Irreversible Rearrangement of Half-sandwich Ruthenium Hydrido-alkynyl Complexes to their Vinylidene Isomers

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The complex [(C$_5$Me$_5$)RuCl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with alk-1-ynes in MeOH in the presence of NaBPh$_4$ yielding the metastable hydrido-alkynyl derivatives [(C$_5$Me$_5$)Ru(H)(C≡CR)(dippe)][BPh$_4$] (R = CO$_2$Me, SiMe$_3$ or Ph), intermediates in the formation of the corresponding vinylidene complexes, to which these compounds rearrange both in solution and in the solid state.

The rearrangement of free acetylene to its vinylidene isomer is a thermodynamically disfavoured process, although it becomes thermodynamically favourable on complexation to a metal fragment.[1] Several possible mechanisms for this conversion have been proposed. One of them involves insertion of the metal into the C–H bond of the acetylene, followed by hydride migration to the β-carbon. Several examples in Rh and Ir chemistry, in which this sort of mechanism operates, are known.[2] However, in the case of ruthenium, this mechanism has been found by extended Hückel calculations to be energetically too costly to occur to an appreciable extent.[3] No stable hydrido-alkynylruthenium complexes that rearrange to vinylidene species have been described.

We now report that the product of the reaction of [(C$_5$Me$_5$)-RuCl(dippe)][4] with alk-1-ynes and NaBPh$_4$ in MeOH is sensitive to the order in which the reagents are added. If a solution of [(C$_5$Me$_5$)RuCl(dippe)] in MeOH is trated with alk-1-yne, and then with NaBPh$_4$, the vinylidene complexes [(C$_5$Me$_5$)Ru=C=CHR(dippe)][BPh$_4$] (R = CO$_2$Me 1, SiMe$_3$ 2 or Ph 3 are formed).† However, if NaBPh$_4$ is added first, followed by the alk-1-yne, then the corresponding hydrido-alkynyl derivative [(C$_5$Me$_5$)Ru(H)(C≡CR)(dippe)][BPh$_4$] (R = CO$_2$Me 4, SiMe$_3$ 5 or Ph 6)† precipitates from the reaction mixture as a white microcrystalline material. Complexes 4–6 are formally derived from the insertion of the metal atom into the C–H bond of the alk-1-yne, and, therefore, must be considered Ru^{IV} species. They display one strong ν(C≡C) band in their IR spectra (Nujol). These compounds rearrange to their corresponding vinylidene isomers 1–3 when they are dissolved in acetone or CH$_2$Cl$_2$ at room temp. The isomerization in solution can be 'frozen' by dissolving the complexes at < −50 °C. In this fashion, it is possible to observe the signals corresponding to the hydride species. The hydride resonances appear as one high-field triplet in all cases, whereas the ^{31}P{^{1}H} NMR spectra consist of one sharp singlet. These data are consistent with a transoid structure for the complexes 4–6, as shown in Scheme 1. When the temperature is raised, the NMR

signals corresponding to [(C$_5$Me$_5$)Ru(H)[C≡CR)(dippe)]$^+$ decrease, whereas the signals of the vinylidene species increase their intensity. For 4, conversion is complete at 0 °C, but the process is lower for 5 and 6. It has been possible to evaluate the kinetic parameters for the rearrangement of 5 to 2. The process is first order, having a constant k = (1.9 ± 0.1) × 10^{-2} s^{-1} at 20 °C. From the study at different temperatures an activation energy of 92 ± 7 kJ mol^{-1} was obtained, a value very similar to that found for the rearrangement of [(C$_5$H$_5$)Ru(η^2-HC≡CR)(PMe$_3$)$_2$]$^+$ to [(C$_5$H$_5$)Ru=C=CHR-(PMe$_3$)$_2$]$^+$ in MeCN (97 ± 1 kJ mol^{-1}).[5] Furthermore, the participation of an hydrido-alkynyl complex of the type [(C$_5$H$_5$)Ru(H)(C≡CR)(PMe$_3$)$_2$]$^+$ as intermediate in the rearrangement process was found possible, but it was not demonstrated. Another recent example of rearrangement of a η^2-alkyne adduct to a metal–vinylidene can be found for the complex [(C$_5$H$_5$)Ru(η^2-HC≡CH)(PMe$_2$Ph)$_2$][BF$_4$], which rearranges to its vinylidene isomer [(C$_5$H$_5$)Ru=C=CH$_2$(PMe$_2$-Ph)$_2$][BF$_4$] above 60 °C in acetone.[6] In our case, there is no evidence for the formation of a η^2-alkyne adduct as previous step to the oxidative addition of the alkyne, although we have isolated and characterized other ruthenium η^2-alkyne derivatives such as [(C$_5$H$_5$)Ru(MeO$_2$CC≡CCO$_2$Me)(dippe)][BPh$_4$],[7] so this possibility cannot be completely ruled out. The isomerization to vinylidene occurs not only in solution, but also in the solid state at room temperature for 5 and 6. Compound 4 seems to be stable as a solid at room temperature. Thus, the ν(C≡C) IR band (Nujol) disappears over a period of 2–3 h, being replaced by the strong ν(C=C) band of the vinylidene ligand, at *ca.* 1600 cm^{-1}. There is a recent precedent for this behaviour in the rhodium complex [RhCl(H)(C≡CSiMe$_3$)-(PPr$^i_3$)$_2$],[8] which rearranges smoothly to [Rh=C=CHSi-Me$_3$(Cl)(PPr$^i_3$)$_2$] both in solution and in the solid state. No hydro-alkynyl complexes have been isolated or detected in the reaction of the cyclopentadienyl complex [(C$_5$H$_5$)RuCl-(dippe)][4] with alk-1-ynes, and only the vinylidene species [(C$_5$H$_5$)Ru=C=CHR(dippe)][BPh$_4$] are observed. If cyclopentadienyl hydrido-alkynyl complexes analogous to 4–6 are involved in these processes, they must be short-lived species that rearrange at room temperature to the corresponding vinylidene species before precipitation as the tetraphenylborate salt occurs. However, from our study it is clear that ruthenium hydrido-alkynyl complexes are feasible intermediates in the transition metal-promoted isomerization of alk-1-ynes to vinylidene complexes.
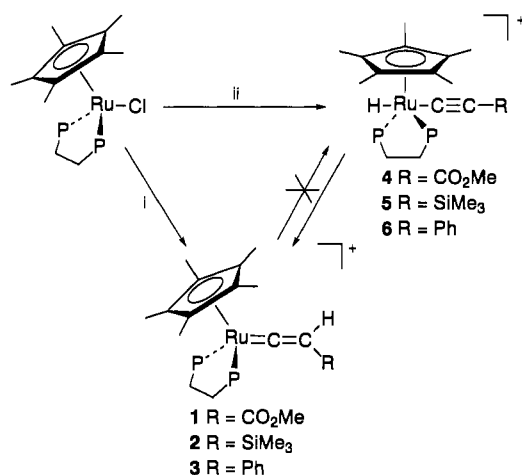
Scheme 1 *Reagents*: i, HC≡CR then Na[BPh$_4$], MeOH; ii, Na[BPh$_4$] then HC≡CR, MeOH

Footnote

† *Selected spectra data* for **1**: IR (Nujol) ν(C=C) 1588, ν(CO) 1689 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.822 [t, J_{HP} 1.2 Hz, C$_5$(CH_3)$_5$], 3.640 (s, CO$_2$CH_3),

4.502 (t br, J_{HP} ca. 8 Hz, Ru=C=CHCO$_2$Me); ^{31}P{^{1}H} NMR δ 75.3(s). For **2**: IR (Nujol) v(C=C) 1604 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.140 [s, Si(CH$_3$)$_3$], 1.813 [t, J_{HP} 2 Hz, C$_5$(CH$_3$)$_5$], 3.158 (t, J_{HP} 12 Hz, Ru=C=CHSiMe$_3$); ^{31}P{^{1}H} NMR δ 81.8 (s). For **3**: IR (Nujol) v(C=C) 1595 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.878 [s, C$_5$(CH$_3$)$_5$], 4.861 (br, Ru=C=CHPh), 7.124, 7.252 (m, C$_6$H$_5$); ^{31}P{^{1}H} NMR δ 83.5(s). Satisfactory elemental analyses were obtained for compounds **1–3**. Compounds **4–6** were not analysed owing to the obvious problems of recrystallization and handling. For **4**: IR (Nujol) v(C≡C) 2108, v(CO) 1680 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$, 223 K) δ −8.549 (t, $^2J_{HP}$ 27.6 Hz, RuH), 2.001 [s, C$_5$(CH$_3$)$_5$], 3.601 (s, CO$_2$CH$_3$); ^{31}P{^{1}H} NMR (223 K) δ 75.5(s). For **5**: IR (Nujol) v(C≡C) 2030 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$, 223 K) δ −9.134 (t, $^2J_{HP}$ 30.4 Hz, RuH), 0.057 [s, Si(CH$_3$)$_3$], 1.849 [s, C$_5$(CH$_3$)$_5$]; ^{31}P{^{1}H} NMR (223 K) δ 72.4(s). For **6**, Ir (Nujol) v(C≡C) 2106 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$, 223 K) δ −8.790 (t, $^2J_{HP}$ 29 Hz, RuH), 1.860 [s, C$_5$(CH$_3$)$_5$], 7.110, 7.503 (m, C$_6$H$_5$); ^{31}P{^{1}H} NMR (223 K) δ 73.5(s).

References

1 M. I. Bruce and A. G. Swincer, Adv. Organomet. Chem., 1983, **22**, 59.
2 J. Wolf, H. Werner, O. Serhadli and M. L. Ziegler, Angew. Chem., Int. Ed. Engl., 1983, **22**, 414; F. J. García-Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, Angew. Chem., Int. Ed. Engl., 1985, **24**, 406; M. Dziallas and H. Werner, J. Chem. Soc., Chem. Commun., 1987, 852.
3 J. Silvestre and R. Hoffmann, Helv. Chim. Acta, 1985, **68**, 1461.
4 I. de los Ríos, M. Jiménez Tenorio, J. Padilla, M. C. Puerta and P. Valerga, J. Chem. Soc., Dalton Trans., submitted for publication.
5 R. M. Bullock, J. Chem. Soc., Chem. Commun., 1989, 165.
6 J. R. Lomprey and J. P. Selegue, J. Am. Chem. Soc., 1992, **114**, 5518.
7 I. de los Ríos, M. Jiménez Tenorio, M. C. Puerta and P. Valerga, manuscript in preparation.
8 H. Werner, M. Baum, D. Schneider and B. Windmüller, Organometallics, 1994, **13**, 1089.