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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.

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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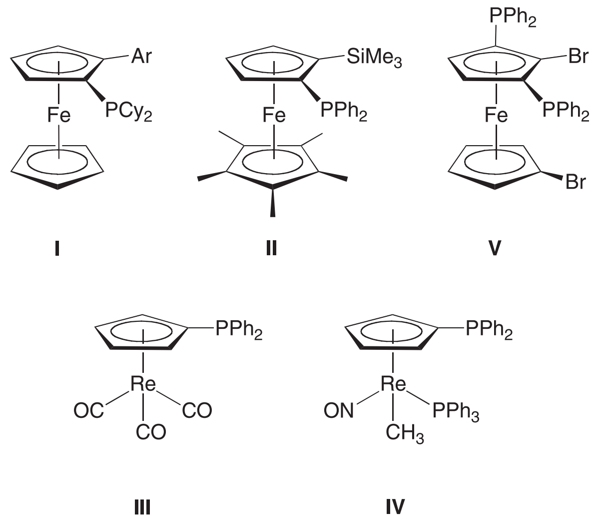


Fig. 1. Relevant literature compounds.

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 $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (**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 $(\eta^5\text{-}C_5H_4HgCl)Re(CO)_3$ (**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 $(\eta^5\text{-}C_5H_4Br)Re(CO)_3$ (**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 $(\eta^5\text{-}1,2\text{-}C_5H_3BrPR_2)Re(CO)_3$ (**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 $(\eta^5\text{-}C_5H_4PR_2)Re(CO)_3$ [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 $[\eta^5\text{-}1,2,5\text{-}C_5H_2Br(PR_2)_2]Re(CO)_3$ (**6a**,**b**) could be isolated in 60% and 80% yields, respectively. This suggests the intermediacy of the dilithio species $(\eta^5\text{-}1,2,5\text{-}C_5H_2BrLi_2)Re(CO)_3$. 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 $LiN(i\text{-}Pr)_2$ 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.

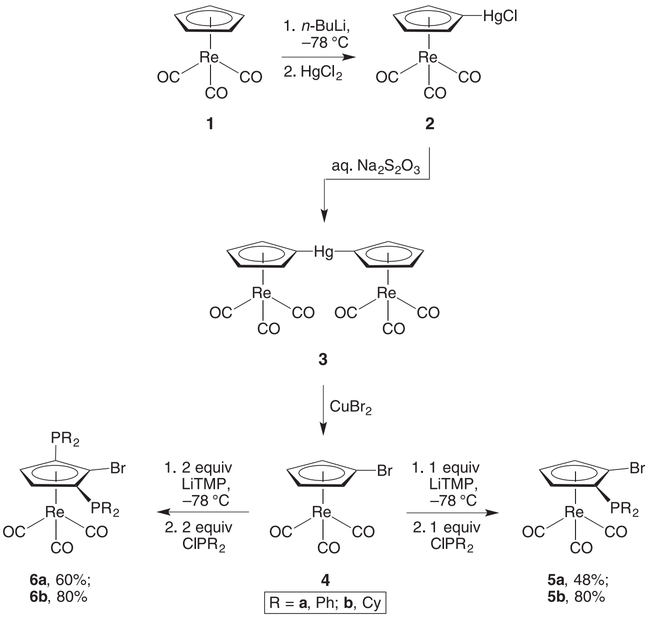
The new complexes **5a**,**b** and **6a**,**b** were obtained as air stable white powders, and characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, in most cases by mass spectrometry, and with **5b** by microanalysis, as summarized in the experimental section. NMR spectra are reproduced in Supporting information. Product identities were evidenced by the strong IR ν_{CO} bands (2029–2025 and 1940–1933 cm^{-1}), ^1H 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 $(\eta^5\text{-}C_5H_4Pt\text{-}Bu)_2Re(NO)(PPh_3)(CH_3)$, which has a



Scheme 1. Syntheses of new complexes.