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Preliminary communication

The reaction of allene with acetylacetonato-π-allylpalladium(II): formation of 2,2'-bi-π-allyl complexes of palladium(II)

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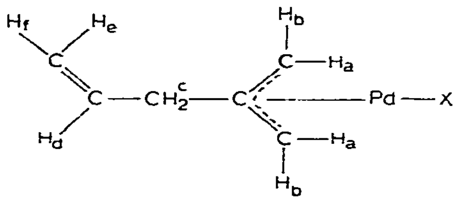
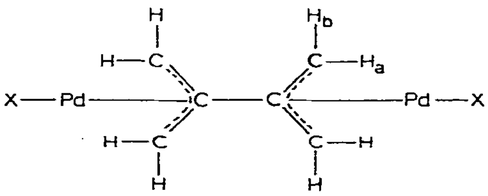
Recently, considerable interest has been focussed on the insertion of dienes into π-allyl–transition metal bonds [1-3]. Although most of the work reported concerns 1,3-dienes, the reaction of halogeno-bridged-π-allylpalladium(II) complexes with allene, a 1,2-diene, has been briefly reported to yield insertion products (similar to (Ib) - see below)[2]. As part of a general study of the nature and reactivity of π-allylic ligands, we have investigated the reaction of allene with acetylacetonato-π-allylpalladium(II) and have noted an unusual side-reaction involving coupling of two molecules of allene and intermolecular coupling of two allyl groups to give a 2,2'-bi-π-allyl complex of palladium(II) and 1,5-hexadiene, respectively. Such coupling reactions may well be important in transition metal catalysed reactions of allene to yield oligomers of unusual structure[4].

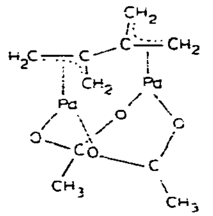
A benzene solution of acetylacetonato-π-allylpalladium(II) reacts with allene to give the insertion product (Ia) in high yield. The structure of (Ia) has been established by analysis and spectroscopic methods IR ν(C=C) 1645 cm^{-1}; NMR H_a 7.24 τ (singlet, 2 H), H_b 6.37 τ (singlet, 2 H), H_c 6.88 τ (doublet, 2 H, J_{cd} = 6 cps), H_d 4.10 τ (multiplet, 1 H), H_e 4.75 τ (multiplet, 1 H), H_f 4.97 τ (multiplet, 1 H), Acac protons 4.65 τ (singlet, 1 H), 8.02 τ (singlet, 6 H), and also by conversion to the dimeric chloride-bridged analogue (Ib) IR, ν(C=C) 1645 cm^{-1}; NMR, H_a 7.09 τ (singlet, 2 H), H_b 6.13 τ singlet, 2 H), H_c 6.94 τ (doublet, 2 H, J_{cd} = 6 cps), H_d 4.01 τ (multiplet, 1 H), H_e 4.73 τ (multiplet, 1 H), H_f 4.86 τ (multiplet, 1 H). A sparingly soluble, white crystalline material is also obtained in low yield. This has been shown to be bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II) (IIa), one of a series of 2,2'-bi-π-allyl complexes of palladium(II) which we have prepared and characterized. Higher reactant concentrations increase the yield of complex (IIa) to *ca.* 40%. The major organic product has been shown by GLC analysis to be 1,5-hexadiene. Treatment of complex (IIa) with dry HCl yields the insoluble chloride-bridged complex (IIb). A high yield synthesis of (IIb) is afforded by reaction of di-μ-chlorobis[β-(3-chloroprop-1-en-2yl)allyl] dipalladium(II)[5,6], with lithium chloropalladite and carbon monoxide in aqueous methanol/chloroform. Treatment of (IIb), prepared by either method, with thallous acetylacetonate, cyclopentadienyl sodium, or silver acetate yields complexes (IIa), (IIc), and (III) respectively. {(IIa): NMR, H_a 7.19 τ (singlet, 4 H), H_b 5.99 τ (singlet, 4H), Acac protons 4.67 τ (singlet, 2 H), 8.04 τ (singlet, 12 H); mass spectrum, *m/e* 490 [$C_{16}H_{22}O_4{}^{106}Pd_2$]$^+$; (IIc): NMR, H_a 7.76 τ (singlet, 4 H),



(Ia, X = Acac;
Ib, X = Cl (dimeric))



(IIa, X = Acac;
IIb, X = Cl (polymeric);
IIc, X = π-C_5H_5)



(III)

H_b 6.35 τ (singlet, 4 H), cyclopentadienyl proton 4.22 τ (singlet, 10 H); mass spectrum, *m/e* 422 $[C_{16}H_{18}\,^{106}Pd_2]^+$; (III): mass spectrum, *m/e* 410 $[C_{10}H_{14}O_4\,^{106}Pd_2]^+$} ★.

The ^1H NMR spectrum of complex (III) exhibits four resonances attributable to protons of the bi-π-allyl ligand {5.86 τ (singlet, 2 H), 6.14 τ (singlet, 2 H), 6.93 τ (singlet, 2 H), 7.33 τ (singlet, 2 H), acetate protons 7.97 τ (singlet, 6 H) [temperature independent from −100° to +60°]} indicating a molecular symmetry lower than C_{2v}. Presumably the rigidity of the dimeric acetato-palladium unit (Pd—Pd distance 2.94 Å)[7] imparts strain on the ligand, causing distortion. The ^1H NMR spectra of the analogous propionate, isobutyrate, phenylacetate and benzoate all show four singlet peaks for the 2,2'-bi-π-allyl protons. An X-ray crystallographic study of complex (III) is now in progress.

The above reaction represents the first example of the formation of a 2,2'-bi-π-allyl ligand from the reaction of allene with a mononuclear transition metal complex. The only other reported examples of 2,2'-bi-π-allyl formation directly from a 1,2-diene involve reaction of allenes with the bi- and tri-nuclear iron carbonyls, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ to give complexes of the type $(C_6H_8)Fe_2(CO)_6$ [8-10].

Further studies of the nature of π-allyl/1,2-diene reactions and of the possible significance of 2,2'-bi-π-allyl intermediates in transition metal catalysed oligomerisation reactions of 1,2'-dienes are being conducted.

ACKNOWLEDGEMENT

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★Satisfactory analyses have been obtained for all 2,2'-bi-π-allyl complexes. NMR spectra were run in $CDCl_3$ solution at 100 MHz using TMS as internal reference.

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