# The Isomerisation of 1,4-Diarylbutenes by Ruthenium–Phosphine Complexes

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The catalytic double-bond migration in 1,4-diarylbutenes and in 2-methyl-1,4-diphenylbutenes by $RuCl_2(PPh_3)_3$ has been studied. The electronic nature of the substituents X in $p$-$XC_6H_4{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2Ph$ does not affect the reaction rate; it does, however, affect the ratio of $p$-$XC_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CHPh$ : $p$-$XC_6H_4{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2Ph$ which is >1 for electron-withdrawing and <1 for electron-releasing substituents. The reaction is sensitive to steric effects and to the electronic nature of the aryl ligands in the triarylphosphine moiety of the catalyst. The experimental results support a modified metal hydride ⟶ alkylmetal mechanism for the reaction and rule out the formation of $\pi$-olefin ⟶ allylmetal intermediates.

DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM (I) is known for its outstanding catalytic properties in numerous organic reactions.[1-10] It is, however, sometimes disadvantageous in being a powerful isomerisation catalyst as well, leading to undesirable side products. In our previous studies on double-bond migration in allylbenzene and phenylbutenes[11] we noticed that compound (I) reacts by a different mechanism than do, *e.g.*, soluble rhodium complexes.[12] The studies of ligand and substitution effects on the isomerisation of 1,4-diphenylbutenes now presented stress this difference and provide new information on the mechanism of the Ru$^{II}$-catalysed reactions.

When peroxide-free[13] *trans*-1,4-diphenylbut-2-ene (II) is treated with $10^{-2}$ mol. equiv. of the ruthenium catalyst (I) at 185 °C in the absence of any solvent, an equilibrium mixture of 7·5% (II), 1·5% *cis*-1,4-diphenylbut-2-ene (III), and 91% *trans*-1,4-diphenylbut-1-ene (IV) (free from the corresponding *cis*-isomer) is formed within 2 h. The maximum rate of conversion is 30·0%

$RuCl_2(PPh_3)_3$ (I) $PhCH_2{\cdot}CH{=}CH{\cdot}CH_2Ph$ (II) *trans* (III) *cis* $PhCH{=}CH{\cdot}CH_2{\cdot}CH_2Ph$ (IV)

$IrCl(CO)(PPh_3)_2$ (V) $RhCl(PPh_3)_3$ (VI) $Rh_2Cl_2O_2(PPh_3)_2(PhH)_2$ (VII)

$[Rh(CO)_2Cl]_2$ (VIII)

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[1] D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, 1965, **208**, 1203.

[2] I. Jardine and F. J. McQuillin, *Tetrahedron Letters*, 1966, 4871.

[3] J. Blum and H. Rosenman, *Israel J. Chem.*, 1967, **5**, 69.

[4] P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1967, 305.

[5] P. S. Hallman, B. R. McGarvay, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143.

[6] P. Abley and F. J. McQuillin, *Discuss. Faraday Soc.*, 1968, **46**, 31.

[7] J. Blum, J. Y. Becker, H. Rosenman, and E. D. Bergmann, *J. Chem. Soc.* (*B*), 1969, 1000.

[8] J. Blum and S. Biger, *Tetrahedron Letters*, 1970, 1825.

[9] J. Blum and G. Scharf, *J. Org. Chem.*, 1970, **35**, 1895.

[10] G. Wilkinson, F.P. 1,459,643/1966 (*Chem. Abs.*, 1967, **67**, 53,652d); B.P. 1,219,763/1971 (*Chem. Abs.*, 1971, **74**, 87,398k).

[11] J. Blum and Y. Pickholtz, *Israel J. Chem.*, 1969, **7**, 723.

[12] R. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272; *Accounts Chem. Res.*, 1968, **1**, 186.

[13] J. E. Lyons, *Chem. Comm.*, 1971, 562.

min$^{-1}$. At 154 °C equilibration is reached after 4·5 h at a maximum rate of 1·06% min$^{-1}$ (see Figure 1).

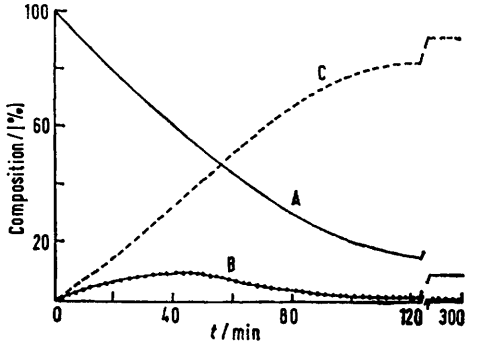


FIGURE 1 Composition–time curves for the isomerisation of *trans*-1,4-diphenylbut-2-ene by $\mathrm{RuCl_2(PPh_3)_3}$ at 154 °C; A, *trans*-Ph·CH$_2$·CH=CH·CH$_2$Ph; B, *cis*-Ph·CH$_2$·CH=CH·CH$_2$Ph; C, *trans*-Ph·CH=CH·CH$_2$·CH$_2$Ph

Similarly, $\mathrm{IrCl(CO)(PPh_3)_2}$ (V) and $\mathrm{RhCl(PPh_3)_3}$ (VI) catalyse double-bond migration in (II). The catalyst (V), however, acts slowly even at 185 °C (equilibration after 8 h; maximum rate 0·49% min$^{-1}$) and the rhodium compound is deactivated when a mixture of 62% (II), 9% (III), and 29% (IV) has been formed (Figure 2). Bubbling oxygen through the reaction catalysed by the rhodium complex (VI) proprovides a new catalytic system which does lead to equilibration (*e.g.*, at 185 °C after 20 min; maximum rate 48% min$^{-1}$). The catalyst in this system differs from that (VII) described by Augustine and Van Peppen,[14] which converts the *cis*-isomer (III) into the equilibrium mixture within 3 min (at 185 °C). The catalytic power of the phosphine-free rhodium compound (VIII) in this isomerisation is of the same order as that of (I), but it exhibits a relative long (10 min) induction period, and is partially converted into metallic rhodium during the process.

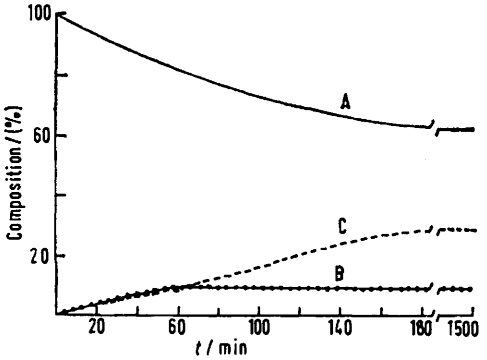
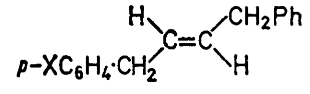
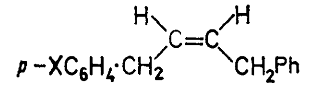


FIGURE 2 Isomerisation of *trans*-1,4-diphenylbut-2-ene by $\mathrm{RhCl(PPh_3)_3}$ at 154 °C; A, B, and C as in Figure 1

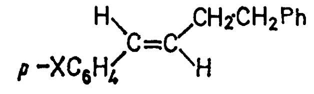
The Ru$^{\mathrm{II}}$-catalysed double bond migration in compound (II) was compared (at 154 °C) with that in asymmetrically substituted *trans*-1-aryl-4-phenylbut-2-enes, *viz.*, 1-(*p*-tolyl)-, 1-(*p*-methoxyphenyl)-, 1-(*p*-chlorophenyl)-, and 1-(*p*-cyanophenyl)-4-phenylbut-2-ene (IX; a—d). Of the six types of olefin [(IX), (XI), (XII), and the corresponding *cis*-isomers] that can be expected to be present in the equilibrium mixtures only (IX), (X), (XI), and (XII) (but neither the *cis*-1-aryl-4-phenylbut-1-enes nor the *cis*-4-aryl-1-phenylbut-1-enes), were formed in significant amounts.



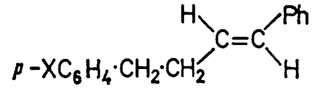
(IX)



(X)



(XI)



(XII)

a, X=Me; b, X=OMe; c, X=Cl; d, X=CN

The reaction curves of the isomerisation of olefins (IX; b—d) resemble those of (IXa) given in Figure 3.

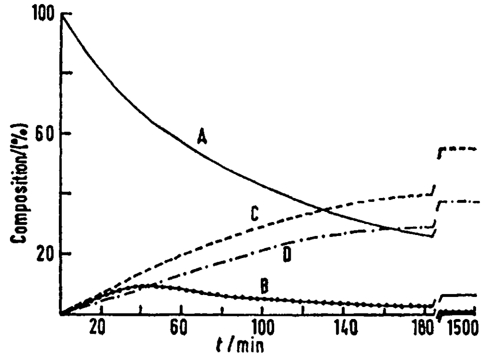


FIGURE 3 Isomerisation of *trans*-1-(*p*-tolyl)-4-phenylbut-2-ene by $\mathrm{RuCl_2(PPh_3)_3}$ at 154 °C; A, *trans*-*p*-MeC$_6$H$_4$·CH$_2$·CH=CH·CH$_2$Ph; B, *cis*-*p*-MeC$_6$H$_4$·CH$_2$·CH=CH·CH$_2$Ph; C, *trans*-*p*-MeC$_6$H$_4$·CH=CH·CH$_2$·CH$_2$Ph; D, *trans*-*p*-MeC$_6$H$_4$·CH$_2$·CH$_2$·CH=CHPh

TABLE 1

Isomerisation of *trans*-*p*-XC$_6$H$_4$·CH$_2$·CH=CH·CH$_2$Ph by $\mathrm{RuCl_2(PPh_3)_3}$ at 154 °C

| | | Maximum rate of isomerisation | Composition of equilibrium mixture(%) [a] | | | |
|---|---|---|---|---|---|---|
| Expt. | X | (% min$^{-1}$) | (IX) | (X) | (XI) | (XII) |
| 1 | H | 1·06 | 8·7 | 0·3 | 91·0 | |
| 2 | Me | 1·10 | 6·4 | 0·5 | 55·4 | 37·7 |
| 3 | OMe | 1·15 [b] | 12·4 | 2·6 | 52·4 | 32·6 |
| 4 | Cl | 1·30 | 4·3 | 1·0 | 40·7 | 54·0 |
| 5 | CN | 4·2 × 10$^{-3}$ | 18·3 | 4·1 | 32·1 | 45·5 |

[a] The equilibrium in expts. 1—4 have been established by isomerisation of both (IX) and (XI) or (XII). The figures in expt. 5 express the composition obtained from (IXd) after 62 h which seems not to change thereafter. Isomerisation of (XId) and (XIId) was too slow to be recorded. [b] After an induction period of 17 min.

The results summarised in Table 1 indicate that the maximum rate of isomerisation of the unsubstituted

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[14] R. L. Augustine and J. Van Peppen, *Chem. Comm.*, 1970, 497.

1,4-diphenylbut-2-ene is practically the same as that of its *p*-methyl-, -methoxy-, and -chloro-derivatives, and that the equilibration is achieved (at 154 °C) after 12—20 h. The extremely slow rate of isomerisation of *trans*-1-(*p*-cyanophenyl)-4-phenylbut-2-ene (IXd) could be explained by the formation of a relatively stable adduct of (IXd) to (I) [compound (XIII)] (see

$$\underset{\text{(XIII)}}{(PhCH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}C_6H_4CN)RuCl_2(PPh_3)_2} \qquad \underset{\text{(XIV)}}{RuCl_2(PPh_3)_2(O_2)}$$

below), which dissociates only very slowly at 154 °C. At high temperature (195 °C) rapid dissociation of (XIII) permits the accumulation of sufficient ' true catalyst ', and double-bond migration proceeds at a rate similar to that of (IXa), (IXb), and (IXc).

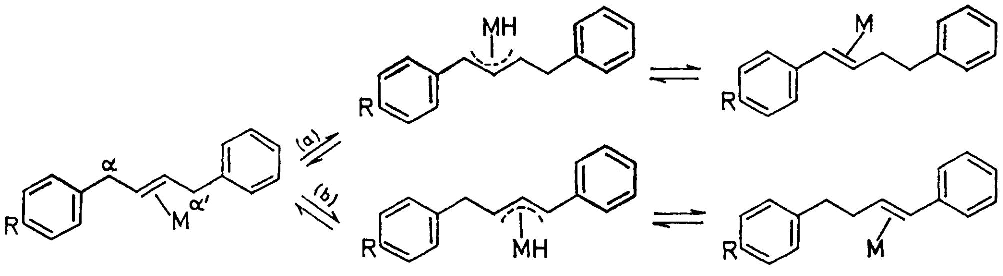
The electronic nature of the substituents in the benzene rings of (IX) seems thus not to affect the rate of isomerisation. It does, however, affect the ratio of the conjugated olefins (XI) : (XII) throughout the entire reaction period, and in the equilibrium mixture. Electron-withdrawing groups favour the formation of the olefins having the double bond conjugated with the unsubstituted phenyl group, while electron-donating groups favour conjugation with the substituted ring.

TABLE 2

Isomerisation of *trans*-*p*-$XC_6H_4{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2Ph$ by sodium methoxide in diglyme at 154 °C

| | Conjugated olefins formed at $t/2$ (%) | |
|---|---|---|
| X | *trans*-*p*-X-$C_6H_4{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2Ph$ | *trans*-*p*-X-$C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CHPh$ |
| Me | 32·0 | 52·0 |
| OMe | 30·8 | 59·5 |
| Cl | 50·0 | 38·2 |
| CN | 58·0 | 33·0 |

In the base-catalysed reaction (0·5 mol. equiv. sodium methoxide in diglyme at 154 °C) the ratio (XI) : (XII) is the reverse one, as electron-withdrawing groups favour the conjugation to the substituted ring and *vice versa* (Table 2). In the basic medium the electronic character exerts also a marked influence on the reaction rate [*e.g.*, maximum rates of isomerisation of (IXb) and (IXc) are 1·05 and 9·15% min$^{-1}$, respectively], as could be expected for the allylic carbanion mechanism suggested for the base-catalysed isomerisation.[15] This type of mechanism does, thus, not apply to our reaction.



SCHEME 1

Although no protic solvent was used in the Ru-catalysed isomerisation of olefins (II) and (IX), a ruthenium hydride is formed during the process. A strong transient band at 1970 cm$^{-1}$ always appears in the initial period of the reaction, followed by small peaks between 2020 and 2060 cm$^{-1}$. In the case of (IXa) and (IXc), in hot benzene (60 °C), the formation of the hydride is followed by the production of σ-bonded alkylruthenium complexes (having neither vinylic nor metal-bonded hydrogen atoms, but showing resonance bands between δ 1·60 and 2·70 p.p.m. in the n.m.r. spectra). Traces of oxygen readily convert both the hydride and the alkyl complexes into the paramagnetic oxido-compound (XIV) ($\nu_{O-O}$ 860 cm$^{-1}$; $g = 2{\cdot}25$).*

TABLE 3

Isomerisation of *trans*-1,4-diphenylbut-2-ene by $[(p\text{-}XC_6H_4)_3P]_3RuCl_2$ at 154 °C

| Catalyst | Initial (maximum) rate of isomerisation(% min$^{-1}$) |
|---|---|
| (XVa) | 6·0 |
| (XVb) | 2·3 |
| (I) | 1·1 |
| (XVc) | 0·6 |
| (XVd) | 0·5 |

The facts that the replacement of the dichloro-compound (I) by $HRuCl(PPh_3)_3$ as catalyst causes 80-fold increase, and that the addition of 3% methanol to the reaction mixture leads to a ten-fold increase in the maximum reaction rate, emphasise the importance of the metal hydride, the formation of which is associated with oxidative protonation of (I) [probably in the dissociated form $RuCl_2(PPh_3)_2$]. In contrast to the Pd$^{II}$-catalysed isomerisation,[17] an increase of the nucleophilicity at the central metal atom [by introduction of Me or OMe groups as in (XVa) and (XVb)] enhances the rate of double-bond migration, and introduction of electron-withdrawing substituents [as in (XVc) and (XVd)] slows it down (Table 3). The same relationship between electronic factors and reaction

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* The difference between compound (XIV) and the recently reported arsine complex $RuCl_2(AsPh_3)_3(O_2)$ [16] is remarkable, as in the latter compound all three neutral ligands are retained while in the phosphine complex one $PPh_3$ is eliminated. This may well be the reason for the superior catalytic activity of the triphenylphosphine containing complex.

[15] D. J. Cram, ' Fundamentals of Carbanion Chemistry,' Academic Press, London and New York, 1965, 209.

[16] M. M. Taqui Khan, R. K. Andul, and P. T. Monoharan, *Chem. Comm.*, 1971, 561.

[17] W. H. Clement and T. Spiedel, *Ind. Eng. Chem.* (*Product Res. and Development*, 1970, **9**, 220.

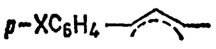
rate has been observed in several other $Ru^{II}$-catalysed hydrogen transfers now being investigated.[18]

Our results can thus not be rationalised by the HCl-addition–elimination mechanism [12] nor by the hydrido-$\pi$-olefin $\longrightarrow$ $\pi$-allylmetal mechanism [19] according to which electron-withdrawing substituents [Cl and CN in (IXc) and (IXd), respectively], should facilitate the abstraction of the $\alpha$-benzylic hydrogen atom leading to (XII) *via* route (a), while electron-releasing groups [Me and OMe in (IXa) and (IXb), respectively] should direct the isomerisation chiefly to (XI) *via* route (b) (Scheme 1).*

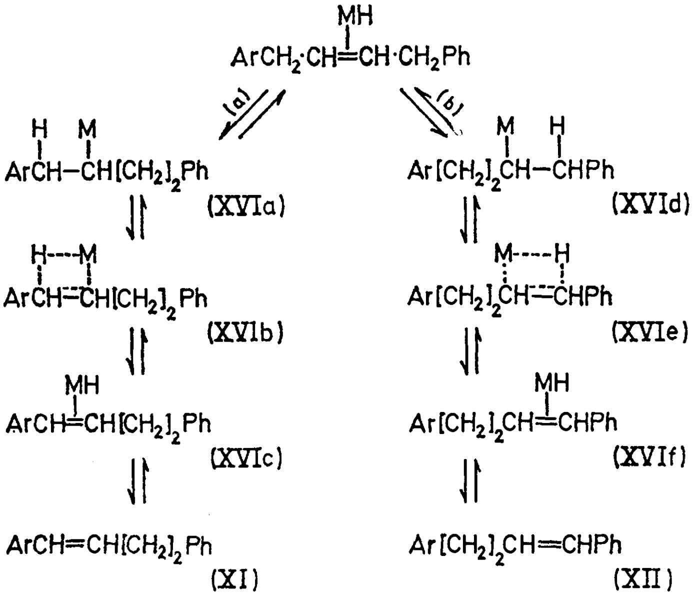
Our results are best explained by a modification of the $\pi$-olefin $\longrightarrow$ alkylmetal mechanism.[20] Dissociation of the catalyst (I) into solvated $RuCl_2(PPh_3)_2$ is followed by the rate-determining step, the formation of a five-co-ordinated ruthenium hydride (the hydrogen atom is abstracted either from the olefinic substrate or, less probably, from the *ortho*-position of the triphenylphosphine ligand [21]).

$[(p\text{-}MeC_6H_4)_3P]_3RuCl_2$ (XVa) $[(p\text{-}MeOC_6H_4)_3P]_3RuCl_2$ (XVb)

$[(p\text{-}ClC_6H_4)_3P]_3RuCl_2$ (XVc) $[(p\text{-}FC_6H_4)_3P]_3RuCl_2$ (XVd)



(1)



SCHEME 2

1,4-Diarylbut-2-ene adds then to the vacant site of the hydrido-complex to give intermediate (XVI) which, in turn, is transformed into (XI) or into (XII) (Scheme 2).

The reason for the formation of compounds (XI) and (XII) in unequal amounts is probably due to polarisation of the C–C double bond and the M–H single bond during the transformation of (XVI) into (XVIa) and (XVId), respectively (Scheme 3). Electron-releasing groups favour, therefore, the route leading to (XI) while 'negative' substituents promote the formation of (XII). Obviously, the polarisation of the $\beta\gamma$-double bond is rather small so that the preferential formation of conjugated olefin does not exceed 20% (Table 1).

In the isomerisation of 2-methyl-1,4-diphenylbut-2-ene (XVII) we observed a steric effect influencing the catalysis. Within 24 h at 154 °C only 21% of (XVII) was isomerised by $RuCl_2(PPh_3)_3$ giving 8% of the isomer (XVIII) and 13% of isomer (XIX). The unexpected ratio (XVIII) : (XIX) indicates at least partial isomerisation by a $\pi$-allyl mechanism, in which the intermediate (2) is formed in preference to (3). Double-bond migration catalysed by $HRuCl(PPh_3)_3$ proceeds at a somewhat higher rate than by (I) (0·46% $min^{-1}$) and gives, after 24 h at 154 °C, a different isomer distribution [28·5% (XVIII) and 12·5% (XIX)] which can be rationalised by the mechanism of Scheme 2.

With regard to factors inhibiting the catalysis, the adduct (XIII) deserves some attention. Unlike the

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* One Referee drew our attention to the fact that there may be an effect of the *para*-substituent on the residue of structure (1) to the metal. This is, of course, theoretically possible. However, there are no data available on such an effect which could be weighed as against the evidence presented in the text.

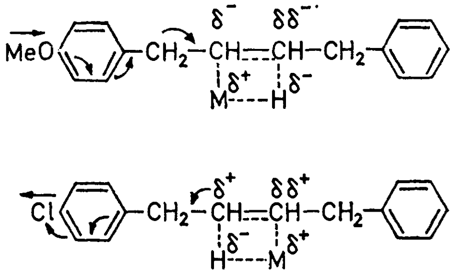
[18] J. Blum and Y. Sasson, unpublished results.

[19] R. E. Rinehart and J. S. Lasky, *J. Amer. Chem. Soc.*, 1964, **86**, 2516.

[20] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 1964, **86**, 1776.

[21] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3011.

nitrile complexes of (I) reported so far,[22] adduct (XIII) has only one cyano-group attached to the ruthenium atom. Spectroscopic measurements indicate that the C=C double bond does not take part in bond formation in the making of the complex. The C=C absorption at 975 cm$^{-1}$ is retained and the vinylic (somewhat shielded) protons give a resonance at δ 4·76 p.p.m. The very small hypsochromic shift (5 cm$^{-1}$) of the C≡N absorption and the paramagnetic nature of the complex (*g* 2·44) suggest σ-bonding *via* the nitrogen atom. Molecular weight determination in cold benzene showed the complex to be monomeric. [In hot solvent, (XIII) is partly dissociated.] The fairly stable nitrile complex is in fact an ' internal ' temperature-dependent inhibitor. Other substances containing strongly complexing groups act as external inhibitors (Table 4).



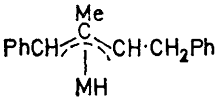
SCHEME 3

$PhCH_2{\cdot}CMe{=}CH{\cdot}CH_2Ph$ (XVII)

$PhCH_2{\cdot}CHMe{\cdot}CH{=}CHPh$ (XVIII)

$PhCH{=}CMe[CH_2]_2Ph$ (XIX)

$HRhCl_2(PPh_3)_3$ (XX)



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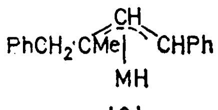

(3)

TABLE 4

Effect of external inhibitors on the isomerisation of 1,4-diphenylbut-2-ene (II) by $RuCl_2(PPh_3)_3$ at 154 °C [a]

| Expt. | Inhibitor | Molar ratio catalyst : additive | Initial rate of isomerisation (% min$^{-1}$) | Maximum % of (II) transformed |
|---|---|---|---|---|
| 1 | None | | 1·06 | 91 |
| 2 | Anisole | 1 : 100 | 0·97 | 78 |
| 3 | Nitrobenzene | 1 : 100 | 0·48 | 76 |
| 4 | Collidine | 1 : 100 | 0·18 | 70 |
| 5 | Benzonitrile | 1 : 1 | 0·92 | 78 |
| 6 | Benzonitrile | 1 : 100 | 0·03 | 61 |
| 7 | 1,2-Bisdiphenylphosphinoethane | 1 : 1 | 0·90 | 74 |
| 8 | 1,2-Bisdiphenylphosphinoethane | 1 : 10 | 0·02 | 15 |
| 9 | 1,2-Bisdiphenylphosphinoethane | 1 : 100 | 0·00 | 2 |

[a] Under argon. In the presence of air, collidine and benzonitrile promote the catalytic oxidation of (II) to give 8 and 15% of 1,4-diphenylbutan-2-one in experiments 4 and 6 respectively.

Lyons has found recently[13] that oxygen is an important factor in the Ru$^{II}$-catalysed isomerisation of 4-vinylcyclohexene and allylbenzene, but we observed only a negligible effect by air on the double-bond migration in the olefin (II). We found, however, and unusual effect of oxygen on the catalysis by $HRhCl_2(PPh_3)_3$ (XX). When air was strictly excluded, compound (II) is rapidly transformed into the equilibrium mixture (max. rate 25% min$^{-1}$). In the presence of small quantities of oxygen, however, an oscillating reaction takes place. At 154 °C the starting non-conjugated olefin is transformed into *cis*- and mainly *trans*-Ph·CH=CH·CH$_2$·CH$_2$Ph (IV) to an extent of 95% (only 92·5% at the equilibrium!) within 4 min. Although the conjugated olefin (IV) has been shown to be more stable than (II) by 4·8 kcal mol$^{-1}$, the reaction reverses itself after 3 min and the starting material (II) is re-formed in 82% yield 3 min later. At this point the reaction reverses again, *etc.* The oscillations damp gradually until at the end of *ca.* 25 min the typical reaction curve of a $RhCl(PPh_3)_3$-catalysed reaction is obtained (Figure 4). The shape of the oscillatory response strongly depends on the oxygen content of the system, but we are not certain what the driving force of the oscillation is. Further studies on this unusual property of $HRhCl_2(PPh_3)_3$ are now in hand.

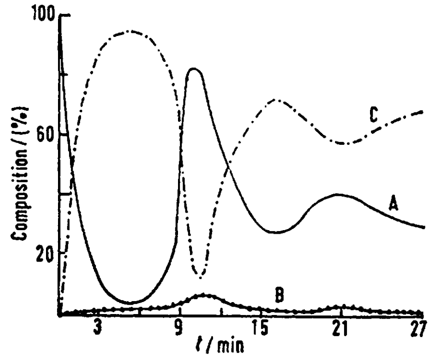

FIGURE 4 Isomerisation of *trans*-1,4-diphenylbut-2-ene by $HRhCl_2(PPh_3)_3$ and oxygen at 154 °C; A, B, and C as in Figure 1

Two other hydrides, *viz.*, $HRh(PPh_3)_3$ and $HIrCl_2(PPh_3)_3$ have been studied under similar conditions. They convert compound (II) at 154 °C into the equilibrium mixture of (II), (III), and (IV) (initial rates 200

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[22] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 1749.

and 3% min$^{-1}$, respectively), but do not cause oscillating reactions in the presence of oxygen.

## EXPERIMENTAL

The catalysts $RuCl_2(PPh_3)_3$,[23] $HRuCl(PPh_3)_3$,[5] $RhCl(PPh_3)_3$,[24] $HRhCl_2(PPh_3)_3$,[25] $HRh(PPh_3)_3$,[26] $IrCl(CO)(PPh_3)_2$,[7] $HIrCl_2(PPh_3)_3$,[27] and the phosphines $(p\text{-}ClC_6H_4)_3P$ [28] and $(p\text{-}FC_6H_4)_3P$ [29] were prepared essentially as described.

*Dichlorotris(triarylphosphine)ruthenium* (XVa—d).—A mixture of $RuCl_3,3H_2O$ (200 mg), triarylphosphine (5 mmol), and MeOH (60 ml) was refluxed under nitrogen for 3 h. Successive washing of the precipitate with EtOH and $Et_2O$ gave the pure catalysts in 66—98% yield. The analyses and physical properties are listed in Table 5.

trans-1,4-*Diphenylbut*-2-*ene* (II).—In a modification of Straus's method,[30] 2·5% sodium amalgam (390 g), 1,4-diphenylbutadiene (10 g), and absolute EtOH (600 ml) were stirred at room temperature for 36 h. The resulting yellow solid was recrystallised twice from MeOH to yield crystals (6·0 g; 60%), m.p. 41·5—43°. Further purification on a 2 m preparative g.l.c. column packed with 15% stabilised diethylene glycol succinate on Chromosorb W (60—80 mesh) at 210 °C afforded compound (II) as needles, m.p. 45·5—46·0° (lit.,[30] 45—45·5°); $\nu_{max.}$ (Nujol) 970 cm$^{-1}$ (*trans*-CH=CH); δ ($CCl_4$) 7·22 (10H, s), 5·74 (2H, m), and 3·42 p.p.m. (4H, m). The crystals were stored under argon in the refrigerator.

TABLE 5

Analyses and physical data for $[(p\text{-}XC_6H_4)_3P]_3RuCl_2$

| | | | | C/% | | H/% | | Cl/% | | P/% | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | X | M.p.(°C) | Colour | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. |
| $C_{63}H_{63}Cl_2P_3Ru$ | Me | 144—145 | Dark tan | 69·5 | 69·7 | 6·2 | 5·8 | 7·0 | 6·6 | 8·0 | 8·6 |
| $C_{63}H_{63}Cl_2O_9P_3Ru$ | OMe | 136—138 | Dark tan | 61·9 | 61·6 | 5·5 | 5·1 | 5·8 | 5·8 | 7·7 | 7·8 |
| $C_{54}H_{36}Cl_{11}P_3Ru$ | Cl | 161—173 | Light tan | 51·2 | 51·2 | 2·8 | 2·8 | | | 6·9 | 7·3 |
| $C_{54}H_{36}Cl_2F_9P_3Ru$ | F | 144—146 | Olive green | 58·0 | 57·8 | 3·6 | 3·2 | 6·4 | 6·3 | | |

The *cis*-isomer was obtained upon irradiation of (II) with a 450 W low-pressure mercury lamp for 5 h followed by separation by g.l.c.; δ ($CCl_4$) 7·10 (10H, s), 5·90 (2H, t, *J* 6 Hz) and 3·42 p.p.m. (4H, d, *J* 6 Hz).

trans-1-(p-*Tolyl*)-4-*phenylbut*-2-*ene* (IXa).—Sodium amalgam–ethanol reduction of *trans,trans*-1-(*p*-tolyl)-4-phenylbutadiene [31] (prepared by the Horner–Wittig reaction from *p*-methylbenzyl chloride and cinnamaldehyde) gave 65% of the butene (IXa) as an oil, b.p. 132—135°/0·6 mmHg. The analytical sample (which was used in the isomerisations) was obtained by preparative g.l.c. purification on the above column at 210°; $n_D^{25}$ 1·5752 (Found: C, 91·9; H, 8·1. $C_{17}H_{18}$ requires C, 91·9; H, 8·0%); $\nu_{max.}$ 975 cm$^{-1}$ (*trans*-CH=CH); δ 6·40 (5H, m), 6·25 (4H, m), 4·86 (2H, m), 2·55 (4H, m), and 1·55 p.p.m. (3H, s).

trans-1-(p-*Methoxyphenyl*)-4-*phenylbut*-2-*ene* (IXb).—As for (II), *trans,trans*-1-(*p*-methoxyphenyl)-4-phenylbutadiene [32] gave the *butene* (IXb) in 80% yield, b.p. 144—152°/5 mmHg. The g.l.c. purified sample is an oil, $n_D^{25}$ 1·5684 (Found: C, 85·5; H, 7·4. $C_{17}H_{18}O$ requires C, 85·8; H, 7·6%); $\nu_{max.}$ 970 and 975 cm$^{-1}$ (*trans*-CH=CH); δ 7·20 (5H, s), 6·90 (4H, g, *J* 8 Hz), 5·60 (2H, m), 3·70 (3H, s), and 3·31 p.p.m. (4H, m).

trans-1-(p-*Chlorophenyl*)-4-*phenylbut*-2-*ene* (IXc).—As for (II), *trans,trans*-1-(*p*-chlorophenyl)-4-phenylbutadiene [33] gave 67% of oily *butene* (IXc), b.p. 135—138°/0·3 mmHg; $n_D^{25}$ 1·5762 (Found: C, 79·5; H, 6·1; Cl, 14·4. $C_{16}H_{15}Cl$ requires C, 79·2; H, 6·2; Cl, 14·6%); $\nu_{max.}$ 975 cm$^{-1}$ (*trans*-CH=CH); δ 6·43 (9H, m), 4·90 (2H, m), and 2·60 p.p.m. (4H, m).

trans,trans-1-(p-*Cyanophenyl*)-4-*phenylbutadiene*.—A solution of *p*-cyanobenzyl chloride (13 g) in triethyl phosphite (14 g) was refluxed gently until evolution of ethyl chloride ceased (45 min). The mixture was cooled and transferred with agitation to a suspension of sodium methoxide (5 g) in dry dimethylformamide (100 ml). To the red solution was added freshly distilled cinnamaldehyde (11·2 g) with external cooling. The temperature was raised from 10 to 40 °C and then kept for 10 min at this level. Upon addition of methanol (40 ml) and water (200 ml) to the cooled mixture, a yellow solid precipitated. It was washed with water and ethanol to yield the diene (8·9 g; 46%); m.p. 168—171° (lit.,[34] 168—171°).

trans-1-(p-*Cyanophenyl*)-4-*phenylbut*-2-*ene* (IXd).—Aluminium amalgam [from aluminium foil (28 g) and 2% mercury(II) chloride solution (1·5 l)] and the foregoing diene (9 g) was covered with moist ether (2 l). The mixture was stirred vigorously at room temperature. When the evolution of hydrogen ceased, water was added dropwise and the stirring continued until all the aluminium dissolved. The ether solution was then concentrated and the oily residue was crystallised from methanol to yield the cyano-olefin (7·8 g; 78%), m.p. 44—46°. As in the case of (II), further purification was accomplished by g.l.c. (at 220 °C). The colourless *needles*, m.p. 54·5—55°, were stored under argon (Found: C, 87·3; H, 6·6. $C_{17}H_{15}N$ requires C, 87·4; H, 6·4%); $\nu_{max.}$ (Nujol) 980 (*trans*-CH=CH) and 2230 cm$^{-1}$ (C≡N); δ ($CCl_4$) 7·41 (4H, q, *J* 7·5 Hz), 7·20 (5H, s), 5·68 (2H, m), and 3·40 p.p.m. (4H, m).

Attempts to prepare (IXd) from the chloro-compound (IXc) and copper(I) cyanide in *N*-methylpyrrolidone gave unsatisfactory results.

[23] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[24] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[25] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc.* (*A*), 1966, 1670.

[26] B. Ilmaier and R. S. Nyholm, *Naturwiss.*, 1969, **56**, 636.

[27] L. Vaska, *J. Amer. Chem. Soc.*, 1961, **83**, 756.

[28] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710.

[29] R. Deketelaere, E. Maylle, W. Vanermer, and E. Claeys, *Bull. Soc. chim. belges*, 1969, **78**, 219.

[30] F. Straus, *Annalen*, 1905, **342**, 190.

[31] R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, 1959, **24**, 1969.

[32] P. L'Ecuyer and F. Turcotte, *Canad. J. Res.*, 1947, **25**, *B*, 575.

[33] R. Y. Hirshberg, E. D. Bergmann, and F. Bergmann, *J. Amer. Chem. Soc.*, 1950, **72**, 5120.

[34] Kodak, S.A., Belg.P. 641,415/1965 (*Chem. Abs.*, 1965, **63**, 3092*g*).

1,4-*Diphenylbutan*-1-*ol*.—This has been reported [35] as an oil. When 3-phenylpropylmagnesium chloride [from 3-chloropropylbenzene (11·6 g) and magnesium (1·8 g)] was reacted with freshly distilled benzaldehyde (8 g), the distilled product (b.p. 190°/1 mmHg) readily solidified to give *crystals* (15·5 g; 92%), m.p. 47° (from heptane) (Found: C, 85·0; H, 8·0. $C_{16}H_{18}O$ requires C, 85·0; H, 8·0%); $\nu_{max.}$ (KBr) 3260 cm$^{-1}$ (OH); δ ($CDCl_3$) 7·20 (10H, d), 4·55 (1H, m), 2·60 (2H, m), 1·98 (1H, m), and 1·66 p.p.m. (4H, m).

trans-1,4-*Diphenylbut*-1-*ene* (IV).—As the method of dehydration of the foregoing compound described by Kuhn and Winterstein [35] gave only the unchanged diphenylbutanol, the following three proceedures were applied to the preparation of (IV).

(*a*) 1,4-Diphenylbutanol (16·3 g) was heated at 280 °C for 30 min. Most of the water formed distilled off. The residue was dissolved in methylene dichloride, dried, and distilled at 165—167°/1 mmHg. Recrystallisation of the distillate from methanol afforded *needles* (3·0 g; 20%), m.p. 38° (lit.,[35] 42—42·5°). Analysis by a 2·5 m g.l.c. column packed as above indicated a purity of 99·9% and attempts to raise the m.p. were unsuccessful (Found: C, 92·25; H, 7·65. $C_{16}H_{16}$ requires C, 92·25; H, 7·75%); $\nu_{max.}$ (Nujol 976 cm$^{-1}$ (*trans*-CH=CH); δ ($CCl_4$) 7·25 (5H, s), 7·11 (5H, s), 6·29 (2H, m), and 2·65 p.p.m. (4H, m).

(*b*) The butanol (2·0 g) and aqueous sulphuric acid (60%) (5 ml) was heated at 70 °C for 30 min. After the usual work-up the oil was separated on a 1·5 m g.l.c. column packed with 20% Carbowax 20M on Chromosorb P at 190 °C to yield 23% *trans*-1,4-diphenylbut-1-ene (m.p. 38°) and 77% *trans*-1,4-diphenylbut-2-ene (m.p. 45·5—46°).

(*c*) To a stirred mixture of thionyl chloride (10·6 g) and dry pyridine (14·2 g) the butanol (20 g) was added in small portions. The mixture was refluxed for 20 min and decomposed with ice and hydrochloric acid. The resulting tan oil was flash-distilled at 1 mmHg to yield the chloride (12 g; 55%), which was then refluxed with pyridine (30 g) for 12 h. Distillation and purification by g.l.c. as above yielded (IV) (1 g, 10%); m.p. 38 °C.

trans-1-(p-*Tolyl*)-4-*phenylbut*-1-*ene* (XIa).—1-(*p*-Tolyl)-4-phenylbutan-1-ol (obtained in 92% yield from 3-phenylpropylmagnesium chloride and *p*-tolualdehyde) [$\nu_{max.}$ 3450 cm$^{-1}$ (OH)] was dehydrated by method (*a*) to give *compound* (XIa) (24%; 99·5% pure by g.l.c.), b.p. 150—153°/0·6 mmHg; $n_D^{25}$ 1·5768 (Found: C, 91·7; H, 8·0. $C_{17}H_{18}$ requires C, 91·9; H, 8·1%); $\lambda_{max.}$ (EtOH) (log ε) 256·5 (4·31), 288·5 (3·21), and 299 nm (3·02); $\nu_{max.}$ 970 cm$^{-1}$ (*trans*-CH=CH); δ ($CCl_4$) 7·15 (9H, s), 6·30 (2H, m), 2·68 (4H, m), and 2·30 p.p.m. (3H, s).

trans-1-(p-*Methoxyphenyl*)-4-*phenylbut*-1-*ene* (XIb).—1-(*p*-Methoxyphenyl)-4-phenylbutan-1-ol [obtained from 3-phenylpropylmagnesium chloride and *p*-anisaldehyde in 89% yield; b.p. 195°/0·5 mm Hg; $\nu_{max.}$ (Nujol) 3450 cm$^{-1}$ (OH)] was dehydrated by method (*a*). A maximum yield of 17% was obtained when the heating at 280 °C was stopped after 10 min giving *plates*, m.p. 55·6—56° (from ethanol) (Found: C, 85·7; H, 7·6. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%); $\lambda_{max.}$ (EtOH) (log ε) 262·5 (4·40), 297 (3·48), and 308 nm (3·25); $\nu_{max.}$ (Nujol) 965 and 978 cm$^{-1}$ (*trans*-CH=CH); δ ($CCl_4$) 7·17 (5H, s), 6·92 (4H, *J* 8 Hz), 6·18 (2H, m), 3·75 (3H, s), and 2·59 p.p.m. (4H, m). G.l.c. analysis indicated a purity of 99%.

trans-1-(p-*Chlorophenyl*)-4-*phenylbut*-1-*ene* (XIc).—Dehydration of the butanol (from 3-chloropropylbenzene and *p*-chlorobenzaldehyde) by method (*a*) (280°; 20 min) afforded (XIc) (18%), b.p. 175—177°/1 mmHg; *crystals*, m.p. 43° (from methanol) (Found: C, 79·0; H, 5·9; Cl, 14·2. $C_{16}H_{15}Cl$ requires C, 79·2; H, 6·2; Cl, 14·6%); $\lambda_{max.}$ (EtOH) (log ε) 260 (4·38), 292 (3·30), and 302 nm (3·05); $\nu_{max.}$ (Nujol) 965 cm$^{-1}$ (*trans*-CH=CH), δ ($CCl_4$) 7·30 (9H, m), 6·30 (2H, m), and 2·60 p.p.m. (4H, m).

trans-1-(p-*Cyanophenyl*)-4-*phenylbut*-1-*ene* (XId).—The yellow viscous butanol obtained from 3-phenylpropylmagnesium chloride and *p*-cyanobenzaldehyde [b.p. 200—205°/1 mmHg; $\nu_{max.}$ 2210 (C≡N) and 3400 cm$^{-1}$ (OH); δ ($CDCl_3$) 7·45 (9H, m), 4·75 (1H, m), 2·60 (2H, m), 2·10 (1H, s), and 1·65 p.p.m. (4H, m)] could not be dehydrated at 280 °C by method (*a*). Dehydration of the butanol (1 g) by method (*c*) yielded a dark tarry mixture from which the expected olefin (50 mg) was isolated by g.l.c. (4 m column, 15% stabilised diethylene glycol succinate on Chromosorb W at 220 °C) to give *crystals*, m.p. 59·5—60° (Found: C, 87·3; H, 6·4; N, 5·8. $C_{17}H_{15}N$ requires C, 87·4; H, 6·4; N, 6·0%); $\nu_{max.}$ (Nujol) 965 (*trans*-CH=CH) and 2205 cm$^{-1}$ (C≡N); δ ($CDCl_3$) 7·25 (9H, m), 8·36 (2H, m), 2·64 p.p.m. (4H, m).

2-*Methyl*-1,4-*diphenylbut*-2-*ene* (XVII).—2-Methyl-1,4-diphenylbutadiene [36] (obtained by the Horner–Wittig reaction in 54% yield from benzyl chloride and α-methylcinnamaldehyde) was reduced in 65% yield by the method described for (II). The mono-olefin, b.p. 192—194°/25 mmHg, proved to be 95% isomerically pure. Further purification was accomplished by g.l.c. on a 10 m × 6·4 mm column packed with diethylene glycol sebacate on Chromosorb W at 235 °C; $n_D^{25}$ 1·5656 (Found: C, 92·2; H, 8·4. $C_{17}H_{18}$ requires C, 91·9; H, 8·1%); δ ($CCl_4$) 7·19 (10H, s), 5·48 (1H, m), 3·35 (4H, m), and 1·61 p.p.m. (3H, s).

2-*Methyl*-1,4-*diphenylbut*-1-*ene* (XVIII).—1,4-Diphenylbutan-2-one [37] [obtained in 65% yield from phenacetyl chloride and the organocadmium derivative of β-phenethyl bromide; b.p. 155—156°/8 mmHg; $\nu_{max.}$ 1710 cm$^{-1}$ (C=O); δ ($CDCl_3$) 7·10 (10H, m), 3·47 (2H, s), and 2·67 p.p.m. (4H, q, *J* 5·8 Hz)] was treated with excess of methylmagnesium iodide. Dehydration of the butanol so formed with 98% formic acid has been reported [37] to give pure (XVIII). The product proved, however, to consist of equal amounts of 2-methyl-1,4-diphenylbut-2-ene (XVII) and 2-methyl-1,4-diphenylbut-1-ene (XVIII) together with 5% of 3-methyl-1,4-diphenylbut-1-ene (XIX). Pure (XVIII) was obtained by g.l.c. separation on a 10 m × 6·4 mm column packed with 15% stabilised diethylene glycol succinate on Chromosorb W as a colourless oil; $n_D^{25}$ 1·5644; δ ($CCl_4$) 7·20 (10H, s), 6·28 (1H, s), 2·67 (4H, m), and 1·90 p.p.m. (3H, s).

*General Procedure for the Isomerisation of Diarylbutenes*.—A reaction tube equipped with a capillary gas inlet was surrounded with the appropriate constant-boiling liquid and charged with the olefin (200 mg) to be isomerised. Argon or nitrogen was passed over the olefin and the temperature of the system was allowed to become homo-

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[35] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 1928, **11**, 116.

[36] T. M. Harris, S. Boatman, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1965, **87**, 3186.

[37] *Cf.* R. D. Haworth, C. R. Mavin, and G. Sheldrick, *J. Chem. Soc.*, 1934, 1423.

geneous and constant. After 30 min a $10^{-2}$ molar ratio of catalyst was dropped into the centre of the reaction tube. The dissolution of the catalyst was instantaneous and never needed more than 30 s. At intervals of 0·5—1 min during the first 10 min and at intervals of 2—40 min thereafter, 2—5 μl samples were withdrawn and frozen to await g.l.c. analysis. When the reaction was completed the components of the mixtures were separated on preparative columns and their structures established by i.r. and n.m.r. spectrometry.

*Dichloro*-[1-(p-*cyanophenyl*)-4-*phenylbut*-2-*ene*]*bis*(*triphenylphosphine*)*ruthenium* (XIII).—A mixture of $RuCl_2(PPh_3)_3$ (I) (200 mg), *trans*-1-(*p*-cyanophenyl)-4-phenylbut-2-ene (IXd) (1·0 g), and benzene (60 ml) was refluxed under argon. After 10 min the red-brown solution turned green and reflux was continued for 50 min. On concentration of the solution *in vacuo* to 5 ml and addition of light petroleum (b.p. 40—60°) (80 ml), yellowish green *crystals* (188 mg; 97%) were obtained; m.p. 149—150° (decomp.) (Found: C, 68·8; H, 5·2; N, 2·0; Cl, 7·4. $C_{53}H_{45}Cl_2NP_2Ru$ requires C, 68·5; H, 4·9; N, 1·5; Cl, 7·6%); $\nu_{max.}$ (Nujol) 975 (*trans*-CH=CH) and 2235 $cm^{-1}$ (C≡N); δ ($C_6D_6$) 8·2—5·8 (39H, m), 4·76 (2H, m), and 2·42 p.p.m. (4H, m); $g = 2{\cdot}44$.

*Dichlorodioxidobis*(*triphenylphosphine*)*ruthenium*.—A mixture of (I) (200 mg), benzene (50 ml), and of either *trans*-1-(*p*-tolyl)-4-phenylbut-2-ene (IXa) or the *p*-chlorophenyl derivative (IXb) (1·5 g) was refluxed under argon for 1 h. Concentration of the solution *in vacuo* to 4 ml. and addition of light petroleum (75 ml) afforded *ca.* 100 mg of greyish blue *crystals*, m.p. 132—134°; $\nu_{max.}$ (Nujol) 1970vs, 2020w, 2035w, and 2060w $cm^{-1}$ (Ru–H). The elemental analysis was close to that required for $HRuCl_2(PPh_3)_2$, but owing to its sensitivity to air no analytically pure sample could be isolated. On exposure to air the complex turns readily into $RuCl_2(PPh_3)_2(O_2)$, $\nu_{max.}$ (Nujol) 860 $cm^{-1}$ (O–O); no band between 1950 and 2100 $cm^{-1}$; $g = 2{\cdot}55$ (Found: C, 59·4; H, 4·2; P, 8·2. $C_{36}H_{30}Cl_2O_2P_2Ru$ requires C, 59·3; H, 4·1; P, 8·5%).

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