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Preliminary communication

Palladium-(II) and -(IV) complexes as intermediates in catalytic C–C bond-forming reactions

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Abstract

Palladium-(II) and -(IV) species active as catalysts in C–C bond-forming reactions have been stabilized by adding phenanthroline as a ligand. The complexes formed have been characterized by chemical and spectroscopic methods and their formation and subsequent fate have been monitored by ^{1}H NMR spectroscopy.

We previously described palladium-catalyzed C–C bond-forming reactions, leading for example to compounds VII and VIII from aryl bromides and bicyclo-[2.2.1]hept-2-ene, and postulated the intermediacy of complexes II–V (Scheme 1) [1–6]. Recent papers on the preparation of some new palladium(IV) complexes [7] prompt us to report our preliminary results aimed at clarifying the mechanism of these reactions.

Complex I was prepared as previously described [8] and a one molar proportion of phenanthroline was added, to give II as a yellow microcrystalline solid. Upon treatment with $NaBD_4$ this complex gave monodeuterated phenylbicycloheptane [8]. Addition of potassium phenoxide to a dichloromethane solution of II gave complex III, which was isolated as an orange microcrystalline solid. The metallacyclic structure of III can be confidently assumed on the basis of the results of hydrogenolysis with $NaBD_4$ and quantitative analysis of its components: the cycloalkylaromatic ligand, isolated as the dideuterated compound (2-(*o-d*-phenyl)-3-*d*-bicycloheptane), and 1,10-phenanthroline are both present in 1/1 ratio to Pd. The complex was fully characterized by ^{1}H NMR spectroscopy. It is noteworthy in this connection that the proton on the carbon atom *ortho* to the palladium-bonded aromatic carbon exerts an Overhauser effect on the facing phenanthroline proton.

Upon addition of CH_3I to III complex IV was formed. This complex is stable at low temperature and can be kept in the solid state at $-80\,^\circ$C. The ^{1}H NMR spectrum recorded at $-20\,^\circ$C clearly shows useful signals particularly those from the methyl group protons and those from the protons on the carbon atoms of the palladacycle and on the aromatic carbon *ortho* to the palladium–carbon bond. The

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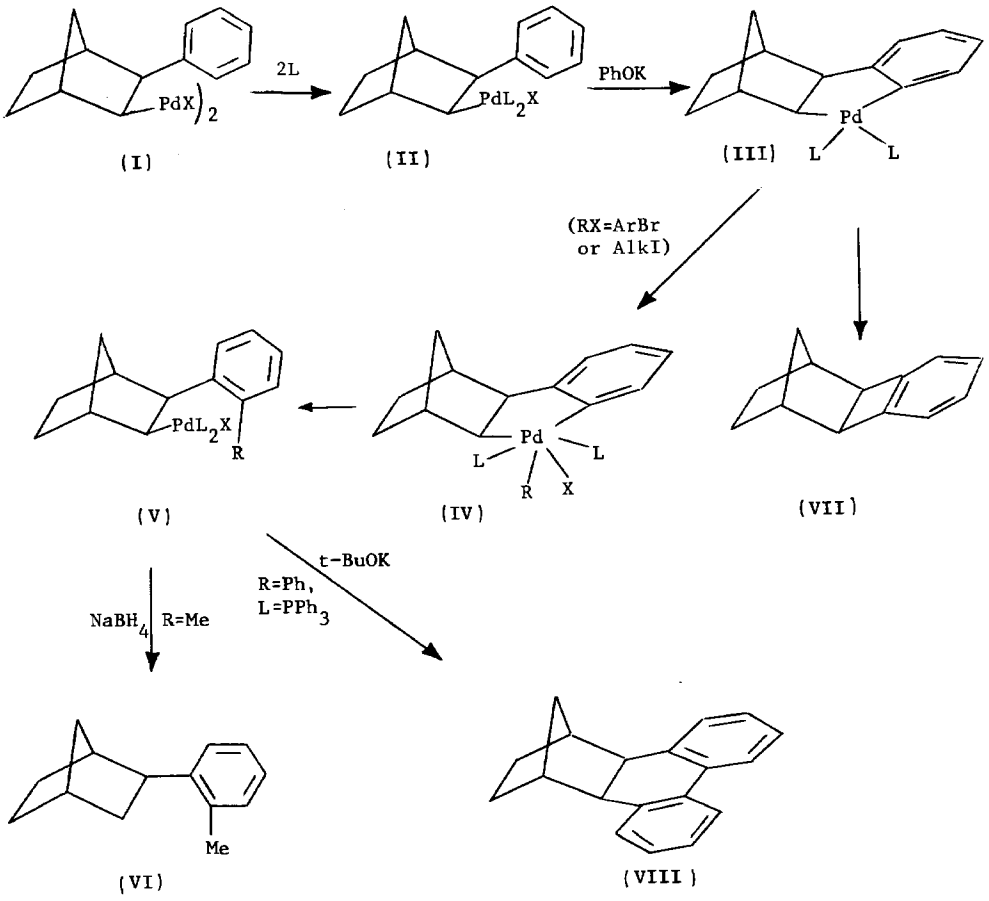


Scheme 1.

relative positions of the Me and I fragments have not so far been determined.

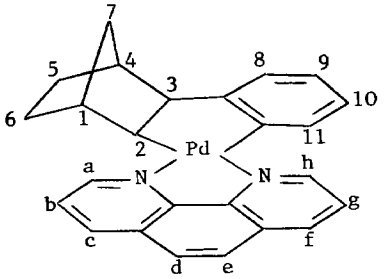
When the solution of complex IV was allowed to warm slowly to room temperature the phenyl group underwent methylation in the *ortho* position (complex V) and compound VI was obtained by treatment with $NaBH_4$. It is relevant to note that we had previously shown that in the catalytic reaction with bromobenzene in the presence of t-BuOK and triphenylphosphine as ligand, the R group (phenyl) migrated in both the aromatic and cycloaliphatic rings before VIII was formed [1c], whereas in the present reaction the methyl group is found exclusively on the aromatic ring.

Palladium(IV) complexes have been postulated as intermediates in coupling reactions [9–18]. In addition to the recently prepared complexes [7], some pentafluorophenyl derivatives described some years ago [19] must be regarded as the first examples of palladium(IV) complexes. In our case the use of phenanthroline as ligand does not favor the formation of substantial amounts of VII and VIII under the mild conditions previously used in catalytic processes [1c,4]. Complexes I–V are therefore to be regarded as stabilized forms of the species involved in the catalytic processes we previously described.

Further work aimed at providing a complete picture of the structure and reactivity of these unusual complexes is in progress.

Preparative and spectroscopic data

To complex I (80 mg, 0.25 mmol) [8] and potassium phenoxide (92 mg, 0.70 mmol) contained under nitrogen in a Schlenk-type flask, was added a solution of *o*-phenanthroline (82 mg, 0.45 mmol) in CH_2Cl_2 (15 ml). The mixture was stirred magnetically at room temperature for 30 min, water (3 ml) was then added, and after 10 min further stirring the organic layer was separated. Concentration of the extract under reduced pressure followed by cooling to $-20\,^{\circ}C$ gave a precipitate of III. Recrystallization from acetone at $-20\,^{\circ}C$ yielded 71 mg (62%) of III as a bright orange microcrystalline solid. More of the complex was isolated by concentrating the mother liquor and adding n-hexane.



Compound III. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 9.48 (1H, H(h), dd, *J* 4.9, 1.6 Hz); 9.14 (1H, H(a), dd, *J* 4.9, 1.6 Hz); 8.36, 8.35 (2H, H(f), H(c), 2 overlapping dd, *J* 8.1, 1.6 Hz); 7.82 (2H, H(d), H(e), s); 7.79, 7.78 (2H, H(g), H(b), 2 overlapping dd, *J* 8.1, 4.9 Hz); 7.54 (1H, H(11), dd, *J* 5.4, 3.2 Hz); 7.15, 6.90 (3H, H(8,9,10), m); 3.36 (1H, H(2), dd, *J* 7.1, 2.2 Hz); 3.03 (1H, H(3), d, *J* 7.1 Hz); 2.52 (1H, H(1), br s); 2.23 (1H, H(4), br s); 1.92 (1H, H(7-*syn*) d, further split, *J* 9.0, 1.7 Hz); 1.71–1.39 (4H, 2H(5) and 2H(6), m); 0.94 (1H, H(7 *anti*), d, further split, *J* 9.0, 1.7 Hz) ppm.

Addition of $NaBD_4$ and methanol-d_1 to the solution of III gave dideuterated phenylbicycloheptane, M^+ 174, the mass spectrum of which was compared with undeuterated and monodeuterated 3-*d*-2-phenylbicycloheptane [8]. In addition to the peak of a dideuterated species at *m/e* 106 (*o*-*d*-2-*d*-styrene), there were relevant peaks at *m/e* 93 ($C_7H_7D^+$) and 92 ($C_7H_6D^+$), both derived from the aromatic part, and another at *m/e* 82 ($C_6H_8D^+$) derived form the cycloaliphatic part.

Complex III (9 mg, 0.02 mmol) was dissolved in $CDCl_3$ (0.5 ml) and treated with MeI (6 mg, 0.04 mmol) at $-20\,^{\circ}C$. The ^1H NMR spectrum, recorded at $-20\,^{\circ}C$, showed remarkable changes. In particular the signals from 2 and 3 protons had shifted to δ 3.92 and 3.33 ppm and, that of the 11 proton to δ 8.67 ppm, and the signal from the palladium-bonded methyl group appeared at δ 2.13 ppm. When the solution was allowed to warm slowly to room temperature, the signal of the methyl group appeared at δ 2.10 ppm, and those from the 2 and 3 protons were shifted to δ 3.26 and 2.93 ppm. On addition of $NaBH_4$ and methanol to this solution product VI [20] was formed (66%).

Complex IV was isolated after removing most of the solvent and MeI and adding n-hexane. A white precipitate formed, and was filtered off and dried at $-40\,^{\circ}C$

under vacuum. The NMR spectra of these complexes show many interesting aspects which are under investigation.

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