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Preliminary communication

Coordination, Oligomerisation and Transfer Hydrogenation of Acetylenes by Some Ruthenium and Osmium Carboxylato Complexes: Crystal and Molecular Structure of (1,4-Diphenylbut-1-en-3-yn-2-yl)trifluoroacetato(carbonyl)bis(triphenylphosphine)ruthenium(II)

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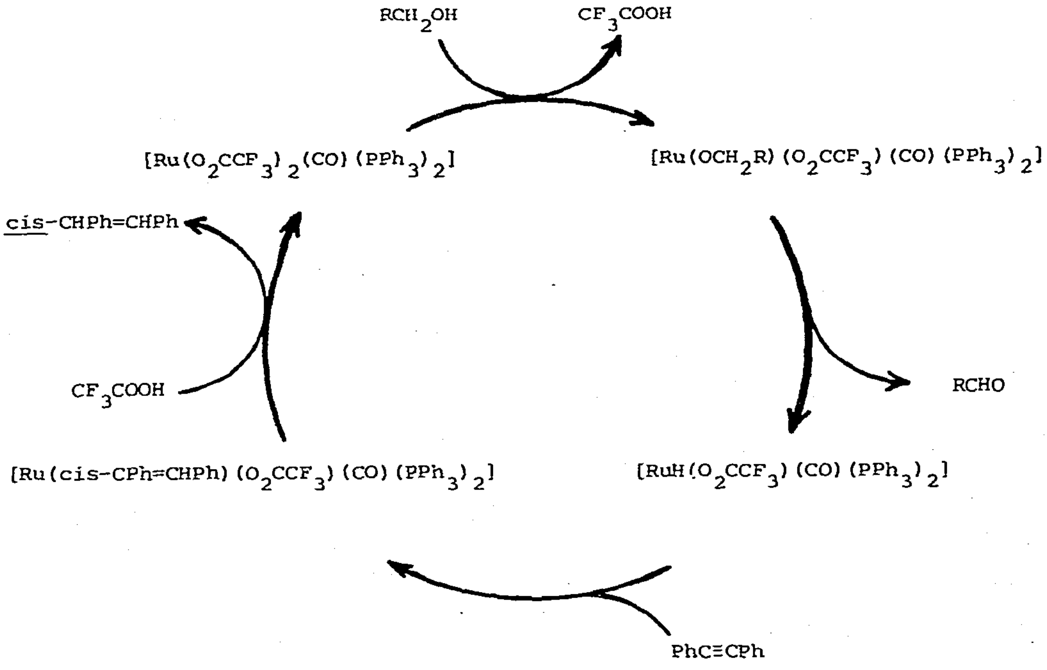
Summary. The complexes $[MH(O_2CCF_3)(CO)(PPh_3)_2]$ and $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ (M = Ru or Os) react with terminal and internal acetylenes to afford oligomerisation and hydrogenation products, respectively, together with vinylic complexes, including the ruthenium species $[Ru(C_4HPh_2)(O_2CCF_3)(CO)(PPh_3)_2]$, which has been shown by X-ray diffraction methods to contain a 1,4-diphenylbut-1-en-3-yn-2-yl ligand.

Current interest in the role of acetylenes as substrates in transition metal catalysed organic reactions[1] prompts this report on some acetylene coordination, oligomerisation and transfer hydrogenation reactions involving the ruthenium and osmium catalyst systems $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$/$[MH(O_2CCF_3)(CO)(PPh_3)_2]$.[2,3]

Diphenylacetylene inserts into the metal-hydrogen bonds of the complexes $[MH(O_2CCF_3)(CO)(PPh_3)_2]$ (M = Ru or Os) to afford 1,2-diphenylvinyl derivatives $[M\{C(Ph)=CHPh\}(O_2CCF_3)(CO)(PPh_3)_2]$ in excellent yield as yellow crystalline solids. Cleavage of the metal vinyl linkage with trifluoroacetic acid under mild conditions (room temperature, 2h) affords the corresponding trifluoroacetato complexes $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ and cis-stilbene. Formation of the latter product, which isomerises readily to the thermodynamically preferred trans isomer if the reaction mixture is heated, implies that the initial 'insertion' of the acetylene into the metal-hydrogen bonds affords cis-vinyl complexes and therefore probably occurs via a four-centre transition state.[1]

The products $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$, liberated during the acidolysis of the vinyl complexes, readily dehydrogenate primary alcohols to afford the corresponding aldehydes, free trifluoroacetic acid and the hydrides $[MH(O_2CCF_3)(CO)(PPh_3)_2]$ thereby completing a cycle for the catalytic transfer hydrogenation of internal acetylenes (scheme) which we have been able to demonstrate experimentally.



Scheme 1. Cycle for catalytic transfer hydrogenation of diphenylacetylene.

Phenylmethylacetylene likewise inserts into the M-H bonds of the hydrides $[MH(O_2CCF_3)(CO)(PPh_3)_2]$. In each case the product is a ca 1/1 mixture of the isomers $[M\{C(Ph)=CHMe\}(O_2CCF_3)(CO)(PPh_3)_2]$ [^1H n.m.r., M = Ru, τ_{Me} 8.97(d), $\tau_{\underline{C}HMe}$ 5.09(q); M = Os, τ_{Me} 8.93(d), $\tau_{\underline{C}HMe}$ 5.20(q)] and $[M\{C(Me)=CHPh\}(O_2CCF_3)(CO)(PPh_3)_2]$ [^1H n.m.r., M = Ru, τ_{Me} 8.29(s), $\tau_{\underline{C}HPh}$ 4.16(s); M = Os, τ_{Me} 8.53(s), $\tau_{\underline{C}HPh}$ 4.17(s)] thus implying that the stereochemistry of 'insertion' is governed by a delicate balance of steric and electronic factors. Cleavage with acid under mild conditions affords cis-PhHC=CHMe thus establishing a cis arrangement of methyl and phenyl groups in the vinylic ligands. In all the above mentioned complexes the ^{31}P n.m.r. data [M = Ru, δ_p 35(s), M = Os, δ_p 17(s)] are consistent with the presence of a trans pair of triphenylphosphine ligands.[4] By virtue of their ability to function as carbon acids, terminal acetylenes are able to cleave metal-hydride and metal-trifluoro acetate linkages in $[MH(O_2CCF_3)(CO)(PPh_3)_2]$ and $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ respectively. However, the acetylides $[M(C\equiv CR)(O_2CCF_3)(CO)(PPh_3)_2]$, which are presumed to be the initial products, react with further acetylene to yield a bright yellow ruthenium complex $[Ru(C_4HPh_2)(O_2CCF_3)(CO)(PPh_3)_2]$ or, when M = Os, a brown hydrocarbon polymer. Formation of the latter product is catalytic since one mole of osmium complex oligomerises ca 100 moles of acetylene. The ruthenium complex and its osmium analogue $[Os(C_4HPh_2)(O_2CCF_3)(CO)(PPh_3)_2]$ are readily obtained in excellent yield by addition of 1,4-diphenylbutadiyne to the hydrides $[MH(O_2CCF_3)(CO)(PPh_3)_2]$. The osmium complex thus formed acts as a catalyst for the oligomerisation of phenylacetylene and is therefore probably an intermediate in the $[OsH(O_2CCF_3)(CO)(PPh_3)_2]$ catalysed reaction.

An X-ray diffraction study of the ruthenium complex $[Ru(C_4HPh_2)(O_2CCF_3)(CO)(PPh_3)_2]$ has been undertaken to establish the coördination stereochemistry and the structure of the hydrocarbon ligand.

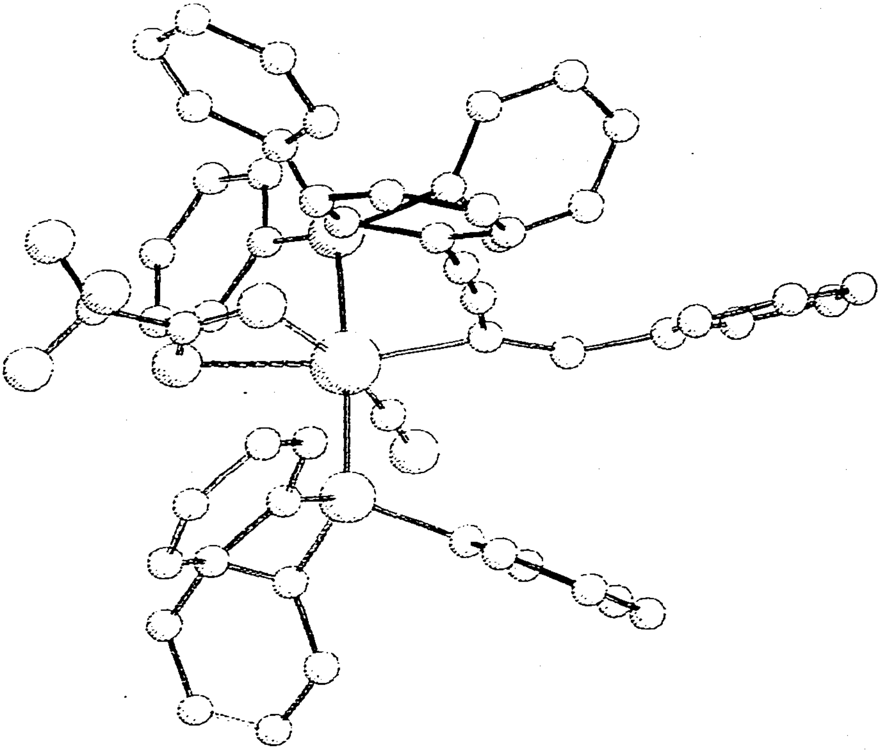


Fig. 1. The molecular structure of $[\mathrm{Ru}\{\mathrm{C(C{\equiv}CPh){=}CHPh}\}(\mathrm{O_2CCF_3})(\mathrm{CO})(\mathrm{PPh_3})_2]$.

Crystallographic data. Air stable yellow triclinic crystals, prepared using phenylacetylene and recrystallised from ethanol, space group $P\bar{1}$ with $\underline{a}$ = 11.526(3), $\underline{b}$ = 12.469(3) and $\underline{c}$ = 18.025(4) Å, α = 88.44(2)°, β = 102.41(2)°, γ = 110.21(2) and Z = 2. Intensity data were recorded on a CAD4 automatic diffractometer using Cu - K_α radiation ($\mu_{\mathrm{Cu-K}_\alpha}$ = 22.36 cm^{-1}) and solved by standard heavy atom methods. R is currently 0.085 following least squares refinement of positional and isotropic thermal parameters using 5475 observed ($F > 5\sigma(F_o)$) from the total of 7784 measured to $\theta_{\max}$ = 60°.

The molecular structure, shown in the figure, reveals the presence of a 1,4-diphenylbut-1-en-3-yn-2-yl ligand formation of which implies the trans-1,2- addition of a second molecule of phenylacetylene across the triple bond rather than the expected "insertion" into the metal-carbon σ-bond of a phenylacetylide ligand. Synthesis of the same complex and its osmium analogue from 1,4-diphenylbutadiyne is rationalised in terms of a *cis*-1,2- addition of the metal-hydride moiety across one of the triple bonds with the metal taking the less sterically hindered site.

References

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3. A. Dobson and S.D. Robinson, *Inorg. Chem.*, 16 (1977) 137.
4. A. Dobson and S.D. Robinson, *Inorg. Chem.*, 16 (1977) 1321.