

Preliminary communication

π -Allylic palladium Schiff-base complexes

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No examples of organopalladium Schiff-base complexes have previously been reported, although some simple Schiff-base complexes of palladium(II) have been synthesized^{1,2}. We now report the preparation of a series of π -allylic palladium(II) complexes of *N*-organo salicylaldimines. Bidentate Schiff-base complexes of the type (All)Pd Sal=N-R* where All = allyl, 2-methylallyl or cycloocta-2,4-dienyl and R = methyl or *p*-tolyl have been synthesized by reaction of the chloro-bridged dimers [(All)Pd Cl]₂^{3,4} with TI Sal=N-R⁵ in benzene and provide examples of π -allyl complexes in which all the allyl protons are non-equivalent, a feature previously observed in allyl palladium phosphine complexes^{6,7}. The ¹H NMR spectra (In CCl₄) of the 2-methylallyl and allyl complexes are shown in Table 1, the numbering of protons being as in Fig. 1, which shows the expected structure of the compounds. The cycloocta-2,4-dienyl complexes have complex NMR spectra which cannot be assigned in detail.

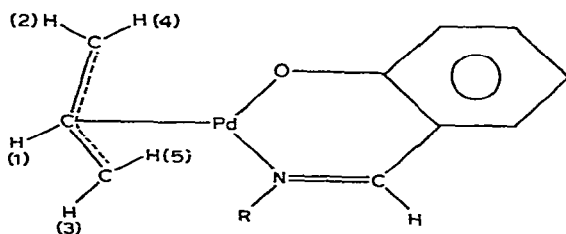


Fig. 1.

The *endo* protons 4 and 5 are assigned on the basis of their larger coupling with the central proton 1 and also their higher τ values, as in the corresponding acetylacetonate derivatives³ and the chloro-bridged dimers⁴. It is interesting to note that

*Sal=N-R = *N*-R substituted salicylaldiminato anion.

TABLE I
¹H NMR SPECTRA

Complex	τ values													Other	
	CH=N	Aromatic	H ₁	H ₂	H ₃	H ₄	H ₅	J ₁₂	J ₁₃	J ₁₄	J ₁₅	J ₂₃			
2-MethylallylPdSal=N-R															
R = methyl	2.21	2.80-3.79		6.31d	6.98d	7.08s	7.53s						2.8	N-CH ₃	6.34
R = <i>p</i> -tolyl	2.10	2.75-3.76		6.32d	7.62d	7.13s	7.58s						2.8	Allyl-CH ₃	7.86
														C ₆ H ₄ -CH ₃	7.67
														Allyl-CH ₃	7.92
Allyl PdSal=N-R															
R = methyl	2.28	2.80-3.79	4.50m	6.16q	6.81q	6.97d	7.47d	7.1	6.6	12.5	11.7	1.9		N-CH ₃	6.45
R = <i>p</i> -tolyl	2.10	2.75-3.85	4.54m	6.13q	7.42q	6.99d	7.60d	6.9	6.4	12.3	11.7	1.8		C ₆ H ₄ -CH ₃	7.68

s = singlet, d = doublet, m = multiplet, q = quadruplet

there is a significant coupling between the *exo* protons 2 and 3 while no coupling between the *endo* protons can be detected. Such coupling has not previously been reported in related compounds but the fact that J_{23} is the largest coupling between the protons 2, 3, 4 and 5 is consistent with predictions⁸. The asymmetry of the π -allylic group is expected from the differing *trans* effects of the co-ordinated oxygen and nitrogen of the salicylaldimine. It would also be expected, by analogy with the phosphine complexes^{6, 7}, that the protons 2 and 4 which have lower τ values are attached to the carbon *trans* to the imine nitrogen (which would have a higher *trans* effect than oxygen) as shown in Fig. 1. A notable feature of the spectra is the relatively large upfield shift of H(3) when the *N*-alkyl salicylaldimine is replaced by an *N*-aryl salicylaldimine, while the other protons are essentially unaffected. This suggests that the shift is not caused by electronic effects through the Pd atom, but by a direct through space shielding from the aromatic ring, thus lending further support to the assignment of this proton to the carbon *cis* to the imine nitrogen.

These complexes all give mass spectra displaying the parent ion, although the fragmentation pattern is variable.

As well as these compounds of bidentate Schiff-bases several novel binuclear complexes of the potentially quadridentate Schiff-base *N,N*-ethylenebis(salicylaldimine) (Salen H₂) *viz.* [(All)Pd]₂Salen where All = allyl, 2-methylallyl or cycloocta-2,4-dienyl, have been synthesized by reaction of the appropriate chloro-bridged dimer [(All)Pd Cl]₂ with Tl₂Salen⁵ in CH₂Cl₂. The compounds presumably have the bridged structure shown in Fig. 2.

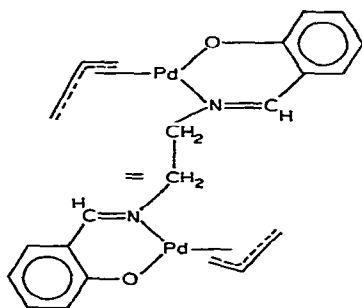


Fig. 2. (Allyl Pd)₂Salen

An extension of the series of allylic palladium Schiff-base complexes and further studies on the compounds are currently being undertaken.

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