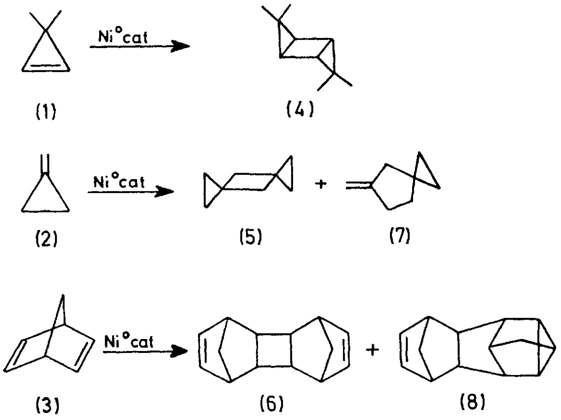
Nickelacyclopentane Derivatives as Intermediates in the Nickel(0)-catalysed Cyclodimerisation of Strained-ring Olefins

By Michael J. Doyle, John McMeeking, and Paul Binger
(*Max-Planck-Institut für Kohlenforschung, D-*4330 *Mülheim a. d. Ruhr, Kaiser-Wilhelm-Platz* 1)

Summary The syntheses of the bipyridylnickelacyclopentane derivatives (**9**)—(**11**) and their displacement reactions with activated olefins, *e.g.* maleic anhydride or the strained-ring olefins (**1**)—(**3**), are reported.

Complexes of zerovalent nickel have been shown to catalyse the [$2\pi + 2\pi$] cycloaddition of strained-ring olefins to give cyclobutane derivatives: *e.g.* 3,3-dimethylcyclopropene (**1**),[1] methylenecyclopropane (**2**),[2] and norbornadiene (**3**)[3] react to give (**4**), (**5**), and (**6**) (a mixture of isomers) respectively. Furthermore, (**2**) and (**3**) undergo catalytic [$2\pi + 2\sigma$] cycloaddition to yield (**7**)[2,4] and (**8**).[3]



Five- and six-membered metallo-carbocycles have been postulated as intermediates in the cyclodimerisation of (**1**) and (**2**).[2,5] Evidence for the formation of such species from olefins has been provided recently by the isolation of iridia- and rhodia-cyclopentane complexes derived from (**3**)[6] and allene.[7]

We now report the isolation and characterisation of the nickelacyclopentane derivatives (**9**) (*trans*-isomer), (**10**), (**11**) (*exo-trans-endo*-isomer), and (**12**). Complexes (**9**)—(**11**) are obtained in > 90% yield by the reaction of 2,2′-bipyridyl(cyclo-octa-1,5-diene)nickel [(bipy)(cod)Ni] with (**1**), (**2**), or (**3**) at 25 °C [equation (1)].

$$\begin{tikzcd}(\mathbf{9}) & {[(\mathrm{bipy})(\mathrm{cod})\mathrm{Ni}]} \arrow[l, "(\mathbf{1})"'] \arrow[r, "(\mathbf{3})"] \arrow[d, "(\mathbf{2})"] & (\mathbf{11}) \\ & (\mathbf{10})\ [+\ (\mathbf{13})?] & \end{tikzcd} \qquad (1)$$

Attempts to obtain the unsubstituted nickelacyclopentane complex (**12**) from an analogous reaction with ethylene have been unsuccessful.† We have, however, isolated (**12**) from [(bipy)(cod)Ni] and 1,4-dibromobutane.[8] Recently a

---

† Evidence for the formation of a titanacyclopentane complex has been presented by a similar method: J. X. McDermott and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 947.

series of di-tertiary-phosphine-nickelacyclopentanes has been prepared from 1,4-dilithiobutane and di-tertiary-phosphine-nickeldihalides.[9]

The complexes (**9**)—(**12**) are air-sensitive, dark-green, crystalline compounds, which are thermally stable up to *ca.* 90 °C. They give satisfactory elemental analyses and their ^{1}H n.m.r. spectra are in agreement with the proposed structures. Subsequent X-ray crystallographic analyses[10] of (**9**) and (**12**) have confirmed these structural assignments and will be reported elsewhere.

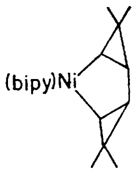
Treatment of (**9**)—(**11**) with activated olefins, *e.g.* maleic anhydride,[11] or with (**1**), (**2**), or (**3**) results in displacement of the hydrocarbon ligands to yield the respective cyclodimers [equations (2) and (3)].

$$\mathbf{(9)}\text{ or }\mathbf{(11)} \xrightarrow[\text{olefins}]{\text{activated}} \mathbf{(4)}\text{ or }\mathbf{(6)} \qquad (2)$$

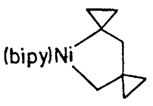
$$\mathbf{(10)}\ [+\ \mathbf{(13)}?] \xrightarrow[\text{olefin}]{\text{activated}} \underset{(92\%)}{\mathbf{(5)}} + \underset{(8\%)}{\mathbf{(7)}} \qquad (3)$$

These displacements occur at 25 °C with maleic anhydride to give (**4**) from (**9**), and (**6**) (predominately *exo-trans-endo* with traces of other isomers) from (**11**) in > 90% yields. A mixture of the two cyclodimers (**5**) and (**7**) [*ca.* 8% of (**7**)] was obtained from (**10**). This suggests that (**10**) may be contaminated by the nickelacyclohexane derivative (**13**).

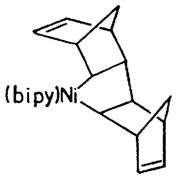
Displacement of the hydrocarbon ligands from (**9**) or (**11**) with (**1**) or (**3**) proceeds at > 90 °C. Since in this process the complexes (**9**) or (**11**) are regenerated, they are catalysts for the cyclodimerisation of (**1**) or (**3**). For example, (**3**) in the presence of (**11**) at 90 °C for 100 h was cyclodimerised in a yield representing *ca.* 50 catalytic turnovers per Ni atom.



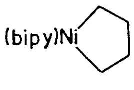
(9)



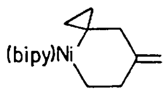
(10)



(11)



(12)



(13)

bipy = 2,2′-bipyridyl

The relevance of these metallo-cyclopentane complexes to the catalytic cyclodimerisation of (**1**)—(**3**) is indicated by their formation from a nickel(0)-compound and (**1**), (**2**), or (**3**) according to equation (1) and by their displacement reactions with activated olefins, *e.g.* maleic anhydride, or more significantly with (**1**), (**2**), or (**3**), to yield the cyclodimers (**4**)—(**7**) which are also produced in the catalytic reactions.[1–4]

(*Received*, 18*th March* 1976; *Com.* 283.)

---

[1] P. Binger, G. Schroth, and J. McMeeking, *Angew. Chem.*, 1974, **86**, 518; *Angew. Chem. Internat. Edn.*, 1974, **13**, 465.

[2] P. Binger, *Angew. Chem.*, 1972, **84**, 352; *Angew. Chem. Internat. Edn.*, 1972, **11**, 309.

[3] *Cf.* G. N. Schrauzer, *Adv. Catalysis*, 1968, **18**, 373.

[4] See also R. Noyori, T. Odagi, and H. Takaya, *J. Amer. Chem. Soc.*, 1970, **92**, 5780.

[5] P. Binger, J. McMeeking, U. Schuchardt, and M. J. Doyle, Abstracts VIIth International Conference on Organometallic Chemistry, Venice, 1975, p. 129.

[6] A. R. Fraser, P. H. Bird, S. A. Bezman, I. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 597.

[7] P. Diversi, G. Ingrosso, A. Immirzi, and M. Zocchi, *J. Organometallic Chem.*, 1976, **104**, Cl. G. Ingrosso, A. Immirzi, and L. Porri, *ibid.*, 1973, **60**, C35.

[8] S. Takahashi, Y. Suzuki, and N. Hagihara, *Chem. Letters*, 1974, 1363.

[9] R. H. Grubbs, D. D. Carr, and P. L. Burk, 'Organotransition-Metal Chemistry,' eds. Y. Ishii and M. Tsutsui, Plenum Press, New York, 1975, p. 135.

[10] C. Krüger and Y.-H. Tsay, unpublished data.

[11] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3350, 3360.