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Alkyne insertion reactions of $[RuH(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$: synthesis of alkenyl, alkynyl and enynyl complexes

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Abstract

The diethyldithiocarbamate hydride ruthenium complex $[RuH(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ reacts with excess phenylacetylene to give the alkynyl complex $[Ru(C{\equiv}CPh)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ via the intermediate alkenyl complex $[Ru(CH{=}CHPh)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ and with 1,4-diphenylbutadiyne to give the enynyl complex $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$. The alkenyl complex $[Ru(CH{=}CHPh)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ is a convenient precursor for alkynyl complexes of the type $[Ru(C{\equiv}CR)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ (R = aryl, alkyl, C_6H_4-4-C≡CH). © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The hydroruthenation of alkynes is a powerful methodology for the synthesis of σ-alkenyl ruthenium complexes. In particular the complex $[RuHCl(CO)(PPh_3)_3]$ (**1**) has been exploited because the reversible de-coordination of one of the triphenylphosphine ligands gives a 16-electron species. This facilitates migratory insertion of alkynes and diynes into the ruthenium-hydride bond generating 16-electron σ-alkenyl and σ-enynyl complexes respectively [1,2]. The ruthenium hydride carboxylate complexes $[RuH(\kappa^2\text{-}O_2CR)(CO)(PPh_3)_2]$ (**2**) also react with alkynes to generate $[Ru\{\eta^1\text{-}C(C{\equiv}CR){=}CHR\}(\kappa^2\text{-}O_2CR)(CO)(PPh_3)_2]$ [3,4] or $[Ru(\eta^1\text{-}CH{=}CR)(\kappa^2\text{-}O_2CR)(CO)(PPh_3)_2]$ [4] complexes depending on the alkyne and the reaction conditions. In these cases the reaction probably proceeds via a 16-electron intermediate formed by the de-coordination of one end of the moderately labile carboxylate ligand. To the best of our knowledge no reports have appeared on migratory insertion reactions of alkynes with the analogous dithiocarbamate complex $[RuH(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ (**3**) [5], presumably because the strong chelation of the dithiocarbamate ligand precludes the facile formation of coordinatively unsaturated intermediates.

2. Results and discussion

Perhaps unsurprisingly in view of its low lability, the complex **3** shows no reaction with excess phenylacetylene in dichloromethane at room temperature. Increasing the temperature did lead to reaction, however the product formed after 3 h in toluene at reflux temperature proved not to be the expected σ-alkenyl complex $[Ru(CH{=}CHPh)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ (**4**) but rather the σ-alkynyl complex $[Ru(C{\equiv}CPh)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ (**5a**) (Scheme 1). The IR spectrum of **5a** shows peaks at 2091 and 1942 cm^{-1} corresponding to $\nu(C{\equiv}C)$ and $\nu(CO)$, respectively. The *trans*-disposition of the phosphine ligands is indicated by the appearance of a singlet in the ^{31}P-NMR spectrum at δ 40.2 ppm, whilst characteristic peaks for the two distinct ethyl groups of the diethyldithiocarbamate ligand are seen in the ^1H-NMR spectrum. The spectroscopic data for this compound compare well with those reported for this type of complex prepared previously from $[RuCl(C{\equiv}CR)(CO)(BSD)(PPh_3)_2]$ and $Na[S_2$-

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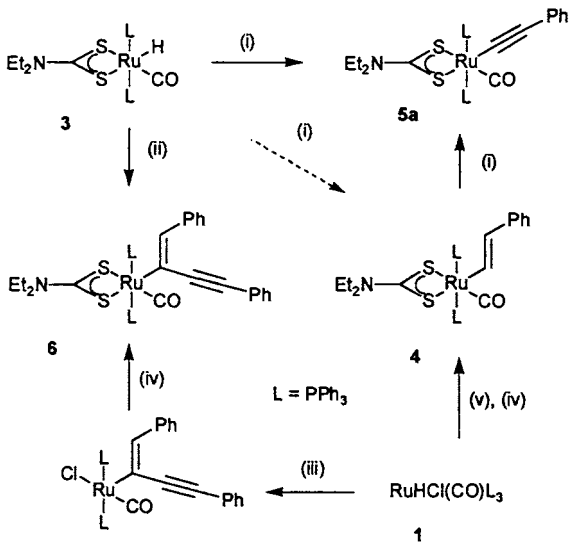
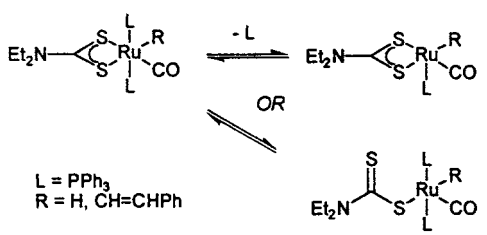


Scheme 1. (i) Phenylacetylene (excess), toluene, reflux temperature; (ii) 1,4-diphenylbutadiyne, toluene, reflux temperature; (iii) 1,4-diphenylbutadiyene, CH_2Cl_2; (iv) $Na[S_2CNEt_2]$, CH_2Cl_2–EtOH; (v) phenylacetylene, CH_2Cl_2.

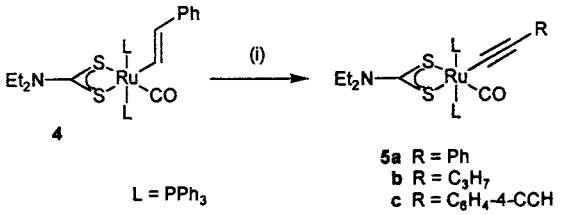
$CNEt_2$] (BSD = 2,1,3-benzoselenadiazole) [6]. The most likely explanation for the isolation of **5a** rather than **4** was that **4** did indeed form but subsequently reacted with the excess phenylacetylene to generate **5a** and styrene. In order to test this hypothesis, **4** was prepared according to a published method by the reaction of **1** with phenylacetylene and then $Na[S_2CNEt_2]$ [7]. Heating **4** with excess phenylacetylene in toluene did indeed generate complex **5a** in 86% yield.

It is highly unlikely that the transformations of **3** to **4** and **4** to **5a** proceed via 20-electron intermediates, therefore it is reasonable to assume that both **3** and **4** are in equilibrium with 16-electron species at elevated temperature. Such species could conceivably be generated either by the loss of a triphenylphosphine ligand or by reversible de-coordination of one sulfur donor of the dithiocarbamate ligand (Scheme 2).

The exchange of a σ-alkenyl for a σ-alkynyl ligand presumably occurs via a Ru(IV) intermediate with subsequent reductive elimination of styrene. Such a mechanism has recently been postulated for the reaction of the osmium complex $[Os(CH{=}CHC_6H_4Me)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ with $HC{\equiv}CC_6H_4Me$, which generates the alkynyl complex $[Os(C{\equiv}CC_6H_4Me)(\kappa^2\text{-}S_2$-



Scheme 2.



Scheme 3. (i) HCCR (excess), toluene, reflux temperature.

$CNEt_2$)(CO)(PPh_3)] [8]. The formation of **5a** from **3** is in contrast to the analogous reaction of phenylacetylene with the carboxylate complex **2**, which generates a σ-enynyl complex [4]. However, the comparable enynyl complex $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ (**6**) can be synthesized from **3** and 1,4-diphenylbutadiyne in toluene at reflux temperature in 54% yield. Similar reactions have been reported previously with the more labile carboxylate complexes **2** and 1,4-diphenylbutadiyne giving the complex $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}(\kappa^2\text{-}O_2CR)(CO)(PPh_3)_2]$, **7** [4]. The complex **6** can also be prepared in 68% yield by the reaction of **1** with 1,4-diphenylbutadiyne [2] followed by addition of sodium diethyldithiocarbamate. The IR spectrum of **6** shows a peak at 1913 cm^{-1} corresponding to the ν(CO). As would be expected this stretch is about 30 cm^{-1} lower than those of the complexes **7** [4] as a result of the greater electron donation of the dithiocarbamate ligand. However, the ν(C≡C) of **6** is about 45 cm^{-1} higher than those of **7**. This indicates that the coordination environment of the enynyl ligand of **6** may be different from that of **7**. The ^{1}H-NMR spectrum of **6** at r.t. shows a broad singlet at δ 6.24 ppm corresponding to the alkenic proton, whilst the ^{31}P-NMR shows a very broad peak at δ 38.7 ppm. This is in contrast to the complexes **7** for which no peak broadenings were reported [4]. At −50°C two peaks corresponding to alkenic protons are observed at δ 6.38 and 6.09 ppm in a 1:3.4 ratio, respectively. The ^{31}P spectrum recorded at this temperature shows two sharp singlets in the same ratio at δ 39.1 (major) and 37.9 ppm (minor). These data indicate that there is restricted rotation about the Ru–C bond of the enynyl ligand in **6** giving two isomers. This may explain why in the IR spectrum the ν(C≡C) of **6** is so different from that of **7**.

Based on the observation with phenylacetylene, the reaction of **4** with terminal alkynes seemed as if it might provide a relatively facile route to σ-alkynyl complexes. Accordingly we investigated the reaction of **4** with excess 1-pentyne which gave the alkynyl complex $[Ru(C{\equiv}CC_3H_7)(\kappa^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2]$ (**5b**) in 76% yield, demonstrating that this reaction could be extended to alkyl-substituted alkynes (Scheme 3). The spectroscopic data for **5b** were comparable with those of **5a** with the exception of those associated with the C_3H_7 group.

The reaction of **4** with excess 1,4-diethynylbenzene gave the mono-ruthenated diyne complex [Ru(C≡CC_6H_4–4-C≡CH)(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] (**5c**) in 91% yield. Again the spectroscopic data for **5c** are broadly similar to those of **5a**. In addition to the ν(C≡C) for the ruthenated alkyne function at 2083 cm^{-1} in the IR spectrum, a peak was also seen at 3294 cm^{-1} corresponding to the ν(≡C–H) of the terminal alkyne function. These data compare well with those reported for [Ru(C≡CC_6H_4-4-C≡CH)$_2$(dppe)$_2$] [9] and [RuCl(C≡CC_6H_4-4-C≡CH)(dppe)$_2$] [10]. The presence of both a metallated and a free alkyne function for the diethynylbenzene ligand was confirmed by ^{1}H-NMR spectroscopy which showed two doublets at δ 7.12 and 6.48 ppm, with a mutual coupling of 8.3 Hz, corresponding to the two aromatic environments of the ligand and a singlet at δ 3.04 ppm for the terminal proton. Ruthenium complexes with mono-metallated diethynylbenzene ligands are of interest as they can act as building blocks for the synthesis of hetero-polymetallic assemblies which allow communication between the metal centers [9–11]. Ordinarily such mono-ruthenated complexes of diethynylbenzene are generated by first protecting one end of the diyne, ruthenating the other end and then de-protecting [9,10]. The methodology reported here therefore provides an attractive alternative as direct mono-metallation of the diyne can be achieved in high yield. Preliminary investigations show that **5c** can indeed be used to fabricate bi- and tri-metallic assemblies and this chemistry will be reported in full elsewhere.

In conclusion we have shown that whilst the 18e ruthenium dithiocarbamate hydride complex **3** is essentially non-labile at r.t., at elevated temperatures it is able to undergo reaction with excess phenylacetylene to generate the σ-alkynyl complex **5a** via the σ-alkenyl species **4**, or with 1,4-diphenylbutadiyne to give the enynyl complex **6**. The complex **4** proves to be a useful building block for the facile generation of σ-alkynyl complexes with aryl, alkyl and alkynyl substituted terminal alkynes.

3. Experimental

The compounds [RuH(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] [5], [Ru(CH=CHPh)(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] [7] and 1,4-diethynylbenzene [12] were prepared according to literature methods. All reactions were performed under nitrogen using degassed solvents. ^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker AC300 spectrometer calibrated against internal $CDCl_3$ (^{1}H) or external H_3PO_4 (^{31}P). IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer.

*3.1. Preparation of [Ru(C≡CPh)(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] (**5a**)*

3.1.1. Method A

A mixture of [RuH(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] (0.100 g, 0.125 mmol) and phenylacetylene (0.07 ml, 0.637 mmol) in toluene (20 ml) was heated at reflux temperature for 3 h. The volatiles were then removed on a rotary evaporator and the resultant solid was recrystallized from dichloromethane–ethanol to give **5a** as a yellow powder (0.093 g, 82%).

3.1.2. Method B

A mixture of [Ru(CH=CHPh)(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] (0.500 g, 0.552 mmol) and phenylacetylene (0.25 ml, 2.28 mmol) in toluene (20 ml) was heated at reflux temperature for 3 h. The solvent was then removed on a rotary evaporator and the residual solid was recrystallized from dichloromethane–ethanol to give **5a** (0.427 g, 86%). Found: C, 65.0; H, 4.9; N 1.4%. $C_{50}H_{45}NOP_2RuS_2CH_2Cl_2$. Anal. Calc.: C, 64.15; H, 4.9; N, 1.5%. IR (ν_{max}/cm^{-1}): 2091 (C≡C), 1942 (CO) and 1261 (SCS) (KBr). P-NMR ($CDCl_3$): δ 40.2. H-NMR ($CDCl_3$): δ 0.61 (t, 3H, CH_3, ^3J(HH) 7.2 Hz), 0.74 (t, 3H, CH_3, ^3J(HH) 7.2 Hz), 2.79 (q, 2H, CH_2, ^3J(HH) 7.2 Hz), 2.98 (q, 2H, CH_2, ^3J(HH) 7.2 Hz), 6.57 (m, 2H, *ortho*-Hs of ≡CC_6H_5), 6.97 (m, 3H, *meta* and *para*-Hs of ≡CC_6H_5), 7.32 (m, 18H, PPh_3) and 7.88 (m, 12H PPh_3).

*3.2. Synthesis of [Ru{η¹-C(C≡CPh)=CHPh}(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] (**6**)*

3.2.1. Method A

A mixture of [RuH(κ²-S_2CNEt_2)(CO)(PPh_3)$_2$] (0.200 g, 0.250 mmol) and 1,4-diphenylbutadiyne (0.063 g, 0.311 mmol) in toluene (20 ml) was heated at reflux temperature for 4 h. The volatiles were removed in vacuo and the brown residue was recrystallized from dichloromethane–ethanol giving **6** as a yellow–ochre powder (0.135 g, 54%).

3.2.2. Method B

A mixture of [RuHCl(CO)(PPh_3)$_3$] (0.504 g, 0.530 mmol) and 1,4-diphenylbutadiyne (0.125 g, 0.618 mmol) in dichloromethane (40 ml) was stirred for 10 min. Then Na[S_2CNEt_2]·3H_2O (0.125 g, 0.550 mmol) and ethanol (60 ml) was added and the mixture was left to stir for 1 h. Concentration of the solution on a rotary evaporator gave **6**, which was collected by filtration and washed with water (2 × 10 ml) and then ethanol (4 × 10 ml) (0.364 g, 68%). Found: C, 67.9; H, 4.9; N 1.25. $C_{58}H_{51}NOP_2RuS_2$·0.5CH_2Cl_2. Anal. Calc.: C, 67.1; H, 5.0; N, 1.3%. IR (ν_{max}/cm^{-1}): 2148 (C≡C), 1913 (CO) and 1271 (SCS) (KBr). P-NMR ($CDCl_3$, 30°C): δ 38.7 (s, broad); ($CDCl_3$, −50°C) 39.1 (s) and

37.9 (s). H-NMR ($CDCl_3$, 30°C): δ 0.71 (t, 3H, CH_3, ^3J(HH) 7.1 Hz), 0.74 (t, 3H, CH_3, ^3J(HH) 7.2 Hz), 2.94 (q, 2H, CH_2, ^3J(HH) 7.1 Hz), 3.05 (q, 2H, CH_2, ^3J(HH) 7.1 Hz), 6.24 (s, br, 1H, =C*H*Ph), 6.94 (m, 1H, aromatic), 7.04 (m, 4H, aromatic), 7.18 (m, 12H, aromatic), 7.24 (m, 6H aromatic), 7.31 (m, 5H aromatic) and 7.60 (m, 12H, aromatic); ($CDCl_3$, -50°C) selected peaks for minor isomer, 0.59 (t, 3H, CH_3, ^3J(HH), 7.4 Hz), (triplet for second CH_3 obscured), 2.77 (q, br, 2H, CH_2, ^3J(HH) $\sim$ 7 Hz), (quartet for second CH_2 obscured), 3.05 (q, 2H, CH_2, ^3J(HH) = 7.1 Hz) and 6.38 (s, 1H, =C*H*Ph); selected peaks for major isomer, 0.68 (t, 3H, CH_3, ^3J(HH) 7.1 Hz), 0.74 (t, $1 \times CH_3$, ^3J(HH) 7.1 Hz + $1 \times CH_3$ of minor isomer), 2.93 (m, $2 \times CH_2 + 1 \times CH_2$ of minor isomer) and 6.09 (s, 1H, =C*H*Ph).

3.3. Preparation of [Ru(C≡CC$_3$H$_7$)(κ^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$] (5b)

As for **5a** above (Section 3.2.2) with [Ru(CH=CHPh)-(κ^2-S_2CNEt_2)(CO)(PPh_3)$_2$] (0.500 g, 0.552 mmol) and 1-pentyne (0.20 ml, 2.0 mmol) to give **5b** as golden flakes (0.366 g, 76%). Found: C, 62.9; H, 5.4; N 1.45. $C_{47}H_{47}NOP_2RuS_2 0.5CH_2Cl_2$. Anal. Calc.: C, 62.6; H, 5.3; N, 1.5%. IR (ν_{max}/cm^{-1}):2112 (C≡C), 1946 (CO) and 1267 (SCS) (KBr). P-NMR ($CDCl_3$): δ 39.8. H-NMR ($CDCl_3$): δ 0.57 (t, 3H, $CH_2CH_2CH_3$, ^3J(HH) 7.2 Hz), 0.75 (t, 6H, $N(CH_2CH_3)_2$, ^3J(HH) 7.2 Hz), 1.13 (m, 2H, $C{\equiv}CCH_2CH_2$), 1.92 (tt, 2H, $C{\equiv}CCH_2$, ^3J(HH) 6.9 Hz, ^5J(PH) 1.8 Hz), 2.76 (q, 2H, NCH_2, ^3J(HH) 7.2 Hz), 3.01 (q, 2H, NCH_2, ^3J(HH) 7.2 Hz), 7.29 (m, 18H, aromatic) and 7.87 (m, 12H, aromatic).

3.4. Preparation of [Ru(C≡CC$_6$H$_4$-4-C≡CH)(κ^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$] (5c)

As for **5a** above (Section 3.2.2) with [Ru(CH=CHPh)-(κ^2-S_2CNEt_2)(CO)(PPh_3)$_2$] (0.940 g, 1.04 mmol) and 1,4-diethynylbenzene (0.655 g, 5.19 mmol) to give **5b** as a tan solid (0.847 g, 91%). Found: C, 66.9; H, 4.9; N 1.05. $C_{52}H_{45}NOP_2RuS_2$. Anal. Calc.: C, 67.4; H, 4.9; N, 1.5%. IR (ν_{max}/cm^{-1}): 3294 (≡C–H), 2083 (C≡C),1938 (CO) and 1271 (SCS) (KBr). P-NMR ($CDCl_3$): δ 40.3. H-NMR ($CDCl_3$): δ 0.61 (t, 3H, CH_3, ^3J(HH) 7.2 Hz), 0.73 (t, 3H, CH_3, ^3J(HH) 7.2 Hz), 2.79 (q, 2H, CH_2, ^3J(HH) 7.2 Hz), 2.97 (q, 2H, CH_2, ^3J(HH) 7.2 Hz), 3.04 (s, 1H, C≡CH), 6.48 (d, 2H, two of $\equiv CC_6H_4C\equiv$, ^3J(HH) 8.3 Hz), 7.12 (d, 2H, two of $\equiv CC_6H_4C\equiv$, ^3J(HH), 8.3 Hz), 7.35 (m, 18H, PPh_3) and 7.86 (m, 12H, PPh_3).

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