

Novel Regioselection in Insertion of a 1,4-Disubstituted-1,3-enyne into Ruthenium-Hydrogen Bonds

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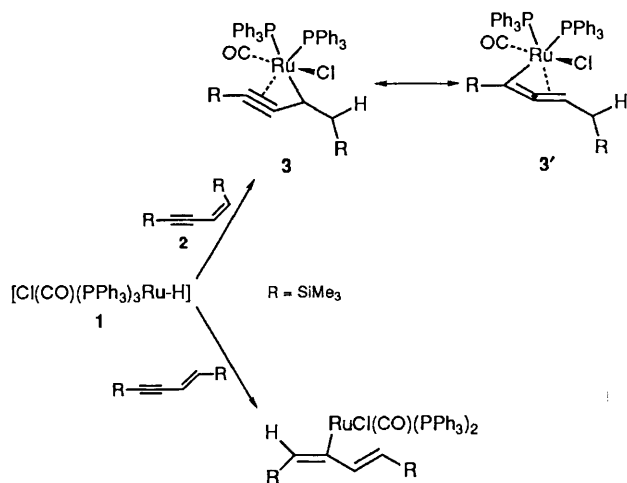
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The reaction of a conjugated enyne, *cis*-(Me₃Si)CH=CHC≡CSiMe₃, with [RuCl(CO)H(PPh₃)₃] gives a quantitative yield of a stable complex whose molecular structure is formally regarded as the result of either 1,2-addition of the H-Ru to the double bond or 1,4-addition of the H-Ru to the conjugated enyne; the former bonding scheme operates when the enyne is hydrogenated by [Ru(CO)H₂(PPh₃)₃] or [RuH₂(PPh₃)₄], the sole product being Me₃SiCH₂CH₂C≡CSiMe₃.

The partial hydrogenation of alkynes to alkenes has been realized by many heterogeneous systems,¹ *e.g.* the Lindlar catalyst (Pd/BaSO₄), and several homogeneous catalysts such as (arene)tricarbonylchromium,² and cationic Rh^I or Fe^{II} complexes.³ The hydrogenation of conjugated enynes by

homogeneous Pd^{II} has been demonstrated to give conjugated dienes in good yields,⁴ suggesting that triple bonds are more reactive than double bonds. The high selectivity observed for the hydrogenation of phenylacetylene to styrene by [OsCl(CO)H(PR₃)₂]-H₂ has been attributed to the thermodynamic



Scheme 1 Complex 4 is the (*p*-MeOC₆H₄)₃P analogue of 3

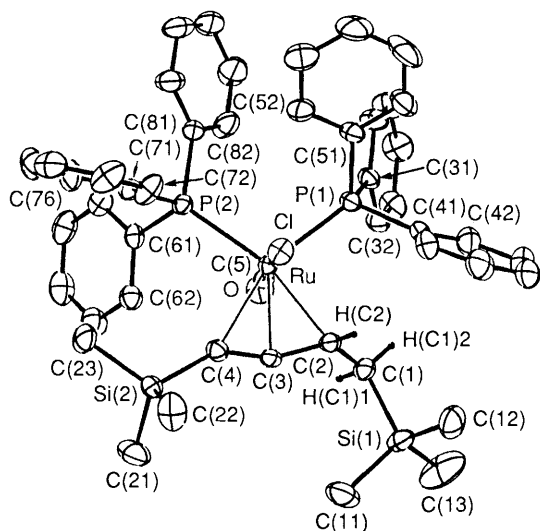
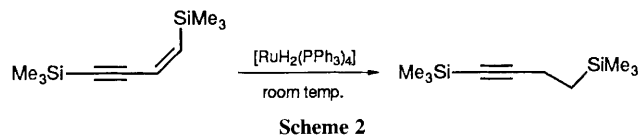


Fig. 1 ORTEP drawing of complex 3. Selected bond distances (Å) and angles (°) are: Ru–C(2) 2.282(5), Ru–C(3) 2.192(5), Ru–C(4) 2.366(5), C(1)–C(2) 1.503(7), C(2)–C(3) 1.398(7), C(3)–C(4) 1.250(7), C(1)–Si(1) 1.890(6), C(4)–Si(2) 1.858(6), P(1)–Ru–C(2) 90.2(1), P(2)–Ru–C(4) 96.8(1), C(1)–C(2)–C(3) 121.4(5), C(2)–C(3)–C(4) 157.1(5), C(2)–C(1)–Si(1) 111.1(4), C(3)–C(4)–Si(2) 141.1(5).

stability of the metal–vinyl intermediate over the metal–alkyl species.⁵ The reaction of an analogous ruthenium complex, [RuCl(CO)H(PPh₃)₃] **1**, with mono- and di-substituted alkynes is known to give stable alkenyl complexes of the type [RuCl(CO)(R'C=CHR)(PPh₃)₂].⁶ Insertion products with simple alkenes, on the other hand, are thermally unstable, because β-hydrogen elimination takes place readily from alkyruthenium complexes.

The reaction of excess of *cis*-(R)CH=CH–C≡C–R **2** (R = SiMe₃) with **1** takes place in tetrahydrofuran (thf) smoothly at room temperature to give orange crystals of **3**,[†] of the composition [RuCl(CO)(H·RCHCHC₂R)(PPh₃)₂] in almost

[†] Complex **3**: m.p. 157–159 °C (decomp.), ¹H NMR (C₆D₆) δ 3.84 (dt, 1H, *J*_{HH} 4 and 13, *J*_{HP} 4 Hz), 1.48 (td, 1H, *J*_{HH} = *J*_{HH} = 13, *J*_{HP} 1.7 Hz), 1.26 (dt, 1H, *J*_{HH} 4 and 13, *J*_{HP} 4 Hz), 0.23 (s, 9H) and 0.04 (s, 9H). Satisfactory C and H analyses were obtained for **3**.



Scheme 2

quantitative yield (Scheme 1). The ¹H NMR spectrum of complex **3** shows two of the three protons of the C₄ chain in the aliphatic region, δ 1.48 and 1.26. That these two protons are attached to the same carbon atom forming a CH₂ group is further confirmed by a 2-D ¹³C–¹H shift correlation NMR spectrum of the P(*p*-MeOC₆H₄)₃ analogue, [RuCl(CO)(H·RCHCHC₂R){P(*p*-MeOC₆H₄)₃}₂] **4** (R = SiMe₃).[‡]

An X-ray structure analysis of **3**[§] revealed that the C₄ skeleton lies approximately in the Ru–P–P plane. Three of the carbon atoms interact with the metal [η^3 -coordination to C(2)–C(3)–C(4)] while the fourth carbon is a CH₂ group. Thus Ru–C(2)–C(3)–C(4) are essentially coplanar, with Ru–C(2) 2.282(5), Ru–C(3) 2.192(5) and Ru–C(4) 2.366(5) Å and a C(2)–C(3)–C(4) angle of 157.1(5)°. The structure may be viewed as a combination of resonance forms **3** and **3'**, but the bonding scheme **3** appears to be more important in an analogous reaction (Scheme 2); when an excess of **2** was treated with [RuH₂(CO)(PPh₃)₃] or [RuH₂(PPh₃)₄], the only product observed was Me₃SiCH₂CH₂C≡CSiMe₃.[¶] To the best of our knowledge, the preferential reduction of the double bond in enynes, leading to alkynes, has not been reported, probably because only *trans*-enynes have been employed. Complexes with the ' η^3 -propynyl' type coordination are also rare and there are only two precedents: [Os(η^3 -PhC₃CHPh)(PMe₃)₄]PF₆ and [Ru(CCPh)(η^3 -PhC₃CHPh)(cyttp)] [cyttp = C₆H₅P{(CH₂)₃P(c-C₆H₁₁)₂}₂], both of which have been synthesized using a coupling reaction of phenylacetylene.^{7,8}

Coordination of the triple bond in **3** appears to be maintained in solution, which should make the complex rather stable. Although it has aliphatic β-hydrogens, decomposition of **3** in benzene is negligible after 10 hours at room temperature. Moreover, the very different ¹H NMR coupling of the methylene protons H(C1)1 and H(C1)2 (Fig. 1) with H(C2) and the P atoms suggests that rotation of the Ru–C(2) and C(1)–C(2) bonds is quite restricted.

In contrast to the unexpected regioselectivity of **2** described above, a similar reaction of *trans*-(R)CH=CHC≡CR (R = SiMe₃) with **1** yielded the conventional product where the Ru–H had added to the triple bond of the enyne.⁹ Isomerization between this complex and **3** is not observed.

[‡] Solubility of the complex was improved by use of P(*p*-MeOC₆H₄)₃ so that the complex could be characterized by ¹³C NMR spectroscopy. Complex **4**: m.p. 100–103 °C (decomp.), ¹³C NMR (CDCl₃) δ 112.03 (–C≡), 59.39 (CH–Ru), 59.05 (≡C–Si), 21.28 (–CH₂–), 1.639 (Si–CH₃) and –1.943 (Si–CH₃). The ¹H NMR spectrum of **4** is similar to that of **3**.

[§] Crystal data for **3** (CH₂Cl₂ solvate): *M* = 971.5, orthorhombic, space group *Pbca*, *a* = 25.846(4), *b* = 20.379(3), *c* = 18.271(2) Å, *U* = 9623.7 Å³, *Z* = 8, *D*_c = 1.34 g cm^{–3}, 12 079 reflections measured for 2.0 < θ < 27.5°, final residual *R* = 0.062 for 9303 observed reflections (*F* > 3.0σ_F). All data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). The structure was solved by direct methods (MULTAN) and refined by block-diagonal least squares. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[¶] ¹H NMR (C₆D₆): δ 2.17 (t, 2H, *J* 7.7 Hz), 0.69 (t, 2H, *J* 7.7 Hz), 0.23 (s, 9H) and –0.04 (s, 9H); ¹³C NMR (C₆D₆) δ 109.97 (–C≡), 83.90 (–C≡), 15.94 (–CH₂–), 14.77 (–CH₂–), 0.28 (Si–CH₃) and –1.62 (Si–CH₃); GCMS, *m/z* 198 (M⁺).

We thank Dr J. Uzawa for measurement and discussion of the NMR spectra.

Received, 7th November 1990; Com. 0105013J

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