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Nucleophilic addition and rearrangement reactions of coordinated olefins

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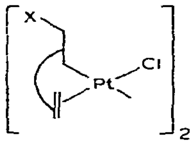
The complexes diene$PtCl_2$ (I; diene = norbornadiene, C_7H_8; dicyclopentadiene, $C_{10}H_{12}$) readily undergo attack by nucleophiles to give derivatives of the type II (*e.g.*, X = $OR^{1,2}$, acac[3], $CH(CO_2Et)_2$[4], O_2CR[5]). We have prepared compounds in which X = PhNH; similar complexes are presumed to exist, but have not been obtained pure[6] The complex I (diene = $C_{10}H_{12}$) in dichloromethane gives initially the intermediate adduct $PhNH_2C_{10}H_{12}PtCl_2$ which, on treatment with one molar equivalent of the amine or with triethylamine, gives II (X = PhNH). The intermediate is not isolated when more basic solvents are used, nor when diene = norbornadiene.



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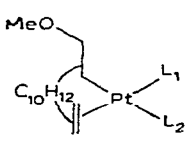
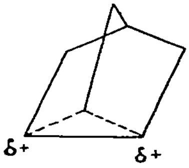


(IIIa: L_1 = Ph_3P, L_2 = Cl;
IIIb: L_1 = Cl, L_2 = py;
IIIc: L_1 = py, L_2 = Cl;
IIId: L_1 = L_2 = ½bipy)

Several reports of the reactions of II (*e.g.*, diene = norbornadiene, dicyclopentadiene; X = OR, O_2CR) with various mono- and bi-dentate ligands have appeared recently [2,7,8] and we now report our independent investigations of some of these systems, which complement and extend the previous reports. The complex $[MeOC_{10}H_{12}PtCl]_2$ undergoes bridge-splitting reactions with triphenylphosphine or pyridine to give $MeOC_{10}H_{12}Pt(L)Cl$ (L = Ph_3P, py)[2,7] On the basis of far infrared measurements it has been suggested[7] that these complexes have the configurations IIIa and IIIb. Our infrared data agree with those reported, but the NMR spectrum of the pyridine complex in deuterochloroform solution shows that it is a mixture of isomers, IIIb and IIIc, in an approximate ratio of 2/1. The signals of the methoxide group, the vinylic protons, and the α-protons of the pyridine are all duplicated. The cationic derivative IIId (as the chloride and tetraphenylborate) has also been obtained by reaction with bipyridyl.

The phosphine complex IIIa undergoes further reaction with methoxide ion in the presence of triphenylphosphine to give the doubly σ-bonded complex $(MeO)_2C_{10}H_{12}Pt(Ph_3P)_2$, and a similar, but less stable derivative is formed from the bipyridyl complex IIId. An analogous compound was reported recently from the reaction of $acacC_{10}H_{12}Ptacac$ with triphenylphosphine[9]. The present method clearly opens the possibility of introducing different functional groups to the same diene, and this is being investigated currently.

The norbornadiene derivative $[MeOC_7H_8PtCl]_2$ also undergoes the bridge-splitting reaction with pyridine, giving the *cis* isomer analogous to IIIb. However, two molar equivalents of triphenylphosphine yield a dimeric, chlorine-bridged product IV, $[MeOC_7H_8Pt(Ph_3P)Cl]_2$. The bridge is cleaved by the further addition of the phosphine. In these complexes the organic ligand has undergone rearrangement to a nortricyclene system, as shown by NMR and IR spectra (absence of signals due to vinylic protons, complex band system in the region τ8–9, characteristic infrared absorption at 820 cm^{-1}). It has previously been suggested that the organic group in $[MeOC_7H_8PdCl]_2$ forms a π-homo-allylic system[10] which rearranges when the complex reacts with a chelating diphosphine[8] Our results show that the rearrangement is sensitive to the nature of the other ligands on the metal atom, since the pyridine and bipyridyl complexes show no tendency to rearrange. However, the addition of triphenylphosphine to the pyridine complex gives IV. The NMR spectra of the dicyclopentadiene derivatives show that the *trans* ligand has a marked effect on the chemical shift of the vinylic protons, since nitrogen donors give high chemical shifts (ca. 5 ppm) and phosphines give low shifts (2–3 ppm). The latter change suggests the withdrawal of charge from the olefin resulting, in the norbornadiene derivatives, in a change towards a coordinated form of the non-classical carbonium ion V[11]. Similar rearrangements are found for complexes in which the substituent X is a carboxyl[12] or anilino group.



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