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Generation and Reactions of Ruthenium Phosphido Complexes $[(\eta^5\text{-}C_5H_5)Ru(PR'_3)_2(PR_2)]$: Remarkably High Phosphorus Basicities and Applications as Ligands for Palladium-Catalyzed Suzuki Cross-Coupling Reactions

José Giner Planas,[a, b] Frank Hampel,[a] and J. A. Gladysz*[a]

Abstract: Reactions of $[(\eta^5\text{-}C_5H_5)Ru(PR'_3)_2(Cl)]$ with $NaBAr_F$ [$BAr_F^- = B\{3,5\text{-}[C_6H_3(CF_3)_2]\}_4^-$; $PR'_3 =$ PEt_3 or $^1/_2Et_2PCH_2CH_2PEt_2$ (depe)] and PR_2H (R = Ph, **a**; *t*Bu, **b**; Cy, **c**) in C_6H_5F, or of related cationic $Ru(N_2)$ complexes with PR_2H in C_6H_5F, gave the secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Ru(PR'_3)_2(PR_2H)]^+$ BAr_F^- ($PR'_3 = PEt_3$, **3a–c**; $^1/_2$depe, **4a**,**b**) in 65–91 % yields. Additions of *t*BuOK (**3a**, **4a**; [D_6]acetone) or $NaN(SiMe_3)_2$ (**3b**,**c**, **4b**; [D_8]THF) gave the title complexes $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PR_2)]$ (**5a–c**) and $[(\eta^5\text{-}C_5H_5)Ru(depe)(PR_2)]$ (**6a**,**b**) in high spectroscopic yields. These complexes were rapidly oxidized in air; with **5a**, $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2\{P(=O)Ph_2\}]$ was isolated (> 99 %). The reaction of **5a** and elemental selenium yielded $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2\{P(=Se)Ph_2\}]$ (70 %); selenides from **5c** and **6a** were characterized in situ. Competitive deprotonation reactions showed that **5a** is more basic than the rhenium analog $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2)]$, and that **6b** is more basic than P*t*Bu_3 and P(*i*PrNCH$_2$CH$_2$)$_3$N. The latter is one of the most basic trivalent phosphorus compounds [pK_a(acetonitrile) 33.6]. Complexes **5a–c** and **6b** are effective ligands for $Pd(OAc)_2$-catalyzed Suzuki coupling reactions: **6b** gave a catalyst nearly as active as the benchmark organophosphine P*t*Bu_3; **5a**, with a less bulky and electron-rich PR_2 moiety, gave a less active catalyst. The reaction of **5a** and $[(\eta^3\text{-}C_3H_5)Pd(NCPh)_2]^+ BF_4^-$ gave the bridging phosphido complex $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2)Pd(NCPh)(\eta^3\text{-}C_3H_5)]^+ BAr_F^-$ in approximately 90 % purity. The crystal structure of **4a** is described, as well as substitution reactions of **3b** and **4b**.

Keywords: basicity · palladium · phosphido complexes · phosphine selenide · ruthenium · Suzuki reaction

Introduction

Transition-metal phosphine complexes catalyze a variety of carbon–carbon bond-forming reactions. In recent years, the activities of many palladium/phosphine systems used for such transformations have been improved by employing bulkier and/or more electron-rich phosphines.[1,2] Our group has sought to develop phosphorus donor ligands which feature a bulky 18-valence-electron transition-metal center α or β to the phosphorus atom that would not directly participate in the bond-breaking/making steps of the catalytic cycle.[3–8] Such systems are much more basic and nucleophilic than organophosphines that lack the metal[8,9] owing to the repulsive interactions between occupied orbitals,[8–11] which are most pronounced in α-substituted or L_nMPR_2 systems (metal lone pair/phosphorus lone pair).[12]

We first tested this design principle with the rhenium(I) phosphido complexes $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(PR_2)]$ (**I**, Scheme 1), which from previous studies are known to be very electron-rich.[8,9] When combined with $Pd(OAc)_2$ in toluene under standard Buchwald conditions,[1a,k] highly active catalysts for Suzuki–Miyaura cross-coupling reactions[13] were obtained.[3,4] The complex with R = *t*Bu gave a particularly active catalyst—close to, but not exceeding, that obtained with the benchmark organophosphine P*t*Bu_3.[1b] Complexes with the rhenium β to the phosphorus atom, either in $ReCH_2PR_2$ or $(\eta^5\text{-}C_5H_4PR_2)Re$ moieties, are less electron-rich and gave less active catalysts.

[a] Dr. J. Giner Planas, Dr. F. Hampel, Prof. Dr. J. A. Gladysz
Institut für Organische Chemie
Friedrich-Alexander-Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax (+49) 9131-852-6865
E-mail: gladysz@organik.uni-erlangen.de

[b] Dr. J. Giner Planas
Current address: Institut de Ciència de Materials de Barcelona (CSIC)
Campus de la U.A.B., 08193 Bellaterra (Spain)

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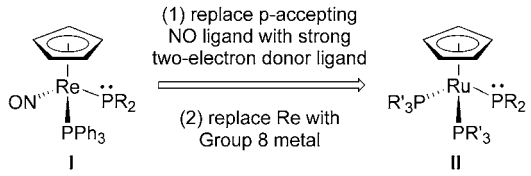


Scheme 1. Design of highly electron-rich ruthenium-containing phosphorus donor ligands.

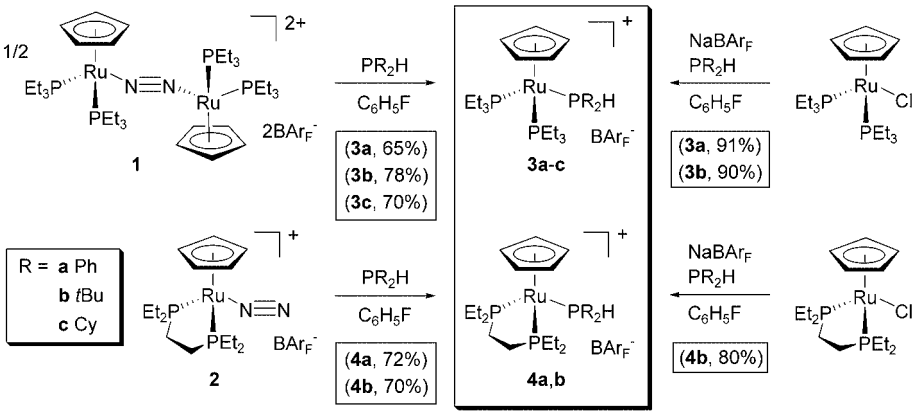
We therefore sought phosphido complexes that would be still more electron-rich than the rhenium systems **I**. As illustrated in Scheme 1, one obvious approach would be to replace the strongly π-accepting NO ligand with a good donor ligand. Since this would in most cases entail the loss of one valence electron, a metal with an additional valence electron—such as, from group eight—would be needed to compensate. Accordingly, our attention was drawn to ruthenium(II) systems of the type $[(\eta^5\text{-}C_5R_5)Ru(PR'_3)_2(PR_2)]$ (**II**). Complexes of the formula $[(\eta^5\text{-}C_5R_5)Ru(PR'_3)_2(X)]$ have an extensive chemistry,[14] and many derivatives with chiral diphosphines have been prepared in an enantiomerically pure form.[15] However, phosphido complexes such as **II** were unknown.[16]

We envisioned that the target complexes **II** could be accessed by deprotonation of the corresponding cationic secondary phosphine complexes, as demonstrated for the rhenium homologues. Herein, we report 1) convenient syntheses of such ruthenium secondary phosphine complexes, 2) their deprotonation to highly reactive phosphido complexes **II**, which have been characterized in situ, 3) facile reactions of **II** with oxygen and selenium to give $[Ru\{P(=X)R_2\}]$ species, 4) proton transfer experiments and NMR data that show **II** to be among the very strongest trivalent phosphorus Brønsted bases found to date, 5) the generation of highly active catalysts for Suzuki–Miyaura couplings[13] from **II** and palladium precursors, and 6) efforts to isolate well-defined palladium complexes of **II**. A portion of this work has already been communicated.[5]

Results

Syntheses of secondary phosphine complexes: At the outset of this study, we were concerned that at least some of the target secondary phosphine complexes based upon **II** would be very sterically congested, and therefore difficult to synthesize. Thus, our attention was drawn to the dinitrogen complexes $[\{(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2\}_2(\mu\text{-}N_2)]^{2+}\,2\,BAr_F^-$ (**1**) and $[(\eta^5\text{-}C_5H_5)Ru(depe)(N_2)]^+\,BAr_F^-$ (**2**) {where $BAr_F^- = B[3,5\text{-}(C_6H_3(CF_3)_2)]_4^-$ and $depe = Et_2PCH_2CH_2PEt_2$}.[17] These complexes can easily be prepared by reactions of the corresponding chloride complexes $[(\eta^5\text{-}C_5H_5)Ru(PR'_3)_2(Cl)]$ with $NaBAr_F$ under dinitrogen in the nonpolar, noncoordinating solvent C_6H_5F. The dinitrogen ligands are readily displaced by a variety of weak donor ligands.

Reactions of the diruthenium complex **1** and secondary phosphines PR_2H (R = Ph, **a**; *t*Bu, **b**; Cy, **c**) gave the secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PR_2H)]^+\,BAr_F^-$ (**3a–c**) in 65–78% yields. Analogous reactions with the monoruthenium complex **2** afforded $[(\eta^5\text{-}C_5H_5)Ru(depe)(PR_2H)]^+\,BAr_F^-$ (**4a**,**b**) in 70–72% yields (Scheme 2). However, as we gained more experience with these complexes, more efficient syntheses could be realized. As shown in Scheme 2, direct, one-pot reactions of the chloride complexes $[(\eta^5\text{-}C_5H_5)Ru(PR'_3)_2(Cl)]$, $NaBAr_F$, and PR_2H in C_6H_5F gave **3a**,**b** and **4b** in higher yields (80–91%).



Scheme 2. Syntheses of ruthenium secondary phosphine complexes.

The secondary phosphine complexes **3a–c** and **4a**,**b** were air-stable, conveniently handled yellow or salmon powders. They were characterized by NMR (^1H, ^{13}C, ^{31}P) spectroscopy and microanalyses, as summarized in the Experimental Section and Tables 1 and 2. The ^{31}P NMR spectra exhibited typical AX_2 patterns arising from the secondary and two equivalent tertiary phosphine ligands ($^2J(P,P) = 31$–42 Hz). The ^1H NMR spectra showed diagnostic doublets of triplets for the PH signals, with $^1J(H,P)$ values ranging from 316 to 353 Hz and $^3J(H,P)$ values from 2 to 5 Hz. A few other cyclopentadienyl ruthenium tris(phosphine) complexes that contain at least one secondary phosphine ligand have been reported,[19] and these exhibit slightly higher $^1J(H,P)$ values (357–370 Hz).

The crystal structure of **4a** was determined as summarized in Table 3 and the Experimental Section. Figure 1 depicts the structure of the cation, and lists key bond lengths and angles. The complex adopts a standard piano-stool geometry, with the bond lengths and angles about ruthenium similar to those in several other structurally characterized cyclo-

Table 1. Key NMR data for $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(X)]^{n+}$ (entries 1–10) and $[(\eta^5\text{-}C_5H_5)Ru(depe)(X)]^{n+}$ (entries 11–17) complexes.[a]

Entry	X	δ(X) [ppm][b]	$^{31}P\{^1H\}$ NMR δ(2PEt$_3$ or depe) [ppm][c]	^2J(P,P) [Hz]	^1H NMR $\delta(C_5H_5)$ [ppm]
1	PPh_2H (**3a**)	41.1[d]	28.0[d]	42.0	5.43[d]
2	PPh_2 (**5a**)	11.8[d,e]	30.4[d,e]	5.0	4.63[d]
3	$P(=O)Ph_2$ (**7a**)	78.3[d]	34.3[d]	50.1	4.87[d]
4	$P(=Se)Ph_2$ (**9a**)	43.3[d]	26.8[d]	40.5[f]	4.71[d]
5	$PtBu_2H$ (**3b**)	71.9[g]	19.0[g]	34.0	5.14[g]
		79.2[d]	20.8[d]	–	5.24[d]
6	$PtBu_2$ (**5b**)	88.0[e,g]	23.7[g]	4.0	4.77[g]
7	PCy_2H (**3c**)	50.7[g]	27.9[g]	38.8	5.17[g]
		49.8[d]	27.9[d]	–	5.28[d]
8	PCy_2 (**5c**)	29.0[g,h]	28.9[g,h]	–[i]	4.67[g]
9	$P(=O)Cy_2$ (**7c**)	108.3[g]	34.3[g]	45.1	4.85[g]
10	$P(=Se)Cy_2$ (**9c**)	57.3[g]	25.7[g]	36.5[f]	4.78[g]
11	PPh_2H (**4a**)	38.2[d]	75.1[d]	39.0	5.40[d]
12	PPh_2 (**6a**)	7.2[d,h]	74.8[d,h]	–[i]	4.63[d]
13	$P(=O)Ph_2$ (**8a**)	92.4[d]	80.5[d]	49.2	5.40[d]
14	$P(=Se)Ph_2$ (**10a**)	44.9[d]	74.2[d]	38.0[f]	4.56[d]
15	$PtBu_2H$ (**4b**)	80.9[g]	62.4[g]	31.4	5.07[g]
		82.3[d]	64.2[d]	–	5.18[d]
16	$PtBu_2$ (**6b**)	84.6[g,h]	64.6[g,h]	–[i]	4.73[g]
17	$P(=O)tBu_2$ (**8b**)	138.3[g]	64.3[g]	38.2	4.83[g]

[a] Conditions are given in the Experimental Section. [b] Triplet unless noted. [c] Doublet unless noted. [d] Data from [D$_6$]acetone. [e] Broad signal. [f] The ^1J(P,Se) value for the selenium satellite associated with this signal is given in Table 2 (^{77}Se = 7.58 %). [g] Data from [D$_8$]THF. [h] Broad singlet. [i] Not resolved.

Table 2. Comparison of the ^1J(P,X) coupling constants of organophosphine compounds and ruthenium phosphorus complexes.

Compound	^1J(P,H) [Hz]	Compound	^1J(P,Se) [Hz]
$[HPPh_3]^+FSO_3^-$	510[a]	$Se{=}PPh_3$	729[b]
$[HPtBu_3]^+BF_4^-$	436[c]	$Se{=}PtBu_3$	711.6[d]
3a	352.9	**9a**	520.0
4a	350.5	**10a**	511.5
3c	327.7	**9c**	507.9
4b	318.9	–	–
3b	316.5	–	–

[a] See ref. [18]. [b] See ref. [25]. [c] See ref. [24b]. [d] See ref. [27].

pentadienyl ruthenium tris(phosphine) complexes.[17,19,20] The coordination environment about the ruthenium atom is obviously congested, and some consequences of this with respect to its reactivity are described below.

Generation of phosphido complexes: Deprotonation reactions of the secondary phosphine complexes were studied in NMR tubes. As shown in Scheme 3, [D$_6$]acetone solutions of the diphenylphosphine complexes **3a** and **4a** were treated with 1.0–1.1 equivalents of *t*BuOK ($pK_a(H_2O)$ *t*BuOH = 19.2).[21] The samples turned bright orange, and the ^1H and ^{31}P NMR spectra were consistent with the formation of the target phosphido complexes $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2)]$ (**5a**; 93 % conversion) and $[(\eta^5\text{-}C_5H_5)Ru(depe)(PPh_2)]$ (**6a**; 90 % conversion). Key NMR data are summarized in Table 1 and the Experimental Section. Both complexes could be similarly generated in toluene, under which conditions the byproduct $KBAr_F$ precipitated. The dialkylphosphine complexes **3b**,**c** and **4b** did not react with *t*BuOK under any conditions.

Table 3. Summary of the crystallographic data for **4a**.

molecular formula	$C_{59}H_{52}BF_{24}P_3Ru$
molecular weight	1421.80
temp. of collection [K]	173(2)
diffractometer	KappaCCD
radiation [Å]	$Mo_{K\alpha}$
crystal system	monoclinic
space group	*Cc*
unit cell dimensions:	
a [Å]	23.1246(5)
b [Å]	12.6360(3)
c [Å]	22.3980(4)
α [°]	90.0
β [°]	113.542(1)
γ [°]	90.0
V [Å^3]	6000.0(2)
Z	4
ρ_{calcd} [g cm^{-3}]	1.574
μ [mm^{-1}]	0.455
crystal dimensions [mm]	$0.45\times0.30\times0.30$
θ range [°]	$1.92\le\theta\le27.48$
range/indices (*h*, *k*, *l*)	−29, 30; −15, 16; −29, 29
no. of reflections	11095
no. of unique data	10375
no. of observed data	11089 [$I>2\sigma(I)$]
no. refined parameters	794
refinement	least-squares on F^2
R_{int}	0.0055
R indices [$I>2\sigma(I)$]	$R_1=0.0407$
	$wR_2=0.1073$
R indices (all data)	$R_1=0.0445$
	$wR_2=0.1104$
goodness of fit	1.035
largest diff. peak, hole [e Å^{-3}]	0.755/−0.540

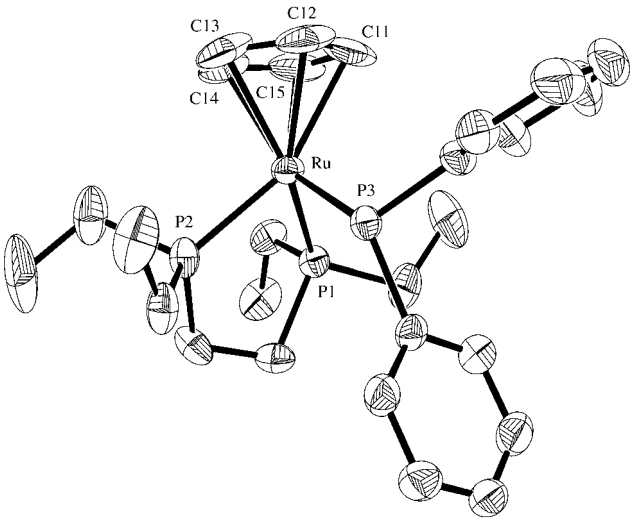
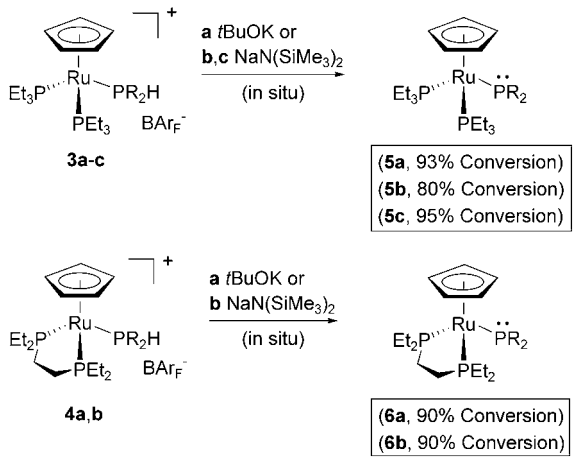


Figure 1. Structure of the cation of **4a**. Key bond lengths [Å] and bond angles [°]: Ru–P1 2.2871(10), Ru–P2 2.2933(11), Ru–P3 2.2867(10), Ru–C11 2.240(5), Ru–C12 2.233(4), Ru–C13 2.236(5), Ru–C14 2.241(4), Ru–C15 2.244(5), P3-Ru-P1 98.86(4), P3-Ru-P2 94.36(4), P1-Ru-P2 81.72(4).

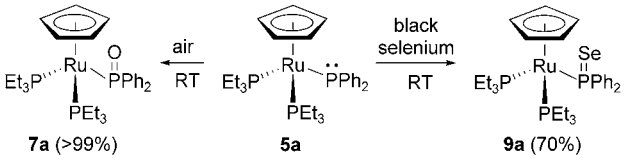


Scheme 3. Generation of ruthenium phosphido complexes.

However, when the stronger base $NaN(SiMe_3)_2$ (pK_a(THF) $HN(SiMe_3)_2 = 25.8$;[22] 1.1–1.5 equiv) was added to [D_8]THF solutions of **3b**,**c** and **4b**, high conversions to the phosphido complexes **5b** (80%), **5c** (95%), and **6b** (90%) were achieved.[5] Deprotonation reactions could also be effected with *n*BuLi. The ^{1}H and ^{31}P NMR spectra of **5c** did not vary significantly in the temperature range of −90 to 55 °C, and the ^{31}P NMR signals of **6b** showed broadening only at −100 °C. Attempts to isolate **5a–c** and **6a**,**b** always gave some of the corresponding phosphine oxide, traces of which were routinely detected in the NMR samples. Preparative oxidation reactions are detailed below.

The NMR data for **5a–c** and **6a**,**b** exhibited several conspicuous trends. First, the cyclopentadienyl ^{1}H signals were 0.5–0.8 ppm upfield from those of the cationic precursors **3a–c** and **4a**,**b**. Second, the $RuPR_2$ ^{31}P signals were 20–30 ppm upfield of the $RuPR_2H$ signals of **3a–c** and **4a**,**b**. Thirdly, the ^2J(P,P) values were much lower than those of **3a–c** and **4a**,**b** (<5 versus 31–42 Hz). Owing to the somewhat broad peaks, they were often too small to measure. Analogous coupling trends have been noted for secondary phosphine and phosphido complexes of other metal fragments and were attributed to higher p character in the metal–phosphorus bonds of the phosphido complexes.[23]

Oxidation reactions of phosphido complexes: When air was deliberately added to the phosphido complexes, oxidation reactions were completed within seconds. Compound **5a** gave the oxide [(η^5-C_5H_5)Ru(PEt_3)$_2${P(=O)Ph_2}] (**7a**) in >99% yield after workup (Scheme 4). The ^{31}P NMR signal



Scheme 4. Representative oxidations of ruthenium phosphido complexes.

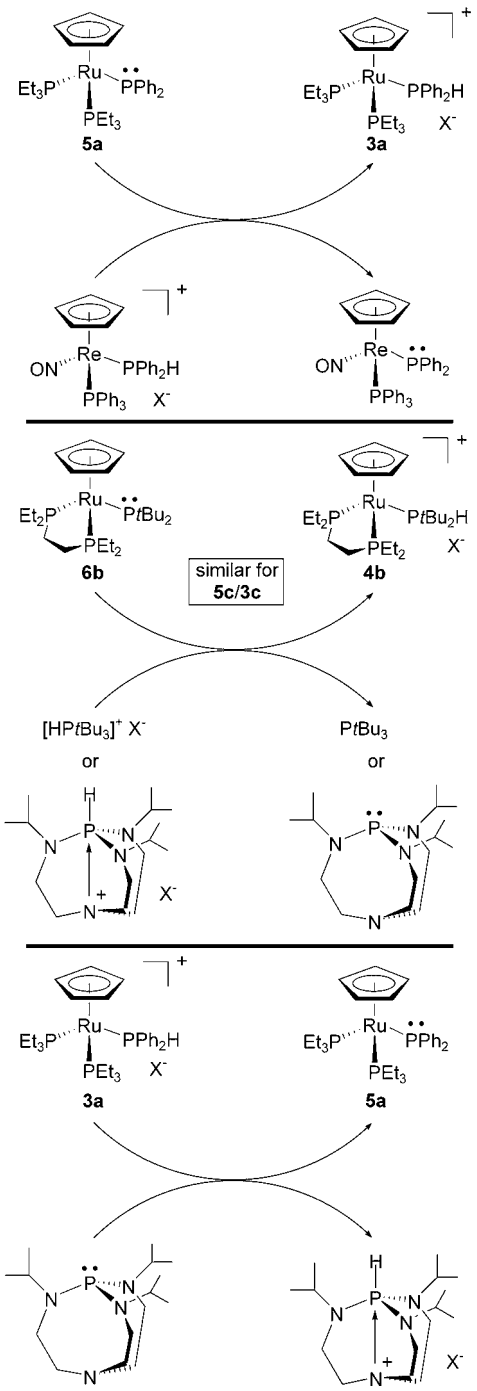
of the P(=O)Ph_2 group of **7a** was 67 ppm downfield from that of the PPh_2 group in **5a**, which is a typical shift for this functional transformation,[9] and the mass spectrum showed a strong molecular ion. Complexes **5c** and **6a**,**b** were treated with substoichiometric amounts of oxygen, and were partially converted to the oxides [(η^5-C_5H_5)Ru(PEt_3)$_2${P(=O)Cy_2}] (**7c**) and [(η^5-C_5H_5)Ru(depe){P(=O)R_2}] (R = Ph, **8a**; *t*Bu, **8b**). These complexes were characterized in situ by NMR spectroscopy and the data are summarized in Table 1.

Phosphine selenides have been extensively reported in the literature,[24] including efforts to correlate the NMR coupling constants $^1J(^{31}P,^{77}Se)$ (henceforth ^1J(P,Se)) with the basicities of the corresponding phosphines.[25] Thus, a slight excess of black selenium powder was added to an NMR tube containing **5a**. After 3 h, the NMR spectra showed complete conversion to a 94:6 mixture of the selenide [(η^5-C_5H_5)Ru(PEt_3)$_2${P(=Se)Ph_2}] (**9a**) and **7a**. A preparative reaction gave **9a** in 70% yield. Interestingly, most tertiary phosphines require at least 20 h in refluxing chloroform or toluene for complete reaction.[26] Similar experiments with **5c** and **6a** gave the corresponding selenides [(η^5-C_5H_5)Ru(PEt_3)$_2${P(=Se)Cy_2}] (**9c**) and [(η^5-C_5H_5)Ru(depe){P(=Se)Ph_2}] (**10a**). However, these transformations were accompanied by side-reactions, including some reprotonation to **3c** and **4a**. Hence, the products were only characterized in situ by NMR spectroscopy and the data are summarized in Table 1 and Table 2. Sometimes bulkier phosphines react with selenium much less efficiently.[25]

As summarized in Table 2, the ^1J(P,Se) values associated with these complexes, 520–508 Hz, are much lower than those of organophosphine selenides, including those derived from bulky, electron-rich phosphines such as Se=P*t*Bu_3 (711.6 Hz).[27] The ^1J(H,P) values of the secondary phosphine complexes exhibit parallel trends. This suggests that the fraction of p character in the phosphorus orbital of the P–Se and P–H bonds is much higher than normal. Hence, as will be discussed further in the discussion section, **5a–c** and **6a**,**b** should be much more basic than most other types of trivalent phosphorus compounds.

Relative Brønsted basicities: We sought to verify the proposal in Scheme 1 regarding the relative basicities of rhenium and ruthenium phosphido complexes **I** and **II**. Thus, an NMR tube was charged with a 1:1 mixture of rhenium and ruthenium secondary phosphine complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(PPh_2H)]$^+$ TfO^-[3,4] and **3a**, and 1.0 equivalents of *t*BuOK in [D_6]acetone was added. The NMR spectra showed the complete conversion of the former to the rhenium phosphido complex [(η^5-C_5H_5)Re(NO)(PPh_3)(PPh_2)],[8] and no reaction of **3a**. Hence, **5a** has a much higher Brønsted basicity than its rhenium counterpart, and the equilibrium shown in Scheme 5 (top) can be formulated.[28]

We sought a comparison with the benchmark organophosphine, P*t*Bu_3. The acidity of the [HP*t*Bu_3]$^+$ ion has been extensively studied and $pK_a(H_2O)$, pK_a(THF), and pK_a(acetonitrile) values of 11.4, 10.7, and 17.0 have been reported.[29] Thus, an NMR tube was similarly charged with a 1:1 mixture



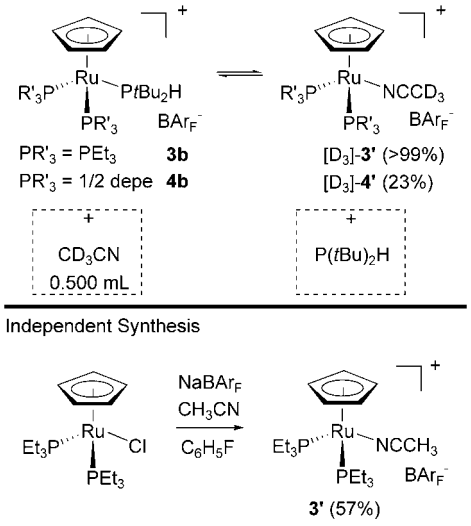
Scheme 5. Proton transfer equilibria.

of **4b** and $[HPtBu_3]^+BF_4^-$,[30] and 1.0 equivalent of $NaN(SiMe_3)_2$ in $[D_8]$THF was added. The NMR spectra showed the complete deprotonation of $[HPtBu_3]^+BF_4^-$ and no reaction of **4b**. Hence, the di(*tert*-butyl)phosphido complex **6b** has a much higher Brønsted basicity than $PtBu_3$, as illustrated in the equilibrium shown in Scheme 5 (middle). We presume that the other phosphido complexes are similarly more basic than the analogous organophosphines PCy_3 and PPh_3 ($pK_a(H_2O)$ and pK_a(THF) for $[HPPh_3]^+$, 2.7 and 3).[29]

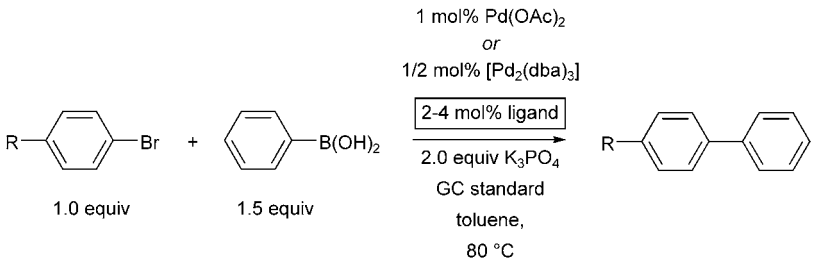
To better bound the basicity of **6b**, one of the most basic trivalent phosphorus compounds, Verkade's proazaphosphatrane superbase $P(iPrNCH_2CH_2)_3N$, was employed.[31] As shown in Scheme 5 (middle), the conjugate acid of this species features a pentacoordinate phosphorus atom and a pK_a(acetonitrile) value of 33.6 has been measured.[32] An NMR tube was charged with a 1:1 mixture of **4b** and $P(iPrNCH_2CH_2)_3N$, and THF was added. No reaction was observed by ^{31}P NMR spectroscopy. An analogous experiment was conducted in $[D_3]$acetonitrile. The ^1H and ^{31}P NMR spectra showed that **4b** had undergone an isotope exchange to give the RuPD species $[D_1]$-**4b**, but no **6b** was detected. However, the proazaphosphatrane underwent about 30% conversion to the deuteriated cation $[DP(iPrNCH_2CH_2)_3N]^+$.

To substantiate the apparent lack of reactions, the equilibrium was approached from the opposite direction. Thus, a THF solution of **6b** was generated and treated with the protonated proazaphosphatrane $[HP(iPrNCH_2CH_2)_3N]^+Cl^-$. The ^{31}P NMR spectrum showed complete conversion to **4b** and the proazaphosphatrane. Hence, **6b** is clearly a stronger Brønsted base than $P(iPrNCH_2CH_2)_3N$. Similar data were obtained with the di(cyclohexyl)phosphido complex **5c**. However, when $P(iPrNCH_2CH_2)_3N$ was added to a $[D_6]$acetone solution of **3a**, complete deprotonation to the diphenylphosphido complex **5a** occurred. Therefore, as illustrated by the equilibrium in Scheme 5 (bottom), $P(iPrNCH_2CH_2)_3N$ is a stronger Brønsted base than **5a** (and presumably **6a**).

Ligand substitution: Whilst characterizing the secondary phosphine complexes, some unexpected substitution reactions were encountered. For instance, **3b** was dissolved in $[D_3]$acetonitrile, as shown in Scheme 6 (top). Over the course of 3 h, the ^1H and ^{31}P NMR spectra showed complete conversion to the acetonitrile complex $[(\eta^5\text{-}C_5H_5)Ru$-



Scheme 6. Representative substitution reactions of ruthenium secondary phosphine complexes.



Scheme 7. Conditions for Suzuki couplings.

$(PEt_3)_2(NCCD_3)]^+ BAr_F^-$ ([D_3]-**3′**) and the free phosphine P*t*Bu_2H. An authentic sample of **3′** was isolated from the reaction of the chloride complex $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(Cl)]$, $NaBAr_F$, and acetonitrile in C_6H_5F (Scheme 6, bottom).[33] When **3b** and 4.5 equivalents of acetonitrile were combined in $ClCD_2CD_2Cl$, complete conversion to **3′** and P*t*Bu_2H also occurred. This indicates an equilibrium constant greater than 1.

However, when the depe chelate **4b** was dissolved in [D_3]acetonitrile (Scheme 6, top), only partial substitution occurred to give a 77:23 **4b**/[D_3]-**4′** equilibrium mixture. From the concentration data (see Experimental Section), an equilibrium constant of 10^{-4} could be calculated. The differences in behavior can be rationalized by the greater effective size of the two PEt_3 ligands in **3b** relative to depe in **4b**. The phenyl- and cyclohexyl-substituted secondary phosphine complexes **3a**,**c** and **4a** were not observed to react in [D_3]acetonitrile solution. Note that the PPh_2H ligands that would be displaced from **3a** and **4a** are less basic than the P*t*Bu_2H displaced from **3b** and **4b**.[24b] This further indicates that substitution is largely driven by steric factors.

Suzuki coupling reactions: Screening experiments were conducted under conditions similar to those developed by Buchwald and co-workers, as summarized in Scheme 7.[1a] Toluene suspensions of **3a–c** or **4b** were treated with either a THF solution of *t*BuOK (**3a**) or a toluene solution of $NaN(SiMe_3)_2$ (**3b**,**c**, **4b**) to generate the phosphido complexes **5a–c** and **6b** (2 or 4 mol%). To better match the conditions of a previous paper,[3,4] twice the amount of base

Table 4. Data for Suzuki coupling reactions under the conditions shown in Scheme 7: conversion [%] of aryl bromides and (in parentheses) yield [%] of biaryl after specified reaction times [h].

Entry	R	Ligand[a] (mol%)	Pd (mol%)	Conversion [%] (yield [%]) after specified reaction time [h] 0.25	0.5	1	2	4	8	24	48
1	H	**5a**	$Pd(OAc)_2$	27	42	55	73	88	93	96	96
		(2)	(1)	(21)	(33)	(46)	(63)	(79)	(88)	(93)	(95)
2	H	**5a**	$Pd(OAc)_2$	43	59	70	84	90	93	95	97
		(4)	(1)	(33)	(48)	(58)	(73)	(81)	(83)	(88)	(91)
3	H	**5a**	$[Pd_2(dba)_3]$	37	48	60	67	72	78	87	92
		(2)	(0.5)	(30)	(38)	(47)	(56)	(65)	(73)	(85)	(86)
4	H	**5a**	$[Pd_2(dba)_3]$	39	51	62	71	74	78	83	84
		(4)	(0.5)	(30)	(42)	(53)	(63)	(66)	(71)	(76)	(76)
5	H	**5b**	$Pd(OAc)_2$	49	81	100	100				
		(2)	(1)	(48)	(80)	(94)	(96)				
6	H	**5c**	$Pd(OAc)_2$	56	77	96	100				
		(2)	(1)	(52)	(74)	(92)	(97)				
7	H	**5c**	$Pd(OAc)_2$	59	82	99	100				
		(4)	(1)	(55)	(79)	(97)	(100)				
8	H	**6b**	$Pd(OAc)_2$	71	93	100					
		(2)	(1)	(66)	(88)	(95)					
9	H	none	$Pd(OAc)_2$	23	30	35	45	49	56	60	63
			(1)	(17)	(27)	(32)	(38)	(44)	(51)	(54)	(59)
10	H	PPh_3	$Pd(OAc)_2$	67	85	98	100				
		(4)	(1)	(50)	(81)	(92)	(92)				
11	H	P*t*Bu_3	$Pd(OAc)_2$	88	96	98	100				
		(4)	(1)	(87)	(95)	(97)	(97)				
12	H_3CO	**5a**	$Pd(OAc)_2$	6	13	26	46	61	68	75	
		(2)	(1)	(9)	(12)	(20)	(34)	(48)	(50)	(55)	
13	H_3C	**5a**	$Pd(OAc)_2$	12	15	21	28	42	64	78	
		(2)	(1)	(9)	(12)	(16)	(22)	(35)	(54)	(68)	
14	H_3C	**5a**	$Pd(OAc)_2$	21	34	49	70	87	93	94	
		(4)	(1)	(15)	(24)	(36)	(54)	(68)	(72)	(75)	
15	$H_3C(O)C$	**5a**	$Pd(OAc)_2$	53	72	86	96	100			
		(2)	(1)	(50)	(62)	(73)	(80)	(90)			
16	$H_3C(O)C$	**5a**	$Pd(OAc)_2$	29	39	55	66	79	89	100	
		(4)	(1)	(29)	(38)	(46)	(61)	(70)	(76)	(84)	

[a] Generated in situ from the conjugate acid as described in the text, except in the case of PPh_3.

used in Scheme 3 was employed (e.g., 4 or 8 mol%). Then $Pd(OAc)_2$ was added (1 mol%), followed by phenylboronic acid (1.5 equiv), the boron-activating base K_3PO_4 (2.0 equiv), bromobenzene (1.0 equiv), and an internal standard. The standard allowed the consumption of bromobenzene and the formation of biphenyl to be continuously monitored by GC. All reactions were carried out at 80 °C.

The first experiments were conducted with 2.0 mol% of the phosphido ligand. The data are summarized in entries 1, 5, 6, and 8 of Table 4 and graphically in Figure 2. In all cases, the bromobenzene conversion was close to the yield

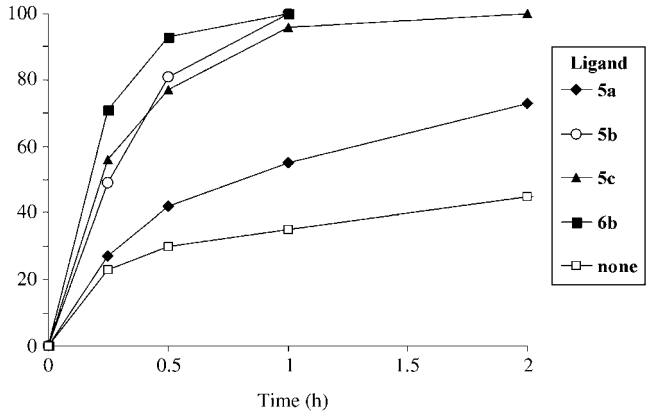


Figure 2. Plots of bromobenzene conversion (%) for entries 1, 5, 6, 8, and 9 of Table 4.

of biphenyl, which reached 95–97%. There was no evidence for any appreciable homocoupling of the boronic acid.[13c,d] The catalysts derived from the *tert*-butyl- and cyclohexyl-substituted phosphido complexes **5b**,**c** were distinctly more reactive than that derived from the less bulky and electron-rich phenyl-substituted **5a**. The *tert*-butyl-substituted depe complex **6b** gave a still more active catalyst. When no ligand was present, the rate decreased dramatically and only partial conversion proved possible (Table 4, entry 9).

Additional experiments were conducted with 4.0 mol% of the phosphido ligands (Table 4, entries 2 and 7). This had only a modest effect with **5a**, and none at all with **5c**. These conditions are strictly comparable to those used with PPh_3, $PtBu_3$, and the rhenium phosphido complexes **I** in previous work.[3,4] The data for the organophosphines are given in entries 10 and 11 in Table 4. Disregarding minor differences due to ligand loading, the following conclusions emerge. First, phenyl-substituted **5a** gives a slightly more active catalyst than the rhenium analogue. Second, the *tert*-butyl-substituted lead ligand **6b** affords a catalyst nearly as active as the rhenium analog. Third, phenyl-substituted **5a** gives a less active catalyst than PPh_3, and *tert*-butyl-substituted **5b** and **6b** give less active catalysts than $PtBu_3$, although the difference in the last case is slight. Hence, catalyst activities do not parallel the basicity strengths established for the various classes of trivalent phosphorus compounds in Scheme 5.

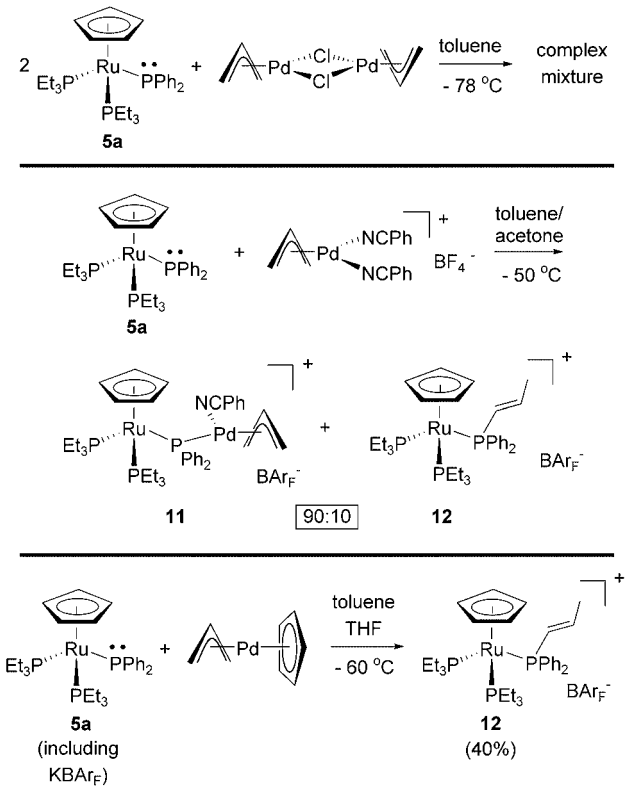
As summarized in entries 12–16 of Table 4, Suzuki coupling reactions of substituted aryl bromides were also examined. Electron-withdrawing groups are commonly activating, and electron-donating groups deactivating. These trends are apparent from the data. Under analogous conditions, chlorobenzene gave only very low yields of biphenyl (5–12% after 48 h with **5c** or **6b**). As shown in entries 3 and 4 in Table 4, $[Pd_2(dba)_3]$ (where dba = dibenzylideneacetone) was also investigated as a palladium source; however, there was no significant improvement in yield or conversion compared to the reactions with $Pd(OAc)_2$. Finally, scouting experiments were conducted under conditions popularized by Fu and coworkers (0.5:1 $[Pd_2(dba)_3]$/**5a**, KF in place of K_3PO_4, THF, 60 °C).[1b] After 96 h, the conversion of bromobenzene and yield of biphenyl were only 55 and 40%, respectively.

We wondered whether the extraordinary basicities of the phosphido complexes and the appreciable acidity of phenylboronic acid ($pK_a(H_2O) = 8.8$)[34] might lead to complications. Indeed, when a toluene solution of **5a** was added to solid phenylboronic acid, rapid proton transfer occurred to give **3a**. However, when $Pd(OAc)_2$ was added first, as in the above procedures, no **3a** was detected, nor were other proton transfer phenomena apparent.

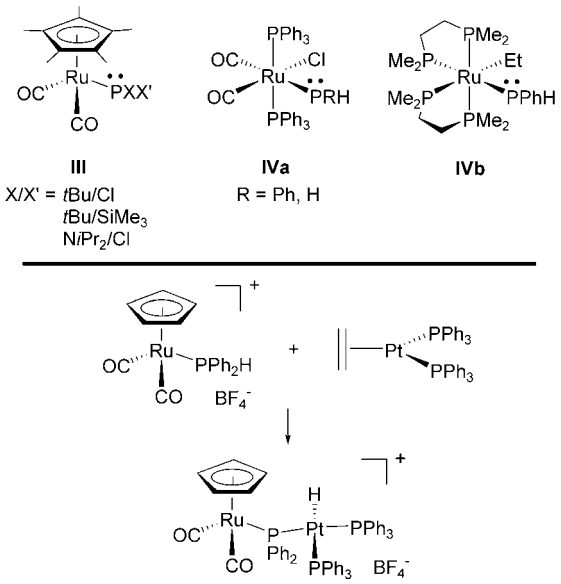
Complexes with $RuPR_2Pd$ linkages: We sought to enhance the activities of the ruthenium/palladium catalyst systems. One limiting factor may be the efficiency with which the catalytic cycle is entered. In other words, is all of the ligand or metal used, or just a portion? In an effort to eliminate the need for substitution at palladium, we set out to prepare palladium adducts of the ruthenium phosphido complexes. Many π-allyl complexes of the type $[(\eta^3\text{-}C_3H_5)Pd(Cl)(L)]$ have been synthesized[35] that can react with *t*BuOK to give low-coordinate PdL species with high catalytic activities.[36] In a standard approach to such species, the phosphido complex **5a** and $[\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2]$ were combined. However, as shown in Scheme 8 (top), complex mixtures of products were formed. Similar observations have sometimes been reported by others.[37]

We speculated that a monomeric, cationic π-allyl complex with a labile two-electron-donor ligand might give cleaner substitution. Thus, the bis(benzonitrile) complex $[(\eta^3\text{-}C_3H_5)Pd(NCPh)_2]^+ BF_4^-$[38] and **5a** were combined at −50 °C. As shown in Scheme 8 (middle), workup gave a high yield of a brown oil that was a 90:10 mixture of the target complex $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2)Pd(NCPh)(\eta^3\text{-}C_3H_5)]^+ BAr_F^-$ (**11**) and another species **12** identified below. The ^1H NMR spectrum of **11** showed signals indicative of the cyclopentadienyl, benzonitrile, PEt_3, and π-allyl ligands, as well as the anion BAr_F^- (present from the generation of **5a**). The ^{31}P NMR spectrum exhibited an AMX pattern consistent with a lack of symmetry and a downfield PPh_2 signal typical of bridging phosphido complexes ($\delta = 209.8$ ppm).[39] However, all efforts to further purify **11** were unsuccessful.[40]

Hence, a third approach to bridging $RuPR_2Pd$ species was investigated. The cyclopentadienyl π-allyl complex $[(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)]$ and many phosphines react to give palladium bis(phosphine) complexes $Pd(PR_3)_2$.[41] Thus, **5a** was



Scheme 8. Reactions of ruthenium phosphido complexes with palladium complexes.



Scheme 9. Other relevant ruthenium complexes and reactions.

added to $[(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)]$ under various conditions. In no case was an adduct cleanly generated. However, when the sequence was carried out in toluene/THF, (*E*)-$[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2CH{=}CHCH_3)]^+ BAr_F^-$ (**12**)—the byproduct obtained in the previous reaction—was isolated in 40% yield (Scheme 8, bottom). The structural assignment was supported by a strong ion for the cation in the mass spectrum, and ^1H and ^{13}C NMR signals typical of a propenyl moiety (see Experimental Section).[42] The $^3J(C,P)$ value associated with the methyl ^{13}C signal (45.2 Hz) was diagnostic of an (*E*)-$PCH{=}CHCH_3$ moiety.[42b] The allylation of phosphines by π-allyl complexes has been previously observed[37] and C=C isomerization reactions are catalyzed by many palladium and ruthenium species. Also, vinylphosphonium salts are normally thermodynamically more stable than allylphosphonium salts.[43]

Discussion

Ruthenium phosphido complexes: The title complexes **II** are easily generated by the deprotonation of cationic secondary phosphine complexes, as outlined in Scheme 3. However, they are by no means the first examples of ruthenium phosphido complexes. Two other classes, **III** and **IV** (Scheme 9), have previously been reported.[16] The species **III** and **IVa** feature two strongly π-accepting carbonyl ligands and should therefore be much less electron-rich and basic than **II**. Complexes **IV** were, as in our study, synthesized by the deprotonation of cationic RuPH compounds. The $^1J(P,H)$ values of **IVa** (388–394 Hz) are greater than those given in Table 2, consistent with lower phosphido complex basicities. However, those of **IVb**, which lacks strongly π-accepting ligands, are much lower (198–189 Hz, depending upon the solvent), which suggests greater basicity.

Although the phosphido complexes **II** were generated and reacted in situ, there remains in our opinion the possibility that some might be isolated, at least in spectroscopically pure form. The best candidates for this are the less electron-rich diphenylphosphido complexes **5a** and **6a**. However, given their high oxygen sensitivities and basicities, the most rigorous anaerobic and protic-impurity-free conditions are necessary. There is also the possibility that they will decompose to bridging phosphido species $Ru(\mu\text{-}PR_2)_nRu$, especially upon concentration of the sample.[12a]

Since the complexes **II** were generated in situ, spectroscopic measurements were conducted in the presence of byproducts such as $KBAr_F$, $NaBAr_F$, *t*BuOH, and $HN(SiMe_3)_2$. However, when **5a** and **6a** were prepared in toluene, $KBAr_F$ precipitates, so that only *t*BuOH remains. The electrophilic portions of these byproducts can in theory interact with the phosphorus lone pair, as illustrated by the crystal structure of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{CH_2PtBu_2\}]$ in a previous paper.[4] This complex, in which the trivalent phosphorus is less basic owing to the intervening methylene group, co-crystallized with *t*BuOH to give a P···H–O hydrogen bond with a phosphorus–hydrogen distance of 2.8–2.9 Å. Hence, some of the NMR properties of **5a–c** and **6a**,**b** may be affected by such interactions.

In work currently in progress, reactions parallel to those in Scheme 2 and Scheme 3 have been conducted with pentamethylcyclopentadienyl ruthenium complexes.[44] Such an-

alogs of phosphido complexes **5** and **6** should be even more bulky and electron-rich. However, the pentamethylcyclopentadienyl secondary phosphine complexes undergo extremely facile ligand substitutions of the type shown in Scheme 6. More weakly coordinating NMR solvents, such as [D$_6$]acetone, participate in such substitution reactions. Hence, although the pentamethylcyclopentadienyl analog of **5a** can be generated, there are additional complications that render the chemistry more challenging.

Brønsted basicities of phosphido complexes: In the various proton transfer reactions involving **5a–c** and **6a**,**b**, a number of equilibrium relationships have been established (Scheme 3 and Scheme 5 and text). First, the pK_a values of the conjugate acids of **5a** and **6a** must be less than that of *t*BuOH. Secondly, those of the conjugate acids of **5b**,**c** and **6b** must be less than that of HN(SiMe$_3$)$_2$. These and other relationships are sketched, incorporating the pK_a(H$_2$O) and/or pK_a(THF) values of HN(SiMe$_3$)$_2$, *t*BuOH, [HP*t*Bu$_3$]$^+$, and [HPPh$_3$]$^+$ cited earlier in the text, in the "basicity ladder" shown in Figure 3.

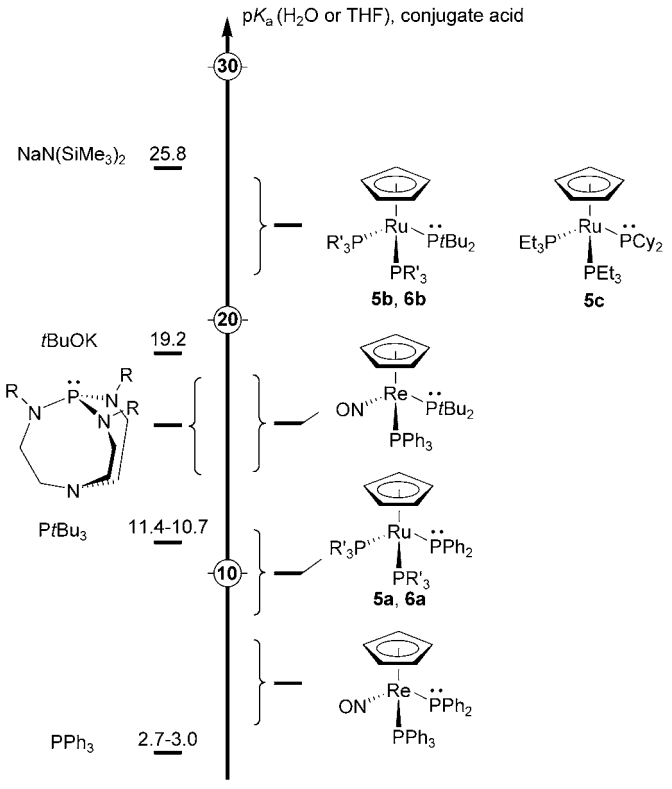


Figure 3. Estimated basicity ladder for trivalent phosphorus compounds and other bases employed in this study (PR′$_3$ = PEt$_3$ or $^1/_2$depe).

The relative basicities of **5a–c**, **6a**,**b**, and Verkade's proazaphosphatrane superbase P(*i*PrNCH$_2$CH$_2$)$_3$N—to our knowledge the most basic isolable trivalent phosphorus compound[32,45]—are of particular interest. The equilibria in Scheme 5 clearly show that **5b**,**c** and **6b** are more basic, and that **5a** and **6a** are less basic. Unfortunately, quantitative data for P(*i*PrNCH$_2$CH$_2$)$_3$N are only available in acetonitrile, a solvent that typically gives pK_a values 7–13 units higher than H$_2$O or THF.[45b] However, the conjugate acid [HP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ Cl$^-$ (pK_a(acetonitrile) = 33.6)[32] is deprotonated by *t*BuOK in THF.[46] Hence, this compound can be placed beneath *t*BuOH on the ladder in Figure 3.

It can also be verified from Scheme 5 that the di(ter*t*-butyl)phosphido complex **6b** is much more basic than P*t*Bu$_3$, an outcome that could have been predicted from the relationships already established with respect to *t*BuOH on the ladder. From this result, we presume that the basicities of the phosphido complexes are at least eight pK_a units higher than the corresponding organophosphines. None of our experiments directly address the relative basicities of P*t*Bu$_3$ and the diphenylphosphido complexes **5a** and **6a**. However, by extrapolating from the pK_a(H$_2$O) and pK_a(THF) values for [HPPh$_3$]$^+$ (2.7–3),[29] a close correspondence would not be surprising.

The situation with the rhenium phosphido complexes **I** is similar. Although Scheme 5 shows that they are less basic than the ruthenium homologues, this was also apparent from other reactions: the conjugate acid of the di(*tert*-butyl)phosphido complex is deprotonated by *t*BuOK, but those of **5b** and **6b** are not.[9] As noted in the introduction, there is excellent evidence that the rhenium complexes are more basic than the corresponding organophosphines.[9,12a] Thus, the di(*tert*-butyl)phosphido complex can be placed between *t*BuOH and [HP*t*Bu$_3$]$^+$ on the ladder, and the diphenylphosphido complex can be placed between **5a**/**6a** and [HPPh$_3$]$^+$.

As noted above, ^1J(H,P) and ^1J(P,Se) values decrease as the p character in the phosphorus orbital of the P–H or P–Se bond increases. For first- and second-row atoms, increased lone-pair p character is commonly associated with greater Brønsted and Lewis basicity. Accordingly, linear correlations of ^1J(H,P) and ^1J(P,Se) values and Brønsted basicities have been found for homologous series of compounds.[25] Such relationships break down when applied to large, structurally diverse, groups of compounds. Nonetheless, the much lower ^1J values of the ruthenium secondary phosphine complexes and selenides in Table 2, relative to those of derivatives of analogous organophosphines or other types of trivalent phosphorus compounds, provide further support for the extraordinary Brønsted basicities of the ruthenium phosphido complexes **II**.

The data in Table 2 suggest that the di(cyclohexyl)phosphido complex **5c** is slightly less basic than the di(*tert*-butyl)-phosphido complexes **5b** and **6b**, in line with the organophosphines.[24b] The ^1J(H,P) values for the protonated rhenium diphenylphosphido and di(*tert*-butyl)phosphido complexes, 397 and 354.8 Hz,[9] are as expected greater than those of the ruthenium analogues. The ^1J(H,P) value of the protonated proazaphosphatrane [HP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ Cl$^-$ is 497.5–501.5 Hz.[46] However, since this compound features a hypervalent phosphorus atom, it is not strictly comparable. Interestingly, the selenium oxidation of **6b** gives a species

with a ^1J(P,Se) value of only 285 Hz ($\delta = 97.2$ ppm), which is to our knowledge the lowest on record. However, since this does not correlate with the trends evident from the data in Table 2, and the spectroscopic yield is low, it is not assigned to a simple selenide derivative.

Catalysis and palladium adducts: Table 4 and Figure 2 show that more bulky and/or electron-rich ruthenium phosphido complexes give more active palladium-based catalysts for Suzuki coupling reactions. Similar trends have been observed for numerous reactions of aryl halides catalyzed by palladium/phosphine systems.[1,2] As discussed in greater detail in a previous paper,[4] these attributes should accelerate oxidative additions to aryl–halide bonds, which are often rate-determining. Unfortunately, the catalysts derived from **II** do not surpass the activities of catalysts derived from less bulky and electron-rich organophosphines or rhenium analogues **I**. Possibly other steps have become rate-determining, for which the ruthenium fragment presents less favorable steric or electronic properties.

Another possible reason for the lower activities of the ruthenium-containing ligands is the efficiency with which the catalytically active palladium adduct is generated. Hence, precursors with $RuPR_2Pd$ linkages may give better results. As summarized in Scheme 8, attempts to isolate well-defined complexes of this type have so far been disappointing. However, these results represent only preliminary data from a brief investigation and we remain confident that such assemblies can be cleanly and easily accessed. For example, it may not be necessary to first generate a phosphido complex. As shown in Scheme 9 (bottom), a cationic ruthenium secondary phosphine complex and a platinum(0) species have been combined directly to give an adduct with a $RuPR_2Pt$ linkage.[47] In any event, we believe that such compounds have exceptional promise as catalyst precursors.

Finally, this study further validates the feasibility of incorporating "spectator" metal fragments into metal catalysts.[8] This enables a wide spectrum of new architectures to be generated, which would not be possible with traditional ligands, as well as unique electronic properties. Although ferrocenyl units are now applied ubiquitously, there are clearly a variety of other robust metal-containing building blocks that can be brought into play. In our initial efforts, we deliberately sought to avoid using a second metal with a direct role in the catalytic cycle. However, various types of secondary interactions are being increasingly recognized as critical factors in palladium-based catalysis.[11,2c,2f] Phosphorus donor ligands of the types **I** and **II** offer excellent platforms for the incorporation of numerous diversity elements and sites for weak interactions, as will be detailed in future reports.[7]

Conclusions

As a result of this study, a series of easily generated, highly bulky, and extremely electron-rich ruthenium phosphido complexes $[(\eta^5\text{-}C_5R_5)Ru(PR'_3)_2(PR_2)]$ (**II**) are now available. Their Brønsted basicities surpass those of all previously characterized trivalent phosphorus compounds. As would be expected, they are readily oxidized by O_2 or selenium to the corresponding oxides or selenides. They are also very effective ligands for palladium-catalyzed Suzuki cross-coupling reactions with activities approaching those of benchmark organophosphines. They represent attractive building blocks for heterobimetallic complexes and other types of potential catalyst precursors, and broad-ranging future applications can be anticipated.

Experimental Section

General: All manipulations were carried out under N_2 unless otherwise noted. NMR spectra were acquired on Bruker FT spectrometers at 400 (^{1}H), 100.6 (^{13}C), or 162 (^{31}P) MHz and referenced to the solvent (^{1}H: residual [D$_5$]acetone, [D$_7$]THF or ClCD$_2$CDHCl; ^{13}C: [D$_6$]acetone or [D$_8$]THF)[48] or PPh$_3$ (^{31}P: a C$_6$D$_6$ solution in an internally sealed capillary, δ −5.00 ppm) unless otherwise noted. When yields were derived from area ratios of ^{31}P NMR signals, appropriate pulse programs were used to maximize integral accuracies (gated decoupled, 10 s delay). Other instrumentation was described in the previous paper.[4]

Chemicals were used as follows: hexane, THF, and toluene, distilled from Na/benzophenone; petroleum ether, distilled from $CaCl_2$; acetone, acetonitrile, and C_6H_5F, distilled from P_2O_5; [D$_6$]acetone, freeze–pump–thaw degassed (×3) and stored under N_2; other deuteriated solvents, opened and stored inside a glove box; *n*BuLi (1.6 M in THF, Acros), standardized;[49] PEt_3, depe, PPh_2H, P*t*Bu$_2$H, PCy$_2$H (5×98–99%, Strem), *t*BuOK (1.0 M in THF, Aldrich), black selenium powder (99.5%, ABCR), P(*i*PrNCH$_2$CH$_2$)$_3$N (Aldrich), 4-bromoanisole, phenylboronic acid, K_3PO_4 (3×97%, Aldrich), Pd(OAc)$_2$ (99%, Lancaster), [Pd$_2$(dba)$_3$] (ABCR), bromobenzene, tridecane, hexadecane, biphenyl (4×99%, Aldrich), 4-bromoacetophenone (98%, Aldrich), and chlorobenzene (99%, Fluka), used as received; [HP*t*Bu$_3$]$^+$BF$_4^-$, prepared by a literature procedure.[30]

$[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2H)]^+BAr_F^-$ (3a):

Method A: A Schlenk flask was charged with $[\{(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2\}_2(\mu\text{-}N_2)]^{2+}2BAr_F^-$ (**1**;[17] 0.988 g, 0.386 mmol) and C_6H_5F (5 mL), and PPh_2H (0.135 mL, 0.786 mmol) was added with stirring. The red solution turned light orange. Within 10 min, a yellow solid started to precipitate. After 1 h, the mixture was concentrated by trap-to-trap distillation under static vacuum, and the remaining solvent was removed with a cannula. The solid was washed with ethanol (2×10 mL) and dried by oil-pump vacuum to give **3a** as a pale yellow powder (0.725 g, 0.250 mmol, 65%), m.p. 202 °C (decomp); elemental analysis calcd (%) for $C_{61}H_{58}BF_{24}Ru$: C 50.46, H 4.03; found: C 50.49, H 3.93.

Method B: A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(Cl)]$ (0.331 g, 0.755 mmol)[50] and C_6H_5F (7 mL), and $NaBAr_F$ (0.671 g, 0.757 mmol)[51] was added with stirring. The orange solution turned red, and NaCl precipitated. After 30 min, the mixture was filtered with a cannula into a new Schlenk flask that had been charged with PPh_2H (0.133 mL, 0.757 mmol). The solution was stirred and turned light yellow. Within 10 min, a yellow solid started to precipitate. After 1 h, the mixture was concentrated by trap-to-trap distillation under a static vacuum, and the remaining solvent was removed with a cannula. The solid was washed with petroleum ether (3×5 mL) and dried by oil-pump vacuum to give **3a** as a pale yellow powder (0.998 g, 0.687 mmol, 91%).

^{1}H NMR ([D$_6$]acetone): $\delta = 7.86$ (m, 4H of PPh$_2$), 7.80 (br s, 8H, *o*-BAr), 7.69 (s, 4H, *p*-BAr), 7.50–7.40 (m, 6H of PPh$_2$), 7.06 (dt, ^1J(H,P) = 352.9 Hz, ^3J(H,P) = 4.0 Hz, PH), 5.43 (s, C$_5$H$_5$), 2.0–1.8 (m, 6PCH$_2$), 0.99 ppm (m, 6CH$_3$); ^{13}C{^{1}H} NMR ([D$_6$]acetone): $\delta = 162.1$ (q, ^1J(C,B) = 50.0 Hz, *i*-BAr), 137.9 (br d, ^1J(C,P) = 46.3 Hz, *i*-PPh), 135.0 (br s, *o*-BAr), 132.6 (d, ^2J(C,P) = 10.1 Hz, *o*-PPh), 130.5 (d, ^4J(C,P) = 2.1 Hz, *p*-PPh),

129.5 (qq, ^2J(C,F) = 31.5 Hz, ^4J(C,F) = 2.9 Hz,[52] *m*-BAr), 129.4 (d, ^3J(C,P) = 9.7 Hz, *m*-PPh), 124.9 (q, ^1J(C,F) = 271.6 Hz, CF_3), 117.9 (sept, ^3J(C,F) = 4.0 Hz, *p*-BAr), 82.4 (s, C_5H_5), 22.5 (m, PCH_2), 8.4 ppm (m, CH_3); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2${P*t*Bu$_2$H}]$^+$ BAr$_F^-$ (3b):

Method A: A procedure similar to Method A used for the preparation of **3a** with **1** (0.810 g, 0.316 mmol), C_6H_5F (5 mL), and P*t*Bu$_2$H (0.160 mL, 0.644 mmol) gave **3b** (washed with hexane and/or toluene) as a pale yellow powder (0.700 g, 0.495 mmol, 78%), m.p. 102–103 °C (decomp); elemental analysis calcd (%) for $C_{57}H_{68}BF_{24}P_3Ru$: C 48.42, H 4.85; found: C 48.45, H 4.59.

Method B: A procedure similar to Method B used for the preparation of **3a** with [(η^5-C_5H_5)Ru(PEt$_3$)$_2$(Cl)] (0.253 g, 0.578 mmol), C_6H_5F (7 mL), and P*t*Bu$_2$H (0.164 mL, 0.868 mmol) gave **3b** (washed with hexane and/or toluene) as a pale yellow powder (0.735 g, 0.520 mmol, 90%).

^{1}H NMR ([D$_6$]acetone): δ = 7.80 (brs, 8H, *o*-BAr), 7.69 (s, 4H, *p*-BAr), 5.24 (s, C_5H_5), 4.93 (dt, ^1J(H,P) = 316.5 Hz, ^3J(H,P) = 2.4 Hz, PH), 2.3–2.0 (m, 6PCH$_2$), 1.45 (d, ^3J(H,P) = 13.6 Hz, 2PC(CH$_3$)$_3$), 1.23 ppm (m, 6PCH$_2$C*H*$_3$); $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 162.1 (q, ^1J(C,B) = 50.0 Hz, *i*-BAr), 135.0 (brs, *o*-BAr), 129.5 (qq, ^2J(C,F) = 31.7 Hz, ^4J(C,F) = 2.9 Hz,[52] *m*-BAr), 124.9 (q, ^1J(C,F) = 271.3 Hz, CF_3), 117.9 (sept, ^3J(C,F) = 4.0 Hz, *p*-BAr), 75.1 (s, C_5H_5), 37.0 (d, ^1J(C,P) = 21.3 Hz, PC(CH$_3$)$_3$), 32.8 (d, ^2J(C,P) = 4.1 Hz, PC(*C*H$_3$)$_3$), 26–18 (m, PCH_2), 7.9 (m, PCH$_2$*C*H$_3$), 5.2 ppm (d, ^2J(C,P) = 4.9 Hz, CH$_2$*C*H$_3$); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2$(PCy$_2$H)]$^+$ BAr$_F^-$ (3c): A procedure similar to Method A used for the preparation of **3a** with **1** (0.429 g, 0.168 mmol), C_6H_5F (6 mL), and PCy$_2$H (0.0695 mL, 0.337 mmol) gave **3c** (washed with toluene) as a pale yellow powder (0.344 g, 0.117 mmol, 70%), m.p. 185–188 °C (decomp); elemental analysis calcd (%) for $C_{61}H_{70}BF_{24}P_3Ru$: C 50.05, H 4.82; found: C 50.12, H 4.95.

^{1}H NMR ([D$_6$]acetone): δ = 7.81 (brs, 8H, *o*-BAr), 7.69 (s, 4H, *p*-BAr), 5.28 (s, C_5H_5), 4.92 (dt, ^1J(H,P) = 327.7 Hz, ^3J(H,P) = 4.0 Hz, PH), 2.2–1.3 (m, 34H, PCy$_2$ and 6PCH$_2$), 1.18 ppm (dt, ^3J(H,P) = 16.0 Hz, ^3J(H,H) = 8.0 Hz, 6CH$_3$); $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 162.6 (q, ^1J(C,B) = 50.0 Hz, *i*-BAr), 135.5 (brs, *o*-BAr), 130.0 (qq, ^2J(C,F) = 28.8 Hz, ^4J(C,F) = 2.8 Hz,[52] *m*-BAr), 125.4 (q, ^1J(C,F) = 271.7 Hz, CF_3), 118.4 (sept, ^3J(C,F) = 4.0 Hz, *p*-BAr), 80.9 (s, C_5H_5), 44.0 (dt, ^1J(C,P) = 27.0 Hz, ^3J(C,P) = 2.1 Hz, PCH), 36.0, 28.7, 28.3 (3 d, *J*(C,P) = 6.6, 9.1, 11.9 Hz, PCH*C*H$_2$*C*H$_2$CH$_2$), 23.6 (m, PCH_2), 9.3 ppm (s, CH_3); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(depe)(PPh$_2$H)]$^+$ BAr$_F^-$ (4a): A procedure similar to Method A used for the preparation of **3a** with [(η^5-C_5H_5)Ru(depe)(N$_2$)]$^+$ BAr$_F^-$ (**2**;[17] 0.255 g, 0.249 mmol), C_6H_5F (4 mL), and PPh_2H (0.044 mL, 0.253 mmol) gave **4a** (washed with hexane (3×4 mL) and ethanol (1×2 mL)) as a pale yellow powder (0.255 g, 0.179 mmol, 72%), m.p. 130 °C; a correct microanalysis was not obtained, but a crystal structure was solved (below).

^{1}H NMR ([D$_6$]acetone): δ = 7.80–7.75 (m, 4H of PPh$_2$), 7.81 (brs, 8H, *o*-BAr), 7.69 (s, 4H, *p*-BAr), 7.50–7.40 (m, 6H of PPh$_2$), 6.61 (dt, ^1J(H,P) = 350.5 Hz, ^3J(H,P) = 5.2 Hz, PH) 5.40 (s, C_5H_5), 2.2–1.1 (m, 6PCH$_2$), 1.09 (dt, ^3J(H,P) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, 2CH$_3$), 0.70 ppm (dt, ^3J(H,P) = 17.2 Hz, ^3J(H,H) = 7.6 Hz, 2C′H$_3$); $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 162.6 (q, ^1J(C,B) = 49.9 Hz, *i*-BAr), 137.6 (brd, ^1J(C,P) = 46.0 Hz, *i*-PPh), 135.5 (brs, *o*-BAr), 133.0 (d, ^2J(C,P) = 10.7 Hz, *o*-PPh), 130.9 (d, ^4J(C,P) = 2.1 Hz, *p*-PPh), 130.0 (qq, ^2J(C,F) = 31.6 Hz, ^4J(C,F) = 2.9 Hz,[52] *m*-BAr), 129.8 (d, ^3J(C,P) = 10.2 Hz, *m*-PPh), 125.4 (q, ^1J(C,F) = 271.8 Hz, CF_3), 118.4 (sept, ^3J(C,F) = 4.0 Hz, *p*-BAr), 83.1 (s, C_5H_5), 25.2 (m, PCH_2), 23.4 (dd, ^1J(C,P) = 23.4 Hz, ^3J(C,P) = 20.7 Hz, PC′H$_2$), 19.3 (m, PC′H$_2$, PC″H$_2$), 8.2 (brs, CH_3), 8.1 ppm (t, ^2J(C,P) = 3.4 Hz, C′H$_3$); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(depe){P*t*Bu$_2$H}]$^+$ BAr$_F^-$ (4b):

Method A: A procedure similar to Method A used for the preparation of **3a** with **2** (0.343 g, 0.335 mmol), C_6H_5F (4 mL), and P*t*Bu$_2$H (0.085 mL, 0.342 mmol) gave **4b** (washed with hexane (3×5 mL)) as a salmon powder (0.324 g, 0.234 mmol, 70%), m.p. 98–99 °C (decomp); elemental analysis calcd (%) for $C_{55}H_{60}BF_{24}P_3Ru$: C 47.81, H 4.38; found: C 47.74, H 4.44.

Method B: A procedure similar to Method B used for the preparation of **3a** with [(η^5-C_5H_5)Ru(depe)(Cl)] (0.343 g, 0.257 mmol),[53] C_6H_5F (6 mL), and P*t*Bu$_2$H (0.160 mL, 0.644 mmol) gave **4b** (washed with petroleum ether (4×6 mL)) as a salmon powder (0.462 g, 0.462 mmol, 80%).

^{1}H NMR ([D$_6$]acetone): δ = 7.81 (m, 8H, *o*-BAr), 7.69 (s, 4H, *p*-BAr), 5.18 (s, C_5H_5), 4.72 (dt, ^1J(H,P) = 318.9 Hz, ^3J(H,P) = 2.0 Hz, PH), 2.5–1.7 (m, 6PCH$_2$), 1.42 (d, ^3J(H,P) = 13.2 Hz, 2PC(CH$_3$)$_3$), 1.28 (dt, ^3J(H,P) = 15.6 Hz, ^3J(H,H) = 7.8 Hz, 2PCH$_2$C*H*$_3$), 1.17 ppm (dt, ^3J(H,P) = 13.2 Hz, ^3J(H,H) = 7.6 Hz, 2PC′H$_2$C′*H*$_3$); $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 162.1 (q, ^1J(C,B) = 50.0 Hz, *i*-BAr), 135.0 (brs, *o*-BAr), 129.5 (qq, ^2J(C,F) = 31.5 Hz, ^4J(C,F) = 3.1 Hz,[52] *m*-BAr), 124.9 (q, ^1J(C,F) = 271.9 Hz, CF_3), 117.9 (sept, ^3J(C,F) = 4.0 Hz, *p*-BAr), 80.9 (s, C_5H_5), 36.0 (d, ^1J(C,P) = 22.2 Hz, PC(CH$_3$)$_3$), 32.8 (d, ^2J(C,P) = 4.4 Hz, PC(*C*H$_3$)$_3$), 25.5 (dd, ^1J(C,P) = 15.9 Hz, ^3J(C,P) = 14.5 Hz, PCH), 25.1 (apparent t, ^1J(C,P) = ^3J(C,P) = 23.1 Hz, PC′H$_2$), 21.4 (m, PC′H$_2$, PC″H$_2$), 9.9 (t, ^2J(C,P) = 2.2 Hz, CH$_3$), 8.2 ppm (t, ^2J(C,P) = 4.4 Hz, C′H$_3$); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2$(PPh$_2$)] (5a): A 5-mm NMR tube was charged with **3a** (0.0226 g, 0.016 mmol) and [D$_6$]acetone (0.500 mL). Then a THF solution of *t*BuOK (0.016 mL, 1.0 M) was added. The pale yellow solution turned bright orange. After 15 min, the ^{1}H and ^{31}P NMR spectra showed 93% conversion of **3a** to **5a**.

^{1}H NMR ([D$_6$]acetone): δ(partial) = 7.45 (brt, 4H of PPh$_2$), 7.07 (t, ^3J(H,H) = 7.2 Hz, 4H of PPh$_2$), 6.96 (t, ^3J(H,H) = 6.8 Hz, 2H of PPh$_2$), 4.63 ppm (s, C_5H_5); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2${P*t*Bu$_2$}] (5b): A 5-mm NMR tube was charged with **3b** (0.0213 g, 0.015 mmol) and [D$_8$]THF (0.6 mL) under argon. Then ^{1}H and $^{31}P\{^1H\}$ NMR spectra were recorded. A second NMR tube was charged with NaN(SiMe$_3$)$_2$ (0.0045 g, 0.023 mmol) and the [D$_8$]THF solution of **3b** was added by syringe. The pale yellow solution turned bright orange. After 10 min, the ^{1}H and ^{31}P NMR spectra showed 80% conversion of **3b** to **5b**. The ratio did not increase further.

^{1}H NMR ([D$_8$]THF): δ = 4.77 (s, C_5H_5), 2.2–1.8 (m, 6PCH$_2$), 1.26 (d, ^3J(H,P) = 8.8 Hz, 2PC(CH$_3$)$_3$), 1.07 ppm (dt, ^3J(H,P) = 12.4 Hz, ^3J(H,H) = 7.6 Hz, 6PCH$_2$C*H*$_3$); $^{31}P\{^1H\}$ NMR ([D$_8$]THF): see Table 1.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2$(PCy$_2$)] (5c): Complex **3c** (0.0213 g, 0.015 mmol), [D$_8$]THF (0.6 mL), and NaN(SiMe$_3$)$_2$ (0.0032 g, 0.017 mmol) were combined in a procedure analogous to that used for the preparation of **5b**. After 10 min, the ^{1}H and ^{31}P NMR spectra showed 95% conversion of **3c** to **5c**.

^{1}H NMR ([D$_8$]THF): δ = 4.67 (s, C_5H_5), 2.1–1.1 (m, 34H, PCy$_2$ and 6PCH$_2$), 1.06 ppm (dt, ^3J(H,P) = 13.2 Hz, ^3J(H,H) = 7.6 Hz, 6CH$_3$); $^{31}P\{^1H\}$ NMR ([D$_8$]THF): see Table 1.

[(η^5-C_5H_5)Ru(depe)(PPh$_2$)] (6a): Complex **4a** (0.013 g, 0.009 mmol), [D$_6$]acetone (0.5 mL), and a THF solution of *t*BuOK (0.010 mL, 1.0 M) were combined in a procedure analogous to that used for the preparation of **5a**. After 15 min, the ^{1}H and ^{31}P NMR spectra showed 90% conversion of **4a** to **6a**. The raio did not increase further.

^{1}H NMR ([D$_6$]acetone): δ(partial) = 7.43 (brm, 4H of PPh$_2$), 7.1–6.8 (brm, 6H of PPh$_2$), 4.69 (brs, C_5H_5), 1.07 ppm (dt, ^3J(H,P) = 14.0 Hz, ^3J(H,H) = 7.6 Hz, 4PCH$_2$C*H*$_3$); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): see Table 1.

[(η^5-C_5H_5)Ru(depe){P*t*Bu$_2$}] (6b): Complex **4b** (0.0211 g, 0.015 mmol), [D$_8$]THF (0.6 mL), and NaN(SiMe$_3$)$_2$ (0.0031 g, 0.016 mmol) were combined in a procedure analogous to that used for the preparation of **5b**. After 15 min, the ^{1}H and ^{31}P NMR spectra showed 90% conversion of **4b** to **6b**. The ratio did not increase further.

^{1}H NMR ([D$_8$]THF): δ = 4.73 (s, C_5H_5), 2.3–1.8 (m, 6CH$_2$), 1.25 (d, ^3J(H,P) = 8.8 Hz, 2PC(CH$_3$)$_3$), 1.17 (dt, ^3J(H,P) = 14.4 Hz, ^3J(H,H) = 7.6 Hz, 2PCH$_2$C*H*$_3$), 1.05 ppm (dt, ^3J(H,P) = 10.2 Hz, ^3J(H,H) = 7.6 Hz, 2PC′H$_2$C′*H*$_3$); $^{31}P\{^1H\}$ NMR ([D$_8$]THF): see Table 1.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2${P(=O)Ph$_2$}] (7a): A Schlenk flask was charged with **3a** (0.093 g, 0.064 mmol) and toluene (4 mL). A THF solution of *t*BuOK (0.1 mL, 1.0 M) was added with stirring. The pale yellow solution turned bright orange (**5a**), and KBAr$_F$ precipitated. The mixture was filtered

with a cannula into a new Schlenk flask and exposed to air for a few seconds. The solution immediately turned pale yellow, and solvent was removed by trap-to-trap distillation under a static vacuum. The solid was washed with hexane (3×2 mL) and dried by oil-pump vacuum to give **7a** as a white solid (0.039 g, 0.064 mmol, >99%), m.p. 192–193°C; elemental analysis calcd (%) for $C_{29}H_{45}P_3ORu$: C 57.70, H 7.51; found: C 57.26, H 7.29.

^{1}H NMR ([D$_6$]acetone): δ=7.82 (brt, ^3J(H,H) 8.0 Hz, 4H of PPh_2), 7.23 (td, ^3J(H,H)=7.4 Hz, J(H,P)=1.6 Hz, 4H of PPh_2), 7.11 (brt, ^3J(H,H)=6.8 Hz, 2H of PPh_2), 4.87 (s, C_5H_5), 2.2–2.0 (m, 6H of 6PCH_2, partially overlapped with residual [D$_5$]acetone), 1.80 (dq, ^2J(H,P)=22.0 Hz, ^3J(H,H)=7.6 Hz, 6H of 6PCH_2), 0.91 ppm (dt, ^3J(H,P)=14.0 Hz, ^3J(H,H)=7.6 Hz, 6CH_3); ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ=154.7 (brd, ^1J(C,P)=35.8 Hz, *i*-PPh), 130.5 (d, ^2J(C,P)=10.0 Hz, *o*-PPh), 126.9, 126.8 (2brs, *m*-PPh/*p*-PPh), 81.1 (s, C_5H_5), 22.3 (apparent t, J(C,P)=13.2 Hz, PCH_2), 8.7 ppm (s, CH_3); ^{31}P{^{1}H} NMR ([D$_6$]acetone): see Table 1. MS:[54] *m*/*z* (%): 605 (100) [*M*H]$^+$, 487 (72) [*M*H−P(CH$_2$CH$_3$)$_3$]$^+$, 403 (44) [*M*−POPh$_2$]$^+$, no other significant peaks at >300.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2${P(=Se)Ph$_2$}] (9a): A Schlenk flask was charged with **3a** (0.082 g, 0.056 mmol) and toluene (5 mL). A THF solution of *t*BuOK (0.06 mL, 1.0 M) was added with stirring. The pale yellow solution turned bright orange (**5a**), and KBAr$_F$ precipitated. The mixture was filtered with a cannula into a Schlenk flask containing a suspension of black selenium powder (0.012 g, 0.150 mmol) in acetone (4 mL). The sample rapidly turned yellow and then gradually green. After 3 h, the sample was filtered using a cannula into a new Schlenk flask, thereby removing excess selenium. The solvent was removed by trap-to-trap distillation under a static vacuum. The green residue was washed with petroleum ether (2× 4 mL) and dried by oil-pump vacuum to give **9a** as a crystalline yellow solid (0.026 g, 0.039 mmol, 70%); elemental analysis calcd (%) for $C_{29}H_{45}P_3RuSe$: C 52.25, H 6.80; found: C 52.57, H 6.87.

^{1}H NMR ([D$_6$]acetone): δ=7.87 (brt, ^3J(H,H) 10.2 Hz, 4H of PPh_2), 7.25 (td, ^3J(H,H)=7.6 Hz, J(H,P)=1.6 Hz, 4H of PPh_2), 7.16 (brt, ^3J(H,H)=6.6 Hz, 2H of PPh_2), 4.71 (s, C_5H_5), 2.28 (dq, ^2J(H,P)=22.4 Hz, ^3J(H,H)=7.6 Hz, 6H of 6PCH_2), 1.92 (dq, ^2J(H,P)=22.4 Hz, ^3J(H,H)=7.6 Hz, 6H of 6PCH_2), 1.03 ppm (dt, ^3J(H,P)=13.6 Hz, ^3J(H,H)=7.6 Hz, 6CH_3); ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ=148.9 (d, ^1J(C,P)=25.6 Hz, *i*-PPh), 133.0 (d, ^2J(C,P)=11.3 Hz, *o*-PPh), 127.3 (d, ^4J(C,P)=2.1 Hz, *p*-PPh), 126.6 (d, ^3J(C,P)=9.2 Hz, *m*-PPh), 81.4 (apparent quartet, ^2J(C,P)=1.4 Hz, C_5H_5), 20.9 (apparent t, J(C,P)=13.3 Hz, PCH_2), 9.2 ppm (apparent t, J(C,P)=2.5 Hz, CH_3); ^{31}P{^{1}H} NMR ([D$_6$]acetone): see Table 1 and Table 2.

[(η^5-C_5H_5)Ru(PEt$_3$)$_2${P(=Se)Cy$_2$}] (9c): A 5-mm NMR tube was charged with **3c** (0.036 g, 0.025 mmol) and [D$_8$]THF (0.600 mL) under argon, and cooled to −50°C. Then *n*BuLi (0.024 mL, 1.6 M in hexane) was added. The pale yellow solution turned bright orange, and was allowed to warm to room temperature (ca. 2 h). The ^{1}H and ^{31}P NMR spectra confirmed the formation of **5c** (>90%). The solution was transferred to a second NMR tube that had been charged with black selenium powder (0.007 g, 0.089 mmol). The solution rapidly turned yellow and then slowly greenish. Over the course of 39 h, the ^{1}H and ^{31}P NMR spectra showed both reprotonation to **3c** (49%) and the formation of **9c** (51%).

^{1}H NMR ([D$_8$]THF): δ(partial)=4.78 ppm (s, C_5H_5); ^{31}P{^{1}H} NMR ([D$_8$]THF): see Table 1 and Table 2.

[(η^5-C_5H_5)Ru(depe){P(=Se)Ph$_2$}] (10a): A 5 mm NMR tube was charged with **4a** (0.0258 g, 0.019 mmol) and [D$_6$]acetone (0.600 mL). A THF solution of *t*BuOK (0.030 mL, 1.0 M) was added. The pale yellow solution turned bright orange. The ^{1}H and ^{31}P NMR spectra confirmed the formation of **6a**. The solution was transferred to a second NMR tube that had been charged with black selenium powder (0.0043 g, 0.054 mmol). The solution rapidly turned yellow and then slowly greenish. Over the course of 24 h, the ^{1}H and ^{31}P NMR spectra showed the formation of **10a** (30%), competing oxidation to **8a** (18%), and other unidentified species.

^{1}H NMR ([D$_6$]acetone): δ(partial)=4.56 ppm (s, C_5H_5); ^{31}P{^{1}H} NMR ([D$_6$]acetone): see Table 1 and Table 2.

Relative Brønsted basicities: These experiments were conducted under argon.

Experiment A: A 5-mm NMR tube was charged with **3a** (0.020 g, 0.014 mmol), [(η^5-C_5H_5)Re(NO)(PPh$_3$)(PPh$_2$H)]$^+$ TfO$^-$ (0.013 g, 0.015 mmol),[4] and [D$_6$]acetone (0.500 mL). Then a THF solution of *t*BuOK (0.015 mL, 1.0 M) was added. The pale yellow solution turned bright orange. After 25 min, the ^{1}H and ^{31}P NMR spectra showed complete conversion of [(η^5-C_5H_5)Re(NO)(PPh$_3$)(PHPh$_2$)]$^+$ TfO$^-$ to [(η^5-C_5H_5)Re(NO)(PPh$_3$)(PPh$_2$)] and <2% of **5a**. Simultaneously, **3a** underwent deuterium exchange to give [(η^5-C_5H_5)Ru(PEt$_3$)$_2$(PPh$_2$D)]$^+$ BAr$_F^-$ ([D$_1$]-**3a**). The product ratio remained constant for 17 h. Additional *t*BuOK (0.015 mL, 1.0 M in THF) was then added. The bright orange color intensified and the NMR spectra showed the complete conversion of [D$_1$]-**3a** to **5a**.

Experiment B: A 5-mm NMR tube was charged with **4b** (0.0169 g, 0.012 mmol), [HP*t*Bu$_3$]$^+$ BF$_4^-$ (0.0039 g, 0.014 mmol), and [D$_8$]THF (0.600 mL). Reference ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded. A second NMR tube was charged with NaN(SiMe$_3$)$_2$ (0.0022 g, 0.011 mmol) and the contents of the first tube were added by syringe. After 1 h, the ^{1}H and ^{31}P{^{1}H} NMR spectra showed the complete conversion of [HP*t*Bu$_3$]$^+$ BF$_4^-$ to P*t*Bu$_3$ and <6% conversion of **4b** to **6b**. The product ratio remained constant for 43 h.

Experiment C: A 5-mm NMR tube was charged with **4b** (0.015 g, 0.011 mmol), P(*i*PrNCH$_2$CH$_2$)$_3$N (0.0035 mL, 0.013 mmol), and [D$_3$]acetonitrile (0.500 mL). After 3 h, the ^{1}H and ^{31}P NMR spectra showed that **4b** had undergone deuterium exchange to give [(η^5-C_5H_5)Ru(PEt$_3$)$_2${P*t*Bu$_2$D}]$^+$ BAr$_F^-$ ([D$_1$]-**4b**). At the same time P(*i*PrNCH$_2$CH$_2$)$_3$N was partially converted to the cation [DP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ (<30%). However, no **6b** was detected. The product ratio remained constant for 20 h.

^{31}P{^{1}H} NMR data for [D$_1$]-**4b** ([D$_3$]acetonitrile): δ=80.5 (tt, ^1J(P,D)=48.8 Hz, ^2J(P,P)=31.3 Hz, P*t*Bu$_2$D), 64.3 (d, ^2J(P,P)=31.3 Hz, 2PEt$_3$). The ^{1}H NMR spectrum was identical to that of **4b** except for the PH signal.

Experiment D: A 5-mm NMR tube was charged with **4b** (0.011 g, 0.008 mmol), P(*i*PrNCH$_2$CH$_2$)$_3$N (0.0025 mL, 0.009 mmol), THF (0.500 mL), and a C_6D_6 solution of PPh_3 in a sealed capillary. After 3 h, the ^{31}P NMR spectra showed no reaction had occurred.

Experiment E: A 5-mm NMR tube was charged with **4b** (0.0372 g, 0.027 mmol), THF (0.400 mL), and a C_6D_6 solution of PPh_3 in a sealed capillary, and placed in a −50°C bath. Then *n*BuLi (0.021 mL, 1.6 M in hexane) was added. The pale yellow solution turned bright orange and was allowed to warm to room temperature (ca. 2 h). The ^{31}P NMR spectrum showed 90% conversion of **4b** to **6b**. The solution was transferred with a cannula to a second NMR tube charged with [D$_3$]acetonitrile (0.200 mL) and [HP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ Cl$^-$ (0.092 g, 0.027 mmol).[46] It rapidly turned yellow and a white solid precipitated. After 30 min, the ^{31}P NMR spectrum showed the complete conversion of **6b** to **4b** and of [HP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ Cl$^-$ (−10.2 ppm, d) to P(*i*PrNCH$_2$CH$_2$)$_3$N (120.5 ppm, s). The signal ratio did not change with time.

Experiment F: A 5-mm NMR tube was charged with **3c** (0.0156 g, 0.011 mmol), P(*i*PrNCH$_2$CH$_2$)$_3$N (0.0030 mL, 0.011 mmol), and [D$_3$]acetonitrile (0.500 mL). After 3 h, the ^{1}H and ^{31}P NMR spectra showed that **3c** had undergone deuterium exchange to give [(η^5-C_5H_5)Ru(PEt$_3$)$_2${P*t*Bu$_2$D}]$^+$ BAr$_F^-$ ([D$_1$]-**3c**). At the same time P(*i*PrNCH$_2$CH$_2$)$_3$N was partially converted to the cation [DP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ (ca. 15%).[46] However, no **5c** was detected. The product ratio remained constant for 15 h.

^{31}P{^{1}H} NMR data for [D$_1$]-**3c** ([D$_3$]acetonitrile): δ=48.3 (tt, ^1J(P,D)=51.0 Hz, ^2J(P,P)=39.4 Hz, P*t*Bu$_2$D), 27.9 ppm (d, ^2J(P,P)=39.4 Hz, 2PEt$_3$). The ^{1}H NMR spectrum is identical to that of **3c** except for the PH signal.

Experiment G: A 5-mm NMR tube was charged with **3a** (0.0200 g, 0.014 mmol) and [D$_6$]acetone (0.500 mL). Then P(*i*PrNCH$_2$CH$_2$)$_3$N (0.0039 mL, 0.015 mmol) was added. The pale yellow solution turned bright orange. After 20 min, the ^{1}H and ^{31}P NMR spectra showed >99% conversion of **3a** to **5a** and of P(*i*PrNCH$_2$CH$_2$)$_3$N to a 40:60 [HP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$/[DP(*i*PrNCH$_2$CH$_2$)$_3$N]$^+$ mixture.

$[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(NCCH_3)]^+ BAr_F^-$ (3′): A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(Cl)]$ (0.0532 g, 0.121 mmol)[50] and C_6H_5F (4 mL), and $NaBAr_F$ (0.107 g, 0.121 mmol)[51] was added with stirring. The orange solution turned red and NaCl precipitated. After 30 min, the mixture was filtered using a cannula into a Schlenk flask containing acetonitrile (0.015 mL, 0.285 mmol). The solution was stirred and turned light yellow. After 1 h, the solvent was removed by trap-to-trap distillation under a static vacuum. The solid was washed with petroleum ether (2×4 mL) and dried by oil-pump vacuum to give **3′** as a pale yellow powder (0.091 g, 0.069 mmol, 57%).

^{1}H NMR ($ClCD_2CD_2Cl$): $\delta = 7.76$ (br s, 8H, *o*-BAr), 7.60 (s, 4H, *p*-BAr), 4.74 (s, C_5H_5), 2.31 (t, $^5J(H,P) = 1.3$ Hz, $NCCH_3$), 2.0–1.8 (m, 3 PCH_2), 1.7–1.5 (m, 3 PCH_2), 1.09 ppm (dt, $^3J(H,P) = 15.0$ Hz, $^3J(H,H) = 7.6$ Hz, 6 CH_2CH_3); $^{31}P\{^1H\}$ NMR ($ClCD_2CD_2Cl$): $\delta = 33.0$ (s, PEt_3).

Phosphine substitution reactions: These experiments were conducted under argon.

Experiment A: A 5-mm NMR tube was charged with **3b** (0.0192 g, 0.0136 mmol) and $ClCD_2CD_2Cl$ (0.400 mL), and sealed with a rubber septum. ^{1}H and ^{31}P NMR spectra were recorded. Acetonitrile (0.003 mL, 0.06 mmol) was added by syringe, which gave a clear solution. The ^{1}H and ^{31}P NMR spectra showed >99% conversion to **3′**.

Experiment B: A 5-mm NMR tube was charged with **3b** (0.0202 g, 0.0143 mmol) and [D$_3$]acetonitrile (0.500 mL), and sealed with a rubber septum. ^{1}H and ^{31}P NMR spectra were recorded. After 3 h, complete conversion to [D$_3$]-**3′** and P*t*Bu$_2$H had occurred.

^{1}H NMR ([D$_3$]acetonitrile): $\delta = 7.70$–6.70 (m, 12H, BAr), 4.77 (s, C_5H_5), 2.00–1.85 (m, CH_2 partially overlapped with residual [D$_2$]acetonitrile), 1.67 (m, CH_2), 1.06 ppm (dt, $^3J(H,P) = 14.4$ Hz, $^3J(H,H) = 7.6$ Hz, 6 CH_3); $^{31}P\{^1H\}$ NMR ([D$_3$]acetonitrile): $\delta = 33.6$ ppm (s, PEt_3).

Experiment C: A 5-mm NMR tube was charged with **4b** (0.0205 g, 0.0148 mmol) and [D$_3$]acetonitrile (0.500 mL), and sealed with a rubber septum. ^{1}H and ^{31}P NMR spectra were recorded. Integration of the C_5H_5 ^{1}H signals of **4b** and [D$_3$]-**4′** indicated a 77:23 ratio. A K_{eq} value, {[[D$_3$]-**4′**][P*t*Bu$_2$H]}/{[**4b**][[D$_3$]acetonitrile]}, was calculated assuming equal quantities of [D$_3$]-**4′** and P*t*Bu$_2$H (0.0035 mmol), that is, {[0.0035/0.5][0.0035/0.5]}/{[0.113/0.5][22.7]} $\approx 10^{-4}$.

^{1}H NMR data for [D$_3$]-**4′** ([D$_3$]acetonitrile): δ(partial) = 4.80 ppm (s, C_5H_5); $^{31}P\{^1H\}$: $\delta = 79.5$ ppm (s, depe).

Suzuki couplings: An oven-dried Schlenk flask was charged with **3a–c** or **4b** (2 or 4 mol%, see Table 4) and toluene (4 mL). A base (a THF solution of *t*BuOK for **3a** or a toluene solution of $NaN(SiMe_3)_2$ for **3b**,**c** and **4b**) was added with stirring to generate **5a–c** and **6b**, but in *twice* the quantity used in Scheme 3 (4 or 8 mol%). With **3b**,**c** and **4b**, THF (0.2–0.5 mL) was added to accelerate deprotonation. After 10–15 min, a toluene solution of $Pd(OAc)_2$ or $[Pd_2(dba)_3]$ (1 mol% palladium) was added followed by phenylboronic acid (1.5 equiv), K_3PO_4 (2.0 equiv), an internal standard (tridecane or hexadecane, 0.050 mL), and the haloarene (0.372–0.583 mmol; 1.0 equiv). The brown suspension was stirred at 80°C. The reaction was monitored by GC until complete conversion or catalyst deactivation. The GC retention time of the biaryl product was identical to that of a commercial sample.

Reaction of 5a with phenylboronic acid: These experiments were conducted under argon.

Method A: A 5-mm NMR tube was charged with **3a** (0.0204 g, 0.014 mmol), a C_6D_6 solution of PPh_3 in an internally sealed capillary, and toluene (0.700 mL). A THF solution of *t*BuOK (0.028 mL, 1.0 M) was added. The pale yellow solution turned bright orange. After 30 min, the ^{31}P NMR spectra showed the quantitative formation of **5a**. Inside a glove box, the sample was transferred by syringe to another NMR tube containing phenylboronic acid (0.0048 g, 0.038 mmol). A yellow solid precipitated (the phenylboronic acid did not completely dissolve). The ^{31}P NMR spectrum showed the complete reprotonation of **5a** to partially soluble **3a**. Then K_3PO_4 (0.012 g, 0.055 mmol) was added. The ^{31}P NMR spectrum showed no further changes.

Method B: Complex **3a** (0.0215 g, 0.015 mmol), toluene (0.400 mL), and a THF solution of *t*BuOK (0.030 mL, 1.0 M) were combined as described in Method A. After 15 min, a toluene solution of $Pd(OAc)_2$ (0.340 mL, 0.022 M) was added. The bright orange solution turned deep red and a dark colloidal precipitate formed. Inside a glove box, the sample was transferred by syringe to another NMR tube containing phenylboronic acid (0.0091 g, 0.072 mmol). No visual changes or ^{31}P NMR signals of **3a** were detected. Then K_3PO_4 (0.016 g, 0.073 mmol) was added. Again, no visual changes or new ^{31}P NMR signals were detected.

$[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2)Pd(NCPh)(\eta^3\text{-}C_3H_5)]^+ BAr_F^-$ (11): A Schlenk flask was charged with $[(\eta^3\text{-}C_3H_5)Pd(NCPh)_2]^+ BF_4^-$ (0.037 g, 0.084 mmol)[38] and acetone (2 mL) and cooled to −50°C. A bright orange solution of **5a**, prepared in situ from **3a** (0.122 g, 0.084 mmol) and *t*BuOK (0.160 mL, 1.0 M in THF) in toluene (4 mL), was added by cannula with stirring. The mixture was allowed to slowly warm and became opaque. After 1 h, the solvent was removed by trap-to-trap distillation under a static vacuum. The brown-orange oil was washed with hexane (1×5 mL) and dissolved in toluene (6 mL). The sample was filtered by cannula, transferred to another Schlenk flask, and dried by oil-pump vacuum to give a brown oil that was an approximately 90:10 mixture of **11** and **12**.

^{1}H NMR ([D$_6$]acetone): $\delta = 8.08$ (m, 2H of *o*-NCPh), 7.80 (br s, 8H, *o*-BAr), 7.68 (s, 4H, *p*-BAr), 7.62 (m, 4H of PPh_2), 7.60–7.40 (m, 5H of Ph), 7.34 (m, 4H of Ph), 5.17 (s, C_5H_5), 5.04 (br t, $^4J(H,H) = 5.2$ Hz, H^4),[55] 3.86 (br tt, $^3J(H,H) = 14.0$ Hz, $^3J(H,H) = 7.2$ Hz, H^5), 3.64 (m, H^1), 2.46 (br dq, $^3J(H,H) = 14.0$ Hz, $J(H,H) = 2.6$ Hz, H^3), 2.10–1.80 (m, 3 PCH_2 partially overlapped with residual [D$_5$]acetone), 1.25–1.05 (m, 3 PCH_2), 1.01 (dt, $^3J(H,P) = 16.8$ Hz, $^3J(H,H) = 7.6$ Hz, 3 CH_3), 0.72 (dt, $^3J(H,P) = 14.8$ Hz, $^3J(H,H) = 7.6$ Hz, 3 C′H_3), 0.37 ppm (apparent td, $^3J(H,H) = {}^3J(H,P) = 12.4$ Hz, $^4J(H,H) = 5.6$ Hz, H^2);[55] $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): $\delta = 209.8$ (dd, $^2J(P,P) = 31.6$ Hz, $^2J(P,P) = 8.6$ Hz, PPh_2), 34.9 (d, $^2J(P,P) = 31.4$ Hz, PEt_3), 11.6 ppm (d, $^2J(P,P) = 8.6$ Hz, P′Et_3).[56] MS:[54] *m*/*z* (%): 735 (100) $[(C_5H_5)Ru(PEt_3)_2(PPh_2)Pd(C_3H_5)]^+$, 694 (30) $[(C_5H_5)Ru(PEt_3)_2(PPh_2)Pd]^+$, 617 (45) $[(C_5H_5)Ru(PEt_3)(PPh_2)Pd]^+$, no other significant peaks at >500.

(*E*)-$[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2CH{=}CHCH_3)]^+ BAr_F^-$ (12): A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)]$ (0.039 g, 0.183 mmol)[57] and toluene (2 mL) and cooled to −60°C. A bright orange solution of **5a**, prepared in situ from **3a** (0.266 g, 0.183 mmol) and *t*BuOK (0.205 mL, 1.0 M in THF) in THF (7 mL), was added by cannula with stirring. The mixture was allowed to slowly warm. After 15 h, the solvent was removed from the deep red solution by trap-to-trap distillation under a static vacuum. The deep red residue was washed with hexane (3×6 mL) and toluene (1×2 mL) and dried by oil-pump vacuum to give **12** as a tan solid (0.110 g, 0.074 mmol, 40%).

^{1}H NMR ([D$_6$]acetone): $\delta =$ 7.80 (br s, 8H, *o*-BAr), 7.68 (s, 4H, *p*-BAr), 7.60–7.40 (m, 2 PPh_2), 6.59 (br dd, $^3J(H,P) = 27.4$ Hz, $^3J(H,H) = 16.2$ Hz, $=CHCH_3$), 5.39 (br apparent tq, $^3J(H,P) = 16.0$ Hz, $^3J(H,H) = 16.0$ Hz, $^3J(H,H) = 6.4$ Hz, PC*H*=), 5.12 (s, C_5H_5), 2.0–1.9 (m, 6 PCH_2, $=CHCH_3$),[58] 1.10 ppm (dt, $^3J(H,P) = 14.0$ Hz, $^3J(H,H) = 7.6$ Hz, 6 PCH_2CH_3); $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): $\delta = 162.1$ (q, $^1J(C,B) = 50.0$ Hz, *i*-BAr), 142.6 (d, $^2J(C,P) = 3.2$ Hz, $=CHCH_3$), 138.7 (br d, $^1J(C,P) = 45.2$ Hz, *i*-PPh), 135.0 (br s, *o*-BAr), 133.6 (d, $^2J(C,P) = 10.9$ Hz, *o*-PPh), 130.5 (d, $^4J(C,P) = 2.0$ Hz, *p*-PPh), 129.5 (qq, $^2J(C,F) = 31.5$ Hz, $^4J(C,F) = 2.9$ Hz,[52] *m*-BAr), 128.8 (d, $^3J(C,P) = 9.8$ Hz, *m*-PPh), 127.9 (d, $^1J(C,P) = 38.5$ Hz, PC*H*=), 124.9 (q, $^1J(C,F) = 271.9$ Hz, CF_3), 117.9 (sept, $^3J(C,F) = 4.0$ Hz, *p*-BAr), 82.6 (br s, C_5H_5), 23.3 (apparent t, $J(C,P) = 13.2$ Hz, PCH_2), 20.1 (d, $^3J(C,P) = 45.2$ Hz, $=CHCH_3$),[59] 8.8 ppm (apparent t, $J(C,P) = 2.3$ Hz, PCH_2CH_3); $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): $\delta = 40.40$ (t, $^2J(P,P) = 37.5$ Hz, $PPh_2CH{=}$), 24.20 ppm (d, $^2J(P,P) = 37.5$ Hz, 2 PEt_3). MS:[54] *m*/*z* (%): 629 (60) $[(C_5H_5)Ru(PEt_3)_2(PPh_2CH{=}CHCH_3)]^+$, 511 (60) $[(C_5H_5)Ru(PEt_3)(PPh_2CH{=}CHCH_3)]^+$, 403 (100) $[(C_5H_5)Ru(PEt_3)]^+$, no other significant peaks at >300.

Crystallography: Pale yellow crystals of **4a** were obtained from ethanol at −30°C and X-ray crystal data were collected as outlined in Table 1. Cell parameters were obtained from 10 frames by using a 10° scan and refined with 5939 reflections. Lorentzian, polarization, and absorption corrections[60] were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined for all data by full-matrix least-squares on F^2 by using SHELXL-97.[61] Non-hydrogen

atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions by means of a riding model. Scattering factors were taken from the literature.[62] The formally achiral complex crystallizes in a chiral conformation, which was solved in the noncentrosymmetric space group *Cc* and refined as a racemic twin (ratio: 49:51).[63]

CCDC-249505 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.

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