Journal of Organometallic Chemistry, 437 (1992) 369–373
Elsevier Sequoia S.A., Lausanne
JOM 22754

A simple direct synthesis of an alkylaromatic palladacycle

Marta Catellani and Gian Paolo Chiusoli
Istituto di Chimica Organica dell'Università, Viale delle Scienze, I-43100 Parma (Italy)

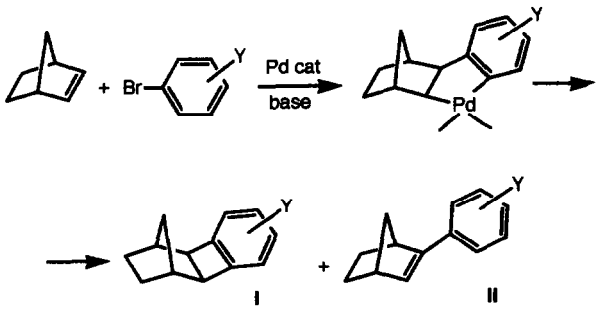
(Received November 20, 1991)

Abstract

The first direct preparation of an alkylaromatic palladacycle is reported. It consists of the reaction of 1-bromo-3-cyanobenzene with norbornene and palladium(0) complexes in the presence of potassium phenoxide.

Introduction

We reported earlier various palladium-catalyzed organic syntheses involving alkylaromatic palladacycles [1,2]. A simple example [1] is given by eq. 1 (Y = substituent; non-reactive ligands are omitted for simplicity).

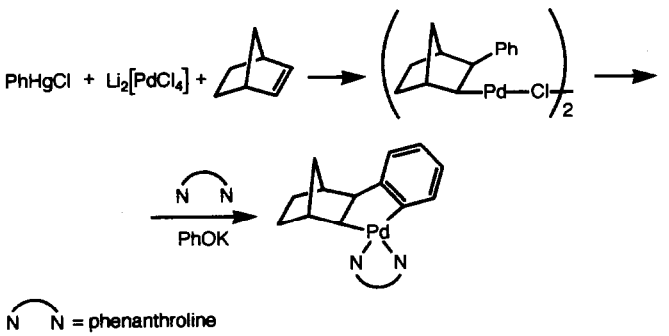


(1)

The palladacycle complex, which also is a key intermediate in other syntheses involving palladium(IV) [3], could be trapped with a stabilizing ligand such as phenanthroline in a stoichiometric reaction according to eq. 2 [4]. The synthesis requires palladium exchange with arylmercury halides followed by norbornene insertion [5] and cyclization [4] in the presence of suitable ligands.

Correspondence to: Professor M. Catellani.

0022-328X/92/$05.00 © 1992 – Elsevier Sequoia S.A. All rights reserved

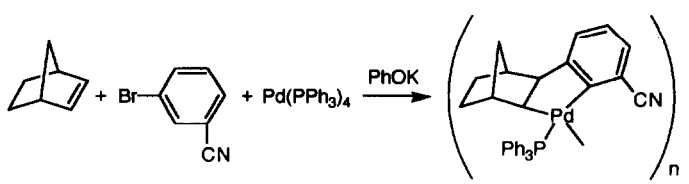


(2)

In an attempt to trap the intermediate directly from a catalytic reaction we have now isolated a palladacyclic complex containing Y = CN *ortho* to Pd–C. To our knowledge this is the first one-pot preparation of a palladacycle by a sequence of oxidative addition, insertion and aromatic substitution.

Results and Discussion

Complex III (eq. 3) is prepared by causing an excess of 1-bromo-3-cyanobenzene to react with norbornene and $[Pd(PPh_3)_4]$ in anisole at 105°C in the presence of potassium phenoxide.

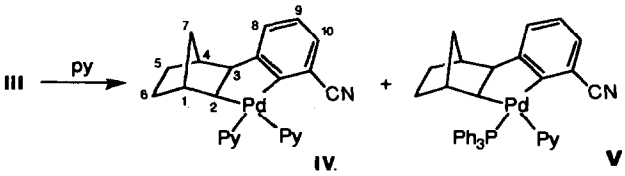


(3)

III

Compound III (*cis, exo*) separates spontaneously from the reaction solution in 67% yield (on Pd). In the absence of a substantial excess of norbornene and bromocyanobenzene compared to palladium (at least more than 5 mol per mol) a small amount of solid complex separates. It is notable that when *p*-bromo- and *o*-bromo-cyanobenzene are used in place of the *m*-cyano-isomer, no insoluble complex is formed. Complex III is an air stable whitish powder and has been characterized analytically, by chemical methods and by IR and NMR spectroscopies. It contains one molecule of triphenylphosphine per molecule of palladium. A coordination site is occupied by the cyano group of another palladacycle unit. This leads to the formation of a species completely insoluble in non-coordinating solvents. The complex should be regarded as polymeric rather than dimeric, in view of the considerable steric presence that would be encountered in the latter. Coordination of the cyano-group is clearly indicated by the absorption of the carbon–nitrogen triple bond at 2242 cm^{-1}. On adding pyridine the complex gradually dissolves when the CN frequency changes to 2212 cm^{-1}. Evidence that the complex is a *cis, exo* palladacycle with the CN group *ortho* to the carbon atom attached to palladium, is provided by NMR spectroscopy. The ^1H NMR spectra of

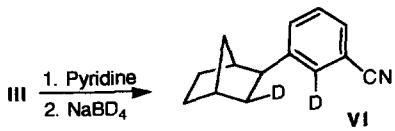
a deuterated pyridine solution of compound III reveal the presence of two species IV and V in a *ca.* 1/3 ratio (eq. 4).



(4)

The $^{31}J(P-H)$ coupling constant (13 Hz) between phosphorus and the *endo* proton of the methyne group attached to palladium provides evidence for a coordinated phosphine *trans* to the aryl group. The presence of two species is confirmed by ^{31}P NMR spectroscopy which shows coordinated and free phosphine in an estimated ratio of *ca.* 1/3.

The structure of the palladacycle is corroborated by its chemical behaviour: treatment of a pyridine solution of III with $NaBD_4$ and methanol-d_1 leads to the formation of the corresponding dideuterated product (2-(2′-*d*-3′-cyanophenyl)-3-*exo*-*d*-bicycloheptane (VI)) (eq. 5). The presence of deuterium at the *exo* position of the norbornyl group is clearly indicated by the multiplicity of the *endo* protons attached to carbon 2 and carbon 3. Both protons resonate as broad doublets.



(5)

After dissolution in pyridine, complex III can be converted again into its polymeric form by removing pyridine. It is worth noting that norbornene and bromocyanobenzene used in excess over palladium for the preparation of III react catalytically giving rise to the cyano derivatives of I (5-CN and 6-CN isomers) and II (*meta*-cyano). In contrast to the metallacycles from norbornene and other aromatic halides, the polymeric intermediate from norbornene and *m*-bromocyanobenzene precipitates directly from the reaction solution. That the reaction leading to the cyano derivatives of I and II proceeds further in the homogeneous solution clearly indicates that complex III corresponds to a catalytic intermediate. Since these metallacycles can also act as intermediates in a rich chemistry involving Pd^{IV} complexes [3] the possibility of directly separating a cyano complex offers a new starting point for synthetic developments.

Experimental

Starting materials were commercial products and were used without further purification. $[Pd(PPh_3)_4]$ and potassium phenoxide were prepared by literature methods [6,7]. Reactions were carried out under dinitrogen. Mass spectra were obtained with a Finnigan 1020 instrument at 70 eV. ^1H NMR spectra were recorded on Bruker CXP-200 and AMX-400 spectrometers. ^{31}P NMR spectra were run on a Bruker CXP-200 at 81 MHz. ^{31}P chemical shifts are reported relative to 85% H_3PO_4 as external standard at 0.00 ppm. IR spectra were recorded

with a Nicolet 5PC FT-IR spectrometer. Elemental analyses were performed by the Analytical Department of Istituto Donegani, Novara.

Preparation and spectroscopic data

A solution of norbornene (0.71 g, 7.55 mmol) and *m*-bromocyanobenzene (1.25 g, 6.88 mmol) in anisole (16 ml) was added to $[Pd(PPh_3)_4]$ (1 g, 0.86 mmol) and potassium phenoxide (0.91 g, 6.89 mmol) contained in a Schlenk-type flask. The mixture was stirred at 105°C for 18 h. The resulting heterogeneous solution was filtered and the very fine solid (III) thus obtained, was washed with water, acetone, methylene chloride and ether, then dried under vacuum. (Yield: 0.32 g, 67%.) After the usual work-up, GLC analysis of the organic solution showed the presence of unreacted bromocyanobenzene (0.53 mg) and compounds I (Y = 5-CN, 0.13 g; Y = 6-CN, 0.36 g) and II (Y = *m*-CN, 0.07 g). The products were separated by flash chromatography on a SiO_2 column using hexane/THF (96/4) as eluents and were characterized by ^1H NMR and mass spectroscopy.

1,2,3,4,4a,8b-Hexahydro-5-cyano-1,4-methanobiphenylene (I; Y = 5-CN). MS (70 eV): M^+ 195, *m/e* 180, 167, 166, 154, 153, 152, 140, 127, 77, 63; ^1H NMR: (200 MHz, $CDCl_3$, TMS; the assignments marked with one or two asterisks may be mutually interchanged): δ 7.43 (H6, br d, $J = 7.8$ Hz), 7.27 (H7, dd, $J = 7.8$, 7.3 Hz), 7.18 (H8, dd, $J = 7.3$, 1.0 Hz), 3.34 (H4a *, d, $J = 3.8$ Hz), 3.25 (H8b *, d, $J = 3.8$ Hz), 2.47 (H4 **, br s), 2.31 (H1 **, br s), 1.72–1.52 (H2-*exo*, H3-*exo*, m), 1.37–1.05 (H2-*endo*, H3-*endo*, m), 1.03 (H7-*anti*, d further split, $J = 10.5$ Hz), 0.77 (H7-*syn*, d further split, $J = 10.5$ Hz). Compound I (Y = 6-CN) has been reported [1].

2-(3'-Cyanophenyl)bicyclohept-2-ene (II; Y = m-CN). MS (70 eV): M^+ 195, *m/e* 168, 167, 166, 140; ^1H NMR: (200 MHz, $CDCl_3$, TMS): δ 7.48 (H2', br s), 7.46–7.30 (H4', H5', H6', m), 6.32 (H3, d, $J = 3.2$ Hz), 3.30 (H1, br s), 3.01 (H4, m), 1.87–1.69 (H5-*exo*, H6-*exo*, m), 1.52 (H7-*syn*, d further split, $J = 8.3$, 2.0 Hz), 1.25 (H7-*anti*, br d, $J = 8.3$ Hz), 1.20–1.05 (H5-*endo*, H6-*endo*, m).

Compound III. Anal. Found: C, 68.68; H, 5.34; N, 2.54; P, 5.02; Pd, 18.02. $C_{32}H_{28}NPPd$ calc.: C, 68.20; H, 4.97; N, 2.48; P, 5.59; Pd, 18.82%. IR: ν(CN) = 2242 (KBr), 2212 cm^{-1} (pyridine solution). No change of the absorption frequency of the triple bond was observed when the IR spectrum of *m*-bromocyanobenzene was examined in the solid state (KBr disc) or in pyridine solution.

Compounds IV and V. ^1H NMR (400 MHz, pyridine-d_5, TMS, * indicates the signals due to compound V): δ 7.78–7.72 * (protons *ortho* to phosphorus, m), 7.47–7.41 (protons *ortho* to the phosphorus of free triphenylphosphine (TPP), m), 7.37 (H10, d partly overlapping with TPP protons), 7.35–7.32 (free and coordinated TPP protons, m), 7.30 (H8, dd, $J = 7.6$, 1.3 Hz), 7.09 * (H9, t, $J = 7.6$ Hz), 7.06 (H9, t, $J = 7.6$ Hz), 3.29 * (H3, br d, $J = 7.4$ Hz), 3.19 (H3, br d, $J = 7.4$ Hz), 2.95 (H2, dd, $J = 7.3$, 2.2 Hz), 2.86 * (H2, ddd, $J = 7.5$, 2.2 Hz, J(P,H) = 13 Hz), 2.33 (H4, br s), 2.32 (H7-*syn*, partly overlapping with H4), 2.24 * (H1, m), 2.21 * (H4, m), 2.17 (H1, br d, $J = 3.2$ Hz), 2.10 * (H7-*syn*, $J = 8.8$ Hz), 1.61–1.52 (H5-*exo*, m), 1.41 (H6-*exo*, dt, $J = 11.6$, 4.3 Hz), 1.38–1.30 (H5-*endo*, m), 1.09–1.02 (H7-*anti*, H6-*endo*, m), 0.91 * (H7-*anti*, br d, $J = 8.8$ Hz). $^{31}P\{^1H\}$ NMR (pyridine-d_5): δ 25.0, coordinated phosphine; −4.6, free phosphine.

Decomposition of IV and V with $NaBD_4$

A solution of III (145 mg, 0.25 mmol) in 20 ml of pyridine, containing 0.5 ml of CH_3OD was treated with $NaBD_4$ in an excess and the mixture was stirred at room temperature for 1 h. The resulting black suspension was filtered and the solvent was removed under vacuum. The residue was treated with dilute sulfuric acid and extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. Compound VI (42 mg, 82% yield) was obtained by flash chromatography on SiO_2 column using hexane/THF (95/5) as eluents and was characterized by ^1H NMR and mass spectroscopy.

Compound VI. MS (70 eV): M^+ 199, *m/e* 132, 82, 68; ^1H NMR: (200 MHz, $CDCl_3$, TMS): δ 7.46–7.42 (H4′, H6′, m), 7.36 (H5′, dd, $J = 8.2$, 7.1 Hz), 2.75 (H2, br d, $J = 8.8$ Hz), 2.38 (H1, H4, br s), 1.78 (H3-*endo*, br d, $J = 8.9$ Hz), 1.68–1.55 (H5-*exo*, H6-*exo*, m), 1.47 (H7-*syn*, ddd, $J = 10.0$, 2.0, 1.6 Hz), 1.40–1.27 (H5-*endo*, H6-*endo*, m), 1.23 (H7-*anti*, ddd, $J = 10.0$, 2.5, 1.6 Hz).

Acknowledgements

This work was supported by Ministero dell'Università e della Ricerca Scientifica (MURST, Roma) and the Consiglio Nazionale delle Ricerche (CNR, Roma). NMR and mass facilities have been provided by Centro Interfacoltà di Misure, Università di Parma.

References

1 M. Catellani, G.P. Chiusoli and S. Ricotti, J. Organomet. Chem., 296 (1985) C11.
2 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 286 (1985) C13.
3 M. Catellani, G.P. Chiusoli and C. Castagnoli, J. Organomet. Chem., 407 (1991) C30.
4 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 346 (1988) C27.
5 H. Horino, M. Arai and M. Inoue, Tetrahedron Lett., (1974) 647.
6 D.R. Coulson, Inorganic Syntheses, Vol. XIII, 1972, p. 121.
7 F. Schmidt in Houben-Weyl, Methoden der organischen Chemie, Vol. 6/2, Sauerstoffverbindungen, 4th ed., Thieme-Verlag, Stuttgart, 1963, p. 38.