JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

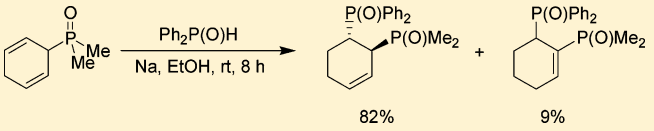
Michael-Type Addition of Secondary Phosphine Oxides to (1,4-Cyclohexadien-3-yl)phosphine Oxides

Marek Stankevič,* Magdalena Jaklińska, and K. Michał Pietrusiewicz

Department of Organic Chemistry, Faculty of Chemistry, Marie Curie-Skłodowska University, Gliniana 33, 20-614 Lublin, Poland

Supporting Information

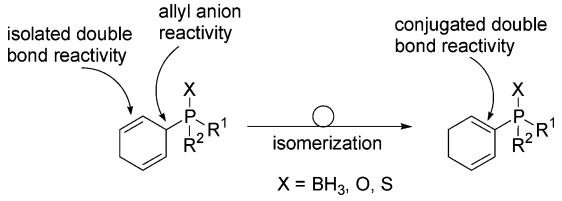
ABSTRACT: Base-induced reaction between (1,4-cyclohexadien-3-yl)phosphine oxides and secondary phosphine oxides gives 3,4-bis(phosphinoyl)cyclohexenes and 2,3-bis(phosphinoyl)cyclohexenes through an in situ isomerization of one of the cyclohexadienyl double bonds and a subsequent Michael-type addition of the secondary phosphine oxide.



INTRODUCTION

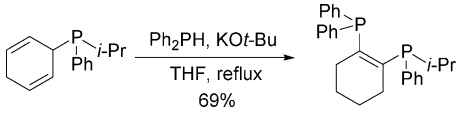
The demand for new compounds having highly targeted properties requires the development of new and efficient methodologies, and this is especially true for organophosphorus compounds, which have found applications as ligands in transition-metal-catalyzed transformations[1,2] and as substrates in material chemistry.[3,4] Organophosphorus derivatives having aryl−phosphorus bonds are particularly attractive because they are easily accessible through simple and practical methods and the preparation of aryl-substituted phosphines for direct use is very common. There is much less precedent for the modification of an arene fragment in arylphosphines, despite the fact that this could provide a simple and direct approach to new organophosphorus compounds. Any brief literature survey shows that simple arene modifications in arylphosphorus compounds can be performed by electrophilic aromatic substitutions[5] but that directed *ortho*-metalation, a very popular transformation in organic chemistry,[6] is rarely used with phosphines and their derivatives.[7,8] A further approach which we have explored recently, the dearomatization of the arene group in arylphosphines and their derivatives by Birch reduction,[9−11] appears to offer great potential for elaboration through chemistry at the isolated or conjugated double bonds or through allyl or pentadienyl anions (Scheme 1).

Scheme 1



While nonphosphorylated 3-substituted 1,4-cyclohexadienes typically undergo classical transformations typical of isolated double bonds, such as dihydroxylation,[12] epoxidation,[13] haloalkoxylation,[14] or Brönsted acid-mediated Friedel−Crafts reactions,[15] the only example of the reactivity of organophosphorus compounds possessing a 1,4-cyclohexadien-3-yl substituent, described by Salem and co-workers, demonstrates that a tricoordinate 3-phosphino-1,4-cyclohexadiene reacts with a secondary phosphine (Scheme 2)[16] to give a 1,2-bis(phosphino)cyclohexene in good yield. This underlines a clear potential for phosphorylated Birch reduction products as ligand precursors for transition-metal-catalyzed transformations, particularly given that Knochel et al. have been able to employ enantiomerically pure *C*-chiral 1,2-bis(phosphino)cyclohexanes as ligands in rhodium-catalyzed hydroboration of styrene derivatives.[17]

Scheme 2



As part of a current research project aimed at developing new methodologies for the synthesis of organophosphorus compounds through the modification of aryl substituents in arylphosphines and their derivatives, we have already communicated the dearomatization of arylphosphine−boranes[18] and arylphosphine oxides[19] into the corresponding (1,4-cyclohexadien-3-yl)phosphine derivatives. Given that the structure of these products appeared to be appropriate for extensive modification, we opted to explore these compounds as precursors for diphosphine derivatives possessing a cyclohexenyl linker. The results are presented here.

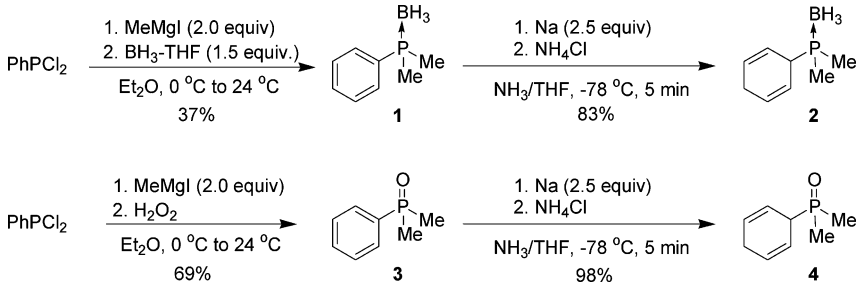
RESULTS AND DISCUSSION

Model reactions were carried out on the (1,4-cyclohexadien-3-yl)dimethylphosphine−borane (**2**) that was obtained as reported previously in 83% yield through the Birch reduction of dimethylphenylphosphine−borane (**1**) (Scheme 3).[18]

Received: January 10, 2012
Published: January 31, 2012

   dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991−2000

Scheme 3



Scheme 4

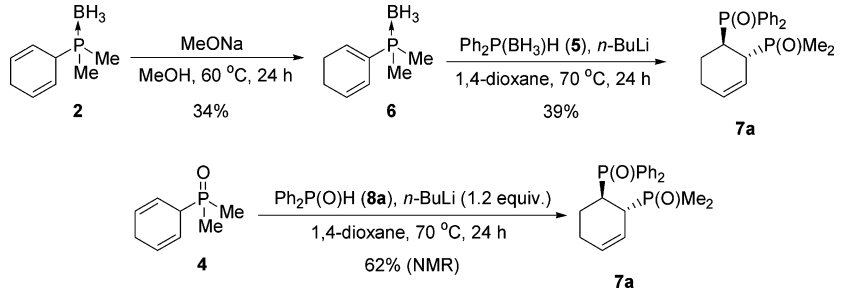
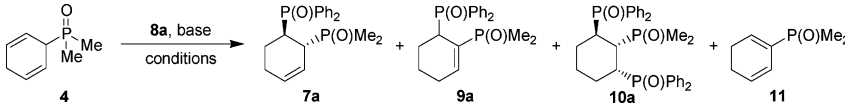


Table 1. Optimization of the Reaction Conditions



			yield (%)			
entry	base (equiv)	conditions	**7a**	**9a**	**10a**	**11**
1	BuLi (1.2)	1,4-dioxane, 70 °C, 24 h	62[a]			
2	BuLi (1.2)	1,4-dioxane, 24 °C, 24 h	no reaction			
3	NaH (1.1)	1,4-dioxane, 70 °C, 24 h	35	8	11	15
4	NaH (0.7)	1,4-dioxane, 70 °C, 24 h	32	13	13	5
5	NaH (0.3)	1,4-dioxane, 70 °C, 24 h	no reaction			
6	NaH (1.1)	1,4-dioxane, 24 °C, 24 h	49			
7	*t*-BuOK (1.0)	1,4-dioxane, 70 °C, 24 h	42[a]	12[a]		15[a]
8	*t*-BuOK (1.0)	1,4-dioxane, 24 °C, 24 h	69	6		16
9	LDA (1.0)	1,4-dioxane, 70 °C, 24 h	50[a]	6[a]		10[a]
10	LDA (1.0)	1,4-dioxane, 24 °C, 24 h	no reaction			
11	DBU (1.0)	1,4-dioxane, 70 °C, 24 h	77[a]	8[a]		
12	DBU (1.0)	1,4-dioxane, 24 °C, 24 h	no reaction			
13	K_2CO_3 (3.0)	1,4-dioxane, 70 °C, 24 h	no reaction			
14	K_2CO_3 (3.0)	1,4-dioxane, 24 °C, 24 h	no reaction			
15	EtONa (0.1)	EtOH, 24 °C, 24 h	no reaction			
16	EtONa (1.0)	EtOH, 24 °C, 24 h	41			
17	EtONa (2.0)	EtOH, 24 °C, 24 h	54[a]	20[a]		10[a]
18	EtONa (3.0)	EtOH, 24 °C, 24 h	65[a]	22[a]		7[a]
19	EtONa (5.0)	EtOH, 24 °C, 24 h	72[a]	28[a]		
20	EtONa (10.0)	EtOH, 24 °C, 8 h	82	9		

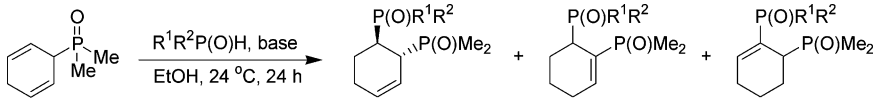
[a]Yields were determined by NMR of the isolated mixture.

Treatment of phosphine−borane **2** with diphenylphosphine−borane (**5**) in the presence of a strong base failed to produce the 1,2-bis(boranatophosphinyl)cyclohexene, so a preisomerization of **2** into **6** was successfully attempted using sodium methoxide in methanol (Scheme 4).

Reaction of this conjugated phosphine−borane **6** with secondary phosphine−borane **5** in the presence of a strong base afforded the corresponding Michael-type addition product as diphosphine dioxide **7a** rather than the anticipated bis(phosphine)−bis(borane), so the reaction is complicated by a competitive BH_3 decomplexation−oxidation. Given this need for a pre- isomerization step of the Birch reduction product **2** and the decomplexation of phosphine−borane that occurs during the reaction, a more convenient system was sought. The (1,4-cyclohexadien-3-yl)dimethylphosphine oxide **4**, prepared as depicted in Scheme 3, was found to undergo

dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991−2000

Table 2. Addition of >P(O)H-type compounds to (1,4-cyclohexadien-3-yl)dimethylphosphine oxide 4



4 7 9 9′

entry		>P(O)H-type compound		base (equiv)	isolated yields (%) 7	9/9′
1	**8a**	Ph	Ph	EtONa (10.0)	82[a]	9[a]/–
2	**8b**	2-Np	2-Np	EtONa (10.0)	41	13/–
3	**8c**	1-Np	1-Np	EtONa (10.0)	69	
4	**8d**	*p*-An	*p*-An	EtONa (10.0)	55	28/–
5	**8e**	*o*-Tol	*o*-Tol	NaH (0.7)[b,c]	32	–/15
6	**8f**	Ph	*o*-An	EtONa (10.0)	70 (54)[d]	20 (27)[d,e]/5 (44)[d,e]
7	**8g**	Ph	Bn	NaH (0.7)[b,f]	complex mixture	
8	**8h**	Ph	*i*-Pr	EtONa (10.0)	43 (15)[d,e]	–/37 (25)[d,e]
9	**8i**	*t*-Bu	Ph	EtONa (10.0)	79 (28)[d]	
10	**8j**	Cy	Cy	NaH (0.7)[b,c]	43	33[e]/–
11	**8k**	*n*-Hex	*n*-Hex	NaH (1.1)[b,c]	24	36/–
12	**8l**	OEt	OEt	NaH (0.7)[b]	no reaction	
13				EtONa (10.0)	no reaction	
14				DBU (1.1)[b]	no reaction	
15	**8m**	Ph	OEt	NaH (0.7)[b]	no reaction	

[a]After 8 h. [b]1,4-Dioxane, 70 °C, 24 h. [c]Reaction performed with EtONa in ethanol failed to give the Michael addition products. [d]In brackets is presented the diastereoisomeric ratio of the products. [e]The yield based on NMR of the isolated mixture of products. [f]Reaction performed with EtONa in ethanol gave lower conversion.

clean reaction with diphenylphosphine oxide (**8a**) under the same reaction conditions to furnish the corresponding diphosphine dioxide **7a** in good yield. The *trans*- formulation was confirmed by two-dimensional NMR spectra. The clear difference in the reactivity of substrates **2** and **4** can be ascribed to the stronger activation of a proton in the α-position in the case of the phosphine oxide because of the better electron-accepting properties of the phosphoryl group. Precedents exist for isomerization–Michael additions of organophosphorus compounds with allyl-substituted phosphonium salts[20] and phosphine oxides;[21] isomerization of one of the double bonds in (1,4-cyclohexadien-3-yl)-substituted phosphine oxides should be facilitated relative to such allylphosphorus compounds by the higher acidity of the proton in the position α-to phosphorus.

These encouraging results led us to optimize the reaction conditions between phosphine oxides **4** and **8a** (Table 1).

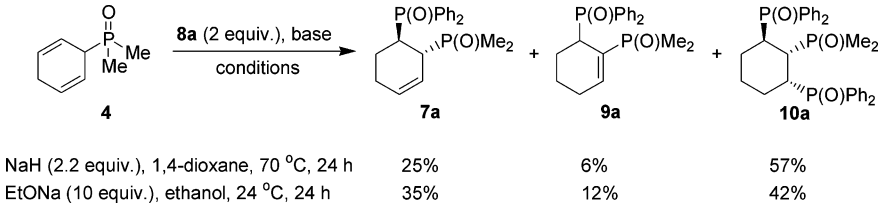
Screening the reaction conditions revealed that two Michael addition products were almost invariably observed: these were the diphosphine dioxide **7a**, which results from a double bond isomerization–-Michael addition sequence, and diphosphine dioxide **9a**, which most probably arises from an isomerization of **7a** through a proton shift. The formation of the latter compound is quite predictable given the basic conditions present in the reaction mixture. In 1,4-dioxane as a solvent, the reaction between the secondary phosphine oxide and the Birch reduction product gives better conversions at elevated temperatures, except with *t*-BuOK (Table 1, entries 7 and 8), which works best at ambient temperatures. K_2CO_3 failed to produce the diphosphine dioxide under both sets of reaction conditions (Table 1, entries 13 and 14). *n*-Butyllithium gave the most selective transformation of the starting compounds into the product (Table 1, entry 1), while sodium hydride, *t*-BuOK or LDA gave significant amounts of either the isomerization product **11** or the double Michael addition product **10a**. The bases giving the highest product yields were those of medium strength like DBU (Table 1, entry 11) or EtONa (Table 1, entry 16–20) whose pK_a is comparable with that of the secondary phosphine oxides.

To investigate the generality of the optimized reaction conditions, we then examined the reaction of **4** with a variety of >P(O)H-type compounds (see Table 2).

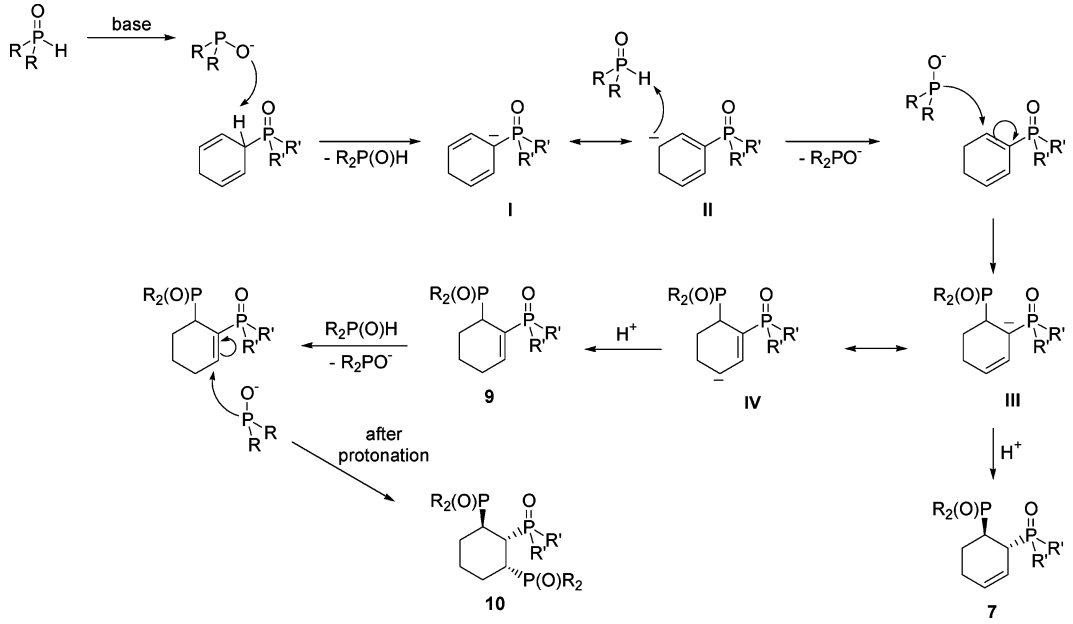
With few exceptions, >P(O)H-type compounds gave the addition products in good to excellent yields. A mixture of *trans*-3,4-(diphosphinoyl)cyclohexene **7** or 2,3-(diphosphinoyl)cyclohexene **9** or **9′** was observed, except when the bulky bis(1-naphthyl)phosphine oxide (**8c**) (Table 2, entry 3) and *tert*-butylphenylphosphine oxide (**8i**) (Table 2, entry 9) were used. Here, the only observed products were *trans*-3,4-(diphosphinoyl)cyclohexenes **7**. The primary Michael addition adduct, the diphosphine dioxide **7**, was the major reaction product except with di-*n*-hexylphosphine oxide (**8k**) (Table 2, entry 11), where the isomerized product **9** dominated. This probably reflects lesser steric crowding generated about the allylic proton by the incoming phosphinoyl fragment when the substituents are primary alkyl groups, which facilitates the arrival of the base during the subsequent deprotonation step. Again, the best substrate conversions were normally achieved using sodium ethoxide as the base, which was optimal for all of the secondary phosphine oxides except di-*c*-hexylphosphine oxide (**8j**) (Table 2, entry 10) and di-*n*-hexylphosphine oxide (**8k**) (Table 2, entry 11) which surprisingly failed to give the addition products. It appears that their lack of reactivity stems from the fact that they have lower acidity than diarylphosphine oxides, so that sodium ethoxide is too weak a base to promote the reaction. In these three cases, using sodium hydride in 1,4-dioxane instead of EtONa in ethanol gave a beneficial effect on the conversion of the substrates into the products. Among the tested secondary phosphine oxides, benzylphenylphosphine oxide (**8g**) appeared

dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991–2000

Scheme 5



Scheme 6



to give the least predictable results as each of three attempts gave a different outcome. In all cases, however, we observed the formation of a mixture of at least several compounds in a different proportions.

When unsymmetrically substituted secondary phosphine oxides were used, the formation of diastereoisomers was observed (Table 2, entries 6–9) but diastereoselectivity was low and reached 54% de in only two cases.

Encouraged by the results concerning the addition of secondary phosphine oxides to **4**, we assumed that the change of reagent from a secondary phosphine oxide $R_2P(O)H$ to a secondary phosphite $(RO)_2P(O)H$ or *H*-phosphinate R(R'O)-P(O)H would provide opportunities for obtaining more highly modified products, since these could allow substitution reactions at the phosphorus atom of the phosphoryl fragment. However, all attempts to obtain these compounds by the addition of $(EtO)_2P(O)H$ (**8l**) or Ph(EtO)P(O)H (**8m**) failed.

The appearance of a product **10a** during the optimization process (see Table 1) points out the possibility of double Michael additions of secondary phosphine oxides to a Birch reduction product. This provides an access to triphosphine trioxides having a cyclohexane core from the readily available Birch reduction products (Scheme 5).

Treatment of phosphine oxide **4** with 2 mol of secondary phosphine oxide **8a** in the presence of an excess of sodium hydride afforded the triphosphine trioxide **10a** in 57% yield, accompanied by the primary Michael addition product **7a** (25%) along with the isomerized Michael addition product **9a** (6%). With sodium ethoxide in ethanol, the yield of the double Michael addition product **10a** fell and the yields of **7a** and **9a** were raised The relative configuration of triphosphine trioxide was found to be *cis,trans* as based on its two-dimensional NMR analysis.

Analysis of the structure of the identified adducts allows a preliminary mechanism to be proposed, as is shown below (Scheme 6).

The first step of the reaction can reasonably be assumed to be the deprotonation of a secondary phosphine oxide, with formation of the corresponding anion. In the next step, this anion removes the acidic 3-proton from the (1,4-cyclohexadien-3-yl)phosphine oxide with the formation of the delocalized anion **I**–**II** which undergoes reprotonation from the secondary phosphine oxide; this affords the isomerized Birch reduction product. It seems likely that the lack of reactivity shown by secondary phosphites and *H*-phosphinates in this trans-formation reflects their low pK_a, so that the weak basicity of the corresponding anions precludes the isomerization. Michael addition of the secondary phosphine oxide anion to the isomerized Birch reduction product then gives the stabilized anion **III**. This can either give rise to **7** directly through protonation, or isomerize into **IV**. In turn, **IV** can evolve through two pathways: protonation provides **9**; treatment with another equivalent of a secondary phosphine affords the triphosphine trioxide **10**.

In summary, we have presented the synthesis of diphosphine dioxides possessing cyclohexenenyl linkers from seconday phosphine oxides and the readily available Birch reduction products of arylphosphine oxides. This protocol provides also an access to tris(phosphorus-substituted) cyclohexanes through

dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991–2000

the reaction of a (1,4-cyclohexen-3-yl)phosphine oxide with an excess of a secondary phosphine oxide.

EXPERIMENTAL SECTION

All reactions were performed under an argon atmosphere by using Schlenk techniques. Only dry solvents were used and the glassware was heated under vacuum prior to use. All chemicals were used as received unless otherwise noted. Solvents for chromatography and crystallization were distilled once before use, and the solvents for extraction were used as received. Dry EtOH was distilled from molecular sieves, and 1,4-dioxane was distilled from KOH. Ammonia was passed through solid NaOH before condensation.

Analytics and Instruments. The NMR spectra were recorded on 500, 400, or 300 MHz spectrometers in $CDCl_3$ as a solvent at room temperature unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak. Mass spectra were recorded in electron ionization (EI) mode, and GC was recorded using the following parameters: pressure, 97.9 kPa; total flow, 19.5 mL/min; column flow, 1.5 mL/min; linear velocity, 44.9 cm/s; split, 10; temperature program (70 °C, hold 3 min; 70−340 °C/12 °C/min, hold 9.5 min; total 35 min). Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution. The reaction mixtures were purified by column chromatography over silica gel (60−240 mesh). (1,4-Cyclohexadien-3-yl)dimethylphosphine−borane (**2**),[18] dimethylphenylphosphine oxide (**3**),[19] (1,4-cyclohexadien-3-yl)dimethylphosphine oxide (**4**),[19] diphenylphosphine−borane (**5**),[22] diphenylphosphine oxide (**8a**), bis-2-naphthylphosphine oxide (**8b**),[23] bis-1-naphthylphosphine oxide (**8c**),[23] bis-*p*-anisylphosphine oxide (**8d**),[24] bis-*o*-tolylphosphine oxide (**8e**),[25] *o*-anisylphenylphosphine oxide (**8f**),[26] benzylphenylphosphine oxide (**8g**),[27] phenyl(isopropyl)phosphine oxide (**8h**),[25] *tert*-butylphenylphosphine oxide (**8i**),[28] di-*c*-hexylphosphine oxide (**8j**),[29] di-*n*-hexylphosphine oxide (**8k**),[30] diethyl phosphite (**8l**),[31] and ethyl phenylphosphinate (**8m**)[32] were synthesized according to well-known procedures.

Dimethylphenylphosphine−Borane (1). Into a flame-dried three-necked round-bottom flask (250 mL) equipped with magnetic stirrer, reflux condenser, argon inlet, and a septum were placed magnesium (2.4 g, 100 mmol) and one piece of iodine in 100 mL of dry degassed diethyl ether. Then methyl iodide (6.23 mL, 100 mmol) was added dropwise through syringe. MeI (10%) was added to initiate the reaction, and after the reaction started the rest of the alkyl halide was added at a rate allowing gentle refluxing of the solvent. After addition of the halide, the mixture was heated to 35 °C and stirred until all magnesium dissolved. Then, the Grignard solution was cooled to 0 °C and dichlorophenylphosphine (5.43 mL, 40 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight under argon atmosphere. BH_3−THF (50 mL, 1 M in THF, 50 mmol) was added, and the reaction mixture was allowed to stir for another 2 h. The mixture was quenched by slow addition of saturated ammonium chloride solution (100 mL), the organic layer was removed, and the aqueous layer was washed with chloroform (3 × 30 mL). The organic fractions were collected, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography using hexane/EtOAc 6:1 as eluent yielding 2.25 g (37%) of title compound as a colorless oil: R_f = 0.38 (hexane/EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.17−0.96 (bm, 3H), 1.50 (d, J_{P-H} = 10.4 Hz, 6H), 7.35−7.45 (m, 3H), 7.61−7.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9 (d, J_{P-C} = 39.1 Hz), 128.8 (d, J_{P-C} = 9.8 Hz), 130.8 (d, J_{P-C} = 9.5 Hz), 130.9 (d, J_{P-C} = 55.2 Hz), 131.1 (d, J_{P-C} = 2.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 3.08; GC t_R = 3.97 min; GCMS (EI, 70 eV) m/z = 138 ($M - BH_3^+$) (100), 123 (80), 121 (78), 107 (11), 91 (49). Anal. Calcd for $C_8H_{14}BP$: C, 63.22; H, 9.28. Found: C, 62.99; H, 9.15.

(1,3-Cyclohexadien-2-yl)dimethylphosphine−Borane (6). A flame-dried Schlenk flask (25 mL) equipped with magnetic stirrer and argon inlet was placed in the water−ice bath. Dry ethanol (5 mL) and pieces of sodium (0.02 g, 0.87 mmol) were then added. After dissolution of sodium (usually 20 min) a solution of (1,4-cyclohexadien-3-yl)dimethylphosphine−borane (0.053 g, 0.34 mmol) in 1 mL of dry ethanol was added at once via syringe. The argon inlet was then replaced with an argon balloon, and the flask was placed in preheated oil bath (60 °C) and heated for 24 h. Then, the mixture was allowed to cool to room temperature, NH_4Cl (satd) was added, and the mixture was extracted with DCM (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was purified with column chromatography using hexane/ethyl acetate 6:1 as eluent yielding 0.04 g (75%) of (1,3-cyclohexadien-2-yl)-dimethylphosphine−-borane containing about 6% of starting material: R_f = 0.70 (hexane/EtOAc = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.23−0.93 (bm, 3H), 1.35 (d, J_{P-H} = 10.4 Hz, 6H), 2.15−2.22 (m, 2H), 2.26−2.34 (m, 2H), 5.99−6.05 (m, 2H), 6.54−6.61 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 11.0 (d, J_{P-C} = 39.1 Hz), 21.1 (d, J_{P-C} = 1.8 Hz), 23.0 (d, J_{P-C} = 11.8 Hz), 120.7 (d, J_{P-C} = 6.4 Hz), 127.0 (d, J_{P-C} = 56.3 Hz), 128.0 (d, J_{P-C} = 8.2 Hz), 128.6 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 0.75; GC t_R = 6.54 min; GCMS (EI, 70 eV) m/z = 141 (9), 140 (100), 139 (31), 125 (39), 123 (10), 109 (13), 97 (33), 92 (11), 91 (23), 83 (10), 80 (11).

Reaction between (1,3-Cyclohexadien-2-yl)-dimethylphosphine−Borane (6) and Diphenylphosphine−Borane 5. To a solution of diphenylphosphine−borane (0.100 g, 0.5 mmol) in 1,4-dioxane (5 mL) was added *n*-butyllithium (0.34 mL, 1.6 M in hexanes, 0.55 mmol), and the reaction mixture was stirred at ambient temperature for 15 min. Subsequently, a solution of (1,3-cyclohexadien-2-yl)dimethylphosphine−borane (**6**) (0.077 g, 0.5 mmol) in 1,4-dioxane (5 mL) was added, and the reaction mixture was heated at 70 °C for 24 h. The reaction was then quenched by addition of saturated NH_4Cl solution (5 mL), diluted with water (5 mL), and extracted with diethyl ether (2 × 15 mL) and dichloromethane (2 × 15 mL). The collected organic phases were dried over $MgSO_4$, filtered through a thin layer of Celite, which was rinsed with dichloromethane (3 × 5 mL), and evaporated to dryness. The crude reaction mixture was examined by TLC and then purified by column chromatography (silica gel, $CHCl_3$/EtOAc/MeOH = 7:7:1) yielding *trans*-3-(dimethylphosphinoyl)-4-(diphenylphosphinoyl)cyclohexene (**7a**) as an colorless oil (0.070 g, 39%): R_f = 0.56 ($CHCl_3$/MeOH = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, J_{P-H} = 12.3 Hz, 3H), 1.43 (d, J_{P-H} = 12.4 Hz, 3H), 1.81−2.05 (m, 3H), 2.45−2.61 (m, 1H), 2.71−2.85 (m, 1H), 3.36−3.46 (m, 1H), 5.52−5.59 (m, 1H), 6.02−6.1 (m, 1H), 7.39−7.57 (m, 6H, Ph), 7.65−8.0 (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0 (d, J_{P-C} = 67.5 Hz), 15.8 (d, J_{P-C} = 67.2 Hz), 19.2 (d, J_{P-C} = 2.9 Hz), 22.1 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 2.2 Hz), 28.7 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 70.0 Hz), 36.2 (d, J_{P-C} = 63.4 Hz), 119.0 (d, J_{P-C} = 5.5 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 128.7 (d, J_{P-C} = 10.9 Hz), 130.9 (d, J_{P-C} = 9.1 Hz), 131.3 (d, J_{P-C} = 8.2 Hz), 131.59 (d, J_{P-C} = 95.7 Hz), 131.62 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 2.7 Hz), 131.9 (d, J_{P-C} = 96.3 Hz), 132.0 (d, J_{P-C} = 5.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 35.22 (d, J_{P-P} = 41.7 Hz), 45.54 (d, J_{P-P} = 41.7 Hz); GC R_T = 26.94 min; GCMS (EI, 70 eV) m/z = 358 [M] (5), 281 (95), 203 (100), 201 (60), 185 (37), 157 (87), 155 (30), 125 (45), 95 (8), 91 (8), 80 (11). Anal. Calcd for $C_{20}H_{24}O_2P_2$: C, 67.03; H, 6.75. Found: C, 67.20; H, 6.85.

Typical Procedure for One-Pot Reaction between (1,4-Cyclohexadien-3-yl)dimethylphosphine Oxide (4) and >P(O)-H-Type Compounds. To a solution of secondary phosphine oxide (0.5 mmol) in 1,4-dioxane or ethanol (5 mL) was added an appropriate amount of a base, and the reaction mixture was stirred at ambient temperature for 15 min. Subsequently, a solution of (1,4-cyclohexadien-3-yl)dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) in 1,4-dioxane or ethanol (5 mL) was added, and the reaction mixture was heated at 70 °C or stirred at room temperature for 24 h. The reaction was then quenched by addition of saturated NH_4Cl solution (5 mL), diluted with water (5 mL), and extracted with diethyl ether (2 × 15 mL) and dichloromethane (2 × 15 mL). The collected organic phases were dried over $MgSO_4$, filtered through a thin layer of Celite, which was rinsed with dichloromethane (3 × 5 mL) and evaporated to dryness. The crude products were purified by column chromatography (silica gel, $CHCl_3$/EtOAc/MeOH = 7:7:1).

dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991−2000

*3-(Dimethylphosphinoyl)-2-(diphenylphosphinoyl)cyclohexene (**9a**).* Prepared from (1,4-cyclohexadien-3-yl)dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and diphenylphosphine oxide (**8a**) (0.101 g, 0.5 mmol): yield 0.016 g (9%); colorless thick oil; R_f = 0.16 ($CHCl_3$/MeOH = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (d, J_{P-H} = 13.0 Hz, 3H), 1.50 (d, J_{P-H} = 13.0 Hz, 3H), 1.57−1.73 (m, 1H), 1.94−2.05 (m, 1H), 2.09−2.31 (m, 3H), 2.35−2.49 (m, 1H), 3.92−4.02 (m, 1H), 6.59−6.69 (m, 1H), 7.42−7.56 (m, 6H), 7.86−7.99 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.9 (d, J_{P-C} = 69.0 Hz), 17.8 (d, J_{P-C} = 1.8 Hz), 18.7 (d, J_{P-C} = 71.8 Hz), 24.3 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 5.5 Hz), 25.3 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 34.6 (dd, J_{P-C} = 7.3 Hz, J_{P-C} = 67.2 Hz), 128.3 (d, J_{P-C} = 11.8 Hz), 128.5 (d, J_{P-C} = 11.8 Hz), 131.1 (d, J_{P-C} = 8.2 Hz), 131.2 (d, J_{P-C} = 8.2 Hz), 131.5 (d, J_{P-C} = 2.7 Hz), 131.9 (d, J_{P-C} = 2.7 Hz), 132.5 (d, J_{P-C} = 94.5 Hz), 132.7 (d, J_{P-C} = 94.5 Hz), 144.8 (dd, J_{P-C} = 9.1 Hz, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.75; 36.86; GC t_R = 17.97 min; GCMS (EI, 70 eV) m/z = 358 (M^+) (5), 281 (82), 203 (93), 201 (82), 185 (35), 183 (19), 157 (100), 155 (37), 125 (49), 95 (13), 80 (20). Anal. Calcd for $C_{20}H_{24}O_2P_2$: C, 67.03; H, 6.75. Found: C, 67.32; H, 6.70.

*trans-3-(Dimethylphosphinoyl)-4-(di(2-naphthyl)phosphinoyl)-cyclohexene (**7b**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di(2-naphthyl)phosphine oxide (**8b**) (0.151 g, 0.5 mmol): yield 0.094 g (41%); white thick oil; R_f = 0.30 ($CHCl_3$/AcOEt/MeOH = 5:5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (d, J_{P-H} = 12.2 Hz, 3H), 1.47 (d, J_{P-H} = 12.9 Hz, 3H), 1.83−2.20 (m, 4H), 2.80−3.00 (m, 1H), 3.58−3.78 (m, 1H), 5.47−5.64 (m, 1H), 6.00−6.16 (m, 1H), 7.40−7.60 (m, 4H), 7.70−8.00 (m, 8H), 8.43−8.58 (m, 1H), 8.62−8.76 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1 (d, J_{P-C} = 68.1 Hz), 15.9 (d, J_{P-C} = 67.2 Hz), 19.4 (d, J_{P-C} = 2.7 Hz), 22.2 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 3.0 Hz), 28.4 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 69.9 Hz), 36.4 (d, J_{P-C} = 63.6 Hz), 119.2 (d, J_{P-C} = 6.4 Hz), 125.66 (d, J_{P-C} = 10.0 Hz), 125.92 (d, J_{P-C} = 9.1 Hz), 126.90 (d, J_{P-C} = 3.6 Hz), 127.74 (d, J_{P-C} = 2.7 Hz), 128.09, 128.14, 128.62, 128,67, 128.76, 128.85, 128.88 (d, J_{P-C} = 95.4 Hz), 128.91 (d, J_{P-C} = 93.6 Hz), 132.15 (d, J_{P-C} = 11.8 Hz), 132.57 (d, J_{P-C} = 5.5 Hz), 132.68 (d, J_{P-C} = 5.5 Hz), 133.06 (d, J_{P-C} = 7.3 Hz), 133.67 (d, J_{P-C} = 8.2 Hz), 134.55 (d, J_{P-C} = 1.8 Hz), 134.59 (d, J_{P-C} = 1.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.55 (d, J_{P-P} = 42.3 Hz), 45.47 (d, J_{P-P} = 42.3 Hz). Anal. Calcd for $C_{28}H_{28}O_2P_2$: C, 73.35; H, 6.16. Found: C, 73.24; H, 6.40.

*2-(Dimethylphosphinoyl)-3-(di(2-naphthyl)phosphinoyl)-cyclohexene (**9b**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di(2-naphthyl)phosphine oxide (**8b**) (0.156 g, 0.5 mmol): yield 0.030 g (13%); pale yellow thick oil; R_f = 0.38 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, J_{P-H} = 13.2 Hz, 3H), 1.52 (d, J_{P-H} = 12.9 Hz, 3H), 1.53−1.72 (m, 2H), 2.05−2.14 (m, 1H), 2.24−2.34 (m, 2H), 2.45−2.56 (m, 1H), 4.19−4.27 (m, 1H), 6.65−6.74 (m, 1H), 7.50−7.60 (m, 4H), 7.81−7.88 (m, 2H), 7.90−7.97 (m, 5H), 7.99−8.05 (m, 1H), 8.54−8.67 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.3 (d, J_{P-C} = 69.9 Hz), 18.0 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 2.7 Hz), 18.8 (d, J_{P-C} = 72.7 Hz), 24.6 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 5.5 Hz), 25.5 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 34.5 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 67.2 Hz), 125.9 (d, J_{P-C} = 10.5 Hz), 126.8, 126.89, 126.91 (d, J_{P-C} = 9.8 Hz), 128.03, 128.08, 128.12, 128.15, 128.5 (d, J_{P-C} = 11.8 Hz), 128.9, 129.0, 130.0 (dd, J_{P-C} = 21.8 Hz, J_{P-C} = 94.5 Hz), 132.3 (d, J_{P-C} = 12.7 Hz, 132.6 (d, J_{P-C} = 12.7 Hz, 133.1 (d, J_{P-C} = 8.2 Hz), 133.86 (d, J_{P-C} = 8.2 Hz), 134.5 (d, J_{P-C} = 1.7 Hz), 134.6 (d, J_{P-C} = 2.9 Hz), 145.0 (dd, J_{P-C} = 9.1 Hz, J_{P-C} = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.41, 37.46. Anal. Calcd for $C_{28}H_{28}O_2P_2$: C, 73.35; H, 6.16. Found: C, 73.10; H, 6.02.

*trans-3-(Dimethylphosphinoyl)-4-(di(1-naphthyl)phosphinoyl)-cyclohexene (**7c**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di(1-naphthyl)phosphine oxide (**8c**) (0.151 g, 0.5 mmol): yield 0.158 g (69%); white solid; mp = 264−266 °C; R_f = 0.47 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, J_{P-H} = 12.6 Hz, 3H), 1.50 (d, J_{P-H} = 12.1 Hz, 3H), 1.59−1.72 (m, 1H), 1.84−1.98 (m, 1H), 2.15−2.24 (m, 1H), 2.44−2.58 (m, 1H), 3.33−3.47 (m, 1H), 3.98−4.98 (m, 1H), 5.61−5.68 (m, 1H), 6.03−6.10 (m, 1H), 7.29−7.38 (m, 2H), 7.42−7.45 (m, 2H), 7.50−7.56 (m, 1H), 7.61−7.66 (m, 1H), 7.74−7.79 (m, 1H), 7.79−7.84 (m, 1H), 7.93−9.98 (m, 2H), 8.24−8.34 (m, 1H), 8.62−8.72 (m, 2H), 8.74−8.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.6 (d, J_{P-C} = 67.2 Hz), 16.6 (d, J_{P-C} = 67.2 Hz), 20.4 (d, J_{P-C} =1.1 Hz), 22.5 (dd, J_{P-C} = 2.3 Hz, J_{P-C} = 3.2 Hz), 28.3 (dd, J_{P-C} = 2.6 Hz, J_{P-C} = 71.0 Hz), 37.2 (dd, J_{P-C} = 1.1 Hz, J_{P-C} = 62.9 Hz), 119.8 (d, J_{P-C} = 5.5 Hz), 124.5 (d, J_{P-C} = 8.3 Hz), 124.7 (d, J_{P-C} = 8.6 Hz), 125.8 (d, J_{P-C} = 4.0 Hz), 126.2 (d, J_{P-C} = 4.6 Hz), 126.7 (d, J_{P-C} = 5.2 Hz), 126.9, 127.4, 128.2 (dd, J_{P-C} = 1.7 Hz, J_{P-C} = 89.7 Hz), 128.7 (d, J_{P-C} = 1.2 Hz), 128.90 (d, J_{P-C} = 1.2 Hz), 128.92 (d, J_{P-C} = 93.7 Hz), 131.5 (d, J_{P-C} = 10.3 Hz), 131.6 (d, J_{P-C} = 9.8 Hz), 132.9 (d, J_{P-C} = 2.9 Hz), 133.0 (d, J_{P-C} = 2.9 Hz), 133.59 (d, J_{P-C} = 9.2 Hz), 133.62 (d, J_{P-C} = 9.2 Hz), 133.8 (d, J_{P-C} = 7.5 Hz), 134.1 (d, J_{P-C} = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.00 (d, J_{P-P} = 40.4 Hz), 45.88 (d, J_{P-P} = 40.4 Hz). Anal. Calcd for $C_{28}H_{28}O_2P_2$: C, 73.35; H, 6.16. Found: C, 73.60; H, 6.22.

*trans-3-(Dimethylphosphinoyl)-4-(di-(p-anisyl)phosphinoyl)-cyclohexene (**7d**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di-*p*-anisylphosphine oxide (**8d**) (0.131 g, 0.5 mmol): yield 0.115 g (55%); white solid; mp =167−169 °C; R_f = 0.20 ($CHCl_3$/AcOEt/MeOH = 5:5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, J_{P-H} = 12.2 Hz, 3H), 1.44 (d, J_{P-H} = 12.4 Hz, 3H), 1.84−2.03 (m, 3H), 2.42−2.59 (m, 1H), 2.74−2.89 (m, 1H), 3.27−3.38 (m, 1H), 3.79 (s, 6H), 5.51−5.60 (m, 1H), 6.00−6.09 (m, 1H), 6.90−7.00 (m, 4H), 7.66−7.74 (m, 2H), 7.81−7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.9 (d, J_{P-C} = 67.2 Hz), 15.8 (d, J_{P-C} = 67.2 Hz), 19.2 (d, J_{P-C} = 2.3 Hz), 22.1 (dd, J_{P-C} = 1.7 Hz, J_{P-C} = 2.3 Hz), 28.9 (dd, J_{P-C} = 3.5 Hz, J_{P-C} = 70.7 Hz), 36.2 (d, J_{P-C} = 63.2 Hz), 55.16, 55.18, 114.1 (d, J_{P-C} = 12.1 Hz), 114.2 (d, J_{P-C} = 12.1 Hz), 119.2 (d, J_{P-C} = 6.0 Hz), 123.2 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 102.3 Hz), 123.3 (d, J_{P-C} = 102.9 Hz), 131.9 (d, J_{P-C} = 11.5 Hz), 132. Seven (d, J_{P-C} = 9.8 Hz), 133.1 (d, J_{P-C} = 9.8 Hz), 162.1 (d, J_{P-C} = 2.9 Hz), 162.2 (d, J_{P-C} = 2.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.39 (d, J_{P-P} = 41.4 Hz), 45.54 (d, J_{P-P} = 41.4 Hz). Anal. Calcd for $C_{22}H_{28}O_4P_2$: C, 63.15; H, 6.75. Found: C, 63.32; H, 6.99.

*2-(Dimethylphosphinoyl)-3-(di-(p-anisyl)phosphinoyl)-cyclohexene (**9d**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di-*p*-anisylphosphine oxide (**8d**) (0.131 g, 0.5 mmol): yield 0.059 g (28%); white thick oil; R_f = 0.36 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (d, J_{P-H} = 12.9 Hz, 3H), 1.53 (d, J_{P-H} = 12.9 Hz, 3H), 1.56−1.69 (m, 1H), 1.86−1.92 (m, 1H), 2.04−2.17 (m, 2H), 2.18−2.29 (m, 1H), 2.31−2.42 (m, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 3.93−3.89 (m, 1H), 6.63−6.71 (m, 1H), 6.94−6.99 (m, 4H), 7.74−7.80 (m, 2H), 7.81−7.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.0 (d, J_{P-C} = 69.9 Hz), 18.0 (dd, J_{P-C} = 1.82 Hz, J_{P-C} = 2.5 Hz), 18.8 (d, J_{P-C} = 72.7 Hz), 24.5 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 5.5 Hz), 25.5 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 35.3 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 68.1 Hz), 55.3, 113.9 (d, J_{P-C} = 12.7 Hz), 114.1 (d, J_{P-C} = 12.7 Hz), 124.2 (dd, J_{P-C} = 17.3 Hz, J_{P-C} = 100.8 Hz), 131.11 (d, J_{P-C} = 94.5 Hz), 131.14 (d, J_{P-C} = 94.5 Hz), 133.0 (d, J_{P-C} = 10.0 Hz), 133.8 (d, J_{P-C} = 10.0 Hz), 144.5 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 8.9 Hz), 162.1 (d, J_{P-C} = 2.7 Hz), 162.4 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 32.18, 37.29. Anal. Calcd for $C_{22}H_{28}O_4P_2$: C, 63.15; H, 6.75. Found: C, 63.35; H, 6.88.

*trans-3-(Dimethylphosphinoyl)-4-(di-(o-tolyl)phosphinoyl)-cyclohexene (**7e**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di-*o*-tolylphosphine oxide (**8e**) (0.115 g, 0.5 mmol): yield 0.062 g (32%); yellow thick oil; R_f = 0.35 ($CHCl_3$/EtOAc/MeOH = 5:5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (d, J_{P-H} = 12.4 Hz, 3H), 1.52 (d, J_{P-H} = 12.1 Hz, 3H), 1.67−1.77 (m, 1H), 1.88−2.01 (m, 2H), 2.22 (s, 3H), 2.89 (s, 3H), 2.35−2.49 (m, 1H), 3.11−3.25 (m, 1H), 3.72−3.82 (m, 1H), 5.60−5.70 (m, 1H), 5.99−6.12 (m, 1H), 7.09−7.18 (m, 2H), 7.25−7.42 (m, 4H), 7.97−8.06 (m, 1H), 8.18−8.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2 (d, J_{P-C} = 67.2 Hz), 16.2 (d, J_{P-C} = 67.2 Hz), 19.7 (d, J_{P-C} = 1.7 Hz), 21.0 (d, J_{P-C}= 4.6 Hz), 21.4 (d, J_{P-C}= 3.5 Hz), 21.9 (dd, J_{P-C}= 2.3 Hz, J_{P-C}= 3.5 Hz), 26.2 (dd, J_{P-C} = 2.9 Hz, J_{P-C}= 70.1 Hz), 36.8 (dd, J_{P-C}= 1.7 Hz, J_{P-C} = 63.2 Hz), 119.7 (d, J_{P-C}= 5.2 Hz), 125.5 (d, J_{P-C} = 10.9 Hz), 125.7 (d, J_{P-C}= 12.1 Hz),

dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991−2000

129.91 (d, J_{P-C}= 90.3 Hz), 129.92 (d, J_{P-C} = 90.9 Hz), 131.3, 131.5 (d, J_{P-C} = 3.5 Hz), 131.61, 131.63 (d, J_{P-C} = 3.5 Hz), 131.9 (d, J_{P-C} = 10.9 Hz), 132.2 (d, J_{P-C} = 10.3 Hz), 133.3 (d, J_{P-C} = 8.7 Hz), 140.9 (d, J_{P-C} = 9.2 Hz), 142.9 (d, J_{P-C} = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.62 (d, J_{P-P} = 39.5 Hz), 46.26 (d, J_{P-P} = 39.5 Hz); GC t_R = 23.83 min; GCMS (EI, 70 eV) m/z = 386 [M] (3), 309 (37), 253 (40), 231 (60), 213 (26), 207 (34), 165 (28), 157 (100), 139 (33), 135 (32), 91 (85). Anal. Calcd for $C_{22}H_{28}O_2P_2$: C, 68.38; H, 7.30. Found: C, 68.65; H, 7.47.

*3-(Dimethylphosphinoyl)-2-(di-(o-tolyl)phosphinoyl)cyclohexene (**9′e**).* Prepared from (1,4-cyclohexadien-3-yl)dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di-*o*-tolylphosphine oxide (**8e**) (0.115 g, 0.5 mmol): yield 0.029 g (15%); colorless thick oil; R_f = 0.26 (EtOAc/$CHCl_3$/MeOH = 5:5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, J_{P-H} = 13.3 Hz, 3H), 1.59 (d, J_{P-H} = 13.4 Hz, 3H), 1.64−1.78 (m, 2H), 1.90−2.03 (m, 2H), 2.25−2.38 (m, 2H), 2.35 (s, 3H), 2.45 (s, 3H), 3.91−4.05 (m, 1H), 6.91−7.03 (m, 1H), 7.18−7.28 (m, 4H), 7.35−7.45 (m, 2H), 7.63−7.72 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.79 (d, J_{P-C} = 69.9 Hz), 18.42 (d, JP-C = 5.5 Hz), 18.62 (d, J_{P-C} = 72.7 Hz), 21.60 (d, J_{P-C} = 3.6 Hz), 21.68 (d, J_{P-C} = 3.6 Hz), 25.16 (d, J_{P-C} = 5.5 Hz), 25.45 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 37.20 (dd, J_{P-C} = 8.4 Hz, J_{P-C} = 63.4 Hz), 125.19 (d, J_{P-C} = 11.8 Hz), 125.33 (d, J_{P-C} = 11.8 Hz), 131.64 (d, J_{P-C} = 96.3 Hz), 131.86 (d, J_{P-C} = 2.7 Hz), 131.88 (d, J_{P-C} = 2.7 Hz), 132.26 (d, J_{P-C} = 10.9 Hz), 132.55 (d, J_{P-C} = 10.9 Hz), 142.87 (d, J_{P-C} = 8.2 Hz), 142.97 (d, J_{P-C} = 8.2 Hz), 145.51 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 9.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.09, 46.79; GC t_R = 23.50 min; GC−MS (EI, 70 eV) m/z = 386 [M] (6), 371 (40), 229 (20), 215 (20), 165 (25), 159 (50), 157 (100), 137 (25), 91 (68). Anal. Calcd for $C_{22}H_{28}O_2P_2$: C, 68.38; H, 7.30. Found: C, 68.54; H, 7.45.

*trans-3-(Dimethylphosphinoyl)-4-(o-anisylphenylphosphinoyl)-cyclohexene (**7f**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and *o*-anisylphenylphosphine oxide (**8f**) (0.116 g, 0.5 mmol): yield 0.134 g (70%). Major diastereoisomer was isolated in pure form. Major diastereomer: light yellow solid; mp =206.0−208.0 °C; R_f = 0.36 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (d, J_{H-P} = 12.1 Hz, 3H), 1.47 (d, J_{H-P} = 12.1 Hz, 3H), 1.77−1.85 (m, 1H), 2.00−2.17 (m, 2H), 2.33−2.45 (m, 1H), 2.75−2.85 (m, 1H), 3.72−3.80 (m, 1H), 3.85 (s, 3H), 5.61−5.67 (m, 1H), 6.06−6.13 (m, 1H), 6.86−6.91 (m, 1H), 7.10−7.14 (m, 1H), 7.40−7.46 (m, 4H), 7.47−7.52 (m, 1H), 8.00−8.06 (m, 2H), 8.12−8.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.18 (d, J_{P-C} = 67.2 Hz), 15.23 (d, J_{P-C} = 67.2 Hz), 19.7 (d, J_{P-C} = 2.7 Hz), 22.2 (d, J_{P-C} = 2.7 Hz), 28.1 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 69.0 Hz), 36.1 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 64.5 Hz), 55.4, 110.5 (d, J_{P-C} = 6.4 Hz), 119.4 (d, J_{P-C} = 6.4 Hz), 121.3 (d, J_{P-C} = 9.1 Hz), 128.2 (d, J_{P-C} = 11.8 Hz), 131.4 (d, J_{P-C} = 2.7 Hz), 131. Six (d, J_{P-C} = 9.1 Hz), 132.1 (d,J_{P-C} = 11.8 Hz), 132.9 (d, J_{P-C} = 83.6 Hz), 133.9 (d, J_{P-C} = 1.8 Hz), 134.7 (d, J_{P-C} = 4.5 Hz), 159.2 (d, J_{P-C} = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.99 (d, J_{P-P} = 44.8 Hz), 44.95 (d, J_{P-P} = 46.3 Hz); GC t_R = 28.10 min; GC−MS (EI, 70 eV) m/z = 389 (M) (7), 312 (20), 311 (48), 233 (47), 231 (16), 215 (45), 201 (11), 199 (48), 196 (10), 158 (16), 157 (81), 155 (26), 153 (12), 152 (28), 141 (19), 139 (17), 138 (10), 137 (17), 125 (10), 91 (100), 80 (15). Anal. Calcd for $C_{21}H_{26}O_3P_2$: C, 64.94; H, 6.75. Found: C, 65.16; H, 7.00. Minor diastereomer: R_f = 0.36 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, J_{H-P} = 12.1 Hz, 3H), 1.42 (d, J_{H-P} = 12.1 Hz, 3H), 1.86−2.14 (m, 2H), 2.27−2.47 (m, 2H), 2.71−2.84 (m, 1H), 3.57−3.79 (m, 1H), 3.84 (s, 3H), 5.57−5.65 (m, 1H), 6.03−6.13 (m, 1H), 6.81−6.89 (m, 1H), 7.06−7.13 (m, 1H), 7.37−7.45 (m, 4H), 7.44−7.51 (m, 1H), 7.93−8.04 (m, 2H), 8.06−8.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3 (d, J_{P-C} = 66.3 Hz), 19.4 (d, J_{P-C} = 2.7 Hz), 22.422 (d, J_{P-C} = 2.7 Hz), 28.6 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 68.1 Hz), 36.4 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 64.8 Hz), 55.4, 110.6 (d, J_{P-C} = 6.4 Hz), 119.1 (d, J_{P-C} = 6.4 Hz), 121.2 (d, J_{P-C} = 9.1 Hz), 128.1 (d, J_{P-C} = 11.8 Hz), 131.4 (d, J_{P-C} = 2.7 Hz), 131.6 (d, J_{P-C} = 9.1 Hz), 132.1 (d,J_{P-C} = 11.8 Hz), 132.9 (d, J_{P-C} = 83.6 Hz), 134.1 (d, J_{P-C} = 1.8 Hz), 135.4 (d, J_{P-C} = 4.5 Hz), 158.9 (d, J_{P-C} = 4.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.13 (d, J_{P-P} = 46.3 Hz), 44.72 (d, J_{P-P} = 44.8 Hz); GC t_R = 28.10 min; GC−MS (EI, 70 eV) m/z = 387 (M) (4), 312 (23), 311 (54), 234 (13), 233 (51), 231 (19), 215 (42), 201 (11), 199 (44), 165 (14), 158 (22), 157 (67), 155 (23), 153 (14), 152 (24), 139 (15), 137 (21), 135 (14), 115 (11), 91 (100), 80 (23).

*2-(Dimethylphosphinoyl)-3-(o-anisylphenylphosphinoyl)-cyclohexene (**9f**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and *o*-anisylphenylphosphine oxide (**8f**) (0.101 g, 0.5 mmol). Isolated as a mixture of diastereoisomers: R_f = 0.36 (15:1, $CHCl_3$/MeOH). Major diastereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, J_{P-H} = 12.9 Hz, 3H), 1.45 (d, J_{P-H} = 12.9 Hz, 3H), 1.53−1.64 (m, 2H), 1.81−1.89 (m, 1H), 2.18−2.26 (m, 2H), 2.47−2.53 (m, 1H), 3.90 (s, 3H), 4.23−4.30 (m, 1H), 6.58−6.68 (m, 1H), 6.85−6.89 (m, 1H), 7.08−7.13 (m, 1H), 7.40−7.57 (m, 4H), 7.96−8.01 (m, 2H), 8.08−8.15 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.5 (d, J_{P-C} = 69.0 Hz), 17.9 (d, J_{P-C} = 71.8 Hz), 18.1 (d, J_{P-C} = 3.6 Hz), 24.9 (dd, J_{P-C} = 1.9 Hz, J_{P-C} = 4.9 Hz), 25.8 (dd, J_{P-C} = 3.1 Hz, J_{P-C} = 13.5 Hz), 33.2 (dd, J_{P-C} = 8.6 Hz, J_{P-C} = 67.7 Hz), 110.3 (d, J_{P-C} = 6.8 Hz), 121.2 (d, J_{P-C} = 10.5 Hz), 127.7 (d, J_{P-C} = 11.7 Hz), 131.6 (d, J_{P-C} = 3.1 Hz), 132.1 (d, J_{P-C} = 9.2 Hz), 133.5 (d, J_{P-C} = 2.5 Hz), 135.0 (d, J_{P-C} = 6.2 Hz), 144.1 (t, J_{P-C} = 9.2 Hz), 159.8 (d, J_{P-C} = 3.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.73 (d, J_{P-P} = 4.1 Hz), 36.22 (d, J_{P-P} = 4.1 Hz). Minor diastereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (d, J_{P-H} = 13.2 Hz, 3H), 1.46 (d, J_{P-H} = 12.9 Hz, 3H), 1.63−1.74 (m, 2H), 1.90−2.00 (m, 1H), 2.04−2.16 (m, 2H), 2.42−2.48 (m, 1H), 4.00 (s, 3H), 4.32−4.41 (m, 1H), 6.58−6.68 (m, 1H), 6.92−6.97 (m, 1H), 7.03−7.07 (m, 1H), 7.40−7.57 (m, 4H), 8.02−8.08 (m, 2H), 8.08−8.15 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.4 (d, J_{P-C} = 69.0 Hz), 17.9 (d, J_{P-C} = 4.5 Hz), 18.8 (d, J_{P-C} = 71.8 Hz), 24.5 (dd, J_{P-C} = 1.9 Hz, J_{P-C} = 4.9 Hz), 25.6 (dd, J_{P-C} = 3.1 Hz, J_{P-C} = 13.5 Hz), 33.6 (dd, J_{P-C} = 8.6 Hz, J_{P-C} = 67.7 Hz), 111.0 (d, J_{P-C} = 7.4 Hz), 120.5 (d, J_{P-C} = 11.1 Hz), 128.0 (d, J_{P-C} = 11.7 Hz), 131.2 (d, J_{P-C} = 3.1 Hz), 131.6 (d, J_{P-C} = 9.2 Hz), 134.1 (d, J_{P-C} = 1.9 Hz), 134.6 (d, J_{P-C} = 4.9 Hz), 144.8 (t, J_{P-C} = 9.2 Hz), 160.3 (d, J_{P-C} = 4.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.20 (d, J_{P-P} = 4.1 Hz), 36.44 (d, J_{P-P} = 4.1 Hz).

*3-(Dimethylphosphinoyl)-2-(o-anisylphenylphosphinoyl)-cyclohexene (**9′f**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and *o*-anisylphenylphosphine oxide (**8f**) (0.101 g, 0.5 mmol). Isolated as a mixture of diastereoisomers: R_f = 0.33 ($CHCl_3$/MeOH = 15:1). Major diastereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66 (d, J_{P-H} = 13.2 Hz, 3H), 1.71 (d, J_{P-H} = 12.9 Hz, 3H), 1.80−1.89 (m, 2H), 1.96−2.08 (m, 2H), 2.25−2.41 (m, 1H), 2.50−2.58 (m, 1H), 2.77−2.86 (m, 1H), 3.75 (s, 3H), 6.29−6.37 (m, 1H), 6.90−6.95 (m, 1H), 6.97−7.02 (m, 1H), 7.39−7.58 (m, 6H), 7.83−7.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.6 (d, J_{P-C} = 67.7 Hz), 18.2 (d, J_{P-C} = 67.1 Hz), 18.7 (d, J_{P-C} = 1.8 Hz), 23.6 (d, J_{P-C} = 3.1 Hz, J_{P-C} = 6.2 Hz), 25.9 (dd, J_{P-C} = 3.1 Hz, J_{P-C} = 14.8 Hz), 36.6 (dd, J_{P-C} = 9.2 Hz, J_{P-C} = 63.4 Hz), 55.4, 111.4 (d, J_{P-C} = 6.2 Hz), 120.9 (d, J_{P-C} = 11.7 Hz), 128.4 (d, J_{P-C} = 11.7 Hz), 131.8 (d, J_{P-C} = 2.7 Hz), 132.0 (J_{P-C} = 9.8 Hz), 131.3 (d, J_{P-C} = 2.5 Hz), 134.8 (d, J_{P-C} = 8.0 Hz), 144.4 (d, J_{P-C} = 11.1 Hz), 161.0 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.70, 47.43. Minor diastereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (d, J_{P-H} = 12.9 Hz, 3H), 1.61 (d, J_{P-H} =12.9 Hz, 3H), 1.80−1.89 (m, 2H), 1.96−2.08 (m, 2H), 2.25−2.41 (m, 1H), 2.57−2.64 (m, 1H), 2.77−2.86 (m, 1H), 3.84 (s, 3H), 6.25−6.32 (m, 1H), 6.93−6.98 (m, 1H), 7.07−7.11 (m, 1H), 7.39−7.58 (m, 6H), 7.92−7.98 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.4 (d, J_{P-C} = 67.1 Hz), 18.1 (d, J_{P-C} = 67.1 Hz), 18.7 (d, J_{P-C} = 1.8 Hz), 23.5 (dd, J_{P-C} = 3.1 Hz, J_{P-C} = 6.2 Hz), 26.0 (dd, J_{P-C} = 3.1 Hz, J_{P-C} = 14.8 Hz), 37.2 (dd, J_{P-C} = 9.2 Hz, J_{P-C} = 63.4 Hz), 55.4, 110.8 (d, J_{P-C} = 6.8 Hz), 121.3 (d, J_{P-C} = 11.1 Hz), 128.1 (d, J_{P-C} = 11.7 Hz), 131.8 (d, J_{P-C} = 2.7 Hz), 131.9 (d, J_{P-C} = 9.8 Hz), 134.3 (d, J_{P-C} = 1.9 Hz), 135.0 (d, J_{P-C} = 5.6 Hz), 144.3 (d, J_{P-C} = 11.1 Hz), 159.9 (d, J_{P-C} = 3.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.68, 47.25.

*trans-3-(Dimethylphosphinoyl)-4-(phenylisopropylphosphinoyl)-cyclohexene (**7h**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and isopropylphenylphosphine oxide (**8h**) (0.084 g, 0.5 mmol): yield 0.070 g (43%). Isolated as a mixture of diastereoisomers. Major diastereomer: R_f = 0.25 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10

dx.doi.org/10.1021/jo300026f | J. Org. Chem. 2012, 77, 1991−2000

(dd, J_{H-H} = 7.2 Hz, J_{P-H} = 16.3 Hz, 3H), 1.17 (dd, J_{H-H} = 7.0 Hz, J_{P-H} = 15.0 Hz, 3H), 1.49 (d, J_{P-H} = 12.3 Hz, 3H), 1.61 (d, J_{P-H} = 12.3 Hz, 3H), 1.58−1.65 (m, 1H), 1.65−1.75 (m, 2H), 1.88−1.97 (m, 1H), 2.30−2.40 (m, 1H), 3.05−3.21 (m, 2H), 5.52−5.62 (m, 1H), 5.85−5.94 (m, 1H), 7.38−7.55 (m, 3H), 7.64−7.74 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.8 (d, J_{P-C} = 67.2 Hz), 14.9 (d, J_{P-C} = 1.8 Hz), 15.9 (d, J_{P-C} = 68.1 Hz), 16.3 (d, J_{P-C} = 1.8 Hz), 20.1 (d, J_{P-C} = 2.7 Hz), 23.1 (d, J_{P-C} = 5.5 Hz), 26.9 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 63.6 Hz), 27.0 (d, J_{P-C} = 68.1 Hz), 36.2 (d, J_{P-C} = 2.7 Hz, J_{P-C} = 63.6 Hz), 119.6 (d, J_{P-C} = 5.5 Hz), 128.3 (d, J_{P-C} = 10.0 Hz), 129.0 (d, J_{P-C} = 84.5 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 131.6 (d, J_{P-C} = 3.6 Hz), 131.8 (d, J_{P-C} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.35 (d, J_{P-P} = 35.6 Hz), 48.77 (d, J_{P-P} =35.6 Hz); GC t_R = 19.62 min; GCMS (EI, 70 eV) m/z = 309 (2), 281 (14), 248 (17), 247 (41), 205 (6), 169 (59), 167 (9), 158 (35), 157 (100), 156 (9), 155 (14), 151 (25), 139 (8), 127 (11), 126 (13), 125 (54), 109 (21), 108 (6), 91 (15), 80 (29). Minor diastereomer: R_f = 0.34 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (dd, J_{H-H} = 6.9 Hz, J_{P-H} = 16.4 Hz), 1.11 (dd, J_{H-H} = 6.9 Hz, J_{P-H} = 14.8 Hz, 3H), 1.30 (d, J_{P-H} = 12.3 Hz, 3H), 1.43 (d, J_{P-H} = 12.3 Hz, 3H), 2.05−2.17 (m, 2H), 2.19−2.30 (m, 1H), 2.52−2.61 (m, 2H), 3.17−3.28 (m, 1H), 5.47−5.54 (m, 1H), 5.98−6.06 (m, 1H), 7.46−7.54 (m, 3H), 7.75−7.82 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.07 (d, J_{P-C} = 68.1 Hz), 15.8 (d, J_{P-C} = 67.2 Hz), 19.5 (d, J_{P-C} = 2.7 Hz), 22.3 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 2.9 Hz), 26.2 (d, J_{P-C} = 67.2 Hz), 26.5 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 66.3 Hz), 36.7 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 63.6 Hz), 119.4 (d, J_{P-C} = 6.4 Hz), 127.8 (d, J_{P-C} = 10.9 Hz), 130.8 (d, J_{P-C} = 86.3 Hz), 131.7 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 3.6 Hz), 132.0 (d, J_{P-C} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.33 (d, J_{P-P} = 37.6 Hz), 49.56 (d, J_{P-P} = 37.6 Hz); GC t_R = 19.37 min; GCMS (EI, 70 eV) m/z = 281 (6), 248 (17), 247 (63), 170 (10), 169 (100), 167 (12), 158 (15), 157 (85), 156 (9), 155 (21), 151 (43), 139 (7), 127 (16), 126 (13), 125 (59), 109 (26), 107 (7), 91 (17), 80 (26).

*3-(Dimethylphosphinoyl)-2-(phenylisopropylphosphinoyl)-cyclohexene (**9′h**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and isopropylphenylphosphine oxide (**8h**) (0.084 g, 0.5 mmol). Isolated as a mixture of diastereoisomers. First diastereoisomer: R_f = 0.34 ($CHCl_3$/EtOAc/MeOH = 5:5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (dd, J_{H-H} = 7.3 Hz, J_{P-H} = 16.7 Hz, 3H), 1.19 (d, J_{P-H} = 12.9 Hz, 3H), 1.24 (dd, J_{H-H} = 6.9 Hz, J_{P-H} = 15.5 Hz, 3H), 1.52 (d, J_{P-H} = 12.9 Hz, 3H), 1.50−1.61 (m, 2H), 1.65−1.74 (m, 1H), 1.96−2.15 (m, 3H), 2.74−2.86 (m, 1H), 3.43−3.51 (m, 1H), 6.32−6.43 (m, 1H), 7.41−7.60 (m, 3H), 7.80−7.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.1 (d, J_{P-C} = 3.6 Hz), 15.97 (d, J_{P-C} = 70.8 Hz), 16.03 (d, J_{P-C} = 2.7 Hz), 18.2 (d, J_{P-C} = 1.8 Hz), 18.4 (d, J_{P-C} = 71.8 Hz), 23.8 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 5.5 Hz), 25.1 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 26.5 (d, J_{P-C} = 63.6 Hz), 33.6 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 60.0 Hz), 128.3 (d, J_{P-C} = 10.0 Hz), 129.1 (d, J_{P-C} = 86.3 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 132.4 (d, J_{P-C} = 8.2 Hz), 142.5 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 10.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.86, 46.80; GC R_T = 18.79 min; GCMS (EI, 70 eV) m/z = 324 (M^+) (10), 323 (4), 282 (27), 281 (78), 267 (6), 253 (4), 205 (35), 201 (10), 188 (10), 158 (30), 157 (100), 156 (10), 155 (18), 142 (17), 141 (11), 140 (10), 139 (20), 126 (11), 125 (59), 124 (12), 112 (6), 109 (17), 95 (22), 93 (15), 92 (10), 91 (32), 80 (15). Second diastereoisomer: R_f = 0.25 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (dd, J_{H-H} = 7.2 Hz, J_{P-H} = 16.5 Hz, 3H), 1.24 (dd, J_{H-H} = 7.2 Hz, J_{P-H} = 15.2 Hz, 3H), 1.28−1.44 (m, 2H), 1.78 (d, J_{P-H} = 13.2 Hz, 3H), 1.80 (d, J_{P-H} = 13.2 Hz, 3H), 1.83−1.96 (m, 2H), 2.00−2.13 (m, 2H), 2.61−2.72 (m, 1H), 3.40−3.49 (m, 1H), 6.70−6.80 (m, 1H), 7.38−7.55 (m, 3H), 7.64−7.74 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.9 (d, J_{P-C} = 1.8 Hz), 16.2 (d, J_{P-C} = 2.7 Hz), 16.4 (d, J_{P-C} = 70.8 Hz), 17.4 (d, J_{P-C} = 3.6 Hz), 19.0 (d, J_{P-C} = 72.7 Hz), 21.7 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 3.6 Hz), 25.0 (d, J_{P-C} = 67.2 Hz), 25.1 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 12.7 Hz), 34.1 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 60.9 Hz), 128.3 (d, J_{P-C} = 10.0 Hz), 130.3 (d, J_{P-C} = 84.5 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 7.3 Hz), 144.8 (dd, J_{P-C} = 8.0 Hz, J_{P-C} = 8.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.15, 46.96; GC t_R = 19.05 min; GCMS (EI, 70 eV) m/z = 324 (M^+) (6), 323 (4), 309 (7), 282 (20), 281 (48), 247 (8), 205 (21), 201 (7), 188 (7), 169 (8), 159 (10), 158 (48), 157 (100), 155 (12), 143 (7), 142 (11), 141 (7), 140 (8), 139 (14), 125 (47), 124 (8), 109 (14), 95 (15), 91 (21), 80 (17).

*trans-3-(Dimethylphosphinoyl)-4-(tert-butylphenylphosphinoyl)-cyclohexene (**7i**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and *tert*-butylphenylphosphine oxide (**8i**) (0.091 g, 0.5 mmol). Major diastereoisomer: yield 0.086 g (51%); white solid; mp =126.8−130.0 °C; R_f = 0.47 ($CHCl_3$/MeOH = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, J_{P-H} = 14.2 Hz, 9H), 1.22 (d, J_{P-H} = 12.1 Hz, 3H), 1.41 (d, J_{P-H} = 12.3 Hz, 3H), 2.05−2.30 (m, 2H), 2.40−2.54 (m, 2H), 2.66−2.82 (m, 1H), 2.30−2.40 (m, 1H), 5.39−5.48 (m, 1H), 5.98−6.07 (m, 1H), 7.40−7.53 (m, 3H), 7.76−7.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 67.8 Hz), 16.2 (d, J_{P-C} = 67.2 Hz), 21.2 (d, J_{P-C} = 3.5 Hz), 22.5 (dd, J_{P-C} = 1.7 Hz, J_{P-C} = 2.9 Hz), 25.8, 26.9 (dd, J_{P-C} = 2.9 Hz, J_{P-C} = 59.2 Hz), 34.3 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 64.4 Hz), 37.7 (dd, J_{P-C} = 2.3 Hz, J_{P-C} = 63.2 Hz), 119.3 (d, J_{P-C} = 6.3 Hz), 128.2 (d, J_{P-C} = 10.3 Hz), 130.7 (d, J_{P-C} = 84.5 Hz), 131.4 (d, J_{P-C} = 2.9 Hz), 131.6 (d, J_{P-C} = 12.1 Hz), 132.1 (d, J_{P-C} = 6.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.65 (d, J_{P-P} = 37.7 Hz), 53.37 (d, J_{P-P} = 37.7 Hz); GC t_R = 21.33 min; GC−MS (EI, 70 eV) m/z = 338 (2), 281 (7), 261 (100), 183 (71), 165 (43), 157 (76), 127 (94), 125 (56), 109 (17), 91 (8), 80 (24). Anal. Calcd for $C_{18}H_{28}O_2P_2$: C, 63.89; H, 8.34. Found: C, 63.95; H, 8.50. Minor diastereoisomer: yield 0.047 g (28%); white solid; mp =168−172 °C; R_f = 0.42 ($CHCl_3$/MeOH = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, J_{P-H} = 14.0 Hz, 9H), 1.47 (d, J_{P-H} = 12.5 Hz, 3H), 1.59 (d, J_{P-H} = 12.0 Hz, 3H), 1.67−1.90 (m, 4H), 3.25−3.44 (m, 2H), 5.56−5.65 (m, 1H), 5.88−5.96 (m, 1H), 7.40−7.54 (m, 3H), 7.72−7.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1 (d, J_{P-C} = 66.7 Hz), 16.3 (d, J_{P-C} = 67.2 Hz), 21.1 (d, J_{P-C} = 2.9 Hz), 21.4 (dd, J_{P-C} = 2.9 Hz, J_{P-C} = 3.2 Hz), 25.5, 26.0 (dd, J_{P-C} = 2.9 Hz, J_{P-C} = 59.2 Hz), 34.8 (d, J_{P-C} = 65.5 Hz), 37.3 (dd, J_{P-C} = 2.3 Hz, J_{P-C} = 63.8 Hz), 119.9 (d, J_{P-C} = 5.8 Hz), 127.9 (d, J_{P-C} = 10.4 Hz), 129.5 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 82.8 Hz), 131.2 (d, J_{P-C} = 2.3 Hz), 131.3 (d, J_{P-C} = 11.5 Hz), 132.2 (d, J_{P-C} = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.67 (d, J_{P-P} = 36.5 Hz), 49.93 (d, J_{P-P} = 36.5 Hz); GC R_T = 22.04 min; GC−MS (EI, 70 eV) m/z = 338 [M] (1), 281 (5), 261 (45), 183 (28), 165 (16), 157 (100), 127 (36), 125 (32), 109 (8), 91 (6), 80 (14). Anal. Calcd for $C_{18}H_{28}O_2P_2$: C, 63.89; H, 8.34. Found: C, 64.10; H, 8.20.

*trans-3-(Dimethylphosphinoyl)-4-(dicyclohexylphosphinoyl)-cyclohexene (**7j**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and dicyclohexylphosphine oxide (**8j**) (0.107 g, 0.5 mmol): yield 0.080 g (43%); colorless thick oil; R_f = 0.18 ($CHCl_3$/MeOH = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17−1.29 (m, 8H), 1.37−1.59 (m, 3H), 1.50 (d, J_{P-H} = 12.3 Hz, 3H), 1.57 (d, J_{P-H} = 12.3 Hz, 3H), 1.76−1.97 (m, 11H), 2.01−2.09 (m, 2H), 2.16−2.30 (m, 2H), 2.80−2.93 (m, 1H), 2.94−3.06 (m, 1H), 5.67−5.74 (m, 1H), 6.12−6.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.3 (d, J_{P-C} = 67.8 Hz), 16.0 (d, J_{P-C} = 66.8 Hz), 21.2 (dd, J_{P-C} = 1.7 Hz, J_{P-C} = 2.3 Hz), 22.7 (dd, J_{P-C} = 3.5 Hz, J_{P-C} = 5.8 Hz), 25.7 (d, J_{P-C} = 4.0 Hz), 25.9 (d, J_{P-C} = 2.9 Hz), 25.96 (d, J_{P-C} = 1.7 Hz), 25.98 (d, J_{P-C} = 2.9 Hz), 26.2 (d, J_{P-C} = 3.2 Hz), 26.5 (d, J_{P-C} = 2.3 Hz), 26.6, 26.7 (d, J_{P-C} = 5.2 Hz), 26.79 (dd, J_{P-C} = 2.9 Hz, J_{P-C} = 55.8 Hz), 26.82 (d, J_{P-C} = 5.2 Hz), 27.0, 35.1 (d, J_{P-C} = 60.4 Hz), 35.6 (dd, J_{P-C} = 2.3 Hz, J_{P-C} = 64.4 Hz), 36.7 (d, J_{P-C} = 61.5 Hz), 120.8 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 7.5 Hz), 132.7 (d, J_{P-C} = 10.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.40 (d, J_{P-P} = 23.4 Hz), 53.50 (d, J_{P-P} = 23.4 Hz); GC R_T = 13.13 min; GC−MS (EI, 70 eV) m/z = 370 [M] (0.1), 323 (8), 322 (46), 321 (100), 307 (5), 229 (9), 213 (15), 165 (8), 152 (7), 133 (5), 115 (6), 92 (10), 91 (13); Anal. Calcd for $C_{20}H_{36}O_2P_2$: C, 64.84; H, 9.80. Found: C, 65.12; H, 9.53.

*2-(Dimethylphosphinoyl)-3-(dicyclohexylphosphinoyl)-cyclohexene (**9j**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and dicyclohexylphosphine oxide (**8j**) (0.107 g, 0.5 mmol). Isolated as a mixture with other compounds: R_f = 0.53 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16−1.31 (m, 7H), 1.36−1.55 (m, 5H), 1.72 (d, J_{P-H} = 13.1 Hz, 3H), 1.75 (d, J_{P-H} = 13.7 Hz, 3H), 1.77−1.87 (m, 8H),

1.88−2.00 (m, 6H), 2.12−2.32 (m, 2H), 3.06−3,18 (m, 1H), 6.94−7.04 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.10, 51.81.

*trans-3-(Dimethylphosphinoyl)-4-(di-n-hexylphosphinoyl)-cyclohexene (**7k**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and dicyclohexylphosphine oxide (**8k**) (0.109 g, 0.5 mmol): yield 0.045 g (24%); pale yellow thick oil; R_f = 0.28 ($CHCl_3$/EtOAc/MeOH = 5:5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79−0.87 (m, 6H), 1.20−1.28 (m, 8H), 1.30−1.38 (m, 4H), 1.47 (d, J_{P-H} = 12.3 Hz, 3H), 1.54 (d, J_{P-H} = 12.1 Hz, 3H), 1.54−1.61 (m, 4H), 1.63−1.76 (m, 3H), 1.83−1.95 (m, 1H), 1.98−2.22 (m, 3H), 2.51−2.70 (m, 2H), 2.73−2.87 (m, 1H), 5.62−5.69 (m, 1H), 6.01−6.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 14.7 (d, J_{P-C} = 67.2 Hz), 15.6 (d, J_{P-C} = 67.8 Hz), 19.5 (d, J_{P-C} = 1.2 Hz), 21.5 (d, J_{P-C} = 4.6 Hz), 21.8 (d, J_{P-C} = 4.6 Hz), 22.1, 22.1 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 5.2 Hz), 22.3, 26.6 (d, J_{P-C} = 61.5 Hz), 26.7 (d, J_{P-C} = 63.8 Hz), 29.5 (dd, J_{P-C} = 2.9 Hz, J_{P-C} = 61.5 Hz), 30.8 (d, J_{P-C} = 8.1 Hz), 31.9 (d, J_{P-C} = 8.1 Hz), 31.2, 35.6 (dd, J_{P-C} = 1.7 Hz, J_{P-C} = 64.4 Hz), 120.2 (d, J_{P-C} = 6.9 Hz), 132.0 (d, J_{P-C} = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.48 (d, J_{P-P} = 34.0 Hz); 52.37 (d, J_{P-P} = 34.0 Hz); GC t_R = 23.43 min; GC−MS (EI, 70 eV) m/z = 374 (2), 297 (36), 219 (23), 205 (13), 157 (100), 91 (6), 80 (7). Anal. Calcd for $C_{20}H_{40}O_2P_2$: C, 64.15; H, 10.77. Found: C, 64.26; H, 10.50.

*2-(Dimethylphosphinoyl)-3-(di-n-hexylphosphinoyl)cyclohexene (**9k**).* Prepared from (1,4-cyclohexadien-3-yl)dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and di-*n*-hexylphosphine oxide (**8k**) (0.109 g, 0.5 mmol: yield 0.067 g (36%); light yellow thick oil; R_f = 0.52 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.83−0.90 (m, 7H), 1.23−2.31 (m, 8H), 1.31−1.40 (m, 3H), 1.53−1.62 (m, 4H), 1.65 (d, J_{P-H} = 13.9 Hz, 3H), 1.68 (d, J_{P-H} = 14.6 Hz, 3H), 1.70−1.76 (m, 4H), 1.76−1.90 (m, 3H), 2.00−2.13 (m, 1H), 2.25−2.31 (m, 2H); 2.98−3.09 (m, 1H), 6.71−6.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 16.0 (d, J_{P-C} = 71.3 Hz), 17.2 (d, J_{P-C} = 71.3 Hz), 18.7 (dd, J_{P-C} = 1.2 Hz, J_{P-C} = 2.0 Hz), 21.4 (d, J_{P-C} = 4.0 Hz), 21.5 (d, J_{P-C} = 4.6 Hz), 22.3, 23.7 (dd, J_{P-C} = 1.7 Hz, J_{P-C} = 6.3 Hz), 25.5 (dd, J_{P-C} = 2.3 Hz, J_{P-C} = 12.6 Hz), 27.9 (d, J_{P-C} = 62.1 Hz), 28.2 (d, J_{P-C} = 63.8 Hz), 30.7 (d, J_{P-C} = 2.3 Hz), 30.8 (d, J_{P-C} = 2.3 Hz), 31.27, 31.31, 35.4 (dd, J_{P-C} = 8.6 Hz, J_{P-C} = 59.2 Hz), 132.5 (dd, J_{P-C} = 5.8 Hz, J_{P-C} = 91.4 Hz), 143.0 (dd, J_{P-C} = 8.1 Hz, J_{P-C} = 8.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.37, 51.31; GC t_R = 22.56 min; GC−MS (EI, 70 eV) m/z = 374 (M^+) (5), 359 (8), 317 (14), 289 (8), 205 (100), 158 (30), 157 (96). 141 (13), 91 (10). Anal. Calcd for $C_{20}H_{40}O_2P_2$: C, 64.15; H, 10.77, Found: C, 64.42; H, 10.65.

*trans,cis-2-Dimethylphosphinoyl-1,3-bis(diphenylphosphinoyl)-cyclohexane (**10a**).* Prepared from (1,4-cyclohexadien-3-yl)-dimethylphosphine oxide (**4**) (0.078 g, 0.5 mmol) and diphenylphosphine oxide (**8a**) (0.202 g, 1.0 mmol): yield 0.160 g (57%); white solid; mp >270 °C; R_f = 0.47 ($CHCl_3$/MeOH = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, J_{H-P} = 12.9 Hz, 3H), 1.64−1.73 (m, 2H), 1.77−1.88 (m, 2H), 2.00 (d, J_{H-P} = 13.6 Hz, 3H), 2.08−2.14 (m, 2H), 2.73−2.84 (m, 1H), 3.87−3.98 (m, 1H), 4.30−4.48 (m, 1H), 7.14−7.20 (m, 2H), 7.41−7.54 (m, 10H), 7.75−7.85 (m, 6H), 8.00−8.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.8 (d, J_{P-C} = 69.0 Hz), 20.2 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 60.9 Hz), 20.7, 22.4, 22.6 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 12.7 Hz), 30.2 (ddd, J_{P-C} = 2.7 Hz, J_{P-C} = 10.9 Hz, J_{P-C} = 69.0 Hz), 34.7 (d, J_{P-C} = 72.7 Hz), 36.1 (d, J_{P-C} = 57.22 Hz), 128.69 (d, J_{P-C} = 10.9 Hz), 128.73 (d, J_{P-C} = 8.2 Hz), 128.8 (d, J_{P-C} = 9.1 Hz), 129.0 (d, J_{P-C} = 10.9 Hz), 130.4 (d, J_{P-C} = 9.1 Hz), 130.5 (d, J_{P-C} = 8.2 Hz), 130.6 (d, J_{P-C} = 9.1 Hz), 131.1 (d, J_{P-C} = 8.2 Hz), 131.5 (d, J_{P-C} = 2.7 Hz), 131.5 (d, J_{P-C} = 2.7 Hz), 131.7 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 121.7 Hz), 131.8 (d, J_{P-C} = 2.7 Hz), 132.0 (d, J_{P-C} = 95.4 Hz), 132.0 (d, J_{P-C} = 96.3 Hz), 132.0 (d, J_{P-C} = 123.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.52 (dd, J_{P-P} = 1.5 Hz, J_{P-P} = 4.1 Hz), 39.12 (dd, J_{P-P} = 2.0 Hz, J_{P-P} = 43.2 Hz), 46.48 (dd, J_{P-P} = 4.1 Hz, J_{P-P} = 43.2 Hz). Anal. Calcd for $C_{32}H_{35}O_3P_3$: C, 68.57; H, 6.29. Found: C, 68.69; H, 6.50.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C, and ^{31}P NMR and GC−MS of pure compounds. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: marek.stankevic@poczta.umcs.lublin.pl.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Ministry of Science and Higher Education (research grant no. N N204 2328 34) is kindly acknowledged. We are grateful to Dr. Duncan Carmichael for his guidance during the preparation of manuscript.

■ REFERENCES

(1) Marinetti, A.; Voituriez, A. *Synlett* **2010**, 174−194.
(2) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338−6361.
(3) Ren, Y.; Baumgartner, T. *J. Am. Chem. Soc.* **2011**, *133*, 1328−1340.
(4) Onoda, M.; Tokuyama, H.; Uchiyama, S.; Mawatari, K.; Santa, T.; Kaneko, K.; Imai, K.; Nakagomi, K. *Chem. Commun.* **2005**, 1848−1850.
(5) Caron, L.; Canipelle, M.; Tilloy, S.; Bricout, H.; Monflier, E. *Tetrahedron Lett.* **2001**, *42*, 8837−8840.
(6) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879−933.
(7) Gray, M.; Chapell, B. J.; Felding, J.; Taylor, N. J.; Snieckus, V. *Synlett* **1998**, 422−424.
(8) Baillie, C.; Xiao, J. *Tetrahedron* **2004**, *60*, 4159−4168.
(9) van Doorn, J. A.; Meijboom, N. *J. Chem. Soc., Chem. Commun.* **1987**, 1700−1701.
(10) Revés, M.; Ferrer, C.; León, T.; Doran, S.; Etayo, P.; Vidal-Ferran, A.; Riera, A.; Verdaguer, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 9452−9455.
(11) León, T.; Riera, A.; Verdaguer, X. *J. Am. Chem. Soc.* **2011**, *133*, 5740−5743.
(12) Purser, S.; Odell, B.; Claridge, T. D. W.; Moore, P. R.; Gouverneur, V. *Chem.—Eur. J.* **2006**, *12*, 9176−9185.
(13) Engelhardt, U.; Linker, T. *Chem. Commun.* **2005**, 1152−1154.
(14) Butters, M.; Elliott, M. C.; Hill-Cousins, J.; Paine, J. S.; Walker, J. K. E. *Org. Lett.* **2007**, *9*, 3635−3638.
(15) Mander, L. N.; McLachlan, M. M. *J. Am. Chem. Soc.* **2003**, *125*, 2400−2401.
(16) Bulbrook, M.; Chu, M.; Deane, K.; Doyle, R. J.; Hinc, J.; Peterson, C.; Salem, G.; Thorman, N.; Willis, A. C. *Dalton Trans.* **2010**, 8878−8881.
(17) Demay, S.; Volant, F.; Knochel, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1235−1238.
(18) Stankevič, M.; Pietrusiewicz, K. M. *Tetrahedron Lett.* **2009**, *50*, 7093−7095.
(19) Stankevič, M.; Włodarczyk, A.; Jaklińska, M.; Parcheta, R.; Pietrusiewicz, K. M. *Tetrahedron* **2011**, *67*, 8671−8678.
(20) Keough, P. T.; Grayson, M. *J. Org. Chem.* **1964**, *29*, 631−635.
(21) Petrov, K. A.; Chauzov, V. A.; Pastukhova, I. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 1425−1426.
(22) Stankevič, M.; Siek, M.; Pietrusiewicz, K. M. *ARKIVOC* **2011**, *v*, 102−126.
(23) Hobbs, C. F.; Knowles, W. S. *J .Org. Chem.* **1981**, *46*, 4422−4427.
(24) Janjah, M.; Alame, M.; Pellet-Rostaing, S.; Lemaire, M. *Tetrahedron: Asymmetry* **2007**, *18*, 2305−2312.

(25) Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277−4280.
(26) Wife, R. L.; van Oort, A. B.; van Doorn, J. A.; van Leeuwen, P. W. N. M. *Synthesis* **1983**, 71−73.
(27) Emmick, T. L.; Letsinger, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 3459−3465.
(28) Holt, J.; Arends, I. W. C. E.; Hanefeld, U.; Schudde, E. P.; Jerphagnon, T.; Minnaard, A. J.; Maj, A. M.; Pietrusiewicz, K. M.; Sieroń, L.; Wieczorek, W. *Synthesis* **2009**, 2061−2065.
(29) Achard, T.; Giordano, L.; Tenaglia, A.; Buono, G.; Gimbert, Y. *Organometallics* **2010**, *29*, 3936−3950.
(30) Arad-Yellin, R.; Zangen, M.; Gottlieb, H.; Warshawsky, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2081−2088.
(31) Ikaev, A. M.; Polezhayeva, O. S.; Mingalev, P. G.; Lisichkin, G. V. *Russ. J. Gen. Chem.* **2008**, *78*, 417−420.
(32) Oms, O.; Le Bideau, J.; Vioux, A.; Leclercq, D. *J. Organomet. Chem.* **2005**, *690*, 363−370.