# The Reactions of σ,η³-Butadienylruthenium Complexes with Donor Ligands and Protons: Structures of [RuC(Ph)=C(Ph)-η²-{(*Z*)-C(Ph)=CH(Ph)}{P(OMe)$_3$}(η-C$_5$H$_5$)] and [RuC(O)C(Ph)=C(Ph)-η²-{(*Z*)-C(Ph)=CH(Ph)}{P(OMe)$_3$}(η-C$_5$H$_5$)]

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σ,η³(5e)-Butadienylruthenium complexes behave as masked σ,η²(3e)-butadienyl complexes in their reactions with P(OMe)$_3$ and PhC$_2$Ph, whereas, protons react on the 'inside' of the σ,η³-butadienyl chain at the α-carbenoid carbon; attempts to expel P(OMe)$_3$ thermally from the resulting σ,η²(3e)-butadienyl complexes results instead in a zeta-H abstraction reaction.

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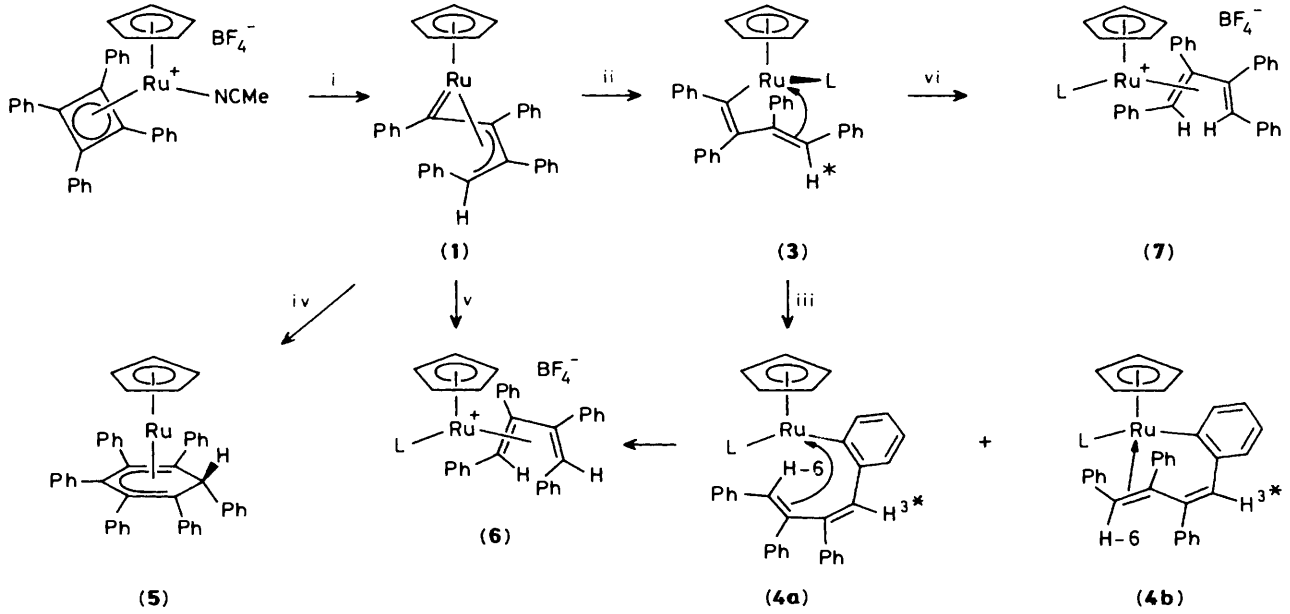
Recently[1] we described a study of ring-opening reactions of cationic η⁴-cyclobutadiene complexes, which led to the characterisation of the first examples[2] of σ,η³(5e)-butadienyl complexes [Ru=C(Ph)-η³-{C(Ph)C(Ph)CH(Ph)}(η-C$_5$H$_5$)] (**1**) and [Ru=C(Ph)-η³-{C(Ph)C(Ph)C(Ph)CHO}(η-C$_5$H$_5$)] (**2**). Not only are these molecules interesting from a bonding viewpoint, but they are also potentially reactive. This reactivity might be expected to be associated with the metal-to-carbon multiple bond. In addition the possibility that these species could behave as masked or latent co-ordinatively



**Scheme 1.** L = P(OMe)$_3$. *Reagents:* i, K[BHBu$^s_3$]; ii, +L; iii, heat; iv, + excess of PhC$_2$Ph; v, + [HP(OMe)$_3$][BF$_4$]; vi, HBF$_4$·Et$_2$O.

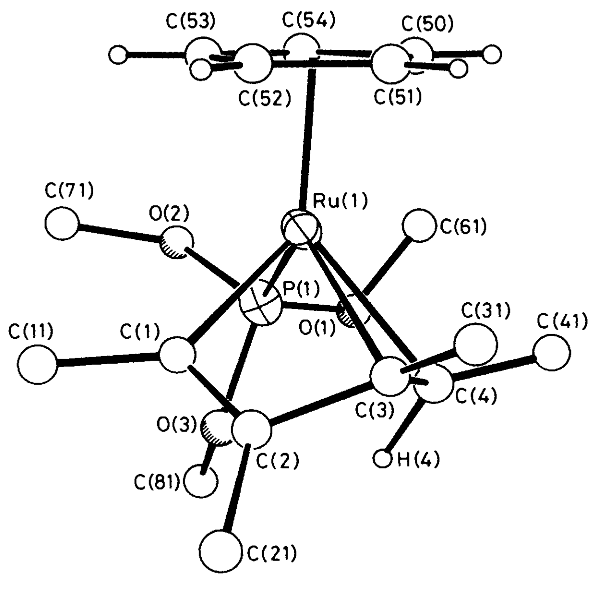
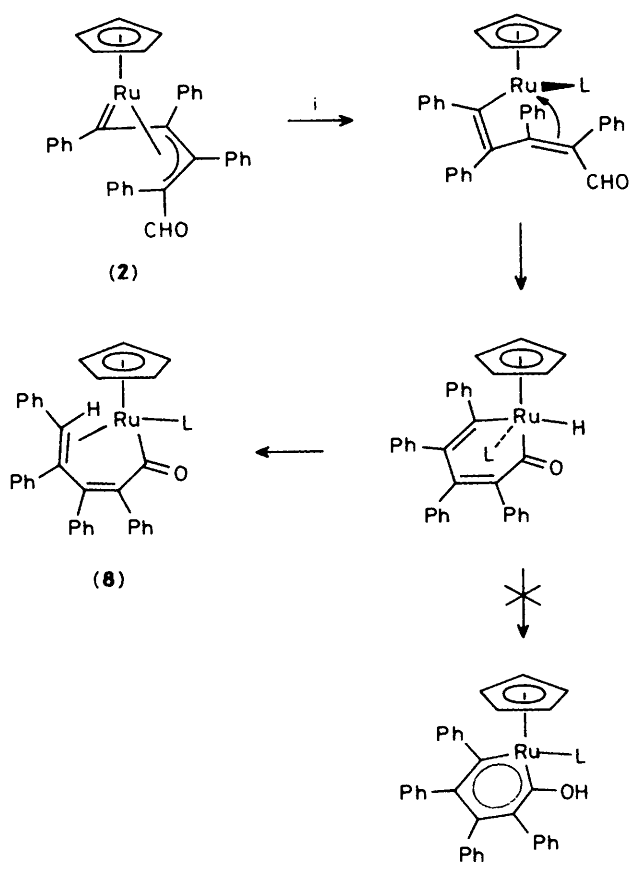


**Figure 1.** Molecular structure of one molecule of (3). For clarity only the *ipso*-carbons of phenyl groups are shown and methyl hydrogens have been omitted. Important geometric parameters, averaged over the two molecules, include; bond lengths (Å): Ru(1)–P(1) 2.220(2), Ru(1)–C(1) 2.070(7), Ru(1)–C(3) 2.248(7), Ru(1)–C(4) 2.253(7), C(1)–C(2) 1.330(9), C(2)–C(3) 1.509(9), C(3)–C(4) 1.418(10); torsion angles (°), C(1)–C(2)–C(3)–C(4) −67.1(8), C(31)–C(3)–C(4)–H(4) 146(4).



**Scheme 2.** L = P(OMe)$_3$. *Reagent:* i, + L.

unsaturated σ,η$^2$(3e)-butadienyl complexes has implication for catalysis. In this paper we report our initial observations.

Addition (room temperature, $CH_2Cl_2$) of the simple donor ligand P(OMe)$_3$ to the purple complex (**1**) resulted in a rapid reaction and the formation of the orange crystalline 1:1 adduct (**3**). Notably absent from the $^{13}$C n.m.r. spectrum† of the adduct was any signal at low field, implying that (**3**) no longer contained the ruthenium-to-carbon double bond which is present in the precursor (**1**).

A single crystal *X*-ray study revealed‡ (Figure 1) that molecules of (**3**) in the solid state consist of a ruthenium atom co-ordinated by η-$C_5H_5$, P(OMe)$_3$, and σ,η$^2$-butadienyl ligands. The butadienyl ligand is co-ordinated to the metal *via* a σ-bond [Ru(1)–C(1) 2.070(7) Å] and a π-olefin bond [Ru(1)–C(3) 2.248(7), Ru(1)–C(4) 2.253(7) Å]. Thus, in this reaction the butadienyl chain modifies its bonding mode [σ,η$^3$(5e) to σ,η$^2$(3e)] providing a co-ordination site for the interacting two electron donor trimethylphosphite. Of added interest is the change in stereochemistry of the CH(Ph) group accompanying the transformation (**1**) to (**3**). Whereas, in the precursor (**1**) the hydrogen substituent occupies a pseudo-*syn*-position, the structure determination of (**3**) shows this stereochemistry to be reversed, with the hydrogen now in the pseudo-*anti*-position, and the phenyl substituent in the pseudo-*syn*-site. This apparent stereomutation reaction is unusual and may be related to the isomerisation of butadienyldithiocarbamatepalladium complexes reported by Maitlis and Taylor[3] and interpreted in terms of a ring-flip process.

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† *Selected spectroscopic data* for compound (**3**): n.m.r. $^1$H ($C_6D_6$), δ 4.22 [d, 1 H, C*H*Ph, *J*(PH) 9.5 Hz]; $^{13}$C{$^1$H}, δ 68.4 [d, *C*HPh, *J*(PC) 7.4 Hz]. Compound (**4a**): n.m.r. $^1$H ($CD_2Cl_2$), δ 6.18 (s, H-3), 4.64 [d, 5H, $C_5H_5$, *J*(HP) 0.98 Hz], 4.31 [d, H-6, *J*(HP) 10.0 Hz], 3.52 [d, 9H, POMe, *J*(HP) 11.0 Hz]. Compound (**4b**): n.m.r. $^1$H ($CD_2Cl_2$), δ 6.37 (s, H-3), 4.58 [d, 5H, $C_5H_5$, *J*(HP) 1.22 Hz], 4.20 [d, H-6, *J*(HP) 11.2 Hz], 3.32 [d, 9H, POMe, *J*(HP) 10.7 Hz]. Compound (**5**): n.m.r. $^1$H ($CDCl_3$), δ 7.56—6.82 (m, 30H, Ph), 4.98 (s, 5H, $C_5H_5$), 4.89 (s, 1H, C*H*Ph). Compound (**6**): n.m.r. $^1$H ([$^2H_6$]acetone), δ 7.36—6.88 (m, 20H, Ph), 5.82 (s, 5H, $C_5H_5$), 5.66 [d, 1H, $H_{syn}$, *J*(PH) 1.4 Hz], 3.76 [d, 1H, $H_{anti}$, *J*(PH) 15.1 Hz], 3.54 [d, 9H, POMe, *J*(PH) 11.5 Hz]; $^{13}$C{$^1$H} ($CD_2Cl_2$), δ 70.3 [d, *C*HPh, *J*(PC) 6.1 Hz], 60.3 [d, *C*HPh, *J*(PC) 4.5 Hz]. Compound (**7**): n.m.r. $^1$H ([$^2H_6$]acetone), δ 7.12 (m, 20H, Ph), 5.85 (s, 5H, $C_5H_5$), 3.79 [d, 9H, POMe, *J*(PH) 11.5 Hz], 2.87 [d, 2H, C*H*Ph, *J*(PH) 16.3 Hz]; $^{13}$C{$^1$H} ([$^2H_6$]acetone), δ 68.8 [d, *C*HPh, *J*(PC) 7.7 Hz]. Compound (**8**): $\nu_{CO}$ 1598w cm$^{-1}$ ($CH_2Cl_2$).

‡ *Crystal data* for (**3**): $C_{36}H_{35}O_3PRu$, *M* = 647.7, monoclinic, space group *Cc* (No. 9), *a* = 18.226(6), *b* = 12.190(4), *c* = 27.447(15) Å, β = 94.31(4)°, *U* = 6080(4) Å$^3$, *T* = 293 K, *Z* = 8, $D_c$ = 1.42 g cm$^{-3}$, *F*(000) = 2972, graphite monochromated Mo-$K_\alpha$ *X*-radiation, λ = 0.71069 Å, μ(Mo-$K_\alpha$) = 5.9 cm$^{-1}$. For (**8**): $C_{37}H_{35}O_4PRu$, *M* = 675.6, monoclinic, space group $P2_1/c$ (No. 14), *a* = 10.627(6), *b* = 21.198(12), *c* = 14.448(6) Å, β = 103.03(4)°, *U* = 3171(3) Å$^3$, *T* = 293 K, *Z* = 4, $D_c$ = 1.42 g cm$^{-3}$, *F*(000) = 1392, graphite monochromated, Mo-$K_\alpha$ *X*-radiation, λ = 0.71069 Å, μ(Mo-$K_\alpha$) = 5.7 cm$^{-1}$.

*X*-Ray intensity data were collected at room-temperature on a Nicolet P3m diffractometer for unique quadrants of reciprocal space in the range $4 < 2\theta < 50°$. All atoms, including hydrogens, were included in the refined model, with phenyl, cyclopentadienyl, and methyl group C–H lengths fixed at 0.96 Å. In both structures phenyl $C_6$ rings were constrained to $D_{6h}$ symmetry with C–C = 1.359 Å, and for (**3**) the cyclopentadienyl $C_5$ ring to $D_{5h}$ with C–C = 1.420 Å. Final residuals were 0.042 and 0.084 for 5066 and 2472 unique, absorption corrected, observed [$I > 2\sigma(I)$ and $> 1.5\sigma(I)$] for (**3**) and (**8**) respectively. In the structure of (**3**) there are two crystallographically distinct molecules which have very similar geometries differing only in phenyl ring orientations.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

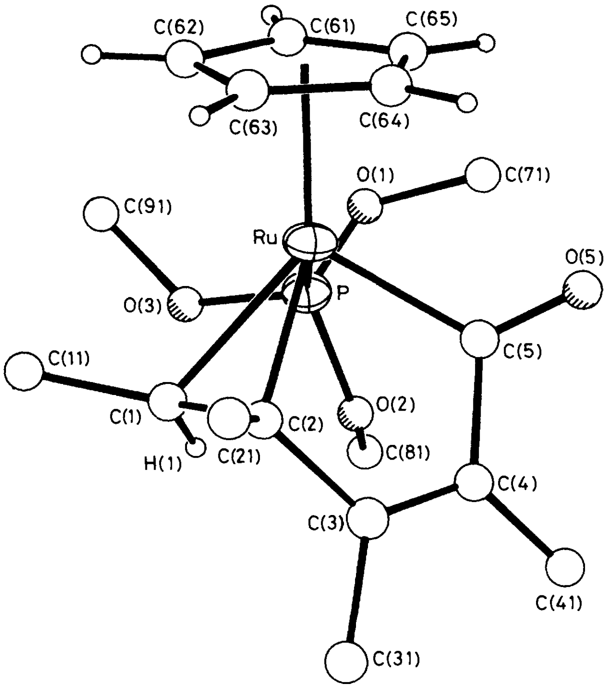

**Figure 2.** Molecular structure of (**8**). For clarity only the *ipso*-carbons of phenyl groups are shown and methyl hydrogens have been omitted. Important geometric parameters include; bond lengths (Å): Ru–P 2.240(4), Ru–C(1) 2.215(9), Ru–C(2) 2.183(11), Ru–C(5) 2.040(12), C(1)–C(2) 1.429(17), C(2)–C(3) 1.494(17), C(3)–C(4) 1.340(16), C(4)–C(5) 1.515(15), C(5)–O(5) 1.213(13); torsion angles (°) C(1)–C(2)–C(3)–C(4) 85.6(13), C(2)–C(3)–C(4)–C(5) 9.3(15).

It was clearly important to examine whether the transformation of (**1**) to (**3**) could be reversed by thermal expulsion of $P(OMe)_3$, because if this was successful it would have implications for the synthesis of other $\sigma,\eta^3$(5e)-butadienyl species. However, in the event a new reaction intervened. In toluene or tetrahydrofuran (thf) at 80 °C (**3**) smoothly isomerised into an $\sigma,\eta^2$-hexatrienyl complex, isolated as a non-equilibrating (at 80 °C) mixture of conformational isomers (**4a**) and (**4b**) (2 : 1 in toluene, 1 : 1 in thf) and identified by analysis, and mass and n.m.r. spectroscopy.† Two observations were made which relate to the mechanism of this reaction. Firstly, dissociative loss of $P(OMe)_3$ from (**3**) does not occur as is evidenced by the absence of exchange with $P(OCD_3)_3$. Secondly, reaction of $K[BDEt_3]$ with $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ followed by addition of $P(OMe)_3$ gave (**3**) deuteriated in the $\eta$-$C_5H_5$ ring and in the C*H*Ph positions in the ratio of 6 : 1. Thermolysis (80 °C) of this deuterium substituted material gave (**4a**) and (**4b**) with deuterium incorporation only in the $C_5H_5$ ring and in the H-3 (starred) position (Scheme 1) of the $\sigma,\eta^3$-hexatrienyl chain. This implies that the butadienyl chain in (**3**) lifts off ($\sigma,\eta^2$ to $\sigma$) the ruthenium leading to a novel zeta-hydrogen abstraction reaction from the end phenyl group followed by hydrogen transfer to the original α-carbon of the butadienyl chain, *i.e.* a metal assisted 1,6-H shift.

Returning to the question of the latent unsaturation of $\sigma,\eta^3$(5e) butadienyl complexes it is interesting that addition of an excess of diphenylacetylene to a solution (thf, 60 °C) of (**1**) led to the catalytic formation of hexaphenylbenzene and the formation of the *endo*-substituted cyclohexadienyl complex (**5**).† It is likely that the initial step in this reaction involves a switch in the bonding mode of the butadienyl ligand thus accommodating the incoming alkyne.

Protons also react with (**1**), but at the α-carbenoid carbon atom. Although direct addition of $HBF_4{\cdot}Et_2O$ to (**1**) led to decomposition, protonation with $[HP(OMe)_3][BF_4]$ [formed by addition of $HBF_4{\cdot}Et_2O$ to $P(OMe)_3$ in $CH_2Cl_2$ at −78 °C] afforded the unsymmetrically substituted (*E,Z*)-1,3-diene cation (**6**) with apparent retention of configuration on the C-4 carbon and placement of the incoming proton on the 'inside' of the $\sigma,\eta^3$-butadienyl chain. The isomeric symmetrically substituted (*Z,Z*)-1,3-diene cation (**7**) was formed on addition of $HBF_4{\cdot}Et_2O$ (−78 °C, $CH_2Cl_2$) to (**3**). Interestingly, the cation (**6**) was also formed on addition (−78 °C, $CH_2Cl_2$) of $HBF_4{\cdot}Et_2O$ to the mixture of (**4a**) and (**4b**) presumably *via* protolysis of the σ-phenyl bond.[4] Evidently the s-*trans*-$\eta^4$-1,3-diene cation obtained from (**4b**) is unstable and isomerises to the s-*cis*-$\eta^4$-bonded cation providing a contrast with recent observations in zirconium[5,6,7] and hafnium[8] chemistry.

Finally, in attempting to observe a phosphite promoted $\sigma,\eta^3$(5e) to $\sigma,\eta^2$(3e) transformation of the formyl substituted $\sigma,\eta^3$-butadienyl complex (**2**) an unusual 1,5-H shift process intervened. Reaction (room temperature, 6 days, $CH_2Cl_2$) again afforded a 1 : 1 adduct (**8**) (Scheme 2), however, examination of the i.r.† and $^{13}C$-off-resonance spectra showed that (**8**) did not contain a formyl group, and an *X*-ray diffraction study‡ (Figure 2) showed that (**8**) is a $\sigma,\eta^2$-bonded acylbutadienyl complex. It is likely that this reaction involves initial co-ordination of $P(OMe)_3$ onto (**2**) with stereomutation at C-4. This places the CHO group in a pseudo-*anti*-position adjacent to the ruthenium such that an oxidative-addition reaction [$Ru^{II}$ to $Ru^{IV}$] of the formyl hydrogen followed by reductive elimination affords (**8**). It is interesting that in this process the postulated hydrido-acyl species does not collapse to a ruthenabenzene.

We thank the S.E.R.C. for support and for studentships (L. B., M. C., and K. R. N.).

*Received, 21st April 1986; Com. 537*

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Typeset and printed by Heffers Printers Ltd, Cambridge, England