2,3-Bis-(π-allyl)propenenickel(0): An Intermediate for the Catalytic Cyclo-oligomerisation of Allene

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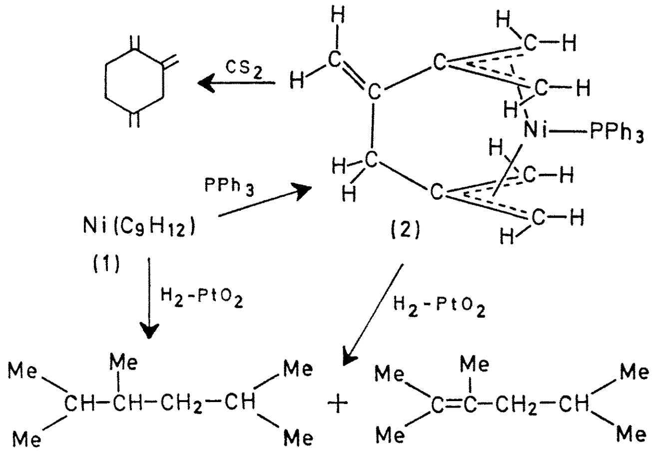
Summary Reaction of allene with $Ni(C_8H_{12})_2$ gave the title complex as an adduct with triphenylphosphine.

PREVIOUSLY we reported an interesting nickel(0)-catalysed cyclo-oligomerisation of allene leading to the exclusive formation of 1,2,4,6,9-pentamethylenecyclodecane.[1] Several oligoallene complexes of Ni^0 which have a bearing on the mechanism of this oligomerisation have been isolated. We describe herein a new allene trimer nickel(0) complex, $Ni(C_9H_{12})(PPh_3)$.

To a pale yellow solution of $Ni(C_8H_{12})_2$ (1 mol. equiv.) (C_8H_{12}=cyclo-octa-1,5-diene) in tetrahydrofuran was added *ca.* 3 mol. equiv. of allene at −70°; a red solution was obtained from which was isolated ***inter alia*** a trimer complex, $Ni(C_9H_{12})$ (**1**), as red needles,[2] which was too unstable to be handled at ambient temperature. Treatment with this solution below −30° with PPh_3 (1 mol. equiv.) afforded an orange-red crystalline complex (**2**), m.p. 97—98°. Structure (**2**) was proposed on the basis of elemental analysis, molecular weight, i.r., and ^1H n.m.r. data. The n.m.r. spectrum indicated that (**2**) had a plane of symmetry.

Treatment of complex (**2**) with CS_2 caused decomposition and the allene-trimer ligand was liberated as 1,2,4-trimethylenecyclohexane. However, a cyclic structure for the C_9 ligand of (**2**) cannot account for the ^1H n.m.r. spectrum and the results of catalytic hydrogenation, which afforded a hydrocarbon mixture consisting of a linear paraffin and a linear C_9 olefin, which were identified as 2,3,5-trimethylhexane and 2,3,5-trimethylhex-2-ene by comparison of their i.r. and n.m.r. spectra with those of authentic samples isolated from the catalytic hydrogenation of allene-trimer–di-iron complexes, $Fe_2(CO)_6(C_9H_{12})$.[3] The same C_9 paraffin and olefin were obtained from the catalytic hydrogenation of a red solution containing (**1**).



The catalytic cyclo-pentamerisation can best be effected with labile Ni^0 complexes such as $Ni(C_8H_{12})_2$. Addition of tertiary-phosphine or a similar biphilic ligand to the system greatly reduces the catalytic activity. At elevated temperature, however, a variety of Ni^0 complexes including NiL_4(L=PPh_3, Bu^tNC) and $Ni(C_2H_4)(PPh_3)_2$ afforded the same cyclic pentamer.[1] We obtained an allene-tetramer complex from $Ni(C_8H_{12})_2$ when it was treated with a large excess of allene in the presence of PPh_3; this liberates a monocyclic allene tetramer, 1,2,4,7-tetramethylenecyclooctane on treatment with CS_2. The mechanistic implication of these results is that a nickel(0) species free from nonreacting ligands acts as a template for the multi-step reaction to yield the pentamer. Under kinetically controlled condition bis(tribiphenyl-2-yl phosphite)nickel(0) acts as a catalyst leading to cyclic trimerisation.[4]

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