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New dimeric phosphine ylide copper (I) complexes: Synthesis, coordination behavior, and application in Suzuki cross-coupling reactions

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ABSTRACT

The reaction of the non-symmetric phosphorus ylides, $Ph_2P(CH_2)_nPPh_2C(H)C(O)PhR$ with CuCl in equimolar ratios using dry methanol as solvent give binuclear complexes of the type $[Cu(\mu\text{-}Cl)\{Ph_2P(CH_2)_nPPh_2C(H)C(O)PhR\}]_2$ ($n = 1$: R = Br (**1**), OCH_3 (**2**); $n = 2$: R = Br (**3**), OCH_3 (**4**)). X-ray analyses of **1** demonstrate the Cl bridged dimeric structures with P,C-chelated ligands. Characterizations of these compounds were carried out by FT-IR and multinuclear NMR technique. Elemental analysis indicate a 1:1 stoichiometry between the ylides and the Cu(I) chloride in the four complexes. The precursor complexes **1** and **3** are found to exhibit high catalytic activity in the Cu-catalyzed Suzuki cross-coupling reactions in an air atmosphere at medium catalyst loading in DMF as a solvent. The use of 5 mol% catalyst in the presence of Cs_2CO_3 allows the coupling reaction to proceed with moderate to excellent yields.

Phosphorus ylides are a group of very interesting ligands in organometallic chemistry; these compounds are also useful intermediates in organic synthesis and have been used as reducing agents in coordination chemistry [1–4]. The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [5–7]. The α-ketostabilized ylides derived from bisphosphines, viz., $Ph_2PCH_2PPh_2 = C(H)C(O)R$ and $Ph_2PCH_2CH_2PPh_2 = C(H)C(O)R$ (R = Me, Ph or OMe) [8], constitute an important class of hybrid ligands containing both phosphine and ylide functionalities and can exist in ylidic and enolate forms. These ligands can therefore engage in different kinds of bonding with metal ions [8–19]. P,C-coordination mode of stabilized phosphorus ylides have been previously observed for Pd(II), Pt(II), Rh(I), Hg(II) species [8–18]. In 1975, Yamamoto et al. [20] reported Cu(I) complexes of phosphorus ylides of the type $(C_6H_5)_3PCHR$ (R = H, CH_3, $CH(CH_3)_2$). The use of copper complexes in the Suzuki coupling has been studied in recent years. Suzuki cross-coupling reactions have proven to be important transformations, as the resulting biaryl products are extremely valuable intermediates in organic synthesis, natural products, and biological molecules [21–27]. The general Suzuki coupling procedures involves the use of palladium phosphine complexes as catalysts [21–23]. Nevertheless, the high price of Pd renders commercial processes based on Pd less attractive unless extremely active and/or recyclable catalysts are available. For these reasons, much recent attention has been attracted on employing less expensive transition metal catalyst complexes, [23–33] in particular, copper, to replace the palladium. However, only a few copper-catalyzed Suzuki cross-coupling procedures exist [21–23,28,29,34,35]. Phosphorus ylides as a particular ligand has been specially used in C–C coupling reactions. Our previous research showed that symmetrical and non-symmetrical phosphorus ylides are versatile ligands and their palladium complexes are quite efficient cross-coupling catalysts [36–39]. Excellent activities observed with Pd (II) complexes of phosphine ylide ligands encouraged us to explore the chemistry of copper compounds. In the first, we have now focused our attention in the study of the coordination modes adopted by the resonance stabilized ylides when ligated to Cu(I). Second, we have worked on catalytic activity of the new copper (I) phosphine mono-ylide Complexes **1** and **3** in Suzuki cross-coupling reactions.

Reaction of the ligands with CuCl in methanol (1:1) yielded the binuclear complexes [40]. The X-ray structure of complex **1** demonstrates the five-membered chelate ring in which the ligands were chelated to the metals through the free phosphine group and the ylidic carbon atom. The ^{31}P NMR spectra of complexes **1** and **2** show two doublets that indicate the presence of the PCH and PPh_2 groups in these molecules (see Supplementary material). The significant downfield shift of the signals due to PCH groups indicates C-coordination of the ligand to Cu center [15]. The strong downfield shifting and broadening of doublets of PPh_2 groups due to rapid equilibrium with non-coordinated forms is other clear evidence for P-coordinating of the ligands [15]. The identical pattern in chemical shift values in the ^{31}P NMR spectra of complexes **3** and **4** suggest similar structures with complexes **1** and **2**. The P, C-chelation of ligands has been previously observed for mercury halide and palladium complexes [41–43]. The downfield shift and broadening of the doublet signal was observed due to methinic (PCH) group in the ^1H NMR spectra of complexes **1** and **2** [41]. Similar behavior was observed earlier in the case of ylide complexes of platinum(II) chloride

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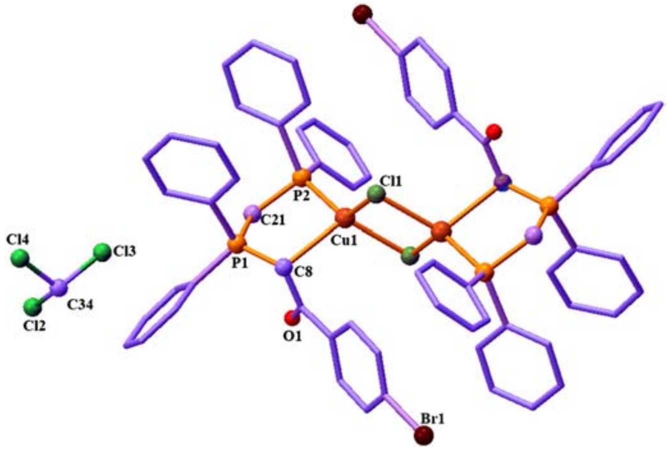


Fig. 1. X-ray crystal structure of **1**. Hydrogen atoms are omitted for clarity.

[44]. In the case of complexes **3** and **4,** these signals are weak and broad due to low solubility in common solvents. The up-field shift of the signals due to ylidic carbons in the ^{13}C NMR spectra of complexes **1** and **2** also are an evidence for C-coordination [45,46]. The ^{13}C NMR shift of the CO signal (180 to 187 ppm) with reference to the parent ylides indicates a much lower shielding of the carbon of the CO group in these complexes. Neither H-Cu nor P-Cu coupling was observed at room temperature in the spectra; possibly a fast equilibrium between the complexes and the free ylides is responsible for the failure to observe NMR coupling or two diastereoisomers. The ν CO for ylides are observed in lower frequencies than those of the related phosphonium salts as in the case of other resonance stabilized ylides [47], suggesting some removal of electron density in the C = O bond. As noted previously [48–50], the coordination of the ylide through carbon or oxygen causes a significant increase or decrease, respectively, in the ν (CO) frequency. The infrared absorption bands observed for these complexes around 1540 cm^{-1} indicate coordination of the ylide through ylidic carbon atom [15].

The crystals of complex **1** were grown by the slow evaporation of the chloroform solution. An ORTEP diagram of the complex with atomic numbering scheme is shown in Fig. 1. Relevant parameters concerning data collection and refinement are given in supplementary material and selected bond distances, and angles are collected in Table S1 and Table S2, respectively.

The complex consists of centrosymmetrical dimeric units with the two chlorine atoms bridging the two copper atoms. The tetrahedral coordination of the copper atoms is achieved by P,C-chelating the ylide. Two ylidic ligands are, respectively, located on the opposite sides to minimize the repulsion between them. The angles subtended by the ligand at the Cu(I) center in **1** vary from 93.48 to 126.11, indicating a distorted tetrahedral environment. The Cu–P bond lengths (~2.19 Å) are in the usual range for Cu(I) complexes. The Cu · · · Cu distance of 3.115 Å (**1**) is longer than two van der Waals radii for copper (2.8 Å) [51], indicating the absence of significant bonding interactions between the Cu atoms in the molecular structures (see Fig. 2). The non-classical C–H…Cl and C = O…H–C hydrogen bonds determine the structural assembly in this compounds and are shown in supplementary material (Fig. S1).

It is well established that palladium complexes containing phosphine ligands, which combines both good donor strength and π-accepting capacity, always have a high catalytic activity in Suzuki cross-coupling reactions [52–55]. The copper-catalyzed Suzuki cross-coupling reaction has received a lot of attention in the past few years and has already been reviewed [28,34,56–60]. Based on these prior examples, our group began a study of using phosphine mono-ylide copper (I) complexes **1** and **3** for Suzuki cross-coupling reactions in the first time. These copper complexes are soluble in a variety of organic solvents that have been shown to be effective as additives in the modern copper-catalyzed cross-coupling reactions. These reactions are general, tolerate a variety of functional groups and substrates, avoid the use of expensive and/or air-sensitive additives and overcome some of the limitations of the palladium-catalyzed analogues. The model reaction of iodobenzene with phenylboranic acid achieved maximum yields when Cs_2CO_3 was used as a base, DMF as a solvent, and the reaction occurred at 130 °C under aerobic conditions (see Ref. [36,37,39]).

Catalyst loading tests were performed to determine the catalytic efficiency of the catalyst in the presence of DMF and Cs_2CO_3. In order to optimize the reaction condition for the coupling reactions, different amounts of catalyst (mol%) were taken and the results are summarized in Table S3 (see supplementary material). Various catalyst concentrations were also tested and 5 mol% gave the best result. These are the indications of an effective catalytic system that merits more downstream explorations.

In the first, the four copper(I) complexes has been observed to catalyze the targeted coupling reactions, but because of their similar structural and catalytic efficiency, we have investigated the catalytic activity of complex **1** and **3** in this work. These Cu(I) complexes were used for the first time in Suzuki cross-coupling reactions.

Under above conditions (base: Cs_2CO_3; solvent: DMF; temperature: 130 °C), we examined the scope of the reaction of phenylboranic acid with various aryl halides bearing electron-donating and electron-withdrawing groups in the presence of 5 mol% of catalyst **1** and the results are shown in Table 1. A number of aryl iodides, bromides, and

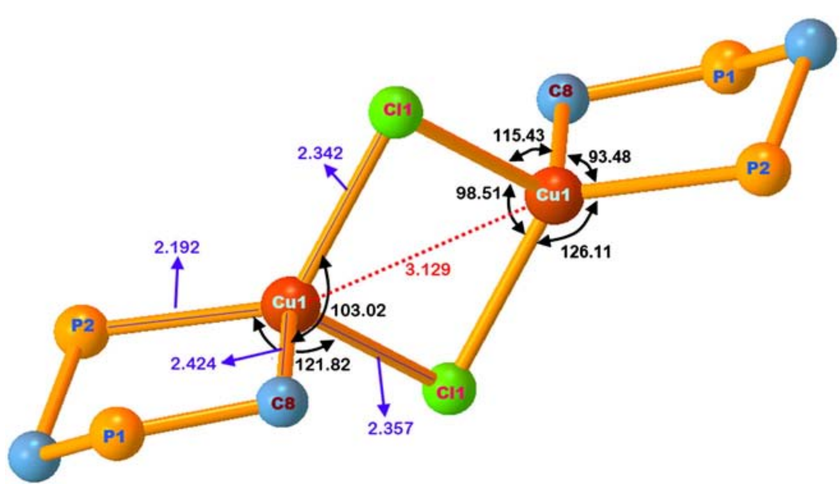


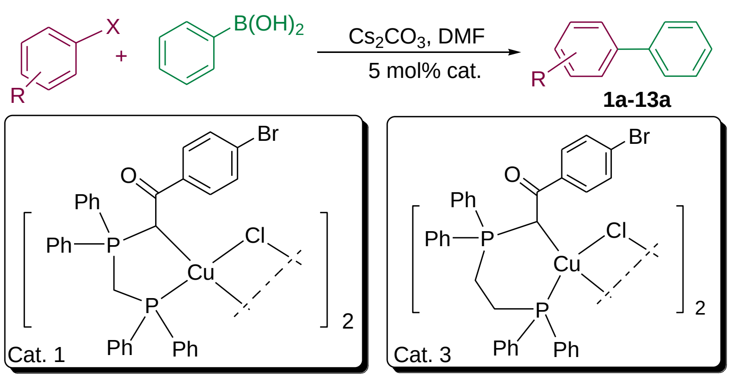
Fig. 2. Selected bond lengths and bond angles for **1**.

chlorides have been successfully coupled with phenylboranic acid. Electron-donating groups (Table 1, **3a**, **11a** and **13a**) and electron-withdrawing groups (Table 1, **1a**, **2a**, **6a**, **8a** and **10a**) were successfully coupled to phenylboranic acid in moderate to good yields. Moderate yields are realized for the coupling of electronically deactivated 4-methyl bromobenzene with phenylboronic acid (Table 1, **3a**, 62%). This condition also allows for the coupling of 2-bromothiophene as a heterocyclic substrate (Table 1, **7a**, 60%). It is notable that the use of deactivated aryl bromides (Table 1, **3a**) as well as activated or electron-poor ones (Table 3, **1a**, **2a** and **8a**) also resulted in good yields. However, the coupling of neutral bromobenzene with phenylboronic acid resulted in coupling with good yield (Table 1, **5a**, 63%). As expected, satisfactory results were obtained with the 1-bromonaphthalene of the phenylboronic acid (Table 1, **4a**, 62%). Then, we tried to examine whether aryl chlorides were active for the Suzuki reaction. Generally, it is difficult to activate C–Cl bonds because of their relative inertness [61–63]. Despite the economical advantages of employing aryl chlorides in the Suzuki reaction, an electron neutral chlorobenzene resulted in a 41 % yield (Table 1, **9a**), and a moderate yield was obtained with an activated chloroarenes (Table 1, **10a**, 50%). The reaction of chlorotoluene proceeded smoothly to provide the desired product in poor yield (Table 1, **11a**, 40%). The experimental data showed that the order of reactivity of the phenyl halides is PhI > PhBr > PhCl with the iodobenzene being most active toward coupling reactions (Table 1, **12a**, 82%). It was gratifying to note that 4-methyl iodobenzene underwent coupling reaction with phenylboronic acid to afford high yield of desired products under similar condition (Table 1, **13a**, 83%). The efficiency of Cu(I) phosphine catalyst precursor relative to Pd(II) catalysts is attributed to the electronic modification of the coordinated phosphorus ylides and bulkiness of the phosphine ligands [64,65].

The catalytic activity of **3** was then evaluated for the Suzuki cross-coupling reaction. In an effort to understand how the complexes **1** (containing five-membered P,C-chelate ring) and **3** (six-membered P,C-chelate ring) could promote the Suzuki cross-coupling reaction most efficiently, different steric properties of phosphine moieties and backbones (derived from dppm or dppe) were examined under similar reaction conditions. The complexes of bulky phosphine ligands is presumed to be able to accelerate the reaction rate and perceived as a potential candidate for an effectively catalytic performance [64–67].

Therefore, we have checked the six-member ring catalyst precursor **3** in Suzuki cross-coupling reaction. Using the available optimal conditions, the scope of the Suzuki cross-coupling reaction was investigated. High catalytic efficiencies were observed for the coupling of a variety of aryl halides with phenylboronic acid (see Table 1). As can be seen in Table 3, the electron-withdrawing groups (Table 1, **1a** (85%), **2a** (80%), **8a** (85%), and **10a** (63%)) and electron-donating groups (Table 1, **3a** (82%), **11a** (61%)) were successfully coupled to phenylboronic acid in good to excellent yields. For instance, the reactions between 4-bromonitrobanzene and phenylboronic acid can be carried out using 5 mol% of **3** in 24 h at 130 °C to give the corresponding of the products (Table 1, **1a** (85%)). The products obtained from the coupling of 1-bromonaphthalene and 2-bromothiophene with phenylboronic acid resulted in 80% and 77% yield, respectively (Table 1, **4a** and **7a**). We further investigated the catalytic activity for the coupling of aryl chloride and their derivatives efficiently reacted with phenylboronic

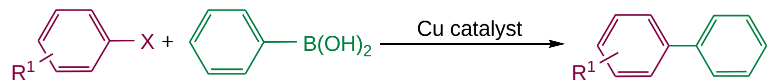
Table 1
Suzuki cross-coupling reaction of various aryl halides with phenyl boronic acid catalyzed by Cu (I) complexes **1** and **3**.[a]



Ar-X	*p*-O_2N-Ph-Ph	Product no.	Catalysts (yield %)[c]
p-O2N-Ph-Br	*p*-OHC-Ph-Ph	**1a**	**1** (64), **3** (85)
p-OHC-Ph-Br	*p*-Me-Ph-Ph	**2a**	**1** (61), **3** (80)
p-Me-Ph-Br	$C_{10}H_7$-Ph	**3a**	**1** (62), **3** (82)
C10H7-Br[d]	Ph-Ph	**4a**	**1** (62), **3** (80)
Ph-Br	*p*-HO_2C-Ph-Ph	**5a**	**1** (63), **3** (83)
p-Br-Ph-CO_2H	C_4H_3S-Ph	**6a**	**1** (67), **3** (85)
C_4H_3SBr[e]	C4H3S-Ph	**7a**	**1** (60), **3** (77)
p-CH_3OC-Ph-Br	*p*-CH_3OC-Ph- Ph	**8a**	**1** (65), **3** (85)
Ph-Cl	Ph-Ph	**9a**	**1** (41), **3** (57)
p-CH_3OC-Ph-Cl	*p*-CH_3OC-Ph- Ph	**10a**	**1** (50), **3** (63)
p-Me-Ph-Cl	*p*-Me-Ph-Ph	**11a**	**1** (40), **3** (61)
Ph-I	Ph-Ph	**12a**	**1** (82), **3** (91)
p-Me-Ph-I	*p*-Me-Ph-Ph	**13a**	**1** (83), **3** (93)

[a] *Reaction conditions:* aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), Cs_2CO_3 (1.5 mmol), DMF (2 ml), catalyst (5 mol%), 130 °C, 24 h, under air.
[b] Products were identified by comparison of their ^1H and ^{13}C NMR spectral data those reported in the literature (see Ref. [36,37]).
[c] Isolated yields.
[d] 1-Bromonaphthalene.
[e] 2-Bromothiophene.

Table 2
Compression with other catalytic system catalyzed with Cu(I) complexes.



Entry	Aryl halide	[Cu] catalyst	mol%	Conditions	Yield (%)	Ref.
1	*p*-Me-Ph-I	Cu colloid	2	K_2CO_3, DMF, 110 °C, 8 h	100	[28]
2	*p*-OHC-Ph-Br	[{Cu(*N*-(aryl)pyridine-2-aldimines)I}$_2$]	5	Cs_2CO_3, PEG[a], 120 °C, 24 h	90	[35]
3	*p*-O_2N-Ph-Br	CuI/DABCO [b]	10	Cs_2CO_3, DMF, 130 °C, 24 h	28	[58]
4	*p*-I-Ph-I	CuI/DABCO/TBAB [c]	10	Cs_2CO_3, DMF, 130 °C, 24 h	80	[59]
5	Ph-Br	Cu powder/I_2	10	K_2CO_3, PEG, 140 °C, 36 h	91	[75]
	Ph-I	Cu powder	10	K_2CO_3, PEG, 110 °C, 12 h	99	[75]
6	Ph-Br	[Cu(μ-Cl){Ph_2PCH_2 Ph_2C(H)C(O)PhBr}]$_2$	5	Cs2CO3, DMF, 130 °C, 24 h	63	This work
	p-Me-Ph-I				83	
7	Ph-Br	[Cu(μ-Cl){$Ph_2P(CH_2$	5	Cs_2CO_3, DMF, 130 °C, 24 h	83	This work
	p-Me-Ph-I	CH_2PPh_2C(H)C(O)PhBr}]$_2$			93	

[a]Polyethyleneglycol.
[b]1,4-Diaza-bicyclo[2.2.2]octane.
[c]n-Bu_4NBr.

acid to yield biphenyls in good yields (Table 1, **9a–11a**). The aryl iodides bearing an electron-donating or neutral were obtained good yields (Table 1, **12a** (91%) and **13a** (93%)).

As can be seen in Table 1, the reaction of aryl bromide with electron donating group, catalyst **1** gave moderate yields of corresponding products, whereas catalyst **3** further increased the yield (Table 1, **3a** (cat. **1**, 62%, cat. **3**, 82%) and **11a** (cat. **1**, 40%, cat. **3**, 61%)). Comparatively, catalyst **3** bears dppe groups on the backbone (forming of six-membered ring) and thus could exhibit a certain steric hindrance on the catalytic center. Similar to previous reports about bulky phosphine ligands [68–71], the bulkier phosphine Cu(I) complex **3** showed higher activities than their analogues **1**. For example, catalyst **1** gave moderate yield with neutral aryl halides (Table 1, **5a**, **9a** and **12a**), which was much less effective than that of catalyst **3**. These results can be ascribed to the increase in steric hindrance of the catalysts, leading to an increase in the rate of the elimination process [72].

According to the literature [64–67,73–75], the best results for Suzuki coupling of aryl halides were achieved with phosphorus-containing complexes or with palladacycles modified by carbenes. A comparison of catalytic efficiency among the most active Cu complexes known to catalyze the Suzuki coupling of aryl halides with phenylboronic acid is discussed in the Table 2. The catalyst precursors **1** and **2** were the first examples of a unsymmetrical phosphine mono-ylide Cu(I) complexes while allowing the use of various aryl halides in Suzuki coupling.

The present study describes the synthesis and characterization of first Cu(I) complexes with stabilized phosphorus ylides. On the basis of the physico-chemical and spectroscopic data, we propose P,C-coordination to the metal, which is further confirmed by the X-ray crystal structures. However, all previous studies focused on Pd(II) systems and no study on the use of dinuclear phosphine mono-ylide Cu(I) complexes as pre-catalysts in Suzuki reactions have been reported to date. The Cu(I) complexes were found to be a highly active catalyst for the Suzuki cross-coupling of a range of various aryl halides with phenylboronic acid.

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Appendix A. Supplementary material

The ligand preparation methods, materials and physical measurements, X-ray crystallography data, determination of catalyst concentration and selected ^{31}P, ^{13}C and ^{1}H NMR spectra of some compounds can be found in the online version. A representation of part of the unit cell contents of **1** and crystal data and structure refinement are presented supplementary material. The crystallographic data for the structural analysis of **1** have been deposited with Cambridge crystallographic center, CCDC No. 864861 Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union roads, Cambridge.CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk). Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.08.010.

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[40] The copper complexes **1–2** were synthesized by the following procedures: To a solution of CuCl (0.5 mmol) in dry methanol (10 ml), a solution of phosphorus ylide (0.5 mmol) also in dry methanol (10 ml) was added dropwise at 25 °C and stirred for 4 h. The separated solid was filtered, and recrystallized in dichloromethane. (**1**): Yield: 0.564 g (83 %). M.p. 155–158 °C. Anal. Calc. for $C_{66}H_{54}Br_2Cl_2Cu_2O_2P_4$: C, 58.25; H, 4.00. Found: C, 58.48; H, 4.13 %. IR (KBr, cm^{-1}): 1533 (CO). ^1H NMR ($CDCl_3$) δ_H (ppm): 3.99 (dd, 2H, CH_2, $^1J_{PH} = 12.8$ Hz), 4.95 (dd, 1H, PCH, $^1J_{PH} = 17.4$ Hz), 7.24–8.05 (m, 24H, Ph). ^{31}P NMR ($CDCl_3$) δ_p (ppm): -17.72 (br, –PPh_2), 20.60 (d, –PC(H), $^2J_{P\text{-}P} = 67.7$ Hz). ^{13}C NMR ($CDCl_3$) δ_C (ppm): 29.63 (dd, CH_2, $^1J_{PC} = 63.2$ Hz), 40.93 (dd, CHP, $^1J_{PC} = 92.6$ Hz), 124.02–137.96 (Ph), 187.04 (s, CO). (**2**) Yield: 0.505 g (80 %). M.p. 156–157 °C. Anal. Calc. for $C_{68}H_{60}Cl_2Cu_2O_4P_4$: C, 64.66; H, 4.79. Found: C, 64.93; H, 4.95%. IR (KBr, cm^{-1}): 1531 (C = O). ^1H NMR ($CDCl_3$) δ_H (ppm): 4.01 (dd, 2H, CH_2, $^1J_{PH} = 12.8$ Hz), 3.81 (s, 3H, OCH_3), 4.95 (dd, 1H, PCH, $^1J_{PH} = 17.2$ Hz), 6.90–8.18 (m, 24H, Ph). ^{31}P NMR (DMSO-d_6) δ_p (ppm): -21.42 (br, –PPh_2), 23.93 (d, –PC(H), $^2J_{P\text{-}P} = 71.0$ Hz).^{13}C NMR ($CDCl_3$) δ_C(ppm): 30.07 (dd, CH_2, $^1J_{PC} = 66.0$ Hz), 38.88 (dd, CHP, $^1J_{PC} = 90.8$ Hz), 55.31 (s, OCH_3), 113.22–161.96 (Ph), 188.09 (s, CO). General procedure for complexes **3–4**: To a solution of CuCl (0.5 mmol) in dry methanol (10 ml), a solution of phosphorus ylide (0.5 mmol) also in dry methanol (10 ml) was added drop wise at 25 °C and stirred for 7 h and then concentrated to a ca. 2 ml in volume and treated with *n*-hexane (ca. 15 ml) to afford a yellow solid. (**3**): Yield: 0.562 g (81 %). M.p. 125 °C (decomposes). Anal. Calc. for $C_{68}H_{58}Br_2Cl_2Cu_2O_2P_4$: C, 58.81; H, 4.21. Found: C, 58.96; H, 4.46 %. IR (KBr, cm^{-1}): 1513 (CO). ^1H NMR ($CDCl_3$): δ_H (ppm): 2.54 (br, 2H, CH_2), 3.12 (br, 2H, CH_2), 4.26 (br, 1H, PCH); 6.92–8.23 (m, 24H, Ph). ^{31}P NMR ($CDCl_3$): δ_p (ppm): -10.42 (br, –PPh_2), 15.46 (d, –PC(H), $^3J_{P\text{-}P} = 61.2$ Hz). (**4**) Yield: 0.529 g (82 %). M.p. 110 °C (decomposes). Anal. Calc. for $C_{70}H_{64}C_{l2}Cu_2O_4P_4$: C, 65.12; H, 5.00. Found: C, 65.41; H, 5.26 %. IR (KBr, cm^{-1}): 1663 (CO). ^1H NMR ($CDCl_3$): δ_H (ppm): 2.05 (br, 2H, C_{H2}), 3.57 (br, 2H, CH_2), 3.80 (s, 3H, OCH_3), 5.60 (br, 1H, PCH), 6.71–7.98 (m, 24H, Ph). ^{31}P NMR ($CDCl_3$): δ_p (ppm): -10.58 (br. d, –PPh_2 $^3J_{P\text{-}P} = 55.0$ Hz), 15.22 (d, –PC(H), $^3J_{P\text{-}P} = 59.3$ Hz).
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