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EVIDENCE FOR (π-ALLYL)PALLADIUM(II)(QUINONE) COMPLEXES IN THE PALLADIUM-CATALYZED 1,4-DIACETOXYLATION OF CONJUGATED DIENES

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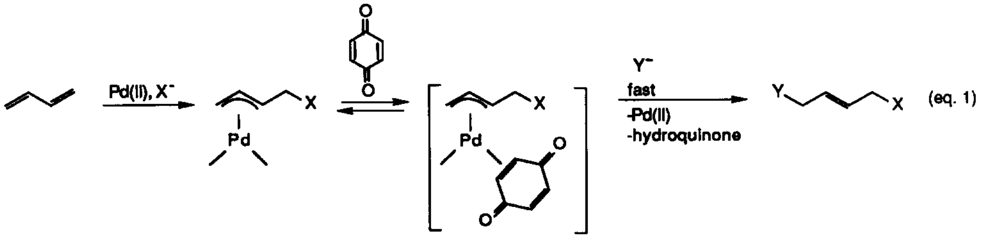
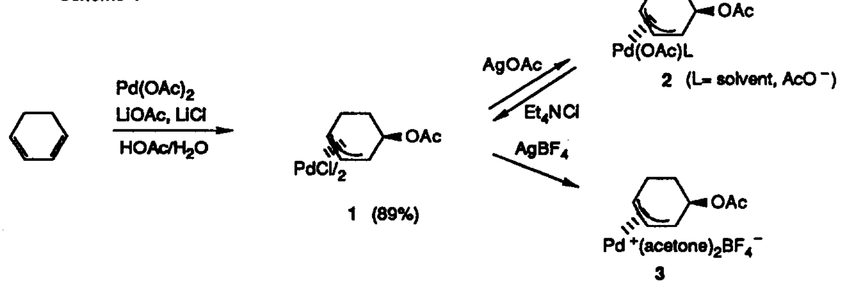
Summary: Evidence for a coordination of p-benzoquinone to palladium in [4-acetoxy-η^3-(1,2,3)-cyclohexenyl]-palladium(II) complexes was provided by changes of the ^{1}H NMR chemical shift values of the π-allyl protons and a decrease of the spin-lattice relaxation time constant for the p-benzoquinone protons.

We have recently developed a number of methods for palladium-catalyzed 1,4-oxidations of conjugated dienes.[1] In all these oxidations, which proceed via (π-allyl)palladium complexes, p-benzoquinone plays a key role as electron transfer mediator (eq. 1). Although kinetic studies suggest formation of (π-allyl)palladium(II)-(benzoquinone) complexes as intermediates in the quinone induced nucleophilic addition,[1, 2a, 2c] direct evidence for their existence is still lacking.[3] In this communication we report for the first time the detection of p-benzoquinone- and 1,4-naphthoquinone-(π-allyl)palladium(II)complexes by NMR spectroscopy.



We first prepared (π-allyl)palladium complexes **1**, **2**, and **3**, which are likely intermediates in the palladium catalyzed 1,4-diacetoxylation of 1,3-cyclohexadiene. Thus, 1,3-cyclohexadiene was converted into the chloro complex **1**, which by ligand exchange gave solutions of the less stable complexes **2** and **3** (Scheme 1). The complexes **1** and **2** were also formed in acetic acid under the actual conditions of the synthetic reactions, as shown by ^{1}H NMR. On addition of p-benzoquinone, **2** was converted to *trans*-1,4-diacetoxy-2-cyclohexene,

Scheme 1



whereas **1** gave mainly *cis*-1,4-diacetoxy-2-cyclohexene in the presence of acetate ions (in the form of Et_4NOAc). Complex **2** reacted much faster than **1**, which reflects the different rates of internal and external acetate attack on the π-allyl moiety.[1a]

Coordination of a quinone to a (π-allyl)palladium complex is expected to result in changes of the ^1H NMR chemical shift values of the π-allyl protons. Such chemical shift changes have been observed on coordination of other ligands to (π-allyl)-palladium complexes.[4] However, addition of p-benzoquinone to **1** or **2** in acetic acid did not result in any detectable chemical shift changes (i.e.> 1 Hz) of the π-allylic protons. Neither did addition of 1,4-naphthoquinone or several other substituted p-benzoquinones (2,6-dimethyl-, 2,6-dimethoxy-, tetramethyl-, or 2,6-diphenyl-) change the ^1H NMR spectrum of **1** or **2** in $CDCl_3$, even in those cases where the reaction to diacetate was very slow.[5] In contrast, there were significant downfield shifts of the π-allylic proton resonances of the cationic complex **3** upon the addition of p-benzoquinone or 1,4-naphthoquinone (Fig. 1 and Table I). These changes suggest a decreased electron density on the π-allyl moiety of the molecule,[4] in accordance with the observed increase in reactivity towards nucleophiles upon addition of a quinone.[6,7] Complex **1** showed no change in chemical shifts on addition of p-benzoquinone or 1,4-naphthoquinone, even at a much higher ligand to complex ratio than used for **3**. This could be interpreted in terms of a less favoured quinone complexation in the presence of the strong binding chloride ligands.

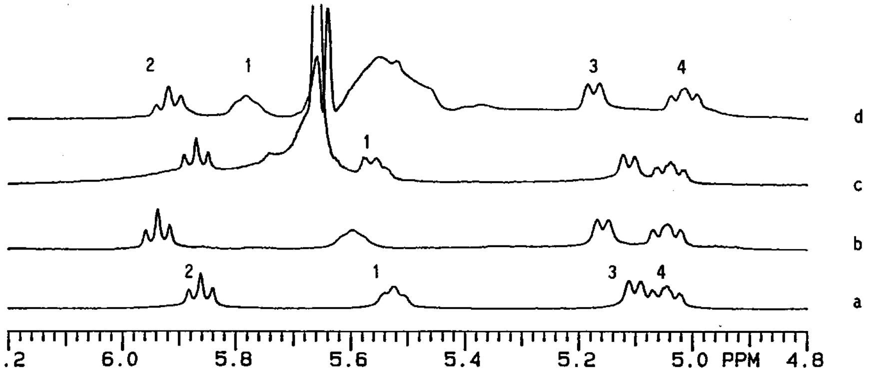


Fig. 1: Chemical shift changes of proton signals for complex 3 upon addition of cyclohexene and p-benzoquinone ligands. ^1H NMR (300 MHz), 0.06 M 3 in $CDCl_3$/acetone-d_6 (2:1), -20°C. (a) 3; (b) 3 + 35.2 equiv. p-benzoquinone; (c) 3 + 4.2 equiv. cyclohexene; (d) 3 + 122 equiv. cyclohexene, partially relaxed inversion-recovery spectrum for suppression of cyclohexene signal.[14b]

For comparison the complexation of **1**, **2** and **3** with cyclohexene was studied. Cyclohexene, which is more electron rich than the quinones, is known to give isolable complexes with Pd(II).[8] Addition of cyclohexene to complex **3** resulted in downfield shifts of the π-allylic proton resonances. The chemical shift changes of H-2 and H-3 were comparable to those observed on addition of p-benzoquinone, whereas the change in the H-1 resonance was larger than in the p-benzoquinone case. The addition of cyclohexene to the complexes **1** and **2** did not affect the chemical shifts of the π-allylic protons, in accordance with the results from the quinone.

That we are not simply dealing with a solvent induced shift was shown by the lack of change in chemical shift on addition of a large excess of p-benzoquinone to **1** (entry 1, Table I). Also for 1,4-naphthoquinone a solvent induced shift was ruled out by comparison with naphthalene. The latter gave an upfield shift as compared to the downfield shift induced by all the quinones (entry 2, Table I).

Table I. Chemical shift changes ($\Delta\delta$) induced in [4-acetoxy-η^3-(1,2,3)-cyclohexenyl]palladium complexes **1** and **3** upon the addition of various ligands.[a]

Entry	Complex	Ligand	ligand/ palladium	$\Delta\delta$ (Hz) of proton[b] H-1	H-2	H-3	H-4
1	**1**	benzoquinone	143:1	–	–	–	–
2	**1**	naphthalene	26.4:1	–7	–5	–5	–2
3	**3**	benzoquinone	17.6:1	13	10	11	6
4	**3**	benzoquinone	35.2:1	24	24	17	5
5	**3**	naphthoquinone	4.5:1	13	9	11	2
6	**3**	cyclohexene	10.5:1	21	5	7	–2
7	**3**	cyclohexene	21:1	30	9	11	–4
8	**3**	cyclohexene	42:1	53	13	17	–6
9	**3**	cyclohexene	122:1	79	18	23	–9

a) The ^{1}H NMR (300 MHz) measurements were performed in $CDCl_3$/acetone-d_6 (2:1) at -20°C using a 0.1 - 0.01 M concentration of **1** and **3**. The chemical shifts (vs. TMS) of the three allylic protons (H-1, H-2, H-3) and CH-O (H-4) were: **1**, δ_1 = 1596 (5.32), δ_2 = 1680 (5.60), δ_3 = 1496 (4.99), δ_4 = 1541 Hz (5.14 ppm); **3**, δ_1 = 1657 (5.52), δ_2 = 1759 (5.86), δ_3 = 1531 (5.10), δ_4 = 1514 Hz (5.05 ppm). b) Refers to the nomenclature [4-acetoxy-η^3-(1,2,3)-cyclohexenyl].

Table II. Proton spin-lattice relaxation time constants (T_1) of p-benzoquinone and cyclohexene (olefinic protons) in the presence of metal complexes.[a]

Metal complex	benzoquinone ligand:metal	T_1	cyclohexene ligand:metal	T_1
–	–	4.2[b]	–	4.4[c]
$AgBF_4$	0.5:1	3.5	0.1:1	2.9
$(PhCN)_2PdCl_2$	0.5:1	2.9	0.7:1	2.9
1	0.05:1	3.5	0.8:1	4.0
2	d	d	0.3:1	3.1[e]
3	0.07:1	3.4	0.4:1	3.7

a) 0.06 M solutions of metal complexes in $CDCl_3$/acetone-d_6 (2:1), -20°C, not degassed.[13] T_1 of protons (300 MHz) determined by inversion-recovery pulse sequence with exponential curve fitting.[14] Error in T_1 measurements 0.2 s. b) 0.02 - 0.2 M p-benzoquinone. c) 0.02 M cyclohexene. d) not determined. e) at -34°C (T_1 = 3.8 s for 0.02 M cyclohexene).

The formation of true complexes, i.e. not just collision complexes,[9] was ultimately indicated by the changes in p-benzoquinone and cyclohexene spin-lattice relaxation time constants (T_1) (Table II). Here, the decreased T_1 values[10] in the presence of the (π-allyl)palladium complexes indicate a lower mobility of the complexed as compared to the free ligands. Pyridine, which is known to bind very tightly to (π-allyl)palladium complexes,[11] showed a comparable decrease of the relaxation time constant in the presence of complex **1** (at ambient temperature, the T_1 value of the 4-pyridine proton changes from 5.1 to 3.5 s on addition of 1.2 equivalents of complex **1**). This complexation was also confirmed by significant shift changes in the ^{1}H NMR spectrum.

Table III. Indication of complex formation by different techniques.

Metal complex	Indications of Complexation[a] p-benzoquinone $\Delta\delta$	p-benzoquinone ΔT_1	cyclohexene $\Delta\delta$	cyclohexene ΔT_1
1	–	+	–	+
2	b	b	–	+
3	+	+	+	+

a) $\Delta\delta$ of π-allyl protons, ΔT_1 of ligand protons. b) not determined.

Surprisingly, the T_1 changes also indicated a complexation of p-benzoquinone with complex **1** and of cyclohexene with complexes **1** and **2** (Table II[12]).

Both the chemical shift changes and the decreased relaxation time constants provide evidence for a complexation between p-benzoquinone and the (π-allyl)palladium complex derived from 1,3-cyclohexadiene. A complexation does not necessarily result in shift changes, whereas the change of relaxation time constants on coordination is more sensitive (Table III).

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