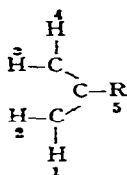


Intramolecular rearrangement of the allyl group in π -allyl complexes of rhodium(III) and platinum(II)

Recently it was found that allyl groups in a number of π -allyl complexes like $Zr(C_3H_5)_4$, $Th(C_3H_5)_4$ ¹, zincdiallyl² and π -allyl palladium complexes containing group V donor ligands³ change with increasing temperature from the π -allyl into the so-called "dynamic" allyl form. The latter form is defined by the equivalence of the syn (1,4) and anti (2,3) protons in the allyl group in the NMR spectrum.



We wish to report here that in the kinetic process involved the allyl group remains bonded to the same metal atom. This is demonstrated for the rhodium $(Ph_3P)_2X_2RhC_3H_5R(A)$ and platinum complexes $(Ph_3P)_2XPtC_3H_5(B)$ ($R = H, CH_3$ and $X = Cl, Br$), which were prepared by reaction of allyl halides with $(Ph_3P)_3RhX$ and $(Ph_3P)_4Pt$ respectively. The rhodium complexes $(Ph_3P)_2Cl_2RhC_3H_4R$ have been reported very recently also by Wilkinson and coworkers⁴. However, they isolated two isomers, namely a σ - and a π -allyl isomer.

The reaction involving the preparation of the platinum complexes, which appeared to be uni-univalent electrolytes, is reversible, since addition of triphenylphosphine to the platinum π -allyl complex (B; $X = Cl, R_{(5)} = H$) in chloroform produced $(Ph_3P)_nPt$ ($n = 3, 4$), allyl chloride and allyltriphenylphosphonium chloride $(Ph_3P)_4Pt + CH_2=CH-CH_2Cl \rightleftharpoons [(Ph_3P)_2PtC_3H_5]Cl + 2Ph_3P$.

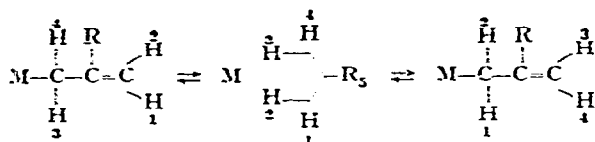
The NMR spectrum of $[(Ph_3P)_2Pt\pi-C_3H_5]Cl$ in deuteriochloroform at $-44^\circ C$ shows the pattern expected for a stable π -allyl complex, *viz.* two broad signals at 3.79 and 2.94 ppm (from TMS) due to the syn and anti protons respectively and a quintet at $\delta = 5.69$ ppm. ($R_{(5)} = H$).

At room temperature, however, protons 1, 2, 3 and 4 absorb at the same magnetic field due to rapid interchange of the syn and anti protons. Superposition of the couplings of the protons 1, 2, 3 and 4 with proton 5 ($R_{(5)} = H$) ($J = 11$ c/s) and with the platinum isotope ^{195}Pt ($J = 22$ c/s), which occurs in 33% natural abundance, gives four signals with the expected intensity ratio 8:42:42:8. The broadness of the phenyl absorption in the above temperature range indicates that the phosphine ligands exchange in solution, which explains why no coupling of the protons 1, 2, 3 and 4 with the phosphor nuclei is observed.

The NMR spectrum of the rhodium methallyl complex (A; $R = CH_3, X = Cl$) in the temperature range of -60 to $+80^\circ C$ consists of two signals at 3.75 and 1.82 ppm in the intensity ratio of 4:3. The low field signal at 3.75 ppm originating from the equivalent protons 1, 2, 3 and 4 is split at room temperature into a triplet ($J = 2.0$ c/s) due to coupling with the two phosphor nuclei (spin $\frac{1}{2}$). The methyl signal at 1.82 ppm is split into four lines in the approximate intensity ratio of 1:3:3:1 due to coupling of the methyl group with the rhodium atom (spin $\frac{1}{2}$) ($J = 1.4$ c/s) and with the two phosphor nuclei ($J = 1.2$ c/s).

At $\pm 80^\circ\text{C}$ exchange of phosphine ligands causes broadening of the phenyl absorptions and collapse of the triplet and the pseudoquartet to a singlet and a doublet ($J = 1.4$ c/s) respectively.

As elaborated elsewhere², the observed equivalence of the syn and anti protons in both the platinum and rhodium compounds is most likely due to an equilibrium between π -allyl and σ -allyl forms:



which in the temperature range investigated, lies almost completely on the side of the π -bonded structure.

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Eine neue Synthese für Alkyl-Metall-Azide

Alkyl- und Arylmetallmonoazide sind bisher ausser vom Kohlenstoff nur von den Elementen Si¹, Ge, Sn, Pb³, B², Tl⁴, Bi⁵ und Hg⁴ bekannt, während Alkylmetalldiazide von Al⁶, Tl⁵ und Bi⁵ dargestellt wurden. Sie werden in erster Linie durch Halogen/Azid-Austauschreaktionen der entsprechenden metallorganischen Halogenide mit salzartigen Aziden in polaren, protonenfreien Lösungsmitteln dargestellt.

Wir fanden im Rahmen von Untersuchungen über Reaktionen von Verbindungen mit elektropositivem Halogen⁷, dass metallorganische Verbindungen mit gasförmigem Chlorazid allgemein nach Gleichung (1) reagieren:



Die Reaktion hat den Vorteil, dass sie sowohl in unpolaren Lösungsmitteln, wie CCl₄ oder Benzol, wie auch ohne Lösungsmittel ausgeführt werden kann. Die Azide entstehen in guter Ausbeute und hoher Reinheit. Nach (1) gelang es, einige bisher unbekannte Alkyl-Metall-Azide herzustellen.

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