromethane (5−7 mL). After the mixture was stirred for 2 h, the solvent was removed under reduced pressure and the resulting brown oily residue purified by column chromatography, with CH_2Cl_2/methanol (97/3) as eluent, to give **16a** as a pale yellow spectroscopically pure solid in 72% yield (0.414 g). An analytically pure sample that was also suitable for X-ray structure determination was grown by slow diffusion of a dichloromethane solution layered with hexane at room temperature. Mp: 186−188 °C dec. ^{31}P{^{1}H} NMR (161.83 MHz, $CDCl_3$, δ): 43.9 (br, minor isomer), 43.2 (br, major isomer). ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): minor + major isomers, 7.97 (m, 1H, Ar-*H*), 7.54 (m, 1H, Ar-*H*), 7.47 (m, 1H, Ar-*H*), 7.44 (d, J = 7.3 Hz, 1H, Ar-*H*), 7.31−7.17 (m, Ar-*H*), 7.08−7.17 (m, Ar-*H*), 6.80 (td, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 6.32 (br d, J = 4.6 Hz, 1H, Ar-*H*), 4.84 (br d, J = 6.0 Hz, 1H, N*H*, major isomer), 4.74 (d, J = 6.4 Hz, 1H, bridgehead C*H*, minor isomer), 4.66 (br, 1H, N*H*, major isomer), 4.59 (br, 1H, N*H*, major + minor isomer), 4.55 (d, J = 6.9 Hz, 1H, bridgehead C*H*, major isomer), 4.36 (br, 1H, bridgehead C*H*, major isomer), 4.30 (br, 1H, bridgehead C*H*, minor isomer), 2.57 (q, J = 6.3 Hz, 1H, Cy-*H*, minor isomer) 2.45 (q, J = 8.3 Hz, 1H, Cy-*H*, major isomer), 2.19−1.9 (m, 3H, Cy-*H* + PC*HCH*$_2$), 1.78−0.85 (m, 19H, Cy-*H* + PC*HCH*$_2$), 0.62 m, 1H, Cy-*H*), 0.27 (m, 1H, Cy-*H*). ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$, δ): minor + major isomers, 152.9 (C_6H_4Q), 152.0 (C_6H_4Q), 146.2 (d, J = 12.4 Hz, C_6H_4Q), 145.8 (d, J = 12.4 Hz, C_6H_4Q), 145.6 (C_6H_4Q), 145.4 (C_6H_4Q), 142.8 (C_6H_4Q), 142.6 (C_6H_4Q), 140.9 (C_6H_4Q), 140.5 (C_6H_4Q), 140.4 (2 × C_6H_4Q), 139.2 (2 × C_6H_4Q), 137.9 (d, J = 7.6 Hz, Ar-*C*H), 137.6 (d, J = 6.7 Hz, Ar-*C*H), 136.1 (C_6H_4Q), 136.0 (C_6H_4Q), 128.3 (Ar-CH), 128.0 (Ar-CH), 127.9 (Ar-CH), 127.5 (Ar-CH), 127.4 (Ar-CH), 127.3 (Ar-CH), 127.2 (Ar-CH), 126.6 (Ar-CH), 126.1 (Ar-CH), 125.9 (Ar-CH), 125.7 (Ar-CH), 125.6 (3 × Ar-CH), 125.5 (Ar-CH), 125.4 (Ar-CH), 125.2 (2 × Ar-CH), 125.0 (2 × Ar-CH), 124.9 (Ar-CH), 124.8 (Ar-CH), 123.9 (Ar-CH), 123.8 (Ar-CH), 123.0 (Ar-CH), 122.7 (2 × Ar-CH), 122.6 (Ar-CH), 119.9 (Ar-CH), 46.8 (d, J = 4.8 Hz, bridgehead *C*H, minor isomer), 45.7 (d, J = 5.2 Hz, bridgehead *C*H, major isomer), 44.6 (d, J = 4.8 Hz, bridgehead *C*H, major isomer), 44.4 (d, J = 4.7 Hz, bridgehead *C*H, minor isomer), 36.8 (d, J = 22.9 Hz, *C*H), 36.0 (d, J = 27.6 Hz, *C*H), 35.8 (d, J = 21.0 Hz, *C*H), 35.3 (2 × d, J = 16.2 Hz, *C*H), 34.8 (d, J = 21.9 Hz, *C*H), 30.9 (Cy-CH_2), 30.7 (Cy-CH_2), 30.4 (Cy-CH_2), 30.3 (Cy-CH_2), 30.0 (2 × Cy-CH_2), 29.7

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($Cy\text{-}CH_2$), 29.8 ($Cy\text{-}CH_2$), 29.6 ($Cy\text{-}CH_2$), 29.4 ($Cy\text{-}CH_2$), 29.2 ($Cy\text{-}CH_2$), 27.9 ($Cy\text{-}CH_2$), 27.8 ($Cy\text{-}CH_2$), 27.7 ($Cy\text{-}CH_2$), 27.6 (2 × $Cy\text{-}CH_2$), 27.5 ($Cy\text{-}CH_2$), 27.4 ($Cy\text{-}CH_2$), 27.3 (2 × $Cy\text{-}CH_2$), 26.2 ($Cy\text{-}CH_2$), 26.0 ($Cy\text{-}CH_2$). LRMS (ESI^+): m/z 676 $[M - Cl]^+$. HRMS (ESI^+): exact mass calcd for $C_{40}H_{45}NPPd$ $[M - Cl]^+$ m/z 675.2332, found m/z 675.2339. Anal. Calcd for $C_{40}H_{45}ClNPPd$: C, 67.42; H, 6.36; N, 1.97. Found: C, 67.79; H, 6.45; N, 2.03.

[Pd{κ^2*N2′*,*C1*-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl{11-(dicyclohexylphosphino)-9-methyl-9,10-dihydro-9,10-ethanoanthracene}] (16b). Compound **16b** was prepared and purified according to the procedure described above for **16a** and isolated as a spectroscopically pure beige solid in 77% yield (0.45 g) by slow diffusion of hexane into a dichloromethane solution at room temperature. Mp: 197−199 °C dec. $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, δ): 45.1 (br, minor), 42.4 (br, major) mixture of rotamers. ^1H NMR (399.78 MHz, $CDCl_3$, δ): minor + major isomers 7.99 (m, 1H, Ar-*H*), 7.47 (m, 1H, Ar-*H*), 7.33−7.18 (m, 7H, C_6H_4), 7.12−6.98 (m, 6H, C_6H_4), 6.78 (br t, J = 7.3 Hz, 1H, Ar-*H*), 6.22 (br, 1H, Ar-*H*), 4.82 (d, J = 6.9 Hz, bridgehead C*H*, minor isomer), 4.74 (br, 1H, N*H*), 4.62 (br, 1H, N*H*), 4.59 (br, 1H, N*H*), 4.50 (d, J = 5.5 Hz, bridgehead C*H* major isomer + N*H*), 2.68 (q, J = 9.16 Hz, 1H, Cy-*H*, minor isomer), 2.54 (q, J = 10.1 Hz, 1H, Cy-*H* major isomer), 1.96 (s, 3H, CH_3 major isomer), 1.90 (s, 3H, CH_3 minor isomer), 1.86−0.31 (m, 24H, Cy-*H* + $PCHCH_2$ major + minor isomer). $^{13}C\{^1H\}$ NMR (100.52 MHz, $CDCl_3$, δ): 152.3 (C_6H_4Q, minor isomer), 151.4 (C_6H_4Q, major isomer), 147.2 (C_6H_4Q, major isomer), 146.9 (C_6H_4Q, minor isomer),146.2 (d, J = 11.4 Hz, C_6H_4Q, minor isomer), 145.8 (d, J = 12.4 Hz, C_6H_4Q, major isomer), 144.6 (C_6H_4Q, minor isomer), 144.4 (C_6H_4Q, major isomer), 140.9 (C_6H_4Q, major isomer), 140.6 (C_6H_4Q, minior isomer), 140.4 (C_6H_4Q, minor isomer), 140.1 (2 × C_6H_4Q, major + minor isomers), 139.5 (C_6H_4Q, major isomer), 137.5 (d, J = 6.9 Hz, Ar-C*H*, minor isomer), 137.3 (d, J = 6.7 Hz, Ar-C*H*, major isomer), 135.6 (C_6H_4Q, major isomer), 135.5 (C_6H_4Q, minor isomer), 128.2 (2 × Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 127.4 (Ar-*C*H), 127.3 (2 × Ar-*C*H), 127.1 (Ar-*C*H), 127.0 (2 × Ar-*C*H), 126.1 (Ar-*C*H), 125.8 (Ar-*C*H), 125.7 (Ar-*C*H), 125.6 (2 × Ar-*C*H), 125.5 (2 × Ar-*C*H), 125.3 (Ar-*C*H), 125.1 (2 × Ar-*C*H), 125.0 (Ar-*C*H), 124.9 (Ar-*C*H), 122.6 (2 × Ar-*C*H), 121.1 (Ar-*C*H), 121.0 (Ar-*C*H), 120.1 (Ar-*C*H), 119.9 (2 × Ar-*C*H), 119.7 (Ar-*C*H), 47.4 (d, J = 3.0 Hz, bridgehead *C*H, minor isomer), 45.8 (d, J = 3.8 Hz, bridgehead *C*H, major isomer), 45.2 (d, J = 2.9 Hz, bridgehead *C*Me, minor isomer), 45.1 (d, J = 2.9 Hz, bridgehead *C*H, major isomer), 37.8 (CH_2, major isomer), 37.1 (d, J = 17.1 Hz, *C*H, minor isomer), 37.0 (d, J = 21.9 Hz, *C*H, major isomer), 36.6 (CH_2, minor isomer), 36.5 (d, J = 16.2 Hz, *C*H, major isomer), 35.9 (d, J = 21.9 Hz, *C*H, major isomer), 35.8 (d, J = 21.7 Hz, *C*H, minor isomer), 35.1 (d, J = 21.9 Hz, *C*H, minor isomer), 30.6 ($Cy\text{-}CH_2$), 30.4 ($Cy\text{-}CH_2$), 30.2 ($Cy\text{-}CH_2$), 30.0 (2 × $Cy\text{-}CH_2$), 29.7 ($Cy\text{-}CH_2$), 29.6 ($Cy\text{-}CH_2$), 29.2 ($Cy\text{-}CH_2$), 27.8 ($Cy\text{-}CH_2$), 27.7 (2 × $Cy\text{-}CH_2$), 27.6 ($Cy\text{-}CH_2$), 27.5 ($Cy\text{-}CH_2$), 27.4 ($Cy\text{-}CH_2$), 27.3 ($Cy\text{-}CH_2$), 27.2 ($Cy\text{-}CH_2$), 26.1 (2 × $Cy\text{-}CH_2$), 26.0 ($Cy\text{-}CH_2$), 25.9 ($Cy\text{-}CH_2$), 18.0 (CH_3, major isomer), 17.7 (CH_3, minor isomer). LRMS (ESI^+): m/z 686 $[M - Cl]^+$. HRMS (ESI^+): exact mass calcd for $C_{41}H_{47}NPPd$ $[M - Cl]^+$ m/z 686.2497, found m/z 686.2480. Anal. Calcd for $C_{41}H_{47}ClNPPd$: C, 67.77; H, 6.52; N, 1.93. Found: C, 67.93; H, 6.66; N, 2.11.

[Pd{κ^2*N2′*,*C1*-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl{11-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}] (17a). Compound **17a** was prepared and purified according to the procedure described above for **16a** and isolated as a spectroscopically pure pale beige powder in 81% yield. Crystals suitable for X-ray structure determination were obtained by slow diffusion of hexane into a dichloromethane solution at room temperature. Mp: 188−188 °C dec. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, δ): 49.5. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.82 (br, 1H, Ar-*H*), 7.46 (br, 1H, Ar-*H*), 7.34 (br, 1H, Ar-*H*), 7.32−7.14 (m, 11H, Ar-*H*), 7.02 (br, 4H, Ar-*H*), 6.96 (t, J = 7.3 Hz, 1H, Ar-*H*), 6.58 (t, J = 7.3 Hz, 1H, Ar-*H*), 6.15 (t, J = 7.3 Hz, 1H, Ar-*H*), 6.10 (t, J = 5.5 Hz, 1H, bridgehead C*H*), 5.72 (t, J = 2.3 Hz, 1H, bridgehead C*H*), 4.86 (br, 1H, N-*H*), 4.53 (br, 1H, N-*H*), 2.84 (br, 1H, Cy-*H*), 2.21 (br, 1H, Cy-*H*), 1.64 (br, 3H, Cy-*H*), 1.43−1.14 (br, 5H, Cy-*H*), 1.03−0.87 (br, 8H, Cy-*H*), 0.74 (br, 2H, Cy-*H*), 0.23 (br, 1H, Cy-*H*), 0.09 (br, 1H, Cy-*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 159.4 (d, J = 22.9 Hz, *C*=CP), 148.2 (C_6H_4Q), 145.0 (C_6H_4Q), 144.7 (C_6H_4Q), 144.4 (C_6H_4Q), 143.8 (C_6H_4Q), 140.4 (d, J = 2.0, C_6H_4Q), 140.1 (C_6H_4Q), 139.3 (C_6H_4Q), 135.9 (d, J = 8.6 Hz, Ar), 135.2 (d, J = 2.1 Hz, C_6H_5Q), 134.9 (d, J = 29.6 Hz, C=*C*P), 128.7 (Ar-*C*H), 128.1 (Ar-*C*H), 127.7 (Ar-*C*H), 127.6 (Ar-*C*H), 126.9 (Ar-*C*H), 126.8 (Ar-*C*H), 126.3 (Ar-*C*H), 125.2 (Ar-*C*H), 125.1 (Ar-*C*H), 125.0 (br, Ar*C*H), 124.7 (br, Ar-*C*H), 123.8 (br, Ar-*C*H), 122.9 (br, Ar-*C*H), 122.6 (br, Ar-*C*H), 120.5 (Ar-*C*H), 62.4 (d, J = 5.3 Hz, bridgehead *C*H), 56.6 (d, J = 12.2 Hz, bridgehead *C*H), 37.4 (d, J = 21.9 Hz, Cy-*C*H), 36.2 (d, J = 25.3 Hz, Cy-*C*H), 32.4 ($Cy\text{-}CH_2$), 30.8 ($Cy\text{-}CH_2$), 30.2 ($Cy\text{-}CH_2$), 29.8 ($Cy\text{-}CH_2$), 28.0 ($Cy\text{-}CH_2$), 27.6 ($Cy\text{-}CH_2$), 27.5 ($Cy\text{-}CH_2$), 27.3 ($Cy\text{-}CH_2$), 26.3 ($Cy\text{-}CH_2$), 25.9 ($Cy\text{-}CH_2$). LRMS (EI^+): m/z 787.2 $[M]^+$. Anal. Calcd for $C_{46}H_{47}ClNPPd$: C, 70.23; H, 6.02; N, 1.78. Found: C, 70.67; H, 6.44; N, 1.91.

[Pd{κ^2*N2′*,*C1*-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl{11-(dicyclohexylphosphino)-9-methyl-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}] (17b). Compound **17b** was prepared and purified according to the procedure described above for **16a** and isolated as a spectroscopically pure light yellow solid in 83% yield. Crystals suitable for X-ray structure determination were obtained by slow diffusion of hexane into a dichloromethane solution at room temperature. Mp: 190 °C dec. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, δ): 51.3. ^1H NMR (399.98 MHz, $CDCl_3$, δ): 7.91 (br, 1H, Ar-*H*), 7.51 (br, 1H, Ar-*H*), 7.32−7.01 (m, 15H, Ar-*H*), 6.98 (t, J = 7.4 Hz, 1H, Ar-*H*), 6.83 (br, 1H, Ar-*H*), 6.59 (t, J = 7.3 Hz, 1H, Ar-*H*), 6.20 (br, 1H, bridgehead C*H*), 6.00 (br, 1H, Ar-*H*), 4.90 (br, 1H, N-*H*), 4.56 (br, 1H, N-*H*), 2.90 (br, 1H, Cy-*H*), 2.75 (br, 1H, Cy-*H*), 1.70 (s, 3H, CH_3), 1.66 (br m, 3H, Cy-*H*), 1.16−0.69 (br, 14H, Cy-*H*), 0.08 (br, 1H, Cy-*H*), −0.14 (br, 1H, Cy-*H*). $^{13}C\{^1H\}$ NMR (100.52 MHz, $CDCl_3$, δ): 160.5 (*C*=CP), 148.7 (C_6H_4Q), 147.1 (C_6H_4Q), 146.4 (C_6H_4Q), 145.8 (C_6H_4Q), 140.1 (C_6H_4Q), 139.2 (C_6H_4Q), 137.5 (d, J = 2.9 Hz, C_6H_4Q), 137.4 (d, J = 29.6 Hz, C=*C*P), 135.5 (C_6H_5Q), 135.3 (d, J = 5.7 Hz, C_6H_4Q), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 129.7 (Ar-*C*H), 129.8 (Ar-*C*H) 129.7 (Ar-*C*H) 125.6 (Ar-*C*H), 125.4 (Ar-*C*H), 126.7 (d, J = 3.8 Hz, Ar-*C*H), 126.0 (Ar-*C*H), 125.1 (Ar-*C*H), 124.9 (Ar-*C*H), 124.7 (Ar-*C*H), 124.6 (2 × Ar-*C*H), 124.5 (Ar-*C*H), 124.3 (Ar-*C*H), 123.4 (Ar-*C*H), 120.3 (Ar-*C*H), 120.2 (2 × Ar-*C*H), 120.1 (Ar-*C*H), 56.1 (d, J = 17.1 Hz, bridgehead *C*H), 55.3 (d, J = 7.0 Hz, bridgehead *C*H), 37.6 (d, J = 7.0 Hz, bridgehead *C*Me), 37.2 (d, J = 25.7 Hz, Cy-*C*H), 36.6 (d, J = 21.1 Hz, Cy-*C*H), 33.1 ($Cy\text{-}CH_2$), 31.7 ($Cy\text{-}CH_2$), 31.1 ($Cy\text{-}CH_2$), 30.1 ($Cy\text{-}CH_2$), 28.1 (d, J = 17.2 Hz, $Cy\text{-}CH_2$), 27.7 ($Cy\text{-}CH_2$), 27.6 ($Cy\text{-}CH_2$), 27.4 (d, J = 17.1 Hz, $Cy\text{-}CH_2$), 26.3 ($Cy\text{-}CH_2$), 25.8 ($Cy\text{-}CH_2$). 15.2 (CH_3). LRMS (EI^+): m/z 797 $[M]^+$. HRMS (ESI^+): exact mass calcd for $C_{41}H_{47}NPPd$ $[M]^+$ m/z 797.2326, found m/z 797.2336. Anal. Calcd for $C_{47}H_{49}ClNPPd$: C, 70.50; H, 6.17; N, 1.75. Found: C, 70.77; H, 6.43; N, 1.88.

[Pd{κ^2*N2′*,*C1*-2-(2′-$NH_2C_6H_4$)C_6H_4}Cl(PCy_2Ph)] (18). Compound **18** was prepared and purified according to the procedure described above for **16a** and isolated as a spectroscopically pure beige solid in 68% yield (0.160 g) by slow diffusion of hexane into a dichloromethane solution at room temperature. Mp: 168−172 °C dec. $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, δ): 41.5. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.49 (br dd, J = 3.2, 2.9 Hz, 1H, Ar-*H*), 7.29−7.17 (m, 8H, Ar-H), 6.92 (t, J = 7.3 Hz, 1H, Ar-*H*), 6.78 (dd, J = 7.8, 4.7 Hz, 1H, Ar-*H*), 6.61 (t, J = 7.4 Hz, 1H, Ar-*H*), 4.78 (br, 2H,. NH_2), 2.37 (br, 2H, Cy-*H*), 2.02 (br 2H, Cy-*H*), 1.9−1.0 (br, 18H, Cy-*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 151.7 (Ar-*C*H), 140.3 (Ar-*C*H), 128.3 (d, J = 9.1 Hz, Ar-*C*H), 135.8 (d, J = 3.1 Hz, Ar-*C*H), 134.3 (d, J = 9.1 Hz, Ar-*C*H), 129.7 (d, J = 2.4 Hz, Ar-*C*H), 127.9 (Ar-*C*H), 127.6 (Ar-*C*H), 127.3 (Ar-*C*H), 127.2 (Ar-*C*H), 127.0 Ar-*C*H), 126.9 (Ar-*C*H), 126.7 (Ar-*C*H), 126.4 (Ar-*C*H), 125.9 (Ar-*C*H), 125.2 (Ar-*C*H), 124.8 (Ar-*C*H), 1201. (Ar-*C*H), 33.2 (br d, J = 25.1 Hz, Cy-*C*H), 32.9 (br d, J = 23.8 Hz, Cy-*C*H), 29.4 (br, $Cy\text{-}CH_2$), 29.1 (br, $Cy\text{-}CH_2$), 28.3 (br, $Cy\text{-}CH_2$), 28.3 (br, $Cy\text{-}CH_2$), 27.0 (br overlapping, $Cy\text{-}CH_2$), 26.2 ($Cy\text{-}CH_2$). Anal. Calcd for $C_{30}H_{37}ClNPPd$: C, 61.65; H, 6.38; N, 2.40. Found: C, 61.79; H, 6.67; N, 2.78.

Preparation of Selenium Adducts. A round-bottomed flask was charged with phosphine (0.125 mmol) and methanol (0.5 mL)

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followed by a solution of KSeCN (0.035 g, 0.025 mmol) in methanol (0.7 mL) and placed under a nitrogen atmosphere, and the mixture was stirred. The reactions were typically complete within 15 min, after which time the solvent was removed under reduced pressure, the solid residue was extracted into chloroform (2 × 2 mL), and the extract was filtered. The products were obtained as either white solids or oils after removing the solvent under reduced pressure and characterized by ^{31}P NMR spectroscopy only. $^{31}P\{^{1}H\}$ NMR (202.46 MHz, $CDCl_3$, δ): **9a**, 60.6 ppm (J_{PSe} = 694 Hz); **9b**, 61.8 ppm (J_{PSe} = 696 Hz); **15a**, 60.5 ppm (J_{PSe} = 702 Hz); **15b**, 60.1 ppm (J_{PSe} = 702 Hz); 2,6-OMeKITPHOS, 59.2 ppm (J_{PSe} = 684 Hz).

General Procedure for the Suzuki−Miyaura Coupling of Aryl Chlorides. A flame-dried Schlenk flask was cooled to room temperature under vacuum, back-filled with nitrogen, and charged with potassium phosphate (0.424 g, 2.00 mmol), boronic acid (1.50 mmol), precatalyst (2.5 μmol, 0.25 mol %), and toluene (2.0 mL). Aryl chloride (1.00 mmol) was added and the resulting mixture heated at the required temperature for the allocated time. After the reaction mixture was cooled to room temperature, decane (0.194 mL, 1.00 mmol), diethyl ether (5 mL), and water (5 mL) were added, the mixture wasshaken vigorously, the organic layer was passed through a short silica plug, and the solution was analyzed by gas chromatography−mass spectrometry to determine the conversion. The solvent was then removed under reduced pressure and the product purified by column chromatography, with hexane/ethyl acetate (typically 5/1 v/v) as eluent. Known products were characterized by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry, and high-resolution mass spectrometry (HRMS).

Computational Details. DFT calculations were performed on the gas-phase molecules with the Gaussian 09 (revision B.01) suite of programs.[56] Geometries were optimized using the hybrid B3LYP functional,[57] with a LanL2DZ effective core potential basis set[58] for Ni and a 6-31G(2d,p)[59] basis set for all other atoms. The location of minima was confirmed by the absence of imaginary vibrational frequencies in each case. The highest ν(CO) vibrational frequency without any scaling factor defines the computed electronic parameter (CEP).

X-ray Crystal Structure Determinations of 12a, 16a, 17a,b, and 18. All data were measured on an Oxford Diffraction (now Agilent Technologies) Gemini A Ultra diffractometer at 150 K, using Mo Kα radiation (λ = 0.71073 Å) for compounds **12a**, **17b**, and **18** or Cu Kα radiation (λ = 1.54178 Å) for compound **17a**, except for compound **16a**, for which data were measured at 120 K using synchrotron radiation (λ = 0.6889 Å) at beamline I19, Diamond Light Source. Semiempirical absorption corrections were applied on the basis of symmetry-equivalent and repeated reflections. Structures were solved by direct methods and refined on all unique F^2 values, with anisotropic non-H atoms and constrained riding isotropic H atoms, except in the case of H atoms bonded to nitrogen and boron, which were located in a difference map and either refined freely or refined with distance restraints. Programs used were Oxford Diffraction CrysAlisPro[60a] (**12a**, **17a,b**, and **18**) or Rigaku CrystalClear[60b] and Bruker APEX2[60c] (**16a**) for data collection, integration, and absorption corrections, SHELXTL[61] for structure solution and refinement, and Olex2[62] for graphics. Where applicable, the absolute configuration was determined using anomalous dispersion effects. The structure of compound **16a** contains two independent molecules in the asymmetric unit and was integrated and refined as a pseudo-nonmerohedral twin (for which symmetry-equivalent reflections cannot be merged before refinement). The structure of compound **17a** contains two independent molecules, one dichloromethane solvent molecule, and half a hexane molecule in the asymmetric unit, the remainder being generated by inversion symmetry. The structure of compound **17b** contains four independent molecules and three dichloromethane solvent molecules in the asymmetric unit. An additional solvent molecule was very disordered and was treated using the PLATON/SQUEEZE[63] algorithm, as it could not be successfully modeled. The structure of compound **18** contains two independent molecules and two toluene solvent molecules, related by a pseudo inversion center. Details are provided in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, text, and CIF files showing the low-temperature ^{31}P NMR EXSY spectrum for **16a** and perspective views of the molecular structures of **12a** and **18**, full details of catalyst optimization studies, details of crystal data, structure solution and refinement, atomic coordinates, bond distances, bond angles, anisotropic displacement parameters for compounds **12a**, **16a**, **17a,b**, and **18**, and details of atomic coordinates and final energies for all calculated geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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