A Key Intermediate in Nickel-catalysed Butadiene Dimerisation; Its Identity in Solution and in the Solid State

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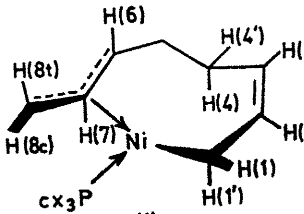
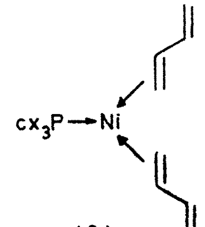
Summary An i.r. spectroscopic study of 1-h^1-6,7,8-h^3-*cis*-2-*trans*-6-octadienediyltricyclohexylphosphinenickel(0) and its dodecadeuterio-analogue shows that this structure persists in solution and in the solid state, and provides no evidence for a rearrangement in the solid state to the bis-butadiene complex.

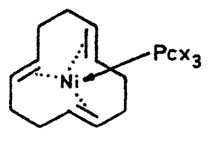
IN continuation of their earlier studies on butadiene oligomerisation catalysed by nickel(0) species, Wilke and his co-workers[1] have recently demonstrated the possibility of forming bis-olefin–nickel(0) tricyclohexylphosphine complexes by displacement of cyclododecatriene from (**3**). Among the reactions carried out was one with butadiene, which gave "a yellow, sparingly soluble compound"[1] assigned structure (**2**) in the solid state. This compound was considered to equilibrate with (**1**) in solution, n.m.r. data indicating (**1**) to be the dominant species in cyclohexane.



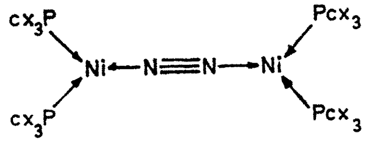
(**1**)



(**2**)



(**3**)



(**4**)

In connection with other studies, we had treated the nickel nitrogen complex (**4**)[2] with butadiene (in toluene/30 min/0—20°) and obtained a yellow crystalline product (87%) apparently identical† with the compound described by Wilke,[1] but which gave us no grounds for suggesting the structural dimorphism signified by the equilibration (**1**)$\rightleftharpoons$(**2**). The 220 MHz ^1H n.m.r. spectrum of our product (in C_6D_6) shows signals at τ 3·80 (q, 1H, $J_{12} \simeq J_{1'2}$ = 10—11 Hz, J_{23} 9 Hz), 4·86 (q, 1H, $J_{34} \simeq J_{34'}$ = 8 Hz, J_{23} 9 Hz), and 5·79 (sextuplet, 1H, $J_{78t} \simeq J_{76}$ = 12—13 Hz, J_{78c} 7·5 Hz) assigned to 2-H, 3-H, and 7-H, respectively, in structure (**1**), by comparison with literature data.[1,3]

Additional signals from the C_8H_{12} fragment and the tricyclohexylphosphine ligand appear above τ 7·3, of which a doublet at τ 7·40 (1H, J_{78c} 7·3 Hz) is assigned to 8-Hc. A 60 MHz n.m.r. spectrum in cyclohexane (containing *ca.* 20% C_6D_6 to aid dissolution of the complex) shows three lower-field signals at positions close to those reported by Wilke (τ 4·35, 5·28, and 5·88).[1] Hence, in benzene solution 2-H and 3-H (but not 7-H) suffer appreciable downfield shifts, possibly on account of a specifically oriented benzene molecule solvating the complex in the vicinity of the *cis*-double bond.[4] The structure (**1**) was also strongly suggested for the solid complex since i.r. spectra in Nujol and benzene were very similar, with a conspicuous band[5] at 1603 cm^{-1} in both phases. However, as a detailed analysis of these i.r. spectra is inherently difficult on account of overlap between phosphine and C_8H_{12} absorbances, we have prepared the dodecadeuterio-analogue of (**1**) by treating (**4**) with hexadeuteriobutadiene.[6] The C–D stretching region in the i.r. spectrum of dodecadeuterio-(**1**) is shown in the Figure where

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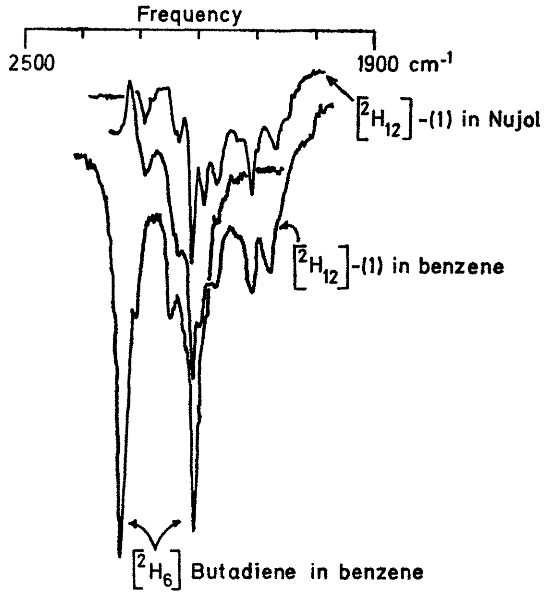
† Recrystallisation from toluene–isopentane gave an analytical sample; n.m.r. and i.r. data are discussed in the text. The substance is unstable in air (pales) and in benzene solution (darkens and deposits a solid), but is stable in an inert atmosphere at −5°. Thermolysis causes decomposition at *ca.* 100°. Wilke and his co-workers[1] have also carried out a reaction between (**4**) and butadiene in toluene, but report the formation of a product of composition $[(C_6H_{11})P_3{\cdot}Ni{\cdot}C_4H_6]_2$,toluene. Whilst the elemental analysis obtained for our product would also agree well with this formulation, it is discounted by the absence from our n.m.r. spectra of signals appropriate to toluene.



(cx = cyclohexyl)

FIGURE.

it can be seen that alteration of the phase‡ has little effect on the spectra. These do not resemble the spectrum of hexadeuteriobutadiene,[7] and the shift towards lower frequency is consistent with the presence of sp^3-hybridised C–D bonds. In contrast, the i.r. spectrum of tetracarbonylbutadieneiron, with ligand bonding analogous to (**2**), is similar to that of butadiene in the C–H region.[8] There is other evidence that co-ordination of an olefinic bond to a transition metal does not alter C–H or C–D stretching frequencies drastically, although there is a trend towards lower values.[9] We conclude that the structure of the complex prepared by Wilke[1] and ourselves is (**1**) in the solid state§ and solution. Compound (**2**) may be an intermediate in its formation and in the reported[1] reaction of (**1**) with triphenylphosphine to give 65% butadiene.

In a preliminary experiment we have observed that (**4**) catalyses the dimerisation of butadiene (in benzene/12h/58°) giving mainly 4-vinylcyclohex-1-ene and cyclo-octa-1,5-diene, probably *via* (**1**).

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‡ The Nujol mull was heterogeneous, microcrystals of dodecadeuterio-(**1**) being observed under a microscope.

§ Crystal structure analysis of (**1**) is in progress with Professor R. Mason (Sussex).

[1] P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 328 and 329.

[2] P. W. Jolly and K. Jonas, *Angew. Chem. Internat. Edn.*, 1968, **7**, 73.

[3] *cf.* L. A. Fedorov, *Russ. Chem. Rev.*, **1970**, **39**, 555.

[4] *cf.* J. Ronayne and D. H. Williams, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **2**, 83.

[5] This band is probably a C=C stretching absorption from the σ-allyl grouping (*cf.* H. A. Martin, P. J. Lemaire, and F. Jellinek, *J. Organometallic Chem.*, 1968, **14**, 149). Wilke[1] reports a value of 1600 cm^{-1} for this absorption and assigns it to the free C=C of (**2**).

[6] D. Craig and R. B. Fowler, *J. Org. Chem.*, 1961, **26**, 713.

[7] Yu. N. Panchenko, Yu. A. Pentin, V. I. Tyulin, and V. M. Tatevskii, *Optics and Spectroscopy*, 1964, **16**, 536.

[8] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, 1962, **45**, 1156; *cf.* R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Analyt. Chem.*, 1956, **28**, 1218.

[9] M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 1968, **88**, 5454.