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Insertion reactions of acetylenes with hydridoruthenium(II) carboxylates

S.S. Deshpande, Sarada Gopinathan and C. Gopinathan *
*Inorganic Chemistry Division, National Chemical Laboratory *, Pune 411008 (India)*

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Abstract

Insertion reactions of acetylene, diphenylacetylene and phenylacetylene into the Ru–H bond of $RuH(CO)(OCOR)(PPh_3)_2$ ($R = CH_3$, C_2H_5, C_3H_7, C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) have been studied in benzene at ambient and reflux temperatures. The vinylic complex formed results from *cis*-addition of the Ru–H bond to the triple bond. An excess of phenylacetylene reacts with $RuH(CO)(OCOR)(PPh_3)_2$ in refluxing benzene to give the σ-vinyl alkynyl complex of formula $Ru(CO)(OCOR)(PPh_3)_2\{C(C{\equiv}CPh){=}CHPh\}$ in good yield. The appearance of a single sharp resonance in the ^{31}P NMR spectra of the complexes suggests that both the phosphorus ligands are equivalent, and *trans* to each other in these octahedral Ru^{II} complexes.

Introduction

The complex $RuHCl(CO)(PPh_3)_3$ is a versatile starting material for the synthesis of ruthenium(II) complexes. Torres et al. [1] have shown that $RuHCl(CO)(PPh_3)_3$ reacts with non-activated alkynes to give five-coordinate alkenyl complexes of the type $RuCl(CO)(RC{=}CHR')(PPh_3)_2$. Furthermore reactions of these five-coordinated alkenyl complexes with dimethyl acetylene dicarboxylate [2], 3,5-dimethylpyrazole [3], 3,3-dimethylacrylate [4], or aliphatic carboxylic acids in the presence of a base result in replacement of the chloride ligand and formation of hexacoordinated Ru^{II} complexes [5]. Robinson et al. [6] have shown that when $RuH(OCOCF_3)(CO)(PPh_3)_2$ or $Ru(OCOCF_3)_2(CO)(PPh_3)_2$ reacts with an excess of phenylacetylene an insertion product of the type $Ru(CO)(OCOCF_3)C(C{\equiv}CPh){=}CHPh\}(PPh_3)_2$ is formed. We recently described the insertion of acrylonitrile into the Ru–H bond of hydridoruthenium(II) carboxylates [7]. We describe below the insertions of non-activated acetylenes into the Ru–H bond in some ruthenium(II) carboxylates.

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Experimental

All reactions were carried out under dry, pure nitrogen. Solvents were dried and freshly distilled [8]. The complexes $RuH(CO)(OCOR)(PPh_3)_2$ with R = CH_3, C_2H_5, C_3H_7, C_6H_5, p-$CH_3C_6H_4$ or p-$CH_3OC_6H_4$ were prepared by a published procedure [9]. Diphenylacetylene and phenylacetylene were purchased from the Aldrich Chemical Co. The acetylene used was of high purity.

IR spectra were recorded on a Perkin-Elmer 1605 FT-IR, spectrometer with KBr pellets or Nujol mulls. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker-90 and a Bruker MSL300 spectrometer, respectively. The chemical shifts were determined relative to internal TMS for ^1H and to external 85% *ortho*-phosphoric acid for ^{31}P, positive value indicates a shift to lower field.

General methods for the preparation of ruthenium(II) vinyl complexes from alk-1-ynes

I. [Ru(CO)(OCOR)(PPh$_3$)$_2$(HC=CH$_2$)]

Acetylene was bubbled through a benzene (25 ml) solution of RuH(CO)(OCOR)$(PPh_3)_2$ (1 mmol) at room temperature for 10 min and the bubbling was continued for a further 30 min at refluxing temperature. The resulting clear yellow solution was concentrated to small volume and cooled overnight to give a white crystalline solid, which was washed with n-hexane and dried *in vacuo*. The following complexes were prepared by this method: $Ru(CO)(OCOCH_3)(PPh_3)_2(HC=CH_2)$ (**1**) (0.35 g; 49%), $Ru(CO)(OCOC_2H_5)(PPh_3)_2(HC=CH_2)$ (**3**) (0.30 g; 42%), $Ru(CO)(OCOC_3H_7)(PPh_3)_2(HC=CH_2)$ (**5**) (0.33 g; 46%), $Ru(CO)(OCOC_6H_5)$-$(PPh_3)_2(HC=CH_2)$ (**7**) (0.49 g; 67%), $Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2(HC=CH_2)$ (**10**) (0.39 g; 54%), and $Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2(HC=CH_2)$ (**13**) (0.42 g; 58%).

II. [Ru(CO)(OCOR)(PPh$_3$)$_2$(PhC=CHPh)]

A mixture of diphenylactylene (0.89 g; 5 mmol) and $RuH(CO)(OCOR)(PPh_3)_2$ (1 mmol) in freshly distilled benzene (25 ml) was refluxed for 6 h, to give a clear orange-yellow solution. This was concentrated to 2 ml and layered with hexane under nitrogen to give light yellow crystals which were washed with diethyl ether and n-hexane. Similarly prepared were: $Ru(CO)(OCOCH_3)(PPh_3)_2(PhC=CHPh)$ (**2**) (0.48 g; 55%), $Ru(CO)(OCOC_2H_5)(PPh_3)_2(PhC=CHPh)$ (**4**) (0.33 g; 38%), $Ru(CO)(OCOC_3H_7)(PPh_3)_2(PhC=CHPh)$ (**6**) (0.55 g; 63%), $Ru(CO)(OCOC_6H_5)$-$(PPh_3)_2(PhC=CHPh)$ (**8**) (0.33 g; 39%), $Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2(PhC$-$=CHPh)$ (**11**) (0.21 g; 24%), and $Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2(PhC=CHPh)$ (**14**) (0.49 g; 57%).

III. [Ru(CO)(OCOAr)(PPh$_3$)$_2$(HC=CHPh)]

Phenylacetylene (0.5 ml, excess) was added to a benzene (25 ml) solution of $RuH(CO)(OCOAr)(PPh_3)_2$ (1 mmol) and the mixture was stirred at ambient temperature for 24 h. The resulting yellow solution was concentrated then cooled to give bright yellow crystals. The complexes prepared were: Ru(CO)-$(OCOC_6H_5)(PPh_3)_2(HC=CHPh)$ (**9**) (0.56 g; 71%), $Ru(CO)(OCOC_6H_4CH_3)$-$(PPh_3)_2(HC=CHPh)$ (**12**), (0.28 g; 36%), $Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2$-$(HC=CHPh)$ (**15**) (0.59 g; 75%).

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

Phenylacetylene (0.5 ml, excess) was added to a benzene (25 ml) solution of $RuH(CO)(OCOR)(PPh_3)_2$ (1 mmol) and the mixture was refluxed for 24 h. The resulting clear yellow solution was concentrated to small volume and diluted with hexane, to give a prepicitate of yellow microcrystals. The product was recrystallized from a CH_2Cl_2/hexane mixture. The products prepared in this way were: $Ru(CO)(OCOCH_3)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$ (**16**) (0.45 g; 62%), $Ru(CO)(OCOC_2H_5)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$ (**17**) (0.62 g; 69%), $Ru(CO)(OCOC_3H_7)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$ (**18**) (0.56 g; 63%), $Ru(CO)(OCOC_6H_5)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$ (**19**) (0.67 g; 76%), $Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$ (**20**) (0.63 g; 72%), $Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$ (**21**) (0.52 g; 59%).

Results and discussion

The complex $[RuH_2(CO)(PPh_3)_2]$ reacts with carboxylic acids to give $RuH(CO)(OCOR)(PPh_3)_2$ isolated as yellow solids. These hydridoruthenium carboxylates undergo insertion on treatment with a stoichiometric amount or an excess of acetylene and diphenylacetylene in refluxing benzene, to give the mono-insertion products $Ru(CO(OCOR)(HC=CH_2)(PPh_3)_2$ and $Ru(CO)(OCOR)(PhC=CHPh)(PPh_3)_2$ respectively (Table 1). The complexes are stable in the air, soluble in benzene, chloroform and methylene chloride, and insoluble in petroleum ether. In

Table 1

Melting points and analytical data for insertion complexes of ruthenium(II) with acetylenes

No.	Compound	M.p. (°C)	Analysis (found (calc.))	
			C	H
1	$Ru(CO)(OCOCH_3)(PPh_3)_2(HC=CH_2)$	228	66.42(66.57)	4.56(4.87)
2	$Ru(CO)(OCOCH_3)(PPh_3)_2(PhC=CHPh)$	185	71.02(71.37)	4.63(4.46)
3	$Ru(CO)(OCOC_2H_5)(PPh_3)_2(HC=CH_2)$	214	66.53(66.92)	4.98(5.04)
4	$Ru(CO)(OCOC_2H_5)(PPh_3)_2(PhC=CHPh)$	198	71.82(71.60)	4.68(4.97)
5	$Ru(CO)(OCOC_3H_7)(PPh_3)_2(HC=CH_2)$	185	67.15(67.26)	5.25(5.21)
6	$Ru(CO)(OCOC_3H_7)(PPh_3)_2(PhC=CHPh)$	229	71.61(71.81)	5.27(5.22)
7	$Ru(CO)(OCOC_6H_5)(PPh_3)_2(HC=CH_2)$	206	68.46(68.70)	4.49(4.74)
8	$Ru(CO)(OCOC_6H_5)(PPh_3)_2(PhC=CHPh)$	247	72.88(73.02)	4.38(4.82)
9	$Ru(CO)(OCOC_6H_5)(PPh_3)_2(HC=CHPh)$	214	70.99(71.13)	4.44(4.78)
10	$Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2(HC=CH_2)$	214	69.07(69.11)	4.79(5.02)
11	$Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2(PhC=CHPh)$	189	72.85(73.17)	4.98(5.06)
12	$Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2(HC=CHPh)$	210	71.31(71.44)	4.86(5.05)
13	$Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2(HC=CH_2)$	216	67.52(67.78)	4.67(4.92)
14	$Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2(PhC=CHPh)$	210	71.69(71.94)	4.96(4.97)
15	$Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2(HC=CHPh)$	193	70.16(70.18)	4.59(4.96)
16	$Ru(CO)(OCOCH_3)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$	242	71.73(72.12)	4.42(4.80)
17	$Ru(CO)(OCOC_2H_5)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$	218	72.30(72.33)	4.77(4.95)
18	$Ru(CO)(OCOC_3H_7)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$	212	72.50(72.52)	4.79(5.08)
19	$Ru(CO)(OCOC_6H_5)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$	243	73.47(73.68)	4.96(4.70)
20	$Ru(CO)(OCOC_6H_4CH_3)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$	200	73.62(73.78)	4.66(4.93)
21	$Ru(CO)(OCOC_6H_4OCH_3)(PPh_3)_2\{C(C\equiv CPh)=CHPh\}$	216	72.16(72.61)	4.84(4.86)

Table 2

IR, ^{1}H NMR data for products formed by insertion of acetylene into ruthenium(II) complexes

No.	IR, ν (cm^{-1})				^{1}H NMR δ (ppm)		
	C≡O	C=C	$_{\text{as}}$(OCO)	$_{\text{s}}$(OCO)	aliphatic protons	vinylic protons	aromatic protons
1	1918	1561	1526	1456	0.57s	4.72ddt,	7.20–7.55
2	1911	1568	1531	1459	0.40s	6.50m	6.08–7.50
3	1919	1562	1524	1467	0.08t, 0.80q	4.65ddt, 4.95ddt	7.20–7.40
4	1911	1566	1517	1466	0.16t, 0.94q	6.37m	6.60–7.46
5	1930	1565	1525	1425	0.30–0.80m	4.60ddt, 4.75ddt	7.00–7.45
6	1913	1567	1516	1433	0.35–0.90m	6.30m	7.05–7.45
7	1925	1560	1515	1435	–	4.63ddt, 5.01ddt	6.80–7.50
8	1917	1568	1512	1432	–	6.35m	6.35–7.50
9	1923	1551	1515	1433	–	5.70dt, 7.86dt	6.35–7.53
10	1910	1550	1505	1410	1.70s	4.69ddt, 5.01ddt	6.36–7.40
11	1917	1564	1508	1432	2.20s	6.35m	6.35–7.40
12	1919	1559	1508	1433	2.20s	5.70dt, 7.90dt	6.37–7.56
13	1925	1560	1500	1410	3.67s	4.7ddt, 5.02ddt	6.36–7.40
14	1919	1562	1504	1426	3.65s	6.30m	6.70–7.40
15	1906	1558	1498	1424	3.62s	5.80dt, 7.91dt	6.38–7.50
16 [a]	1942	1592	1518	1461	0.54s	6.22m	6.83–7.50
17 [a]	1943	1593	1511	1471	0.60t, 0.71q	6.22m	6.82–7.50
18 [a]	1945	1595	1513	1434	0.30–0.85m	6.20m	6.80–7.50
19 [a]	1945	1592	1504	1434	–	6.30m	6.80–7.60
20 [a]	1946	1595	1498	1434	2.15s	6.28m	6.65–7.50
21 [a]	1946	1599	1495	1434	3.65s	6.30m	6.80–7.50

[a] C≡C 2103–2105 cm^{-1}; nos. as in Table 1.

chlorinated solvents, the colour of the solution changes to brown from colourless on storage.

The IR spectra of the hydridoruthenium(II) carboxylates show bands at ~ 2000 cm^{-1} and 1930 cm^{-1} attributable to ν(Ru–H) and terminal ν(C≡O), respectively. A band between 1500 and 1530 cm^{-1} is due to ν_{as}(OCO) of the chelated carboxylate. The ν_s(OCO) band is discernible at ~ 1440 cm^{-1}.

Acetylene and diphenylacetylene insertion products (Table 2) show complete absence of the ν(Ru–H) band and the presence of vinylic ν(C=C) bands between 1550 and 1560 cm^{-1}, consistent with addition of Ru–H to the –C≡C– bond. The ν(C≡O) band is shifted to lower frequency (1920 cm^{-1}), indicating increased Ru–CO bond order. The values of $\Delta\nu$(OCO), i.e. [ν_{as}(OCO) – ν_s(OCO)], are lower than those for the corresponding hydridoruthenium carboxylates, because of the strong chelation.

The ^{1}H NMR spectra of the insertion products show an upfield shift for the carboxylic protons suggesting an increase of the electron density at ruthenium compared to that in the starting hydrido complex. The complexes Ru(CO)(OCOR)(HC=CH$_2$)(PPh$_3$)$_2$ show resonances at ~ 4.7 ppm, ^3J(HH)$_{trans}$ = 16 Hz and ~ 5 ppm, ^3J(HH)$_{cis}$ = 6 Hz due to =CH$_2$ protons. The Ru–CH= signal appears along with those from the aromatic protons at ~ 7.4 ppm.

In the case of Ru(CO)(OCOR)(PPh$_3$)$_2$(PhC=CHPh), the alkenyl proton (=CHPh) resonates at 6.3 ppm as a multiplet with ^4J(PH) = 3 Hz. The ^{31}P NMR spectra of the acetylene insertion complexes (Table 3) show a singlet at 38.4 ppm, confirming the

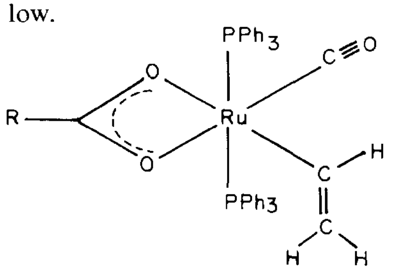
Table 3

^{31}P NMR data for some hydrido ruthenium carboxylates and the products of their reactions with acetylenes

No.		RuH(CO)(OCOR)-(PPh_3)$_2$	Ru(CO)(OCOR)-(PPh_3)$_2$($R^1C{=}CR^2$)
1	R = $OCOCH_3$	44.50s	39.46s [a]
2	= $OCOC_2H_5$	45.43s	39.15s [a]
3	= $OCOC_3H_7$ $R^1 = R^2 = H$	45.07s	38.42s
4	= $OCOC_6H_5$ $R^1 = R^2 = H$	45.23s	38.90s, 39.00s [a]
5	= $OCOC_6H_4CH_3$ $R^1 = R^2 = H$	45.11s	38.43s
6	= $OCOC_6H_4OCH_3$ $R^1 = R^2 = H$	45.14s	38.49s
7	= $OCO_6H_4CH_3$ $R^1 = R^2 = Ph$	45.11s	35.07s
8	= $OCOC_6H_4OCH_3$ $R^1 = R^2 = Ph$	45.14s	35.07s

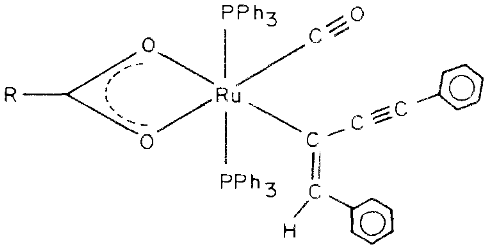
[a] Insertion products of the type Ru(CO)(OCOR)(PPh_3)$_2${C(C≡C–Ph)=CHPh}.

trans disposition of the phosphine ligands. These resonances are at higher field than those for the corresponding hydrido ruthenium carboxylates. The shielding observed for the ^{31}P resonance may be attributed to the presence of the vinylic groups in place of hydrido ligand. A similar upfield shift was also observed for diphenylacetylene insertion compounds. Thus IR, ^{1}H and ^{31}P NMR data are consistent with the stereochemistry of the complex Ru(CO)(OCOR)(PPh_3)$_2$($HC{=}CH_2$) shown below.



An excess of phenylacetylene reacts with RuH(CO)(OCOR)(PPh_3)$_2$ complexes in refluxing benzene to give coordinately saturated σ-vinyl complexes of the formula Ru(CO)(OCOR)(PPh_3)$_2${C(C≡CPh)=CHPh} in good yield. These complexes are also formed in stoichiometric reactions of 1,4-diphenylbutadi-1,3-yne with the appropriate ruthenium hydrido carboxylates [10]. The formation of Ru–{C(C≡CPh)=CHPh} bonds is confirmed by the IR spectra. The ν(C≡C) band of HC≡CPh is shifted only slightly, from 2111 to 2103 cm^{-1}, which rules out metal-acetylide formation. The vinylic ν(C=C) frequency gives rise to a medium band (1595 cm^{-1}). The ν(C≡O) band has been shifted to higher frequency ~ 1940 cm^{-1}, suggesting that the Ru–CO bond order is lower than in the mono-insertion products. The carboxylate chelation is strengthened in these complexes, as can be seen from the Δν(OCO) values. ^{1}H NMR spectra include a multiplet at 6.2 ppm (^4J(PH) = 3 Hz) attributable to the vinylic =CHPh proton. The ^{31}P NMR spectra show a singlet at 39 ppm due to *trans* phosphine ligands.

The ^{13}C NMR spectrum of the complex Ru(CO)($OCOC_6H_4OCH_3$)(PPh_3)$_2$(PhC=CHPh) shows resonances due to terminal and carboxylate carbons at 206 and 176 ppm, respectively. The upfield shift for the terminal carbonyl (204 ppm) accompanied by a downfield shift for the carboxylate carbon (178 ppm) is consistent with the observed reduction in the $\Delta\nu$(OCO) values for the complexes of the type Ru(CO)(OCOR)$(PPh_3)_2$\{C(C≡CPh)=CHPh\}. The data suggest that the complex has the stereochemistry shown below.



The phenylacetylene, being a terminal acetylene, reacts in a different way with the Ru–H bond in ruthenium(II) aromatic carboxylate complexes. Reaction with an excess of phenylacetylene at ambient temperature gives mono-insertion products of the type Ru(CO)(OCOR)$(PPh_3)_2$(HC=CHPh) which were isolated as yellow microcrystals. The IR spectra show features similar to those of acetylene and diphenylacetylene complexes. ^{1}H NMR spectra show a doublet of triplets at 5.7 ppm [$^3J(HH)_{trans}$ = 16 Hz, $^4J(HP)$ = 2 Hz] due to the =CH proton. A similar signal from the Ru–CH= proton is observed at ~ 7.9 ppm. However, aliphatic carboxylates did not give pure mono-insertion compounds in their reactions with phenylacetylene at ambient temperature in either benzene or methylene chloride, but instead a mixture of two products was formed. Even with a 1 : 1 molar proportion the product was a mixture of Ru(CO)(OCOR)$(PPh_3)_2$(HC=CHPh) and Ru(CO)(OCOR)$(PPh_3)_2$\{C(C≡CPh)=CHPh\}. Attempts to separate them in a pure state by fractional crystallization or column chromatography on Florisil were unsuccessful. The IR spectra of the mixtures show a ν(C≡C) band at 2105 cm^{-1} and two carbonyl bands at 1945 and 1925 cm^{-1}. The ^{1}H NMR spectra also show resonances for vinylic protons for both products. The ^{13}C NMR spectra do not show signals due to Ru=C at ~ 360 ppm, which rules out the formation of a Ru–vinylidene bond such as that reported by Robinson et al. [6].

Work in progress is aimed at establishing the mechanism of the reaction giving rise to formation of the alkynyl alkene ruthenium(II) complexes.

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