

Preliminary communication

Magnetically nonequivalent groups in substituted allylpalladium compounds

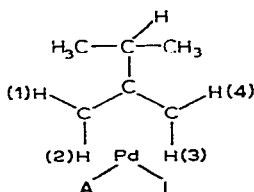
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In continuation of our NMR studies¹ on the temperature-dependent behaviour of allylmetal complexes, we wish to report some preliminary data on 1- and 2-alkylallylpalladium compounds (chlorides and acetates). The substituents with the general formula R₂H-carbon or H₂R-carbon on the carbon-2 atom (2-ethyl-, 2-isopropyl-, 2-isobutyl-, and 2-isoamyl-) have nonequivalent R groups or H atoms only in the compounds of the type (anion)allylpalladium(phosphine) owing to the absence of symmetry. In the dimers bis-[chloro(allylpalladium)] the respective groups are equivalent since the molecule has a plane of symmetry. It should be stressed that the nonequivalence is not necessarily due to restricted rotation² but it must be ascribed to the absence of a symmetry operation, or rotation interchanging the groups.

It is a well-known fact that *syn*- and *anti*-protons of the allyl group exchange under certain conditions in the NMR time-scale. Recently¹ the mechanism of this process was definitely shown to involve a σ -intermediate. This was established using phenyldimethylphosphine as a ligand which has two nonequivalent methyl groups in the (chloro)-allylpalladium adduct. We now propose a method similar to that used by Marks and Cotton³ which is more general in that it does not require the presence of a phosphine. When a π, σ -mechanism is operative the nonequivalences present in the substituents on the allyl group should be time-averaged, as according to this mechanism the metal ion becomes bonded to the other face of the allyl plane. This is not the case in the mechanism of Beconsall and O'Brien⁴. It should be noted that exchange of chemical environments of asymmetric substituents on carbon-2 may also take place via left-right interchange of anion (Cl⁻ or OAc⁻) and ligand (PPh₃ or AsPh₃). This does not hold for 1-substituted allyl complexes, which form two chemically different compounds with carbon-1 either *cis* or *trans* to the ligand.



The compounds (A)-2-isopropyl- π -allylpalladium-(L) (A = Cl⁻ or OAc⁻; L = PPh₃ or PPhMe₂) show an interchange of H(3) and H(4) in the range between -30 and +10° with a simultaneous exchange of the nonequivalent methyl groups on the 2-isopropyl substituent whereas H(1) and H(2) remain sharp below +10° thus proving that they do not exchange with H(4) and H(3), *i.e.* no left-right interchange of A and L occurs.

The corresponding compounds with bulky substituents like 2-isoamyl and 2-isobutyl have markedly different behaviour. In this case no π,σ -reaction is found in this temperature region in the NMR time scale. Molecular models indicate that the bulky groups will occupy a position opposite to the metal of the allyl plane. During a (3,4)-interchange according to the π,σ -mechanism the metal moves to the other face of the allyl plane and so will the large 2-alkyl group. This latter rotation, however, is hindered by the (1) and (4) protons of the allyl group, which explains the absence of a π,σ -reaction in the usual temperature range.

The 1-isopropyl-substituted compounds provide a good evidence that the palladium changes sides of the allyl plane simultaneously with the H(3) and H(4) interchange.

REFERENCES

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