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Preliminary communication

Diyne coordination chemistry: Reactions of $[RuClH(CO)(PPh_3)_3]$ with diphenylbutadiyne and bis(phenylethynyl)mercury

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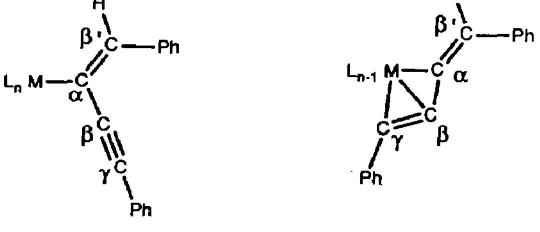
Abstract

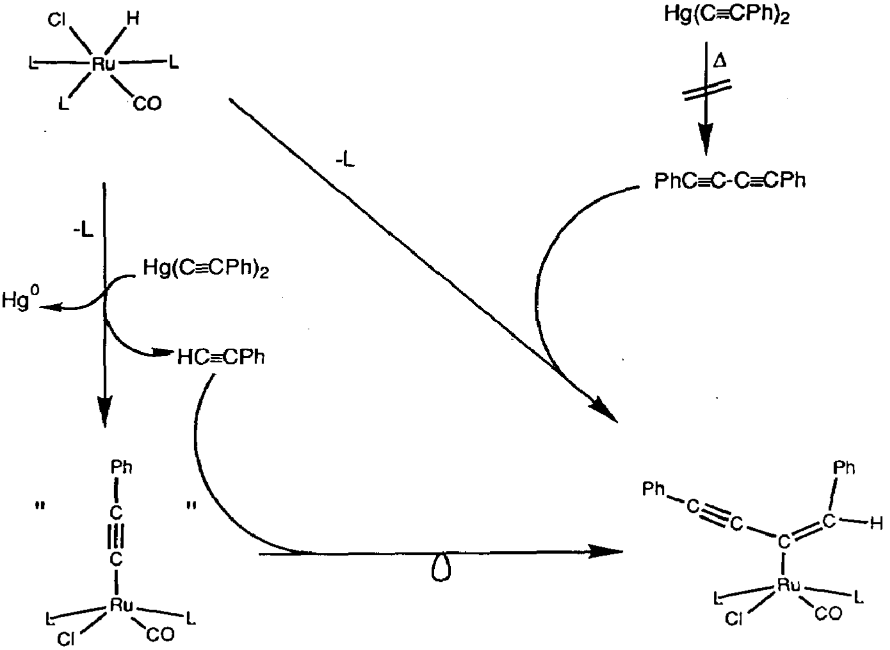
The reaction of the hydridometal complex $[RuClH(CO)(PPh_3)_3]$ with 1,4-diphenyl-butadi-1,3-yne has been investigated and found to proceed with monoinsertion to give a coordinatively unsaturated σ-vinyl complex $[Ru\text{-}\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$, which is also the major product of the reaction of $[RuClH(CO)(PPh_3)_3]$ with $[Hg(C{\equiv}CPh)_2]$.

Recent interest in the unusual 1,4-diphenylbut-1-en-3-yn-2-yl ligand (Scheme 1) centres on its possible intermediacy in alkyne oligomerisation [1–3]. This highly unsaturated ligand may coordinate as either a one [1] or three [2,3] electron donor depending upon the requirements of the metal centre which, in the cases studied, are quite clear.

The complexes $[RuRCl(CO)(PPh_3)_2]$ (R = aryl [4], vinyl [5]) are stable 16-electron species even though the latter might be expected to coordinate in a bidentate manner as observed for σ–π-vinyl complexes of molybdenum [6]. It was therefore of interest to prepare such a complex with a potentially bidentate 1,4-diphenylbut-1-en-3-yn-2-yl ligand. Such a complex was the unexpected product of an unsuccessful attempt to obtain the corresponding hypothetical σ-alkynyl derivative



Scheme 1. Bonding modes for coordinated C_4HPh_2.



Scheme 2. Mechanisms for the formation of $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)L_2]$, L = PPh_3.

$[Ru(C{\equiv}CPh)Cl(CO)(PPh_3)_2]$ from the reaction of $[RuClH(CO)(PPh_3)_3]$ and di(phenylethynyl)mercury. Elemental mercury was deposited and a bright yellow compound obtained upon chromatography and characterised as $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ [7*].

Two plausible explanations for the course of this reaction are (Scheme 2) (a) thermolysis of $[Hg(C{\equiv}CPh)_2]$ to provide 1,4-diphenyl-butadi-1,3-yne, which subsequently reacts with the hydridoruthenium complex by insertion, or (b) reaction of $[RuClH(CO)(PPh_3)_3]$ with the organomercurial to provide the desired complex $[Ru(C{\equiv}CPh)Cl(CO)(PPh_3)_x]$ ($x = 2$ or 3), which under the reaction conditions inserts the equivalent of phenylacetylene which is liberated in the initial reaction. Both these mechanisms could ultimately lead to the same product $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$. Treating $[RuClH(CO)(PPh_3)_3]$ with one equivalent of the preformed diyne provides $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ in high yield and a similar reaction has been reported for the trifluoroacetato complex $[RuH(O_2CCF_3)(CO)(PPh_3)_2]$ [1]. However, heating $[Hg(C{\equiv}CPh)_2]$ in tetrahydrofuran under reflux does not lead to deposition of mercury and therefore the extrusion of mercury must be in some way mediated *by the ruthenium centre*. In the absence of a preparative route to $[Ru(C{\equiv}CPh)Cl(CO)(PPh_3)_2]$, mechanism (b) remains unvalidated; however, the required second step, i.e., insertion reactions of acetylenes in this metal–ligand system, has a precedent in the reaction of $[Ru(CH{=}CH^tBu)Cl(CO)(PPh_3)_2]$ with $HC{\equiv}CCO_2Me$ [8].

Mawby and co-workers have described a related ligand system which arises from the reaction of $[RuCl_2(CO)_2(PMe_2Ph)_2]$ with $[Hg(C{\equiv}CPh)_2]$ via the proposed

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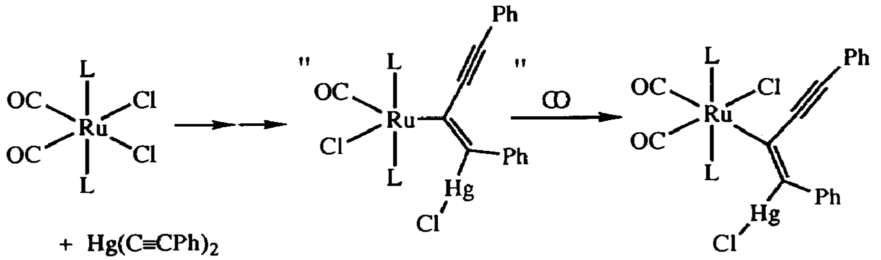
* Reference number with asterisk indicates a note in the list of references.



Scheme 3. Chlororuthenation of bis(phenylethynyl)mercury (ref. 9); L = PMe_2Ph.

intermediacy of a 16-electron vinyl complex [Ru{C(C≡CPh)=C(HgCl)Ph}-$Cl(CO)(PMe_2Ph)_2$] related to [Ru{C(C≡CPh)=CHPh}$Cl(CO)(PPh_3)_2$]; however, in this case the mercury remains incorporated in the final ligand as a vinyl β-substituent (Scheme 3).

The complex [Ru{C(C≡CPh)=CHPh}$Cl(CO)(PPh_3)_2$], being coordinatively unsaturated, reacts with a range of ligands, viz, carbon monoxide, isonitriles, pyrazole, 2,1,3-benzoselenadiazole, 2,2′-bipyridyl, 1,4,7-trithiacyclononane, and poly(azol-1-yl)chelates [7b]. We are currently investigating the generality of the insertion of diphenylbutadiyne into platinum–metal hydride bonds.

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7 (a) Data for [Ru{C(C≡CPh)=CHPh}$Cl(CO)(PPh_3)_2$]: IR ν(CO) 1910 (Nujol), 1923 (CH_2Cl_2) cm^{-1}. ^{31}P-{^1H} NMR ($CDCl_3$), δ 35.0 ppm. ^1H NMR ($CDCl_3$) δ 5.26 [s(br) 1 H, C=C*H*Ph], 7.05–7.40, 7.70–7.80 [m×2, 40 H, PC_6H_5 and CC_6H_5]. FAB-MS (nitrobenzyl alcohol) *m/z* 890 $[M]^+$, 628 $[M - PPh_3]^+$, 626 $[Ru(PPh_3)_2]^+$, 600 [$RuCl(PPh_3)_2${C(C≡CPh)=CHPh}]$^+$, 565 [$Ru(PPh_3)$-{C(C≡CPh)=CHPh}]$^+$, 492 $[Ru(PPh_3)(HCCCCPh)]^+$, 364 $[RuPPh_3]^+$. Yield, via PhC_4Ph route, 84%. (b) The characterisation of [Ru{C(C≡CPh)=CHPh}$Cl(CO)(PPh_3)_2$] included its reaction with $K[HB(pz)_3]$ (pz = pyrazol-1-yl) to provide [Ru{C(C≡CPh)=CHPh}$(CO)(PPh_3)${$HB(pz)_3$}], the structure of which was determined by X-ray crystallography: N.W. Alcock and A.F. Hill, unpublished results.

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