

Preliminary communication

Pallada(IV)cyclopentane chemistry, including the synthesis of tris(pyrazol-1-yl)borate complexes

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Abstract

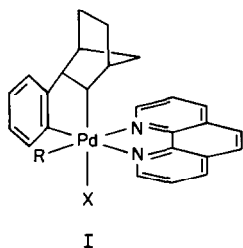
Pallada(IV)cyclopentane complexes, $\text{PdBr}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{R})(\text{bpy})$ (R *trans* to Br), have been obtained by oxidative addition of organohalides to $\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})$, and related tris(pyrazol-1-yl)borate complexes, $\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{R})(\text{pz})_3\text{BH}$, have been obtained on addition of $\text{K}[(\text{pz})_3\text{BI}]$ to $\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{tmeda})$ followed by addition of organohalides.

Hydrocarbylpalladium(IV) chemistry has developed only recently [1,2], and includes the preparation of simple alkyl- and aryl-palladium(IV) complexes containing polydentate nitrogen or sulfur donor ligands, e.g. the octahedral 2,2'-bipyridyl complexes $\text{PdMe}_3(\text{bpy})$ [1] and $\text{PdBrMePh}(\text{CH}_2\text{Ph})(\text{bpy})$ [3]. Some potential roles for palladium(IV) intermediates in organic synthesis and catalysis have been identified [2] and, for one catalytic system, bicycloheptylphenyl complexes (I) have been synthesized as models for processes that may proceed *via* palladium(IV) phosphine complexes [4,5]. In view of these reports, and the recognition that metallacyclic species are relevant to organic synthesis [6], we have commenced studies of the chemistry of simple pallada(IV)cycloalkanes related to the more complex systems represented by I. We report here results of some initial studies of the synthesis and decomposition of pallada(IV)cyclopentanes.

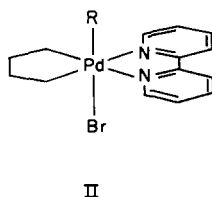
Complexes of 2,2'-bipyridyl (II) were formed by direct oxidative addition of organic bromides to the known complex $\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})$ [7,8] in acetone. The synthesis of tris(pyrazol-1-yl)borate complexes (III) required the development of a different strategy, since the analogous palladium(II) substrate has not been reported. Noting that tetramethylethylenediamine is readily displaced from organopalladium(II) complexes [9], we have found that III may be obtained in one step by addition of $\text{K}[(\text{pz})_3\text{BH}]$ to $\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{tmeda})$ [7,8] followed by addition of the appropriate organic halide [10] *.

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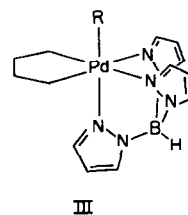
* Reference number with asterisk indicates a note in the list of references.



RX = MeI (configuration uncertain [4])
 $\text{CH}_2=\text{CHCH}_2\text{Cl}$ [5]
 $\text{CH}_2=\text{CHCH}_2\text{Br}$ [5]



RX = (a) PhCH_2Br ,
 (b) PhCOCH_2Br
 (c) $\text{PhCH}=\text{CH}-\text{CH}_2\text{Br}$



RX = (a) MeI
 (b) PhCH_2Br

The complexes exhibit ^1H NMR spectra in CDCl_3 consistent with configurations II and III; *e.g.* for the palladacyclopentane group in II, four broad resonances of equal intensity appear in the region 1.8–4.4 ppm, corresponding to resonances for protons adjacent to and far from the bromine atom. The CH_2 resonance for R in II(a) and II(b) appears as a singlet, indicating that R is *trans* to bromine, since an AB pattern would be expected for R *trans* to bpy [11].

Palladium(IV) complexes containing simple alkyl or aryl groups generally decompose by reductive elimination; *e.g.* $\text{PdBrMe}_2(\text{CH}_2\text{Ph})(\text{bpy})$ gives ethane and $\text{PdBr}(\text{CH}_2\text{Ph})(\text{bpy})$ at *ca.* 40°C in $(\text{CD}_3)_2\text{CO}$ [2]. The pallada(IV)cyclopentane complexes II are stable in CDCl_3 solution at ambient temperature, and when kept at 40°C in solution they decomposed slowly. When decomposition was complete (*ca.* 16 h) an orange crystalline product was readily identified by infrared spectroscopy as $\text{PdBr}_2(\text{bpy})$. In view of the complexity of the decomposition, apparently involving reactions of both palladium(IV) and palladium(II) species, preliminary studies of decomposition were confined to short reaction times prior to deposition of solid products. Analysis of the volatile products (GC-MS) after 2 h at 40°C in acetone revealed that the major volatile product from II is 1-butene (75–98%), accompanied by *cis*- and *trans*-2-butenes (2–25%).

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References and notes

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