

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

By SEI OTSUKA,* AKIRA NAKAMURA, SUMIO UEDA, and KAZUHIDE TANI

(Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan)

Summary Reaction of allene with $\text{Ni}(\text{C}_8\text{H}_{12})_2$ gave the title complex as an adduct with triphenylphosphine.

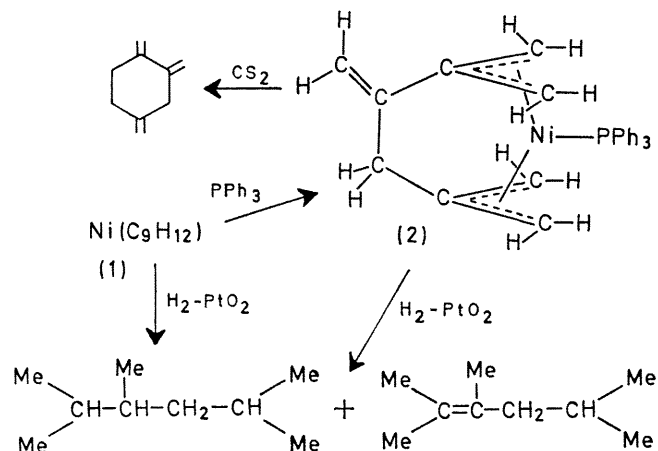
PREVIOUSLY we reported an interesting nickel(0)-catalysed cyclo-oligomerisation of allene leading to the exclusive formation of 1,2,4,6,9-pentamethylenecyclodecane.¹ Several oligoallene complexes of Ni^0 which have a bearing on the mechanism of this oligomerisation have been isolated. We describe herein a new allene trimer nickel(0) complex, $\text{Ni}(\text{C}_9\text{H}_{12})(\text{PPh}_3)$.

To a pale yellow solution of $\text{Ni}(\text{C}_8\text{H}_{12})_2$ (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, $\text{Ni}(\text{C}_9\text{H}_{12})$ (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. $97-98^\circ$. 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, $Fe_2(CO)_8(C_3H_4)_2$.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-tetramethylenecyclo-octane on treatment with CS_2 . The mechanistic implication of these results is that a nickel(0) species free from non-reacting 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

(Received, May 25th, 1971; Com. 844.)

¹ (a) S. Otsuka, A. Nakamura, K. Tani, and S. Ueda, *Tetrahedron Letters*, 1969, 297; (b) S. Otsuka, A. Nakamura, S. Ueda, and H. Minamida, *Kogyo Kagaku Zasshi*, 1969, **72**, 1809.

² S. Otsuka, K. Mori, and F. Imaizumi, *J. Amer. Chem. Soc.*, 1965, **87**, 3017.

³ S. Otsuka, A. Nakamura, and K. Tani, *J. Chem. Soc. (A)*, 1971, 154.

⁴ M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 77.