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The Iminophosphorane-Phosphane $Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2$: Synthesis, Reactivity, and Catalytic Activity in Suzuki Cross-Coupling and the Homogeneous Hydrogenation of Olefins

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Keywords: Monoimination / Monophosphane / Iminophosphorane-phosphane / Staudinger reaction / Suzuki cross-coupling

The iminophosphorane-phosphane ligand $Ph_2PC_6H_4OC_6H_4$-PPh_2=NP(O)$(OPh)_2$ (**1**) has been synthesized by partial imination of bis[2-(diphenylphosphanyl)phenyl] ether (DPEphos) with phosphoryl azide $(PhO)_2P(O)N_3$. A similar reaction in a 1:2 stoichiometry affords the bis(iminophosphorane) O-$\{C_6H_4PPh_2$=NP(O)$(OPh)_2\}_2$ (**2**). The chalcogen derivatives O$\{C_6H_4P(E)Ph_2\}_2$ [E = S (**3**) and Se (**4**)] and $Ph_2P(E)$-$C_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2$ [E = S (**5**) and Se (**6**)] are also synthesized by treating DPEphos and **1** with elemental sulfur and selenium, respectively. The mononuclear complexes *trans*-[$MCl_2\{\kappa^1$-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2\}_2$] [M = Pt (**7**) Pd (**8**)] and *trans*-[Rh(CO)Cl{κ^1-*P*-Ph_2PC_6-$H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2\}_2$] (**12**) are prepared by the reaction of **1** with $[Pt(COD)Cl_2]$, $[Pd(COD)Cl_2]$, and $[\{Rh(CO)_2$-$Cl\}_2]$, respectively. Treatment of **1** with $[Pd_2(dba_3)]$ (dba = dibenzylideneacetone) affords the mononuclear complex $[Pd^0\{\kappa^2$-*P,O*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2\}_2]$ (**9**) in which ligand **1** coordinates through its P and O centers in a κ^2-*P,O* chelating fashion. The monocoordinated Au^I complex [AuCl{κ^1-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2\}$] (**10**) has been prepared by the reaction of **1** and $[AuCl(SMe_2)]$ and its structure has been confirmed by X-ray crystallography. The reaction of **1** with $[\{Rh(COD)Cl\}_2]$ in the presence of AgOTf affords the cationic Rh^I complex *cis*-[Rh(COD)$\{\kappa^2$-*P,O*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2\}$][OTf] (**11**). The catalytic activity of the Pd^0 complex **9** has been investigated in Suzuki cross-coupling reactions. Homogeneous catalytic hydrogenation of olefins has also been studied using the cationic Rh^I complex **11**.

Introduction

There has been considerable interest in recent years in the chemistry of iminophosphorane-phosphane ligands due to their interesting coordination chemistry and applications in organic syntheses such as aza-Wittig reactions.[1] These iminophosphorane-phosphane ligands have been synthesized by selective imination of bis(phosphanes) in a Staudinger reaction.[2–4] Various types of organic azides have been employed for the synthesis of such ligands, including R'_3SiN_3 and $R'_2P(O)N_3$.[5–11] The monoimination of bis(phosphanes) with phosphoryl azide $R'_2P(O)N_3$ leads to the formation of the hemilabile iminophosphorane-phosphane ligands R_2P-X-P$\{$=NP(O)$R'_2\}R_2$ (X = divalent bridging group). These ligands have the ability to offer different coordination modes such as κ^1-*P*, κ^2-*P,N*, κ^2-*P,O*, and κ^3-*P,N,O*, and its hemilabile behavior has been successfully utilized in homogeneous catalysis such as hydrogenation of olefins,[12] olefin oligomerization,[13] transfer hydrogenation of ketones,[14,15] and cross-coupling of secondary amines with aryl halides.[16] Surprisingly, their involvement in Suzuki cross-coupling reaction still remains unexplored.

van Leeuwen and co-workers[17] and others[18] have extensively studied the coordination chemistry and the catalytic utility of the bis[2-(diphenylphosphanyl)phenyl] ether $Ph_2PC_6H_4OC_6H_4PPh_2$. The complexes of this large-bite bis(phosphane) are found to be very effective in catalyzing a variety of organic transformations.[19–21]As a continuation of our work in designing new phosphorus-based ligands in order to explore their coordination chemistry[22–29] and catalytic activity,[30–33] we report herein the synthesis, coordination chemistry, and catalytic activity of the iminophosphorane-phosphane $Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2$ (**1**) derived from $Ph_2PC_6H_4OC_6H_4PPh_2$.

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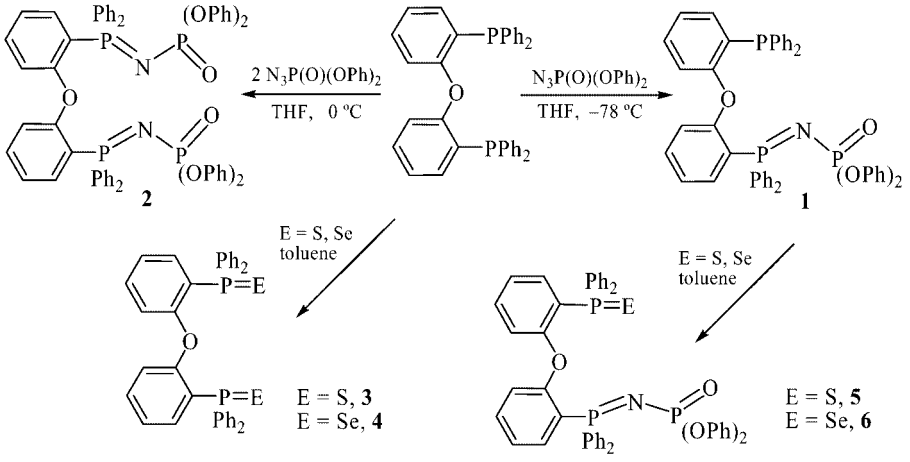
Results and Discussion

Synthesis of the Ligand and Chalcogen Derivatives

Reaction of the phosphoryl azide $(PhO)_2P(O)N_3$ with bis[2-(diphenylphosphanyl)phenyl] ether (DPEphos) (1:1 molar ratio) in thf at –78 °C affords the iminophos-



Scheme 1.

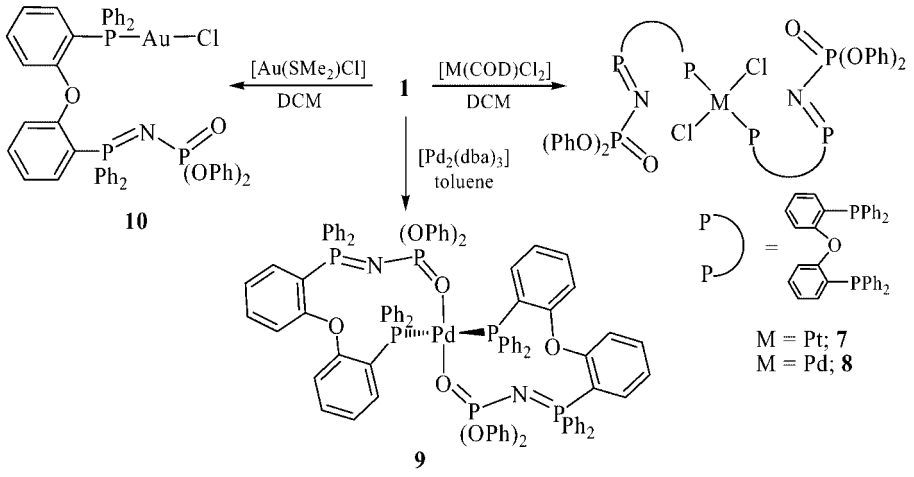
phorane-phosphane $Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2$ (**1**) in good yield. A similar reaction in a 2:1 molar ratio at 0 °C affords the bis(iminophosphorane) $O\{C_6H_4PPh_2{=}NP(O)(OPh)_2\}_2$ (**2**). Compounds **1** and **2** are moderately air stable and highly soluble in dichloromethane, diethyl ether, acetonitrile, and toluene.

The $^{31}P\{^1H\}$ NMR spectrum of ligand **1** shows three well-separated phosphorus signals with equal relative intensities. The terminal phosphoryl $P^V_{[O]}$ (δ = –10.5 ppm) and iminophosphorane $P^V_{[N]}$ (δ = 10.4 ppm) signals appear as simple doublets with a $^2J_{P,P}$ value of 37.7 Hz. The trivalent phosphorus appears as a singlet at δ = –20.1 ppm. The EI mass spectrum supports the structure as it shows the molecular ion peak at *m*/*z* 786.47 $[M + H]^+$. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets of equal intensity [δ = 10.9 ($P^V_{[N]}$) and –10.6 ppm ($P^V_{[O]}$); $^2J_{P,P}$ = 40.4 Hz] with chemical shift values comparable to those described for analogous compounds of the type $[RNPPh_2NP(O)(OPh)_2]_2$.[8,10,11] The EI mass spectrum of compound **2** shows the molecular ion peak at *m*/*z* 1033.57 $[M + H]^+$. Treatment of DPEphos and **1** with elemental sulfur and selenium results in the isolation of the bis-chalcogenides $O\{C_6H_4P(E)Ph_2\}_2$ [E = S (**3**) and Se (**4**)] and the thio- and selenoyl derivatives $Ph_2P(E)$-$C_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2$ [E = S (**5**) and Se (**6**)], respectively, in good yield. The $^{31}P\{^1H\}$ NMR spectra of compounds **3** and **4** show single resonances at δ = 39.1 and 29.4 ppm ($^1J_{Se,P}$ = 734.1 Hz), respectively. The EI mass spectrum of **4** shows the molecular ion peak at *m*/*z* 699.04 $[M + H]^+$. The $^{31}P\{^1H\}$ NMR spectra of **5** and **6** show three resonances, similar to the parent compound **1**. The ^{31}P resonances due to the chalcogenide phosphorus centers in **5** and **6** show a considerable downfield shift and appear at δ = 37.7 and 27.6 ppm, respectively, whereas the chemical shift values of the other two phosphorus centers are almost the same as those of compound **1**. The selenoyl derivative **6** shows a $^1J_{Se,P}$ coupling of 744 Hz. The mass spectra of compounds **5** and **6** support their structure, with molecular ion peaks at *m*/*z* 818.15 $[M + H]^+$ and 866.13 $[M + H]^+$, respectively (Scheme 1).

Synthesis of Metal Complexes

The reactions of **1** with $[M(COD)Cl_2]$ (M = Pt, Pd), irrespective of the stoichiometry, afford the mononuclear complexes *trans*-$[MCl_2\{\kappa^1$-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}_2]$ [M = Pt (**7**) and Pd (**8**)]. These complexes were therefore prepared in good yield from the reagents in 2:1 molar ratio. The $^{31}P\{^1H\}$ NMR spectroscopic data are very diagnostic for characterizing the complexes. The ^{31}P chemical shift due to the coordinated PPh_2 group is shifted considerably downfield as a result of coordination whereas the resonances due to the $P^V_{[N]}$ and $P^V_{[O]}$ groups do not exhibit such a large change in their chemical shift and $^2J_{P,P}$ values, thereby indicating their non-involvement in the complex formation. The $^{31}P\{^1H\}$ NMR spectrum of complex **7** shows a singlet at δ = 10.3 ppm corresponding to the coordinated phosphorus with a $^1J_{Pt,P}$ value of 2642 Hz and two doublets at δ = 11.4 (P=N) and –10.6 ppm (P=O) with a $^2J_{P,P}$ value of 37.9 Hz. The low $^1J_{Pt,P}$ value suggests a *trans* geometry for complex **7**.[34] The EI mass spectrum of complex **7** shows the molecular ion peak at *m*/*z* 1838.01 $[M + H]^+$. The $^{31}P\{^1H\}$ NMR spectrum of complex **8** shows one singlet at δ = 14.2 ppm for the coordinated phosphorus and two doublets at δ = 11.7 and –10.6 ppm ($^2J_{P,P}$ = 38.1 Hz) for the other two phosphorus centers.

The reaction of **1** with $[Pd_2(dba)_3]$ in a 2:1 molar ratio in toluene affords the Pd^0 complex **9** in good yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of $[Pd\{\kappa^2$-*P*,*O*-$Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}_2]$ (**9**) shows three resonances at δ = 23.6, 11.7, and –7.8 ppm for the PPh_2, $P^V_{[N]}$, and $P^V_{[O]}$ centers, respectively. The reaction of **1** with $[AuCl(SMe_2)]$ in CH_2Cl_2 affords $[AuCl\{\kappa^1$-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}]$ (**10**) in quantitative yield as a colorless crystalline solid. The $^{31}P\{^1H\}$ NMR spectrum of complex **10** shows three well-separated signals with equal intensities. The coordinated phosphorus center exhibits a singlet at δ = 19.0 ppm; there is no major change in the chemical shift values for the other two phosphorus centers with respect to ligand **1**. The elemental analysis and



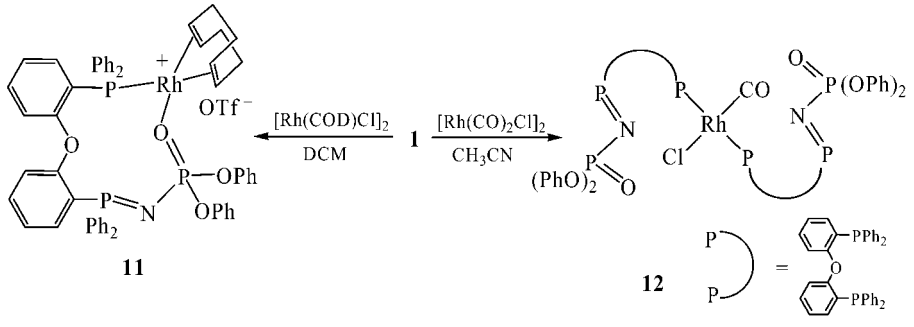
Scheme 2.

mass spectrum of complex **10** are in accordance with the proposed structure, which was further confirmed by single-crystal X-ray diffraction studies.

The mononuclear rhodium complex *cis*-[Rh(COD){κ²-*P*,*O*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)$(OPh)_2$}][OTf] (**11**) was prepared by the reaction of **1** with [{Rh(COD)Cl}$_2$] followed by the addition of AgOTf in an equimolar ratio. The ^{1}H NMR spectrum of **11** confirmed the presence of a cyclooctadiene group, which exhibits broad signals at around δ = 1.27–2.37 ppm for the four CH_2 groups and two doublets at δ = 2.90 and 5.13 ppm for the olefin protons with $^2J_{Rh,H}$ values of 119.2 and 115.6 Hz, respectively. The formation of an 11-membered chelate ring by binding of the P and O atoms of the phosphoryl group was confirmed by its ^{31}P NMR spectroscopic data. The ^{31}P{^{1}H} NMR spectrum of **11** consists of three resonances with equal intensities. The coordinated phosphorus appears as a doublet at δ = 12.9 ppm with a $^1J_{Rh,P}$ value of 149.3 Hz while the iminophosphorane and phosphoryl groups show mutually coupled doublets centered at δ = 8.8 and –11.1 ppm, respectively, with a $^2J_{P,P}$ value of 39 Hz. The doublet due to the phosphoryl group shows an additional $^2J_{Rh,P}$ coupling of 6.6 Hz, thus indicating the coordination of the phosphoryl oxygen to the rhodium center, similar to an analogous compound reported in the literature.[5b] The EI mass spectrum of cationic complex **11** shows the molecular ion peak at *m*/*z*

Table 1. Summary of ^{31}P{^{1}H} NMR data for compounds **1**–**12** [δ in ppm and *J* in Hz].

Compound	δ_{PPh_2}	$\delta_{Ph_2P=N}$	$\delta_{(PhO)_2P=O}$	$^2J_{P,P}$
1	–20.1 (s)	10.4 (d)	–10.5 (d)	37.7
2		10.9 (d)	–10.6 (d)	40.4
3	39.1 (s)			
4	29.4 (s), $^1J_{Se,P}$ = 734.1			
5	37.7 (s)	10.8 (d)	–10.5 (d)	38.9
6	27.6 (s), $^1J_{Se,P}$ = 744.0	10.8 (d)	–10.5 (d)	39.0
7	10.3 (s), $^1J_{Pt,P}$ = 2642	11.4 (d)	–10.6 (d)	37.9
8	14.2 (s)	11.7 (d)	–10.6 (d)	38.1
9	23.6 (s)	11.7 (d)	–7.8 (d)	39.5
10	19.0 (s)	10.4 (d)	–10.5 (d)	37.9
11	12.9 (d), $^1J_{Rh,P}$ = 149.3	8.8 (d)	–11.1 (dd), $^2J_{Rh,P}$ = 6.6	39.0
12	22.5 (d), $^1J_{Rh,P}$ = 140.3	11.3 (d)	–10.6 (d)	37.9



Scheme 3.

996.2 $[M - OTf]^+$. The reaction of $[\{Rh(CO)_2Cl\}_2]$ with **1** in a 1:2 molar ratio affords *trans*-$[Rh(CO)Cl\{\kappa^1$-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}_2]$ (**12**), as is evident from the $^{31}P\{^1H\}$ NMR, mass, and elemental analysis data. The $^{31}P\{^1H\}$ NMR spectrum of complex **12** consists of three doublets. The doublet at δ = 22.5 ppm with a $^1J_{Rh,P}$ coupling of 140 Hz is due to the coordinated phosphorus whereas the remaining two doublets at δ = 11.3 and –10.6 ppm are assigned to $P^V_{[N]}$ and $P^V_{[O]}$, respectively, with a $^2J_{P,P}$ coupling of 37.9 Hz. The mass spectrum of **12** exhibits the molecular ion peak at *m*/*z* 1701.1 $[M - Cl]^+$. The IR spectrum of **12** shows ν_{CO} at 1958 cm^{-1} (Table 1 and Scheme 3).

Crystal Structure of Complex 10

A perspective view of the molecular structure of complex **10** with the atom numbering scheme is shown in Figure 1. Crystal data and details of crystal structure determination are given in the Experimental Section, while the selected bond lengths [Å] and bond angles [°] are displayed in Table 2. The P(1)–Au(1)–Cl(1) bond angle of 177.81(7)° indicates that the gold is in a slightly distorted linear geometry. The Au(1)–Cl(1) and Au(1)–P(1) bond lengths are 2.284(1) and 2.230(1) Å, respectively, and are close to the reported values for $[O(C_6H_4PPh_2AuCl)_2]$.[18b] There is an intermolecular interaction between O(2_j) and H(34), as is evident from the bond length of 2.402 Å (less than the sum of the van der Waal's radii)[35] and the C(34)–H(34)–O(2_j) bond angle of 172°.

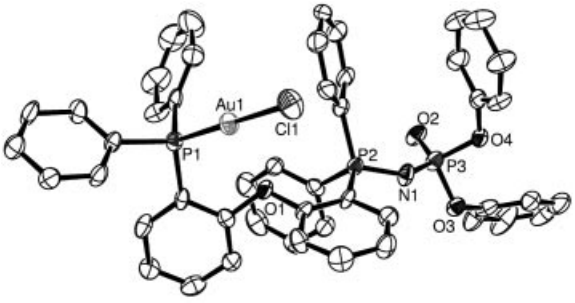


Figure 1. Molecular structure of $[AuCl\{\kappa^1$-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}]$ (**10**). All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] and bond angles [°] for **10**.

Bond lengths		Bond angles	
Au(1)–Cl(1)	2.284(1)	Au(1)–P(1)–C(1)	112.90(2)
Au(1)–P(1)	2.230(1)	P(1)–Au(1)–Cl(1)	177.81(7)
P(2)–N(1)	1.586(5)	N(1)–P(3)–O(2)	122.40(3)
P(3)–N(1)	1.570(5)	N(1)–P(3)–O(3)	103.20(2)
P(3)–O(2)	1.463(4)	P(2)–N(1)–P(3)	135.40(3)
P(3)–O(3)	1.605(4)	C(18)–O(1)–C(19)	118.10(4)
P(3)–O(4)	1.623(5)	C(34)–H(34)–O(2_j)	172.00
H(34)–O(2_j)	2.402		
C(34)–O(2_j)	3.325(7)		

Catalytic Studies

Suzuki Cross-Coupling Reactions

Although iminophosphorane-phosphane ligands have been employed in homogeneous catalysis, there are no re-

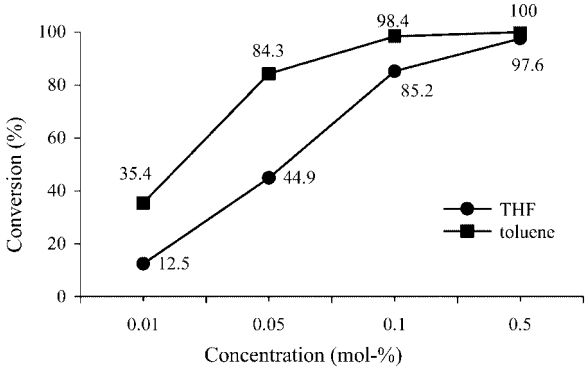
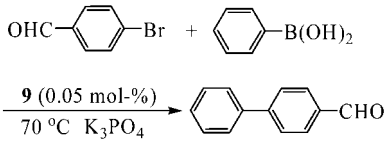


Figure 2. Influence of catalyst concentration on the coupling of 4-bromobenzaldehyde (1.0 mmol) and phenylboronic acid (1.5 mmol). Conditions: K_3PO_4 (2.0 mmol), toluene/thf (10 mL), *t* = 15 min, *T* = 70 °C.

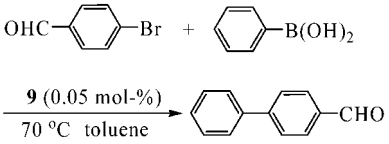
Table 3. Effect of solvent on the coupling of 4-bromobenzaldehyde with phenylboronic acid.



Entry	Solvent	Base	Time [h]	Conversion [%][a]
1	tetrahydrofuran	K_3PO_4	2	84.6
2	dioxane	K_3PO_4	2	63.2
3	dimethylformamide	K_3PO_4	2	100
4	toluene	K_3PO_4	2	100
5	acetonitrile	K_3PO_4	2	63.7
6	methanol	K_3PO_4	2	69.8

[a] Conversion to coupled product determined by GC, based on aryl halides; average of two runs.

Table 4. Effect of base on the coupling of 4-bromobenzaldehyde with phenylboronic acid.

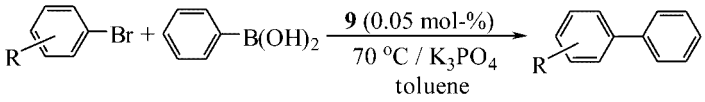


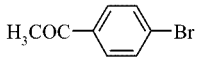
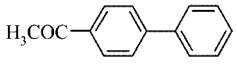
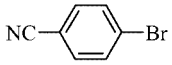
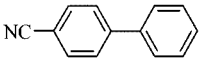
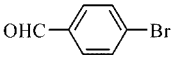
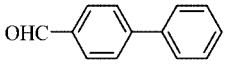
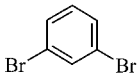
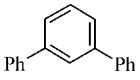
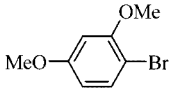
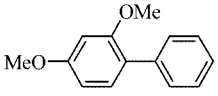
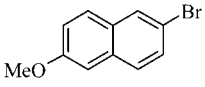
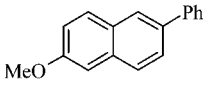
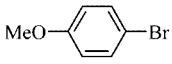
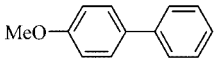
Entry	Base	Solvent	Time [h]	Conversion [%][a]
1	Cs_2CO_3	toluene	2	100
2	K_3PO_4	toluene	2	100
3	K_2CO_3	toluene	2	97.1
4	NaOH	toluene	2	73.5
5	TMEDA	toluene	2	15.6
6	none	toluene	2	1.6

[a] Conversion to coupled product determined by GC, based on aryl halides; average of two runs.

ports of their application in Suzuki cross-coupling reactions. Interestingly, the iminophosphorane-phosphane ligand **1** shows excellent activity for Suzuki cross-coupling reactions with high turnover numbers at very low catalyst concentrations. The Pd^0 complex **9** effectively catalyzes the Suzuki cross-coupling reactions of a variety of aryl bromides and phenylboronic acids to afford the desired biaryls in remarkably high yields. These reactions were studied systematically to find the optimal conditions to afford biaryls in good yield. It is important to achieve good yields using minimum amounts of catalyst, therefore we examined the effect of catalyst loading on the coupling between 4-bromobenzaldehyde and phenylboronic acid (Figure 2 and Tables 3, 4, and 5). Complete conversion of the starting materials into 4-phenylbenzaldehyde was achieved with 0.5 mol-% of catalyst in 1 h or 0.05 mol-% in 2 h, therefore a concentration of 0.05 mol-% was selected as the optimal concentration for catalytic loading.

Table 5. Suzuki cross-coupling of aryl halides (1 mmol) with phenylboronic acid (1.5 mmol) catalyzed by **9** in the presence of K_3PO_4 (2 mmol) in toluene (10 mL).



Entry	Substrate	Product	Time (h)	Conversion[a] (%)	Yield (%)
1			2	100	99
2			2	99.5	99
3			2	100	98
4			4	94.8	90
5			8	90.7	89
6			4	78.9	78
7			12	79.4	70
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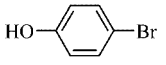
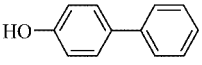
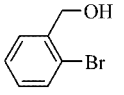
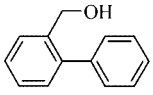
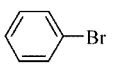
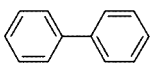
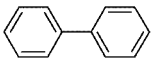
9			10	77.5	73
10			10	68.3	66
11			4	83.3	83
12			4	100	98

The above investigations showed that the reaction rate and the catalyst activity are significantly influenced by the base and the solvent employed. Various solvents were tested in the coupling reaction with K_3PO_4 as base. Toluene and dmf allowed complete conversion of 4-bromobenzaldehyde into 4-phenylbenzaldehyde. Considering the ease of separation of the product, toluene was chosen as the best solvent.

Inorganic bases such as Cs_2CO_3, K_3PO_4, K_2CO_3, and NaOH gave excellent yields whereas the reaction proceeded very slowly with TMEDA. Considering the high activity and cost effectiveness, K_3PO_4 was chosen as the base.

Under these optimized reaction conditions, a wide array of aryl bromides react with phenylboronic acid to provide the cross-coupling products in excellent yields (Table 5). The palladium(0) catalyst **9** is very effective in Suzuki cross-coupling reactions and exhibits remarkable tolerance towards both "deactivating" electron-donating substituents (Table 5, entries 7, 9 and 10) and sterically encumbering *ortho* substituents (Table 5, entry 5) on aryl bromides. The catalytic activity of **9** is found to be better than that of the catalyst $[Pd_2(dba)_3]$ + [1,1′-bis(diphenylphosphanyl)ferrocene (dppf)], which catalyzes the coupling of 4-bromoacetophenone and phenylboronic acid in toluene at 70 °C (2 h) in 86.5% yield,[36a] whereas it is similar to that of the parent compound DPEphos. However, DPEphos shows better activity only at higher temperature and higher catalytic loading.[36b]

Catalytic Hydrogenation of Styrene

The cationic Rh^I complex **11** was tested as a catalyst for the hydrogenation of styrene. The catalyst (0.0005 mol-%) shows effective conversions under mild conditions (4 atm of H_2 at room temperature). The conversion rate was monitored periodically by gas chromatography and the product formation was confirmed by ^1H NMR spectroscopy. The results are displayed in Figure 3.

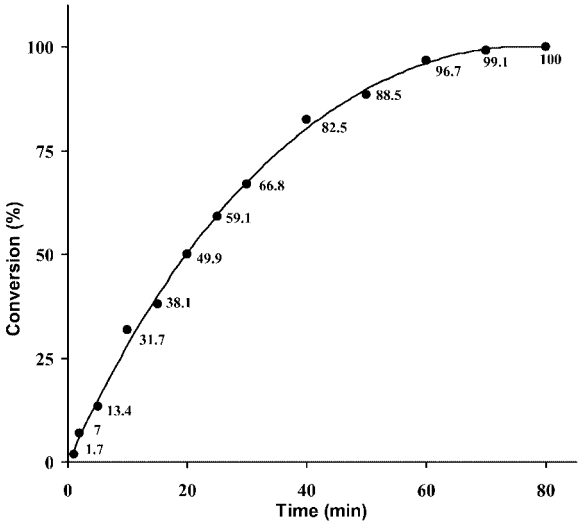


Figure 3. Hydrogenation of styrene. Conditions: styrene (1.0 mmol), Et_3N (0.1 mmol), **11** (0.0005 mol-%), thf (20 mL); H_2 pressure: 4 atm; room temperature; stirring speed: 400 rpm.

The turnover number (TON) for the conversion of styrene to ethylbenzene was 200,000 and the turnover frequency (TOF) at 50% conversion was 300,000 h^{-1}. The TOF improved to 600,000 h^{-1} when the pressure of H_2 was increased to 10 atm and the temperature to 70 °C. The catalytic activity was tested on other substrates such as α-methylstyrene, 4-methylstyrene, and phenylacetylene with a catalyst loading of 0.005 mol-%. The results are displayed in Table 6. Complex **11** was found to be more effective in homogeneous hydrogenation under mild conditions than $[RhCl(PPh_3)_3]$, for which complete conversion was observed under the following conditions: [styrene]/[catalyst] = 1200, T = 80 °C, t = 2 h, H_2 pressure: 28 atm.[37]

Table 6. Hydrogenation of olefins using complex **11**.[a]

Entry	Substrate	Time [min]	Conversion [%]	TOF [h^{-1}]
1	styrene	30	100	40,000
2	α-methylstyrene	40	100	30,000
3	4-methylstyrene	30	100	40,000
4	phenylacetylene	70	100	17,143
5[b]	styrene	20	100	600,000

[a] Conditions: olefin (1.0 mmol), Et_3N (0.1 mmol), **11** (0.005 mol-%), thf (20 mL); H_2 pressure: 4 atm; room temp.; stirring speed: 400 rpm. [b] **11** (0.0005 mol-%), H_2 pressure: 10 atm; T: 70 °C.

Summary

The hemilabile iminophosphorane-phosphane ligand **1** has been synthesized by monoimination of bis[2-(diphenylphosphanyl)phenyl] ether by a Staudinger reaction and its chalcogen derivatives **3**–**6** have been prepared and characterized. The imino-phosphorane shows both a monodentate and bidentate (κ^2-*P*,*O*) chelating coordination mode. The platinum(II), palladium(II), and rhodium(I) complexes **7**, **8**, and **12**, respectively, are obtained as *trans* isomers with simple monodentate coordination modes. The Pd^0 complex **9**, in which ligand **1** binds in a chelating (κ^2-*P*,*O*) fashion, has been synthesized by the reaction of **1** with $[Pd_2(dba)_3]$. The reaction of **1** with $[\{Rh(COD)Cl\}_2]$ and AgOTf affords the 11-membered macrocyclic square-planar complex **11** with the imino-phosphorane ligand showing a chelating bidentate mode of coordination. The cationic rhodium(I) complex **11** is catalytically active for the hydrogenation of olefins with a TON of 2×10^5 and a TOF of 6×10^5 h^{-1}. The Pd^0 complex **9** is catalytically active for Suzuki cross-coupling reactions of various aryl bromides and phenylboronic acid. A lower catalytic loading of 0.05 mol-% of **9** allows complete conversion of several aryl bromides into biaryls.

Experimental Section

Reagents and Techniques: All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.

All the solvents were purified by conventional procedures and distilled under nitrogen prior to use. The compounds DPEphos,[17a] $[M(COD)Cl_2]$ (M = Pd, Pt),[38] $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$,[39] $[\{Rh(CO)_2(\mu\text{-}Cl)\}_2]$,[40] $[Pd_2(dba)_3]$,[41] and $[AuCl(SMe_2)]$[42] were prepared according to published procedures. $(PhO)_2P(O)N_3$ was purchased from Lancaster and used as received. The ^1H and $^{31}P\{^1H\}$ NMR spectra (δ in ppm) were recorded with Varian 300 or 400 mercury plus spectrometers operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. Microanalyses were performed with a Carlo–Erba Model 1112 elemental analyzer. The IR spectra were recorded with a Nicolet Impact 400 FT-IR instrument as KBr disc. Electrospray ionization (EI) mass spectrometry experiments were carried out with a Waters Q-Tof micro-YA-105 spectrometer. Melting points were recorded in capillary tubes and are uncorrected. GC analyses were performed with a Perkin–Elmer Clarus 500 GC fitted with a packed column.

Synthesis of $Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2$ (1): A thf solution (20 mL) of $(PhO)_2P(O)N_3$ (0.153 g, 0.557 mmol) was added dropwise to a solution of DPEphos (0.300 g, 0.557 mmol) in thf (20 mL) at –78 °C. After stirring the mixture for 8 h at room temperature, all the solvents were removed under vacuum and the residue washed with petroleum ether (b.p. 60–80 °C), then extracted with Et_2O (15 mL) and dried to give an analytically pure white solid. Yield: 85% (0.372 g); m.p. 76–78 °C. $C_{48}H_{38}NO_4P_3$ (785.7): calcd. C 73.37, H 4.87, N 1.78; found C 72.81, H 4.43, N 1.93. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.93–8.18 (m, 38 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = –20.1 (s, P^{III}), 10.4 (d, $^2J_{P,P}$ = 37.7 Hz, $P^V_{[N]}$), –10.5 (d, $^2J_{P,P}$ = 37.7 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 786.47 $[M + H]^+$.

Synthesis of $O\{C_6H_4PPh_2{=}NP(O)(OPh)_2\}_2$ (2): A solution of DPEphos (0.2 g, 0.371 mmol) in thf (10 mL) was added dropwise to a solution of $(PhO)_2P(O)N_3$ (0.204 g, 0.742 mmol) in thf (10 mL) at 0 °C. After stirring the mixture for 8 h at room temperature, all the solvents were removed under vacuum and the residue washed with petroleum ether, then extracted with Et_2O (10 mL) and dried to give **2** as a white solid. Yield: 90% (0.350 g); m.p. 72–74 °C. $C_{60}H_{48}N_2O_7P_4$ (1032.9): calcd. C 69.77, H 4.68, N 2.71; found C 70.26, H 4.51, N 2.84. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.12–7.65 (m, 48 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 10.9 (d, $^2J_{P,P}$ = 40.4 Hz, $P^V_{[N]}$), –10.6 (d, $^2J_{P,P}$ = 40.4 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 1033.57 $[M + H]^+$.

Synthesis of $O\{C_6H_4P(S)Ph_2\}_2$ (3): A mixture of DPEphos (0.200 g, 0.371 mmol) and sulfur (0.024 g, 0.093 mmol) was refluxed in toluene (10 mL) for 24 h with constant stirring to give a white precipitate of **3**. The solution was then cooled to room temperature, filtered, and recrystallized from hot $CHCl_3$. Yield: 92% (0.206 g); m.p. > 250 °C. $C_{36}H_{28}OP_2S_2$ (602.7): calcd. C 71.74, H 4.68, S 10.64; found C 71.62, H 4.81, S 10.88. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.20–7.68 (m, 28 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 39.1 (s) ppm.

Synthesis of $O\{C_6H_4P(Se)Ph_2\}_2$ (4): A mixture of DPEphos (0.200 g, 0.371 mmol) and selenium (0.059 g, 0.742 mmol) was refluxed in toluene (10 mL) for 24 h with constant stirring to give a white precipitate of **4**. The solution was then cooled to room temperature, filtered, and recrystallized from hot $CHCl_3$. Yield: 90% (0.233 g); m.p. > 250 °C. $C_{36}H_{28}OP_2S_2$ (696.5): calcd. C 62.08, H 4.05; found C 62.45, H 4.26. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.30–7.67 (m, 28 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 29.4 (s, $^1J_{Se,P}$ = 734.1 Hz) ppm. MS (EI): *m*/*z* 699.04 $[M + H]^+$.

Synthesis of $Ph_2P(S)C_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2$ (5): A mixture of **1** (0.100 g, 0.127 mmol) and sulfur (0.003 g, 0.016 mmol) was refluxed in toluene (5 mL) for 24 h with constant stirring. The solution was then cooled to room temperature and petroleum ether (5 mL) was added to give white precipitate **5**. Yield: 93% (0.096 g); m.p. 98–100 °C. $C_{48}H_{38}P_3O_4NS$ (817.8): calcd. C 70.49, H 4.68, N 1.71, S 3.92; found C 70.52, H 4.44, N 1.82, S 4.09. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.87–7.97 (m, 38 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 37.7 (s, $P^V_{[S]}$), 10.8 (d, $^2J_{P,P}$ = 38.9 Hz, $P^V_{[N]}$), –10.5 (d, $^2J_{P,P}$ = 38.9 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 818.15 $[M + H]^+$.

Synthesis of $Ph_2P(Se)C_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2$ (6): A mixture of **1** (0.100 g, 0.127 mmol) and Se (0.010 g, 0.127 mmol) was refluxed in toluene (5 mL) for 24 h with constant stirring. The solution was then cooled to room temperature and petroleum ether (5 mL) was added to give a white microcrystalline solid of **6**. Yield: 98% (0.108 g); m.p. 120–122 °C. $C_{48}H_{38}NO_4P_3Se$ (864.7): calcd. C 66.67, H 4.42, N 1.61; found C 66.97, H 4.21, N 1.73. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.89–7.92 (m, 38 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 27.6 (s, $^1J_{Se,P}$ = 744.0 Hz, $P^V_{[Se]}$), 10.8 (d, $^2J_{P,P}$ = 39.0 Hz, $P^V_{[N]}$), –10.5 (d, $^2J_{P,P}$ = 39.0 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 866.13 $[M + H]^+$.

Synthesis of *trans*-$[PtCl_2\{\kappa^1\text{-}P\text{-}Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}_2]$ (7): A solution of $[Pt(COD)Cl_2]$ (0.034 g, 0.091 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of **1** (0.144 g, 0.183 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred for 8 h to give a pale-yellow solution, which was concentrated to 5 mL. Et_2O (10 mL) was added to give a pale-yellow precipitate of **7**, which was then filtered, washed, and dried. Yield: 87% (0.145 g); m.p. > 250 °C. $C_{96}H_{76}Cl_2N_2O_8P_6Pt$ (1837.5): calcd. C 62.75, H 4.16, N 1.52; found C 62.58, H 4.15, N 1.58. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.87–8.21 (m, 76 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 10.3 (s, $^1J_{Pt,P}$ = 2642 Hz, $P_{[Pt]}$), 11.4 (d, $^2J_{P,P}$ = 37.9 Hz, $P^V_{[N]}$), –10.6 (d, $^2J_{P,P}$ = 37.9 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 1838.01 $[M + H]^+$.

Synthesis of *trans*-$[PdCl_2\{\kappa^1\text{-}P\text{-}Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}_2]$ (8): A solution of $[Pd(COD)Cl_2]$ (0.031 g, 0.109 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **1** (0.170 g, 0.217 mmol) in CH_2Cl_2 (10 mL) at room temperature. The bright yellow solution was stirred for 8 h then concentrated to 5 mL. Addition of Et_2O (10 mL) gave the mononuclear *trans* complex **8** as a yellow solid. Yield: 83% (0.158); m.p. 210–212 °C. $C_{96}H_{76}Cl_2N_2O_8P_6Pd$ (1748.8): calcd. C 65.93, H 4.38, N 1.60; found C 65.24, H 3.99, N, 1.75. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.85–8.20 (m, 76 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 14.2 (s, $P_{[Pd]}$), 11.7 (d, $^2J_{P,P}$ = 38.1 Hz, $P^V_{[N]}$), –10.6 (d, $^2J_{P,P}$ = 38.1 Hz, $P^V_{[O]}$) ppm.

Synthesis of $[Pd\{\kappa^2\text{-}P,O\text{-}Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}_2]$ (9): A solution of $[Pd_2(dba)_3]$ (0.05 g, 0.048 mmol) in toluene (20 mL) was added dropwise to a stirring solution of **1** (0.152 g, 0.193 mmol) in toluene (10 mL) at room temperature. After 4 h the solution had turned yellow and all the solvents were removed in vacuo. The residual solid was washed several times with petroleum ether to remove dba and dried. Yield: 78% (0.126 g); m.p. 112 °C (dec). $C_{96}H_{76}N_2O_8P_6Pd$ (1677.9): calcd. C 68.72, H 4.57, N 1.67; found C 68.48, H 4.76, N 1.80. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.93–8.30 (m, 38 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 23.6 (s, $P_{[Pd]}$), 11.7 (d, $^2J_{P,P}$ = 39.5 Hz, $P^V_{[N]}$), –7.8 (d, $^2J_{P,P}$ = 39.5 Hz, $P^V_{[O]}$) ppm.

Synthesis of $[AuCl\{\kappa^1\text{-}P\text{-}Ph_2PC_6H_4OC_6H_4PPh_2{=}NP(O)(OPh)_2\}]$ (10): A solution of $[AuCl(SMe_2)]$ (0.03 g, 0.102 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of **1** (0.08 g, 0.102 mmol)

in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred for 12 h, then concentrated to 2 mL and layered with Et_2O (5 mL) to give colorless crystals of analytical purity. Yield: 92% (0.095 g); m.p. 216–218 °C. $C_{48}H_{38}AuClNO_4P_3$ (1018.2): calcd. C 56.62, H 3.76, N 1.38; found C 56.64, H 3.79, N 1.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.15–7.88 (m, 38 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 19.0 (s, $P_{[Au]}$), 10.4 (d, $^2J_{P,P}$ = 37.9 Hz, $P^V_{[N]}$), –10.5 (d, $^2J_{P,P}$ = 37.9 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 982.49 $[M - Cl]^+$.

Synthesis of *cis*-[Rh(COD){κ^2-*P*,*O*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP(O)-(OPh)$_2$}][OTf] (11): A mixture of **1** (0.066 g, 0.083 mmol), [{Rh(COD)Cl}$_2$] (0.021 g, 0.042 mmol), and AgOTf (0.021, 0.083 mmol) in CH_2Cl_2 (10 mL) was stirred for 8 h at room temperature. The yellow solution was concentrated to 2 mL and Et_2O (10 mL) added to give a yellow oily substance. The supernatant liquid was discarded and dried to give a yellow foamy substance **11**, which was washed with Et_2O and dried. Yield: 78% (0.044 g, 0.025 mmol); m.p. 144–146 °C. $C_{57}H_{50}F_3NO_7P_3RhS$ (1145.9): calcd. C 59.74, H 4.39, N 1.22, S 2.80; found C 60.11, H 4.08, N 1.30, S 2.85. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27–2.37 (br. m, 8 H, CH_2), 2.90 (br. d, $^2J_{Rh,H}$ = 119.2 Hz, 2 H, CH), 5.13 (br. d, $^2J_{Rh,H}$ = 115.6 Hz, 2 H, CH), 6.26–7.99 (m, 38 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 12.9 (d, $^1J_{Rh,P}$ = 149.3 Hz, $P_{[Rh]}$), 8.8 (d, $^2J_{P,P}$ = 39.0 Hz, $P^V_{[N]}$), –11.1 (dd, $^2J_{P,P}$ = 39.0, $^2J_{Rh,P}$ = 6.6 Hz, $P^V_{[O]}$) ppm. MS (EI): *m*/*z* 996.29 $[M - OTf]^+$.

Synthesis of *trans*-[Rh(CO)Cl{κ^1-*P*-$Ph_2PC_6H_4OC_6H_4PPh_2$=NP-(O)(OPh)$_2$}$_2$] (12): A CH_3CN (8 mL) solution of [{$Rh(CO)_2Cl$}$_2$] (0.015 g, 0.039 mmol) was added dropwise to a solution of **1** (0.121 g, 0.154 mmol) in CH_3CN (10 mL) at room temperature. The reaction mixture was stirred for 4 h to give the *trans* complex **12** as a yellow precipitate, which was then filtered, washed with CH_3CN (2 mL), and dried. Yield: 88% (0.118 g, 0.068 mmol); m.p. 242–244 °C. $C_{97}H_{76}ClN_2O_9P_6Rh$ (1737.9): calcd. C 67.04, H 4.41, N 1.61; found C 66.37, H 4.80, N 1.82. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77–8.12 (m, 76 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 22.5 (d, $^1J_{Rh,P}$ = 140.3 Hz, $P_{[Rh]}$), 11.3 (d, $^2J_{P,P}$ = 37.9 Hz, $P^V_{[N]}$), –10.6 (d, $^2J_{P,P}$ = 37.9 Hz, $P^V_{[O]}$) ppm. FT-IR (KBr disc): $\tilde{\nu}$ = 1958 cm^{-1} [ν_{CO}]. MS (EI): *m*/*z* 1701.70 $[M - Cl]^+$.

Crystal Structure Determination: Single crystals of **8** suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a dichloromethane solution and mounted on a glass fiber with epoxy resin. Unit cell determination and data collection of **8** were performed with an Oxford Diffraction XCALIBUR-S CCD system using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 (SHELXL program package).[43] The absorption corrections were done by multi-scan and all the data were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model (Table 7).

CCDC-616229 (for **9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Suzuki Cross-Coupling Reactions of Aryl halides with Boronic Acids: The appropriate amount of catalyst **9** (0.05 mol-%) was placed into a two-necked, round-bottomed flask under an atmosphere of nitrogen and 10 mL of toluene was added. After stirring for 15 min, aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), and K_2CO_3 (2 mmol) were added. The mixture was stirred at 70 °C under an atmosphere of nitrogen until the conversion stopped (the course of the reaction was monitored by GC analysis). The solvent was then removed under reduced pressure. The resultant residual mixture was quenched with H_2O (10 mL) and extracted twice with Et_2O (2 × 10 mL). The combined organic fraction was dried ($MgSO_4$), the solvent removed under vacuum, and the residue dissolved in CH_2Cl_2 (5 mL). An aliquot of the solution was subjected to GC analysis. Yields were calculated with respect to aryl halides or dodecane as an internal standard.

Catalytic Hydrogenation of Olefins: A mixture of Rh^I complex **11** (0.0005 or 0.005 mol-%), olefin (1.0 mmol), and triethylamine (0.1 mmol) was dissolved in 20 mL of thf and was introduced into a 50-mL glass vessel, which was placed into a steel autoclave and the reactor sealed. The vessel was purged three times with hydrogen and then the autoclave was pressurized with 4 atm of hydrogen. The reaction mixture was stirred at a room temperature for the required time. The extent of conversion was determined by periodic GC analysis until complete conversion was observed.

Table 7. Crystallographic data for complex **10**.

Formula	$C_{48}H_{38}AuClNO_4P_3$
Molecular weight	1018.12
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	15.9417(14)
b [Å]	10.9513(16)
c [Å]	25.3394(18)
α [°]	90
β [°]	101.717(7)
γ [°]	90
V [Å^3]	4331.6(8)
Z	4
ρ_{calc} [g cm^{-3}]	1.561
μ (Mo-K_a) [mm^{-1}]	3.614
F(000)	2024
Crystal size [mm^3]	0.26 × 0.21 × 0.18
T [K]	150(2)
2θ range [°]	2.95–25.00
Total number of reflections	21719 [R_{int} = 0.0702]
GOF [F^2]	0.778
R_1[a]	0.0349
wR_2[b]	0.0563

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

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