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Structural features and catalytic reactivity of

$[Pd{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3-\kappa P, P']I_2]$ and related complexes in

hydroalkoxycarbonylation and Suzuki-Miyaura C-C cross-coupling reactions

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Dedicated to Professor Spyros Perlepes, on the occasion of his 65th birthday.

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Abstract

The synthesis, as well as the structural and spectroscopic characterization of the palladium(II) complex $[Pd\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3-\kappa P, P^{-1}I_2]$, bearing the bis(phosphino)amine ligand $(P,P) = (Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$, is described. X-ray crystallography studies revealed a square planar PdP₂I₂ coordination sphere, the structural features of which are compared with those of analogous nickel(II), palladium(II) and platinum(II) complexes. The three complexes $[Pd(P,P)X_2]$, X = Cl, Br, I, along with $[Pd\{(Ph_2P)_2N((S)-CHPhMe)-\kappa P, P^{-1}Cl_2]$ and $[Pd\{(Ph_2PSe)(Ph_2P)N((S)-CHMePh)-\kappa P, Se\}Cl_2]$, were tested as catalysts in homogeneous hydroalkoxycarbonylation reactions. The hydroalkoxycarbonylation of styrene proved to be perfectly regioselective towards the branched ester. Complex $[Pd(P,P)Cl_2]$ showed remarkably higher activity compared with that of $[Pd(P,P)X_2]$, X = Br, I. Furthermore, complex $[Pd(P,P)I_2]$ was studied as a homogeneous catalyst precursor in the Suzuki-Miyaura C–C coupling reaction between aryl bromides and phenylboronic acid. Complex $[Pd(P,P)I_2]$ was immobilized onto STx–1 montmorillonite clay and the catalytic reactivity of the heterogenized catalyst was also investigated in both hydroalkoxycarbonylation and Suzuki-Miyaura reactions.

1. Introduction

The organo-transition-metal chemistry has reached the stage of specific applications both in the synthesis of simple building blocks and of more complex structures of practical importance, via selective functionalization reactions catalyzed by transition metal complexes [1, 2]. In many instances, the catalytic activity and (chemo-, regio- and enantio-) selectivity can be finely tuned by the steric and electronic properties of the ligands [3]. In this respect, phosphino-ligands, containing P as donor atoms, are of special importance. In addition to fundamental "text-book" examples, many general treatises in related books [4-6], reviews [7], as well as numerous original research papers, demonstrate the increasing role of transition metal-phosphine complexes, both in chemical synthesis and catalysis. Among various classes of P-containing ligands, the P,N-heterobidentate and P,N,P-heteroterdentate ligands, containing soft and hard donor atoms, have been extensively explored [8]. These ligands are of high interest because of their hemilabile character, since they contain both substitutionally inert and labile donor atoms. In addition, their PNP backbone is amenable to a great variety of modifications, altering the stereochemical or electronic properties of the system. Along these lines, the coordination chemistry of bis(phosphino)amine type of ligands, (R₂P)N(R')(PR₂), has been extensively investigated [9]. These ligands are readily coordinated to a host of transition metals in a bidentate fashion, affording, in many instances, catalytically active metal complexes, as recently reviewed by Braunstein and co-workers [10]. More specifically, chromium complexes have been shown to be catalytically active in the oligomerization of olefins [11-14], while nickel(II) complexes in the polymerization [15] and oligomerization [16, 17] of ethylene, the vinyl type polymerization of norbornene [18, 19] and the Kumada C-C coupling reactions [20, 21]. It should be stressed that among the Kumada coupling nickel(II) catalysts, complex [Ni{(Ph₂P)₂N(CH₂)₃Si(OCH₃)₃- $\kappa P, P'$ Cl₂], containing the (P,P) = (Ph₂P)₂N(CH₂)₃Si(OCH₃)₃ ligand, has been immobilized onto

siliceous mesoporous sieves via its $-Si(OCH_3)_3$ anchoring group, affording an active heterogenized catalyst [21]. The analogous $[Pd(P,P)X_2]$, X = Cl, Br, complexes have been recently synthesized and investigated by some of us, as either homogeneous or heterogenized (onto STx–1 montmorillonite clay) catalysts in Suzuki-Miyaura C–C coupling reactions [22], following previously reported studies on analogous palladium(II) complexes [23-27].



Scheme 1. Drawings of complexes (a) $[Pd(P,P)X_2]$, X = Cl, Br, I; (b) $[Pd\{(Ph_2P)_2N((S)-CHPhMe)-\kappa P, P'\}Cl_2]$ [28]; (c) $[Pd\{(Ph_2PSe)(Ph_2P)N((S)-CHMePh)-\kappa P, Se\}Cl_2]$ [29].

In the work presented herein, the synthesis, as well as the X-ray crystallographic and spectroscopic characterization of $[Pd(P,P)I_2]$, is described. Furthermore, the three complexes $[Pd(P,P)X_2]$, X = Cl, Br, I, along with $[Pd\{(Ph_2P)_2N((S)-CHPhMe)-\kappa P, P'\}Cl_2]$ [28] and $[Pd\{(Ph_2PSe)(Ph_2P)N((S)-CHMePh)-\kappa P, Se\}Cl_2]$ [29] (Scheme 1), were tested as catalysts in homogeneous hydroalkoxycarbonylation reactions. With respect to the latter, it has been well known for a long time, that the pharmacological importance of the 2-aryl-propionates, the intermediates for nonsteroidal antiinflammatory agents (NSAI), rendered the corresponding vinylaromatics favorite substrates in hydroalkoxycarbonylation reactions [30-33]. In addition to

vinylaromatics, various other unsaturated compounds of biological importance have been used as substrates and were converted to the corresponding esters, revealing the synthetic potential of the hydroalkoxycarbonylation reaction. For instance, this reaction has been employed for the functionalization of steroid and terpene frameworks [34-39]. It has also been shown that lactones can be synthesised via high-yielding intramolecular hydroalkoxycarbonylation reactions, *i.e.* in the carbonylation of hydroxy-olefins [40]. Comparisons among the $[Pd(P,P)X_2]$, X = Cl, Br, I, catalyst precursors enable the study of the effects of the halogeno X⁻ ligand nature on the observed catalytic reactivity exerted by palladium(II) complexes containing similar Pd-P-N-P four-membered chelate rings. Furthermore, the reactivity of [Pd(P,P)I₂], as a homogeneous catalyst precursor in Suzuki-Miyaura cross-coupling reactions, was also explored. Complex [Pd(P,P)I₂] was immobilized onto STx-1 montmorillonite clay and the catalytic reactivity of the $[Pd(P,P)I_2]/Mont,$ heterogenized catalyst, also investigated in both was hydroalkoxycarbonylation and Suzuki-Miyaura reactions.

2. Experimental

2.1 Materials, equipment and methods

An inert (Ar) atmosphere and Schlenk techniques were employed for all synthetic experiments. Prior to their use, all solvents (DMF, dichloromethane, n-hexane) were dried by standard techniques [41]. The $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ ligand was synthesized via the reaction between Ph_2PCl and $NH_2(CH_2)_3Si(OCH_3)_3$, according to a published method [42]. The synthesis of complexes $[Pd(COD)X_2]$, X = Cl, Br; COD = 1,5-cyclooctadiene [43], $[Pd(P,P)X_2]$, X = Cl, Br [22], $[Pd\{(Ph_2P)_2N(CHMePh)-\kappa P, P^{-1}Cl_2]$ [28] and $[Pd\{(Ph_2PSe)(Ph_2P)N(CHMePh)-\kappa P, P^{-1}Cl_2]$ [28] and $[Pd\{(Ph_2PSe)(Ph_2P)N(Ph_2P)$

 $\kappa P, Se$ [Cl₂] [29], was carried out according to literature procedures. All the other chemicals were commercially available.

¹H and ³¹P NMR spectra were recorded in CDCl₃ on a Varian 300 MHz spectrometer. Chemical shifts δ are reported in ppm relative to CHCl₃ (7.26 ppm) in ¹H NMR spectra. ³¹P NMR spectra are referenced to H₃PO₄ (85%). Samples of the catalytic reactions, as well as of the isolated epimers, were analysed with an MS (Agilent 6300) (electronspray ionizer, eluent: methanol (0.1 v/v% formic acid), GC-Varian 3400 CX equipped with FID detector and Varian Saturn 2000 GC-MS-MS System. The FT-IR spectra were monitored in the region of 400-4000 cm⁻¹ in KBr pellets, using an IRAffinity-1 SHIMADZU spectrometer. HRMS were recorded with a Thermo Scientific LTQ OrbitrapVelos (ESI) spectrometer.

2.2 Synthesis of $[Pd(P,P)I_2]$ and preparation of $[Pd(P,P)I_2]/Mont$

To a solution of complex $[Pd(P,P)Cl_2]$ (100 mg, 0.138 mmol) in 10 mL of acetone, were added 207 mg of NaI (1.380 mmol), under inert atmosphere and vigorous stirring. The dark yellow solution was stirred at room temperature for 2 h. After acetone was completely removed under vacuum, 10 mL of CH₂Cl₂ were added to the resulting solid. The mixture was filtered in order to remove the inorganic salts. Subsequent addition of n-hexane (20 mL) to the filtrate led to the formation of a yellow solid, which was filtered and dried under vacuum. Yield: 103 mg, 82 %. HRMS (positive ESI-MS, Fig. S1, Supplementary Material): calcd for C₃₀H₃₅I₂NNaO₃P₂PdSi [M+Na]⁺ 929.8878, found 929.8898; calcd for C₃₀H₃₅I₂KNO₃P₂PdSi [M+K]⁺ 945.8617, found 945.8634. IR (KBr, cm⁻¹): 513 (s), 558 (m), 693 (s), 741 (s), 869 (s), 1098 (s), 1430 (s), 2820 (w), 2931 (w). ¹H NMR (300 MHz, CDCl₃): δ 0.20 (t, 2H, Si-CH₂), 1.20 (m, 2H, -CH₂-CH₂-Si), 1.60, 2.80 (m, 2H, N-CH₂), 3.40 (s, 9H, Si-OCH₃), 7.30, 7.4 - 8.0 (m, 20H, H_{arom}). ³¹P NMR

(121.5 MHz, CDCl₃): δ 24.2. UV-Vis (CH₂Cl₂), [λ (nm), ϵ (M⁻¹cm⁻¹)]: (418, 6800), (292, 23000), (263, 26150).

The $[Pd(P,P)I_2]$ complex was immobilized onto Na⁺-saturated STx–1 montmorillonite clay (Clay Minerals Society Repository, University of Missouri - Columbia), by following a procedure described in the literature [22]. A typical electronic spectrum of $[Pd(P,P)I_2]$ dissolved in CH₂Cl₂ is presented in Fig. S2. For the immobilization experiment, the appropriate amount of $[Pd(P,P)I_2]$ was added onto the clay in CH₂Cl₂, so that after centrifugation of the mixture, the supernatant became colourless, indicating saturation of the immobilization capacity of the clay, under the conditions employed. Following this procedure, the Pd content of $[Pd(P,P)I_2]/Mont$ was determined to be 0.98% w/w (0.0496 mmol Pd per 540 mg of clay).

2.3 X-ray crystallography

Selected crystallographic data for complex [Pd(P,P)I₂] are listed in Table 1. A crystal of this complex (0.14×0.33×0.43 mm) was taken from the mother liquor and immediately cooled to -113 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer, using graphite monochromated Cu K α radiation. Data collection (ω -scans) and processing (cell refinement, data reduction and numerical absorption correction) were performed using the CrystalClear program package [44]. The structures were solved by direct methods using SHELXS-97 [45] and refined by full-matrix least-squares methods on F^2 with SHELXL2014/6 [46]. Further experimental crystallographic details: $2\theta_{max} = 130.00$ °; 224 parameters refined; $(\Delta/\sigma)_{max} = 0.031$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 1.07/-1.50$ e/Å³. Two of the methyl groups of the ligand are in disordered positions. Both oxygen and carbon atoms of the OCH₃ group are disordered with occupancies of 0.52(1) and 0.48(1). The hydrogen atoms were refined

isotropically at positions located either from difference Fourier Maps or at calculated ones using a riding model. All non-hydrogen atoms for both complexes were refined anisotropically.

2.4 Hydroalkoxycarbonylation reaction

In a typical experiment, 0.020 mmol of the palladium(II) complex was dissolved in 10 mL of toluene under argon. To this solution, 0.115 mL (1 mmol) of styrene and 1 mL of ethanol was added. The atmosphere was changed to carbon monoxide and the reaction mixture was kept at 100 °C for 24 h. After the given reaction time, the autoclave was depressurized and the reaction mixture was analysed by GC.

2.5 Suzuki-Miyaura reaction

In a typical experiment, 0.001 mmol of $[Pd(P,P)I_2]$, 1 mmol of substrate, 1.5 mmol of phenyl boronic acid and 2 mmol of K₂CO₃ were transferred in a Schlenk tube under argon. To this mixture, 1 mL of DMF (solvent) was added and the reaction mixture was kept at 25 °C or 100 °C for 24 h. The tube was allowed to cool at room temperature and the reaction was quenched by adding 5 mL of H₂O and then 5 mL of dichloromethane. The organic layer was separated, dried with Na₂SO₄, and analyzed by GC and GC-MS.

For the investigation of $[Pd(P,P)I_2]/Mont$ as an heterogenized catalyst, 218 and 11 mg of $[Pd(P,P)I_2]$ were used in the hydroalkoxycarbonylation and Suzuki-Miyaura C-C coupling reactions, respectively, to ensure the molar equivalent (0.02 and 0.001 mmol, respectively) of $[Pd(P,P)I_2]$.

Formula	C ₃₀ H ₃₅ I ₂ NO ₃ P ₂ PdSi
Fw	907.82
T (K)	160
radiation	Cu K _a
Crystal system	Orthorhombic
Space group	Pcmn
a (Å)	8.8958 (1)
b (Å)	18.2965 (3)
c (Å)	21.6512 (3)
Volume (Å ³)	3523.99 (9)
Ζ	4
D(calc), Mg m ⁻³	1.711
Abs. coef., μ , mm ⁻¹	19.43
GOF on F ²	1.04
Measured/ unique/	20868/3026/
reflections with $I>2\sigma(I)$	2893
R _{int}	0.106
R1 / wR2 (total)	0.044/0.116
R1 / wR2 [for I>2σ(I)]	0.043/0.114

Table 1.	Crystallographic	data for	$[Pd(P,P)I_2]$
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 $R_{1} = \sum (|F_{o}| - |F_{c}|) / \sum (|F_{o}|) \text{ and } wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}\}^{1/2}$ $w = 1 / [\sigma^{2}(F_{o}^{2}) + (\alpha P)^{2} + bP] \text{ and } P = [F_{o}^{2} + 2F_{c}^{2}] / 3, \alpha = 0.0561, b = 11.5547$

3. Results and Discussion

3.1. Synthesis and characterization of $[Pd(P,P)I_2]$.

Complex $[Pd(P,P)I_2]$ was prepared by employing $[Pd(P,P)CI_2]$ as a starting material and an excess of NaI in acetone, in order to substitute CI⁻ of the latter by I⁻ (Scheme 2). In the FT-IR spectrum of $[Pd(P,P)I_2]$, the band at 2831 cm⁻¹ is assigned to the $\{v_{sym}(C-H) Si(OCH_3)\}$ of the $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ ligand [42]. The assignment of the ¹H-NMR spectrum of $[Pd(P,P)I_2]$ is shown shown in Fig. S3. In the corresponding ³¹P-NMR spectrum, only one singlet at 24.2 ppm is observed (Fig. S4), suggesting the equivalence of the two P atoms of $[Pd(P,P)I_2]$. This signal is significantly upfield shifted compared with that of the ligand $(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$ at 62.2 ppm [42], due to shielding effects exerted by the metal-ligand coordination. Positive ESI-MS of the complex (Figure S1) showed peaks corresponding exactly to $[M+Na]^+$ and $[M+K]^+$.



Scheme 2. Synthesis of complex [Pd(P,P)I₂].

Suitable crystals of $[Pd(P,P)I_2]$ were grown by slow diffusion of hexane into a dichloromethane solution of the complex (CH₂Cl₂/n-hexane 1:3 v/v). The most important structural data are listed in Table 2. The structure of complex $[Pd(P,P)I_2]$ contains discrete

molecules exhibiting a square planar PdP_2I_2 core (Fig. 1). Palladium(II) is coordinated to the (P,P) chelate forming a four-membered Pd-P-N-P ring. The PdP_2I_2 core is almost planar, showing a minimal (0.003 Å) mean deviation from the best plane defined by the Pd, P and I atoms, with the Pd atom exhibiting the largest deviation (0.008 Å). The four-membered Pd-P1-N-P2 ring is essentially planar, with the mean deviation from the best plane defined by these four atoms being 0.026 Å. The structure exhibits a mirror plane of symmetry containing the atoms Pd, N, C21, C22, C23, C24, Si, O21 and C24 (Fig. 1).



Figure 1. Molecular structure and atom numbering of $[Pd(P,P)I_2]$ (ORTEP diagram, 50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. The atoms at disordered sites are shown in gray. Symmetry code: ('): x,-y+0.5,z.

A search in the Cambridge Structural Database (CSD) [47] for $[M\{(R_2P)_2N(R')-\kappa P, P'\}I_2]$ type of complexes (M = Ni, Pd, Pt), showed only one structure for M = Pd (bearing one Me and three Ph as R groups and R' = ⁱPr, CSD code TEXCAA [48]). In addition, the structure of the following M = Ni, Pt, complexes are reported: i) the nickel(II) complexes bearing the ligand with

R = ⁱPr and R' = H (CSD code UTEMOX) [49], R = Ph and R' = EtO₂CCH₂ (CSD code XEBGET) [50], R = Ph and R' = *p*-MeC₆H₄CH₂ (CSD code XEBGAP) [50], ii) [Ni(P,P)I₂] (CSD code PELGIZ) [17], iii) the platinum(II) complexes bearing the ligands with R = Ph, R' = 3-methoxycarbonylphenyl (CSD code BATQET) [51], R = [μ_2 -N-(dinaphtho[2,1-d:1',2'-g][1,3,6,2]dioxathiaphosphocin-8-yl-P)dinaphtho[2,1 d:1',2'g][1,3,6,2]dioxathiaphosphocin-8-amine-P'] and R' = Ph (CSD code SIYLIW) [52]. Selected bond lengths and angles of these structures, as well as those of complexes [Pd(P,P)X₂], X = Cl, Br [22], are also listed in Table 2.

Complex $[Pd(P,P)I_2]$ exhibits smaller bond lengths than those of the structurally characterized literature palladium(II) analogue (CSD code TEXCAA, Table 2). More specifically, the Pd–P and Pd–I bond lengths of $[Pd(P,P)I_2]$ are shorter by 0.0593 / 0.0513 Å and 0.099 / 0.0809 Å, respectively. Similarly, the P–N and N–C(R') bond lengths of $[Pd(P,P)I_2]$ are smaller by 0.04 / 0.048 Å and 0.04 Å, respectively, than those of the TEXCAA structure [48].

As expected, the Pd–I bond lengths of $[Pd(P,P)I_2]$ [2.5553(4) and 2.555(4) Å] are bigger compared with the Pd–Cl [2.3581(11) and 2.3536(11) Å] and Pd–Br [2.4609(5) Å] ones of the complexes $[Pd(P,P)X_2]$, X = Cl, Br [22] (Table 2). Interestingly, the Pd–P bond lengths of $[Pd(P,P)I_2]$ [2.1707(11) Å] are smaller compared with those of the X = Cl [2.2128(12) and 2.2210(11) Å], Br [2.2210(9) and 2.2210(9) Å], analogues. In the latter, the difference between the corresponding bonds is very small. Similarly, the P–N bond lengths of $[Pd(P,P)I_2]$ [1.646(3) Å)] are slightly smaller, compared with those of the X = Cl [1.688(4) and 1.690(4) Å], Br [1.688(3) Å], analogues, in which they are almost the same [22]. The endocyclic P-Pd-P angle of $[Pd(P,P)I_2]$ [71.01(6)°] is slightly smaller than those of the X = Cl [71.49(4)°] and X = Br [71.53(5)°] analogues [22].

The Pd–P bond lengths of $[Pd(P,P)I_2]$ ([2.1707(11) Å] are slightly larger compared with the Ni–P ones [2.1383(11) Å] of the analogous literature complex $[Ni(P,P)I_2]$ [17]. The same trend is also observed for the Pd–I bond lengths of the former [2.5553(4) and 2.555(4) Å] and the latter [2.5013(6) and 2.5013(6) Å]. As far as the bond angles are concerned, complex $[Pd(P,P)I_2]$ exhibits a significantly smaller endocyclic P-Pd-P angle [71.01(6)°] compared with the P-Ni-P one of $[Ni(P,P)I_2]$ [73.59(5)°], revealing the impact of the metal atom on the magnitude of this angle. On the other hand, the P-N-P angle of the former [100.0(3)°] is larger compared with that [98.6(2)°] of $[Ni(P,P)I_2]$.

The two platinum(II) complexes listed in Table 2 exhibit slightly larger P-Pt-P angles $\{72.89(4)^{\circ} [51] \text{ and } 71.35(5)^{\circ} [52]\}$ compared with the P-Pd-P angles of the palladium(II) complexes. The narrow range of the latter in $[Pd(P,P)I_2]$ [71.01(6)°] and the TEXCAA structure $[71.14(5)^{\circ}]$ [48], irrespective of the nature of their R and R' groups, suggests that the P-Pd-P angle in the two palladium(II) complexes is controlled by the formation of the Pd-P-N-P fourmembered ring.

13

Table 2. Selected bond lengths and angles of $[Pd(P,P)I_2]$ and related complexes. (P,P) denotes a $(R_2P)N(R')(PR_2)$ ligand.^{(a)-(f)}

Complex			bond	lengths (Å)			
Complex							
	M-P1	M-P2	M-X1	M-X2	N-P1	N-P2	N–C or H
$[Pd(P,P)I_2]$	2.1707(11)	2.1707(11)	2.5553(4)	2.555(4)	1.646(3)	1.646(3)	1.460(8)
$[Pd(P,P)Cl_2]$ [22]	2.2128(12)	2.2210(11)	2.3581(11)	2.3536(11)	1.688(4)	1.690(4)	1.494(6)
$[Pd(P,P)Br_2]$ [22]	2.2210(9)	2.2210(9)	2.4609(5)	2.4609(5)	1.688(3)	1.688(3)	1.483(7)
$[Pd(P,P)I_2] [48]^{(a)}$	2.222(1)	2.230(2)	2.6362(9)	2.6540(9)	1.694(5)	1.686(6)	1.50(1)
[Ni(P,P)I ₂] [17]	2.1383(11)	2.1383(11)	2.5013(6)	2.5013(6)	1.690(3)	1.690(3)	1.493(6)
$[Ni(P,P)I_2] [49]^{(b)}$	2.1463(8)	2.1443(8)	2.5197(5)	2.5396(5)	1.688(2)	1.681(2)	0.80(3)
$[Ni(P,P)I_2] [50]^{(c)}$	2.130(1)	2.132(1)	2.4935(7)	2.5107(7)	1.697(3)	1.696(3)	1.484(5)
$[Ni(P,P)I_2] [50]^{(d)}$	2.1366(8)	2.1285(8)	2.5150(6)	2.5093(7)	1.699(2)	1.699(2)	1.475(3)
$[Pt(P,P)I_2] [51]^{(e)}$	2.210(1)	2.211(1)	2.6381(6)	2.6545(8)	1.715(4)	1.710(4)	1.431(5)
$[Pt(P,P)I_2] [52]^{(f)}$	2.219(1)	2.230(1)	2.6363(4)	2.6265(4)	1.673(4)	1.675(4)	1.437(7)

Complex	bond angles (°)						
	X1-M-X2	X1-M-P1	X2-M-P2	P1-M-P2	M-P1-N	M-P2-N	P1-N-P2
$[Pd(P,P)I_2]$	95.31(2)	96.84(3)	96.84(3)	71.01(6)	94.40(14)	94.40(14)	100.0(3)
$[Pd(P,P)Cl_2]$ [22]	94.31(4)	96.08(4)	98.11(4)	71.49(4)	94.22(14)	93.93(13)	100.2(2)
$[Pd(P,P)Br_2]$ [22]	95.24(2)	96.60(3)	96.60(3)	71.53(5)	93.88(12)	93.88(12)	100.5(2)
$[Pd(P,P)I_2] [48]^{(a)}$	97.98(2)	94.37(4)	96.48(4)	71.14(5)	94.40(2)	94.40(2)	100.1(3)
[Ni(P,P)I ₂] [17]	97.65(3)	94.38(2)	94.38(2)	73.59(5)	93.83(11)	93.83(11)	98.6(2)
$[Ni(P,P)I_2] [49]^{(b)}$	99.75(2)	94.29(2)	94.38(2)	73.16(3)	93.49(9)	93.76(9)	98.7(1)
$[Ni(P,P)I_2] [50]^{(c)}$	99.56(2)	94.22(3)	93.85(3)	73.78(4)	94.2(1)	94.1(1)	97.9(2)
$[Ni(P,P)I_2] [50]^{(d)}$	100.18(2)	92.66(2)	93.64(2)	74.00(3)	93.58(7)	93.87(7)	98.1(1)
$[Pt(P,P)I_2] [51]^{(e)}$	97.00(1)	92.54(3)	97.71(3)	72.89(4)	93.4(1)	93.5(1)	100.1(2)
$[Pt(P,P)I_2] [52]^{(f)}$	89.73(1)	98.36(3)	100.52(3)	71.35(5)	93.7(2)	93.3(2)	101.6(2)

(a) The complex contains three R = Ph and one R = Me; R' = i Pr

(b) $R = {}^{i}Pr, R' = H$

(c) $R = Ph, R' = EtO_2CCH_2$

(d) $R = Ph, R' = p-MeC_6H_4CH_2$

(e) R = Ph, R' = 3-methoxycarbonylphenyl

(f) $R = [\mu_2-N-(dinaphtho[2,1-d:1',2'-g][1,3,6,2]dioxathiaphosphocin-8-yl-P)dinaphtho[2,1 d:1',2'g][1,3,6,2]dioxathiaphosphocin-8-amine-P')], R' = Ph_2 =$

3.3. Hydroethoxycarbonylation of styrene

In this work, styrene as a model substrate, was reacted with carbon monoxide and ethanol, in the presence of palladium(II) catalyst precursors $[Pd(P,P)X_2]$, X = Cl, Br, I. Toluene was used as solvent, under harsh carbonylation conditions (100 °C; 100-120 bar CO pressure) (Scheme 3).



Scheme 3. Potential products formed during the hydroethoxycarbonylation of styrene.

Although, in general, in the hydroalkoxycarbonylation of styrene (**A**), the formation of both branched (ethyl 2-phenylpropionate, **B**) and linear (ethyl 3-phenylpropionate, **C**) ester regioisomers (Scheme 3) is expected, in our experiments **C** was detected only in traces (< 0.2%) by GC-MS. In that sense, excellent regioselectivity towards the branched ester (**B**) was observed (Table 3). It has to be added that, in all cases, oligomerization (polymerization) of styrene took place to a very small extent, resulting in the formation of only traces of dimerization/polymerization products.

The activity of the $[Pd(P,P)X_2]$ catalysts was found to be strongly dependent on the nature of the coordinated halogeno X⁻ ligand. More specifically, 51%, 2% and <1% conversion was observed for X = Cl, Br and I, respectively (Table 3, entries 1-3). The activity of $[Pd(P,P)I_2]/Mont$ was also negligible (entry 4). For the best catalyst precursor, namely $[Pd(P,P)Cl_2]$, a higher conversion (89%) was observed for greater reaction time and at elevated pressure (entry 7).

For comparison, the palladium(II) literature complexes $[Pd\{(Ph_2P)_2N((S)-CHPhMe)-\kappa P, P'\}Cl_2]$ (b) and $[Pd\{(Ph_2PSe)(Ph_2P)N((S)-CHMePh)-\kappa P, Se\}Cl_2]$ (c) (Scheme 1) were also tested as catalysts in hydroethoxyarbonylation reactions. For the former complex, low activities were observed (entries 9, 10), providing TONs of 9 and 4, respectively, compared to a TON of 26 by complex $[Pd(P,P)Cl_2]$ (entry 1). The latter complex (c) was not stable under the harsh conditions used in the hydroalkoxycarbonylation reaction. The activity was negligible and some elemental selenium was formed in the reaction mixture during the catalytic experiments (entries 11, 12).

Adding $HCl_{(aq)}$ to the catalytic reaction mixtures was shown to be either detrimental (entries 5,10) or not to significantly increase the substrate conversion (entries 6, 12). On the other hand, addition of PPh₃ enhanced the catalytic activity (entry 8).

With respect to the hydroaryloxycarbonylation of styrene, according to a generally accepted mechanism, the "rate determining step" is considered to be the reaction between the $[PhCH_2CH_2C(O)PdX(P,P)]$ or $[Ph(CH_3)CHC(O)PdX(P,P)]$, X = Cl, Br, I, intermediates and ROH [53]. Our results provide evidence that the transformation of the latter, *via* nucleophilic attack of ROH on the palladium-coordinated acyl moiety, is significantly favoured when $[Pd(P,P)Cl_2]$ is the catalyst precursor. This observation may be explained on the basis of smaller steric hindrance, for the nucleophilic attack step, exerted by the chloro ligand compared with that of the bulkier bromo and iodo ligands in the coordination sphere of the intermediates. A thorough experimental and computational mechanistic investigation can shed more light on this matter, but it is beyond the scope of this work.

Entry	Catalyst precursor	p(CO)	Conversion ^(b)	TON ^c
- J	JF	[bar]	[%]	
1	$[Pd(P,P)Cl_2]$	100	51	26
2	$[Pd(P,P)Br_2]$	100	2	1
3	$[Pd(P,P)I_2]$	110	<1	-
4	[Pd(P,P)I ₂]/Mont	110	<1	7 -
5^{d}	$[Pd(P,P)Cl_2]$	100	2	1
6 ^d	$[Pd(P,P)Br_2]$	100	3	2
$7^{\rm e}$	$[Pd(P,P)Cl_2]$	120	89	45
8^{f}	$[Pd(P,P)Cl_2]$	100	74	37
9	$[Pd{(Ph_2P)_2N(S-CHPhMe)-\kappa P, P'}Cl_2]$	100	17	9
10^{d}	$[Pd{(Ph_2P)_2N(S-CHPhMe)-\kappa P, P'}Cl_2]$	100	8	4
11 ^g	$[Pd{(Ph_2PSe)(Ph_2P)N(S-CHMePh)-\kappa P, Se}Cl_2]$	100	2	1
$12^{d,g}$	$[Pd{(Ph_2PSe)(Ph_2P)N(S-CHMePh)-\kappa P,Se}Cl_2]$	100	2	1

Table 3.	Hydroethox	ycarbonylatior	of styrene	catalyzed by	y palladium(II)	precursors. ^a
	J	J				

^aReaction conditions (unless otherwise stated): 0.02 mmol of palladium(II) catalyst, 0.115 mL (1 mmol) of styrene, 1 mL of ethanol, 10 mL of toluene (solvent), 100 °C, reaction time: 20 h.

^bDetermined by GC (GC-MS).

^cTON: turnover number (moles of styrene transformed per mole of Pd).

^d3 drops of $HCl_{(aq)}$ (37% w/w) was added.

^eReaction time: 67 h.

^fAddition of 0.02 mmol PPh₃

^gSome metallic Se was formed in the reaction mixture.

3.4. Suzuki-Miyaura cross-coupling reaction

The catalytic activity of complex $[Pd(P,P)I_2]$ was also tested in the Suzuki-Miyaura reaction of aryl bromides with phenylboronic acid in DMF employing K₂CO₃ as base, at 25 or 100 °C for 24 h, using a relatively low palladium loading (0.1 mol%) (Scheme 4, Table 4). At room temperature, conversion of bromobenzene to biphenyl was only 5%, which was increased to 20% by addition of PPh₃ or to 50% by using the heterogenized $[Pd(P,P)I_2]/Mont$ catalyst (compare entries 1–3). As expected, substrates bearing electron-withdrawing moieties, such as 1-bromo-4nitrobenzene, are more reactive, affording the corresponding coupling product in 67% yield at room temperature (entry 7), while the use of $[Pd(P,P)I_2]/Mont$ resulted a higher conversion

(75%; entry 8) with TONs of 670 and 750, respectively. The evaluation of the free complex at elevated temperature (100 °C) led to satisfactory results with 58 and 100% conversion of the bromobenzene and 1-bromo-4-nitrobenzene, respectively (entries 4, 9; TONs: 580 and 1000, respectively). The conversion of 4-bromoanisole, bearing an electron-donor moiety, was found to be very low at room temperature and moderate at 100 °C, even in the presence of PPh₃ (entries 5, 6). The results listed in Table 4 providing TONs in the range 50–750 at 25 °C and 580–1000 at 100 °C, clearly indicate that the catalytic activity of the [Pd(P,P)I₂] complex is lower compared to that of the analogous [Pd(P,P)X₂], X = Cl, Br, as recently reported by some of us [22], and this order of reactivity is in accordance to that observed for the hydroalkoxycarbonylation of styrene, as explained in the previous section. Concerning the Suzuki reaction, the lower activity of [Pd(P,P)I₂] compared to [Pd(P,P)Cl₂] coupler to [Pd(P,P)Cl₂] couplex to chlorine, and thus, the metal center has a higher electron density in complex [Pd(P,P)Cl₂], facilitating a possible primary reduction of Pd(II) to Pd(0) before the oxidative addition of the aryl bromide.

ArBr + PhB(OH)₂
$$\frac{Pd \text{ cat. (0.1 mol%)}}{DMF/K_2CO_3} \text{ ArPh}$$
25 or 100 °C

Scheme 4. Suzuki-Miyaura cross-coupling.

Entry	Catalyst	ArBr	Tempe	Conversion (%) ^b	TON ^c
	precursor		rature		
			(°C)		
1	$[Pd(P,P)I_2]$	PhBr	25	5	50
2^{d}	$[Pd(P,P)I_2]$	PhBr	25	20	200
3	[Pd(P,P)I ₂]/Mont	PhBr	25	50	500
4	$[Pd(P,P)I_2]$	PhBr	100	58	580
5^{d}	$[Pd(P,P)I_2]$	4-MeO-C ₆ H ₄ Br	25	10	100
6^{d}	$[Pd(P,P)I_2]$	4-MeO-C ₆ H ₄ Br	100	54	540
7	$[Pd(P,P)I_2]$	$4-O_2N-C_6H_4Br$	25	67	670
8	[Pd(P,P)I ₂]/Mont	$4-O_2N-C_6H_4Br$	25	75	750
9	$[Pd(P,P)I_2]$	$4-O_2N-C_6H_4Br$	100	100	1000

Table 4. Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid catalyzed by complex $[Pd(P,P)I_2]$ and immobilized complex $[Pd(P,P)I_2]/Mont.^a$

^aReaction conditions: ArBr (1.0 mmol), PhB(OH)₂ (1.5 mmol), K₂CO₃ (2.0 mmol), DMF (1 mL), ArBr/Pd molar ratio = 1000:1, 24 h, argon.

^bConversion to cross-coupling product ArPh as determined by GC.

^cTON: turnover number (moles of ArBr transformed to ArPh per mole of Pd).

^dPPh₃ (1 μ mol) was added.

4. Conclusions

The catalytic activity of a series of palladium(II) complexes was tested in hydroalkoxycarbonylation and Suzuki-Miyaura C–C cross-coupling reactions. Among the complexes investigated, complex $[Pd(P,P)Cl_2]$ was the most efficient catalyst for the hydroalkoxycarbonylation reaction. Although the catalytic activity was moderate, the regioselectivity toward the branched ester was excellent. Complexes $[Pd(P,P)X_2]$, X = Br, I, are practically inactive catalysts in the hydroalkoxycarbonylation of styrene. The catalytic activity of complex $[Pd(P,P)I_2]$ was also evaluated in the Suzuki-Miyaura reaction of aryl bromides with phenylboronic acid, and found to be lower compared to that of the analogous complexes $[Pd(P,P)X_2]$, X = Cl, Br. The addition of PPh₃ improved the catalytic efficiency of $[Pd(P,P)I_2]$.

Similarly, immobilization of the latter onto STx–1 montmorillonite afforded a remarkably more active catalyst.

Appendix A. Supplementary data

CCDC 1831665 (for [Pd(P,P)I₂]) contains the supplementary crystallographic data, which can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>, or via <u>www.ccdc.cam.ac.uk/data_request/cifhttp://www.ccdc.cam.ac.uk/conts/retrieving.html</u>.

Supplementary data associated with this article can be found, in the online version, at xxx.

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The $[Pd{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3-\kappa P, P']I_2}$ complex was prepared and characterized by X-ray crystallography and spectroscopic methods. Its structural features were compared with those of $[Pd{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3-\kappa P, P']X_2], X = Cl, Br, and other related complexes. The$, aio catalytic activity of these and related complexes in hydroalkoxycarbonylation and Suzuki-