The Palladium catalysed Carbonylation of Nitrobenzene into Phenyl Isocyanate: A Metallacyclic Intermediate

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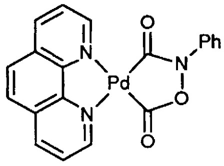
A metallacyclic complex has been isolated from the reaction of $PhNO_2$ with CO using the Palladium(II)–*o*-phenanthroline system known to produce phenyl isocyanate or carbamates catalytically; reactions of this metallacycle have been studied and its rôle in the catalytic reaction discussed.

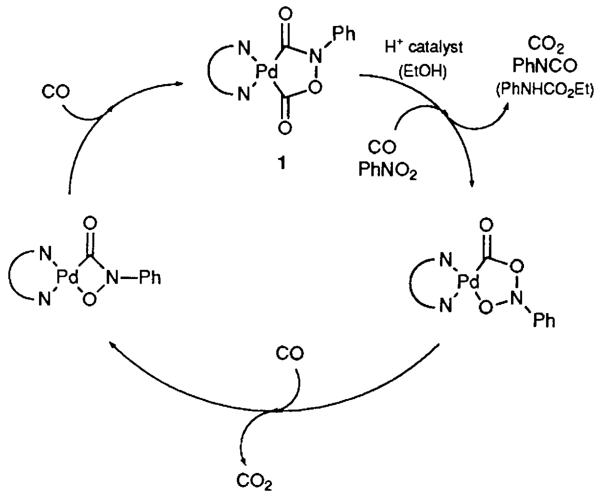
The direct carbonylation of nitroaromatics into the corresponding isocyanates (or carbamates if alcohol is present), *e.g.* eqn. (1), is of great commercial potential. Among homogeneous catalyst systems, the combination Pd^{II}–1,10-phenanthroline (*o*-phen)–H^+, studied by Drent[1] and Mestroni,[2] is one of the most efficient and selective, but the mechanism of this multistep process remains unclear. In general, a variety of possible intermediates have been proposed for such carbonylation processes, such as metal–nitrenes,[3] clusters[3] and metallacycles.[2c,3c,4] We report here the isolation and characterisation of a metallacyclic complex which appears to be directly involved in the catalytic process and whose structure helps throw light on the overall mechanism.

$$PhNO_2 \xrightarrow[-2CO_2]{+3CO} PhNCO \xrightarrow{ROH} PhNH(CO_2R) \qquad (1)$$

When $Pd(OAc)_2$, *o*-phen (3 equiv.) and $PhNO_2$ (40 equiv.) are heated in ethanol under CO (30 bar) at 80 °C, a yellow complex[1] precipitates in *ca.* 80% yield (based on Pd). Under the conditions normally used for efficient catalysis (135–180 °C), the complex remains soluble in $PhNO_2$. The IR spectrum of **1** shows notably two absorptions at 1620 and 1690 cm^{-1} as well as coordinated *o*-phen. The ^1H NMR spectrum (in CD_2Cl_2) indicates the presence of one monosubstituted phenyl group and an unsymmetrical coordinated *o*-phen ligand (*e.g.* 2-H, 9-H at δ 9.94 and 10.13). In the ^{13}C MAS NMR spectrum, two characteristic carbonyl resonances at δ 185 and 190 are observed. The microanalysis is consistent with



(A)



Scheme 1

the formula Pd(*o*-phen)(C_6H_5)(C_2NO_3). The FAB MS of **1** (dimethylacetamide-*o*-nitrobenzyl alcohol) shows two families of peaks at *m/z* 450 (M + 1), 422 (M + 1-CO), 378 (M + 1-CO-NCO), 331 (M + 1-C_6H_5NCO), as well as at 393 (M-2CO), 363 (M-CO_2-NCO), 314 (M-CO-C_6H_5NO), 302 (M-CO-C_6H_5NCO) and 286 (most intense) (M-CO_2-C_6H_5NCO). All peaks have isotope profile structures corresponding to a monomeric species. Weak peaks above 450 result from ion-molecule and matrix interactions.

From these data and the chemical reactivity of **1** (*vide infra*), structure (**A**) is proposed.

Compounds **1** can be looked at in two ways. The metallacycle appears to result from the coupling a PhNO group with two molecules of CO. Alternatively, opening of the cycle with N–O cleavage would yield PhNCO and CO_2, both products of the catalytic reaction. The FAB fragmentation patterns illustrate both processes.

Complex **1** is surprisingly stable; only heating in *o*-dichlorobenzene under CO (20 bar) at 170 °C causes conversion to PhNCO (0.2 equiv.), $(PhNH)_2CO$ (0.1 equiv.),† $(PhNHCO)_2NPh$ (0.1 equiv.) and CO_2 (1 equiv.). However, if 1.6 equiv. of H^+ is added (as 2,4,6-trimethylbenzoic acid) under otherwise identical conditions, 0.6 equiv. of PhNCO is formed along with $(PhNH)_2CO$ (0.1 equiv.) and CO_2 (1 equiv.). An increase both in rate and selectivity to PhNCO is observed on addition of H^+, an observation which is also found in the catalytic process. If the above experiments are carried out with ethanol as solvent at 90 °C, carbamate ($PhNHCO_2Et$) (0.8 equiv.), $(PhNH)_2CO$ (0.1 equiv.) and CO_2 (1 equiv.) are produced. On addition of H^+ an increase in rate but little selectivity change is observed.

The ring opening of the metallacycle is hence catalysed by H^+, possibly by protonation at the amide oxygen (or nitrogen) atom. The effect of the presence of ethanol is twofold. Firstly, metallacycle opening is easier, occurring at much lower temperatures. We suggest that this takes place by nucleophilic attack of the alcohol on the carbonyl group attached to nitrogen thus directly yielding carbamate, a process which would be accelerated if the amide were also protonated. Secondly, ethanol increases the produce yield by thus removing the isocyanate as carbamate, avoiding subsequent reactions of free isocyanate by which by-products such as triphenylbiuret may be formed.

Finally, if a mixture of **1** (1 mmol), $PhNO_2$ (150 mmol), EtOH (125 ml), under CO (60 bar), with 2,4,6-trimethylbenzoic acid (10 mmol) is heated at 135 °C for 2 h, 100% of the $PhNO_2$ is converted to $PhNH(CO_2Et)$ in 91% selectivity.

These results are strongly indicative that **1** is a key intermediate in the carbonylation of $PhNO_2$ using these catalysts. We propose as a working hypothesis a sequence of transformations between metallacycle intermediates for this catalytic reaction where, interestingly, no nitrene or cluster intermediates need to be invoked (Scheme 1). Studies which will confirm or deny such a hypothesis are underway.

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References

1 E. Drent and P. van Leeuwen, E.V. Patent 0086281 A1 (1983); *Chem. Abs.*, 1984, **100**, 6109x.

2 (*a*) E. Alessio and G. Mestroni, *J. Mol. Cat.*, 1984, **26**, 337; (*b*) E. Alessio and G. Mestroni, *J. Organomet. Chem.*, 1985, **291**, 117; (*c*) A. Bontempi, E. Alessio, G. Chanos and G. Mestroni, *J. Mol. Cat.*, 1987, **42**, 67.

3 (*a*) S. Bhaduri, H. Khwaja, N. Sapre, K. Sharma, A. Basu, P. G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.*, 1990, 1313 and ref. therein; (*b*) S. Cenini, C. Crotti, M. Pizzotti and F. Porta, *J. Org. Chem.*, 1988, **53**, 1243; (*c*) S. Hwan Han and G. L. Geoffroy, *Polyhedron*, 1988, **7**, 2331; (*d*) S. Hwan Han, J. S. Song, P. D. Macklin, S. T. Nguyen and G. L. Geoffroy, *Organometallics*, 1989, **8**, 2127.

4 A. J. Kunin, M. D. Noirot and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1989, **111**, 2739.

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† The source of protons is probably trace H_2O (or H_2) present.