Rearrangement of a Metal (η^2-Alkyne) Complex to a Metal Vinylidene and Subsequent Reaction of the Metal Vinylidene to Regenerate the Alkyne

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The η^2-alkyne complex $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CMe)^+PF_6^-$, which was isolated from a reaction of $HC{\equiv}CMe$ with $(C_5H_5)(PMe_3)_2RuCl$, undergoes first-order rearrangement to give $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+\ PF_6^-$; at higher temperatures in MeCN, this vinylidene complex cleanly regenerates $HC{\equiv}CMe$ and forms $(C_5H_5)(PMe_3)_2Ru(MeCN)^+\ PF_6^-$.

The rearrangement of acetylene to vinylidene ($H_2C{=}C{:}$) requires temperatures in excess of 500 °C,[1] but the rearrangement of metal η^2-alkyne complexes occurs under mild conditions and provides a convenient route to metal vinylidenes.[2] Free vinylidene rearranges to acetylene on a picosecond time-scale;[3] organometallic analogues of this reaction have been briefly mentioned,[4] but are not well known. This communication reports the first organometallic system which demonstrates conversion of a free alkyne through isolable η^2-alkyne and metal vinylidene complexes, and then back into the free alkyne.

The η^2-alkyne complex $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CMe)^+\ PF_6^-$† precipitates as a pale yellow powder when $HC{\equiv}CMe$ is bubbled through a methanol solution of $(C_5H_5)(PMe_3)_2RuCl$ containing excess of NH_4PF_6 at room temperature for 15 min (Scheme 1). This complex rearranges to the previously reported[5] $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+\ PF_6^-$‡ in methanol or acetonitrile. The kinetics of this rearrangement were determined by monitoring the rate of appearance of the λ_{max} = 478 nm band of $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+PF_6^-$. Evaluation of the temperature dependence of the first-order rate constants obtained at six temperatures from 15 to 40 °C in MeCN gave the activation parameters $\Delta H^\ddagger = 23.4 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = 3.9 \pm 0.9$ cal K^{-1} mol^{-1} (cal = 4.184 J). Werner and co-workers have isolated alkynyl–hydride complexes which are intermediates in the conversion of Rh and Ir

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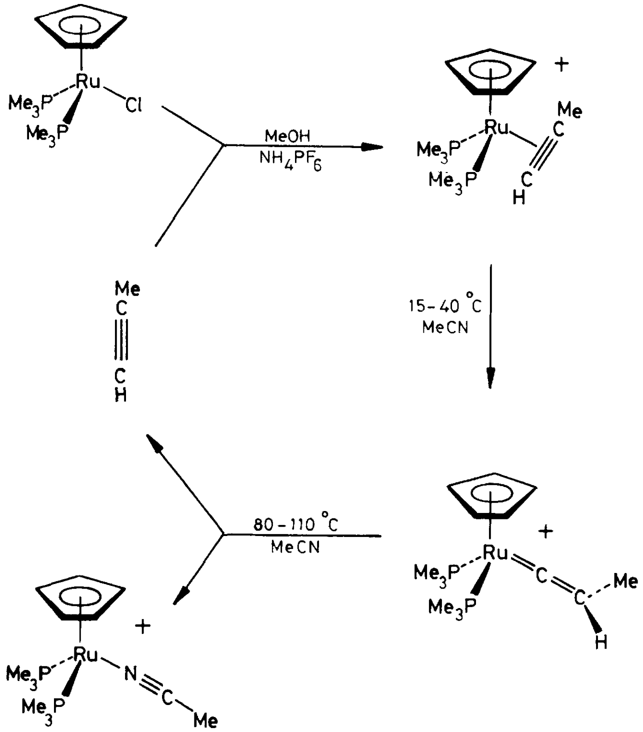
† $(C_5H_5)(PMe_3)_2Ru(\eta^2\text{-}HC{\equiv}CMe)^+\ PF_6^-$: ^{1}H n.m.r. ($CD_3CN$) δ 5.02 (s, 5H, C_5H_5), 4.02 (tq, J_{PH} 10.5, $^4J_{HH}$ 2.4 Hz, 1H, ≡CH), 2.44 (dt, $^4J_{HH}$ 2.4, J_{PH} 0.6 Hz, 3H, $\equiv CCH_3$), 1.47 ('filled-in doublet,' separation between outer lines = $^2J_{PH} + {}^4J_{PH}$ = 9.5 Hz, 18H, PMe_3); $^{13}C\{^1H\}$ [$(CD_3)_2CO$, 0.07 M $Cr(acac)_3$ (acac = pentane-1,4-dionato), −48 °C] δ 87.1 (s, C_5H_5), 73.0 (s, $\equiv CCH_3$), 53.6 (s, $\equiv CH$), 20.0 (d, J 33 Hz, PMe_3), 13.1 (s, $\equiv CCH_3$); i.r. (KBr) $\nu_{C\equiv C}$ ν(C≡C) 1890 cm^{-1}.

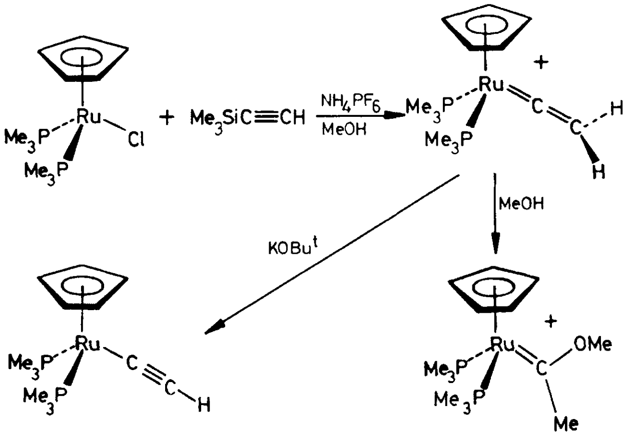
$(C_5H_5)(PMe_3)_2Ru(\eta^2\text{-}HC{\equiv}CH)^+\ PF_6^-$: ^{1}H n.m.r. ($CD_3CN$) δ 5.02 (s, 5H, C_5H_5), 4.98 (t, J_{PH} 7.2 Hz, 2H, $\equiv CH$), 1.47 ('d,' $^2J_{PH} + {}^4J_{PH}$ = 9.7 Hz, 18H, PMe_3); $^{13}C\{^1H\}$ [$(CD_3)_2CO$, 0.07 M $Cr(acac)_3$, −23 °C] δ 87.2 (s, C_5H_5), 62.4 (s, $\equiv CH$), 20.3 (apparent triplet, observed $J = {}^1J_{PC} + {}^3J_{PC}$ = 17.5 Hz); i.r. (KBr) ν(C≡C) 1748 cm^{-1}.

‡ $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)(CH_3)^+PF_6^-$: ^{1}H n.m.r. ($CD_3CN$) δ 5.41 (s, 5H, C_5H_5), 4.31 (qt, $^3J_{HH}$ 7.6, $^4J_{PH}$ 2.3 Hz, 1H, CH), 1.77 (d, $^3J_{HH}$ 7.6 Hz, 3H, CH_3), 1.56 ('filled in doublet,' separation between outer lines = $^2J_{PH} + {}^4J_{PH}$ = 10.3 Hz, 18H, PMe_3); $^{13}C\{^1H\}$ n.m.r. [CD_3CN, 0.07 M $Cr(acac)_3$] δ 347.9 (br. s, Ru=C), 103.4 (s, Ru=C=C), 91.7 (s, C_5H_5), 23.0 (apparent triplet, observed $J = {}^1J_{PC} + {}^3J_{PC}$ = 18 Hz, PMe_3), 4.5 (s, CH_3); i.r. (MeCN) ν(CC) 1695, 1662 cm^{-1}; visible (MeCN) λ_{max} 478 nm, ε 62 dm^3 mol^{-1} cm^{-1}.

$(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2{}^+PF_6^-$: ^{1}H n.m.r. ($CD_3CN$) δ 5.43 (s, 5H, C_5H_5), 3.78 (t, $^4J_{PH}$ 2.4 Hz, 2H, CH_2), 1.57 ('d,' $^2J_{PH} + {}^4J_{PH}$ = 10.4 Hz, 18H, PMe_3); $^{13}C\{^1H\}$ [CD_3CN, 0.07 M $Cr(acac)_3$] δ 343.9 (br. s, Ru=C), 92.7 (s, $Ru{=}C{=}CH_2$), 92.0 (s, C_5H_5), 22.3 ('t,' $^1J_{PC} + {}^3J_{PC}$ = 19 Hz, PMe_3); i.r. (CH_2Cl_2) ν(CC) 1633 cm^{-1}; visible (MeCN) λ_{max} 488 nm; ε 55 dm^3 mol^{-1} cm^{-1}.

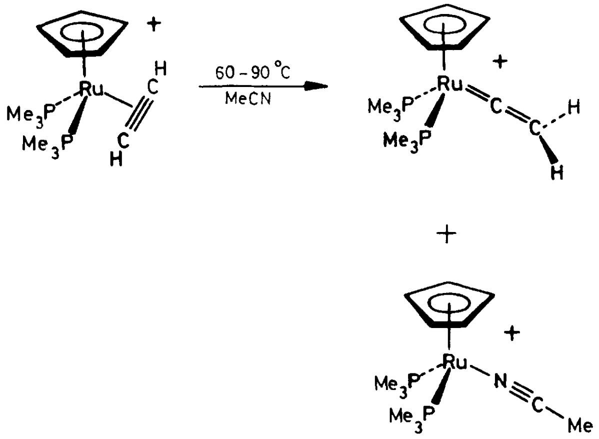


Scheme 1



Scheme 2

η^2-alkynes to vinylidene complexes.[6] A similar intermediate might be possible for the $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CMe)^+$ to $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+$ rearrangement, and would be consistent with the relatively low entropy of activation. However, the 18e$^-$ cationic complexes studied here would be less likely to facilitate the intramolecular oxidative addition required to convert an η^2-alkyne complex into a alkynyl-hydride, compared to the neutral, electronically unsaturated complexes studied by Werner. Further experiments are in progress to discern between this and other plausible mechanisms.



Scheme 3

At higher temperatures (80—110 °C, in sealed tubes) in acetonitrile, the metal vinylidene complex $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+$ PF_6^- regenerates $HC{\equiv}CMe$ in high yield; acetonitrile replaces the vacant co-ordination site created by loss of the vinylidene ligand, forming $(C_5H_5)(PMe_3)_2Ru(MeCN)^+$ PF_6^-.[7] This reaction also exhibits clean first-order kinetics; activation parameters of $\Delta H^{\ddagger} = 26.8 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.9 \pm 1.9$ cal K^{-1} mol^{-1} were determined.

The η^2-acetylene complex $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CH)^+$ PF_6^-† was isolated from a reaction similar to that used for the synthesis of the analogous η^2-methylacetylene complex.§ Vinylidene complex $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ PF_6^-‡ was isolated from the reaction of $Me_3SiC{\equiv}CH$ with $(C_5H_5)(PMe_3)_2RuCl$ in the presence of NH_4PF_6 (Scheme 2). While this complex can be isolated in pure form soon after it precipitates from the methanol solution, it reacts slowly with methanol to give the carbene complex $(C_5H_5)(PMe_3)_2Ru{=}C(OMe)Me^+$ PF_6^-. Deprotonation of $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ by $KOBu^t$ in tetrahydrofuran (THF) gave $(C_5H_5)(PMe_3)_2Ru{-}C{\equiv}CH$. The rearrangement of $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CH)^+$ to $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ is significantly slower than the $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CMe)^+$ to $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+$ rearrangement. For example, at 40 °C $t_{\frac{1}{2}}$ for the isomerization of $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CMe)^+$ to $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)Me^+$ is 5.5 min, while the half-life for the analogous rearrangement of $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CH)^+$ to $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ is over 5 h at 60 °C. The kinetics of the latter reaction are complicated by formation of $(C_5H_5)(PMe_3)_2Ru(MeCN)^+$ (Scheme 3). This acetonitrile complex appears to be formed in competition with $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ rather than in a secondary reaction of it since preliminary studies indicate that the formation of $(C_5H_5)(PMe_3)_2Ru(MeCN)^+$ from $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ is very slow ($t_{\frac{1}{2}} > 1$ day at 90 °C).

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the United States Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy

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§ N.m.r. and i.r. spectra of $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CH)^+$ and $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ suggest that the product previously characterized[5] as $(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2^+$ was actually $(C_5H_5)(PMe_3)_2Ru(HC{\equiv}CH)^+$.

Sciences. Helpful discussions with Professor J. L. Templeton are gratefully acknowledged.

Received, 27th July 1988; Com. 8/03066I

References

1 R. P. Durán, V. T. Amorebieta, and A. J. Colussi, *J. Am. Chem. Soc.*, 1987, **109**, 3154.
2 M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 59.
3 Y. Osamura, H. F. Schaefer, S. K. Gray, and W. H. Miller, *J. Am. Chem. Soc.*, 1981, **103**, 1904.
4 R. M. Bullock, *J. Am. Chem. Soc.*, 1987, **109**, 8087.
5 M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2203.
6 A. Höhn, H. Otto, M. Dziallas, and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1987, 852; F. J. G. Alonso, A. Höhn, J. Wolf, H. Otto, and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 406.
7 M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1398.