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A highly active palladium complex catalyst in the synthesis of N,N′-diphenylurea from nitrobenzene, aniline and carbon monoxide

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A catalyst system comprising palladium acetate and bidentate bis(diphenylphosphino)alkane ligand of general formula $Ph_2P(CH_2)_nPPh_2$ ($n = 3$–5) was highly active in N,N′-diphenylurea synthesis from nitrobenzene, aniline and carbon monoxide and showed different reactivity from the system with the more common monodentate triphenylphosphine ligand.

Keywords: N,N′-diphenylurea; palladium complex catalyst; bidentate phosphine ligands

1. Introduction

A great deal of recent research has been directed toward alternative routes to isocyanates without using phosgene. These routes comprise catalytic carbonylation of nitrobenzene or aniline as a key step. N,N′-diphenylurea (DPU) has been proposed as a convenient intermediate in the phosgene-free synthesis of diphenylmethane diisocyanate (MDI) [1]. The DPU can be synthesized effectively from nitrobenzene, aniline and carbon monoxide in the presence of a catalyst system comprising a palladium salt, a halogen promoter, and a ligand. By using triphenylphosphine (PPh_3) as a ligand, we reported that the reaction proceeded according to the following two stoichiometries [2,3]:

$$PhNO_2 + PhNH_2 + 3CO \rightarrow PhNHCONHPh + 3CO_2\,, \qquad (1)$$

$$PhNO_2 + 5PhNH_2 + 3CO \rightarrow 3PhNHCONHPh + 2H_2O\,. \qquad (2)$$

During the course of our study on the effect of ligands in DPU synthesis, we have

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found that bidentate phosphine ligands were highly active and showed different reactivity compared to monodentate phosphine ligands, PPh_3.

2. Experimental

The reactions were performed in a batch reactor having a total volume of 300 cm^3. In a typical run, 300 mmol of aniline, 0.60 mmol of palladium acetate, 1.71 mmol of a bidentate ligand, 1.8 g of NEt_4Cl,and 70 ml of xylene were charged into the reactor. When PPh_3 was employed, twice as much of the amount (3.42 mmol) was used in order to keep the number of donor atoms in the system to be the same. After flushing with 60 psig CO three times, the gas phase in the reactor was pressurized to 620 psig. The reactor was then heated to 120°C. After temperature was stabilized, 50 mmol of nitrobenzene or deuterated nitrobenzene(d_5) was pumped rapidly into the reactor by a metering pump. The reaction mixture was sampled during the reaction and the liquid phase was analyzed quantitatively by a GC equipped with FID detector and HP-17 megabore column (0.53 mm i.d. × 10 m) with 1,4-di-tert-butylbenzene as an internal standard. After the reactor was cooled, solid products were isolated and recrystallized for mass spectroscopy (MS) analysis. A direct inlet probe was employed for sample feed to mass spectrometer.

3. Results and discussion

As shown in fig. 1, a great difference in activity was observed when phosphines of general formula $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–6) were used as ligands. The initial rate was calculated from the average value during the initial 15 min of the reaction. The variation of a distance between two donor atoms, n, resulted in significant changes in reaction rate. The rate was negligible for $n = 1$, increased slowly for $n = 2$, and increased greatly for $n = 3$. After reaching a maximum value for $n = 4$, the rate decreased as n increased further up to 6. Bidentate ligands with nitrogen donor atoms such as 1,10-phenanthroline (Phen) and 3,4,7,8-tetramethyl-Phen showed good activity as well. The initial rate for 1,4-bis(diphenylphosphino)-butane (DPB, $n = 4$) was higher by a factor of 3.2 than the value for PPh_3, the most commonly used ligand in this reaction [2,3]. Furthermore, the time required to achieve complete conversion of nitrobenzene was much shorter in case of DPB (10 min) than that of PPh_3 (150 min). This indicates an increase by a factor of 15 in the average rate. As these bidentate phosphine ligands are known to have similar electron donating ability [4], it appears that steric property of the ligands plays a significant role in catalytic activity.

Another interesting point to be noted is that the use of a halogen promoter NEt_4Cl, which was indispensable in case of PPh_3, yet inhibited the reaction if used with bidentate phosphine ligands. In case of 1,3-bis(diphenylphosphino)propane

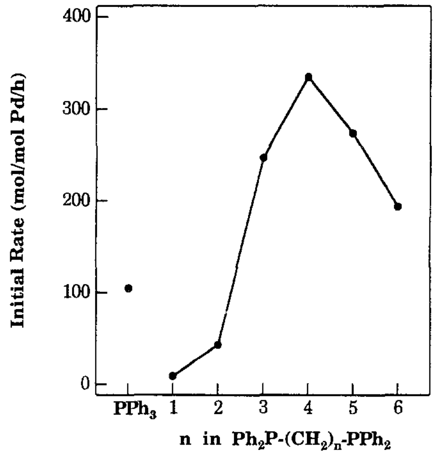


Fig. 1. Effect of phosphine ligands with different distance between two donor atoms on the initial rate of Pd-catalyzed N,N'-diphenylurea synthesis: nitrobenzene 50 mmol; aniline 300 mmol; palladium acetate 0.6 mmol; Et_4NCl 1.8 g; 120°C; CO 620 psig; ligand 1.71 mmol (PPh_3 = 3.42 mmol); xylene 70 ml; initial rate = mmol of consumed nitrobenzene/mmol of Pd/h.

($n = 3$) with NEt_4Cl, the reaction temperature rose from 120 to 125°C as soon as nitrobenzene was introduced and the reaction was completed after 30 min. However, when NEt_4Cl was not used, the reaction proceeded explosively with liberation of heat that raised the temperature to 155°C. The reaction was completed within 10 min.

The difference in reactivity between mono- and bidentate phosphine ligands was also investigated by utilizing fully deuterated nitrobenzene(d_5) and normal aniline as reactants. The results are summarized in table 1. Three forms of DPU are formed according to the number of deuterated phenyl rings involved in DPU formation. We denote these as x, y and z forms when the numbers of deuterated phenyl

Table 1
Effect of phosphine ligands on synthesis of N,N'- diphenylurea[a]

Ligand	Relative abundance[b] $x : y : z$	$C_6H_5NH_2/C_6D_5NO_2$ consumed[c]
PPh_3	3.25 : 1.00 : 0.04	6.94
$PPh_2(CH_2)_nPPh_2$		
$n = 3$	1.25 : 1.00 : 0.04	3.24
$n = 4$	1.48 : 1.00 : 0.06	3.54
$n = 5$	1.53 : 1.00 : <0.01	4.06
$n = 6$	2.05 : 1.00 : <0.01	5.10
Phen	1.54 : 1.00 : 0.13	3.24

[a] Nitrobenzene(d_5) 50 mmol; aniline 300 mmol; palladium acetate 0.6 mmol; Et_4NCl 1.8 g; 120°C; CO 620 psig; ligand 1.71 mmol (PPh_3 = 3.42 mmol); xylene 70 ml.

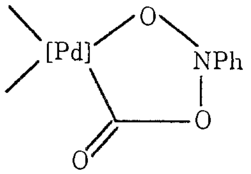
[b] The mole ratio of x, y, and z forms of DPU analyzed by MS.

[c] The mole ratio of C_6H_5 to C_6D_5 group contained in DPU.

rings in DPU molecule are 0, 1, and 2, respectively. Thus x, y and z forms are originated from, respectively, two molecules of aniline, each molecule of nitrobenzene and aniline, and two molecules of nitrobenzene. The abundance of x, y and z species in DPU was determined from the relative height of molecular peaks at m/e of 212 (x), 217 (y), and 222 (z) of MS analysis. A great difference in the distribution of these DPU forms between mono- and bidentate ligands was observed. The x form of DPU is formed in much greater propensity with PPh_3 than with bidentate phosphines. Therefore, much more aniline is consumed in the case of PPh_3 than that of bidentate phosphines, when an equal amount of nitrobenzene is consumed. As the distribution of DPU results from the relative rates of reaction (1) and (2), this indicates that the catalyst with bidentate ligands promotes reaction (1) to a greater extent than the catalyst with monodentate triphenylphosphine ligand. Phenanthrolines also showed a similar trend to that of bidentate phosphines. Among bidentate phosphines, the relative abundance of the x form DPU increased with the length of ligand backbone.

Since Pd(II) complex is a d_8, 16-electron species, it would be expected to assume a square planar geometry of the type $[PdL_2X_2]$, where L and X denote different types of ligand. When monodentate tertiary phosphine is employed as a ligand (L), two PPh_3 will tend to coordinate with trans stereochemistry, due to the high trans effect of the phosphine, the lability of the groups coordinated to Pd(II), and steric crowding of two PPh_3 molecules, even though the cis complexes are thermodynamically more stable [5,6]. However, bidentate ligands with short chelate backbones ($2 \leqslant n \leqslant 5$) prefer to form cis chelate complexes since the length of the chelate backbone is not sufficient to span the trans position in a square planar complex [5]. For Pd(II) complexes with bis(diphenylphosphino)methane ($n = 1$), the ligand backbone is so short that a bridging configuration between two Pd atoms is more likely to be formed instead of chelation to a single palladium atom [5]. On the other hand, if the length of the ligand backbone increases sufficiently to span the trans position ($n \geqslant 6$), it would favor trans chelation [5]. In this regard, it should be noted in table 1 that the abundance of x form DPU and the ratio of $C_6H_5NH_2/C_6D_5NO_2$ consumed to produce DPU showed the largest difference between $n = 5$ and 6.

Thus contrary to trans coordination of the monodentate PPh_3 ligand, diphosphines with $n = 2$–5 are likely to bind to a single palladium(II) center in a cis configuration as the case of Phen. Then, what is the impact of this different stoichiometry between monodentate and bidentate ligands on catalysis of the resulting Pd complexes? In earlier works [2,7], we proposed that reaction (1) involved a nitrene intermediate, PhN[Pd], while reaction (2) a carbamoyl intermediate, PhNHCO[Pd]. The choice of the reaction path between (1) and (2) depends on whether nitrobenzene or aniline is coordinated first to the metal. If nitrobenzene is initially coordinated to the metal, a nitrene intermediate is formed by the deoxygenation with CO. Insertion of CO into the nitrene complex produces phenyl isocyanate complex PhNCO[Pd], which reacts with aniline to form DPU according to the stoichiometry of reaction (1). Hence, the configuration of the catalyst which favors coordination of nitrobenzene over aniline would promote reaction (1) more effectively than reaction (2). For the coordination of nitrobenzene, a metallocycle intermediate such as I has been proposed as a precursor to nitrene complex [8]. Alternatively, Leconte et al. [9] isolated metallocyclic intermediate II from the reaction of nitrobenzene with CO using the Pd(II)–Phen system and proposed this as an active intermediate for the catalytic cycle where no nitrene or cluster intermediates needed to be invoked.



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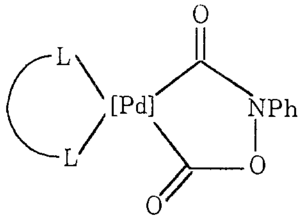

II

In either case, for the intermediate I or II to be formed effectively, the cis form of ligand coordination is required inevitably. Therefore, it is inferred that the cis coordination of bidentate ligands to palladium preferentially promotes the reaction (1).

The proposed reaction paths for reactions (1) and (2) involve a series of CO insertion, attacks by reactant and substitutions at square-planar palladium(II) complexes [3,7]. It is commonly believed that such transformations proceed via a trigonal-bipyramidal transition state. Therefore, bidentate ligands which are able to stabilize both the square-planar ground state and the trigonal-bipyramidal transition state ($n = 3$–5 here) can catalyze the reaction effectively, and thus show higher activity. The effectiveness of bidentate ligands in palladium complex-catalyzed reactions, which showed different activity with monodentate ligands, due to cis coordination of ligands has been reported for other systems as well [10,11].

The role of NEt_4Cl is not clear although there have been a number of reports on its promotion effects in similar reactions [12,13]. However, the observation that it promotes the reaction with monodentate ligands, yet inhibits it with bidentate ligands, is interesting and has not been reported to the best of our knowledge.

4. Conclusion

Bidentate bis(diphenylphosphino)alkane ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 3$–5) show much improved activity in Pd-catalyzed N,N′-diphenylurea synthesis from nitrobenzene, aniline and carbon monoxide relative to the usual monodentate triphenylphosphine ligand. Furthermore, they show different reactivity as reflected by the opposite response to NEt_4Cl and different selectivity between reactions (1) and (2). The preference of the bidentate ligands to assume the cis chelate form of square-planar Pd complexes appears to be the major reason for these effects.

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