Synthesis and Crystal Structure of a Palladium Metallacyclic Complex: A Key Intermediate in the Carbonylation of Azobenzene to *N*-Phenyl Urethane

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The reductive carbonylation of azoxybenzene to *N*-phenyl urethane via azobenzene is promoted by the catalytic system based on palladium, bidentate nitrogen-donor chelating ligands N-N [N-N = 1,10-phenanthroline (phen) and its substituted derivatives] and the acid cocatalyst [(N-N)H][PF_6], the same catalyst as for the reductive carbonylation of nitroaromatic compounds to the corresponding carbamates. The possible key intermediate of the azobenzene → *N*-phenyl urethane transformation has been synthesised and fully characterised.

Introduction

Since 1962 the reductive carbonylation of nitroaromatic compounds has been an interesting field of research, both from the academic and industrial point of view, due to the demand for a new, phosgene-free method for the synthesis of carbamates.[1]

The industrial development of a powerful catalytic system is dependent both on its catalytic activity and on the selectivity towards the carbamate. In this system the main by-products are: aniline, *N*,*N*′-diphenylurea, azobenzene and azoxybenzene. Therefore, the comprehension of the factors which control both the formation and the transformation of these side-products are of great interest.

This reaction is homogeneously catalysed by systems based on different metals, such as ruthenium, rhodium and palladium.[1] The palladium-based system with nitrogen-donor chelating ligands, in the presence of a weak Brønsted acid as cocatalyst, is the most promising up to now.[2,3]

Mechanistic studies have been carried out based mainly on either the isolation or the spectroscopic detection of several metallacyclic derivatives, which should be directly involved in the catalytic cycle.[4−6] In particular, the structural characterization of two metallacyclic intermediates of general formula [(N-N)Pd*C*(O)N(Ar)O*C*(O)] **(1)** (**1a:** N-N = phen, Ar = Ph; **1b:** N-N = 4,4′-di(*tert*-butyl)-2,2′-bipyridyl, Ar = *p*-*tert*-butylphenyl; the italic letters indicate the atoms of the metallacyclic fragment bound to the palladium centre), which differ in the N-N ligand and the aryl group, has been reported by Osborn[4c] and by us.[5]

In this paper we report the isolation and the complete characterization, both in the solid state and in solution, of the symmetric metallacycle [(N-N)Pd*C*(O)N(Ph)N(Ph)*C*(O)] **(2)** [**2a:** N-N = phen; **2b:** N-N = 3,4,7,8-tetramethyl-1,10-phenanthroline (tm-phen)]. This complex is proposed as a "key-intermediate" for the carbonylation of azobenzene to *N*-phenyl urethane. Some preliminary catalytic results are also presented.

Results and Discussion

During the investigation of the catalytic cycle involved in the reductive carbonylation of nitroaromatic compounds to urethanes, we isolated, in high yield, the metallacyclic derivative [(phen)Pd*C*(O)N(Ph)O*C*(O)] **(1a)**, starting from [Pd(phen)($CH_3COO)_2$] in a nitrobenzene/alcohol mixture, under mild reaction conditions.[5] When the same precursor was treated with azobenzene, instead of nitrobenzene, at room temperature, in the presence of free phen and under a CO pressure of 40 atm., a pale yellow solid, formulated as [(phen)Pd*C*(O)N(Ph)N(Ph)*C*(O)], was obtained. After 24 h the yield was about 20% and this increased to 50% on prolonging the reaction time to 60 h. The addition of an excess of chelating ligand was necessary to prevent the formation of palladium metal, which occurs on increasing the reaction temperature. Moreover, no solid was isolated when the reaction was carried out under atmospheric CO pressure. The yield of the reaction is also affected by the nature of the nitrogen ligand. Actually, it further decreases when the tm-phen is used instead of phen (from 20% to 5%). All these data indicate that the formation of the metallacycle **2a** occurs with more difficulty than that of the corresponding derivative **1a**.

Yellow crystals of **2a** suitable for an X-ray analysis were obtained by slow diffusion of diethyl ether into a chloroform solution of the compound. Its molecular structure is shown in Figure 1.

The Pd centre exhibits the expected square-planar coordination geometry with Pd−N and Pd−C distances of 2.148(6) and 2.173(5) Å, and 1.947(7) and 1.963(7) Å, respectively, which are comparable to those observed in the closely related Pd metallacyclic complexes [(N-N)Pd*C*(O)N(Ar)O*C*(O)].[4c,5] The phenyl rings are structurally disor-

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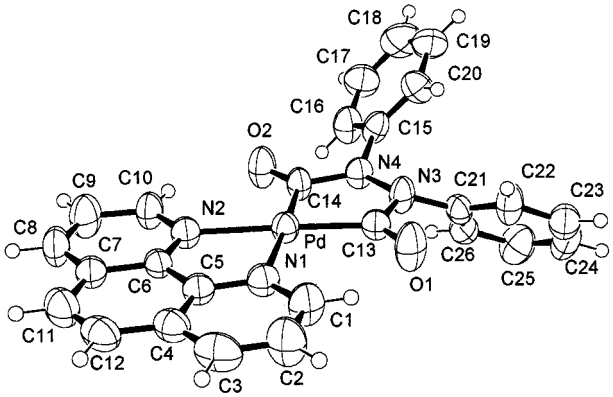

Figure 1. An ORTEP drawing (50% probability thermal ellipsoids) of the metallacycle **2a** with atom numbering scheme; selected bond lengths (Å) and angles (°): Pd−C(14) 1.947(7), Pd−C(13) 1.963(7), Pd−N(2) 2.148(6), Pd−N(1) 2.173(5), N(3)−N(4) 1.419(7); C(14)−Pd−C(13) 81.8(3), C(14)−Pd−N(2) 100.9(3), C(13)−Pd−N(2) 177.3(3), C(14)−Pd−N(1) 177.0(3), C(13)−Pd−N(1) 101.1(3), N(2)−Pd−N(1) 76.2(2), C(1)−N(1)−Pd 126.5(5), C(5)−N(1)−Pd 113.5(5), C(10)−N(2)−Pd 127.5(5), C(6)−N(2)−Pd 114.4(5)

dered over two positions since the phenanthroline and the atoms of the metallacycle Pd*C*(O)NN*C*(O) lie on a crystallographic mirror plane (see Experimental Section). In Figure 1 the rings are represented in a *trans* arrangement, which is the most likely configuration, with their mean planes forming dihedral angles of 48.7 and 45.4° with the crystallographic plane.

The N−N azo bond length of 1.419(7) Å is indicative of considerable single bond character when compared with the value of 1.26−1.27 Å measured in a series of (*E*)-azobenzenes.[7] On the other hand, the nitrogen atoms display a bonding geometry close to planarity, as shown by the summation of the bond angles about them (ca. 355°), and by the value of the torsion angle C(Ph)−N−N−C(Ph) [50.0(6)°], an aspect that may suggest a π delocalization in the azodioxo ring, although packing forces are not to be excluded in driving the observed configuration. In fact, in the crystal structure the [(phen)Pd*C*(O)NN*C*(O)] moieties stack at 3.38 Å (i.e. half of the *b* axis) in a head-to-tail arrangement.

For complexes **2** the IR spectra in the solid state show the typical band of ketonic CO stretching at 1627 cm^{-1}.

Their ^1H NMR spectra in $CDCl_3$ solution present one set of signals for the N-N ligand and one for the *C*(O)N(Ph)N(Ph)*C*(O) moiety. The number of signals of the N-N ligand and their integration confirm the equivalence of the two halves of the ligand in solution, as already observed in the solid state. All the signals of the nitrogen ligand are shifted with respect to those of the free ligand; in particular, the signals attributed to $H^{2,9}$ are deshielded by about 1.00 ppm.

The addition of one equivalent of tm-phen to a solution of [(phen)Pd*C*(O)N(Ph)N(Ph)*C*(O)], **(2a)**, resulted in an exchange of the two ligands at the palladium centre, in agreement with the higher coordinating capability of tm-phen with respect to phen. Indeed, immediately after the dissolution, the spectrum shows the signals of both coordinated and free ligands, indicating that the exchange process is slow on the NMR time scale. Although the frequencies of $H^{2,9}$ of the coordinated phen and tm-phen are quite broad, from their integration it is possible to follow the proceeding of the reaction with time. After five min, 64% of **2a** is transformed into **2b** and the equilibrium is reached after 30 min. The equilibrium mixture is formed from 83% of **2b** with the remainder being unchanged **2a**. Working in the presence of an excess of tm-phen (two equivalents with respect to Pd), the exchange process is accelerated and after five min the phen-metallacycle is completely transformed into the tm-phen derivative. In agreement with this behaviour the metallacycle [(tm-phen)Pd*C*(O)N(Ph)N(Ph)*C*(O)] **(2b)** is easily obtained by a ligand exchange reaction starting from [(phen)Pd*C*(O)N(Ph)N(Ph)*C*(O)], in chloroform, at room temperature.

We have previously reported that the catalytic system formed by $[Pd(phen)_2][PF_6]_2$ in combination with free phen and the acid cocatalyst $[(phen)H][PF_6]$ is very active in the reductive carbonylation of nitroaromatic compounds to the corresponding carbamates.[2b,8] We have now found that the same catalytic system promotes the carbonylation of both azoxy- and azobenzene to urethane (Table 1). The preliminary results reported in Table 1 show that 94% of azobenzene is converted into carbamate in two hours, with aniline as the main by-product. On the other hand, when azoxybenzene is the substrate, azobenzene is the main product. These data indicates that azoxybenzene is transformed in azobenzene, which further reacts to give the carbamate.

Table 1. Carbonylation of azoxy- and azobenzene to carbamate; catalytic system: $[Pd(phen)_2][PF_6]_2$ + phen + $[(phen)H][PF_6]$[a]

Substrate	Conv. (%)	Selectivity (%)			
		Carbamate	Aniline	Azobenzene	Other
Azobenzene	94	80	14		6
Azoxybenzene	75	29	3	41	2

[a] Reaction conditions: n_{Pd} = 0.02 mmol; $n_{free\ phen}$ = 0.08 mmol; $n_{[(phen)H][PF6]}$ = 0.12 mmol; substrate: 2.5 mmol; methanol: V = 8.0 mL; 2,2′-dimethoxypropane: V = 0.4 mL; T = 155 °C; P_{CO} = 40 atm; t = 2 h.

On the basis of the catalytic results and on the isolated metallacycles (**2**) we propose a catalytic cycle (Figure 2) which may be operative contemporary to that of the main reaction.[4] The carbonylated species **A**, which is also supposed to be the active species for the conversion of nitrobenzene to carbamate, reacts with azoxybenzene yielding the metallacycle **B**. From the latter, azobenzene is obtained and the active species **A** is restored. Azoxy- and azobenzene may compete for the intermediate **A**. When azobenzene interacts with **A** the metallacycle **C** is formed. This intermediate can follow two different pathways: in one case it reacts with methanol and protons yielding one equivalent of carbamate and aniline, which was found to be the main by-product. In the other, the insertion of carbon monoxide into the Pd−N bond is possible yielding the metallacycle **D**, which corresponds to **2**. The attack of methanol on this

species generates two equivalents of carbamate and regenerates the active species **A**.[9]

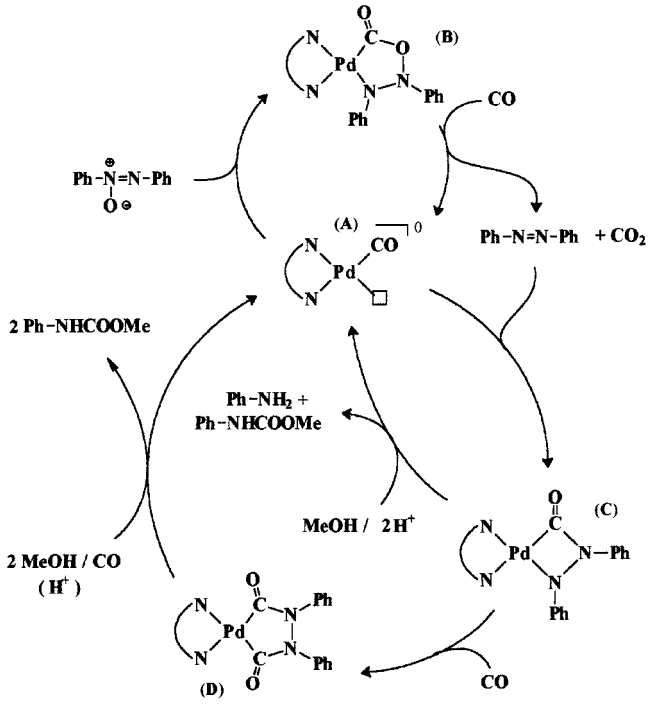

Figure 2. Proposed catalytic cycle

Conclusion

The isolation of the new metallacylic derivatives [(N-N)Pd*C*(O)N(Ph)N(Ph)*C*(O)] has allowed us to propose another catalytic cycle which should be operative contemporary to that of direct conversion of nitrobenzene to carbamate. In agreement with this hypothesis azoxy- and azobenzene are better regarded as intermediates of the reaction rather than by-products.

Moreover, a comparison of the two metallacycles [(phen)Pd*C*(O)N(Ph)O*C*(O)] **(1a)** and [(phen)Pd*C*(O)N-(Ph)N(Ph)*C*(O)] **(2a)** shows that, in the former, the N−O bond of the *C*(O)N(Ph)O*C*(O) moiety is polar, and therefore more likely to be broken than the N−N bond of the *C*(O)N(Ph)N(Ph)*C*(O) fragment of the second one. Therefore, the high amount of azobenzene obtained in the reductive carbonylation of nitrobenzene to urethane might be related to the more difficult formation and reaction of the metallacycles **2** than of **1**. The use of unsymmetrically substituted phenanthrolines, such as 3,4-dimethyl-1,10-phenanthroline, might favour the transformation of the corresponding metallacycle **2** into carbamate, increasing the selectivity of the overall reaction.

Experimental Section

The nitrogen-donor ligands were used as supplied (Aldrich). Azoxybenzene was synthesised from nitrosobenzene (Aldrich) in 0.2 M NaOH ethanolic solution. Azobenzene (Fluka) and methanol (Baker) were used without further purification. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

IR spectra were recorded on a Perkin−Elmer 983G spectrometer as KBr pellets.

^{1}H NMR spectra were recorded at 400 MHz on a Jeol EX 400 spectrometer operating in Fourier-transform mode, with tetramethylsilane (TMS) as internal standard.

The GC analyses were conducted on a gas-chromatograph DANI 6800 on a column 10% SE 30 (2 m), equipped with a Carlo Erba DP700 data processor.

Synthesis: The complexes [Pd(N-N)($CH_3COO)_2$], [Pd(N-N)$_2$][PF_6]$_2$ and compounds [(N-N)H][PF_6] were synthesised according to the procedures reported in literature.[10,11]

Synthesis of [(N-N)Pd*C*(O)N(Ph)N(Ph)*C*(O)] [N-N = phen (2a), tmphen (2b)]: The reaction was carried out in a Berghof stainless steel autoclave (100 mL), equipped with a Teflon liner and magnetic stirrer. [Pd(phen)($CH_3COO)_2$] (0.30 g, 0.7 mmol), phen (0.27 g, 1.5 mmol), azobenzene (0.77 g, 4.2 mmol) and methanol (10 mL) were placed in the reactor, which was then pressurised at 40 atm. with CO. The system was stirred at room temperature for 24 h. After releasing the residual gas, the pale-yellow solid was filtered at reduced pressure, washed with methanol and dried under vacuum.

The same procedure was followed for the complex with the tmphen ligand.

2a: Yield: 75 mg, 20%. − $C_{26}H_{18}N_4O_2Pd$ (524.85): calcd. C 59.5, H 3.46, N 10.7; found C 58.5, H 3.26, N 10.2. − IR (KBr): ν(CO) = 1627 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.05 (t, 2 H, *p*-Ph), 7.28 (overlapped with $CDCl_3$, *m*-Ph), 7.46 (d, 4 H, *o*-Ph), 7.91 (dd, 2 H, H^{3,8}), 7.95 (s, 2 H, H^{5,6}), 8.47 (d, 2 H, H^{4,7}), 10.25 (d, 2 H, H^{2,9}).

Synthesis of [(tm-phen)Pd*C*(O)N(Ph)N(Ph)*C*(O)] (2b): A chloroform (2.5 mL) solution of [(phen)Pd*C*(O)N(Ph)N(Ph)*C*(O)] (0.05 g, 0.1 mmol) was treated with tm-phen (0.03 g, 0.12 mmol). After stirring for 3 h at room temperature, a few drops of diethyl ether were added. The solid was filtered off, washed with cold chloroform and diethyl ether and dried under vacuum.
Yield: 53 mg, 90%. − $C_{30}H_{26}N_4O_2Pd$ (580.96): calcd. C 62.0, H 4.51, N 9.64; found C 61.5, H 4.26, N 9.52. − IR (KBr): ν(CO) = 1627 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.59 (s, 6 H, CH_3 of tm-phen), 2.70 (s, 6 H, CH_3 of tm-phen), 7.05 (t, 2 H, *p*-Ph), 7.28 (overlapped with $CDCl_3$, *m*-Ph), 7.45 (d, 4 H, *o*-Ph), 8.01 (s, 2 H, H^{5,6}), 9.74 (s, 2 H, H^{2,9}).

X-ray Structure Determination: A yellow single crystal of **2a**, prism shaped (0.40 × 0.20 × 0.18 mm) was mounted on an Enraf−Nonius CAD4 diffractometer, equipped with graphite monochromator and Mo-K_α radiation. Unit cell dimensions were obtained from a least-squares fit of the setting angles of 25 reflections in the θ range 10.0−14.5°. Intensity data were corrected for Lorentz-polarisation effects and absorption by an empirical ψ-scan method. The structure was solved by conventional Patterson and Fourier techniques[12] and refined by a full-matrix anisotropic least-squares method.[13] All the calculations were performed using the WinGX System, Ver 1.61.[14]

The choice of space group $P2_1/m$ involves a structural disorder of the phenyl rings, the Pd(phen) moiety being located on a symmetry mirror. On the other hand, an attempted structure solution in the

noncentrosymmetric space group $P2_1$ did not produce satisfactory results (large correlation matrix elements and nonpositive definite thermal ellipsoids for some atoms).

$C_{26}H_{18}N_4O_2Pd$, M = 524.84, monoclinic, space group $P2_1/m$ (No. 11), a = 10.125(5), b = 6.766(2), c = 15.468(3) Å, β = 94.97(2)°, U = 1055.7(6) Å^3, Z = 2, ρ_{calcd} =1.651 g cm^{-3}, μ (Mo-K_α) = 0.912 mm^{-1}, F(000) = 528; 2902 measured reflections at room temperature ($2\theta_{max}$ = 56°, octants $-14 \leq h \leq 14$; $0 \leq k \leq 9$; $0 \leq l \leq 20$), 2783 unique reflections [R(int) = 0.0708], 1568 observed [$I > 2\sigma(I)$], 229 parameters, $R1$ = 0.0524, $wR2$ = 0.0939, GoF = 0.953; hydrogen atoms in idealized geometries; weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0410P)^2]$, where P = (Max (F_o^2, 0) + $2F_c^2$)/3; max positive and negative peaks in ΔF map 0.460 and −0.909 e Å^{-3}, respectively. Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100492. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Catalysis: The carbonylation reactions were carried out in the Berghof reactor (see above). After introducing the catalyst precursor, the ligand and the acid cocatalyst the autoclave was closed. Nitrobenzene, methanol and 2,2′-dimethoxypropane were placed in a two necked flask connected both to the reactor and to the CO bomb through a PTFE tube. This solution was flushed with CO for 20 min and it was then transferred to the reactor. The autoclave was charged at 40 atm. of CO and heated to the proper temperature. At the end of the run the autoclave was cooled and the residual gas vented. The reaction mixture was filtered off over fine paper and analysed by GC.

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