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Syntheses, structures, and reactions of cyrhetrenylphosphines; applications in palladium catalyzed Suzuki cross-coupling reactions

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ABSTRACT

Reaction of bromocyrhetrene $(\eta^5\text{-}C_5H_4Br)Re(CO)_3$ with lithium tetramethylpiperidide (LiTMP; 1.0 equiv, −78 °C) and then $ClPR_2$ (R = **a**, Ph; **b**, Cy) gives $(\eta^5\text{-}1,2\text{-}C_5H_3BrPR_2)Re(CO)_3$ (**5a**, 48%; **5b**, 80%). Analogous reactions with 2.0 equiv of LiTMP and $ClPR_2$ give the 1-bromo-2,5-diphosphidocyclopentadienyl complexes $[\eta^5\text{-}1,2,5\text{-}C_5H_2Br(PR_2)_2]Re(CO)_3$ (**6a**, 60%; **6b**, 80%). These rhenium containing or cyrhetrenylphosphines are combined with $Pd(OAc)_2$ (2:1 mol ratio) to give catalysts for Suzuki couplings of phenylboronic acid and *p*-bromotoluene or *p*-bromoacetophenone (1 mol%; Cs_2CO_3, toluene, 100 °C). The catalyst with **5b** exhibits much higher activities than the others, with conversions of 92–64% after 20 min. The crystal structures of **5b** and **6a**,**b** are determined.

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1. Introduction

The development of new phosphine ligands has had a huge impact in transition metal catalyzed organic reactions [1–3] and continues to attract great interest [4–7]. One growing subclass would be organometallic or "transition metal containing" phosphines, in which the metal is a spectator that does not participate in any of the bond breaking or bond making steps [8–10]. These are being evaluated as ligands in increasing numbers of metal catalyzed reactions.

The success of phosphine ligands in catalysis is a function of both steric and electronic properties, and it is desirable to be able to vary both independently. This allows fine tuning of the coordinated species, thus enabling the various steps of the catalytic cycle to be optimized [11]. One recurring theme in metal catalyzed carbon–carbon bond forming reactions has been the use of bulky phosphine ligands, often with electron releasing substituents [12].

In a relevant example involving ferrocenyl phosphines, the addition of an *ortho* aryl substituent to $(\eta^5\text{-}C_5H_4PCy_2)Fe(\eta^5\text{-}C_5H_5)$, as exemplified by **I** in Fig. 1 (Ar = Ph, *o*-$MeOC_6H_4$, 1-naphthyl, 9-phenanthrenyl), enhances the rates of palladium catalyzed Suzuki cross-coupling reactions [13]. Similarly, the air stable 2-trimethylsilyl ferrocenyl phosphine, $(\eta^5\text{-}C_5H_3SiMe_3(PPh_2))Fe(\eta^5\text{-}C_5Me_5)$ (**II**), is a superb ligand for the Suzuki reaction [14]. It has been proposed that an increase in steric bulk enhances the rate of the product forming reductive elimination step in the catalytic cycle [15].

We have previously demonstrated that the rhenium containing or cyrhetrenylphosphine $(\eta^5\text{-}C_5H_4PPh_2)Re(CO)_3$ (**III**) [10] as well as the related chiral-at-rhenium phosphine $(\eta^5\text{-}C_5H_4PPh_2)Re(NO)(CH_3)(PPh_3)$ (**IV**) [9e] are effective ligands for palladium catalyzed Suzuki cross coupling reactions. These provide coordination environments that are complementary to substituted ferrocenes. We wondered whether adding appropriate substituents to the former at the *ortho* cyclopentadienyl positions could have a beneficial effect. Accordingly, in this paper we describe syntheses, crystal structures, and palladium catalyzed Suzuki reactions involving cyrhetrenylphosphines that contain 1-bromo-2-phosphidocyclopentadienyl and 1-bromo-2,5-diphosphidocyclo pentadienyl units.

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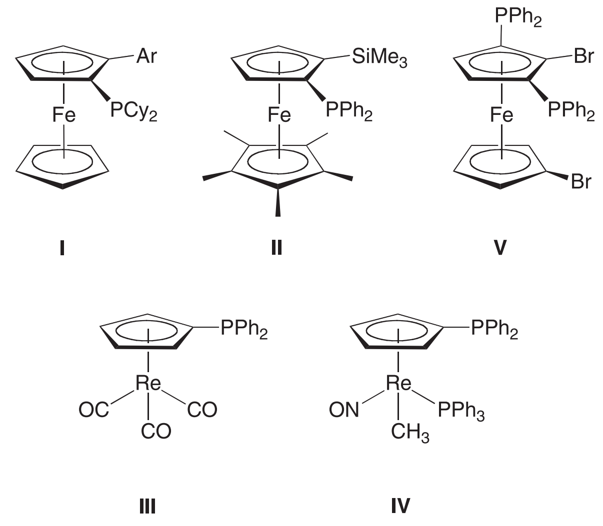


Fig. 1. Relevant literature compounds.

2. Results and discussion

2.1. Syntheses of rhenium complexes

The new rhenium-containing or cyrhetrenylphosphines evaluated in this study were synthesized by the four step pathway depicted in Scheme 1, starting with the readily available cyclopentadienyl tricarbonyl complex (η^5-C_5H_5)Re(CO)$_3$ (**1**) [16]. Following a previously reported protocol [17], the cyclopentadienyl ligand was lithiated with *n*-BuLi, and subsequent addition of mercuric chloride afforded the chloromercuriocyclopentadienyl complex (η^5-C_5H_4HgCl)Re(CO)$_3$ (**2**). The reaction of **2** and $Na_2S_2O_3$ afforded a bis(cyclopentadienyl)mercury species (**3**) [17], which was treated with $CuBr_2$ to give the bromocyclopentadienyl complex (η^5-C_5H_4Br)Re(CO)$_3$ (**4**) [18]. This constituted the starting point for new chemistry, with the bromide group viewed as a possible means of introducing additional functionality by metal catalyzed substitution reactions.

The dialkylamide base lithium tetramethylpiperidide (LiTMP) has previously been used to deprotonate cyclopentadienyl ligands [19]. Accordingly, reactions of **4** with LiTMP (1.0 equiv) and then the chlorophosphines ClPR$_2$ (R = **a**, Ph; **b**, Cy) at −78 °C afforded the 1-bromo-2-phosphidocyclopentadienyl complexes (η^5-1,2-C_5H_3BrPR$_2$)Re(CO)$_3$ (**5a**,**b**) in 48% and 80% yields, respectively, after chromatographic workups (Scheme 1). In some cases, the samples contained small amounts of the corresponding phosphidocyclopentadienyl complexes (η^5-C_5H_4PR$_2$)Re(CO)$_3$ [9d], presumably generated via initial bromide/lithium exchange. These could be removed by repeating the chromatography, or recrystallization.

Next, analogous reactions were conducted, but using 2.0 equiv of LiTMP and the chlorophosphine. After comparable workups, the 1-bromo-2,5-diphosphidocyclopentadienyl complexes [η^5-1,2,5-C_5H_2Br(PR$_2$)$_2$]Re(CO)$_3$ (**6a**,**b**) could be isolated in 60% and 80% yields, respectively. This suggests the intermediacy of the dilithio species (η^5-1,2,5-C_5H_2BrLi$_2$)Re(CO)$_3$. Indeed, at least one other rhenium dilithiocyclopentadienyl complex has been previously characterized [20]. Also, an analogous dilithiation/diphenylphosphination product, **V** in Fig. 1, has been isolated in low yield from the reaction of 1,1′-dibromoferrocene with the dialkylamide base LiN(*i*-Pr)$_2$ and ClPPh$_2$ [21]. As with **5a**,**b**, some samples of **6a**,**b** showed small amounts of impurities, and these could be removed by repeating the chromatography or crystallization.

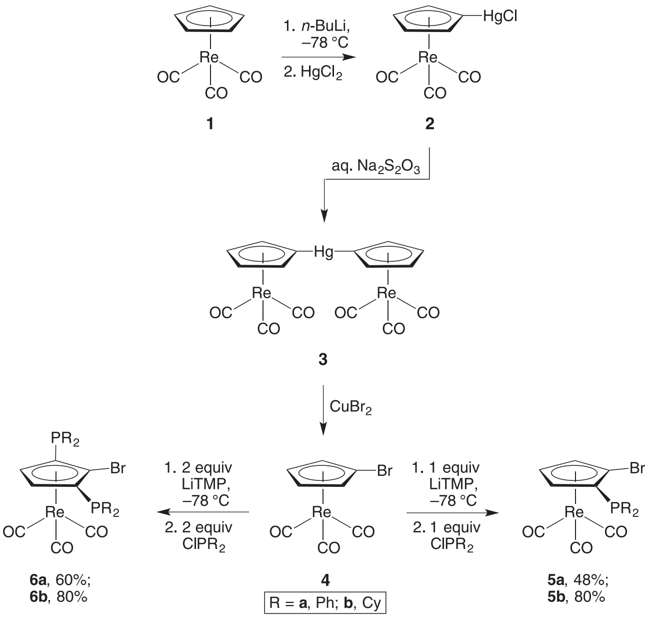
The new complexes **5a**,**b** and **6a**,**b** were obtained as air stable white powders, and characterized by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, in most cases by mass spectrometry, and with **5b** by microanalysis, as summarized in the experimental section. NMR spectra are reproduced in Supporting information. Product identities were evidenced by the strong IR ν_{CO} bands (2029–2025 and 1940–1933 cm^{-1}), ^{1}H and ^{13}C NMR signal patterns characteristic of substituted cyclopentadienyl ligands (see Supporting information), and intense molecular ions in the mass spectra. Also, the planar chirality associated with the substituted cyclopentadienyl ligands rendered the PR$_2$ groups diastereotopic, resulting in two sets of ^{13}C NMR signals.

2.2. Crystallography

Single crystals of **5b** and **6a**,**b** could be grown, and the X-ray crystal structures were determined as summarized in Table 1 and the experimental section. These confirmed the structural assignments, and key bond lengths and angles are provided in supporting information (Table 1s). Thermal ellipsoid plots of the molecular structures are depicted in Fig. 2. In order to facilitate comparisons between structures, the atom numbering schemes of some have been altered from those in the CIF files (Supporting information).

Most of the metrical parameters (see Table 1s) are quite similar and routine, conforming to those of many other formally octahedral, three-legged piano stool cyclopentadienyl rhenium complexes. For example, the OC—Re—CO bond angles fall into the narrow range of 91.81(11)° to 87.5(2)°. Complex **6a** adopts a conformation in which two phenyl groups on opposite diphenylphosphido moieties are nearly eclipsed (Fig. 2, middle), as evidenced by a C9—P1—P2—C21 torsion angle of 18.75°. Curiously, this motif has also been observed in ferrocene **V** (Fig. 1), which features an identical cyclopentadienyl ligand (analogous torsion angle 8.06°) [21].

The sums of the bond angles about the phosphorus atoms reflect the degree of pyramidalization. Interestingly, all are significantly less than that of an idealized tetrahedral atom, 328.4° (**5b**, 306.1°; **6a**, 302.3° and 304.2°; **6b**, 304.5° and 308.5°). To our knowledge, no other cyrhetrenylphosphines have been crystallographically characterized. However, for the di(*t*-butyl)phosphidocyclopentadienyl complex (η^5-C_5H_4P*t*-Bu)$_2$Re(NO)(PPh$_3$)(CH$_3$), which has a



Scheme 1. Syntheses of new complexes.

Table 1
Crystallographic data for **5b**, **6a**, and **6b**.

Complex	**5b**	**6a**	**6b**
Empirical formula	$C_{20}H_{25}BrO_3PRe$	$C_{32}H_{22}BrO_3P_2Re$	$C_{32}H_{46}BrO_3P_2Re$
Formula weight	610.48	782.55	806.74
Temperature [K]	110(2)	110(2)	110(2)
Diffractometer	Bruker GADDS	Bruker Smart 1000	Bruker GADDS
Wavelength [Å]	1.54178	0.71073	1.54178
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	P2(1)/c	P-1	P2(1)2(1)2(1)
Unit cell dimensions			
a [Å]	12.0944(7)	10.162(2)	10.6760(4)
b [Å]	15.0884(9)	12.083(3)	12.0665(5)
c [Å]	12.4653(8)	13.648(3)	24.9980(9)
α [°]	90	104.308(2)	90
β [°]	115.301(3)	97.445(3)	90
γ [°]	90	113.747(2)	90
Volume [Å^3]	2056.5(2)	1435.8(6)	3220.3(2)
Z	4	2	4
ρ_{calcd} [mg/m^3]	1.972	1.810	1.664
μ [mm^{-1}]	14.706	5.767	10.009
F(000)	1176	756	1608
Crystal size [mm^3]	0.25 × 0.08 × 0.04	0.30 × 0.20 × 0.20	0.09 × 0.08 × 0.02
Range for data collection (Θ, °)	4.04 to 60.80	1.95 to 25.00	4.07 to 60.00
Index ranges	$-13 \le h \le 13$ $-17 \le k \le 17$ $-13 \le l \le 14$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-16 \le l \le 16$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-28 \le l \le 28$
Reflections collected	15,171	13,397	25,217
Independent reflections	3038 [R(int) = 0.0496]	5008 [R(int) = 0.0360]	4688 [R(int) = 0.4661]
Max. and min. transmission	0.5908 and 0.1201	0.5963 and 0.2766	0.8249 and 0.466
Data/restraints/parameters	3038/0/235	5008/0/352	4688/0/353
Goodness-of-fit on F^2	1.030	1.002	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0282$, $wR2 = 0.0729$	$R1 = 0.0193$, $wR2 = 0.0488$	$R1 = 0.0181$, $wR2 = 0.0442$
R indices (all data)	$R1 = 0.0349$, $wR2 = 0.0751$	$R1 = 0.0203$, $wR2 = 0.0494$	$R1 = 0.0190$, $wR2 = 0.0444$
Largest diff. peak & hole [eÅ^{-3}]	01.339 and −1.393	0.916 and −0.922	0.894 and −0.580

more π basic rhenium fragment, the sum of the bond angles about the t-Bu$_2$P moiety is greater (315°) [9e]. In contrast, the values for the trisubstituted cyclopentadienyl ligand in ferrocene **V** (305.1° and 299.1°) are comparable to those in **6a**. Hence, in all of the new complexes, the phosphorus-carbon bonds must have higher degrees of phosphorus p character. This requires the phosphorus lone pairs to have enhanced s character, and thereby decreased basicities.

2.3. Catalysis

The rhenium-containing monophosphines and diphosphines **5a**,**b** and **6a**,**b** were evaluated as ligands for palladium catalyzed Suzuki cross coupling reactions of phenylboronic acid under the standard conditions summarized in Scheme 2. In the interest of identifying the most active system, conversions were assayed after 20 min. With both coupling partners assayed, p-bromotoluene and p-bromoacetophenone, the monodicyclohexylphosphine ligand **5b** exhibited much higher activity than the others, with conversions of 64–92% (entries 2, 5).

However, this activity is lower than when the non-brominated diphenylphosphido analog (η^5-$C_5H_4PPh_2$)Re(CO)$_3$ is used as a ligand, as well as the 1,2-disubstituted ferrocenyl phosphines **I** and **II** described in previous reports [10,13,14]. This may be due to the

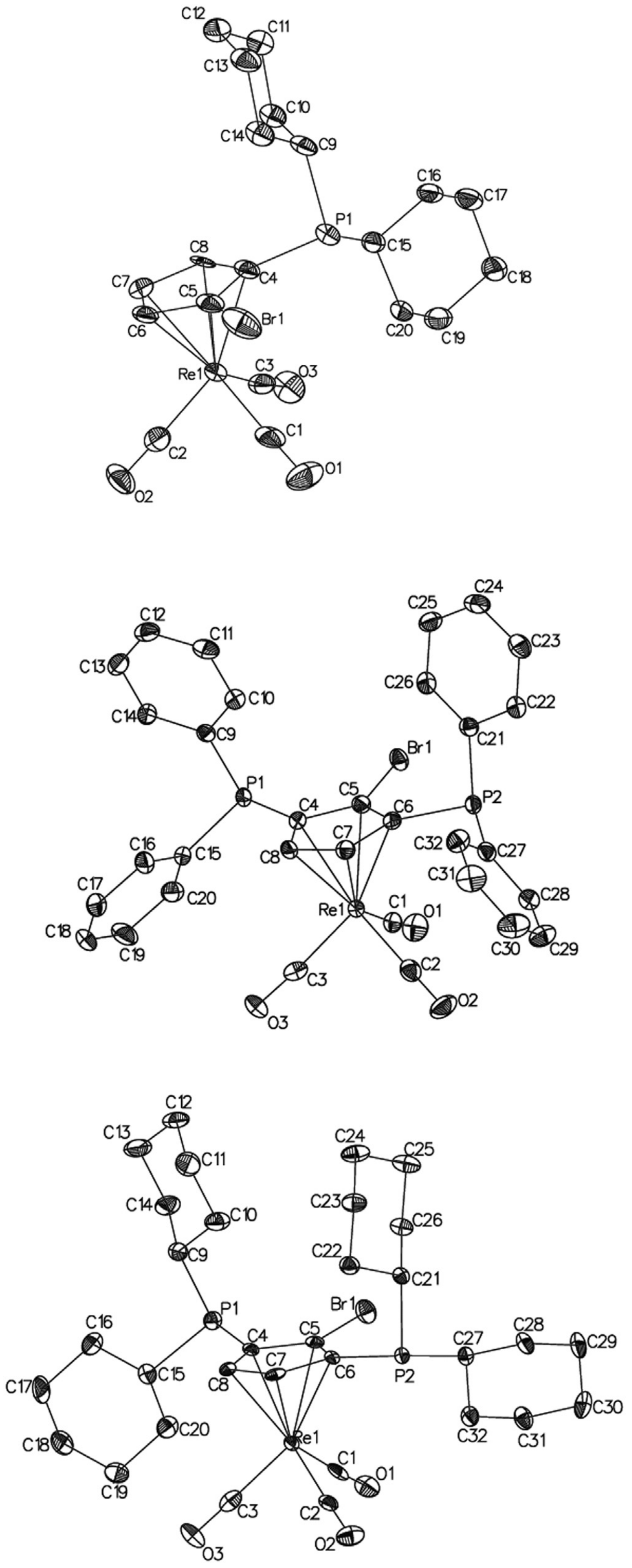
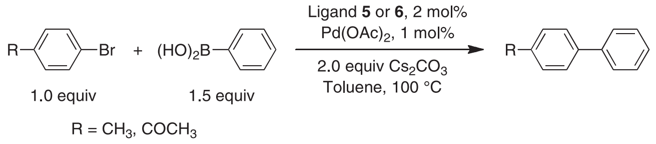


Fig. 2. Thermal ellipsoid plots (50% probability levels) of the molecular structures of **5b** (top), **6a** (middle), and **6b** (bottom).



Entry	Ligand	ArBr	Conversion, 20 min
1	**5a**	*p*-BrC$_6$H$_5$CH$_3$	6%
2	**5b**		64%
3	**6a**		<1%
4	**6b**		5%
5	**5a**	*p*-BrC$_6$H$_4$COCH$_3$	7%
6	**5b**		92%
7	**6a**		<1%
8	**6b**		15%

Scheme 2. Suzuki cross coupling reactions using rhenium containing phosphine ligands.

electron withdrawing effect of the bromide substituent, which renders all of these ligands less basic and capable of promoting the oxidative addition step of the catalytic cycle [22,23]. The marked decrease of activity with **5a** (entries 1, 5) would in turn reflect the lower basicity of the diphenylphosphido moiety. A parallel reactivity trend with **6b** and **6a** is evident (entries 4 and 8 vs. 3 and 7). Nonetheless, with longer reaction times, both **5a** and **6b** should give synthetically useful conversion levels.

The lower activities of **6a**,**b** relative to **5a**,**b** might be ascribed to the electron withdrawing effect of the additional phosphido substituent. However, note the absence of any correlation to the sums of the bonds angles about the phosphorus donor groups. Finally, although the Suzuki conditions employed are not strictly identical, the diphenylphosphidocyclopentadienyl complex (η^5-C$_5$H$_4$PPh$_2$)Re(NO)(PPh$_3$)(CH$_3$) appears to give a catalyst with an activity similar to that with **5b** [9e].

2.4. Conclusions

This study has shown that bromocyrhetrene, **4**, is easily converted to brominated cyrhetrenyl*mono*phosphines and cyrhetrenyl-1,3-*di*phosphines by monodeprotonation/monophosphination and dideprotonation/diphosphination sequences, respectively. All of these complexes exhibit planar chirality, and therefore constitute highly attractive phosphorus donor ligands for metal-catalyzed reactions, especially those in which chiral products are generated from achiral reactants. However, initial screening results with palladium catalyzed Suzuki coupling reactions, in which the basicities of the phosphorus donor groups are often important, are disappointing. In retrospect, the non-coordinating electronegative cyclopentadienyl substituents appear to be a step in the wrong direction for this particular application. Accordingly, future efforts will be directed at replacing the bromine functionality, and the introduction of more basic and/or bulkier phosphido moieties. Nonetheless, the new ligands may prove useful for other types of metal catalyzed transformations, and additional exploratory chemistry, including efforts to resolve the enantiomers, will be reported in due course.

3. Experimental section

3.1. General methods

All reactions were conducted under nitrogen atmospheres, and workups were carried out in air. Chemicals were treated as follows: THF, dried over an alumina column and degassed by aspirating with argon; toluene, freshly distilled from Na/benzophenone; TMPH (tetramethylpiperidene), *n*-BuLi (2.5 M in hexane), ClPPh$_2$, ClPCy$_2$, Pd(OAc)$_2$, Cs$_2$CO$_3$, *p*-bromotoluene, *p*-bromoacetophenone, and phenylboronic acid, used as received from common commercial sources.

The complexes (η^5-C$_5$H$_5$)Re(CO)$_3$ (**1**) [16], (η^5-C$_5$H$_4$HgCl)Re(CO)$_3$ (**2**) [17], the corresponding bis(cyclopentadienyl) mercurial **3** [17], and (η^5-C$_5$H$_4$Br)Re(CO)$_3$ (**4**) [18] were synthesized by literature procedures. LiTMP was freshly prepared as follows [24]. A Schlenk flask was charged with TMPH (0.14 mL, 0.84 mmol) and a stir bar and cooled to 0 °C. Then *n*-BuLi (2.5 M in hexane; 0.34 mL, 0.85 mmol) was slowly added with stirring. After 15 min, the faint yellow LiTMP suspension was added to the reaction mixture via cannula.

NMR spectra were recorded on Varian NMRS 500 and Bruker AVANCE 400 spectrometers at ambient probe temperatures and referenced as follows: ^{1}H, residual internal CHCl$_3$ (δ, 7.24 ppm); ^{13}C, internal CDCl$_3$ (δ, 77.0 ppm); ^{31}P, external 85% H$_3$PO$_4$ (δ, 0.00 ppm). FT IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR in a NaCl solution cell. MS and GC–MS analyses were conducted using a Shimadzu QP5050 instrument with a direct injection capability for non-volatile samples.

3.2. (η^5-1,2-C$_5$H$_3$BrPR$_2$)Re(CO)$_3$ (**5**; R = a, Ph; b, Cy)

A Schlenk flask was charged with **4** (0.350 g, 0.840 mmol) and THF (10 mL) and placed in a −78 °C cold bath. A solution of freshly prepared LiTMP (0.84 mmol) was slowly added via cannula with stirring. After 0.5 h, the flask was transferred to a −40 °C cold bath. After 3.0 h, the flask was transferred to a −78 °C cold bath, and ClPR$_2$ (0.84 mmol) was slowly added with stirring. The cold bath was allowed to warm overnight. The solvent was removed by oil pump vacuum. The yellow oil was chromatographed on a silica gel column that was eluted first with hexane to give unreacted **4** and then with 9:1 v/v hexanes/dichloromethane to give (η^5-C$_5$H$_4$PR$_2$)Re(CO)$_3$ [18] followed by **5**. The solvent was removed from the product containing fractions by rotary evaporation and oil pump vacuum to give **5** as a white amorphous powder (**5a**: 0.243 g, 0.406 mmol, 48%; **5b**: 0.410 g, 0.672 mmol, 80%) [25]. Crystallization of **5b** from hot hexanes afforded colorless needles suitable for X-ray diffraction. Calcd for C$_{20}$H$_{25}$BrO$_3$PRe (610.49): C, 39.35; H, 4.19; C, 39.44, H, 4.19.

Data for **5a**. IR ν_{CO} (cm^{-1}, CH$_2$Cl$_2$): 2029 (vs), 1938 (vs). NMR (δ, CDCl$_3$ (ppm)): ^{1}H (400 MHz) 7.48–7.29 (m, 10H, Ph), 5.80 (m, 1H, C$_5$H$_3$), 5.24 (m, 1H, C$_5$H$_3$), 4.91 (m, 1H, C$_5$H$_3$); ^{13}C{^{1}H} (101 MHz) 192.5 (s, ReCO), 136.6 (d, J_{CP} = 12 Hz, *i*-Ph), 134.7 (d, J_{CP} = 10 Hz, *i*-Ph′), 134.5 (d, J_{CP} = 21 Hz, *o*-Ph), 132.3 (d, J_{CP} = 19 Hz, *o*-Ph′), 129.8 (s, *p*-Ph), 129.0 (s, *p*-Ph′), 128.8 (d, J_{CP} = 7 Hz, *m*-Ph) [26], 128.7 (d, J_{CP} = 7 Hz, *m*-Ph′) [26], 98.2 (d, J_{CP} = 21 Hz, C$_5$H$_3$), 92.9 (d, J_{CP} = 30 Hz, C$_5$H$_3$), 91.1 (d, J_{CP} = 4 Hz, C$_5$H$_3$), 89.7 (s, C$_5$H$_3$), 82.8 (s, C$_5$H$_3$); ^{31}P{^{1}H} (162 MHz) −18.7 (s, PPh$_2$).

Data for **5b**. IR ν_{CO} (cm^{-1}, CH$_2$Cl$_2$): 2027 (vs), 1933 (vs). NMR (δ, CDCl$_3$ (ppm)): ^{1}H (500 MHz) 5.68 (dt, J = 2.9, 1.6 Hz, 1H, C$_5$H$_3$), 5.44 (dd, J = 3.1, 1.8 Hz, 1H, C$_5$H$_3$), 5.26 (ddd, J = 3.2, 2.7, 0.7 Hz, 1H, C$_5$H$_3$), 2.09 (m, 2H, C$_6$H$_{11}$), 1.91–1.58 (m, 10H, C$_6$H$_{11}$), 1.40–1.10 (m, 10H, C$_6$H$_{11}$); ^{13}C{^{1}H} (101 MHz) 193.0 (s, ReCO), 95.6 (d, J_{CP} = 38 Hz, C$_5$H$_3$), 93.8 (d, J_{CP} = 27 Hz, C$_5$H$_3$), 91.4 (s, C$_5$H$_3$), 88.8 (s, C$_5$H$_3$), 82.6 (s, C$_5$H$_3$), 35.1 (apparent t, J_{CP} = 14 Hz, C$_6$H$_{11}$), 31.7 (d, J_{CP} = 17 Hz, C$_6$H$_{11}$), 30.8 (d, J_{CP} = 17 Hz, C$_6$H$_{11}$), 30.0 (d, J_{CP} = 8 Hz, C$_6$H$_{11}$), 29.6 (d, J_{CP} = 10 Hz, C$_6$H$_{11}$), 27.6–26.7 (apparent m, C$_6$H$_{11}$), 26.2 (d, J_{CP} = 7 Hz, C$_6$H$_{11}$); ^{31}P{^{1}H} (202 MHz) −8.1 (s, PCy$_2$). Mass spectrum (EI, *m*/*z*): 610 [M$^+$], 582 [M$^+$ − CO], 503 [M$^+$ − CO − Br].

3.3. [η^5-1,2,5-C$_5$H$_2$Br(PR$_2$)$_2$]Re(CO)$_3$ (**6**; R = a, Ph; b, Cy)

These compounds were synthesized by procedures analogous to those for **5a**,**b** using **4** (0.175 g, 0.420 mmol), freshly prepared LiTMP

(0.84 mmol), and $ClPR_2$ (0.84 mmol). An identical chromatographic workup afforded (η^5-$C_5H_4PR_2$)$Re(CO)_3$ and then **6a** (0.197 g, 0.252 mmol, 60%) or **6b** (0.336 g, 0.335 mmol, 80%) as white powders [25]. Recrystallizations of **6a**,**b** from hot hexanes yielded colorless needles suitable for X-ray diffraction.

Data for **6a**. IR ν_{CO} (cm^{-1}, CH_2Cl_2): 2029 (vs), 1940 (vs). NMR (δ, $CDCl_3$ (ppm)): ^1H (400 MHz) 7.50–7.30 (m, 20H, Ph), 4.82 (s, 2H, C_5H_2); $^{13}C\{^1H\}$ (101 MHz) 192.4 (s, ReCO), 136.4 (d, J_{CP} = 12 Hz, *i*-Ph), 134.7 (d, J_{CP} = 23 Hz, *o*-Ph), 134.0 (d, J_{CP} = 10 Hz, *i*-Ph′), 132.5 (d, J_{CP} = 20 Hz, *o*-Ph′), 130.0 (s, *p*-Ph), 129.1 (s, *p*-Ph′), 128.9–128.74 (apparent m, *m*-Ph) [26], 128.72–128.6 (apparent m, *m*-Ph′) [26], 102.5 (d, *J* = 21 Hz, PC_5H_2), 99.9 (s, C_5H_2), 89.0 (t, *J* = 3 Hz, BrC_5H_2); $^{31}P\{^1H\}$ (202 MHz) −19.0 (s, PPh_2). Mass spectrum (EI, *m*/*z*): 782 [M^+], 754 [M^+ − CO], 726 [M^+ − 2CO], 698 [M^+ − 3CO], 617 [M^+ − 3CO − Br].

Data for **6b**. IR ν_{CO} (cm^{-1}, CH_2Cl_2): 2025 (vs), 1933 (vs). NMR (δ, $CDCl_3$ (ppm)): ^1H (500 MHz) 5.42 (s, 2H, C_5H_2), 2.06 (m, 4H, C_6H_{11}), 1.91–1.63 (m, 20H, C_6H_{11}), 1.39–1.12 (m, 20H, C_6H_{11}); $^{13}C\{^1H\}$ (126 MHz) 193.1 (s, ReCO), 101.4 (t, J_{CP} = 20 Hz, BrC_5H_2), 99.2 (d, J_{CP} = 39 Hz, PC_5H_2), 90.0 (d, J_{CP} = 5 Hz, C_5H_2), 34.7 (d, J_{CP} = 13 Hz, C_6H_{11}), 31.7 (d, J_{CP} = 16 Hz, C_6H_{11}), 30.7 (d, J_{CP} = 18 Hz, C_6H_{11}), 30.4 (d, J_{CP} = 9 Hz, C_6H_{11}), 30.0 (d, J_{CP} = 10 Hz, C_6H_{11}), 27.5–26.9 (apparent m, C_6H_{11}), 26.3 (d, J_{CP} = 7 Hz, C_6H_{11}); $^{31}P\{^1H\}$ (202 MHz) −4.6 (s, PCy_2). Mass spectrum (EI, *m*/*z*): 778 [M^+ − CO], 750 [M^+ − 2CO], 670 [M^+ − 2CO − Br], 582 [M^+ − CO − PCy_2].

3.4. Catalysis

A Schlenk flask was charged with phenylboronic acid (0.0836–0.0850 g, 0.68–0.69 mmol; 1.5 equiv), an aryl bromide (0.450 mmol, 1.0 equiv), Cs_2CO_3 (0.298–0.300 g, 0.914–0.920 mmol; 2.0 equiv), spectroscopically pure rhenium containing phosphine ligand (0.0090 M in toluene; 1.0 mL, 0.0090 mmol; 2 mol%) and dry toluene (12.0 mL) with stirring. The flask was immersed in a 100 °C oil bath, and a solution of $Pd(OAc)_2$ (0.0045 M in toluene; 1.0 mL, 0.0045 mmol; 1 mol%) was added. The product identities were verified by GC–MS, and conversions were calculated by relative integrations of GC peaks.

3.5. Crystallography

Data were collected as outlined in Table 1. Cell parameters for **5b** and **6b** were obtained from 180 data frames taken at widths of 0.5°; those for **6a** were obtained from 60 frames at widths of 0.3°. Integrated intensity information for each reflection was obtained by reduction of data frames with the program APEX2 [27]. Data were corrected for Lorentz and polarization factors using APEX2, and were subsequently treated for absorption and crystal decay effects using SADABS [28]. The structures were solved by direct methods using SHELXTL (SHELXS) [29]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions, and refined using a riding model. The parameters were refined by weighted least squares refinement on F_2 to convergence [29]. During the final stages of refinement of **6b**, the possibility of twinning was indicated; the structure refined to a BASF (batch scale factor) of 0.261.

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Appendix A. Supplementary material

CCDC-953402 (for **5b**), 953403 (for **6a**), and 953404 (for **6b**) contain 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. Also provided are ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **5a**,**b** and **6a**,**b**.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.10.029.

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