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Preliminary communication

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

Anthony F. Hill * and Richard P. Melling

Department of Chemistry, University of Warwick, Coventry CV4 7AL (U.K.)

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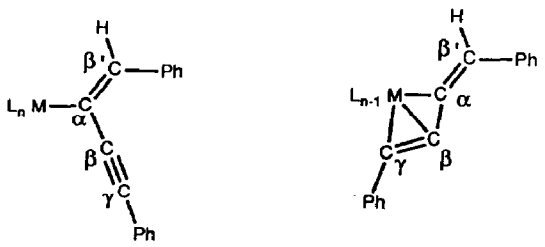
Abstract

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 $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$, 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.

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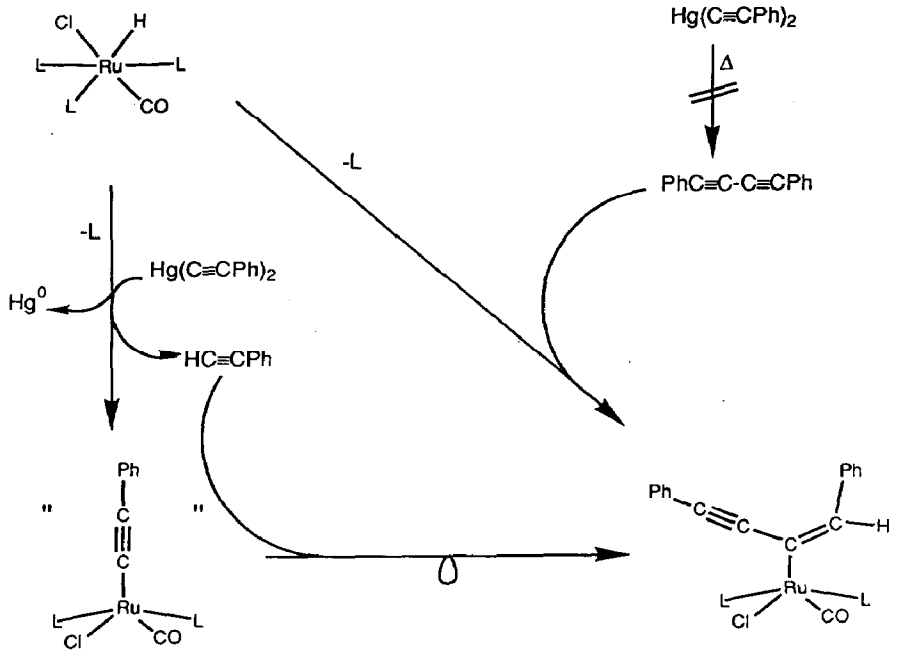


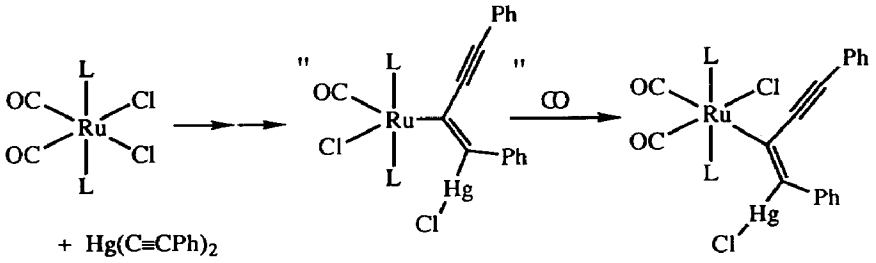
Scheme 2. Mechanisms for the formation of [Ru{C(C≡CPh)=CHPh}Cl(CO)L_2], L = PPh_3.

[Ru(C≡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≡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≡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≡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≡CPh)=CHPh}Cl(CO)(PPh_3)$_2$]. Treating [RuClH(CO)(PPh_3)$_3$] with one equivalent of the preformed diyne provides [Ru{C(C≡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≡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≡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^{t}Bu)Cl(CO)(PPh_3)$_2$] with HC≡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≡CPh)$_2$] via the proposed

* 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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References and notes

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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=CHPh], 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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