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Conformational effects in elementary steps in catalytic reactions. Oxidative addition of 3-bromoprop-1-ene to a palladium(II) metallacyclic complex

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Abstract

The solution structure of an η^1-allylpalladium(IV) complex formed by oxidative addition of bromopropene to a palladium(II) metallacyclic species has been determined by ^{1}H NMR spectroscopy. A *cis* attack from the less-hindered side is implied.

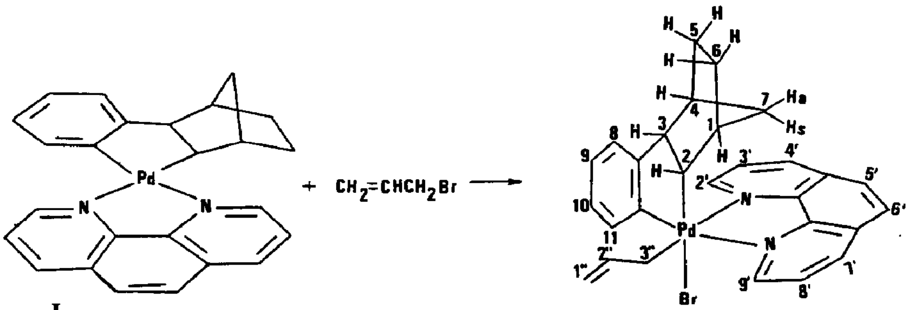
Introduction

In previous papers [1,2] several catalytic syntheses involving palladacyclic intermediates were reported, and interpretations based on the intermediacy of palladium(IV) complexes were advanced. Isolation of some palladium-(II) and -(IV) complexes supported these hypotheses, and allowed clarification of the mechanism [2,3]. The way in which a palladium(II) complex could be attacked to form palladium(IV) and the stereochemistry of the resulting complex remained unknown, however. Since the $Pd^{II} \rightarrow Pd^{IV}$ oxidative addition process could be extended to other substrates, we decided to study a complex suitable for investigation by NMR techniques.

Results and discussion

Complex I was chosen as substrate for oxidative addition of 3-bromoprop-1-ene (eq. 1).

When freshly distilled 3-bromoprop-1-ene (8 μl, ca. 0.09 mmol) was added to I (21 mg, 0.046 mmol) in 0.5 ml $CDCl_3$ at room temperature, a new compound, II,



I

II

was formed. This compound decomposes slowly at room temperature, but is stable for several days at −20 °C. It was characterized at −20 °C by NMR spectroscopy. The ^1H NMR spectrum shows, in addition to the expected signals due to the coordinated phenanthroline and bicycloheptylphenyl moieties present in I, the

Table 1

Complete proton NMR spectral assignment for II

Proton	Chemical shift (ppm)	Coupling constants (Hz)	multiplicity
1	0.88		m
2	3.87	$J(2,3)$ 7.0	br d
3	3.43	$J(3,2)$ 7.0	br d
4	2.32		m
5x	1.41	$J(5x,5n)$ 12.0; $J(5x,6x)$ 12.0; $J(5x,6n)$ 4.3; $J(5x,4)$ 4.0	tt
5n	1.21		m
6x	0.88		m
6n	0.88		m
7a	0.47	$J(7a,7s)$ 9.4	br d
7s	1.07	$J(7s,7a)$ 9.6	br d
8	7.03	$J(8,9)$ 7.2; $J(8,10)$ 1.8; $J(8,11)$ 0.9	ddd
9	7.13	$J(9,8)$ 7.2; $J(9,10)$ 7.2; $J(9,11)$ 1.4	td
10	7.18	$J(10,9)$ 7.4; $J(10,11)$ 7.4; $J(10,8)$ 1.8	td
11	8.47	$J(11,10)$ 8.0	br d
2′	8.73	$J(2',3')$ 5.0	br d
3′	7.67	$J(3',4')$ 8.0; $J(3',2')$ 5.0	dd
4′	8.41	$J(4',3')$ 8.0; $J(4',2')$ 1.5	dd
5′, 6′	7.95, 7.96	$J(5',6')$ 9.0	AB system
7′	8.51	$J(7',8')$ 8.3; $J(7',9')$ 1.5	dd
8′	7.90	$J(8',7')$ 8.3; $J(8',9')$ 5.0	dd
9′	9.51	$J(9',8')$ 5.0; $J(9',7')$ 1.5	dd
1″a	5.44	$J(1''a,2'')$ 17.0	br d
1″b	5.35	$J(1''b,1''a)$ 2.2	dd [a]
2″	6.57		br m
3″a or 3″b	3.94 [b]	$J(3''a,3''b)$ 8.0; $J(3''a,2'')$ 8.0	t
3″b or 3″a	3.21	$J(3''b,3''a)$ 9.0; $J(3''b,2'')$ 9.0	t

[a] $J(1''b,2'')$ obscured by excess allyl bromide. [b] Partly obscured by allyl bromide.

Table 2

Significant NOE values [a] for II. Observed protons (% enhancement [b]) versus irradiated protons

	2	3	4	5x	5n	7a	7s	8	10	11	2′	3′	8′	9′	1″a	1″b	2″	3″a	3″b
3	4		3		2			2											
4		3		2		1	1	10											
7a			2				16												
7s			2			13					5								
8		1	4																
11									6		2								
2′							3			3		12							
9′													9				6	4 [c]	
2″														8		3		2	
3″a														7			5		13
3″b														1	2 [c]		2	10 [c]	

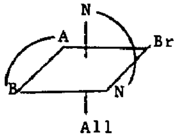
[a] NOE values produced by irradiating the proton for 5 s. [b] Note these percentage enhancements do not represent equilibrium enhancements, but are quoted to give a measure of the observed enhancement. [c] Estimated values.

signals due to an η^1-allyl group with prochiral methylene protons (see Table 1). The NMR spectrum is consistent with the formation of the palladium(IV) complex, $[Pd(C_6H_4\text{-bicycloheptyl})(phen)(C_3H_5)Br]$. The ^1H NMR spectrum reveals large shifts for several of the protons, notably H(1) and H(7 *syn*) of the bicycloheptyl group, indicating that these protons are very close to an aromatic ring. The structure was determined from NOE measurements. The results are given in Table 2. Many Nuclear Overhauser effects can be observed within the palladium-coordinated groups, but the significant ones in determining the structure are those between H(7 *syn*) and H(2′), and between H(9′) and both H(2″) and H(3″). These NOEs are consistent with structure II, as are the shifts observed for H(1) and H(7 *syn*), which are above the phenanthroline ring. The low frequency shifts, due to ring current effects, calculated [4] for H(1) and H(7 *syn*) in structure II are in good agreement with those observed for complex I (H(1): calculated −1.6 ppm, observed −1.54 ppm; H(7 *syn*): calculated −0.8 ppm, observed −0.85 ppm).

The NMR data, reported in Tables 1 and 2, help to exclude other possible structures. First of all they clearly indicate that the phenylylbicycloheptyl ligand (denoted by A–B, with A the aromatic ring and B the upwards-pointing bicycloheptyl group) remains essentially unchanged [2]. Under these conditions all the possible combinations of the other ligands (N–N = phenanthroline), give ten structures (II–XI).

Of these, IV and V can be discarded from considerations of steric interactions. Structures VIII–XI are less likely because of steric hindrance to the approach of bromopropene to palladium from the bridge side. In addition structure VIII has the allyl group *trans* to the bicycloheptyl.

In structures VI–XI the H(1) and H(7 *syn*) do not occupy positions relative to the phenanthroline ring, which would give rise to the observed shifts. Futhermore in



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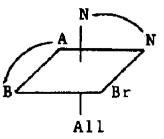
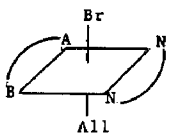
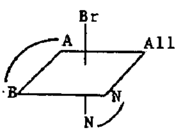


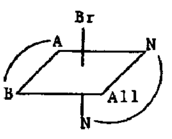
IV



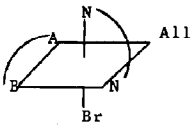
VI



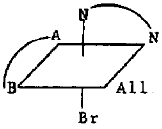
VIII



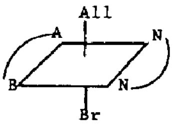
X



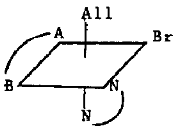
III



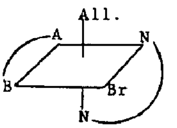
V



VII



IX



XI

VI, VII, VIII and X no NOE would be observed between the allyl and phenanthroline protons. In the case of IX and XI (restricted rotation of the allyl group) no NOE is observed (as expected) between the allyl protons and H(7 *syn*). Two structures (II and III) are left, and these would result from attack of bromopropene on the less hindered side of the palladium. Although the chemical shifts are consistent with both structures, the second one must be discarded on the ground that no NOEs would be observed between the allyl protons and H(9′). Moreover structure III has the allyl *trans* to the bicycloheptyl group. A similar spectrum was obtained for 3-chloro- in place of 3-bromoprop-1-ene. In keeping with the relative *trans* and field effects of chloride and bromide, the following low frequency shifts are observed: H(2) (0.12); H(3) (0.05); H(11) (0.18); H(2′) (0.06); H(9′) (0.05); H(2″) (0.10); H(3″a) or H(3″b) (0.15). The remaining protons show only very small shifts./

We conclude that only structure II is fully consistent with the NMR data. This finding has the mechanistic consequence that a *cis* oxidative addition of bromopropene must occur from the less sterically hindered side of the complex. This conclusion is in agreement with the observations recently reported by Canty [3] for a different complex.

Experimental

Starting 3-chloro- and 3-bromo-propene were commercial products and distilled prior to the use. Complex I was prepared as described previously [2]. The NMR spectra were recorded on a Bruker WH400 NMR spectrometer in $CDCl_3$, with TMS as internal standard. The NOE measurements were performed by difference spectroscopy as described in ref. 5.

Acknowledgements

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