Journal of Organometallic Chemistry, 458 (1993) C12–C15

JOM 23881PC

Preliminary Communication

Regioselective ring opening of a palladium(IV) alkylaromatic metallacycle by benzyl group migration from palladium to the aromatic carbon and X-ray structure of the resulting palladium(II) complex

Gabriele Bocelli

Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., V. le delle Scienze, 43100 Parma (Italy)

Marta Catellani

Istituto di Chimica Organica dell'Università, V. le delle Scienze, 43100 Parma (Italy)

Stefano Ghelli

Dipartimento di Chimica dell'Università, Via Campi, 41100 Modena (Italy)

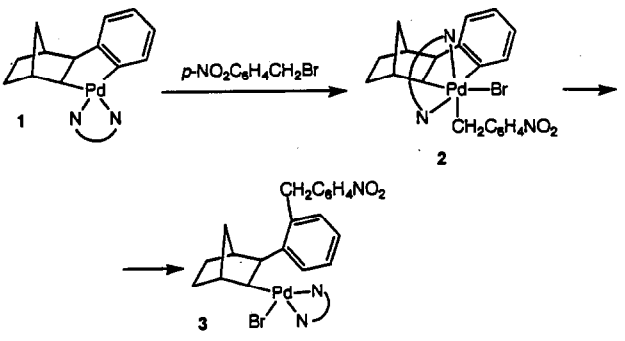
(Received March 30, 1993)

Abstract

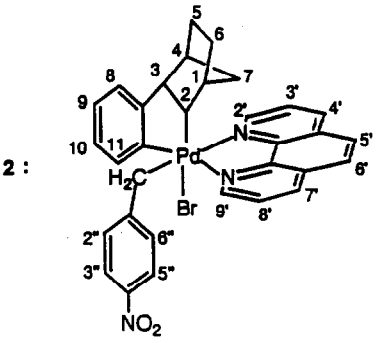
The stereochemical course of a $Pd^{II} \rightarrow Pd^{IV} \rightarrow Pd^{II}$ transformation is described for the first time through isolation of organometallic species containing the entire carbon skeleton.

In the key step of many processes catalyzed by metal complexes, carbon–carbon bond formation is accompanied by a change in metal oxidation state and in complex stereochemistry. Information on this process is of paramount importance in order to control selectivity in organic reactions. We now wish to report the isolation and crystal structure determination of a palladium(II) complex (**3**) derived from the rearrangement of a new palladium(IV) metallacycle (**2**) (eqn. (1)).

Correspondence to: Professor M. Catellani.



(1)

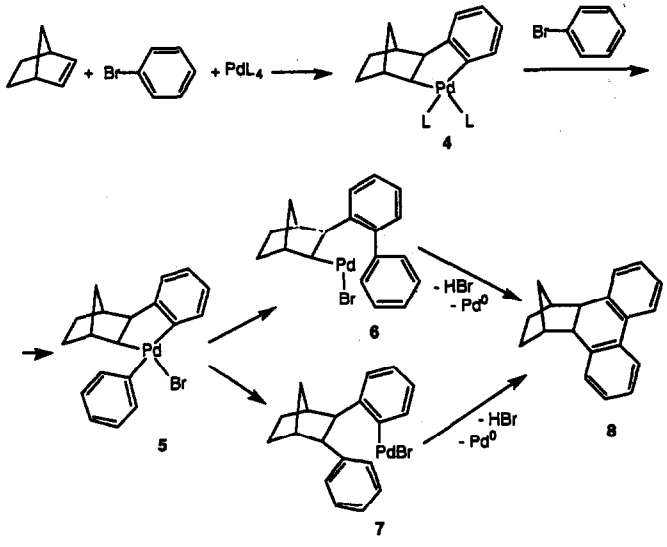


Reactions involving palladium(IV) intermediates with three Pd–C bonds have been often postulated [1] but only recently have these species been isolated [2]. In particular the sequence shown above corresponds to a model of the key steps of the catalytic synthesis of methanotriphenylene derivatives (**8**) we described some years ago. (Scheme 1, L = triphenylphosphine) [1i].

A palladium(IV) complex (**5**) formed by oxidative addition of the aryl halide to Pd^{II} was postulated as intermediate but is yet to be isolated. By using substituted aryl bromides we showed that two pathways, involving migration of the phenyl ring of **5** either to the aryl (complex **6**) or to the norbornyl group (complex **7**) were at work. For example, with *p*-fluoro-substituents, two, organic products of type **8**, corresponding to intermediates **6** and **7**, were obtained in *ca.* 3/1 molar ratio [1i].

The reaction described here stems from the isolation of a palladium(IV) complex (**2**) by reaction of palladacycle **1** (*exo*) [2e] with *p*-nitrobenzyl bromide. In solution, the complex is stable for some hours at room temperature, then benzyl group migration to the aromatic site slowly occurs. The process corresponds to a strictly regioselective rearrangement with concomitant change of the palladium oxidation state, and offers an opportunity to check a stereochemical course probably common to other palladium(IV)-mediated reac-

0022-328X/93/$6.00



Scheme 1. Mechanism proposed for the reaction of norbornene with aryl bromides.

tions [3]. The resulting palladium(II) complex was isolated and the X-ray analysis of a crystal was carried out. The structure of **3** is shown in Fig. 1 *.

It is worth noting the distortion from planarity of the square coordination of palladium, which causes a moderately *twisted* conformation with a dihedral angle between the N2–Pd–N3 and Br–Pd–C13 mean planes of 8.5(3)°. The dihedral angle between the two pyridine rings (2.5(4)°), reveals a little bowing of the phenanthroline ligand, which compensates for the significant narrowing of the N2–Pd–N3 angle and the enlargement of the Br–Pd–C13 angle, with bromine moving away from the norbornyl group. The chloroform solvent is disordered in two different positions.

Information concerning the stereochemistry of the palladium(IV)–palladium(II) transformation was acquired from NMR analysis of the palladium(IV) complex (**2**). In the latter, the phenanthroline was shown to be perpendicular to the metallacycle, favouring a *cis* arrangement of the two fragments deriving from the oxidative addition of *p*-nitrobenzyl bromide to the metal. This arrangement was clearly indicated by NMR spectroscopy **.

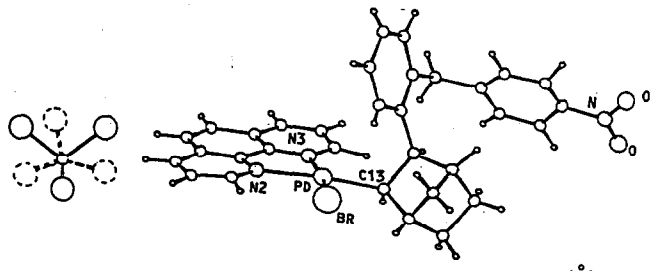


Fig. 1. Projection of the complex. Selected bond distances (Å) and angles (°): Pd–Br = 2.453(2), Pd–C13 = 2.042(10), Pd–N2 = 2.185(8), Pd–N3 = 2.071(9), Br–Pd–C13 = 96.6(3), Br–Pd–N2 = 92.1(2), Br–Pd–N3 = 169.8(3), N3–Pd–C13 = 93.6(4), N2–Pd–N3 = 77.9(4), N2–Pd–C13 = 168.1(4).

The assignment of proton resonances was obtained by observing COSY, TOCSY and NOESY spectra. As previously observed for an analogous compound [2f], the large shifts shown by protons 1 and 7*syn* of the norbornyl group were particularly helpful. These low frequency shifts are due to ring current effects and indicate the proximity of the corresponding protons to an aromatic ring. The NOEs between H7*syn* and H2′ and between H9′ and H2*endo* confirm that phenanthroline is in close proximity to the upper and lower part of the norbornyl ring, with one side near the bridge and the other one close to H2*endo*. Moreover, the phenanthroline proton 9′ showed NOEs with the benzylic protons and the aromatic hydrogens of the benzyl ring, indicating that the benzyl group is *cis* to a phenanthroline nitrogen. All other NOE effects are consistent with the arrangement shown in complex **2**.

* Crystal data for complex **3**: $C_{32}H_{28}BrN_3O_2Pd \cdot CHCl_3$, M = 792.27, monoclinic, $P2_{1/c}$; cell parameters: a = 18.223(2), b = 9.788(2), c = 17.931(3) Å, β = 101.43(2)°; V = 3134.9 (Å^3); $F(000)$ = 1584; D_c = 1.68 (g cm^{-3}); μ = 21.39 (cm^{-1}); Z = 4; crystal dimensions = 0.09×0.12×0.19 mm; θ range = 3–25°; total reflections collected = 6082; total observed = 3701; total independent = 3569; limit = $I \geq 2\sigma(I)$; R_{int} = 0.018; final R = 0.058. Cell parameters obtained from least-square on angular $(\theta, \chi, \phi)_{hkl}$ values of 28 reflections automatically centered on a Siemens AED diffractometer using the Mo-Kα radiation (λ = 0.71069 Å). The intensities were corrected for Lorentz and polarisation effects. The structure was solved with automated Patterson methods with XFPS90 and refined by full-matrix anisotropic cycles. The hydrogens were found in a final ΔF map and refined isotropically. All the calculations were performed on an IBM PS2/80 personal computer with the CRYSRULER package. Further details of the crystal structure investigation and Tables of deposited data are availble from the Cambridge Crystallographic Data Centre.

** ^{1}H NMR data for complex **2**: (400 MHz, $CDCl_3$, 243 K): δ = 8.69 (dd, J = 4.9, 1.4 Hz, 1 H, H2′), 8.49 (dd, J = 8.2, 1.4 Hz, 1 H, H4′), 8.44 (dd, J = 8.2, 1.4 Hz, 1 H, H7′), 8.42 (dd partly overlapping with H7′, J = 7.1, 2.1 Hz, 1 H, H11), 8.50–8.10 (AA′ part of an AA′BB′ system, 2 H, H3″, H5″), 7.97 (br s, 2 H, H5′, H6′), 7.84 (dd, J = 4.9, 1.4 Hz, 1 H, H9′), 7.71–7.63 (m, 4 H, H3′, H8′, H2″, H6″), 7.15–7.06 (m, 2 H, H9, H10), 6.94 (dd, J = 6.8, 2.1 Hz, 1 H, H8), 4.36 (d, J = 7.4 Hz, 1 H, benzylic-H), 4.03 (d further split, J = 6.5 Hz, 1 H, H2*endo*), 3.99 (d, J = 7.4 Hz, 1 H, benzylic-H), 3.05 (d further split, J = 6.9 Hz, 1 H, H3*endo*), 2.28 (m, 1 H, H4), 1.44–1.33 (m, 1 H, H5*exo*), 1.18–1.08 (m, 1 H, H5*endo*), 1.01 (d further split, J = 9.5 Hz, 1 H, H7*syn*), 0.96–0.84 (m, 1 H, H6*exo*), 0.84–0.73 (m, 2 H, H1, H6*endo*), 0.46 (d further split, J = 9.5 Hz, 1 H, H7*anti*).

The structure appears to be rather rigid, even in solution at 243 K, as shown by the shielding effect experienced by proton 9′, probably in front of the aromatic ring of the benzyl group and the NOEs. Benzyl group migration to the aromatic part of the complex causes ring opening to complex **3**. In contrast with the earlier described pathways leading from **5** to **8**, the migration is completely regioselective towards the aryl site. Migration to the cycloaliphatic part is probably prevented by the shielding of the phenanthroline. Concomitantly with benzyl migration, phenathroline reverts to a square planar arrangement, which is stabilized in the crystal by weak interaction with the phenanthroline ligand of another molecule.

At the present stage of our research, a detailed mechanism involving the stereochemistry of the oxidative addition to palladium (II) and of the reductive elimination step from palladium(IV) cannot be proposed. Isolated palladium(IV) complexes are formed by oxidative addition of alkyl or benzyl groups while the formation of analogous complexes from aromatic halides could not be observed, although the organic products obtained point to their intermediacy. This circumstance has certainly to do with different mechanisms. S_N2-type mechanisms have been shown to be operative with alkyl or benzyl halides [4] while other mechanisms, such as single electron-transfer could be at work with aromatic halides. Different mechanisms would have different electronic and steric requirements. [5].

Sterically demanding groups and geometrical rigidity [6,7] are expected to influence both the oxidative addition and the reductive elimination steps. Thus the first attack on an axial position could be followed by the appropriate rearrangement placing the halide and the organic groups in the *cis* position actually observed. Reductive elimination from this position probably requires further modification of the complex geometry to enable the groups undergoing coupling to place themselves in axial-equatorial rather than equatorial *cis* position in respect to the plane defined by phenanthroline and palladium (thus avoiding the need for an unlikely N–Pd–N widening) [8]. This process will require breaking of a ligand-to-Pd bond, probably the halide [9].

It is interesting at this point to contrast the behaviour of our complex in eqn. (1) with the recently described [PdBrMe(CH_2Ph)Ph(bpy)] (bpy = 2,2′-bipyridine) [6]. This complex eliminates toluene exclusively, while in our case the reaction occurs between the benzyl and the aryl group, selectively. Although the two situations are quite different, the elimination process should be regarded in both cases as an axial-equatorial coupling between *cis* ligands with the phenyl group in axial position in respect to the plane defined by the phenanthroline or bipyridine ligand. In the bipyridine complex the methyl group couples with the phenyl group because the possible competitor (benzyl group) is more strongly bound to the metal, while in our case the benzyl group reacts more easily with the aromatic nucleus than the norbornyl one because of the stability of the metallacycle ring.

1. Experimental details

1.1. Complex 2

To a 10 ml dichloromethane solution of **1** (0.140 g, 0.30 mmol) prepared as described elsewhere [2e], was added *p*-nitrobenzyl bromide (0.066 g, 0.30 mmol) in 2 ml of dichloromethane. The resulting solution was stirred under dinitrogen for 5 min at room temperature. By removal of most of the solvent and addition of hexane, complex **2** was precipitated as a light yellow solid, filtered and dried *in vacuo* (yield 0.165 g, 82%).

1.2. Complex 3

To a 5 ml chloroform solution of **1** (0.100 g, 0.22 mmol) was added *p*-nitrobenzyl bromide (0.052 g, 0.24 mmol) in 1 ml of chloroform. The resulting solution was left under dinitrogen overnight at room temperature and then cooled at *ca.* −15°C. Orange crystals of **3** (0.115 g, 78%) were isolated and dried *in vacuo*.

Acknowledgements

This research was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Roma) and by Consiglio Nazionale delle Ricerche (C.N.R, Roma). We thank Bruker Italiana, Milano, for access to their AMX-400 spectrometer.

References

1 (a) P.M. Maitlis and F.G.A. Stone, *Chem. Ind.*, (1962) 1865; (b) J.K. Stille and K.S.Y. Lau, *J. Am. Chem. Soc.*, *98* (1976) 5841; (c) D. Milstein and J.K. Stille, *J. Am. Chem. Soc.*, *101* (1979) 4981, 4992; (d) A. Gillie and J.K. Stille, *J. Am. Chem. Soc.*, *102* (1980) 4933; (e) S.J. Tremont and H.U. Rahman, *J. Am. Chem. Soc.*, *106* (1984) 5759; (f) B.M. Trost, C. Chan and G. Ruhter, *J. Am. Chem. Soc.*, *109* (1987) 3486; (g) T. Ito, H. Tsuchiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, *50* (1977) 1319; (h) P. Diversi, D. Fasce and R. Santini, *J. Organomet. Chem.*, *269* (1984) 285; (i) M. Catellani and G.P. Chiusoli, *J. Organomet. Chem.*, *286* (1985) C13.

2 (a) P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, *J. Chem. Soc. Chem. Commun.*, (1986) 1722; (b) P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Commun., (1987) 1093; (c) P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, J. Organomet. Chem., 336* (1987) C55; (d) B.A. Markies,

A.J. Canty, M.D. Janssen, A.L. Spek, J. Boersma and G. van Koten, *Recl. Trav. Chim. Pays-Bas, 110* (1991) 477; (e) M. Catellani and G.P. Chiusoli, *J. Organomet. Chem., 346* (1988) C27; (f) M. Catellani and B.E. Mann, *J. Organomet. Chem., 390* (1990) 251. For a recent review on palladium(IV) complexes see: A.J. Canty, *Acc. Chem. Res., 25* (1992) 83.

3 O. Reiser, M. Weber and A. de Meijere, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1037.

4 P.K. Byers, A.J. Canty, M. Crespo, R.J. Puddephatt and J.D. Scott, *Organometallics, 7* (1988) 1363; K. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott and A.A. Watson, *Organometallics, 8* (1989) 1518.

5 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Application of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987; F. Ozawa, M. Fujimori, T. Yamamoto and A. Yamamoto, *Organometallics, 5* (1986) 2144.

6 W. de Graaf, J. Boersma and G. van Koten, *Organometallics, 9* (1990) 1479.

7 L. Zhang and K. Zetterberg, *Organometallics, 10* (1991) 3806.

8 P.S. Braterman, in P.S. Braterman (ed.), *Reactions of Coordinated Ligands*, Vol. 1, Plenum Press, New York, 1986, p. 60; S. Komiya, T.A. Albright, R. Hoffmann and J.K. Kochi, *J. Am. Chem. Soc., 98* (1976) 7255; S. Komiya, T.A. Albright, R. Hoffmann and J.K. Kochi, *J. Am. Chem. Soc., 99* (1977) 8440; K. Tatsumi, R. Hoffmann, A. Yamamoto and J.K. Stille, *Bull. Chem. Soc. Jpn., 54* (1981) 1857; R.J. McKinney, D.L. Thorn, R. Hoffmann and A. Stockis, *J. Am. Chem. Soc., 103* (1981) 2595.

9 P.K. Byers, A.J. Canty, B.W. Skelton, P.R. Trail, A.A. Watson and A.H. White, *Organometallics, 9* (1990) 3080.