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Reactions of $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$ and $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ with terminal alkynes: synthesis and characterization of new five- and six-coordinate bis(alkynyl) and alkynyl(vinyl) derivatives of ruthenium(II)

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Abstract

The reaction of the complex $[RuHCl(CO)(P^iPr_3)_2]$ with C_3H_5MgBr affords $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$ (**2**). This complex reacts with terminal alkynes. With CyC_2H it yields $[Ru(C_2Cy)_2(CO)(P^iPr_3)_2]$ (**3**), whereas with Me_3SiC_2H it gives a mixture of $[Ru(C_2SiMe_3)_2(CO)(P^iPr_3)_2]$ (**4**) and $[Ru(C_2SiMe_3)\{(E)\text{-}CH{=}CHSiMe_3\}(CO)(P^iPr_3)_2]$(**5**). **4** was obtained as a spectroscopically pure oil by reaction of $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ (**15**) with Me_3SiC_2H. **2** also reacts with PhC_2Ph giving $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ (**6**), which with RC_2H then yields $[Ru(C_2R)\{(E)\text{-}CH{=}CHR\}(CO)(P^iPr_3)_2]$ (R = Cy (**11**), or $-CO_2CH_3$ (**12**)). Under CO, **3** and **4** give $[Ru(C_2R)_2(CO)_2(P^iPr_3)_2]$(R = Cy (**7**) or ($Me_3Si$ (**8**)), but **5**, **11** and **12** afford $[Ru(C_2R)\{(E)\text{-}CH{=}CHR\}(CO)_2(P^iPr_3)_2]$ (R = Me_3Si (**9**), Cy (**13**), or $-CO_2CH_3$ (**14**)). **15** catalyzes the cyclotrimerization of methyl propiolate to give a mixture of $1,3,5\text{-}C_6H_3(CO_2CH_3)_3$ and $1,2,4\text{-}C_6H_3(CO_2CH_3)_3$ in a 2 : 1 molar ratio.

Keywords: Ruthenium; Bis(alkynyl) complexes; Alkynyl(vinyl) complexes; Allyl complexes; Reactions

1. Introduction

Reactions of late transition metal complexes with terminal alkynes have attracted a great deal of attention in recent years [1–6]. Much of this has been stimulated by their connection with important homogeneous catalytic processes such as oligomerization [7], reduction [8], hydrosilylation [9] and silylformylation [10] of alkynes, condensation of allylic alcohols with terminal alkynes to provide γ,δ-unsaturated ketones [11], and addition of alkenes to alkynes [12].

We have reported previously that the five-coordinate hydridoruthenium complex $[RuHCl(CO)(P^iPr_3)_2]$ reacts with $NaBH_4$ in benzene–methanol to give the octahedral compound $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ [13], which by reaction with diphenylacetylene affords $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ [14]. We have now observed that the reaction of $[RuHCl(CO)(P^iPr_3)_2]$ with allylmagnesium bromide leads to $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$.

We also report the reactivity of $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$ and $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ with cyclohexylacetylene, trimethylsilylacetylene and methyl propiolate. In addition, we describe the catalytic activity of the tetrahydridoborato-complex $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ in the cyclotrimerization of methyl propiolate.

2. Results and discussion

2.1. *Synthesis and reactions of $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$*

Treatment of a THF solution of the five-coordinate carbonylhydrido-complex $[RuHCl(CO)(P^iPr_3)_2]$ (**1**) with 1.8 equivalents of a diethyl ether solution of C_3H_5MgBr results in the formation of $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$ (**2**), which was isolated in 80% yield. This compound, which is a yellow air-sensitive solid, is stable for one week if kept under argon at

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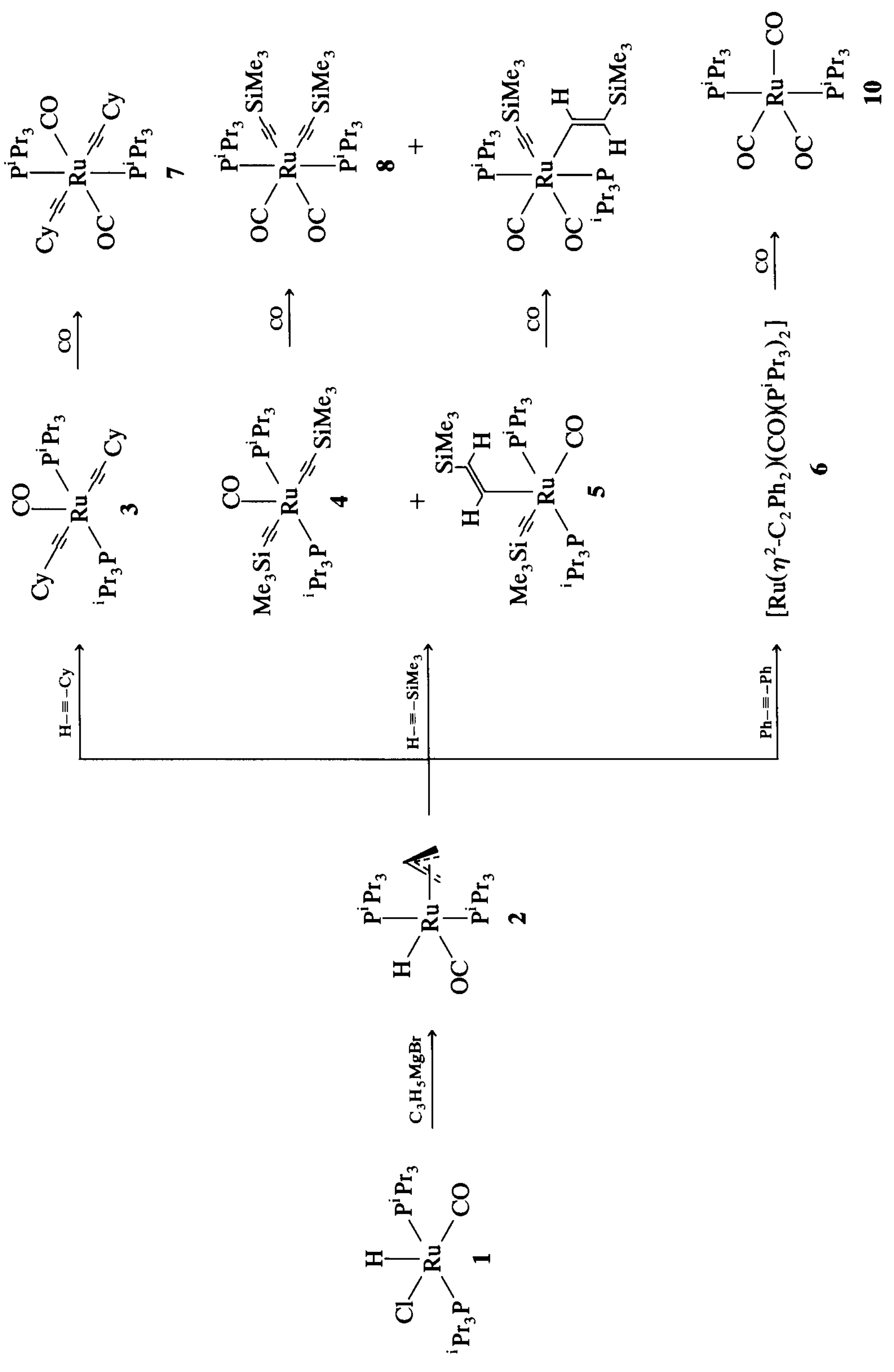

1
C_3H_5MgBr
2
H–≡–Cy
H–≡–$SiMe_3$
Ph–≡–Ph
3
4
5
[Ru(η^2-C_2Ph_2)(CO)(P^iPr_3)$_2$]
6
CO
7
8
10

Scheme 1.

−20°C. However, it decomposes in solution to an ill-defined straw-coloured solid after 20 min.

The ^{1}H NMR spectrum of **2** in benzene-d_6 shows a hydride resonance at −8.55 ppm, which appears as a doublet of doublets with P–H coupling constants of 19.8 and 33.1 Hz, and the resonances of five nonequivalent protons corresponding to the η^3-C_3H_5 group, with no molecular plane of symmetry containing the central allyl carbon. The $^{31}P\{^1H\}$ NMR spectrum exhibits an AB pattern with $J(AB) = 232.5$ Hz, which requires two mutually *trans* phosphines. The nonequivalence of the two phosphines shows that the molecule has no plane of symmetry containing the P–Ru–P unit. These spectroscopic data are in good agreement with those previously reported for the related compounds $[MH(\eta^3\text{-}C_3H_5)(CO)(P^tBu_2Me)_2]$(M = Ru [15] or Os [16]) and $[OsH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$ [16], and suggest that the structure of **2** is that shown in Scheme 1.

Complex **2** reacts with terminal alkynes such as cyclohexylacetylene and trimethylsilylacetylene, and also with diphenylacetylene (Scheme 1). The reaction of **2** with cyclohexylacetylene leads to the five-coordinate bis(alkynyl) derivative **3**, whereas the reaction of **2** with trimethylsilylacetylene affords a mixture of the bis(alkynyl) complex **4** and the alkynyl(vinyl) compound **5** in a 1:3 molar ratio. The bis(alkynyl) complex **4** was prepared as a spectroscopically pure oil by reaction of the tetrahydridoborato-compound $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ with trimethylsilylacetylene. The reaction of **2** with diphenylacetylene leads to the previously reported complex $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ (**6**) [14].

Complex **3** was isolated as a pure solid in 72% yield. The structure proposed in Scheme 1 is strongly supported by the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra in benzene-d_6. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 52.8 ppm, indicating that the phosphines are equivalent and mutually *trans*. In the $^{13}C\{^1H\}$ NMR spectrum, only one acetylide C_α triplet at 112.66 ppm ($J(PC) = 14.1$ Hz) is observed, suggesting that both alkynyl groups are equivalent and mutually *trans*. Similar structures have been proposed for the complexes $[Ru(C_2Ph)_2(CO)(PR_3)_2]$ ($PR_3 = P^iPr_3$ [17] or PBu^t_2Me [18]) on the basis of their $^{13}C\{^1H\}$ NMR spectra.

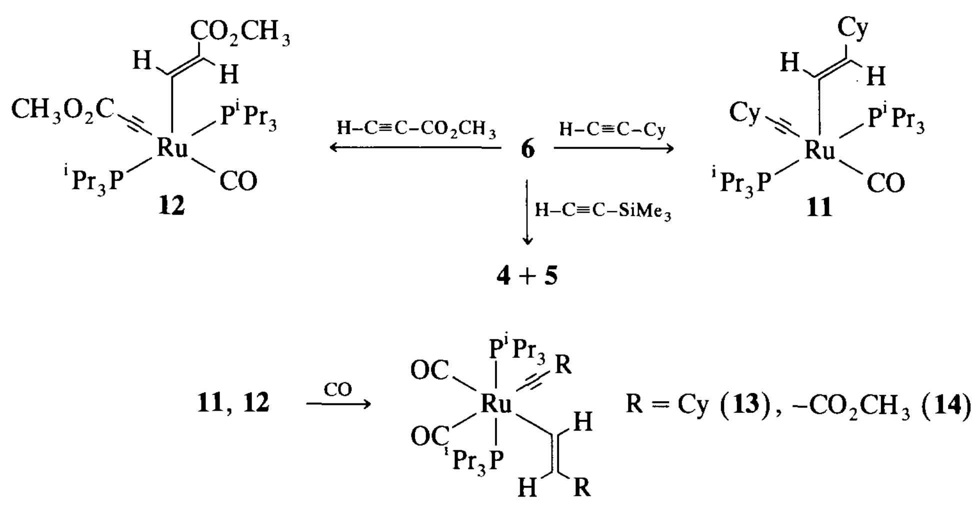
The equivalence of both alkynyl ligands of **4** is demonstrated by the ^{1}H NMR spectrum of the compound, which contains only one resonance, at 0.30 ppm, for their methyl groups. In the ^{1}H NMR spectrum of **5** the methyl groups of the alkynyl and the vinyl display singlets at 0.11 and 0.30 ppm. Furthermore, the spectrum contains two doublets of triplets at 8.30 and 5.62 ppm assigned to the α- and β-protons of the vinyl, respectively. The *trans* stereochemistry at the carbon–carbon double bond of the group $RuCH{=}CH(SiMe_3)$ is strongly supported by the proton–proton coupling constant of 13.7 Hz, which is a typical value for this arrangement in similar pentacoordinate compounds [19].

The coordination number six for **3**–**5** can be achieved by reaction with carbon monoxide. On passing a slow stream of carbon monoxide through an hexane solution of **3**, or methanol solutions of **4** and **5**, the dicarbonyl compounds **7**–**9** are formed (Scheme 1). As the IR spectrum of **7** shows only one $\nu(C{\equiv}O)$ band we assume that the two carbonyls of this complex are *trans*. However, and in agreement with a *cis* disposition for the two carbonyls in **8** and **9**, the corresponding IR spectra contain two $\nu(CO)$ bands at 2015 and 1980 (**8**), and at 2000 and 1950 (**9**) cm^{-1}.

Under carbon monoxide the π-alkyne complex **6** affords **10** in 27% yield (Scheme 1) and diphenylacetylene [14].

2.2. Reactivity of $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ with terminal alkynes

These investigations are summarized in Scheme 2. Whereas the reactions with cyclohexylacetylene and methyl propiolate lead to the five-coordinate alkynyl-



Scheme 2.

(vinyl) derivatives **11** and **12**, the reaction with trimethylsilylacetylene affords a mixture of the bis(alkynyl) complex **4** and the alkynyl(vinyl) compound **5** in a 1 : 1 molar ratio. During these reactions, diphenylacetylene is hydrogenated to *cis*- (three parts) and *trans*-stilbene (one part), suggesting that the reactions involve the formation of hydride intermediates.

Complex **11** was isolated as a brown solid in 80% yield, and was characterized by elemental analysis and IR, ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectroscopies. The most noticeable absorptions in the IR spectrum in Nujol are three bands at 1995, 1910 and 1580 cm^{-1}, which are assigned to $\nu(C{\equiv}C)$, $\nu(C{\equiv}O)$ and $\nu(C{=}C)$, respectively. The α and β protons of the vinyl give rise to two resonances in the ^{1}H NMR spectrum at 6.95 and 5.04 ppm. The *trans* stereochemistry at the carbon–carbon double bond is supported by the proton–proton coupling constant of 12.7 Hz. In the $^{13}C\{^{1}H\}$ NMR spectrum the α and β carbon atoms of the vinyl display triplets at 136.6 and 140.6 ppm, with P–C coupling constants of 10.8 and 6.8 Hz, respectively. The Ru–C≡ carbon atom appears at 120.1 ppm as a triplet with a P–C coupling constant of 18.9 Hz. The $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet at 43.0 ppm.

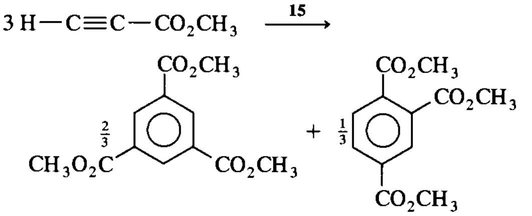
Complex **12** was isolated as a red–brown oil, and characterized by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. In the ^{1}H NMR spectrum, the vinyl gives rise to two doublets at 10.18 and 6.25 ($J(HH) = 13.8$ Hz) ppm, assigned to the α and β protons. The protons of the $-OCH_3$ groups of the alkynyl and vinyl appear as singlets at 3.51 and 3.46 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum has a singlet at 44.5 ppm.

Similarly to **5**, complexes **11** and **12** react with carbon monoxide to give the dicarbonyl derivatives, **13** and **14**, which were isolated as white solids. The IR and NMR spectra of these compounds are consistent with the proposed structures. The IR spectra show two $\nu(CO)$ bands at 2000 and 1945 cm^{-1} (**13**), and at 2010 and 1960 cm^{-1} (**14**). The most noticeable signals in the ^{1}H NMR spectra are the resonances due to the vinyl ligands. The vinyl protons of **13** display a doublet at 7.05 ppm with a H–H coupling constant of 17.3 Hz and a doublet of doublets at 5.80 ppm with H–H coupling constants of 17.3 and 6.8 Hz. The first signal is assigned to the α proton, and the second to the β proton. In the ^{1}H NMR spectrum of **14**, the RuCH=CH– unit gives rise to two doublets of triplets at 9.79 (H_α; $J(HH) = 18.2$ Hz, $J(PH) = 4.8$ Hz) and 5.37 (H_β; $J(HH) = 18.2$ Hz, $J(PH) = 4.4$ Hz) ppm. The $^{31}P\{^{1}H\}$ NMR spectra show singlets at 40.9 (**13**) and 41.9 (**14**) ppm.

2.3. Cyclotrimerization of methyl propiolate catalyzed by [RuH(η²-H₂BH₂)(CO)(PⁱPr₃)₂]

It has been previously mentioned that $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ (**15**) reacts with trimethylsilylacetylene to give the bis(alkynyl) compound **4**, isolated as a spectroscopically pure oil. The reaction was carried out in hexane at reflux temperature and with a ruthenium–alkyne molar ratio of 1 : 6. Under the same conditions, the treatment of a hexane solution of **15** with methyl propiolate in a 1 : 6 molar ratio leads to a mixture of **15**, $1,3,5\text{-}C_6H_3(CO_2CH_3)_3$ and $1,2,4\text{-}C_6H_3(CO_2CH_3)_3$.

This unexpected finding prompted us to study the catalytic activity of **15** in the cyclotrimerization of methyl propiolate (Eq. 1). The formation of 0.05 M of $1,3,5\text{-}C_6H_3(CO_2CH_3)_3$ and 0.03 M of $1,2,4\text{-}C_6H_3(CO_2CH_3)_3$ by treatment of 0.24 M of methyl propiolate with 2.4×10^{-3} M of **15** in hexane at 69°C was observed after 13 h.



(1)

It has been reported previously that **15** is a catalyst (or catalyst precursor) for hydrogen transfer reactions of 2-propanol to cyclohexanone, acetophenone [20], benzylideneacetophenone [21] and phenylacetylene [17], and for the addition of triethylsilane to phenylacetylene [22]. Our evidence indicates that **15** is also a catalyst for the cyclotrimerization of methyl propiolate. This type of reaction is one of the most interesting processes in organometallic chemistry [23].

3. Experimental details

All reactions were carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $[RuHCl(CO)(P^iPr_3)_2]$ [24] and $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ [13] were prepared by published methods.

NMR spectra were recorded on a Varian 200 XL or on a Varian UNITY 300 spectrometer. Chemical shifts are expressed in ppm upfield from Me_4Si ($^{13}C\{^{1}H\}$, ^{1}H) and 85% H_3PO_4 ($^{31}P\{^{1}H\}$). Coupling constants *J* and *N* are given in Hz. IR spectra were run on a Perkin Elmer 783 spectrophotometer (Nujol mulls on polyethylene sheets). C, H and N analyses were carried out with a Perkin Elmer 240C microanalyzer. Gas chromatography (GC) analysis was performed on a Perkin Elmer 8500 gas chromatograph with a flame ionizator detector and an FFAP (Free Fatty Acids Phase) on Chromosorb GHP 80/100 mesh (3.6 × 1/8 in) column at 200°C (*cis*- and *trans*-stilbene) or at 100°C (methyl propiolate). Mass spectral analyses were performed with a VG

AutoSpec instrument connected to a Konik HRGC-3000 gas chromatograph equipped with an HP-1 capillary column (Crosslinked Methyl Silicone Gum; 25 m × 0.2 mm × 0.33 μm film thickness). Ionization was by electron impact, operating at 70 eV.

3.1. Preparation of $[RuH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2]$ (2)

A solution of **1** (200 mg, 0.41 mmol) in 10 ml of THF was treated with $BrMgCH_2CH{=}CH_2$ (1.7 ml, 1.0 M in diethyl ether, 0.75 mmol). The orange solution became yellow upon addition of the reagent. The solvent was removed in vacuo and the crude product was extracted with 40 ml of hexane. The suspension was filtered and concentrated to ca. 2 ml. Yellow crystals were formed. Yield: 161 mg (80%). ^1H NMR (300 MHz, C_6D_6): δ 5.00 (dtt, 1H, $J(HH_{syn}) = 6.8$, $J(HH_{anti}) = 10.4$, $J(PH) = 3.5$, CH_2CHCH_2), 2.93 (d, 1H, $J(HH_{syn}) = 6.8$, H_{syn}), 2.57 (dd, 1H, $J(HH_{anti}) = 10.8$, $J(PH) = 3.1$, H_{anti}) (the resonance due to the other *anti* hydrogen atom is masked by one Pr^i resonance), 2.05 (m, 3H, $PCHCH_3$), 1.87 (m, 3H, $PCHCH_3$), 1.76 (d, 1H, $J(HH_{syn}) = 5.5$, H_{syn}), 1.2 (m, 36H, $PCHCH_3$), −8.55 (dd, 1H, $J(PH) = 19.8$, $J(P'H) = 33.1$, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): AB spin system, $\delta_A = 68.5$, $\delta_B = 59.8$, $J = 232.5$.

3.2. Preparation of $[Ru(C_2Cy)_2(CO)(P^iPr_3)_2]$ (3)

A solution of **2** (160 mg, 0.33 mmol) in 10 ml of hexane was treated with a 4:1 excess of CyC_2H (170 μl, 1.32 mmol). After stirring for 12 h at room temperature, 10 ml of hexane were added. MS analysis of a sample of this solution showed the presence of $C_6H_3(Cy)_3$ (*m/e* 324). The solution was then filtered and the solvent was removed in vacuo. Addition of MeOH caused the precipitation of a purple solid which was repeatedly washed with MeOH and dried in vacuo. Yield: 158 mg (72%). Anal. Calc. for $C_{35}H_{64}OP_2Ru$: C, 63.32; H, 9.72%. Found: C, 63.82; H, 8.27%. IR (Nujol, cm^{-1}): $\nu(CO)$ 1925 vs. ^1H NMR (300 MHz, C_6D_6): δ 3.00 (m, 6H, $PCHCH_3$), 2.68, 2.00 1.77, 1.50 (all m, 22H, Cy), 1.30 (dvt, 36H, $N = 13.7$, $J(HH) = 7.1$, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 52.8 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 208.15 (t, $J(CP) = 12.9$, CO), 126.77 (s, ≡CCy), 112.66 (t, $J(PC) = 14.1$, Ru–C≡), 35.07, 33.23, 26.76, 25.95 (all s, Cy), 25.44 (vt, $N = 22.1$, $PCHCH_3$), 20.30 (s, $PCHCH_3$).

3.3. Preparation of $[Ru(C_2SiMe_3)_2(CO)(P^iPr_3)_2]$ (4)

A solution of **15** (117.9 mg, 0.25 mmol) in 6 ml of hexane was treated with a 6:1 excess of Me_3SiC_2H (215 μl, 1.50 mmol). After stirring for 7 h at reflux temperature, the solution was concentrated to dryness. A brown oil was obtained. ^1H NMR (300 MHz, C_6D_6): 2.70 (m, 6H, $PCHCH_3$), 1.26 (dvt, 36H, $N = 13.8$, $J(HH) = 7.2$, $PCHCH_3$), 0.30 (s, 18H, $SiMe_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): 51.3 (s).

3.4. Preparation of $[Ru(C_2SiMe_3)_2(CO)(P^iPr_3)_2]$ (4) and $[Ru(C_2SiMe_3)\{(E)\text{-}CH{=}CHSiMe_3\}(CO)(P^iPr_3)_2]$ (5)

3.4.1. Route (a): reaction of 2 with Me_3SiC_2H

A solution of **2** (160 mg, 0.33 mmol) in 8 ml of hexane was treated with a 4:1 excess of Me_3SiC_2H (188 μl, 1.33 mmol). After stirring for 18 h, the solution was filtered and the solvent was removed. Addition of MeOH caused the precipitation of a cream solid which became red–brown when dried in vacuo. Crude yield: 109 mg (60%). The solid was characterized by NMR spectroscopy as a mixture of compounds **4** and **5** in a 1:3 molar ratio.

3.4.2. Route (b): reaction of 6 with Me_3SiC_2H

A suspension of **6** (94 mg, 0.15 mmol) in 5 ml of hexane was treated with a 2:1 excess of Me_3SiC_2H (44 μl, 0.30 mmol). After stirring for 1 h at room temperature, the mixture was filtered and the solution was taken to dryness. The residue was treated with 5 ml of MeOH and a red–brown solid was formed, which was filtered off, washed with MeOH and dried in vacuo. Crude yield: 46 mg (55%). The solid was identified by NMR spectroscopy as a mixture of compounds **4** and **5** in a 1:1 molar ratio. Spectroscopic data for **5**: ^1H NMR (300 MHz, C_6D_6): 8.30 (dt, 1H, $J(H_\alpha H_\beta) = 13.7$, $J(PH) = 0.9$, Ru–CH=), 5.62 (dt, 1H, $J(H_\alpha H_\beta) = 13.7$, $J(HP) = 2.3$, $=CHSiMe_3$), 2.90 (m, 6H, $PCHCH_3$), 1.26 (dvt, 18H, $N = 13.8$, $J(HH) = 7.2$, $PCHCH_3$), 1.17 (dvt, 18H, $N = 13.3$, $J(HH) = 7.1$, $PCHCH_3$), 0.30 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): 43.7 (s).

3.5. Preparation of $[Ru(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]$ (6). Reaction of 2 with PhC_2Ph

A solution of **2** (160 mg, 0.33 mmol) in 10 ml of hexane was treated with a 3:1 excess of PhC_2Ph (178 mg, 1 mmol). After stirring for 3 h, the solvent was removed and 3 ml of acetone were added. The purple crystals obtained were washed several times with cold acetone and dried in vacuo. Yield: 161 mg (78%). IR (Nujol, cm^{-1}): $\nu(CO)$ 1850s, $\nu(C{=}C)$ 1650m, 1590w. ^1H NMR (300 MHz, C_6D_6): δ 7.50–7.00 (m, 10H, Ph), 2.22 (m, 6H, $PCHCH_3$), 1.19, 1.16 (both dvt, 18H each, N = 13.2, $J(HH) = 7.1$, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 71.5 (s).

3.6. Preparation of $[Ru(C_2Cy)_2(CO)_2(P^iPr_3)_2]$ (7)

A stream of CO was bubbled through a solution of **3** (158 mg, 0.23 mmol) in 6 ml of hexane for 2 min. The dark purple solution became yellow instantaneously. After concentration to ca. 1 ml, addition of MeOH caused the precipitation of white crystals. The solid was washed several times with MeOH and dried in vacuo. Yield: 129 mg (81%). Anal. Calc. for $\mathrm{C_{36}H_{64}O_2P_2Ru}$: C, 62.49; H, 9.32%. Found: C, 62.70; H, 7.05%. IR (Nujol, $\mathrm{cm^{-1}}$): ν(CO), 1975 vs. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 2.70 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 2.50, 1.90 1.70, 1.20 (all m, 22H, Cy), 1.40 (dvt, 36H, $N = 13.7$, J(HH) = 7.1, $\mathrm{PCHC}H_3$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (80.9 MHz, $\mathrm{C_6D_6}$): δ 46.5 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 203.54 (t, J(CP) = 12.9, CO), 115.39 (s, ≡CCy), 86.43 (t, J(PC) = 13.3, Ru–C≡), 35.21, 32.99, 26.78 (all s, Cy), 25.02 (vt, $N = 23.0$, $\mathrm{P}C\mathrm{HCH_3}$), 19.99 (s, $\mathrm{PCH}C\mathrm{H_3}$).

3.7. Preparation of $[\mathrm{Ru(C_2SiMe_3)_2(CO)_2(P^iPr_3)_2}]$ (8)

A solution of **15** (117.9 mg, 0.25 mmol) in 6 ml of hexane was treated with $\mathrm{Me_3SiC_2H}$ (215 μl, 1.5 mmol) and left to stir for 7 h at reflux temperature. After taking dryness, 15 ml of MeOH were added and carbon monoxide was then bubbled through for 15 min. The solution was concentrated to ca. 1 ml and then stored at −78°C. The white solid that separated was filtered off, washed with cold MeOH, and dried in vacuo. Yield: 70 mg (42%). Anal. Calc. for $\mathrm{C_{30}H_{60}O_2P_2RuSi_2}$: C, 53.62; H, 9.00%. Found: C, 53.51; H, 9.75%. IR (Nujol, $\mathrm{cm^{-1}}$): ν(C≡C) 2060m, ν(CO) 2015s, 1980s. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 2.70 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.37 (dvt, 36H, $N = 13.8$, J(HH) = 7.1, $\mathrm{PCHC}H_3$), 0.26 (s, 18H, $\mathrm{SiMe_3}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (80.9 MHz, $\mathrm{C_6D_6}$): δ 46.1 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 202.01 (t, J(CP) = 11.0, CO), 132.02 (t, J(PH) = 15.0, Ru–C≡), 119.01 (s, $\mathrm{{\equiv}CSiMe_3}$), 26.03 (vt, $N = 23$, $\mathrm{P}C\mathrm{HCH_3}$), 19.72 (s, $\mathrm{PCH}C\mathrm{H_3}$), 1.30 (s, $\mathrm{Si(CH_3)_3}$).

3.8. Reaction of a mixture of 4 and 5 with carbon monoxide: preparation of $[\mathrm{Ru(C_2SiMe_3)\{(}E\mathrm{)\text{-}CH{=}CHSiMe_3\}(CO)_2(P^iPr_3)_2}]$ (9)

Carbon monoxide was bubbled through a mixture of complexes **4** and **5** (90 mg, 0.16 mmol) in a 1 : 1 ratio, in 20 ml of methanol for 15 min. Concentration of the solution to ca. 2 ml caused the precipitation of a white solid, which was filtered off, washed with methanol and dried in vacuo. Crude yield: 55 mg. The solid was identified by NMR and IR spectroscopies as a mixture of **8** and **9** in a 1 : 2 ratio. By comparison of the spectra of the mixture with those of a pure sample of **8** we were able to assign the signals due to compound **9**. Spectroscopic data for **9**: IR (Nujol, $\mathrm{cm^{-1}}$): ν(CO) 2000vs, 1950vs. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.50 (dt, 1H, $J(\mathrm{H_\alpha H_\beta}) = 21.4$, J(PH) = 2.5, Ru–CH=), 6.71 (dt, 1H, $J(\mathrm{H_\alpha H_\beta}) = 21.4$, J(HP) = 1.8, $\mathrm{{=}CHSiMe_3}$), 2.60 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.38 (dvt, 18H, $N = 14.0$, J(HH) = 7.3, $\mathrm{PCHC}H_3$), 1.19 (dvt, 18H, $N = 12.6$, J(HH) = 7.1, $\mathrm{PCHC}H_3$), 0.29 (s, 9H, $\mathrm{SiMe_3}$), 0.22 (s, 9H, $\mathrm{SiMe_3}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (80.9 MHz, $\mathrm{C_6D_6}$): 40.4 (s).

3.9. Preparation of $[\mathrm{Ru(C_2Cy)\{(}E\mathrm{)\text{-}CH{=}CHCy\}(CO)(P^iPr_3)_2}]$ (11)

A suspension of **6** (90 mg, 0.14 mmol) in 5 ml of hexane was treated with a 2 : 1 excess of $\mathrm{CyC_2H}$ (37.3 μl, 0.29 mmol). After stirring for 1 h at room temperature, the solution was filtered and taken to dryness. Addition of 5 ml of MeOH caused the precipitation of a brown solid which was washed with MeOH and dried in vacuo. Yield: 73 mg (80%). Anal. Calc. for $\mathrm{C_{35}H_{66}OP_2Ru}$: C, 63.12; H, 9.99%. Found: C, 63.35; H, 10.72%. IR (Nujol, $\mathrm{cm^{-1}}$): ν(C≡C) 1995vw, ν(CO) 1910vs, ν(C=C) 1580m. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 6.95 (d, 1H, $J(\mathrm{H_\alpha H_\beta}) = 12.7$, Ru–CH=), 5.04 (ddt, 1H, $J(\mathrm{H_\alpha H_\beta}) = 12.7$, J(HP) = 2.6, $J(\mathrm{H_\alpha H_{Cy}}) = 7.4$, J(HP) = 2.6, =CHCy), 2.77 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 2.64, 2.15–1.44, 1.15 (all m, 22H, Cy), 1.33 (dvt, 18H, $N = 13.4$, J(HH) = 7.0, $\mathrm{PCHC}H_3$), 1.25 (dvt, 18H, $N = 13.0$, J(HH) = 6.9, $\mathrm{PCHC}H_3$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.4 MHz, $\mathrm{C_6D_6}$): 43.0 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 205.06 (t, J(CP) = 12.9, CO), 140.57 (t, J(PC) = 6.8, =CHCy), 136.58 (t, J(PC) = 10.8, Ru–CH), 120.10 (t, J(PC) = 18.9, Ru–C≡), 45.18, 34.89, 34.45, 34.20, 32.81, 26.59, 26.55, 26.44, 25.68 (all s, Cy), 25.14 (vt, N = 19.4, $\mathrm{P}C\mathrm{HCH_3}$), 20.03, 19.77 (both s, $\mathrm{PCH}C\mathrm{H_3}$). GC analysis of 0.2 μl of the mother liquor shows the presence of *cis*- and *trans*-stilbene in a 3 : 1 molar ratio.

3.10. Preparation of $[\mathrm{Ru(C_2CO_2Me)\{(}E\mathrm{)\text{-}CH{=}CHCO_2Me\}(CO)(P^iPr_3)_2}]$ (12)

A suspension of **6** (132.8 mg, 0.21 mmol) in 8 ml of hexane was treated with a 2 : 1 excess of $\mathrm{HC_2CO_2Me}$ (37 μl, 0.42 mmol). After stirring for 1 h at room temperature the solution was filtered through Celite, and the clear solution obtained was taken to dryness. A red–brown oil was formed. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 10.18 (d, 1H, $J(\mathrm{H_\alpha H_\beta}) = 13.8$, Ru–CH=), 6.25 (d, 1H, $J(\mathrm{H_\alpha H_\beta}) = 13.8$, $\mathrm{{=}C}H\mathrm{CO_2CH_3}$), 3.51 (s, 3H, $\mathrm{CO_2C}H_3$), 3.46 (s, 3H, $\mathrm{CO_2C}H_3$), 2.49 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.14 (dvt, 18H, $N = 13.8$, J(HH) = 7.2, $\mathrm{PCHC}H_3$), 1.03 (dvt, 18H, $N = 13.7$, J(HH) = 7.1, $\mathrm{PCHC}H_3$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.4 MHz, $\mathrm{C_6D_6}$): 44.5 (s).

3.11. Preparation of $[\mathrm{Ru(C_2Cy)\{(}E\mathrm{)\text{-}CH{=}CHCy\}(CO)_2(P^iPr_3)_2}]$ (13)

Carbon monoxide was bubbled through a solution of **11** (87 mg, 0.13 mmol) in 10 ml of hexane for 15 min. The solution was taken to dryness. Addition of 3 ml of methanol caused the precipitation of a white solid which was filtered off, washed with methanol and dried in vacuo. Yield: 70 mg (78%). Anal. Calc. for

$C_{36}H_{66}O_2P_2Ru$: C, 62.31; H, 9.59%. Found: C, 62.02; H, 10.73%. IR (Nujol, cm^{-1}): ν(CO), 2000s, 1945s. ^1H NMR (300 MHz, C_6D_6): δ 7.05 (d, 1H, $J(H_\alpha H_\beta) = 17.3$, Ru–CH), 5.80 (dd, 1H, $J(H_\alpha H_\beta) = 17.3$, $J(H_\alpha H_{Cy}) = 6.8$, =CHCy), 2.68 (m, 6H, PC*H*CH_3), 2.5–1.2 (m, 22H, Cy), 1.45 (dvt, 18H, $N = 14.1$, $J(HH) = 7.0$, PCHCH_3), 1.22 (dvt, 18H, $N = 12.6$, $J(HH) = 6.7$, PCHCH_3). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 40.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 203.59 (t, $J(CP) = 9.2$, CO), 199.95 (t, $J(CP) = 9.2$, CO), 146.56 (t, $J(PC) = 13.3$, Ru–CH), 145.83 (s, =CHCy), 114.48 (s, ≡CCy), 97.60 (t, $J(PC) = 20.6$, Ru–C≡), 48.10, 34.72, 33.69, 33.06, 26.96, 26.72, 26.20 (all s, Cy), 25.08 (vt, $N = 21.6$, P*C*HCH_3), 20.68, 19.28 (both s, PCH*C*H_3).

3.12. Preparation of $[Ru(C_2CO_2Me)\{(E)\text{-}CH=CHCO_2Me\}(CO)_2(P^iPr_3)_2]$ (14)

A suspension of **7** (100 mg, 0.16 mmol) in 10 ml of hexane was treated with a 2:1 excess of HC_2CO_2Me (30 μl, 0.32 mmol). A brown solution was formed. After stirring for 30 min, carbon monoxide was bubbled through the solution for 15 min. The solution was concentrated to ca. 2 ml and a white solid separated, which was filtered off, washed with hexane and dried in vacuo. IR (Nujol, cm^{-1}): ν(C≡C) 2110m, ν(CO) 2010s, 1960s, ν(C=O) 1705m, 1685s. ^1H NMR (300 MHz, C_6D_6): δ 9.79 (dt, 1H, $J(H_\alpha H_\beta) = 18.2$, $J(PH) = 4.8$, Ru–CH), 5.37 (dt, 1H, $J(H_\alpha H_\beta) = 18.2$, $J(PH) = 4.4$, =C*H*CO_2CH_3), 3.56 (s, 3H, $-CO_2CH_3$), 3.43 (s, 3H, $-CO_2CH_3$), 2.41 (m, 6H, PC*H*CH_3), 1.29 (dvt, 18H, $N = 14.4$, $J(HH) = 7.1$, PCHCH_3), 1.04 (dvt, 18H, $N = 13.3$, $J(HH) = 7.1$, PCHCH_3). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 41.9 (s).

3.13. Reaction of $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ (15) with HC_2CO_2Me

A solution of **15** (117.9 mg, 0.25 mmol) in 6 ml of hexane was treated with a 6:1 excess of HC_2CO_2Me (137 μl, 1.50 mmol). After stirring for 7 h at reflux temperature, the solution was concentrated to ca. 2 ml. A yellow solid precipitated, which was washed with cold hexane and dried in vacuo. The IR and ^1H NMR spectra showed this to be a mixture of **15**, 1,3,5-$C_6H_3(CO_2CH_3)_3$ and 1,2,4-$C_6H_3(CO_2CH_3)_3$. Recrystallization from methanol afforded **15**. Spectroscopic data for **15**: IR (C_6H_6, cm^{-1}) ν(BH), 2420, 2320, ν(RuH), 2010, ν(CO), 1930. ^1H NMR (300 MHz, C_6D_6): δ 2.45 (m, 6H, PC*H*CH_3), 1.35 (dvt, 36H, $N = 12$, PCHCH_3), −14.12 (t, 1H, $J(PH) = 20$, Ru–H). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 60.2 (s). Spectroscopic data for 1,3,5-$C_6H_3(CO_2CH_3)_3$: ^1H NMR (C_6D_6, 300 MHz): 8.99 (s, 3H), 3.35 (s, 9H). MS: *m/e* 252 (M^+), 221 (M^+ −31, $-OCH_3$), 75 (M^+ −177, $-(CO_2CH_3)_3$. Spectroscopic data for 1,2,4-$C_6H_3(CO_2CH_3)_3$: ^1H NMR (C_6D_6, 300 MHz): 8.48 (d, 1H, $J = 1.7$), 7.88 (dd, 1H, $J = 8.2$ and 1.7), 7.32 (d, 1H, $J = 8.2$), 3.47, 3.38 and 3.33 (all s, 3H each). MS: *m/e* 252 (M^+), 75 (M^+ −177, $-(CO_2CH_3)_3$).

3.14. Cyclotrimerization of methyl propiolate catalyzed by $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2]$ (15)

The catalytic reaction was carried out under argon in a 50 ml, two-necked flask fitted with a condenser and provided with a septum cap. HC_2CO_2Me (161 μl, 1.92 mmol) in 4 ml of hexane was added to a solution of **15** (9.1 mg, 1.92×10^{-2} mmol) in 4 ml of hexane. The mixture was magnetically stirred for 13 h at reflux temperature (69°C). The reaction was followed by measuring the substrate consumption using GC. After 13 h of reaction 60% of the substrate was converted. Solvent evaporation yielded a mixture of the catalyst, 1,3,5-trimethylbenzene carboxylate (66%) and 1,2,4-trimethylbenzene carboxylate (34%), which was analyzed by ^1H NMR, GC and MS.

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