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Novel usage of palladium complexes with P–N–P ligands as catalysts for diphenyl carbonate synthesis[†]

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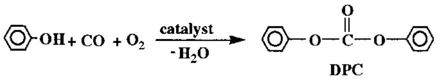
Two palladium complexes with P–N–P ligands [Pd{(SPPh$_2$)$_2$N}$_2$]{Pd(S,S)} and [Pd{(SePPh)$_2$N}$_2$] {Pd(Se,Se)} were prepared and investigated as novel polladium catalysts for oxidative carbonylation of phenol using carbon monoxide and oxygen along with a redox catalyst (for *in situ* regeneration of palladium) and ammonium halide. The efficiency of these new catalysts was compared with that of a PdCl$_2$-based catalyst system. In order to obtain the maximum efficiency, the effects of various parameters such as concentration of redox catalyst and ammonium halide, the effect of solvent, the influence of a quinone-type redox catalyst in addition to inorganic redox catalyst, and the effect of temperature were studied. Under the reaction conditions employed, the Pd(S,S) catalyst was found to perform better than PdCl$_2$-based catalyst system, whereas the Pd(Se,Se) catalyst had extremely low efficiency. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: palladium; complexes catalyses; oxidative carbonylation; diphenyl carbonate

INTRODUCTION

Polycarbonates are highly useful as engineering thermoplastics, owing to their good thermal and mechanical properties. For their synthesis, a transesterification process using diphenols and diphenyl carbonate (DPC) has been given more recognition lately than interfacial polycondensation because of its advantages, such as the absence of toxic phosgene, solvent and salt formation. However, the most common method employed for DPC synthesis is based on the reaction of phenol with phosgene in the presence of bases. Therefore, it is of the utmost importance to find a phosgene-free synthesis route for DPC synthesis. Direct synthesis of DPC by oxidative carbonylation of phenol in the presence of a palladium-based catalyst system using CO and O$_2$ (Eqn [1]) seems to be a good alternative, but in the reactions reported units now the efficiency of catalyst is too low for such processes to be commercially viable.[1–13]



[1]

Recently we demonstrated the successful usage of a PdCl$_2$–Ce(OAc)$_3$–bis(triphenylphosphoranylidene) ammonium bromide (PPNBr) - based catalyst system for DPC synthesis in yields as high as 76%, and for direct synthesis of polyarylcarbonates in 90–95% yield and average molecular weight (M_w) up to 5000.[14–16] An efficient catalyst system is the key to the success of this process and there is still scope for finding new palladium complexes which can act as highly efficient catalysts for oxidative carbonylation of phenols.

Dichalcogenoimidodiphosphinato anions,

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$[R_2P(E)—N—(E)PR_2]$ (E = O, S, Se; R = Ph, OPh) are versatile P–N–P-type ligands with a strong tendency to form inorganic (carbon-free) chelate rings.[17] For many years after their introduction by Schmidpeter *et al.*[18] dichalcogenoimidodiphosphinates received only scant attention, but recently the interest in their complexes have been renewed.[19–21] Although known for several years, diselenoimidodiphosphinate was only recently been used as a ligand.[22] In this work we prepared two $[Pd\{Ph_2P(E)—N—(E)PPh_2\}_2]$ complexes with P–N–P ligands where E was either S [Pd(S,S)] or Se [Pd(Se,Se)], and tested their activity for oxidative carbonylation of phenol.

EXPERIMENTAL

Materials

All chemicals were commercial products and were used without any further purification. The starting materials $Ph_2PNHPPh_2$, $Ph_2P(S)NHP(S)Ph_2$ and $Ph_2P(Se)NHP(Se)Ph_2$ were prepared according to the literature methods.[22–24] The solvents were distilled and stored in activated 3 Å molecular sieves before use. 3 Å molecular sieves were activated by heating at 350 °C under nitrogen for 10 h.

Instrumentation

Elemental analysis was performed on a Fisoin's EA 1108 instrument. The ^{31}P NMR spectra were recorded in CH_2Cl_2 on a Bruker Avance DRX 500 instrument using H_3PO_4 (85%) as external reference. The oxidative carbonylation reaction products were identified and quantified by gas chromatography using a Hewlett-Packard HP 6890 series GC system (TC-1 column).

Synthesis of Pd(S,S) and Pd(Se,Se)

Though the synthesis of $[Pd\{(SPPh)_2N\}_2]$ and $[Pd\{(SePPh_2)_2N\}_2]$ is already reported in the literature,[22] in the present work we used a modified method reported below.

$[Pd\{(SPPh)_2N\}_2]$
A solution of $Pd(OAc)_2$ (0.112 g; 0.5 mmol) in methanol (40 mmol) was added to a clear solution of $Ph_2P(S)NHP(S)Ph_2$ (0.449 g; 1 mmol) and KOtBu (0.112 g; 1 mmol) in methanol (50 mmol) and these were stirred together for 2 h. The product (orange crystals) was recrystallized from CH_2Cl_2. Yield 0.371 g, 74% (after recrystallization). Elemental analysis: Found: C, 57.24; H, 3.84; N, 2.42. Calcd for $C_{48}H_{40}N_2P_4PdS_4$: C, 57.45; H, 4.00; N, 2.80%. $^{31}P\{^1H\}$ NMR: $\delta = 37.8$. IR data (cm^{-1}): $\nu(P_2N)$ = 1207m, 1174m, 804s; $\nu(P{=}S)$ = 565vs.

$[Pd\{(SePPh_2)_2N\}_2]$
A solution of $Pd(OAc)_2$ (0.112 g; 0.5 mmol) in methanol (40 mmol) was added to a clear solution of $Ph_2P(Se)NHP(Se)Ph_2$ (0.543 g; 1 mmol) and KOtBu (0.112 g; 1 mmol) in methanol (50 mmol) and these were stirred together for 2 h. The product (brown–red crystals) was recrystallized from CH_2Cl_2. Yield 0.423 g, 78% (after recrystallization). Elemental analysis: Found: C, 48.12; H, 3.04; N, 2.22. Calcd for $C_{48}H_{40}N_2P_4PdSe_4$: C, 48.40; H, 3.40; N, 2.35%. $^{31}P\{^1H\}$ NMR: $\delta = 26.7$ $[^1J(^{31}P–^{77}Se) = 543\ Hz]$. IR data ($cm^{-1}$): $\nu(P_2N)$ = 1172m, 1174m, 800s; $\nu(P{=}Se)$ = 537vs.

Oxidative carbonylation of phenol

Palladium complex (0.0125 mmol), $Ce(OAc)_3$ (25 mg; 0.075 mmol), PPNBr (231 mg; 0.375 mmol), and 1 g activated 3 Å molecular sieves were loaded into a 50-ml stainless steel autoclave and dried at 70 °C for 2 h under vacuum before the reaction.

After the drying, addition of 3.011 g (32 mmol) phenol and 5 ml dichloromethane was followed by charging with 6.0 MPa CO and 0.3 MPa O_2, and the autoclave was placed in an oil bath preheated to 100 °C. After the desired reaction time, the reaction was quenched immediately by cooling the autoclave in a water bath.

RESULTS AND DISCUSSION

The utility of Pd(S,S) and Pd(Se,Se) complexes was investigated as novel catalysts for the oxidative carbonylation of phenol to diphenyl carbonate. Other components of the catalyst system included PPNBr and $Ce(OAc)_3$ as an inorganic redox catalyst for *in-situ* regeneration of reduced palladium. Short reaction times were used with unexcess of phenol, in order to understand the efficiency of these complexes clearly. 3 Å molecular sieves were used as dehydrating agents to remove the water produced during the reaction and prevent the hydrolysis of the DPC produced to phenol. The

Table 1 Efficiency of Pd(S,S) catalyst in oxidative carbonylation of phenol[a]

Run no.	Pd. catalyst	Redox catalyst	Solvent	HQ (mmol)	DPC[b] (%)	TOF (mol DPC (mol Pd)$^{-1}$ h^{-1})	PS[b] (%)
1	$PdCl_2$	$Ce(OAc)_3$	CH_2Cl_2	—	4.96	21.3	0.09
2	Pd(S,S)	$Ce(OAc)_3$	CH_2Cl_2	—	3.57	15.2	0.07
3	Pd(S,S)	$Ce(OAc)_3$	—	—	3.67	15.6	0.07
4	Pd(S,S)	$Ce(TMHD)_4$[a]	CH_2Cl_2	—	10.8	46.1	0.1
5	Pd(S,S)	$Ce(trop)_4$	CH_2Cl_2	—	8.3	35.4	0.08
6	Pd(S,S)	$Mn(TMHD)_3$	CH_2Cl_2	—	8.8	37.5	0.098
7	Pd(S,S)	$Mn(trop)_3$	CH_2Cl_2	—	2.97	12.7	0.03
8	Pd(S,S)	$Co(TMHD)_3$	CH_2Cl_2	—	0.17	0.74	0.02
9	Pd(S,S)	$Ce(TMHD)_4$	CH_2Cl_2	0.375	6.6	28.4	0.07

[a] Reaction conditions: Pd catalyst (0.012 mmol) redox catalyst (0.075 mmol), PPNBr (0.375 mmol), CH_2Cl_2 (5 ml), 3 Å molecular sieves (1 g), phenol (32 mmol) CO (6.0 MPa), O_2 (0.3 MPa), 100 °C, 3 h.
[b] Yield based on phenol.
[c] TMHD, tetrakis (2,2,6,6-tetramethyl-3,5-heptanedionato).

results obtained were compared with those obtained from $PdCl_2$–$Ce(OAc)_3$–PPNBr-based catalyst systems reported earlier by us.[14–16] From the results given in Table 1 (Run 2), it is clear that the turnover frequency (TOF) of the Pd(S,S) catalyst was marginally lower than that of the $PdCl_2$-based catalyst system under the reaction conditions employed and further optimization is required to obtain the the best efficiency. Besides diphenyl carbonate, phenyl salicylate (PS) and a few oxidation products of phenol were obtained in low yields. The selectivity of diphenyl carbonate was found to be more than 90%. Assuming that solvent might be decreasing the catalytic efficiency, a reaction was performed in the absence of solvent. However, as evident from the result reported in Table 1 (Run 3), no difference in the TOF of catalyst could be observed, suggesting that the solvent does not affect the activity of the catalyst in these reaction conditions. Therefore, all further reactions were carried out in the presence of solvent, as usage of a solvent is essential if we wish to use this reaction for direct polycarbonate synthesis.

Choosing a suitable inorganic redox catalyst is very important for *in-situ* regeneration of palladium (0). Thus, various redox catalysts with different ligands were investigated; the results are listed in Table 1, Runs 4–8. Among the different metal complexes, $Ce(TMHD)_4$ was found to give the highest TOF of 46.1 mol DPC (mol Pd)$^{-1}$h^{-1}.

From our previous work we know that incorporating hydroquinone or benzoquinone as an additive substantially improved the efficiency of the $PdCl_2$–$Ce(OAc)_3$–PPNBr catalyst system.[15,16] In the palladium catalysed reactions, benzoquinone (BQ) is reported to work as a redox catalyst for regeneration of reduced palladium. In addition it is also known that benzoquinone can act as a ligand and can prevent the aggregation of palladium (0) by the formation of Pd–BQ complexes which can easily be oxidized to palladium(II) complexes by metallic redox agents.[25] However, addition of 0.375 mmol hydroquinone with the Pd(S,S) complex led to the reduction of the TOF from 46.1 to 28.4 mol DPC (mol Pd)$^{-1}$h^{-1} (Table 1, Run 9). This behaviour indicates that a Pd(S,S) complex which contains a P–N–P ligand does not require any additional ligand for stabilizing its palladium metal, and any additional ligand such as benzoquinone will make palladium unavailable for further reaction.

Although all the reports on oxidative carbonylation of phenol confirm the need for an ammonium halide for the reaction to progress efficiently, the role of this component of catalyst system is not clear. Furthermore, it has been confirmed from all these reports that among the various ammonium halides, only ammonium bromides are useful for this reaction. Ammonium bromide is not a catalyst for the reaction, nor can it help in regeneration of palladium. Recently, Vavasori and Toniolo[9] have suggested that ammonium bromide works as a stabilizer and prevents undesirable palladium metal formation. If ammonium bromide is actually acting as a surfactant, then its concentration in the reaction should be above its critical micelle concentration. We therefore performed some experiments with the PPNBr/Pd ratio (mol mol^{-1}) varying from 30 to 80, to find a suitable concentration of PPNBr. As shown

Table 2 Optimization of PPNBr/Pd and Ce/Pd ratios for oxidative carbonylation of phenol[a]

Run no.	PPNBr/Pd ratio (mol mol^{-1})	Ce/Pd ratio[b] (mol mol^{-1})	DPC[c] (%)	TOF (mol DPC (mol Pd^{-1}) h^{-1})	PS[c] (%)
1	30	6	10.8	46.1	0.1
2	60	6	16.8	71.6	0.15
3	70	6	17.3	73.7	0.12
4	80	6	16.0	68.4	0.13
5	60	4	12.8	54.5	0.12
6	60	2	11.3	48.2	0.09

[a] Reaction conditions:Pd catalyst (0.012 mmol), CH_2Cl_2 (5 ml), 3 Å molecular sieves (1 g) phenol (32 mmol) CO (6.0 MPa), O_2 (0.3 MPa), 100 °C, 3 h.
[b] Ce as Ce(TMHD)$_4$.
[c] Yield based on phenol.

Table 3 Temperature dependence of the efficiency of the Pd(S,S) complex for oxidative carbonylation of phenol[a]

Run no.	Temp. (°C)	DPC[a] (%)	TOF (mol DPC (mol Pd^{-1}) h^{-1})	PS[a] (%)
1	80	12.1	52.0	0.09
2	100	16.8	71.6	0.15
3	120	6.18	26.4	0.10
4	140	2.06	8.82	0.09

[a] Reaction conditions: Pd(S,S) (0.012 mmol), Ce(TMHD)$_4$ (0.15 mmol) PPNBr (0.75 mmol), CH_2Cl_2 (5 ml), 3 Å molecular sieves (1 g), phenol (32 mmol), CO (6.0 MPa), O_2 (0.3 MPa), 3 h.
[b] Yield based on phenol.

in Table 2 (Runs 1–4), the DPC yield as well as the TOF of the catalyst increased substantially on raising the PPNBr/Pd ratio from 30 to 60, but with further increases in the PPNBr/Pd ratio to 80 no significant improvement in catalytic activity could be observed. Thus it can be assumed that, for the catalyst system under investigation, the amount of PPNBr required to achieve the best results is 60–70 times of that of the palladium.

In further reactions, the concentration of the oxidation catalyst, Ce(TMHD)$_4$ (TMHD is defined in Table 1) was optimized. The Ce(TMHD)$_4$/Pd ratio (mol mol^{-1}) was varied from 2 to 6, keeping the PPNBr/Pd ratio constant at 60; the results obtained are given in Table 2 (Runs 2, 5 and 6). On reducing the Ce/Pd ratio from 6 to 2 the efficiency of the catalyst system in terms of TOF was reduced from 71.6 to 48.2 mol DPC (mol Pd)$^{-1}$ h^{-1}. This trend shows that more redox catalyst is required for an efficient regeneration of palladium.

Furthermore, the temperature dependence of the efficiency of the catalyst system was studied by varying the reaction temperature from 80 to 140 °C. It is evident from the results given in Table 3 that maximum TOF of 71.6 mol DPC (mol Pd)$^{-1}$ h^{-1} and DPC yield of 16.8% were obtained at 100 °C. Any further increase in temperature led to substantial decreases in the TOF of the catalyst as well as in the DPC yield, presumably due to degradation.

After various reaction parameters had been optimized with the Pd(S,S) catalyst, the efficiency of the Pd(Se,Se) catalyst system was investigated at optimum temperature, using optimum concentrations of Ce(TMHD)$_4$ and PPNBr. The results showed a TOF of 0.17 mol DPC (mol Pd)$^{-1}$ h^{-1}. At present we have no explanation for such a drastic difference in the efficiency of these two palladium complexes with same ligand but different donor atoms.

In summary, the Pd(S,S) complex with P–N–P ligands and an S donor was found to be an efficient catalyst for oxidative carbonylation of phenol to diphenyl carbonate. The Pd(Se,Se) complex, on the other hand, did not show any activity for this reaction. Efforts to understand this substantial difference in the efficiency of these two similar complexes and to further improve the activity of the Pd(S,S) complex are currently being made.

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