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Short communication

Dicyclohexylphosphino cyrhetrene: Synthesis, characterization and catalytic evaluation toward Suzuki-Miyaura cross-coupling reaction of aryl bromides and chlorides

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ABSTRACT

Reaction of cyrhetrene ((η^5-C_5H_5)Re(CO)$_3$) with *n*-butyllithium (1.0 equiv, −78 °C) and then ClPCy$_2$ (Cy = cyclohexyl) gives the new cyrhetrenyl-phosphino ligand (η^5-$C_5H_4PCy_2$)Re(CO)$_3$ which was isolated as a pure sample in 86% yield and characterized by standard spectroscopic techniques (FT-IR, ^{1}H, ^{13}C and ^{31}P NMR), MS, X-ray diffraction and Elemental Analysis). This rhenium containing cyrhetrenyl phosphine combined with Pd(OAc)$_2$ (2:1 mol ratio) resulted an efficient catalytic system for Suzuki couplings of aryl bromides and aryl chlorides with phenylboronic acid. The catalyst exhibits a high activity, with conversions of 100% after 20 min.

Over the last twenty years, palladium catalyzed Suzuki cross-coupling reaction has become one of the most frequently employed reaction in organic chemistry [1,2]. Furthermore, this reaction has been applied industrially to the production of compounds such as losartan®, an antihypertensive drug produced by Merck [3]. This popularity is attributable to a variety of factors, such as the commercial availability of a large number of boronic acids, as well as their nontoxic nature and stability to heat, air, and moisture. Furthermore, the boron-containing by-product of the Suzuki cross-coupling can readily be separated from the desired compound [4].

During this time numerous efforts have been aimed at optimizing the catalytic systems used in this reaction, most of them involve the modulation of the electronic and steric properties of the ligands, improving the activity and selectivity of the catalytic system. An important part of these studies has been focused in the use of organometallic ligands, mainly ferrocene-based phosphines, since the bulky and electron-rich metallocene fragment provides the electronic and steric characteristics that are often required to form a highly active catalyst [5,6,7]. Although in a much lesser extent than their ferrocene analogues, cyrhetrenylphosphine ligands such as (η^5-$C_5H_4PR_2$)Re(CO)$_3$ (R = Ph, *t*-Bu) and (η^5-$C_5H_4PR_2$)Re(NO)(CH$_3$)(PPh$_3$) (R = Ph, *t*-Bu) [8], has also received attention, because they have demonstrated to be efficient components of Pd(II) systems for the Suzuki cross-coupling reaction, showing comparable activities to those catalytic systems based on organic phosphines. Furthermore, the easiness of perform electronic and structural modifications by exchanging the ligands coordinated to the rhenium center in these species offers exciting possibilities to improve the performance of these organometallic ligands [9,10,11].

As a part of our continued interest in cyrhetrenyl containing ligands here in, we would like to describe the synthesis and characterization of the unreported phosphinocyrhetrenic ligand (η^5-$C_5H_4PCy_2$)Re(CO)$_3$ (Cy = cyclohexyl). We also include in this report, the study of the catalytic systems based on this metalloligand, toward the palladium catalyzed Suzuki-Miyaura cross-coupling reaction of aryl bromides and aryl chlorides.

It is important to mention that in a previous publication we have used this cyrhetrenylphosphine as a precursor for the preparation of the corresponding oxides, boranes and selenides [12] but without any details of it spectroscopic characterization neither it X-ray diffraction study.

Experimentally, the cyrhetrenyl dicyclohexylphosphine was prepared by the reaction of cyrhetrene and n-BuLi, according to Scheme 1 (See SI).

The resulting compound was isolated as pure material after purification by column chromatography and recrystallization from a supersaturated solution in hexane. This compound was thermally stable, soluble in polar organic solvents and moderately soluble in hexane and benzene.

Spectroscopic parameters of (η^5-$C_5H_4PCy_2$)Re(CO)$_3$ are similar to those reported for the complexes (η^5-$C_5H_4PPh_2$)Re(CO)$_3$ [8,13] and (η^5-$C_5H_4PCy_2$)Fe(η^5-C_5H_5) [14]. For example, the IR spectra showed a characteristic pattern for *three-legged piano stool* geometry, of ν_{CO} absorptions bands at 2022 and 1926 cm^{-1}. These frequencies are slightly

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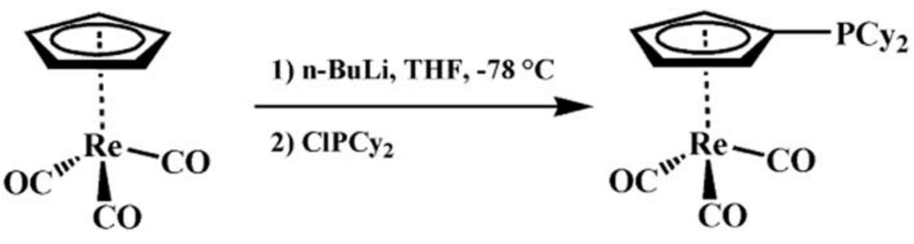

Scheme 1. Synthesis of (η^5-$C_5H_4PCy_2$)$Re(CO)_3$.

shifted to a lower energy, respect to those measured for (η^5-$C_5H_4PPh_2$)$Re(CO)_3$ (2024 and 1930 cm^{-1}), [8,13] which indicate a higher electron-donor capability of the PCy_2 group respect to PPh_2. ^1H NMR spectra, shown two signals at 5.39 and 5.44 assigned to the hydrogen atoms of the cyclopentadienyl ring, displaced to high field respect to the resonances reported for (η^5-$C_5H_4PPh_2$)$Re(CO)_3$, in agreement with the electron-donor properties of the PCy_2 group. ^{31}P NMR spectra showed, as expected, only one signal at −4.9 ppm value comparable to the ferrocenyl analog (−8.8 ppm) [14]. Finally, the mass spectra of the metalloligand exhibit the typical fractioning pattern for the cyclopentadienyl rhenium tricarbonyl complexes, showing a signal with an m/z of 532 (based in ^{187}Re), assigned to the molecular ion [M^+], following by two important peaks with a value of 504 and 421 assigned to the loss of a CO ligand and the subsequent loss of a Cy group respectively.

Single crystals for X-ray diffraction studies, of (η^5-$C_5H_4PCy_2$)$Re(CO)_3$ was obtained by an supersaturated solution of the cyrhetrenylphosphine ligand in hexane (50 °C), the solution was sealed in a Schlenk tube under N_2 and keep to reach room temperature. The colorless crystals were separated from the solution and dried with a slow N_2 flow. Crystal data, data collection and refinement parameters are given in the Supplementary material (Table S1). The ORTEP drawings with the corresponding atom-labeling scheme and key bond lengths and angles, are shown in Fig. 1.

Most of the metrical parameters are quite similar to those measured in 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 92.0(2)° to 88.7(2)°, additionally, the bond distance Re—Cp(Centroid) present a value (1.958(14) Å) comparable to the reported for the (η^5-$C_5H_3Br(PCy_2)$)$Re(CO)_3$ ligand (1.971 Å) [13,15].

The degree of pyramidalization of the phosphorus atom can be estimated by the sums of the bond angles about the phosphorus, for this organometallic ligand the value is 306.02°. Interestingly, this parameter is significantly lower than the expected for idealized tetrahedral atom (328.4°), but comparable to those found in complexes (η^5-$C_5H_3BrPCy_2$)$Re(CO)_3$ and (η^5-$C_5H_2Br(PCy_2)_2$)$Re(CO)_3$ (306.1° and 304.5°; 308.5°, respectively). This behavior reflects the enhancement in the s character of the electronic lone pair over the phosphorous atom, mainly due to the electron-withdrawing effects of the cyrhetrenyl group, and thereby decreasing the basicity [15].

With the aim to get more inside on the catalytic activity of rhenium based phosphines we carried out a study of the catalytic properties of the dicyclohexilphosphino cyrhetrene, as part of a palladium (II) catalytic system, toward the Suzuki cross-coupling reaction of aryl bromides and chlorides (Scheme 2). The results of these studies are presented in Table 1.

Catalytic reactions were conducted under conditions similar to those popularized by Buchwald [16], using $Pd(OAc)_2$ as the palladium source (1 mol%), twice this amount (2 mol%) of the rhenium-containing phosphorus donor ligand, Cs_2CO_3 as the boron-activating base, toluene solvent, and elevated temperatures. The conversion of the biphenyls was determined by GC-chromatography in a Shimadzu GCMS-QP5050 and in a Thermo-Fisher TRACE GC 1300 chromatographer and conversions were calculated by relative integrations of GC peaks.

Data indicates, high activity of this catalytic system toward electronically and sterically un-activated substrates such as p-bromotoluene and 1-bromo-2,6-dimethylbenzene (Entry 1 and 4 respectively). As

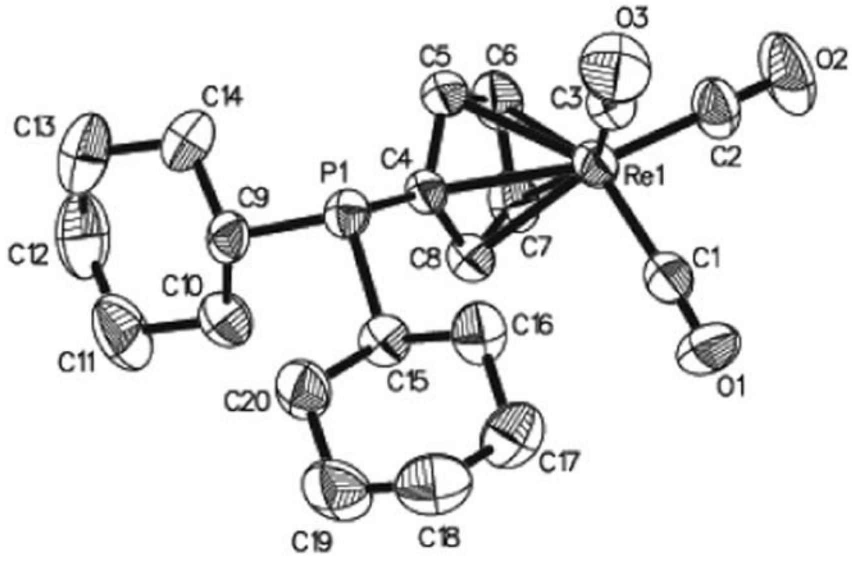

Fig. 1. ORTEP plot of dicyclohexylphosphinocyrhetrene, (η^5-$C_5H_4PCy_2$)$Re(CO)_3$, with displacement ellipsoids at the 50% probability level. Selected bond lengths (in Å) and bond angles (in deg.): Re1—C2, 1.909(5); Re1—C3, 1.915(6); Re1—Cp(Centroid), 1.958(14); P1—C4, 1.834(4); P1—C9, 1.848(5); P1—C15, 1.861(5); C1—Re1—C2, 88.7(2); C1—Re1—C3, 90.3(2); C2—Re1—C3, 92.0(2); Re1—C1—O1, 176.6(4); Re1—C2—O2, 177.9(5); Re1—C3—O3, 176.0(5); C4—P1—C9, 99.44(19); C4—P1—C15, 103.38(19) and C9—P1—C15, 103.2(2).