Rhenium-Containing Phosphorus Donor Ligands for Palladium-Catalyzed Suzuki Cross-Coupling Reactions: A New Strategy for High-Activity Systems

Sandra Eichenseher, Olivier Delacroix,† Klemenz Kromm,‡ Frank Hampel, and J. A. Gladysz*

Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraβe 42, 91054 Erlangen, Germany

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The chiral racemic methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) is converted to the rhenium-containing phosphorus donor ligands (η^5-C_5H_5)Re(NO)(PPh_3)($(CH_2)_nPR_2$) (*n*/R = **3a**, 0/Ph; **3b**, 0/*t*-Bu; **3c**, 0/Me; **5a**, 1/Ph; **5b**, 1/*t*-Bu) and (η^5-$C_5H_4PR_2$)Re(NO)(PPh_3)(CH_3) (**7**; R = **a**, Ph; **b**, *t*-Bu) via standard reactions (**3**, TfOH/CH_2Cl_2 or HBF_4/chlorobenzene, then PR_2H, then *t*-BuOK; **5**, $Ph_3C^+X^-$, then PR_2H, then *t*-BuOK; **7**, *n*-BuLi, then PR_2Cl). (η^5-$C_5H_4PR_2$)Re(CO)$_3$ (R = Ph, *t*-Bu) is prepared from (η^5-C_5H_5)Re(CO)$_3$ analogously to **7**. Most of these species are effective ligands for palladium-catalyzed Suzuki couplings. Typical conditions involve toluene solvent, an aryl bromide (1.0 equiv), phenylboronic acid (1.5 equiv), K_3PO_4 (2.0 equiv), $Pd(OAc)_2$ (1 mol %), the rhenium/PR_2 species (4 mol %), and 60−100 °C. In the cases of **3** and **5**, the rhenium/PR_2 species are generated in situ from indefinitely stable conjugate acids [rhenium/PR_2H]$^+$ and *t*-BuOK (2 equiv or 8 mol %). The bulkier and more electron-rich rhenium/P(*t*-Bu)$_2$ systems generally give more active catalysts than the rhenium/PPh_2 analogues. Under many conditions, the activities of **3a** and **3b** approach (but do not exceed) those of the corresponding organophosphines PPh_3 and P(*t*-Bu)$_3$, the latter being a benchmark ligand for Suzuki couplings. Turnover numbers of >1000 are easily realized. Chloroarenes can be coupled, but at much slower rates and in lower yields. The crystal structures of **5b** and **7b** are determined. The trigonal phosphorus atoms become increasingly pyramidalized in the series **5b** < **5a** < **7b**.

Introduction

The importance of the Suzuki or Suzuki−Miyaura cross-coupling of arylboronic acids and aryl halides in organic synthesis has grown dramatically over the past decade.[1] During this period, there have been intense efforts to optimize the palladium catalysts commonly used for these transformations.[1−4] Many involve phosphine donor ligands, and enhanced activities have often been found by substituting phosphines that are bulkier and/or more electron-rich.[2−5] Although there are many obvious approaches to such phosphines, we sought new paradigms that were far removed from earlier investigations.

Thus, we set out to develop new catalysts based upon monodentate phosphorus donor ligands that feature a novel and untested design element: an 18-valence-electron transition metal center α or β to the phosphorus atom. These "spectator metals" would not directly participate in the bond-breaking or bond-making steps of the catalytic cycle. Such coordinatively saturated L_nMPR_2 and $L_nMCH_2PR_2$ species have an extensive literature. They, and/or nitrogen or sulfur analogues, have been shown to be much more basic and nucleophilic than model compounds without the metal.[6−12] As analyzed elsewhere, this can be attributed to repulsive interactions between occupied orbitals (metal lone pair/heteroatom lone pair or M−C bond/heteroatom lone

† Current affiliation: LCMT, UMR CNRS 6507, ENSICAEN, France.
‡ Current affiliation: Dynamit Nobel, Leverkusen, Germany.

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pair).[7,9,11−14] Furthermore, most metal fragments constitute bulky substituents.

Accordingly, we set out to probe whether effective palladium catalysts can be generated from L_nMPR_2 and $L_nMCH_2PR_2$ species, where L_nM is the chiral rhenium fragment (η^5-C_5H_5)Re(NO)(PPh_3). Such complexes are easily synthesized in both racemic and enantiomerically pure form.[7,15] Certain ferrocenyl-PR_2 systems are also very effective ligands for palladium-catalyzed Suzuki couplings.[3b] Hence, we also sought to survey related PR_2-substituted cyclopentadienyl complexes. However, in the case of ferrocene such phosphines are less electron-rich than the organic analogues PR_3.[16] As described in the narrative below, these types of rhenium-containing phosphorus donor ligands often give highly active palladium-based Suzuki catalysts. A portion of these data have been communicated,[17] and complementary work with ruthenium complexes is described elsewhere.[8]

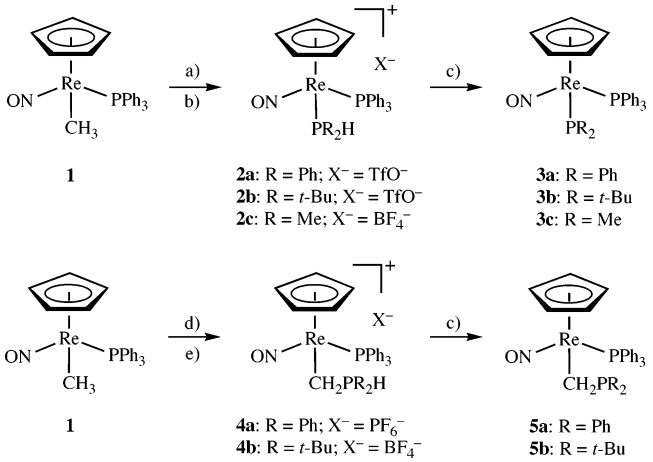
One potential concern—that the spectator metal fragment might somehow compromise catalyst lifetimes or stabilities—merits note at the outset. However, metal-containing ligands of all types—not just the familiar ferrocenes—are playing rapidly increasing roles in catalysis.[6] Furthermore, chelating diphosphines of the formula (η^5-$C_5H_4PR_2$)Re(NO)(PPh_3)((CH_2)$_n$$PR_2$) ($n$ = 0, 1), which feature a chiral rhenium fragment in the backbone, give long-lived rhodium hydrogenation and hydrosilylation catalysts.[18] High enantioselectivities are obtained, consistent with molecular catalysts. Furthermore, a logical step for future studies would be to exploit the second, coordinatively saturated metal more directly in the catalytic cycle, perhaps as a hydrogen-bond or proton acceptor. Various types of secondary interactions are being increasingly recognized as key factors in palladium-based catalysts.[2b]

Results

1. Rhenium-Containing Phosphorus Donor Ligands. The rhenium-containing ligands were prepared as summarized in Schemes 1 and 2. First, the racemic methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**1**)[19] was treated with TfOH/CH_2Cl_2 or HBF_4/chlorobenzene. Methane evolved, and subsequent additions of secondary phosphines PR_2H gave the corresponding adducts [(η^5-C_5H_5)Re(NO)(PPh_3)(PR_2H)]$^+X^-$ (**2**; R/X^- = **a**, Ph/TfO^-; **b**, *t*-Bu/TfO^-; **c**, Me/BF_4^-) in 82−56% yields. Next, deprotonations with *t*-BuOK afforded the phosphido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(PR_2) (**3**; R = **a**, Ph, 86%; **b**, *t*-Bu, 92%; **c**, Me). Compounds **2b** and **3a**,**b** were originally reported some time ago,[7] as were tosylate and tetrafluoroborate analogues of **2a**.[7,18a,20] Whereas **2a**−**c** are stable for years, **3a**−**c** oxidize quite rapidly to the corresponding oxides in solvents that are not rigorously deoxygenated.[7]

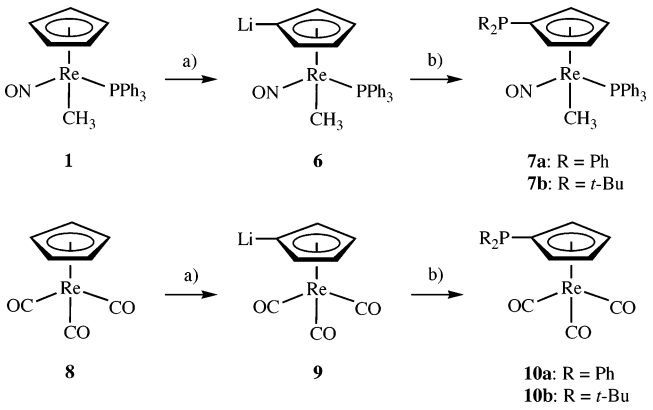
Next, **1** was treated with $Ph_3C^+X^-$, which generates an electrophilic methylidene complex, and secondary phosphines PR_2H were added (Scheme 1, bottom). Workups gave the phosphonium salts [(η^5-C_5H_5)Re(NO)-(PPh_3)(CH_2PR_2H)]$^+X^-$ (**4**; R/X^- = **a**, Ph/PF_6^-; **b**, *t*-Bu/BF_4^-) in 94−85% yields. Deprotonations with *t*-BuOK then afforded the rhenium-containing phosphines (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PR_2) (**5**; R = **a**, Ph; **b**, *t*-Bu) in 94−76% yields. Complex **5a** has been described previously, as has the tetrafluoroborate analogue of **4a**.[18a,20] Due to the extra methylene group, **5a**,**b** are much more

Scheme 1. Synthesis of Complexes with $Re(CH_2)_nPR_2$ Linkages[a]



[a] (a) CH_2Cl_2, TfOH, 0 °C (R = Ph, *t*-Bu) or chlorobenzene, HBF_4, −41 °C (R = Me). (b) PR_2H; CH_2Cl_2, rt (R = Ph) or benzene, reflux (R = *t*-Bu) or chlorobenzene, −41 °C to rt (R = Me). (c) *t*-BuOK, THF, rt. (d) $Ph_3C^+X^-$ (X^- = PF_6^- or BF_4^-), CH_2Cl_2, −60 °C. (e) PR_2H, −60 °C to rt.

Scheme 2. Synthesis of Complexes with (η^5-$C_5H_4PR_2$)Re Linkages[a]



[a] (a) *n*-BuLi, THF, −78 °C to rt. (b) PR_2Cl, THF, −78 °C to rt.

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(20) To help consolidate a fragmented literature, updated syntheses and characterization of the previously reported rhenium complexes in Scheme 1 (and alternative salts for some cations) are provided in the Supporting Information.

stable toward oxidation than **3a**,**b**, and show no deterioration after several hours in air.

As shown in Scheme 2, **1** was next treated with *n*-BuLi to generate the lithiocyclopentadienyl complex (η^5-C_5H_4Li)Re(NO)(PPh_3)(CH_3) (**6**).[21] Subsequent additions of chlorophosphines PR_2Cl gave the phosphocyclopentadienyl complexes (η^5-$C_5H_4PR_2$)Re(NO)(PPh_3)(CH_3) (**7**; R = **a**, Ph; **b**, *t*-Bu) in 60−42% yields. These were also more stable toward oxidation than **3a**,**b**. Similar sequences have been executed with other (η^5-C_5H_5)Re(NO)(PPh_3)(X) species.[18] The many interesting NMR properties associated with all of the preceding compounds—such as distinct signals for the diastereotopic PR_2 or PR_2H groups and dynamic behavior arising from pyramidal inversion at phosphorus—have been detailed in earlier papers.[7,18a,b]

We also sought reference compounds for **7** with somewhat different electronic properties. Accordingly, (η^5-C_5H_5)Re($CO)_3$ was similarly converted to the lithiocyclopentadienyl complex (η^5-C_5H_4Li)Re($CO)_3$ (**9**).[22] Subsequent additions of PR_2Cl gave the target compounds (η^5-$C_5H_4PR_2$)Re($CO)_3$ (**10**; R = **a**, Ph; **b**, *t*-Bu) in 98−30% yields. The *tert*-butyl-substituted species **10b** could only be isolated in ca. 95% spectroscopic purity, so it was not tested in catalysis.

2. Structural Data. During the course of the preceding syntheses, single crystals of *tert*-butyl-substituted **5b** were obtained. Since the structures of **3a**,**b** and nonracemic (*S*)-**5a** had been previously determined,[7,18a] X-ray data were collected as described in Table 1 and the Experimental Section. To our surprise, refinement revealed a solvate of the composition **5b**·*t*-BuOH·1.5CH_2Cl_2, with the *t*-BuOH retained from the deprotonation of **4b** despite an intermediate vacuum-drying step. Two independent molecules were present in the unit cell, differing slightly in the $ReCH_2$−PC bond conformations or torsion angles. One (but not the other) showed hydrogen bonding from the phosphorus lone pair to a *t*-BuOH proton, as depicted in Figure 1 (top). Key metrical parameters are summarized in Table 2.

The bond lengths and angles about rhenium and the Re−CH_2 bond conformation were similar to those in (*S*)-**5a**. The hydrogen atom in the hydrogen bond could not be located. However, from the phosphorus−oxygen separations, 3.744 Å, phosphorus−hydrogen distances of 2.8−2.9 Å could be estimated. A related type of hydrogen bond has been found between the cation and anion of the complex [(η^5-C_5H_5)Re(NO)(PPh_3)(P(*t*-Bu)H_2)]$^+Cl^-$.[15] The trivalent phosphorus atoms of the two independent molecules were similarly pyramidalized, as reflected by the sums of the bond angles (337.8−338.5°). As would be expected from their bulky *tert*-butyl substituents, they were much less pyramidal (more planarized) than the trivalent phosphorus atom in (*S*)-**5a** (305°). The corresponding values for **3b** and **3a**, in which the phosphorus atoms are directly bound to rhenium, are 332° and 323°.[7] Some possible consequences for catalysis are discussed below.

Crystals of another *tert*-butyl-substituted species, **7b**, were also obtained. The structure was similarly determined and is depicted in Figure 1 (bottom). The trivalent phosphorus in this complex is much more pyramidal than those in **3b** or **5b**·*t*-BuOH·1.5CH_2Cl_2, as reflected by the sum of the bond angles (315°). The cyclopentadienyl ligand adopts a conformation that maximizes the distances between the bulky P(*t*-Bu)$_2$ and PPh_3 moieties. One *tert*-butyl group is approximately anti to the cyclopentadienyl−rhenium bond, as reflected by C−P−C−C torsion angles of ca. ±90° (Table 2). As would be intuitively expected, the rhenium−carbon σ bond (2.163(5) Å) was slightly shorter than those in **5b**·*t*-BuOH·1.5CH_2Cl_2 (2.199(5)−2.209(6) Å) and related benzyl and secondary alkyl complexes (2.203(8)−2.215(4) Å).[23]

Table 1. Summary of Crystallographic Data

	5b·*t*-BuOH·1.5CH_2Cl_2	**7b**
formula	$C_{37.50}H_{53}Cl_3NO_2P_2Re$	$C_{32}H_{40}NOP_2Re$
fw	904.30	702.79
temperature [K]	173(2)	173(2)
wavelength [Å]	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a [Å]	14.2299(1)	9.3511(3)
b [Å]	15.8221(2)	25.5777(4)
c [Å]	17.9834(2)	13.0351(3)
α [deg]	69.791(1)	90
β [deg]	89.882(1)	105.2548(9)
γ [deg]	87.044(1)	90
V [Å^3]	3794.06(7)	3007.88(13)
Z	4	4
ρ_{calc} [Mg/m^3]	1.583	1.552
absorp coeff [mm^{-1}]	3.532	4.171
F(000)	1828	1408
cryst size [mm^3]	0.40 × 0.35 × 0.35	0.20 × 0.20 × 0.20
θ limit [deg]	1.21−27.50	1.80−27.50
index ranges (*h*, *k*, *l*)	−18, 18; −20, 20; −23, 22	−12, 12; −22, 32; −16, 16
no. of reflns collected	32 633	12 403
no. of indep reflns	17 355 [*R*(int) = 0.019]	6838 [*R*(int) = 0.0214]
no. of reflns [$I > 2\sigma(I)$]	14 128	5857
max. and min. transmn	0.3711 and 0.3323	0.4892 and 0.4892
no. of data/restraints/params	17 355/27/852	6838/0/334
goodness-of-fit on F^2	1.017	1.118
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$ $wR_2 = 0.1250$	$R_1 = 0.0325$ $wR_2 = 0.0890$
R indices (all data)	$R_1 = 0.0577$; $wR_2 = 0.1377$	$R_1 = 0.0407$; $wR_2 = 0.0981$
largest diff peak and hole [e·Å^{-3}]	2.477 and −1.840	1.203 and −1.505

3. Relative Ligand Reactivities in Palladium-Catalyzed Suzuki Couplings. Experiments were first conducted under conditions similar to those popularized by Buchwald,[2a] using $Pd(OAc)_2$ as the palladium source (1 mol %), twice this amount (2 mol %) of the rhenium-containing phosphorus donor ligand, K_3PO_4 as the boron-activating base, toluene solvent, and elevated temperatures. Scouting reactions showed good activities. However, as noted above, some of the rhenium complexes are easily oxidized. Hence, for operational convenience, experiments were conducted with the conjugate acids **2a**−**c** or **4a**,**b**, and *t*-BuOK (2.0 equiv) was added to effect deprotonation in situ. The similar use of protonated organophosphines in several palladium-catalyzed reactions has been reported.[24]

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Table 2. Key Distances [Å], Bond Angles [deg], and Torsion Angles [deg] for 5b·*t*-BuOH·1.5CH_2Cl_2 and 7b

5b·*t*-BuOH·1.5CH_2Cl_2[a]		**7b**	
Re−N1	1.750(5)/1.758(5)	Re−N1	1.753(4)
Re−C1	2.199(5)/2.209(6)	Re−C1	2.163(5)
Re−P2	2.3582(13)/2.3578(13)	Re−P1	2.3475(11)
N1−O1	1.216(6)/1.205(7)	N1−O1	1.208(6)
P1−C1	1.787(5)/1.787(5)	P2−C11	1.829(5)
P1−C50	1.847(6)/1.830(8)	P2−C50	1.908(6)
P1−C60	1.846(7)/1.865(8)	P2−C60	1.894(6)
P1−O80	3.744/−		
N1−Re−C1	100.3(2)/102.2(3)	N1−Re−C1	95.19(17)
N1−Re−P2	91.39(15)/90.96(17)	N1−Re−P1	93.08(14)
C1−Re−P2	87.05(14)/86.86(15)	C1−Re−P1	87.24(12)
O1−N1−Re	175.0(5)/171.9(5)	O1−N1−Re	177.1(4)
C1−P1−C50	112.9(3)/112.7(3)	C11−P2−C50	106.0(2)
C1−P1−C60	109.2(3)/109.7(3)	C11−P2−C60	100.0(2)
C50−P1−C60	115.7(3)/116.1(4)	C60−P2−C50	108.7(3)
N1−Re−C1−P1	−73.7(4)/−71.1(4)	C60−P2−C11−C12	−88.1(5)
P2−Re−C1−P1	−164.6(3)/−161.4(4)	C60−P2−C11−C15	79.8(4)
C50−P1−C1−Re	64.1(4)/93.3(5)	C50−P2−C11−C12	24.8(5)
C60−P1−C1−Re	−165.8(3)/−135.7(4)	C50−P2−C11−C15	−167.3(4)

[a] The doubled values represent the two independent molecules in the unit cell.

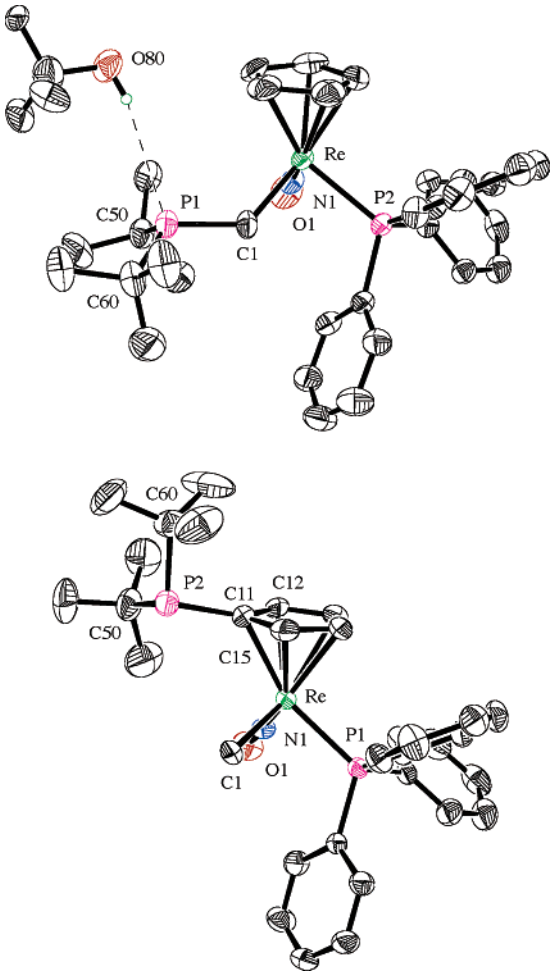

Figure 1. (top) Partial structure of **5b**·*t*-BuOH·1.5CH_2-Cl_2 (one of two independent molecules); (bottom) Structure of **7b**.

Thus, as summarized in Scheme 3, the coupling of bromobenzene and phenylboronic acid was studied using 1 mol % of $Pd(OAc)_2$ and Pd/Re/*t*-BuOK mol ratios of 1:4:8. Phenylboronic acid was used in excess over bromobenzene (1.5:1), as some homocoupling can occur under Suzuki conditions.[1c,d] An internal standard was

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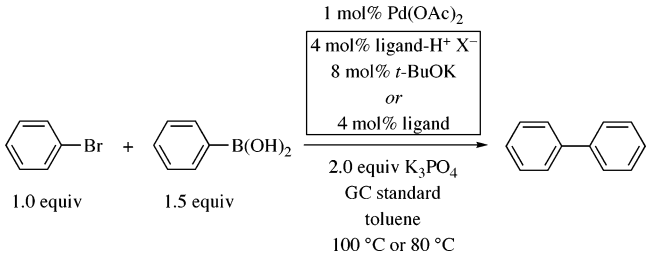
Scheme 3. Standard Screening Conditions for Suzuki Couplings



employed, so that the amount of bromobenzene consumed and biphenyl formed could be continuously quantified by gas chromatography. The first set of experiments was conducted at 100 °C, and the results with **2a**−**c** and **4a**,**b** are summarized in entries 1−5 of Table 3. The conversion of bromobenzene is plotted as a function of time in Figure 2 (top). The yields of biphenyl were normally very similar, suggesting little if any homocoupling of phenylboronic acid.

The catalysts derived from the phenyl- and *tert*-butyl-substituted $RePR_2$ systems **3a**,**b** are distinctly more reactive than those derived from methyl-substituted **3c** (less bulky) or the corresponding $ReCH_2PR_2$ systems **5a**,**b** (less bulky and electron-rich). Curiously, the rate with **5b** is less than that in the absence of a donor ligand, and factors that may be in play are analyzed in the discussion section. Although *tert*-butyl-substituted **3b** gives the most reactive catalyst, coupling was so fast that the rate could not be distinguished from that of P(*t*-Bu)$_3$, the benchmark organophosphine (entry 10).[3a] The reactivity of the catalyst with phenyl-substituted **3a** also appeared close to that with the organic analogue PPh_3 (entry 9).

To improve the time resolution and allow better reactivity comparisons, rates with selected ligands were monitored at 80 °C. These data are summarized in entries 12−16 of Table 3 and Figure 2 (bottom). Again, the catalyst derived from **3b** appeared close in activity to that from P(*t*-Bu)$_3$. However, **3a** gave a somewhat slower catalyst than PPh_3. To still better define the relative reactivities of the **3b**/P(*t*-Bu)$_3$ systems, two experiments were conducted at 60 °C (Table 3, entries 17, 18). Now it becomes clear that the organophosphine

Table 3. Data for Suzuki Couplings under the Conditions of Scheme 3: Conversion [%] of Bromobenzene and (in parentheses) Yield [%] of Biphenyl as Determined by GC

entry	donor ligand[a] (temp, °C)	time (h) 0.25	0.5	1	2	4	8	24	48	96	168
1	**3a**	66	85	97	100						
	(100 °C)	(60)	(77)	(90)	(93)						
2	**3b**	97	100								
	(100 °C)	(92)	(100)								
3	**3c**	14	24	38	58	84	96	99	100		
	(100 °C)	(8)	(14)	(29)	(50)	(76)	(90)	(95)	(96)		
4	**5a**	71	81	86	89	93	98	100			
	(100 °C)	(64)	(72)	(77)	(80)	(83)	(87)	(90)			
5	**5b**	19	21	25	26	31	33	40	45	60	76
	(100 °C)	(10)	(12)	(13)	(16)	(19)	(24)	(28)	(33)	(44)	(57)
6	**7a**[b]	33	49	63	70	77	83	96	100		
	(100 °C)	(32)	(47)	(60)	(69)	(75)	(80)	(94)	(96)		
7	**7b**[b]	64	81	89	95	98	100				
	(100 °C)	(62)	(81)	(88)	(95)	(96)	(98)				
8	**10a**[b]	53	74	90	96	100					
	(100 °C)	(53)	(70)	(85)	(96)	(100)					
9	PPh_3[b]	78	91	100							
	(100 °C)	(65)	(86)	(95)							
10	P(*t*-Bu)$_3$	98	100								
	(100 °C)	(98)	(100)								
11	none	41	44	49	52	55	60	60	61	64	66
	(100 °C)	(35)	(38)	(42)	(45)	(50)	(53)	(54)	(55)	(55)	(59)
12	**3a**	15	27	61	84	93	98	100			
	(80 °C)	(7)	(18)	(51)	(78)	(83)	(89)	(98)			
13	**3b**	84	99	100							
	(80 °C)	(79)	(94)	(96)							
14	**3c**	12	12	12	14	21	48	95	99	99	
	(80 °C)	(2)	(2)	(2)	(4)	(12)	(41)	(92)	(97)	(99)	
15	PPh_3[b]	67	85	98	100						
	(80 °C)	(50)	(81)	(92)	(92)						
16	P(*t*-Bu)$_3$	88	96	98	100						
	(80 °C)	(87)	(95)	(97)	(97)						
17	**3b**	21	74	95	100						
	(60 °C)	(8)	(69)	(91)	(97)						
18	P(*t*-Bu)$_3$	79	86	91	96	99	100				
	(60 °C)	(77)	(81)	(87)	(93)	(97)	(98)				
19	**3b**	11	11	11	11	11	11	16		76	80
	(rt)	(0)	(0)	(0)	(0)	(0)	(0)	(0)		(69)	(75)
20	P(*t*-Bu)$_3$	24	30	41	58	87	97	99		99	99
	(rt)	(19)	(24)	(34)	(55)	(86)	(97)	(99)		(99)	(99)

[a] Generated in situ from the conjugate acid and *t*-BuOK unless noted. [b] This ligand was added directly and not generated from the conjugate acid.

gives the more reactive catalyst, at least through 86% conversion. The catalyst derived from **3b** remains active at room temperature (entry 19). However, the conversion plateaus at 11% for a considerable period, suggesting that the initially generated species is not responsible for most of the catalysis.

The phosphocyclopentadienyl donor ligands in Scheme 2 were tested next. These were used in their unprotonated forms, and data from reactions at 100 °C are summarized in entries 6−8 of Table 3. Consistent with the trend for **3a**,**b**, *tert*-butyl-substituted **7b** gave a more active catalyst than phenyl-substituted **7a**. However, as is readily seen from Figure 2, rates are much slower than with **3a**,**b**. The rhenium atoms in the donor ligands **10a**,**b** have three good π-accepting ligands, which should lead to less electron-rich systems than **7a**,**b**. Nonetheless, **10a** gave a more active catalyst than **7a**. Had **10b** been available in pure form and tested, it would likely have been more reactive yet. Thus, other factors clearly play roles in the relative rates.

4. Substrate Scope and Other Experiments. The two most active rhenium-containing ligands from Table 3, **3a**,**b**, were applied to Suzuki couplings of substituted aryl bromides as shown in Scheme 4. The conditions were analogous to those in Scheme 3. Substrates containing electron-withdrawing groups, such as **11**, are generally activated, whereas those containing electron-donating groups, such as **12**−**14**, are usually deactivated. In all cases, complete conversions and good to excellent yields were obtained over the course of a few minutes to hours at 100 °C, as summarized in entries 1−8 of Table 4. Parallel experiments were conducted with ligands **7a**,**b**, as summarized in entries 9−16.

As seen for bromobenzene, the catalyst derived from **3b** was more reactive than that from **3a**. Reactions with aryl bromides **11**, **13**, and **14** were essentially complete within 15 min, and **12** within 30 min. In contrast, **3a** required ca. 2 h for the complete conversion of **12** and **13**. As expected from Table 3, the catalyst derived from **7b** was slower still, requiring 4−8 h for nonactivated **12**−**14**. The catalyst derived from **7a** required days for the complete conversion of the nonactivated substrates. Entry 8 with **3b** and the aryl bromide **14** was repeated on a 5-fold greater scale. Column chromatography gave the phenylnaphthalene **18** in 97% yield.

Aryl chlorides are especially desirable substrates for metal-catalyzed carbon−carbon bond forming reactions.[25] However, they are much less reactive than aryl bromides. Screening experiments with chlorobenzene and phenylboronic acid were conducted at 100 °C under

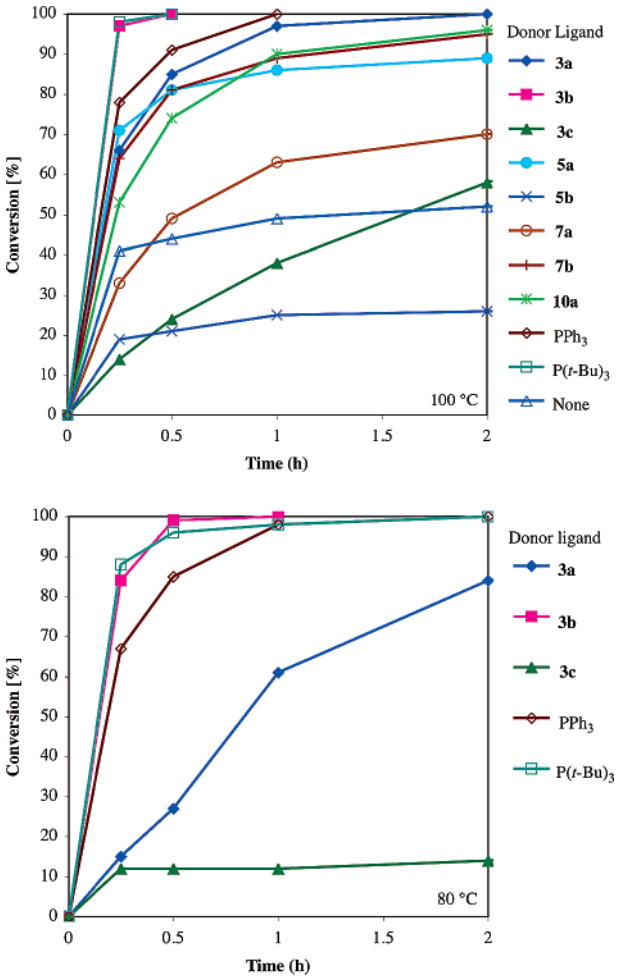


Figure 2. Plots of bromobenzene conversion (Table 3) under the conditions of Scheme 3: (top) data at 100 °C; (bottom) data at 80 °C.

conditions analogous to Scheme 3. After 168 h, ligands **3a**,**b** gave conversions of only 5% and 40%, corresponding to yields of 2% and 31%. After 96 h under identical conditions, PPh_3 and P(*t*-Bu)$_3$ gave conversions of 12% and 83%, corresponding to yields of 7% and 76%. This provides another example where P(*t*-Bu)$_3$ is superior to **3b**. For comparison, **3a**,**b** were also tested with the more activated substrate 4-chloroacetophenone. After 168 h, conversions were 46% and 88%, and the yields of 4-phenylacetophenone (**15**) were 28% and 51%.

Under the conditions of Schemes 3 or 4, turnover numbers cannot exceed 100, which is insufficient for industrial applications. Thus, entries 7 and 8 of Table 4 were repeated, but with reduced palladium and rhenium loadings of 0.1 and 0.4 mol %. After 1.0 and 0.5 h, complete conversions and quantitative yields were again obtained. This establishes that turnover numbers of ≥1000 are easily realized.

The boron-activating base K_3PO_4 is only slightly less strong than the *t*-BuOK used to deprotonate the ligand precursors **2a**−**c** and **4a**,**b** ($\Delta pK_a(H_2O)$ ca. 6).[26] We therefore wondered whether the *t*-BuOK was needed at all. Accordingly, when a toluene solution of **2b** was treated with K_3PO_4 (2.0 equiv) at 100 °C, the characteristic orange-red color of **3b** was generated. Entry 2 of Table 3 was repeated with this sample. After 0.5 h, the conversion and yield were 100% and 99%, virtually equivalent to the results with *t*-BuOK. A similar reaction was conducted, but with all components mixed simultaneously. After 0.5 h, the data were identical.

The effectiveness of the lead ligand **3b** was also screened under Suzuki conditions popularized by Fu.[3a] These involved bromobenzene, phenylboronic acid (1.1 equiv), $Pd_2(dba)_3$ (1.5 mol %), **3b** (3.6 mol %, generated in situ from **2b** and *t*-BuOK (1:2)), and KF (3.3 equiv). Although detailed studies were not conducted, **3b** gave a more active catalyst than P(*t*-Bu)$_3$ at room temperature. However, P(*t*-Bu)$_3$ was more reactive in couplings conducted at 60 °C.

Discussion

The preceding data constitute another in an ongoing series of examples where bulky and/or electron-rich phosphorus donor ligands give more active catalysts for Suzuki or other palladium-catalyzed carbon−carbon bond forming reactions.[4] It is often overlooked that bulkier phosphorus donor ligands are less pyramidal, as reflected in the crystal structure of **5b** versus **5a** and **3b** versus **3a**. This trend is very pronounced in trialkyl phosphines (PH_3, $P(CH_3)_3$, P(*t*-Bu)$_3$) and results in more lone pair p character.[27] Hence, such species are intrinsically more basic or electron-rich. In any event, electron-rich ligands should help to facilitate oxidative addition steps, which are often rate-determining in catalytic cycles. Bulkier ligands furthermore promote lower coordination numbers, which can also facilitate oxidative addition.

However, the basicity-enhancing rhenium moieties in **3a**,**b** do not result in catalytic activities higher than those of the corresponding organophosphines, at least for Suzuki couplings of aryl bromides or chlorides under the Buchwald conditions. Perhaps a non-oxidative-addition step of the catalytic cycle has become rate determining, for which the rhenium fragment imparts unfavorable steric or electronic properties. The lower activity of the catalyst derived from **7b** versus **3b** is consistent with its increased pyramidalization (Figure 1) and inductive effects previously observed with ferrocene-substituted PR_2 moieties.[16] However, the greater activity of **10a** as compared to **7a** is curious. Although we have no quantitative data on their relative basicities, the latter is almost certainly more electron-rich. Hence, other factors clearly play roles in the relative reactivities.

We originally speculated that $ReCH_2PR_2PdX$ systems derived from **5a**,**b** might be shorter-lived or less active due to possible equilibration with $^{+}Re{=}CH_2$ and $[R_2PPdX]^{-}$ species.[17,28] However, we have since found that **5a** is in fact cyclometalated by $Pd(OAc)_2$ to give a novel palladacycle with rhenium in the backbone.[29] This system has catalytic activity in its own right and will

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Scheme 4. Suzuki Reactions of Other Aryl Bromides

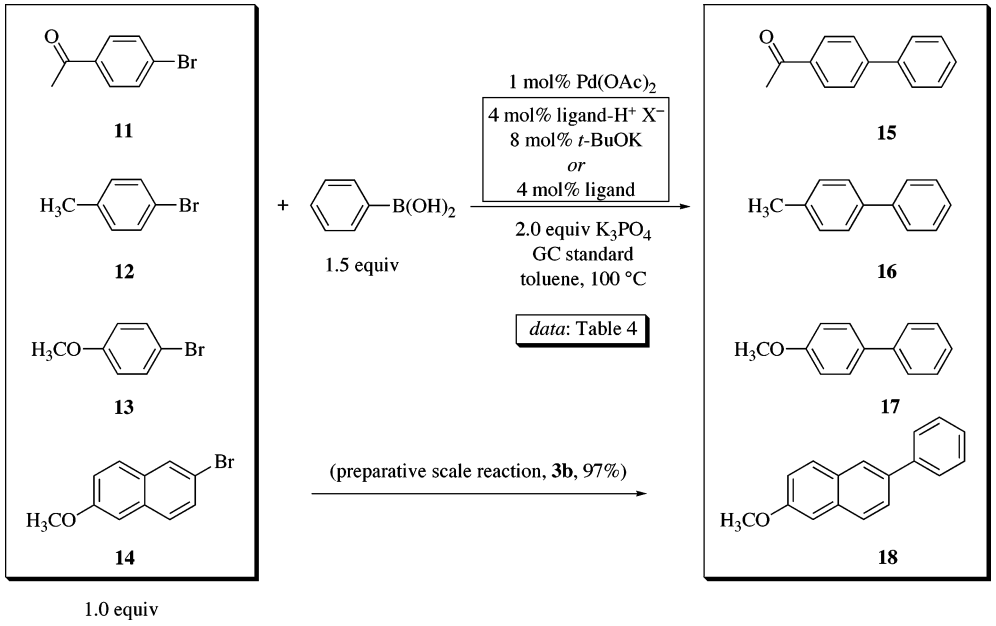

Table 4. Data for Suzuki Couplings under the Conditions of Scheme 4: Conversion [%] of Aryl Bromides and (in parentheses) Yield [%] of Biaryl as Determined by GC

			time (h)								
entry	educt	ligand	0.25	0.5	1	2	4	8	24	48	96
1	**11**	**3a**[a]	100 (86)								
2	**11**	**3b**[a]	100 (78)								
3	**12**	**3a**[a]	20 (20)	41 (40)	82 (82)	97 (92)	100 (100)				
4	**12**	**3b**[a]	70 (70)	98 (98)	100 (100)						
5	**13**	**3a**[a]	81 (64)	91 (83)	97 (85)	99 (87)	100 (88)				
6	**13**	**3b**[a]	100 (88)								
7	**14**	**3a**[a]	100 (100)								
8	**14**	**3b**[a]	98 (98)	100 (100)							
9	**11**	**7a**[b]	79 (70)	86 (85)	94 (90)	100 (99)					
10	**11**	**7b**[b]	92 (90)	99 (96)	100 (96)						
11	**12**	**7a**[b]	66 (63)	71 (68)	76 (71)	80 (75)	83 (76)	86 (77)	91 (81)	97 (82)	100 (84)
12	**12**	**7b**[b]	66 (63)	79 (77)	86 (85)	93 (91)	99 (98)	100 (98)			
13	**13**	**7a**[b]	44 (38)	57 (45)	69 (58)	75 (64)	80 (65)	84 (67)	91 (70)	95 (74)	100 (76)
14	**13**	**7b**[b]	58 (50)	74 (64)	83 (75)	94 (86)	100 (92)				
15	**14**	**7a**[b]	66 (57)	73 (63)	79 (67)	84 (75)	89 (76)	90 (76)	95 (79)	100 (79)	
16	**14**	**7b**[b]	52 (50)	55 (55)	60 (60)	74 (70)	88 (87)	99 (95)	100 (97)		

[a] Generated in situ from the conjugate acid and *t*-BuOK. [b] This ligand was used directly and not generated from the conjugate acid.

be described separately. For this reason, we do not place any special significance on the relative reactivities of the catalysts from **5a**,**b**. We also considered the possibility that palladium might somehow catalyze the scrambling of the bonds to the trivalent phosphorus atoms in the rhenium complexes, giving PPh_3 or P(*t*-Bu)$_3$ (and other species). However, when **3b** and $Pd(OAc)_2$ were combined in C_6D_6 (4:1 mol ratio), no P(*t*-Bu)$_3$ or other decomposition process was detected by ^{31}P NMR.

Another approach to enhancing catalyst activities is to achieve a more direct entry into the catalytic cycle. For example, the phosphorus donor ligand might be precoordinated to palladium, rendering substitution steps unnecessary. However, there have been to our

(29) Friedlein, F. K.; Hampel, F.; Gladysz, J. A. Manuscript in preparation.

knowledge no spectroscopic investigations of the nature of the catalyst under Buchwald-type conditions or any procedure involving $Pd(OAc)_2$. NMR data for Fu-type catalysts that use $Pd_2(dba)_3$ suggest that monophosphine adducts LPd play key roles.[3a] Accordingly, experiments involving preformed MPR_2Pd species will be described in our next paper,[8b] using metal fragments that are more electron-rich than the rhenium systems described herein.

There is also increasing interest in enantioselective Suzuki couplings that lead to chiral biaryls.[30] Since rhenium-containing phosphorus donor ligands of the types in Schemes 1 and 2 are easily prepared in enantiomerically pure form,[7,15,18,19] this represents an attractive possible extension of this work. At the same time, note that the use of chiral *racemic* rhenium complexes in the present study allows for the possibility of diastereomeric species on the reaction coordinate, e.g., whenever at least two such ligands are coordinated to palladium or are present in a Pd_x complex. This poses another potential complication in interpreting the relative reactivity data in Tables 3 and 4.

In summary, this study has extended the types of metal-containing phosphorus donor ligands that can be employed in metal-catalyzed reactions,[6] as well as the scope of reactions in which rhenium-containing ligands can be applied. In most cases (but not all), the rhenium-containing ligands appear to be innocent, in line with past experience.[18] However, there are also fascinating possibilities for incorporating secondary interactions, which appear to be important attributes of many highly active palladium catalysts.[2b] Future papers will describe similar experiments that utilize ruthenium-containing ligands of the type $(\eta^5\text{-}C_5H_5)Ru(PR'_3)_2(PR_2)$.[8b] These are considerably more electron-rich than **3a**,**b**, as confirmed by quantitative basicity measurements. Also, applications of **3a**,**b**, **5a**,**b**, and **7a**,**b** in additional types of catalytic reactions will be reported.

Experimental Section

General Procedures. All experiments were carried out under nitrogen or argon. NMR spectra were recorded on standard 300−500 MHz FT spectrometers, referenced to a residual solvent signal (^{1}H: $CHCl_3$, 7.24 ppm; C_6D_5H, 7.15 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6, 128.00 ppm) or H_3PO_4 (^{31}P, internal capillary, 85%, 0.00 ppm) and recorded at 25−28 °C unless noted. IR spectra were recorded on an ASI React IR-1000 spectrometer. Mass spectra were obtained using a Micromass Zabspec instrument. Gas chromatography was conducted on a ThermoQuest Trace GC 2000 instrument (OPTIMA-5-0.25 μm capillary column, 25 m × 0.32 mm). Elemental analyses were determined with a Carlo Erba EA1110 CHN instrument (in-house).

Solvents were freshly dried before use, as described in the Supporting Information. The *n*-BuLi (≈1.6 M in hexanes, Acros) was standardized by titration versus *N*-benzylbenzamide (2×),[31] PPh_2Cl (98%, Acros) was vacuum distilled, chlorobenzene (for Suzuki reactions) was distilled, and $P(t\text{-}Bu)_3H^+BF_4^-$ was prepared by a literature procedure.[32] The quality of commercial $Ph_3C^+X^-$ can vary, and crystallization from CH_2Cl_2/hexane or CH_2Cl_2/benzene[33] is recommended. All other materials were obtained from standard sources as summarized in the Supporting Information and used without purification.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2H)]^+TfO^-$ (2a).[34] A Schlenk flask was charged with **1** (6.145 g, 11.00 mmol)[19,35] and dry degassed CH_2Cl_2 (100 mL) and cooled to 0 °C. Then TfOH (1.4 mL, 2.4 g, 16 mmol) was slowly added with stirring. After 20 min, the mixture was filtered through a medium frit containing 1 cm of silica gel. The silica gel was eluted with dry CH_2Cl_2 (50 mL) and then dry CH_2Cl_2/acetone (95:5 v/v; 50 mL). Solvent was removed from the eluate via oil pump vacuum. The red powder was dissolved in dry CH_2Cl_2 (150 mL), and PPh_2H (3.80 mL, 4.09 g, 22.0 mmol) was added with stirring. After 48 h, the mixture was concentrated in vacuo to ca. 50 mL. Dry ether (100 mL) was added, and the sample was stored in the freezer overnight. The precipitate was collected by filtration (medium frit), washed with dry ether, and dried by oil pump vacuum to give **2a** (7.879 g, 8.965 mmol, 82%) as a yellow powder, mp 125−126 °C. Anal. Calcd (%) for $C_{36}H_{31}F_3NO_4P_2ReS$ (878.85): C 49.20, H 3.56, N 1.59, S 3.65. Found: C 48.71, H 3.72, N 1.51, S 3.69. IR (thin film, cm^{-1}): $\tilde{\nu}$ 1710 (s, NO), 1262 (vs, CF). ^{1}H NMR (400 MHz, $CDCl_3$): PPh_3 and PPh_2 at δ 7.49−7.00 (m, 25H); 7.31 (dd, 1H, ^1J(H,P) = 394.0 Hz, ^3J(H,P) = 4.8 Hz, PH), 5.26 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): PPh_3 at δ 133.0 (d, ^2J(C,P) = 11.1 Hz, o), 131.7 (d, ^4J(C,P) = 2.7 Hz, p), 129.3 (d, ^3J(C,P) = 11.1 Hz, m); PPhPh′ at 133.0 (d, ^2J(C,P) = 10.7 Hz, o), 131.6 (d, ^4J(C,P) = 2.3 Hz, p), 131.5 (d, ^4J(C,P) = 2.3 Hz, p′), 131.3 (d, ^2J(C,P) = 10.6 Hz, o′), 129.6 (d, ^3J(C,P) = 11.2 Hz, m), 129.5 (d, ^3J(C,P) = 11.6 Hz, m′); 120.9 (q, ^1J(C,F) = 323.7 Hz, CF_3), 92.6 (s, C_5H_5).[36] ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$): δ 12.7 (d, ^2J(P,P) = 13.3 Hz, PPh_3), −7.8 (d, ^2J(P,P) = 13.3 Hz, PPh_2H).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PMe_2H)]^+BF_4^-$ (2c). A Schlenk flask was charged with **1** (0.5600 g, 1.002 mmol)[19,35] and chlorobenzene (50 mL) and cooled to −41 °C. Then HBF_4 (7.3 M in ether; 0.151 mL, 1.10 mmol) was added with stirring. The flask was immersed in liquid N_2, evacuated, and transferred under vacuum to a glovebox. To the almost thawed mixture was added cold PMe_2H (0.12 g, 2.0 mmol, −32 °C).[37] The flask was removed from the glovebox and placed in a cold bath (−60 °C). An oil pump vacuum was applied. The mixture was warmed to room temperature and concentrated to ca. 30 mL. The yellow precipitate was collected by filtration, washed with ether (3 × 10 mL), and dissolved in CH_2Cl_2. A layer of ether was added. After 1 day, the supernatant was decanted and the yellow oil dried by oil pump vacuum to give **2c**·$(CH_2Cl_2)_{0.5}$ (0.550 g, 0.794 mmol, 79%) as yellow fibers, mp 135 °C. Anal. Calcd (%) for $C_{25}H_{27}BF_4NOP_2Re\cdot(CH_2Cl_2)_{0.5}$ (734.92): C 41.68, H 3.84, N 1.91. Found: C 41.69, H 3.79, N 1.71. IR (thin film, cm^{-1}): $\tilde{\nu}$ 1691 (s, NO), 1050 (s, BF). ^{1}H NMR (400 MHz, $CDCl_3$): δ PPh_3 at 7.51−7.50 (m, 9H), 7.29−7.24 (m, 6H); 5.56 (apparent dsext, 1H, ^1J(H,P) = 381 Hz, ^3J(H,P) = 6 Hz, PH), 5.51 (s, 5H, C_5H_5), 1.80/1.53 (2 dd, 18H, ^2J(H,P) = 12 Hz, ^4J(H,P) = 6 Hz, CH_3/CH_3'), 5.32 (s, 1H, 0.5 CH_2Cl_2). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ PPh_3 at 133.0 (d, ^2J(C,P) = 11 Hz, o), 132.6 (d, ^1J(C,P) = 56 Hz, i), 131.6 (d, ^4J(C,P) = 2 Hz, p), 129.3 (d, ^3J(C,P) = 11 Hz, m); 91.5 (s, C_5H_4), 53.8 (s, CH_2Cl_2), 13.1 (d, ^1J(C,P) = 39 Hz, CH_3), 12.2 (d, ^1J(C,P) = 41 Hz,

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(36) The *ipso* PPh_3 and PPhPh′ signals were not observed.

(37) **Caution**: PMe_2H is pyrophoric and was stored at −32 °C in a glovebox. Preparation: (a) Parshall, G. W. *Inorg. Synth.* **1968**, *11*, 157. (b) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 46.

C′H_3). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 13.1 (d, $^2J(P,P)$ = 16 Hz, PPh_3), −62.2 (d, $^2J(P,P)$ = 16 Hz, PMe_2H). MS (FAB, 3-NBA): *m/z* (%) 606 (100) $[M]^+$, 544 (8) $[M - PMe_2H]^+$.

[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]$^+PF_6^-$ (4a).[38] A Schlenk flask was charged with **1** (4.500 g, 8.055 mmol)[19,35] and dry CH_2Cl_2 (200 mL) and cooled to −60 °C. Then $Ph_3C^+PF_6^-$ (3.441 g, 8.862 mmol) was added with stirring. Within 30 min, the orange suspension became a light yellow solution. Then PPh_2H (1.70 mL, 1.83 g, 9.83 mmol) was added dropwise with stirring. After 10 min, the cold bath was removed. The solution turned orange and then red. After 1.5 h, the mixture was concentrated to ca. 50 mL by oil pump vacuum. Dry pentane (150 mL) was added. After 2 h, the precipitate was collected by filtration, washed with dry pentane (2 × 25 mL), and dried by oil pump vacuum to give **4a** (6.719 g, 7.560 mmol, 94%) as a yellow powder, mp 197−198 °C dec. Anal. Calcd (%) for $C_{36}H_{33}F_6NOP_3Re$ (888.78): C 48.65, H 3.74, N 1.58. Found: C 48.52, H 3.86, N 1.52. IR (thin film, cm^{-1}): $\tilde{\nu}$ 1656 (m, NO), 834 (vs, PF_6). ^1H NMR (400 MHz, CD_2Cl_2): PPh_3 and PPh_2 at δ 7.87−7.32 (m, 25H); 7.11 (ddd, 1H, $^1J(H,P)$ = 489.5 Hz, $^3J(H,H)$ = 12.9 Hz, $^3J(H,H')$ = 3.2 Hz, PH), 4.89 (s, 5H, C_5H_5), 2.65−2.55 (m, 1H, C*H*H′), 2.42−2.30 (m, 1H, CH*H*′). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2): PPh_3 at δ 134.4 (d, $^1J(C,P)$ = 55.5 Hz, i), 133.8 (d, $^2J(C,P)$ = 11.1 Hz, o), 131.4 (d, $^4J(C,P)$ = 1.9 Hz, p), 129.4 (d, $^3J(C,P)$ = 10.2 Hz, m), PPhPh′ at 134.4 (s, p), 132.5 (d, $^2J(C,P)$ = 10.2 Hz, o), 131.9 (d, $^2J(C,P)$ = 10.2 Hz, o′), 130.4 (d, $^3J(C,P)$ = 12.0 Hz, m), 130.1 (d, $^3J(C,P)$ = 12.0 Hz, m′), 124.6 (d, $^1J(C,P)$ = 69.4 Hz, i), 122.5 (d, $^1J(C,P)$ = 86.0 Hz, i′); 90.9 (s, C_5H_5), −35.7 (dd, $^1J(C,P)$ = 28.7 Hz, $^2J(C,P)$ = 3.7 Hz, CH_2). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2): δ 29.6 (d, $^3J(P,P)$ = 10.6 Hz, PPh_2H), 21.5 (d, $^3J(P,P)$ = 11.9 Hz, PPh_3), −143.3 (sep, $^1J(P,F)$ = 708.1 Hz, PF_6).

[(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2P(t\text{-}Bu)_2H$)]$^+BF_4^-$ (4b). A Schlenk flask was charged with **1** (0.632 g, 1.13 mmol)[19,35] and dry CH_2Cl_2 (30 mL) and cooled to −60 °C. Then $Ph_3C^+BF_4^-$ (0.448 g, 1.36 mmol) was added with stirring. Within 30 min, the orange suspension became a light yellow solution. Then $P(t\text{-}Bu)_2H$ (0.230 mL, 0.182 g, 1.24 mmol) was added dropwise with stirring. The solution turned red. The mixture was stirred for 12 h while the cold bath warmed to room temperature. All volatiles were removed by oil pump vacuum. The orange residue was extracted with benzene (10 mL). The extract was filtered through a syringe filter and added dropwise to vigorously stirred hexanes (100 mL). The beige precipitate was collected and analogously reprecipitated from CH_2Cl_2/hexanes (5/100 mL). The precipitate was collected by filtration, washed with hexanes (10 mL), and dried by oil pump vacuum to give **4b** (0.760 g, 0.961 mmol, 85%) as an orange powder, mp 190−192 °C. Anal. Calcd (%) for $C_{32}H_{41}BF_4NOP_2Re$ (790.64): C 48.61, H 5.23, N 1.77. Found: C 48.68, H 5.17, N 1.65. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1642 (s, NO), 1054 (s, BF). ^1H NMR (400 MHz, $CDCl_3$): PPh_3 at δ 7.54−7.42 (m, 7H), 7.42−7.28 (m, 8H); 6.88 (dd, 1H, $^1J(H,P)$ = 410 Hz, $^3J(H,H)$ = 11 Hz, PH), 5.24 (s, 5H, C_5H_5), 1.72/1.46 (2 m, 2H, CHH′), 1.35/1.31 (2 d, 18H, $^3J(H,P)$ = 10 Hz, CH_3/CH_3'). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ PPh_3 at 134.0 (d, $^1J(C,P)$ = 51.5 Hz, i), 133.3 (d, $^2J(C,P)$ = 11 Hz, o), 130.9 (s, p), 128.9 (d, $^3J(C,P)$ = 11 Hz, m); 91.0 (s, C_5H_5), 33.6 (d, $^1J(C,P)$ = 33 Hz, PC), 32.3 (d, $^1J(C,P)$ = 37 Hz, PC′), 28.3 (s, CH_3), 27.2 (s, C′H_3), −44.1 (d, $^1J(C,P)$ = 26 Hz, CH_2). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 73.9 (d, $^3J(P,P)$ = 23 Hz, $P(t\text{-}Bu)_2$), 20.3 (d, $^3J(C,P)$ = 23 Hz, PPh_3). MS (FAB, 3-NBA): *m/z* (%) 704 (80) $[M]^+$, 558 (100) $[M - P(t\text{-}Bu)_2H]^+$.

(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2P(t\text{-}Bu)_2$) (5b). An oven-dried Schlenk tube was charged with **4b** (0.500 g, 0.633 mmol) and dry THF (25 mL). Then *t*-BuOK (1.0 M in THF; 0.70 mL, 0.70 mmol) was added with stirring. The orange mixture turned red. After 1 h, the solvent was removed by oil pump vacuum. Dry CH_2Cl_2 (25 mL) was added. The mixture was filtered through a Celite plug (4 × 2 cm, oven dried at 120 °C, cooled to room temperature under vacuum). The filtrate was concentrated to ca. 10 mL and layered with dry pentane (30 mL). After 3 days, orange prisms had formed. The supernatant was decanted and the product dried by oil pump vacuum to give **5b** (0.338 g, 0.481 mmol, 76%) as orange prisms, mp 172 °C dec. Anal. Calcd (%) for $C_{32}H_{40}NOP_2Re$ (702.83): C 54.69, H 5.74, N 1.99. Found: C 54.53, H 5.80, N 1.89. IR (thin film, cm^{-1}): $\tilde{\nu}$ 1639 (s, NO). ^1H NMR (400 MHz, C_6D_6): δ PPh_3 at 7.57−7.52 (m, 6 H), 7.06−6.96 (m, 9 H); 4.92 (s, 5H, C_5H_5), 1.91−1.84 (m, 1H, C*H*H′), 1.68 (dd, 1H, $^2J(H,P)$ = 15 Hz, $^3J(H,P)$ = 5 Hz, CH*H*′), 1.50/1.16 (2 d, 18H, $^3J(H,P)$ = 10 Hz, CH_3/CH_3'). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ PPh_3 at 136.7 (d, $^1J(C,P)$ = 51 Hz, i), 133.9 (d, $^2J(C,P)$ = 11 Hz, o), 130.1 (s, p), 128.4 (d, $^3J(C,P)$ = 11 Hz, m); 91.2 (s, C_5H_5), 33.3 (d, $^1J(C,P)$ = 31 Hz, PC), 32.0 (d, $^1J(C,P)$ = 26 Hz, PC′), 31.3/30.0 (2d, $^2J(C,P)$ = 13 Hz, CH_3/CH_3'), −25.4 (d, $^1J(C,P)$ = 44 Hz, CH_2). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 52.9 (d, $^3J(P,P)$ = 7 Hz, $P(t\text{-}Bu)_2$), 24.1 (d, $^3J(P,P)$ = 7 Hz, PPh_3). MS (FAB, 3-NBA): *m/z* (%) 704 (15) $[MH]^+$, 558 (100) $[M - P(t\text{-}Bu)_2]^+$.

(η^5-$C_5H_4PPh_2$)Re(NO)(PPh_3)(CH_3) (7a). A Schlenk flask was charged with **1** (0.300 g, 0.537 mmol)[19,35] and dry THF (15 mL) and cooled to −78 °C. Then *n*-BuLi (1.6 M in hexanes; 0.36 mL, 0.58 mmol) was added dropwise with stirring. The orange solution was stirred at −30 °C for 5.5 h and then briefly warmed to room temperature. The red sample was cooled to −78 °C, and a solution of PPh_2Cl (0.106 mL, 0.130 g, 0.590 mmol) in dry THF (5 mL) was slowly added. The mixture was allowed to warm to room temperature overnight and filtered through layered silica/Celite (1.5 cm/1.5 cm) with THF rinses (4 × 5 mL). The combined filtrates were taken to dryness by oil pump vacuum. Dry benzene (10 mL) was added. The mixture was filtered through layered silica/Celite (1.5 cm/1.5 cm) with benzene rinses (5 × 10 mL). The combined filtrates were concentrated by oil pump vacuum to ca. 2 mL and layered with dry pentane (60 mL). After 1 day, the precipitate was collected by filtration (medium frit), washed with dry pentane, and dried by oil pump vacuum to give **7a** (0.240 g, 0.323 mmol, 60%) as an orange powder, mp 205−207 °C dec. Anal. Calcd (%) for $C_{36}H_{32}NOP_2Re$ (742.81): C 58.21, H 4.34, N 1.89. Found: C 57.01, H 4.38, N 1.90. IR (thin film, cm^{-1}): $\tilde{\nu}$ 1629 (s, NO). ^1H NMR (400 MHz, C_6D_6): PPh_3 and PPh_2 at δ 7.66−7.50 (m, 10H), 7.20−6.95 (m, 15H); C_5H_4 at 4.75, 4.67, 4.63, 3.79 (4 br s, 4H); 1.54 (d, 3H, $^3J(H,P)$ = 6.0 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): PPh_3 at δ 136.9 (d, $^1J(C,P)$ = 50.9 Hz, i), 134.1 (d, $^2J(C,P)$ = 11.1 Hz, o), 130.0 (s, p), 128.5 (d, $^3J(C,P)$ = 6.4 Hz, m); PPhPh′ at δ 138.6 (d, $^1J(C,P)$ = 66.6 Hz, i), 138.5 (d, $^1J(C,P)$ = 64.7 Hz, i′), 134.3 (d, $^2J(C,P)$ = 10.2 Hz, o), 133.9 (d, $^2J(C,P)$ = 6.5 Hz, o′), 130.4 (s, p), 128.8 (d, $^3J(C,P)$ = 6.4 Hz, m), 128.7 (d, $^3J(C,P)$ = 6.5 Hz, m′); C_5H_4 at 101.0 (d, $^2J(C,P)$ = 3.7 Hz), 100.6 (d, $^1J(C,P)$ = 18.5 Hz, CP), 91.0 (s), 87.5 (d, $^2J(C,P)$ = 4.6 Hz), 86.4 (s); −34.3 (d, $^2J(C,P)$ = 6.0 Hz, $ReCH_3$). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 25.2 (d, $^3J(P,P)$ = 1.9 Hz, PPh_3), −18.0 (s, $C_5H_4PPh_2$). MS (FAB, 3-NBA): *m/z* (%) 759 (52) $[MO]^+$, 743 (64) $[M]^+$, 579 (100).

(η^5-$C_5H_4P(t\text{-}Bu)_2$)Re(NO)(PPh_3)(CH_3) (7b). A Schlenk flask was charged with **1** (0.300 g, 0.537 mmol)[19,35] and dry THF (15 mL) and cooled to −78 °C. Then *n*-BuLi (1.6 M in hexanes; 0.36 mL, 0.58 mmol) was added dropwise with stirring. The orange solution was stirred at −30 °C for 5.5 h and then briefly warmed to room temperature. The red sample was cooled to −78 °C, and a solution of $P(t\text{-}Bu)_2Cl$ (0.112 mL, 0.107 g, 0.590 mmol) in dry THF (5 mL) was slowly added. The mixture was allowed to warm to room temperature overnight, becoming deep red-brown, and was filtered through layered silica/Celite (2 cm/2 cm) with THF rinses (2 × 10 mL). The combined filtrates were taken to dryness by oil pump vacuum. Dry benzene (20 mL) was added. The mixture was filtered through layered silica/Celite (2 cm/2 cm) with benzene rinses (4 × 10 mL). The combined filtrates were concentrated

(38) An analogous tetrafluoroborate salt has been reported.[18a]

by oil pump vacuum to ca. 5 mL and layered with dry pentane (80 mL). After 1 day, the solvent was decanted, and the residue dried under oil pump vacuum to give **7b** (0.157 g, 0.223 mmol, 42%) as orange blocks, mp 220−221 °C dec. Anal. Calcd (%) for $C_{32}H_{40}NOP_2Re$ (702.83): C 54.69, H 5.74, N 1.99. Found: C 54.58, H 5.72, N 2.07. IR (thin film, cm^{-1}): $\tilde{\nu}$ 1629 (s, NO). ^1H NMR (400 MHz, C_6D_6): PPh_3 at δ 7.61−7.56 (m, 6H), 7.05−6.95 (m, 9H); C_5H_4 at 5.20, 5.11, 4.99, 3.12 (4 br s, 4H); 1.49 (d, 3H, ^3J(H,P) = 6.1 Hz, CH_3), 1.41 (d, 9H, ^3J(H,P) = 11.7 Hz, CH_3), 1.20 (d, 9H, ^3J(H,P) = 11.0 Hz, CH'_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): PPh_3 at δ 137.1 (d, ^1J(C,P) = 50.9 Hz, i), 134.0 (d, ^2J(C,P) = 11.1 Hz, o), 130.0 (s, ^4J(C,P) = 1.9 Hz, p), 128.5 (d, ^3J(C,P) = 10.2 Hz, m); C_5H_4 at 112.3 (d, ^1J(C,P) = 29.6 Hz, CP), 95.8 (d, ^2J(C,P) = 6.5 Hz), 89.6 (s), 87.4 (s), 82.2 (s); 33.3 (d, ^1J(C,P) = 21.3 Hz, PC), 32.7 (d, ^1J(C,P) = 22.2 Hz, PC′), 30.8 (d, ^2J(C,P) = 4.6 Hz, CH_3), 30.7 (d, ^2J(C,P) = 4.6 Hz, C′H_3), −35.0 (d, ^2J(C,P) = 8.3 Hz, $ReCH_3$). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 25.6 (s, PPh_3), 24.9 (s, $C_5H_4P(t\text{-}Bu)_2$).[39] MS (FAB, 3-NBA): *m/z* (%) 719 (25) $[MO]^+$, 703 (100) $[M]^+$, 646 (60).

(η^5-$C_5H_4PPh_2$)Re(CO)$_3$ (10a). A Schlenk flask was charged with **8** (0.180 g, 0.537 mmol)[19] and dry THF (15 mL) and cooled to −78 °C. Then *n*-BuLi (1.6 M in hexanes; 0.36 mL, 0.58 mmol) was added dropwise with stirring. The light yellow solution was stirred at −30 °C for 5.5 h and then briefly warmed to room temperature. The sample was cooled to −78 °C, and a solution of PPh_2Cl (0.106 mL, 0.130 g, 0.590 mmol) in dry THF (5 mL) was slowly added. The mixture was allowed to warm to room temperature overnight and filtered through layered silica/Celite (2 cm/2 cm) with THF rinses (4 × 5 mL). The combined filtrates were taken to dryness by oil pump vacuum. Dry benzene (10 mL) was added. The mixture was filtered through layered silica/Celite (2 cm/2 cm) with benzene rinses (3 × 10 mL). The combined filtrates were concentrated by oil pump vacuum to ca. 5 mL and layered with dry pentane (60 mL). After 1 day, the precipitate was collected by filtration (medium frit), washed with dry pentane, and dried by oil pump vacuum to give **10a** (0.273 g, 0.525 mmol, 98%) as an off-white powder, mp 129−131 °C. Anal. Calcd (%) for $C_{20}H_{14}O_3P_2Re$ (519.51): C 46.24, H 2.72. Found: C 46.36, H 2.72. IR (thin film, cm^{-1}): $\tilde{\nu}$ 2019 (s, CO), 1922 (s, CO). ^1H NMR (400 MHz, C_6D_6): PPh_2 at δ 7.32−7.28 (m, 4H), 7.07−7.01 (m, 6H); C_5H_4 at 4.76 (dd, 2H, ^3J(H,H′) = 2.0 Hz, ^3J(H,P) = 3.6 Hz), 4.42 (dd, 2H, ^3J(H′,H) = 2.0 Hz, ^4J(H′,P) = 2.0 Hz). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ 193.6 (s, CO), PPh_2 at δ 137.6 (d, ^1J(C,P) = 10.7 Hz, i), 133.6 (d, ^2J(C,P) = 19.8 Hz, o), 129.3 (s, p), 128.8 (d, ^3J(C,P) = 7.6 Hz, m); C_5H_4 at 96.6 (d, ^1J(C,P) = 21.4 Hz, CP), 92.6 (d, ^2J(C,P) = 13.8 Hz), 85.6 (s). $^{31}P\{^1H\}$ NMR (161.80 MHz, C_6D_6): δ −17.1 (s, C_5H_4-PPh_2).

(η^5-$C_5H_4P(t\text{-}Bu)_2$)Re(CO)$_3$ (10b). A Schlenk flask was charged with **8** (0.180 g, 0.537 mmol)[19] and dry THF (15 mL) and cooled to −78 °C. Then *n*-BuLi (1.6 M in hexanes; 0.36 mL, 0.58 mmol) was added dropwise with stirring. The colorless solution was stirred at −30 °C for 5.5 h and then briefly warmed to room temperature. The light yellow sample was cooled to −78 °C, and a solution of $P(t\text{-}Bu)_2Cl$ (0.112 mL, 0.107 g, 0.590 mmol) in dry THF (5 mL) was slowly added. The mixture was allowed to warm to room temperature overnight, becoming deep yellow, and was filtered through layered silica/Celite (2 cm/2 cm) with THF rinses (2 × 10 mL). The combined filtrates were taken to dryness by oil pump vacuum. Dry benzene (20 mL) was added. The mixture was filtered through layered silica/Celite (2 cm/2 cm) with benzene rinses (4 × 10 mL). The combined filtrates were concentrated by oil pump vacuum to ca. 5 mL and layered with dry pentane (80 mL). After several days, the precipitate was collected by filtration (medium frit), washed with dry pentane, and dried by oil pump vacuum to give **10b** (0.078 g, 0.16 mmol, 30%) as a light brown powder of ca. 95% spectroscopic purity, mp 227−230 °C dec. IR (thin film, cm^{-1}): $\tilde{\nu}$ 2030 (s, CO), 1922 (vs, CO). ^1H NMR (400 MHz, C_6D_6): δ C_5H_4 at 4.99 (dd, 2H, ^3J(H,H′) = 2.0 Hz, ^3J(H,P) = 4.0 Hz), 4.46 (dd, 2H, ^3J(H′,H) = 2.0 Hz, ^4J(H′,P) = 2.0 Hz); 1.05 (d, 18H, ^3J(H,P) = 11.6 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ 194.3 (s, CO), C_5H_4 at 95.3 (d, J(C,P) = 15.7 Hz), 84.8 (s), 84.1 (d, J(C,P) = 15.7 Hz); 32.7 (d, ^1J(C,P) = 22.2 Hz, PC), 30.5 (d, ^2J(C,P) = 13.9 Hz, CH_3). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 27.9 (s, $C_5H_4P(t\text{-}Bu)_2$).

Suzuki Couplings. A (Tables 3, 4). An oven-dried Schlenk flask was charged with a phosphorus donor ligand (protonated form unless noted; 0.0179 mmol, 4 mol %) and dry toluene (4 mL). Then *t*-BuOK (1.0 M in THF; 0.036 mL, 0.036 mmol) was added with stirring (omitted for ligands used in deprotonated form). The yellow mixture turned red. After 5 min, $Pd(OAc)_2$ (0.0045 M in toluene; 1.0 mL, 0.0045 mmol, 1 mol %; higher-turnover experiments: 0.100 mL, 0.000448 mmol, 0.1 mol %), phenylboronic acid (0.0820 g, 0.673 mmol), K_3PO_4 (0.1900 g, 0.8950 mmol), an internal standard (tridecane (0.050 mL, 0.038 g, 0.205 mmol), hexadecane (0.060 mL, 0.046 g, 0.204 mmol), or eicosane (0.0577 g, 0.2042 mmol)), and an aryl halide (0.45 mmol) were added. The red-brown suspension was stirred at the indicated temperature and monitored by GC until complete conversion or catalyst deactivation (up to 168 h). The product was identified by comparison of the GC retention time to that of an authentic sample. **B.** An oven-dried Schlenk flask was charged with a protonated ligand (0.0161 mmol, 3.6 mol %) and dry THF (4 mL). Then *t*-BuOK (1.0 M in THF; 0.032 mL, 0.032 mmol) was added with stirring. The yellow mixture became red. After 5 min, $Pd_2(dba)_3$ (0.0062 g, 0.0068 mmol, 1.5 mol %), phenylboronic acid (0.0600 g, 0.492 mmol), KF (0.0859 g, 1.48 mmol), tridecane (0.050 mL, 0.038 g, 0.205 mmol), and an aryl halide (0.45 mmol) were added. The suspension was stirred at room temperature or 60 °C and analyzed as described in procedure A. **C** (preparative experiment). Complex **2b** (0.0752 g, 0.0896 mmol, 4 mol %) and dry toluene (15 mL), *t*-BuOK (1.0 M in THF; 0.18 mL, 0.18 mmol, 2.0 equiv/ligand), $Pd(OAc)_2$ (0.0050 g, 0.022 mmol, 1 mol %), phenylboronic acid (0.4097 g, 3.360 mmol), K_3PO_4 (0.9510 g, 4.480 mmol), and 6-methoxy-2-bromonaphthalene (0.5311 g, 2.240 mmol) were combined in a procedure analogous to A. The red-brown suspension was stirred at 100 °C. After 1 h, the mixture was cooled to room temperature, diluted with ether (15 mL), and washed with aqueous NaOH (2 N, 5 mL). The NaOH layer was separated and washed with ether (10 mL). The combined organic layers were washed with brine (10 mL) and dried ($MgSO_4$). The solvents were removed by rotary evaporation, and the residue was chromatographed (silica gel column, 17.5 × 3 cm, 9:1 v/v hexanes/ethyl acetate). Solvent was removed from the product-containing fractions (R_f = 0.56, TLC) to give 6-methoxy-2-phenylnaphthalene as a white mother-of-pearl solid (0.511 g, 2.18 mmol, 97%). The NMR data closely matched literature values:[40] ^1H NMR (300 MHz, $CDCl_3$): Np and Ph at δ 7.97 (d, ^4J(H,H) = 1.2 Hz, 1H), 7.79 (m, 2H), 7.71 (m, 3H), 7.46 (m, 2H), 7.35 (m, 1H), 7.17 (m, 2H); 3.93 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): Np and Ph at δ 157.7, 141.2, 136.4, 133.8, 129.7, 129.2, 128.8, 127.2, 127.1, 126.1, 125.6, 119.2, 105.6 (13 s); 55.3 (s, OCH_3).

Crystallography. A. A CH_2Cl_2 solution of **5b** that had been dried under 0.006 Torr for 1 h was layered with hexane. After 3 days, the orange prisms were taken to a Nonius KappaCCD diffractometer for data collection as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 16 382 reflections. Lorentz, polarization, and absorption corrections[41] 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 with all data by full-matrix least-squares on F^2 using SHELXL-97.[42] Non-hydrogen

(39) Tentative assignment

(40) Zapf, A.; Beller, M. *Chem. Eur. J.* **2000**, *6*, 1830.

atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from the literature.[43] The asymmetric unit contained two independent molecules of **5b**, two *t*-BuOH molecules, and three CH_2Cl_2 molecules. The carbon atoms were disordered in two of the CH_2Cl_2 molecules and were refined to 55:45 (C70/C70A) and 84:16 (C90/C90A) occupancies. The chlorine atoms of the other CH_2Cl_2 molecule were disordered over six positions (C120−C125) and were refined with a fixed occupancy of 1/3. **B.** A benzene solution of **7b** was layered with pentane. After 1 day, the orange blocks were analyzed as described for **5b** (cell parameters from 10 frames using a 10° scan; refined with 6330 reflections). The structure was solved and refined as described for **5b**.

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Supporting Information Available: Additional experimental details and preparations of rhenium complexes,[20] and a cif file of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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