Mechanistic Studies on the Course of a σ-But-3-enyl- to 1—3-η-But-2-enyl-nickel Transformation

By **John M. Brown** and **Konstantinos Mertis,** Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

σ-But-3-enyl-π-cyclopentadienyltriphenylphosphinenickel (10b) is converted into *trans*-1—3-η-but-2-enyl-π-cyclopentadienylnickel on thermolysis at 75° or photolysis through Pyrex in benzene solution. By employing (10b) labelled with deuterium in the 1- or 4-position of the butenyl group the course of rearrangement was deduced and showed that in thermolysis C-1 and -4 became equivalent but that the photochemical reaction was regioselective, and involved a predominant [1,3] hydrogen shift. Mechanistic implications are discussed. Synthesis and reactions of the cyclopropyl and cyclobutyl analogues of (10b) and attempts to form the cyclopropylmethyl analogue are reported.

In contrast to the considerable body of work which has accumulated on organometallic complexes derived from planar conjugated ligands of formula C_nH_{n+2}, very few studies have been reported on their homoconjugated counterparts. Simple examples of the latter include the homoallyl (1), 1—2:4—5-η-homodienyl (2), and 1—3-η-homodienyl (3) systems. Derivatives of (1) are unknown, although Green and Smith[1] have prepared a complex of the dimethyl analogue (4) which lacks the potential for rearrangement *via* hydrogen-atom migration. This latter pathway is in evidence in several reactions which might have been expected to give rise to homoallyl complexes but instead produce 1—3-η-but-2-enyls or related species.[2] The addition of aluminium[3] and boron hydrides[4] to butadiene proceeds in 1,2-fashion with metal bonded to a terminal carbon atom so that a σ-but-3-enyl derivative is the initial product. In contrast, transition metal hydrides usually react with butadiene to form 1—3-η-but-2-enyls,[5] and this could in principle be interpreted as a consequence of either initial 1,4-addition or the implementation of a 1,2-addition in which the metal is initially bonded to an internal carbon atom with formation of a σ-but-2-enyl. It may very well be, however, that derivatives of (1) are often produced in the first instance, but rearrange by hydrogen-atom migration sufficiently rapidly for the 1—3-η-but-2-enyl derivative to be the only observed product. Some analogues of (1) are known, and thus Green and Hancock[6] found that the σ–η-norbornenylpalladium complex (5) formed by reaction of sodium methoxide with norbornadienepalladium dichloride showed spectroscopic properties more in accord with a delocalised homoallylic structure than a non-interacting σ–η-formulation. Other examples of (formally) homoallylic complexes exist, although no evidence is available on the possibility of delocalisation.[7]

Organometallic derivatives of penta-1,4-diene (2) are unknown, and reaction of the hydrocarbon with iron carbonyl leads directly to tricarbonyl-*trans*-penta-1,3-dieneiron.[8] A considerable degree of angle strain would be required in order to achieve good overlap between metal and olefin in (2), and we note that bicyclo[2.2.1]-heptadiene, where this stereoelectronic problem is removed, behaves significantly differently in its complexes

---

[1] M. L. H. Green and M. J. Smith, *J. Chem. Soc.* (*A*), 1971, 3220.

[2] J. Y. Merour, C. C. Charrier, J. Benaim, J. L. Roustan, and D. Commereuc, *J. Organometallic Chem.*, 1972, **39**, 320 and references therein.

[3] L. I. Zakharkin and L. A. Savina, *Isvest Akad. Nauk. S.S.S.R.*, 1967, 78.

[4] H. C. Brown and E. Brewer, *J. Amer. Chem. Soc.*, 1969, **91**, 4164; H. C. Brown, E-i. Negishi and P. L. Burke, *ibid.*, 1971, **93**, 3400.

[5] W. R. McClellan, H. H. Hoehn, H. N. Gripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601; M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189; J. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, 1963, **2**, 601; C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6777; C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 850; R. D. Cramer, *J. Amer. Chem. Soc.*, 1967, **89**, 1633.

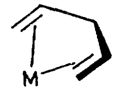
[6] M. Green and R. I. Hancock, *J. Chem. Soc.* (*A*), 1967, 2054.

[7] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1668.

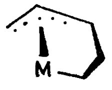
[8] G. F. Emerson, J. E. Mahler, R. Kockhar, and R. Pettit, *J. Org. Chem.*, 1964, **29**, 3620.

from other chelating diolefins, and indeed more like a conjugated diene. Its superior π-acceptor properties are demonstrated in the high degree of shielding observed in the ^{13}C chemical shift of the olefinic carbons in norbornadienerhodium(I) acetylacetone, (relative to cycloocta-1,5-diene)[9] or the ^{1}H chemical shifts of olefinic carbons in cationic rhodium complexes of norbornadiene and cyclo-octa-1,5-diene.[10]

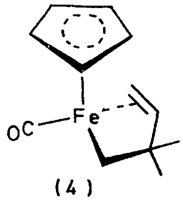
(1)



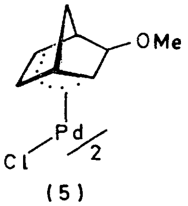
(2)



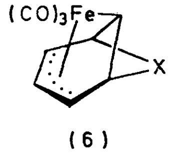
(3)



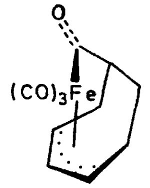
(4)



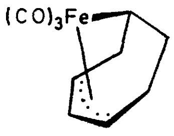
(5)



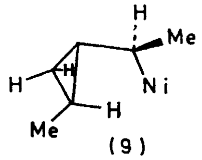
(6)



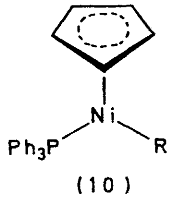
(7)



(8)

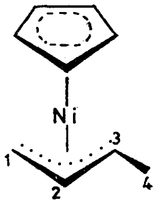


(9)



(10)

a; R = Cl
b; R = $CH_2CH_2CH{:}CH_2$
c; R = $CH_2CH_2CH{:}CD_2$
d; R = $CD_2CH_2CH{:}CH_2$

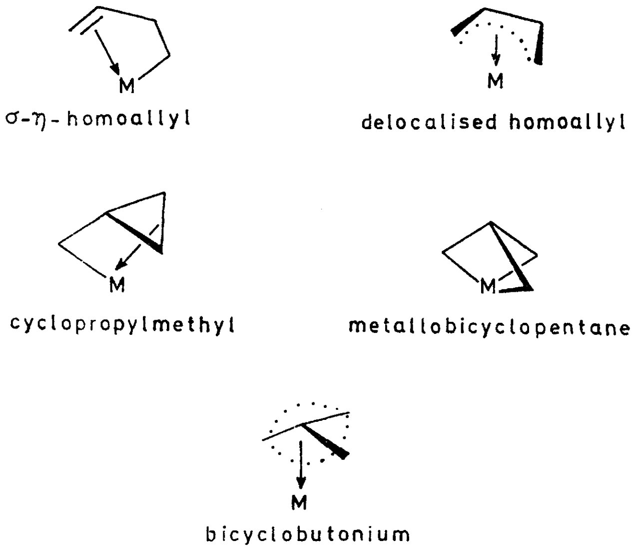


(11)

The major contribution to complexes of type (3) has come from the work of Aumann.[11] Reaction of a range of bridged and fused vinylcyclopropanes with enneacarbonyldi-iron gives rise to (6) or the corresponding derivatives. The reactivity of these complexes towards carbon monoxide and the position of alkyl $\rightleftharpoons$ acyl equilibrium varies very markedly with the nature of the bridging group and the stereochemical relationship of the σ- and η-linkages. For example complex (7) decarbonylates at 30° and the product (8) is stable to 120°, whereas the corresponding six-membered ring compound cannot be decarbonylated below 120° and then gives rise to a cyclohexa-1,3-diene complex by a hydrogen shift. Although not explicitly considered in this manner, it may be fruitful to regard the complexes (6) as derived from a delocalised homoconjugated ligand, and the apparent increase in stability with decreasing bridge size could support this viewpoint.

DISCUSSION

Our attempts to form homoallylic complexes of nickel had two motivating factors. One was the intervention of intermediates of this type in the nickel hydride catalysed interconversion of *cis*-hexa-2,4-diene and 2-methylpenta-1,3-diene[12] in which the key intermediate (9) has been indicated by the elegant labelling studies of Miller.[13] Butenyl $\rightleftharpoons$ cyclopropylmethyl $\rightleftharpoons$ cyclobutyl interconversions are well known in carbonium-ion chemistry and the former occurs in free radical and anionic systems.[14] Its demonstration in a simple isolable organometallic derivative might be a useful model for extending the range of metal-catalysed skeletal rearrangements. From a structural standpoint, there are a variety of ways in which a C_4H_7 unit may bind to a transition-metal (Scheme 1), thus providing a further impetus for studying their complexes.



SCHEME 1 Bonding patterns for η-C_4H_7 metal complexes.

Synthesis and Reactions.—Our choice of starting materials was dictated by a number of factors, namely

---

[9] G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Comm.*, 1970, 1530.

[10] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 2397; M. Green and T. A. Kuc, *J.C.S. Dalton*, 1972, 832.

[11] R. Aumann, *J. Organometallic Chem.*, 1973, **47**, C29; R. Aumann and B. Lohmann, *ibid.*, 1972, **44**, C51; R. Aumann, *Angew Chem. Internat. Edn.*, 1972, **11**, 522.

[12] R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Amer. Chem. Soc.*, 1967, **89**, 3756.

[13] R. G. Miller, P. A. Pinke, and D. J. Barker, *J. Amer. Chem. Soc.*, 1970, **92**, 4490; R. G. Miller, P. A. Pinke, R. D. Tauffer, and H. J. Golden, *J. Organometallic Chem.*, 1971, **29**, C42.

[14] *E.g.* G. A. Olah, L. Jeuell, P. Kelly, and D. Porter, *J. Amer. Chem. Soc.*, 1972, **94**, 147; J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, 1969, **91**, 1877; A. Maerecker and K. Weber, *Annalen*, 1972, **756**, 20.

structural simplicity, ready availability, the absence of carbonyl and other ligands having the potential for formation of insertion products, and a ligand readily displaced by an internal double bond. The alkyl-π-cyclopentadienyltriphenylphosphinenickels fulfil the first three of these criteria, and evidence for the fourth is provided by the observation that the σ-allyl derivative expels triphenylphosphine at —40°.[15] The chloride (10a) is readily prepared in near-quantitative yield by reaction of nickelocene and triphenylphosphine in carbon tetrachloride, as reported by Ustynyuk.[16] Reaction of (10a) with butenylmagnesium bromide in ether produced an air-sensitive green solid with spectroscopic properties appropriate for the σ-but-3-enyl derivative. The multiplets from 1-H_2 and 2-H_2 in the ^1H n.m.r. spectrum of (10b) (Figure 1) both broadened and eventually collapsed at *ca.* $-90°$; an explanation based on the inherent chiral properties of triphenylphosphine has been reported elsewhere.[17] Compound (10b) was thermally stable at room temperature and above, but underwent slow thermolysis at 75° in benzene solution ($t_{\frac{1}{2}}$ 12 h). The product after work-up by chromatography and vacuum distillation was shown to be *trans*-1—3-η-but-2-enyl-π-cyclopentadienylnickel (11). Photolysis of (10b) in benzene or ether through Pyrex (Hanovia black-light) produced (11) as the only major organometallic product, together with triphenylphosphine. Under these conditions, photolysis of other alkyls related to (10) did not lead to appreciable change.

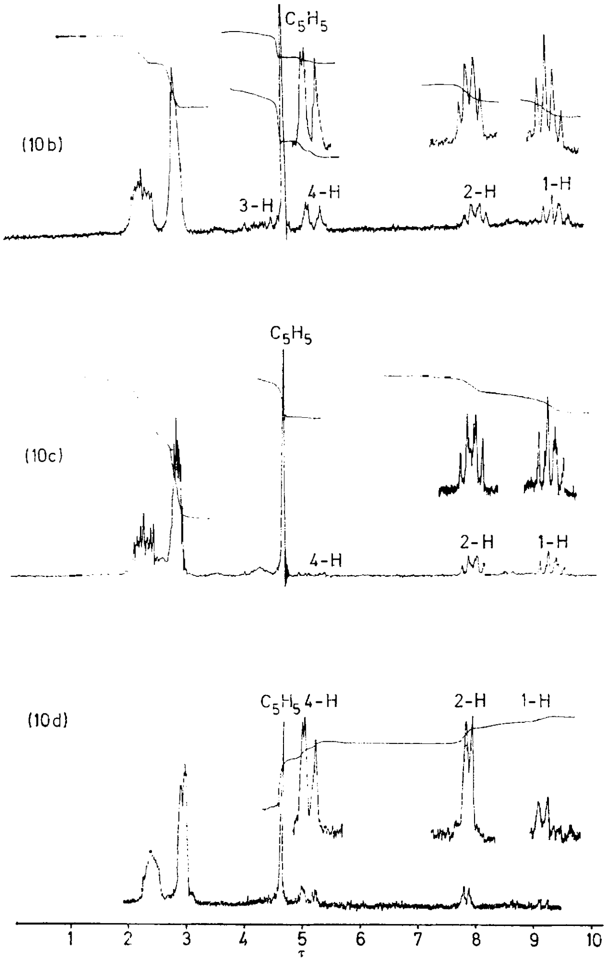


FIGURE 1 N.m.r. spectra of (10b—d) in C_6D_6 at 60 MHz

In order to determine the detailed mechanism of these transformations, deuteriated analogues of (10b) were prepared. Reaction of [$^2H_2$]bromomethylcyclopropane[18] with magnesium in ether and subsequently with (10a) gave, *via* 4,4-dideuterio-but-3-enylmagnesium bromide, the deuteriated analogue (10c) contaminated by $<5\%$ of other isotopomers (Figure 1). [1,1-$^2H_2$]But-3-enylmagnesium[18b] chloride reacted with (10a) to give the analogue (10d), in this case contaminated with 24·5% of the [2,2-$^2H_2$]isotopomer. Since the preparation of the Grignard reagent and its subsequent reaction were conducted entirely below 20°, and isotopic scrambling is known to be slow at this temperature ($t_{\frac{1}{2}}$ 28 h at 30°) we suspect that (10a) is capable of catalysing scrambling, possibly through production of but-1-enyl radicals which are known to be in rapid equilibrium with cyclopropylmethyl radicals.[14] The deuteriated compounds were separately subjected to thermolysis and photolysis under the previous conditions and in each case the product was purified by chromatography on alumina followed by vacuum distillation. The deuterium distribution in (11) was derived in each case by analysis of the 220 MHz n.m.r. spectrum in benzene solution (Figure 2) and values are recorded in the Table.

Deuterium distribution upon rearrangement of compounds (10c and d) into (II)

	No. of hydrogen atoms at				
	C-1	C-2	C-3	C-4	[1,3] Shift (%)
(10c) Photolysis	1·66	1·00	1·07 *	1·31	84
(10d) Photolysis	0·66	0·86	0·97	2·54	*ca.* 82
(10c) Thermolysis	0·98	1·02	1·05	1·97	50
(10d) Thermolysis	1·21	0·92	1·00	1·88	*ca.* 44

* Value enhanced by trace impurities.

Deuterium distribution was estimated by triplicate peak weighing (Mettler H20 microbalance) of expanded portions of the 220 MHz n.m.r. spectra at 500 Hz sweep width. The errors are $< \pm 5\%$.

Taking first the thermolysis of (10c) it is apparent that deuterium is distributed equally between the 1- and 4-positions of the but-2-enyl group without disruption of the integrity of the CD_2 unit. This observation is not consistent with any conceivable pattern which might arise from a homoallylic intermediate with rapid carbon scrambling, for homoallyl–cyclopropylmethyl interconversion causes interchange of C-1 and -2, and homoallyl–cyclobutyl interconversion causes interchange of C-1

---

[15] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometallic Chem.*, 1966, **6**, 86.

[16] Yu. A. Ustynyuk, T. I. Voevodskaya, N. A. Zharikova, and N. A. Ustynyuk, *Dodklady Akad. Nauk. S.S.S.R.*, 1968, **181**, 372.

[17] J. M. Brown and K. Mertis, *J. Organometallic Chem.*, 1973, **47**, C5.

[18] M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1960, **82**, 2646.

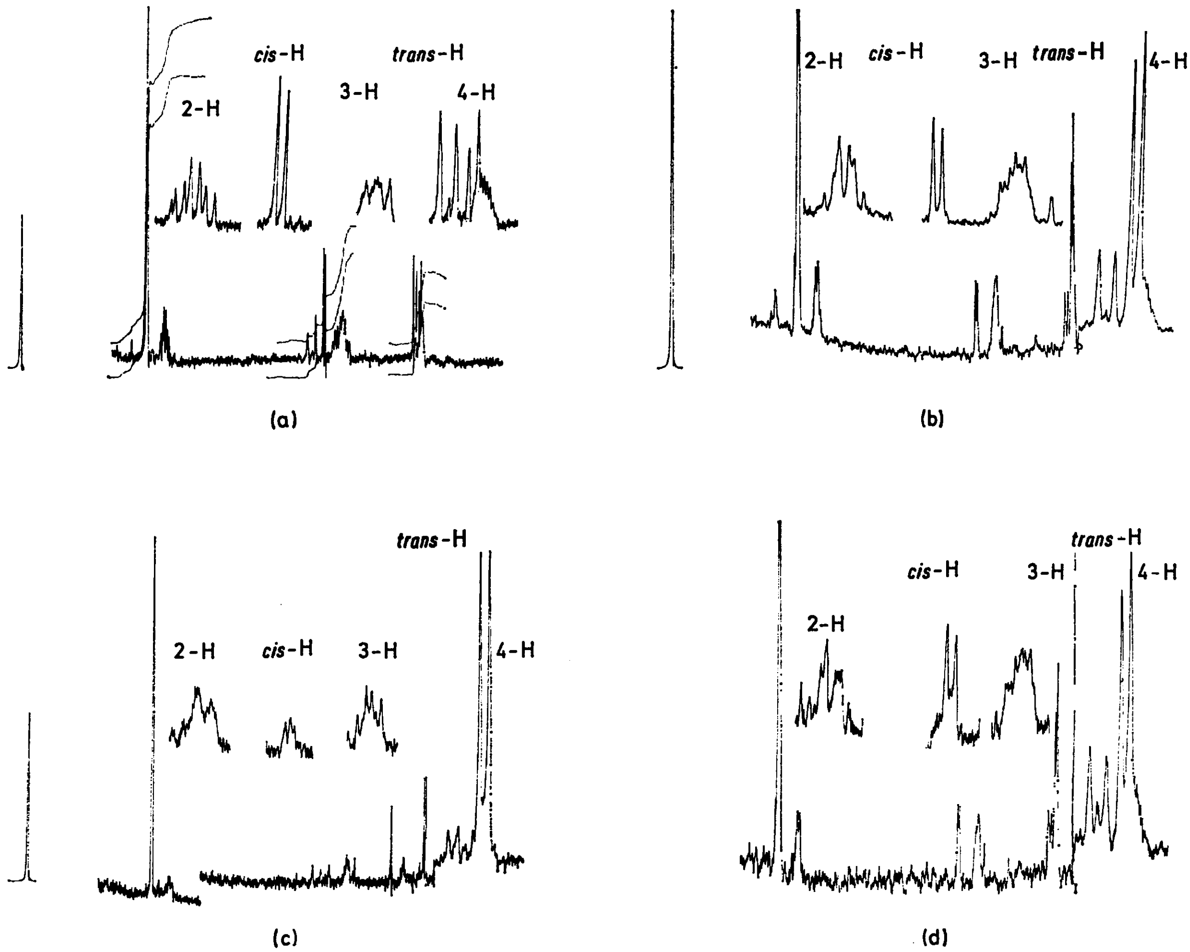
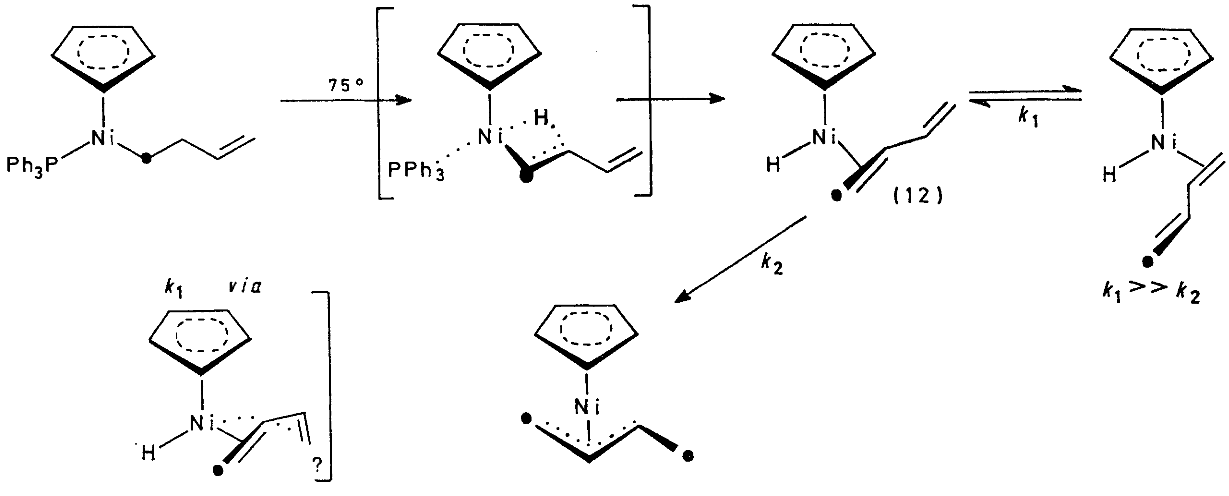


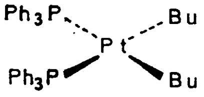
FIGURE 2 220 MHz N.m.r. spectra of deuteriated (11) in C_6D_6 pertaining to thermolysis and photolysis experiments: (a) photolysis of (10c), (b) thermolysis of (10c), (c) photolysis of (10d), (d) thermolysis of (10d) (main sweep 2500 Hz, insets 500 Hz; for chemical shifts see Experimental section)



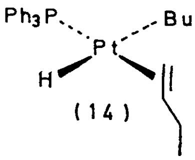
SCHEME 2 Mechanism of thermolysis of (10b).

and -4. A similar result, here complicated by the non-specificity of labelling is obtained from thermolysis of (10d). These may readily be explained by the mechanism of Scheme 2 in which the 1—2-η-butadiene complex (12) is formed in the rate-determining step. This then undergoes a hydride migration step in which (11) is produced. Either bond switching in (12) is rapid, or butadiene is cisoid in the final step so that the terminal carbon atoms have become indistinguishable in the product. Reaction is irreversible, for no change was observed in the deuterium distribution of (10d) when the thermolysis was monitored by n.m.r. spectroscopy. The possibility that free butadiene is produced during the reaction and recombines with a nickel hydride can be discounted since addition of a three molar excess of isoprene to (10b) under thermolysis did not result in the formation of π-allyls other than (11). There are precedents for expecting that butadiene and isoprene would react with a nickel hydride at similar rates.[19] Compound (11), from both thermolysis and photolysis, is 98% *trans* but this does not cast any light on the initial product geometry. Thus a mixture of the isomers of (11) (40% *cis*, 60% *trans*) prepared by reaction of nickelocene with but-2-enylmagnesium bromide isomerised slowly to the equilibrium mixture of 98% *trans*, 2% *cis*, at 120°. In the presence of an equivalent quantity of triphenylphosphine, however, isomerisation was rapid at room temperature, in accord with other examples of ligand catalysed $\eta \longrightarrow \sigma \longrightarrow \eta'$ transformations.[20]

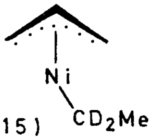
Formation of a hydrido-olefin metal complex in the thermolysis of an alkylmetal has considerable precedent, and is now thought to be the preferred pathway in these reactions when a β-hydrogen atom is present. A recent thorough study of the thermolysis of di-n-butylbistriphenylphosphineplatinum (13) by Whitesides and his co-workers showed that triphenylphosphine expulsion occurred in a rate-determining stage, and that the resulting co-ordinatively unsaturated intermediate underwent β-hydrogen abstraction to give (14). The latter collapsed to equimolar amounts of n-butane, but-1-ene, and an uncharacterised platinum(II) product.[21] The [1,1-$^2H_2$]-butyl analogue of (13) undergoes thermolysis similarly, but gives rise to but-1-ene in which deuterium is scrambled between C-1 and -2 and no scrambling is observed in the starting material. Reaction is strongly inhibited by triphenylphosphine, but α-deuteriated analogue of (13) is scrambled in its presence. Further evidence for the intermediacy of hydrido-olefinmetal in alkyl decomposition is due to Wilke, who showed that (15) reacts above —70° to form undeuteriated propene, 1,1-dideuterioethylene, and metallic nickel.[22] The stability of alkylmetals lacking the opportunity for this mode of decomposition has been exploited, notably by Wilkinson and Lappert.[23]



(13)

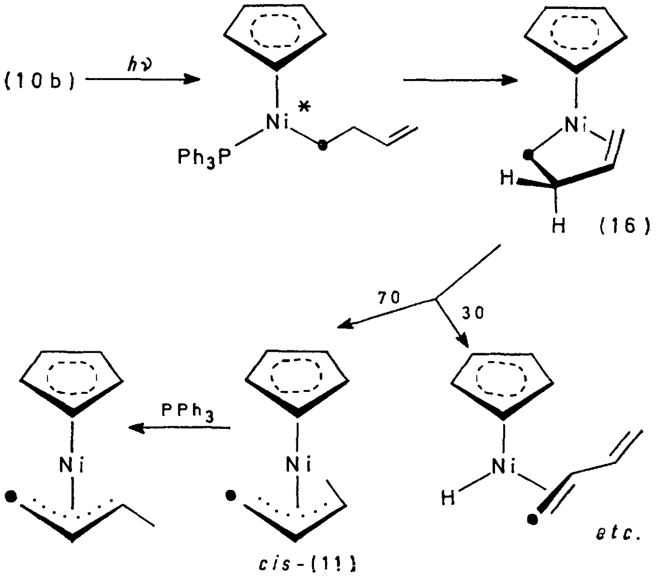


(14)



(15)

Irradiation of (10c) also produced (11), but with a strikingly different deuterium distribution. More than 80% of the product now arises by a formal [1,3] deuterium shift, and again the integrity of the CD_2 group has been maintained. This is very clearly demonstrated in the n.m.r. spectrum, which shows the methyl group to be a mixture of 84% CHD_2 and 16% CH_3 (the former 7 Hz to higher field!)[24] with no evidence for any CH_2D species. Similarly the proton signals from 4-H_2 show no more than traces of signals derived from CH_2=CD. Photolysis is strongly inhibited by triphenylphosphine, and this suggests that phosphine expulsion from a photo-excited intermediate is involved. Solvent co-ordination to this intermediate may be unimportant for a similar deuterium distribution was obtained in one reaction carried out in ether. The evidence indicates that olefin co-ordination to form (16) occurs (Scheme 3), particularly since simple saturated alkyls (*e.g.* the corresponding σ-cyclobutyl) do not photolyse under these conditions.



SCHEME 3 Mechanism of photolysis of (10b).

---

[19] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6785.

[20] J. Lukas, J. E. Ramakers-Blum, T. G. Hewitt, and J. J. de Boer, *J. Organometallic Chem.*, 1972, **46**, 167; R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 4438.

[21] G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.

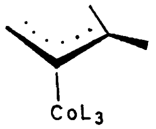
[22] G. Wilke and co-workers, unpublished work; reported at the Chemical Society Anniversay Meeting, Brighton, 1971.

[23] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533 and references therein.

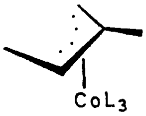
[24] *Cf.* E. W. Garbisch and M. G. Griffiths, *J. Amer. Chem. Soc.*, 1968, **90**, 6543; G. W. Smith, W. A. Boyd, and C. C. Hinckley, *ibid.*, 1971, **93**, 6319; A. L. Allred and W. D. Wilk, *Chem. Comm.*, 1969, 273.

The conversion of (16) to (11) involves predominant [1,3] hydrogen migration, and this could be envisaged to occur in one of a number of ways, including a spontaneous [1,3] shift involving metal participation, a photochemical step, or even proton transfer promoted by triphenylphosphine (the reaction would be expected to be highly exothermic). In attempts to identify (16) we carried out photolyses of (10b) in chlorobenzene at low temperature with a xenon lamp, and monitoring by n.m.r. spectroscopy. A broad featureless spectrum was obtained which on standing at 33° showed an increase in intensity of the doublet at τ 8·85 ascribed to the methyl group of (11). Although this is indicative of a thermally labile intermediate, it cannot be taken as conclusive evidence for participation of the homoallyl (16).

There is a possibility that the distribution of deuterium in (11) derived from thermolysis might be a consequence of a selective [1,3] hydrogen shift followed by a [1,4] sigmatropic shift in the *cis*-isomer of (11). A similar rearrangement has recently been observed by Nixon and his co-workers,[25] who show that (17) is in equilibrium with (18) at 60°. Thermolysis of the product from photolysis of (10c) for protracted periods at 75° in the presence or absence of triphenylphosphine, however, did not result in any subsequent change in deuterium distribution. The experiment additionally rules out the possibility of reversible formation of (16) from (11).



(17)

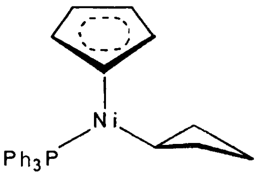


(18)

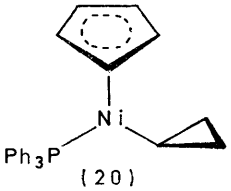
We conclude from these results that thermal and photochemical transformations occur by distinct mechanistic pathways. Since the photolysis is carried out at 20°, and the thermolysis at 75°, there remains the possibility that a common intermediate (I) is produced, which undergoes [1,3] shift to form the 1—3-η-but-2-enyl (P) in competition with a scrambling reaction which makes C-1 and -4 equivalent [(I) $\rightleftarrows$ (I′)]. This would entail the kinetic Scheme 4 and at the temperature of photolysis, 293 K, $k_1 = 0{\cdot}4k_2$, and at the temperature of thermolysis, 348 K, $k_1 > 10k_2$. For two competitive reactions to vary in relative rate by this extent implies a difference in $\Delta S^{\ddagger}$ of *ca.* 35 cal mol^{-1} K^{-1}, or a difference * in pre-exponential factor of 10^8. Clearly this is an unlikely situation, demanding rather unusual activation parameters for one of the two competing reactions.

$$\begin{tikzcd}
(\mathrm{I}) \arrow[rr, shift left, "k_1"] \arrow[dr, "k_2"'] & & (\mathrm{I'}) \arrow[ll, shift left] \arrow[dl, "k_2"] \\
& \mathrm{P} &
\end{tikzcd}$$

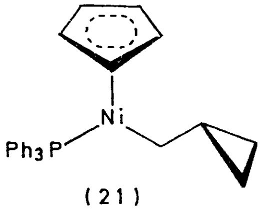
SCHEME 4



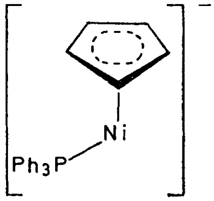
(19)



(20)



(21)



(22)

Cyclopropyl, Cyclobutyl, and Cyclopropylmethyl Derivatives.—The cyclobutyl derivative (19) was prepared as before from cyclobutylmagnesium chloride and (10a), and is an air-sensitive solid whose n.m.r. (Figure 3) and mass spectrum are in accord with the structure. Thermolysis led to slow general decomposition above 100° without any evidence for rearrangement to σ-but-3-enyl or 1—3-η-but-2-enyl derivatives. Compound (19) proved to be photochemically inert under conditions where (10) was completely transformed. For comparison purposes the σ-cyclopropyl complex (20) was synthesised and shown not to rearrange to π-allyl-π-

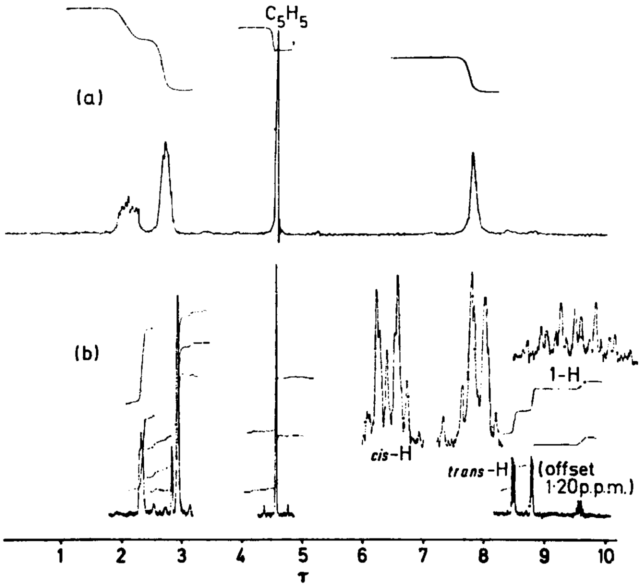


FIGURE 3 N.m.r. spectra of (a) cyclopropyl- and (b) cyclobutyl-π-cyclopentadienyltriphenylphosphinenickel in C_6D_6. No further resolution was obtained by running the former at 220 MHz

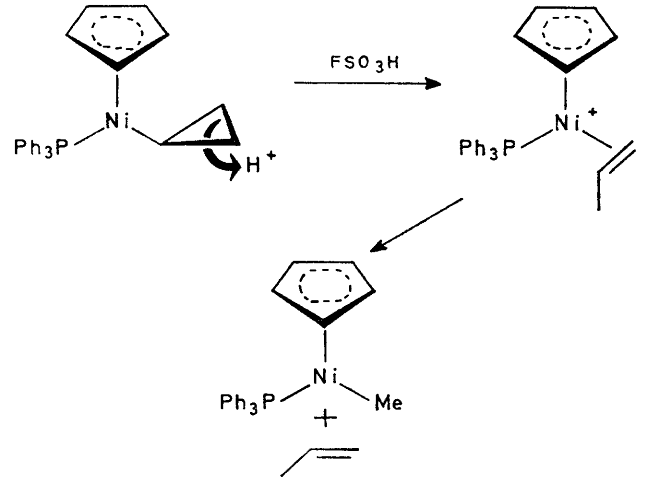
---

* Sample calculations: $E_2 = 12$ kcal mol^{-1}, $A_2 = 10^8$; then $E_1 = 23{\cdot}4$ kcal mol^{-1}, $A_1 = 10^{16\cdot1}$; $E_2 = 18$ kcal mol^{-1}, $A_2 = 10^{12}$, then $E_1 = 29{\cdot}5$ kcal mol^{-1}, $A_1 \simeq 10^{20}$.

[25] M. A. Cairns, J. F. Nixon, and B. Wilkins, *Chem. Comm.*, 1973, 86.

cyclopentadienylnickel under thermal or photochemical conditions. Thermolysis of (20) proceeded quite slowly at 120° and gave traces of cyclopropane together with an uncharacterised crimson phosphinenickel complex. The high thermal stability of (20) suggests a resistance to β-elimination because of the high energy of cyclopropene, and perhaps also a high barrier to homolysis of the metal–carbon bond on account of the high *s* character of the carbon orbital involved, and consequent net electron-withdrawing character. This would be in line with the higher stability of primary than of secondary alkylmetals (*vide* the preferred direction of addition of metal hydrides to primary olefins) and the higher stability of fluoroalkyls than of alkyls (including $M-CF_2CF_2H$ species). Comparison of the n.m.r. spectra of (19) and (20) is most informative. Whereas the cyclobutyl M–C–H resonance is at τ 8·1 ($\tau_{\square}$ 8·01) the cyclopropyl M–C–H signal is at τ 10·95 ($\tau_{\triangle}$ 9·80) in the same solvent. Evidently the shielding, and by implication the acceptor characteristics of cyclopropyl metals are closer to those of primary than of secondary alkylmetals.

Reaction of (20) with fluorosulphonic acid in methylene chloride at −80° produced a dark red solution which reacted with excess of methyl-lithium to give the corresponding σ-methyl derivative. By analogy with the results of Rosenblum,[26] we ascribe this to the formation of a π-propenyl complex, which subsequently reacts with methyl-lithium by displacement of propene (Scheme 5).



SCHEME 5 Protonation of (20).

Our attempts to form (21), the third member of the C_4H_7-nickel family, met with little success.[2] Roberts, Lansbury *et al.* have established the lability of organo-lithium and -magnesium derivatives derived from halogenomethylcyclopropanes,[18,28] but the latter succeeded in preparing cyclopropylmethyl-lithium at low temperatures by metal–halogen exchange between iodomethylcyclopropane and s-butyl-lithium. Following this procedure we treated cyclopropylmethyl-lithium with (10a) at −85° but obtained a low yield of (10b) as the only isolable product. The reaction of (10a) with anthracenyl-lithium at low temperatures gave a yellow-brown solution which contained the anion (22), at least in part, for reaction with methyl iodide formed the corresponding σ-methyl derivative. Under these conditions, bromomethylcyclopropane reacted to form (10b) as the only isolated product. Given the reactivity of cyclopropanes to proton and Lewis acids and the very powerful carbonium ion stabilising effect of the nickel, carrying as it does two powerful σ-donor ligands, one might expect that (21) would readily isomerise to (10b) under acidic conditions. Even if produced, the inevitable presence of lithium chloride or lithium bromide in the reaction mixture may be sufficient to promote rearrangement.

EXPERIMENTAL

M.p.s were taken on a Reicher heated microscope stage and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 grating machine and u.v. spectra on a Unicam SP 800 instrument. Mass spectra were recorded at the University of Hull or at P.C.M.U., Harwell, on an AEI MS 902. ^1H N.m.r. spectra at 60 MHz were taken on a Perkin-Elmer R12, at 100 MHz on a Varian HA 100, through P.C.M.U., and at 220 MHz on a Varian HR 220 instrument at the Corporate Laboratories, I.C.I., Runcorn. Air-sensitive compounds were manipulated under nitrogen by Schlenck tube techniques. Microanalyses were carried out by Alfred Bernhardt, Mulheim.

Chloro-π-cyclopentadienyltriphenylphosphinenickel (10a).—To an ice-cold solution of nickelocene (1·88 g, 10 mmol) in carbon tetrachloride (30 ml) was added a solution of triphenylphosphine (2·67 g, 10·2 mmol) in carbon tetrachloride (30 ml). The bright red solution was evaporated to 15 ml and product was precipitated with n-hexane. Recrystallisation from benzene–hexane gave chloro-π-cyclopentadienyltriphenylphosphinenickel (4·01 g, 95%), m.p. 138—139° (decomp.).

Alkyl-π-cyclopentadienyltriphenylphosphinenickel Complexes. General Procedure.—To an ice-cold solution of the appropriate Grignard reagent from alkyl halide (4 mmol) and magnesium (4 mg-atom) in ether (50 ml) was added slowly solid complex (10a) (4·27 gm, 1 mmol). The dark green mixture was transferred to a double-armed Schlenck tube cooled to 0° and treated with triethylamine (1 ml) followed by aqueous ammonium chloride (50 ml). The tube was cooled to −50° and the ether layer transferred to the other arm of the Schlenck tube under nitrogen pressure. The solution was dried over K_2CO_3 and chromatographed under nitrogen or deaerated neutral alumina. The olive-green eluate was reduced to *ca.* 10 ml, n-hexane added, and the solution cooled to −20° overnight giving dark green crystals [average yield *ca.* 80% (based on nickel halide)]. There were thus obtained: *σ-but-3-enyl-π-cyclopentadienyltriphenylphosphinenickel*, m.p. 87—89°, $\lambda_{max.}$ (Et_2O) 409sh

---

[26] A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1972, **94**, 4354.

[27] The corresponding carbonylcyclopropylmethyl-π-cyclopentadienylnickel has been prepared, K. Mertis, unpublished work; *cf.* W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299.

[28] P. T. Lansbury, V. A. Rahison, W. A. Clement, and J. D. Silver, *J. Amer. Chem. Soc.*, 1964, **86**, 2247.

and 578sh nm, $\nu_{max.}$ (Nujol) 3010w, 1630m, 1430s, 1190m, 1120w, 1100s, 1030w, 1015w, 1000w, 910w, 790s, 750s, 725m, and 700s cm^{-1}, τ (C_6D_6) 2·33—2·75 (15H, m, Ph); 4·75 (5H, s, C_5H_5, partly obscuring 3-H), 5·2 (2H, d, 4-H), 8·2 (2H, dt, $J_{2,3}$ 6 Hz, 2-H), and 9·45 (2H, dt, $J_{1,2}$ 7, $J_{^{31}P}$ 6 Hz, 1-H), *m/e* 440, 385, 320, 276, and 262 (Found: C, 72·65; H, 6·1; P, 7·45. $C_{27}H_{27}NiP$ requires C, 73·6; H, 6·1; P, 7·0%); *cyclopropyl-π-cyclopentadienyltriphenylphosphinenickel*, m.p. 122—125°, $\nu_{max.}$ (Nujol) 3025w, 1590vw, 1440s, 1250s, 1180w, 1100s, 1030vw, 1000m, 760s, 730s, and 675s cm^{-1}, τ (C_6D_6) 2·08 (*ortho*) and 2·85, (*meta* and *para*) (15H, PPh_3), 4·75 (5H, s, C_5H_5), 9·65 (2H, m, J_{gem} 5, J_{vic} 8 Hz, *cis*-2-H), 10·05 (2H, m, J_{vic} 6 Hz, *trans*-2-H), and 10·95 (1H, m, $J_{^{31}P,1}$- 14·5 Hz, 1-H), *m/e* 426, 385, 320, 262, and 58; and *cyclobutyl-π-cyclopentadienyltriphenylphosphinenickel*, m.p. 121—124°, $\nu_{max.}$ (Nujol) 3030vw, 1590vw, 1435s, 1190s, 1120m, 1100s, 790s, 750s, 730s, 700s, and 650s cm^{-1}, τ (C_6D_6) 2·10—3·10 (15H, m, PPh_3), 4·7 (5H, s, C_5H_5), and 8·0br (7H, s, C_4H_7), *m/e* 440, 387, 320, 262, and 58 (Found: C, 73·25; H, 6·25; P, 7·26. $C_{27}H_{27}NiP$ requires C, 73·6; H, 6·1; P, 7·0%).

Attempts to form Cyclopropylmethyl-π-cyclopentadienyltriphenylphosphinenickel.—A. To a solution of cyclopropylmethyl-lithium [6 mmol; in hexane–ether (9 : 1); prepared according to the procedure of Lansbury at −78°] at −90° was added slowly complex (10a) (0·92 g, 2 mmol) in toluene. The solution was stirred at −90° for 30 min, warmed to −70°, and maintained at −70° with stirring for a further 2 h. Work-up as before and chromatographic elution with pentane–ether (9 : 1) gave complex (10b) (0·080 g, 9%), characterised by n.m.r. comparison with an authentic sample.

B. Complex (10a) (0·421 g, 1 mmol) was dissolved in ether (10 ml) and tetrahydrofuran (2 ml), and cooled to −78° with stirring. Anthracenyl-lithium (1 mmol) in tetrahydrofuran was added by syringe and the mixture stirred for 30 min at −78°. The deep red colour of the chloride rapidly changed to golden brown. Bromomethylcyclopropane (0·137 g, 1 mmol) in tetrahydrofuran (2 ml) was added slowly to the cold solution, causing a colour change to deep green. After 30 min, work-up as usual and alumina chromatography gave complex (10b) in low yield (characterised by n.m.r. spectroscopy).

*Synthesis of Deuteriated But-*3-*enylnickel Complexes.*—[1,1-$^2H_2$]But-3-enyl iodide and [1,1-$^2H_2$]bromomethylcyclopropane were prepared by published procedures and shown to be essentially free from isomeric or isotopic impurities. Complex (10a) (0·842 g, 2 mmol) was treated with the Grignard reagent from [1,1-$^2H_2$]bromomethylcyclopropane (0·82 g, 6 mmol) in ether (50 ml). Work-up by the standard procedure gave complex (10c) (0·685 g, 78%), τ (C_6D_6) 2·1—2·9 (15H, m, PPh_3), 4·40br (1H, m, 3-H), 5·4 (<0·1H, residual 4-H), 8·1 (2H, q, 2-H), and 9·45 (2H, q, 1-H). Similarly, reaction of the Grignard reagent from [1,1-$^2H_2$]but-3-enyl iodide gave complex (10d) (0·57 g, 65%), τ (C_6D_6) 2·1—2·9 (15H, m, Ph), 4·75 (6H, s, C_5H_5, obscuring 2-H), 5·3 (2H, d, 4-H), 8·1 (1·51H, d, 2-H), and 9·45 (0·49H, d, 1-H).

Thermal and Photochemical Reactions.—The butenylnickel complexes (10b—d) (0·21 g) in benzene (1 ml) were sealed under nitrogen in an n.m.r. tube and maintained at 75°. The reaction was monitored by n.m.r. spectroscopy and appeared complete after 30 h. The resulting deep red solutions were rapidly chromatographed on basic alumina, and the red-purple solutions eluted with isopentane were evaporated, and the residues purified by double molecular distillation at 10^{-3} mmHg, giving complex (11). Photolysis was likewise carried out in sealed n.m.r. tubes using unfiltered light from a Hanovia model 16, 100 W medium pressure Hg lamp. Samples of complexes (10b—d) (0·220 g) in benzene (1·5 ml) were photolysed within 6 in of the lamp, the sample being cooled within the cavity of a running water condenser. The reaction was monitored by n.m.r. spectroscopy and showed only signals for the starting material and complex (11) and broad resonances at τ *ca.* 8·5 corresponding to ill-defined decomposition products. On completion of reaction the product was isolated and characterised as before.

Preparation of 1—3-*η-But-2-enyl-π-cyclopentadienylnickel* (11).—To an ice-cold solution of but-2-enylmagnesium bromide (2 mmol) in ether (50 ml) was added a solution of nickelocene (1·89 g, 1 mmol) in tetrahydrofuran (*ca.* 30 ml). The resulting brown solution was stirred overnight at room temperature, and solvent was removed at 0° (100 mmHg). The residue was extracted with n-pentane and solvent again removed *in vacuo* to give an air-sensitive purple oil which was purified by molecular distillation (20°; 10^{-3} mmHg). There were obtained the *cis-* (35%) and *trans-* (65%) isomers of complex (11), $\nu_{max.}$ 3050w, 3020w, 1480m, 1350s, 1100m, 1030m, 920m, 780s, and 6·0s cm^{-1}, τ (*cis*) (C_6D_6) 4·7 (6H, s, C_5H_5, obscuring 2-H multiplet), 6·25 (1H, dq, $J_{3,4} = J_{2,3} =$ 6·5 Hz, 3-H), 7·08 (1H, dm, $J_{1,2}$ 12 Hz, *trans*-H), and 9·21 (3H, d, $J_{3,4}$ 6·5 Hz, 4-H), τ (*trans*) (C_6D_6) 4·7 (5H, s, C_5H_5), 4·97 (1H, ddd, 2-H), 7·41 (1H, d, $J_{1,2}$ 6·0 Hz, *cis*-1-H), 7·75 (1H, dq, 3-H), 8·80 (1H, d, $J_{1,2}$ 12 Hz, *trans*-1-H), and 8·90 (3H, d, $J_{3,4}$ 6·0 Hz, 4-H).

Control Experiments.—Thermolysis in the presence of isoprene. A mixture of complex (10b) (0·440 g, 1 mmol) and isoprene (0·3 ml, 3 mmol) in benzene (15 ml) was heated to 75° in a sealed n.m.r. tube. In the later stages of reaction products derived from the dimerisation and oligomerisation of isoprene were apparent, but work-up and chromatography in the normal manner gave only (10b) and no π-allyl intermediates derived from isoprene.

Thermolysis of deuteriated photolysis product. The n.m.r. solution from photolysis of (10c) was heated to 75° and monitored for changes in the τ 8·5—9·5 region. After 24 h none was apparent, there being no change in the relative heights of the peaks at τ 8·80 and 8·90 due to *trans*-1- and 4-H respectively.

cis–trans-*Isomerisation of complex* (11). Samples of the *cis–trans*-mixture prepared as above were transferred under nitrogen to septum-sealed n.m.r. tubes and spectra were taken for a benzene solution. In the absence of triphenylphosphine, reaction was observed to occur rather slowly at 120°. In the presence of one mol. equiv. of triphenylphosphine, reaction occurred rapidly at the n.m.r. probe temperature.

Photolysis in the presence of triphenylphosphine. Samples of complex (10b) (100 mg, 0·25 mmol) in C_6D_6 and C_6D_6 containing triphenylphosphine (130 mg, 05 mmol) were sealed in n.m.r. tubes under nitrogen and photolysed in the previous manner with frequent interchange of the position of the tubes. The reaction was monitored at intervals of 6 h by following the growth of the cyclopentadienyl resonance at τ 4·7 and the decline of the resonance at τ 4·75. The sample containing triphenylphosphine was photolysed at a rate approximately one-third of the standard sample.

Reactions of Cyclopropyl-π-cyclopentadienyltriphenylphos-

phinenickel (20).—A. The complex (0·106 g, 0·25 mmol) was dissolved in methylene chloride (2 ml) and cooled to −75°. Fluorosulphonic acid (0·05 g, 0·5 mmol) in CH_2Cl_2 (1 ml) was added slowly and the green solution observed to change to deep red. To this solution was slowly added methyl-lithium (0·6M in ether, 1·35 ml, 1 mmol) and the colour rapidly changed to dark green. After stirring for an hour, and work-up according to the previously described procedure, π-cyclopentadienyl(methyl)triphenylphosphinenickel was obtained, and identified by spectroscopic comparison with an authentic sample.

B. The complex (100 mg) in C_6D_6 (0·5 ml) was heated to 120° in a nitrogen-filled sealed n.m.r. tube and monitored at intervals. Over 48 h the green colour changed to bright red and a sharp singlet at τ 9·8 (τ_{Δ} 9·8) was apparent. A nickel mirror was gradually deposited on the walls of the tube.

[3/841 *Received, 19th April,* 1973]