The Metallacyclopentane–Olefin Interchange Reaction

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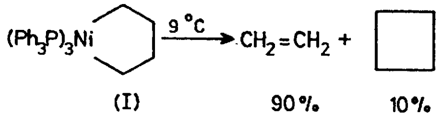
Summary Tris(triphenylphosphine)tetramethylenenickel(II) and biscyclopentadienyltetramethylenetitanium, prepared from the reaction of a 1,4-dilithiobutane and the transition metal dihalides, react with olefins to produce substituted metallacyclopentanes; the stereochemistry and substitution pattern of the metallocycles formed from propene, octa-1,7-diene, and norbornadiene has been determined.

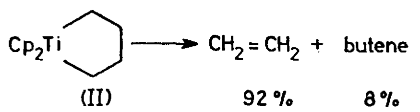
METALLACYCLOPENTANES have been suggested as intermediates in a number of transition metal–olefin reactions.[1] This type of complex has been prepared from 1,4-lithium or Grignard reagents,[2–4] by the reaction of low-valent metals with strained olefins[5] and by the insertion of low-valent metals into strained cyclobutanes.[6] Owing to their unique geometry, these complexes are more stable than acyclic dialkyl metal complexes.[2]

In our studies of nickelacyclopentanes,[7] we found that 5-co-ordinate phosphine complexes decomposed to produce ethylene as the major product [equation (1)]. To determine if this was a general reaction, an early transition element analogue was reinvestigated. A highly purified sample of biscyclopentadienyltetramethylenetitanium(IV)[3] also produced ethylene as the major product [equation (2)]. This and other results suggested that the metallocycles were in equilibrium with the bis-olefin complexes[8,9] [equation (3)].



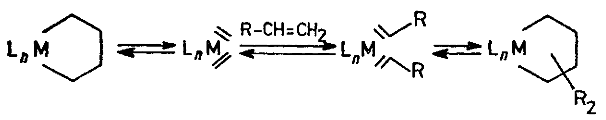
(I)

(1)



(II)

(2)



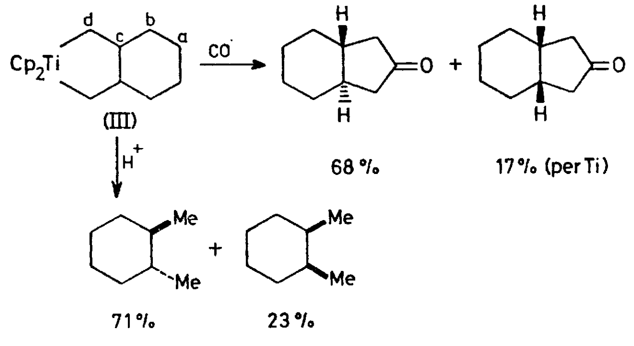
(3)

Cp = η-cyclopentadienyl

Exchange of the olefins in the bis-olefin complex would result in the formation of a new metallocycle. As seen in the Table, metallocyclopentanes can be produced in good yields by this method. Most of the metallocycles were characterized by acidolysis of the metal complex to produce the reduced dimer of the added olefin.[2,6] Protonolysis has been demonstrated to give good quantitative results from simple metallocycles. As a further characterization, some of the complexes were carbonylated to cyclopentanone derivatives. This reaction has been found to be characteristic of metallacyclopentanes.

TABLE

Complex	Olefin	[Olefin]/[Complex] (temp./°C)	Protonolysis product	Yield % based on the complex
(I)	Octa-1,7-diene	68 (−5)	1,2-Dimethylcyclohexane	*trans* 97% *cis* 0%
(I)	Propene	86 (−10)	Hexane	53
			2-Methylpentane	3
			2,3-Dimethylbutane	6
(I)	Norbornadiene (NBD)	58 (0)	(Thermal) $(NBD)_2$	57
(II)	Octa-1,7-diene	10 (−25)	1,2-Dimethylcyclohexane	*trans* 71% *cis* 23%
(II)	Propene	63 (−20)	Hexane	49
			2-Methylpentane	11
			2,3-Dimethylbutane	6



SCHEME

The metallocycle (III) from the reaction of biscyclopentadienyltetramethylenetitanium (II) and octa-1,7-diene has been isolated and analysed. The ^{13}C n.m.r. spectrum† of (III) was consistent with it being a mixture of *cis*-and *trans*-isomers. Addition of carbon monoxide produced a mixture of *cis*- and *trans*-hydrindanone in good yield[3] (Scheme). Attempts to isolate the metallocycle formed from (I) and octa-1,7-diene resulted in recovery of octa-1,7-diene, and production of 2-methylmethylenecyclohexane and nickel(0)–phosphine complexes. Spectroscopic studies (^{13}C and ^{1}H n.m.r.) were hampered by low solubility and stability, and large P couplings. Treatment of this complex with carbon monoxide produced *trans*-hydrindanone (no *cis*) in 78% yield together with the above decomposition products.

The two complexes (I) and (II) differed in the stereochemistry of the products formed with octa-1,7-diene. The reaction of the titanium complex (II) produced a *ca.* 3:1 ratio of *trans*- to *cis*-isomer, reflected both in the ^{13}C n.m.r. spectrum, and carbonylation and protonolysis studies, whereas the nickel complex (I) produced only the *trans*-isomer as shown by protonolysis and carbonylation studies. Thermal decomposition of the metallocycle produced from norbornadiene produced the *exo-trans-endo* norbornadiene dimer. This is analogous to the results obtained from the nickel dipyridyl-norbornadiene metallocycle produced from Ni° complexes.[7]

Of particular interest was the production of n-hexane as the major dimer from the reaction of propene with either complex. This suggests that the more stable isomer of the metallocycle contains the alkyl groups adjacent to the metal. The nickel complex was only stable below −20 °C or under propene atmosphere and the titanium analogue decomposed above −50 °C.

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† ^{13}C{^{1}H} n.m.r. spectrum of (III) at −30 °C: δ 114·3 (Cp), 56·7 (C^d), 34·1 (C^c, *trans*), 32·5 (C^c, *cis*), and 30·4 and 30·1 (C^a and (C^b) p.p.m. The shift for C^d is similar to that in a tantalum metallocycle (ref. 9).

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