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Palladacycle formation by electrophilic aromatic substitution, as monitored by ^{1}H NMR spectroscopy

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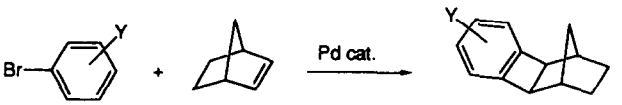
Abstract

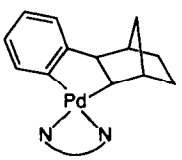
The formation of alkylaromatic palladacycles proceeds through an electrophilic aromatic substitution, as shown by monitoring by ^{1}H NMR spectroscopy the reactions of variously substituted aromatic compounds.

Some syntheses of cyclic compounds involving palladium-catalyzed C–C bond formation processes have been reported by us during the last decade [1,2]. One of the simplest is the following [1] (eq. 1).

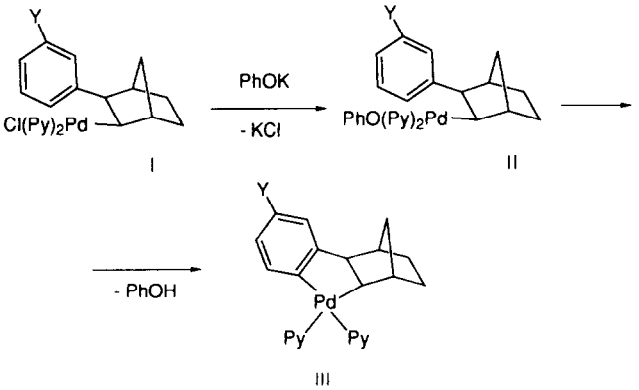


(1)

We proved that this reaction involves the formation of a palladacyclic species by trapping the intermediate with phenanthroline (N⌣N) [2].



However the way in which the ring closure proceeded was not clear because reaction (1) is favoured both by electron-withdrawing and electron-releasing substituents, Y. In some related reactions involving similar palladacyclic rings [3] electron-withdrawing substituents gave even better results in terms of selectivity. These facts posed the problem of possible oxidative addition or nucleophilic substitution processes leading to the formation of the intermediate palladacycle, rather than an electrophilic substitution. Although electrophilic substitution is a general feature of palladium chemistry [4], to our knowledge no information is available on the mechanism of intramolecular palladacycle formation from Pd–C precursors containing aromatic groups. To establish which pathway was followed in



(2)

our reactions, we studied the relative reactivity of different complexes under ring-forming conditions.

The NMR technique is a valuable tool to monitor the course of the reactions. The presence of protons which exhibit different chemical shifts in the starting complex and in the metallacyclic complex allows a clear-cut determination of the evolution of the system. We studied the formation of three metallacyclic complexes **III** containing Y = H, OMe, or NO_2 *para* to the Pd–C bond to be formed from appropriate complexes **I**, by ^{1}H NMR spectroscopy.

Complexes **I** were prepared from their dinuclear precursors (see Experimental) in chloroform solution by addition of pyridine. On further addition of potassium phenoxide, new species (**II**) were observed before the cyclization products (**III**) appeared. Intermediates **II**, which are likely to be derived from **I** by replacement of the chloride by the phenoxy anion, were stable at −50°C, but changed to **III** at −30°C. Type **III** complexes with pyridine as ligands were isolated. Their ^{1}H NMR spectra are similar to those of the analogous complexes with phenanthroline. However, the two pyridine units do not lie in the plane of the phenylnorbornyl group but are perpendicular to it, as indicated by the chemical shifts of the aromatic protons α to the Pd-bonded carbon atoms. Owing to ring current effects, these protons are observed at frequencies lower than expected (δ 6.16, 6.27 and 6.47 for Y = OMe, H, and NO_2, respectively). The metallacycle formation was monitored following the intensities of the signals corresponding to the Pd-bonded CH and the benzylic protons. The latter are particularly suitable for this purpose because of their sensitivity to structural changes and the absence of other interfering signals in the region of interest.

The chemical shifts of benzylic H and of H–C–Pd for complexes **I–III** are shown in Table 1. Under the reported conditions and using a 0.03 *M* concentration of compound **I**, half conversion of **II** to **III** (Y = OMe, H, or NO_2) occurred in approximately 10, 100, or 240 min, respectively. Half conversion allowed a satisfactory quantitative determination. Lower conversions in a given time, however, reflected the same trend. Competitive experiments were also carried out, but the overlap of some peaks prevented a complete observation of the species involved. The reactivity sequence is that to be expected from the substituent effects on electrophilic aromatic substitution.

Table 1

Chemical shifts of benzylic H and H–C–Pd relative to $CHCl_3$ at −30°C for complexes **I–III**

Y	H-benzylic (δ)			H-C-Pd (δ)		
	I	**II**	**III**	**I**	**II**	**III**
H	2.36	2.44	2.93	2.73	2.58	2.74
OMe	2.30	2.36	2.90	2.73	2.53	2.68
NO_2	2.40	2.41	2.98	2.80	2.64	2.78

The results are relevant to the understanding of the course of catalytic reactions of type 1. The fact that electron-releasing and electron-withdrawing substituents give comparable results in these reactions (1) must be attributed to opposing substituent effects in metallacycle ring formation and in reductive elimination to yield organic compounds.

Experimental

Starting materials were commercial products, and were used without further purification. Phenylmercuric chloride was an Aldrich product. *m*-Nitrophenyl- and *m*-anisyl-mercuric chloride were prepared by published methods [5,6]. Complexes **I** (Y = H or OMe) were obtained by adding pyridine to the dinuclear precursors, prepared according to the literature [7], while complex **I** (Y = NO_2) was obtained by recrystallizing the corresponding dinuclear complex from a solution of pyridine (2%) in dichloromethane. Palladium complex preparation and reactions were carried out under dinitrogen.

Complexes **III** (Y = H, OMe, or NO_2) were prepared as described previously [2], using an excess of pyridine (2–3 fold) in place of phenanthroline.

Complex **III**: ^{1}H NMR (200 MHz, $CDCl_3$/pyridine 99.5/0.5, TMS) (Y = H): δ 6.92 (1H, d, J = 8.1 Hz), 6.78 (1H, t, J = 8.1 Hz), 6.58 (1H, t, J = 8.2 Hz), 6.27 (1H, d, J = 8.2 Hz), 2.88 (1H, brd, J = 7.0 Hz), 2.69 (1H, dd, J = 6.9, 1.9 Hz), 2.16 (1H, m), 2.07 (1H, brd, J = 8.7 Hz), 1.75 (1H, m), 1.50–1.05 (3H, m), 1.05–0.75 (2H, m); (Y = OMe): 6.59 (1H, d, J = 2.6 Hz), 6.27 (1H, dd, J = 8.2, 2.5 Hz), 6.16 (1H, d, J = 8.2 Hz), 3.70 (3H, s), 2.91 (1H, brd, J = 7.1 Hz), 2.69 (1H, dd, J = 7.1, 1.9 Hz), 2.23 (1H, m), 2.12 (1H, d, J = 8.8 Hz), 1.78 (1H, m), 1.55–1.10 (3H, m), 1.10–0.75 (2H, m); (Y = NO_2): 7.79 (1H, d, J = 2.5 Hz), 7.53 (1H, dd, J = 8.3, 2.6 Hz), 6.47 (d, J = 8.3 Hz), 2.98 (1H, brd, J = 6.9 Hz), 2.78 (1H, dd, J = 7.1, 1.8 Hz), 2.24 (1H, m), 1.94 (1H, brd, J = 8.7 Hz), 1.82 (1H, m), 1.60–1.20 (3H, m), 1.05 (1H, m), 0.95 (1H, brd, J = 8.5 Hz).

Spectral monitoring

^{1}H NMR spectra were recorded with a Bruker CXP-200 spectrometer at −30°C using $CDCl_3$ solution containing ca. 0.03 *M* compound **I** (Y = H, OMe, NO_2). Excesses of pyridine and potassium phenoxide (molar ratio 3:1 and 2:1, respectively) were used. Addition of potassium phenoxide was carried out at −50°C.

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