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SELECTIVE HYDROGENATION BY A NOVEL PALLADIUM(II) COMPLEX

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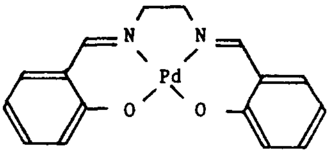
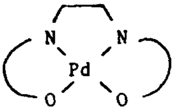
Abstract: A novel insoluble green complex of palladium(II) and salicylidene ethylene diamine (salen) has been prepared and found to be an active and selective heterogeneous hydrogenation catalyst especially for the reduction of alkynes in the presence of alkenes and of alkenes in the presence of other functional groups.

Our earlier work on selective biomimetic reactions showed that micelles could influence the course of aromatic substitution[1-3] and we wished to extend the scope of this method of control to further reactions. There were several reports of the ability of palladium(II) salen (**1**) to mediate catalytic hydrogenation[4-6] and, in view of the similarity of this complex to some of the metal complexes in our earlier work,[1] we chose to prepare the N-alkylbenzylidene imine complexes of palladium (**2a-c**). These diamagnetic yellow complexes were prepared and purified but surprisingly showed no catalytic activity at all. Similarly a highly purified sample of palladium salen (**1**) was inactive. On examining the original literature, it was evident that the samples of (**1**) used had not been rigorously purified; indeed for one example, the complex was prepared in situ.[5] Repetition of this work revealed that the complex prepared was not bright yellow like our pure samples but was tinged with a green impurity. By modifying the conditions of preparation of the complex using triethylamine as a base and potassium tetrachloropalladate, we obtained a dull green insoluble compound (**3**). The product was washed extensively with warm dimethylformamide at 60°C to remove the yellow palladium(II) salen (**1**). After drying under reduced pressure, (**3**) was tested for its ability to catalyse hydrogenation; unlike (**1**), a suspension of (**3**) in ethanol under an atmosphere of hydrogen led to smooth and quantitative reduction of cyclohexene and nitrobenzene. Many batches of (**3**) have been prepared by this method with identical spectroscopic-catalytic properties.

The extreme insolubility of (**3**) made complete characterisation difficult. Elemental analysis established that (**3**) was essentially a 1:1 complex of salen and palladium although a little residual chlorine was always detected (ca. 1%). The mass spectra of the green complex (**3**) and the yellow complex (**1**) showed the same molecular ion (372 for Pd^{106}). The infra red spectra as KCl discs indicated that (**3**) was less symmetrical than (**1**); whereas (**1**) showed sharp bands at 1627 and 1595 cm^{-1} corresponding to the imine and benzene ring respectively, (**3**) showed a broader band with a maximum at 1620 cm^{-1} and shoulders at 1625, 1615, and 1595 cm^{-1}. The fingerprint regions of the spectra were completely different. ^{13}C nmr spectra of the two complexes in the solid state confirmed the lack of symmetry in (**3**). The spectrum of (**1**) showed resonances at 157.9 and 121.5 ppm for the amine carbon and the quaternary carbon of





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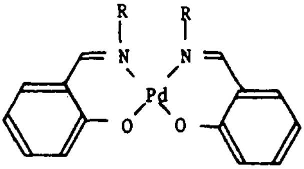
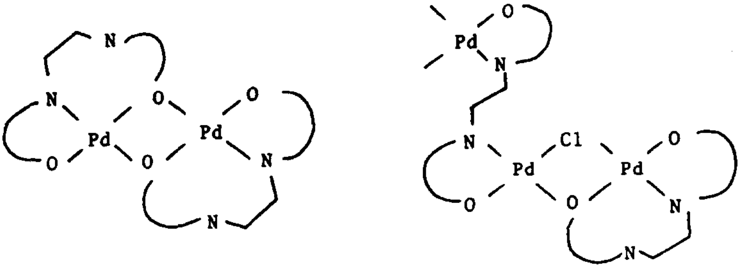


2 a $R = C_4H_9$

b $R = C_8H_{17}$

c $R = C_{12}H_{25}$

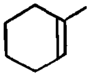
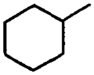


3 Some possible structures for the green complex.

the benzene ring whereas the green complex (3) showed resonances at 167.5 and 164.1 for the imine carbon and 120.9 and 119.2 ppm for the quaternary carbon. The available data is insufficient to define a unique structure for (3) but a possibility consistent with the data is shown. Bridging oxygen ligands are a feature of this structure and several isomeric dimeric structures can be written. There is some precedent for this type of bonding.[7] However in view of the extreme insolubility of (3) and the residual chlorine observed in the analysis, it could be that (3) is an oligomer constructed through a series of bridging oxygen ligands with a terminal chlorine. Whatever structure proves to be correct, it is notable that the palladium atoms would be anticipated to be more susceptible to ligand exchange in these structures than in the yellow complex (1), a factor which is probably relevant to the catalytic activity of (3).

The green complex (3) exhibits interesting selectivity in its catalytic activity. Unlike palladium/charcoal, it is much more reactive towards alkenes and alkynes than towards aromatic nitro compounds (Table: entries 1-8). Nevertheless, it reduces aromatic nitro compounds cleanly to aromatic amines without appreciable formation of coupled products such as azobenzenes. Alkynes are reduced rapidly and it is easily possible to stop reduction of an alkyne at the alkene stage. For example, although phenylacetylene can be hydrogenated to ethylbenzene (entry 1), it is greater than 98% hydrogenated to styrene before ethylbenzene is detectable in the reaction mixture. Similarly hex-1-yne is completely reduced to hex-1-ene before n-hexane is detectable. Terminal alkenes are reduced faster than internal alkenes (entries 2 and 3) and trisubstituted alkenes are reduced but slowly (entry 4). Reduction of internal alkynes affords the cis-alkene (entry 6). Carbonyl groups in simple esters, aldehydes, and ketones are not reduced at atmospheric pressure and neither hydrogenolysis of dibenzylether nor reductive dehalogenation of iodobenzene was observed. Cyclopropylbenzene is not a substrate.

TABLE Representative examples of reduction by **(3)**

	Substrate	[substrate] M		**(3)** M	Reaction time	Product	(yield %)
1.	$PhC{\equiv}CH$	0.27	a	$8.95\mathrm{x}10^{-4}$	51 min	$PhCH_2CH_3$	(100)
2.	$PhCH{=}CH_2$	0.27	a	$8.95\mathrm{x}10^{-4}$	19 min	$PhCH_2CH_3$	(100)
3.		0.24	a	$4.00\mathrm{x}10^{-3}$	3 h		(>99)
4.		0.24	a	$4.00\mathrm{x}10^{-3}$	9 h		(6)
5.	$PhNO_2$	0.24	b	$4.00\mathrm{x}10^{-3}$	4 h	$PhNH_2$	(100)
6.	$HO(CH_2)_2C{\equiv}CC_2H_5$	0.27	c	$8.95\mathrm{x}10^{-4}$	17 min	cis-$HO(CH_2)CH{=}CHC_2H_5$	(100)
7.	$C_4H_9C{\equiv}CH$	0.27	c	$8.95\mathrm{x}10^{-4}$	21 min	$C_4H_9CH{=}CH_2$	(98)
8.	..	..	c	..	2.5 h	C_6H_{14}	(2)

a in methanol, b in ethanol, c in pyridine. Yields determined by glc in comparison with authentic samples.

The catalytic properties of (3) might be considered due to metallic palladium released by decomposition of the complex. Several lines of evidence argue against this view. Firstly, the complex (3) can be recovered from reactions and reused after washing with dimethyl formamide without perceptible loss of activity. Dimethylformamide washing removes small quantities of the catalytically inactive yellow complex that form during reaction. Secondly, and more significantly, the selectivity characteristics of the green complex (3) and palladium on charcoal are distinct as shown by the reduction of hex-1-yne. Whereas Pd-C in pyridine reduces hex-1-yne rapidly to hex-1-ene with concomitant further reduction to hexane and isomerisation to hex-2-ene, the green complex (3) under the same conditions reduces hex-1-yne to hex-1-ene essentially without competing reduction to hexane and with very slow isomerisation to hex-2-ene. Both catalysts are comparably active in the first stage of reduction but after 6 h at room temperature and atmospheric pressure the reaction mixture from Pd-C was composed of hexane (75%) and hex-2-ene (25%) with no hex-1-ene. In contrast the reaction mixture with (3) contained hex-1-ene (55%), hex-2-ene (8%), and hexane (37%). It is, of course, possible to stop reduction at the hex-1-ene stage with either catalyst; these reaction times were chosen to emphasise the differences between the two catalysts.

The selectivity observed for terminal alkynes has only previously been reported for homogeneous catalysts.[8] Since we find that the rate of alkene hydrogenation is approximately 25-30% greater than that of the corresponding alkyne, the observed selectivity for alkynes is probably due to the better donor ability of the triple bond compared with the double bond.[9] The consequences of coordination to palladium are further illustrated by the virtual suppression of alkene reduction when pyridine is used as a solvent (entries 7 and 8). Presumably the coordination of pyridine to the catalytically active palladium is too strong for displacement by hydrogen or an alkene. These properties have again been observed for homogeneous catalysts.[10]

In conclusion, these results show that the novel green complex (**3**) has some potentially useful properties for selective catalytic hydrogenation. The preferential reduction of alkenes or alkynes in the presence of other easily reducible groups such as nitro or cyclopropyl and the selectivity for reducing alkynes in the presence of alkenes is especially notable.

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