Stereoselective Cobalt-catalysed [2 + 2 + 2] Cross-addition of Norbornadiene and Norbornene

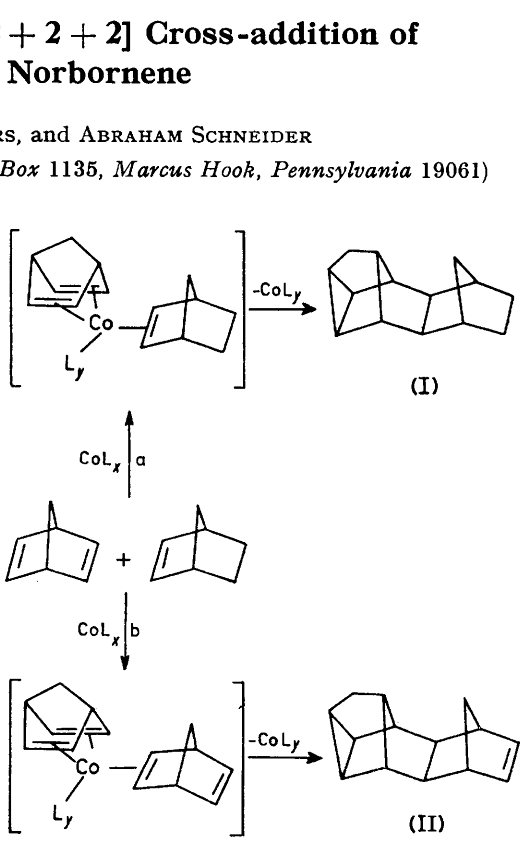
By James E. Lyons,* Harry K. Myers, and Abraham Schneider
(*Suntech, Inc., Research and Engineering Division, P.O. Box* 1135, *Marcus Hook, Pennsylvania* 19061)

Summary A cobalt complex, formed by reducing [Co(acac)$_3$] (Hacac = acetylacetone) with diethylaluminium chloride in the presence of the bidentate ligand bis(1,2-diphenylphosphino)ethane, is an active catalyst for the stereoselective [2+2+2] cycloaddition of norbornene to norbornadiene.

Olefins which are not activated by electron withdrawing groups resist both thermal and catalytic Diels–Alder co-dimerization with norbornadiene.[1] While metal complexes accelerate and direct the reaction of dienophiles such as butadiene,[2] 1,1-dimethylallene,[3] and methylenecyclopropane[4] with norbornadiene, they do not readily promote the Diels–Alder addition of simple olefins such as ethylene or propene. To the best of our knowledge, the Diels–Alder coupling of norbornadiene and norbornene has not been achieved.[5]

We report that a catalyst system comprised of cobalt(III) acetylacetonate {[Co(acac)$_3$]}, diethylaluminium chloride (DEAC), and bis(1,2-diphenylphosphino)ethane (DIPHOS) readily promotes [2+2+2] cycloaddition of norbornene to norbornadiene in a stereoselective manner to give (I) (Scheme 1). It is interesting that this catalyst system promotes the stereoselective dimerization of norbornadiene itself to give (II). The stereochemical similarity of these reactions implies that in each case only three double bonds may be involved and suggests similar pathways a and b (Scheme 1).

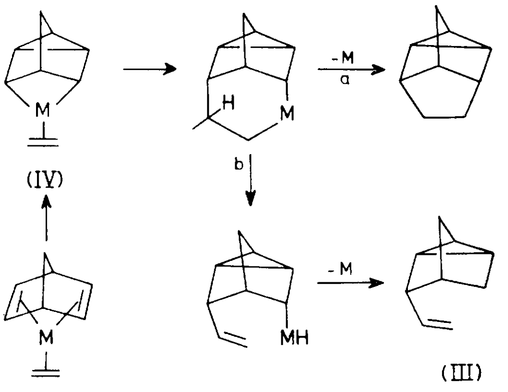
The reaction between norbornadiene (100 mmol) and norbornene (330 mmol) was carried out at 50 °C in toluene (40 ml) to which [Co(acac)$_3$] (1 mmol), DIPHOS (1·5 mmol), and DEAC (15 mmol) had been added. After quenching with aqueous HCl, g.l.c. analysis showed that norbornadiene was converted (22%) into (I) and (II) with 42 and 44% selectivity, respectively.



Scheme 1. L = Ligand.

The cobalt complex appears to be unique in catalysing the reaction (a) (Scheme 1). If one substitutes triphenylphosphine for DIPHOS, the major reaction product is BINOR-S[6] formed from coupling of norbornadiene. If [Fe(acac)$_3$], [Fe(acac)$_2$], or [Ni(acac)$_2$] is substituted for [Co(acac)$_3$], no co-dimerization with norbornene occurs, and various norbornadiene homodimers are obtained.[7]

The cobalt complex is also capable of co-dimerizing ethylene and norbornadiene in a unique and selective manner to give vinyl norticyclene (III). To our knowledge this reaction has not been reported. This result could be



Scheme 2

rationalized in the manner shown in Scheme 2. Stable complexes analogous to the metallocycle (IV) have been reported.[8] Insertion of olefin into a metal–carbon bond of (IV) would give an intermediate which could either cyclize (Scheme 2, pathway a) or eliminate a β-hydrogen (Scheme 2, pathway b). The accessibility of the β-hydrogen to the metal might then determine whether path a (norbornene) or b (ethylene) is operative.

Again the cobalt catalyst is unique in its co-dimerization activity since $[Fe(acac)_3]$ and $[Fe(acac)_2]$ show no activity of this type. We have found $[Ni(acac)_2]$ also to be inactive; however, other low-valent nickel complexes have been shown to catalyse co-dimerization of ethylene and norbornadiene[9] to give vinylnorbornene.

Norbornadiene (115 mmol) was treated with ethylene (345 mmol) in a glass pressure vessel at 59 °C in toluene (41 ml) to which $[Co(acac)_3]$ (1 mmol), DIPHOS (1·5 mmol), and DEAC (15 mmol) had been added. After quenching with aqueous HCl, the reaction mixture was analysed by g.l.c. The conversion of norbornadiene was 80·2%. The co-dimer (III) was formed in 70·5% yield and (II) was formed in 2·5% yield based on norbornadiene. Other norbornadiene dimers comprised the remainder of the product (7·2% yield). Compound (III) was isolated in 98% purity by preparative g.l.c. and its structure was determined by i.r., n.m.r., and mass spectroscopy.

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