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Preliminary communication

THE STRUCTURE OF A MODEL INTERMEDIATE FOR THE NICKEL-CATALYZED CYCLODIMERIZATION OF ALLENE

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Summary

The stoichiometric reaction between allene, zerovalent nickel and a chelating diphosphane leads to the formation of a bis-methylenenickelacyclopentane derivative whose structure has been established by X-ray crystallography.

The nickel-catalyzed oligomerization of allene has been investigated in considerable detail [1] and nickel complexes have been isolated which are regarded as plausible intermediates in the cyclotrimerization to 1,2,4-trimethylenecyclohexane [2,3] and in the cyclotetramerization to 1,2,4,7-tetramethylenecyclooctane [3]. We report here the preparation and structure of a model intermediate for the cyclodimerization of allene to 1,2 —bismethylenecyclobutane.

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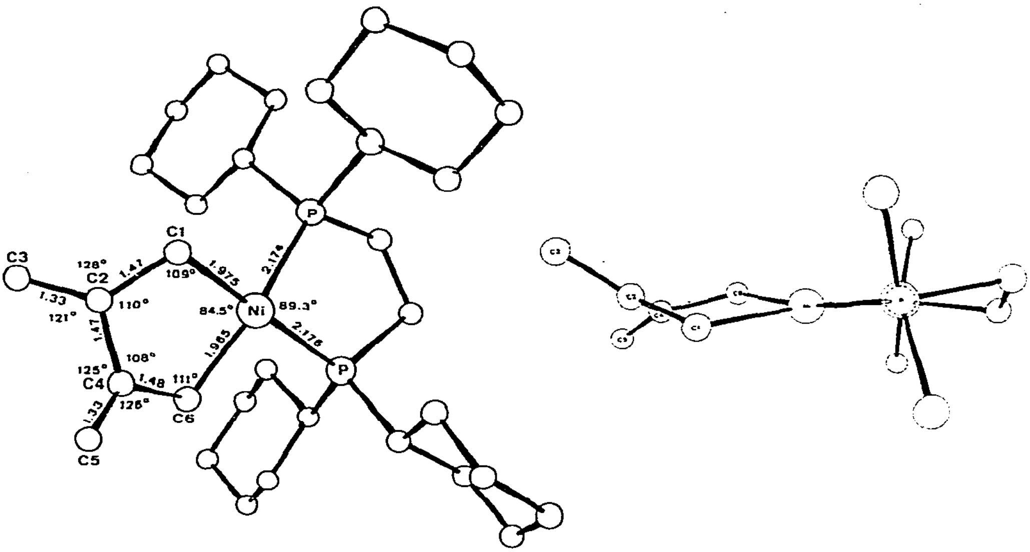
[++] X-ray structure.

Reaction between bis(cycloocta-1,5-diene)nickel, bis-dicyclohexylphosphino-ethane and allene at -20 ° to 0 ° in toluene leads to formation of a crystalline yellow compound having the composition $(C_3H_4)_2Ni[P(C_6H_{11})_2]_2C_2H_4 \cdot$toluene [Ni 9.2, C 71.2, H 9.9, P 9.7 %; calc$^{\underline{d}}$ for $C_{39}H_{64}P_2Ni$ Ni 9.0, C 71.7, H 9.8, P 9.5 %]. The complex releases toluene in the mass spectrometer at 60 ° and at 160 ° a molecular peak at m/e 560 is observed. The complex reacts with hydrogen in the presence of Raney nickel to give 2,3-dimethylbutane as the principal organic product and with CO at room temperature and atmospheric pressure to give a cyclic ketone (m/e 108), presumably 3,4-dimethylenecyclopentanone, as the only organic product. The bisallene nickel complex is also formed on reaction of allene with the chelating phosphane nickel-benzene or -butadiene complexes [4,5].

The crystal structure has been determined by X-ray methods (Fig. 1). The two allene molecules and the nickel atom form a nonplanar 2,3-bismethylenenickelacyclopentane system. The four atoms attached to the central nickel atom deviate by 0.2 - 0.35 Å from planarity towards a tetrahedral geometry. In addition to the torsional angles $C_1C_2C_4C_6$ (44 °) and $C_3C_2C_4C_5$ (55 °), the distances in the exo-methylene part of the ring indicate the absence of conjugation of the twisted diene fragment. Both independent molecules in the unit cell have slightly different conformations about the nickel atom. Selected averaged distances and angles for both independent molecules are shown in Fig. 1. The geometry around the nickel should be compared to that observed in the dipyridylnickelacyclopentane complex isolated from a reaction involving 3,3'-dimethylcyclopropene [6].

The ^{13}C-NMR spectrum (D_6-benzene, +60 °) indicates that the molecule adopts a similar arrangement in solution (δ_{C_2/C_4}



The structure of $C_6H_8Ni[(C_6H_{11})_2P]_2C_2H_4$ [7].

161.00 (m), δ_{C_3/C_5} 93.97 (m), δ_{C_1/C_6} 33.00 (m) ppm). Interestingly, all of the C-atoms in the metalla-ring system couple to both phosphorus atoms of the ligand [8].

References

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C. Krüger and Y.-H. Tsay unpublished results.

7 Crystal data: a = 17.2539(6), b = 42.834(1), c = 20.2804(8) Å, Z = 16, space group Pbca; 8927 reflexions collected, of which 5740 were considered unobserved (2σ), R: 0.051 (R_w: 0.056), d_{calc} = 1.016 gcm^{-3} with two molecules of solvent (toluene) (included in refinement). Hydrogen atoms at computed positions not refined.

8 A detailed analysis of the ABX spectrum found in this and related systems is in preparation (R. Mynott).