Notes

[(2−4-η)-Butadienyl]- and [(3−5-η)-Pentatrienyl]ruthenium Complexes from Vinylidene and Allenylidene Precursors[1]

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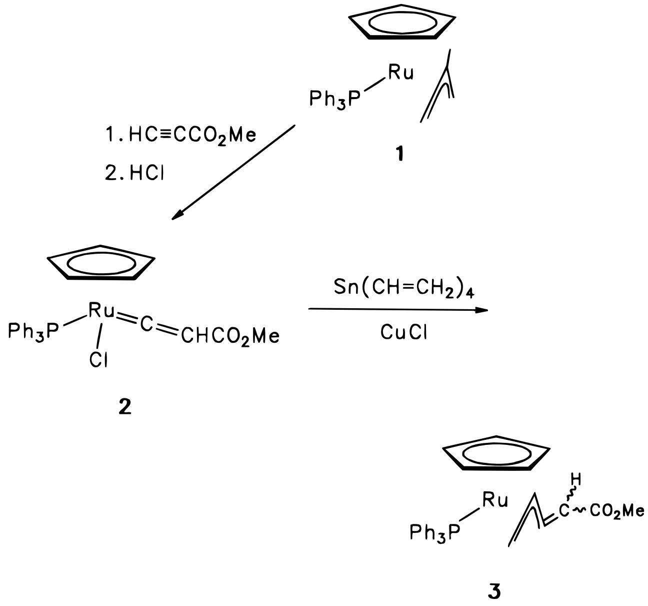
*Summary: The vinylideneruthenium complex $[C_5H_5RuCl(=C=CHCO_2Me)(PPh_3)]$ (**2**), which is obtained on stepwise treatment of $[C_5H_5Ru(\eta^3\text{-}C_3H_4Me)(PPh_3)]$ (**1**) with $HC\equiv CCO_2Me$ and HCl in aromatic solvents, reacts with $Sn(CH=CH_2)_4$ in the presence of CuCl to give the (2−4-η)-butadienyl compound $[C_5H_5Ru(\eta^3\text{-}CH_2CHC=CHCO_2Me)]$ (**3**) in abut 70% yield. A similar C−C coupling reaction leading to the formation of the (3−5-η)-pentatrienyl metal complex $[C_5H_5Ru\{(3-5\text{-}\eta)\text{-}CH_2CHC=C=CPh_2\}(PPh_3)]$ (**5**) occurs on treatment of the allenylidene compound $[C_5Me_5RuCl(=C=C=CPh_2)\{\kappa(P)\text{-}iPr_2PCH_2CO_2Me\}]$ (**4**) with $CH_2=CHMgBr$ in C_6H_6/THF.*

We have recently shown that migratory insertion of vinylidene ligands into metal−alkyl, metal−aryl, and metal−vinyl bonds provides a novel route to (η^3-allyl)- and (η^3-butadienyl)rhodium complexes.[2] Since we argued that the C−C coupling reaction leading to the allyl and butadienyl units might be facilitated by the coordinative unsaturation at the rhodium(I) center, we were interested to find out whether a similar process could also occur in the coordination sphere of a (cyclopentadienyl)ruthenium(II) compound where the metal has an *18-electron configuration*. We note that recently both Wakatsuki and Bianchini described the metal-assisted coupling of an alkynyl and a vinylidene unit by using dichlororuthenium(II) complexes as precursors.[3,4]

The starting material $[C_5H_5RuCl(=C=CHCO_2Me)(PPh_3)]$ (**2**) was obtained by stepwise treatment of the allyl complex **1**[5] with $HC\equiv CCO_2Me$ and HCl in toluene/benzene. The lability of the allyl−metal bond in **1** and in the related compound $[C_5H_5Ru(\eta^3\text{-}C_3H_5)(CO)]$ in the presence of acids has already been illustrated by us[6] as well as by Green[7] and used for the synthesis of neutral as well as cationic C_5H_5Ru complexes.

Scheme 1



The orange, only moderately air-sensitive compound **2** reacts with tetravinyltin in the presence of CuCl to give the [(2−4-η)-butadienyl]ruthenium(II) complex **3** in about 70% yield. The structural proposal shown in Scheme 1 is supported by the ^{1}H and ^{13}C NMR data, which are in good agreement with those of similar [(2−4-η)-butadienyl]metal compounds.[2,8] Like other $C_5H_5(PPh_3)Ru$ derivatives containing a η^3-allyl ligand in the *exo* configuration (i.e., with the central CH unit of the allyl group pointing toward the C_5H_5 plane), the ^{1}H NMR spectrum of **3** displays a signal for the proton H^3 at the terminal allylic carbon atom at δ 1.79 (doublet of doublets) with a much larger P−H coupling (13.5 Hz) than expected for the *endo* isomer.[9] As far as the stereochemistry at the noncoordinated C=C bond of the butadienyl ligand is concerned, we assume that the CO_2Me substituent is directed away from the metal (i.e. *trans* disposed), as has also been found by X-ray diffraction studies of $[C_5H_5Ru(\eta^3\text{-}CHRCRC=CHPh)$-

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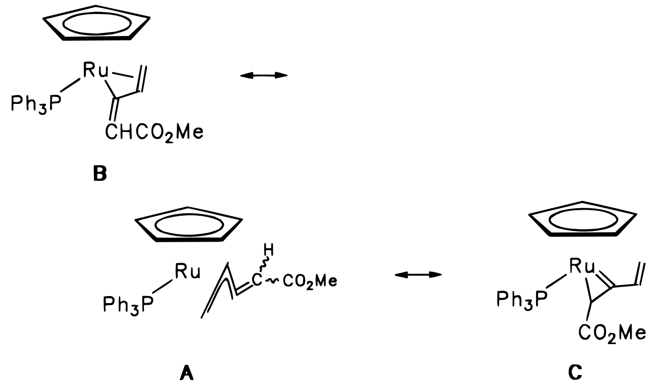
Scheme 2

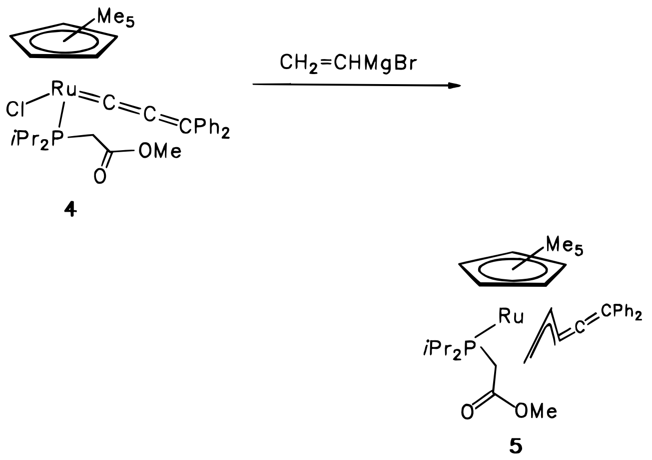


(PPh$_3$)] (R = CO$_2$Me)[10] and [RuCl(η^3-*C*HR*C*H*C*=CHR′)(CO)(PPh$_3$)$_2$] (R = R′ = SiMe$_3$; R = Et, R′ = *t*Bu),[11] respectively.

For the description of the bonding mode of the butadienyl unit to the metal, probably more than one resonance formula should be considered. Besides the usual allyl-type coordination (see **A** in Scheme 2), a η^1:η^2-butadienyl as well as a η^2(3e)-vinylcarbene structure (**B** and **C**) are conceivable and would explain the chemical shift at δ 199.6 of the ^{13}C NMR signal for the quaternary carbon atom C^2.[12] The reason why we, in contrast to Wakatsuki et al., favor the carbene-type structure **C** instead of **B** is that in the ^{1}H NMR spectrum the signal of the proton H^2 (for assignment, see the Experimental Section) is observed at δ 2.88, while in the crystallographically characterized complex [RuCl{η^3-*C*H(SiMe$_3$)*C*H*C*=CHSiMe$_3$}(CO)(PPh$_3$)$_2$] it appears at 5.39.[11] An analogous bonding mode to that in **C** has also been proposed by Green for [C$_5$H$_5$Mo{η^2-=*C*(Ph)-*C*=CHPh}{P(OMe)$_3$}$_2$] in order to explain the chemical shift of the signal for the carbene carbon atom at δ 253.[13]

The allenylidene complex **4**, which was prepared from [C$_5$Me$_5$RuCl{κ^2(*P,O*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] and HC≡CCPh$_2$OH,[14] also undergoes a C–C coupling reaction with a vinyl unit. Treatment of a solution of **4** in benzene with a solution of CH$_2$=CHMgBr in THF led to a rapid change of color from red to yellow and finally to the isolation of yellow microcrystals of **5** in good yield. Since the IR spectrum of **5** indicates that the functionalized phosphine is only attached via phosphorus to the metal, a η^3-allyl bonding mode can be assumed for the pentatrienyl ligand. The ^{13}C NMR spectrum of **5** displays two low-field signals for the allene-like carbon atoms C^1 and C^2 at δ 105.0 and 198.0 and three resonances (each split into a doublet) for the allyl carbons C^3–C^5 at δ 109.2, 54.3, and 34.7, respectively. These data are quite similar to those found for the pentatrienylrhodium complex [Rh{(3–5-η)-*C*H$_2$*C*H-*C*=C=CPh$_2$)}(P*i*Pr$_3$)$_2$][2] and, together with the data of the ^{1}H NMR spectrum of **5**, leave no doubt that the structural proposal shown in Scheme 3 is correct.

Scheme 3



With regard to the mechanism of formation of the η^3-allyl-type compounds **3** and **5**, we assume that initially a nucleophilic substitution of the chloro ligand takes place and a vinylmetal intermediate is generated. This could rearrange by migratory insertion of the vinylidene or allenylidene unit into the Ru–CH=CH$_2$ bond to give the final product. In this context it is important to note that the rhodium complexes *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = *t*Bu, Ph) react with CH$_2$=CHMgBr to yield the *isolable* intermediates *trans*-[Rh(CH=CH$_2$)(=C=CHR)(P*i*Pr$_3$)$_2$], which upon heating to 45–50 °C in benzene isomerize to give almost quantitatively the butadienyl derivatives [Rh{(2–4-η)-*C*H$_2$*C*H*C*=CHR}(P*i*Pr$_3$)$_2$].[2] An alternative pathway leading to **3** and **5**, namely the addition of the vinyl nucleophile to the α-carbon atom of the vinylidene or allenylidene ligand followed by elimination of chloride with concomitant η^1 to η^3 rearrangement, could also be considered but seems less likely.

Since compound **2** does not react with Sn(CH=CH$_2$)$_4$ *in the absence of CuCl*, this electrophilic substrate seems to play a crucial role in the formation of **3**. Although it is possible that copper(I) chloride adds to the Ru=C bond of **2** to activate the vinylidene unit,[15] we assume that CuCl interacts with the ruthenium-bonded chloride and thus supports the substitution process. Lewis et al. have recently shown that mono- and polynuclear alkynylruthenium complexes are accessible from the corresponding chlorometal precursors and SnMe$_3$-substituted alkynes and diynes, but only in the presence of CuI.[16]

Experimental Section

All experiments were carried out under an atmosphere of argon by using Schlenk tube techniques. The starting materials **1**[4] and **4**[14] were prepared as described in the literature. Melting points were determined by DTA. IR spectra were measured with Perkin-Elmer 1420 and NMR spectra with Bruker AC 200 and AMX 400 instruments.

Preparation of [C$_5$H$_5$RuCl(=C=CHCO$_2$Me)(PPh$_3$)] (2). A solution of **1** (176 mg, 0.36 mmol) in 5 mL of toluene was treated with HC≡CCO$_2$Me (158 μL, 1.82 mmol). A 0.16 M solution of HCl (2.76 mL, 0.44 mmol) in benzene was added, and the reaction mixture was stirred for 5 min at room temperature. After the solvent was removed, the residue was

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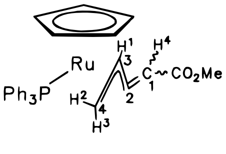
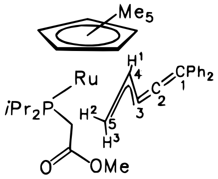
washed twice with 5 mL of pentane. An orange microcrystalline solid was obtained: yield 184 mg (94%); mp 134 °C dec. Anal. Calcd for $C_{27}H_{24}ClO_2PRu$: C, 59.18; H, 4.41. Found: C, 59.42; H, 4.46. IR (KBr): ν(C=O) 1680, ν(C=C) 1580 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.73, 6.99 (both m, 15H, C_6H_5), 5.04 (s, 5H, C_5H_5), 4.48 (s, 1H, =C*H*CO_2CH_3), 3.33 (s, 3H, CO_2CH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 335.3 (d, *J*(PC) = 22.8 Hz, Ru=C), 166.3 (s, *C*O_2CH_3), 139.4 (d, *J*(PC) = 39.5 Hz, *i*-C of C_6H_5), 134.2 (d, *J*(PC) = 10.3 Hz, *o*-C of C_6H_5), 130.5 (d, *J*(PC) = 2.0 Hz, *p*-C of C_6H_5), 128.3 (d, *J*(PC) = 10.4 Hz, *m*-C of C_6H_5), 109.0 (s, =*C*HCO_2CH_3), 93.4 (s, C_5H_5), 50.6 (s, CO_2*C*H_3). ^{31}P NMR (81.0 MHz, C_6D_6): δ 54.3 (s).

Preparation of [$C_5H_5Ru\{(2-4-\eta)$-*C*H_2CH*C*=CHCO_2Me$\}(PPh_3)$] (3). A solution of **2** (220 mg, 0.40 mmol) in 10 mL of THF was treated with $Sn(CH=CH_2)_4$ (0.50 mL, 2.75 mmol) and CuCl (2.0 mg, 0.02 mmol). The reaction mixture was heated for 3 h to 60 °C, and upon cooling to 25 °C, the solution was brought to dryness in vacuo. The residue was dissolved in 10 mL of ethanol, and the mixture was stirred for 1 h at room temperature. The solvent was removed, the residue was extracted with 2 mL of toluene, and the solution was chromatographed on Al_2O_3 (basic, activity grade V, length of column 6 cm). With toluene, a yellow fraction was eluted, from which the solvent was removed in vacuo. The residue was washed with 2 mL of pentane to give a yellow microcrystalline solid: yield 145 mg (67%); mp 125 °C dec. Anal. Calcd for $C_{29}H_{27}O_2PRu$: C, 64.55; H, 5.04. Found: C, 64.08; H, 4.85. IR (C_6H_6): ν(C=O) 1695 cm^{-1}.



^{1}H NMR (400 MHz, C_6D_6): δ 7.67, 7.43, 7.01 (all m, 15H, C_6H_5), 6.79 (dd, *J*(PH) = 2.8, *J*(H^1H^4) = 1.6 Hz, 1H, H^4), 4.46 (s, 5H, C_5H_5), 3.50 (s, 3H, CO_2CH_3), 3.40 (m, 1H, H^1), 2.88 (d, *J*(H^1H^2) = 7.1 Hz, 1H, H^2), 1.79 (dd, *J*(PH) = 13.5, *J*(H^1H^3) = 9.8 Hz, 1H, H^3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 199.6 (d, *J*(PC) = 13.1 Hz, C^2), 169.5 (s, *C*O_2CH_3), 137.5 (d, *J*(PC) = 42.6 Hz, *i*-C of C_6H_5), 134.5 (d, *J*(PC) =10.5 Hz, *o*-C of C_6H_5), 129.2 (s, *p*-C of C_6H_5), 127.6 (d, *J*(PC) = 9.7 Hz, *m*-C of C_6H_5), 110.8 (d, *J*(PC) = 5.7 Hz, C^1), 82.6 (s, C_5H_5), 50.0 (s, CO_2*C*H_3), 42.3 (s, C^3), 33.4 (d, *J*(PC) = 4.4 Hz, C^4). ^{31}P NMR (162.0 MHz, C_6D_6): δ 58.7 (s).

Preparation of [$C_5H_5Ru(3-5-\eta)$-*C*H_2CH*C*=C=$CPh_2\}(PPh_3)$] (5). A solution of **4** (69 mg, 0.11 mmol) in 5 mL of benzene was treated with a 0.75 M solution of CH_2=CHMgBr (157 μL, 0.11 mmol) in THF and stirred for 5 min at room temperature. A change of color from red to yellow occurred. After the solvent was removed, the residue was extracted with 3 mL of benzene and the extract was brought to dryness in vacuo. A yellow solid was obtained, which was washed with 2 mL of pentane at 0 °C and dried in vacuo: yield 46 mg (68%); mp 76 °C dec. Anal. Calcd for $C_{36}H_{47}O_2PRu$: C, 67.16; H, 7.36. Found: C, 67.30; H, 7.56. IR (THF): ν(C=C=C) 1930, ν(C=O) 1720 cm^{-1}.



^{1}H NMR (400 MHz, C_6D_6): δ 7.76 (d, *J*(HH) = 7.4 Hz, 2H, *o*-H of C_6H_5), 7.45 (d, *J*(HH) = 7.2 Hz, 2H, *o*-H of C_6H_5), 7.25, 7.08, 6.70 (all m, 6H, C_6H_5), 3.18 (s, 3H, OCH_3), 2.92 (ddd, *J*(PH) = 2.9, *J*(H^1H^3) = 8.8, *J*(H^1H^2) = 7.2 Hz, 1H, H^1), 2.27 (dsept, *J*(PH) = 2.6, *J*(HH) = 6.9 Hz, 1H, PC*H*CH_3), 2.05 (dd, *J*(H^1H^2)= 7.1, *J*(H^2H^3) = 2.1 Hz, 1H, H^2), 2.00 (sept, *J*(HH) = 7.1 Hz, 1H, PC*H*CH_3), 1.87 (part of an ABX pattern, d in ^{1}H-$\{^{31}P\}$, *J*(HH) = 14.0 Hz, 1H, PCH_2), 1.81 (part of an ABX pattern, d in ^{1}H$\{^{31}P\}$, *J*(HH) = 14.0 Hz, 1H, PCH_2), 1.59 (d, *J*(PH) = 0.8 Hz, 15H, C_5Me_5), 1.13 (dd, *J*(PH) = 14.6, *J*(HH) = 6.6 Hz, 3H, PCHC*H*$_3$), 1.08 (dd, *J*(PH) = 15.2, *J*(HH) = 7.1 Hz, 3H, PCHC*H*$_3$), 1.01 (dd, *J*(PH) = 15.2, *J*(HH) = 7.1 Hz, 3H, PCHC*H*$_3$), 0.97 (dd, *J*(PH) = 11.0, *J*(HH) = 6.9 Hz, 3H, PCHC*H*$_3$), signal of H^3 covered by the singlet of the C_5Me_5 protons. ^{13}C NMR (100.6 MHz, C_6D_6): δ 190.0 (d, *J*(PC) = 13.1 Hz, C^2), 170.9 (d, *J*(PC) = 9.4 Hz, *C*O_2CH_3), 141.0 (s, *J*(PC) = 42.6 Hz, *i*-C of C_6H_5), 129.6, 128.5, 128.3, 128.0, 125.7, 125.5 (all s, C_6H_5), 109.2 (d, *J*(PC) = 12.7 Hz, C^3), 105.0 (s, C^1), 90.6 (s, *C*$_5Me_5$), 54.3 (d, *J*(PC) = 2.1 Hz, C^4), 50.9 (s, CO_2*C*H_3), 34.7 (d, *J*(PC) = 6.3 Hz, C^5), 28.3 (d, *J*(PC) = 20.2 Hz, P*C*HCH_3), 28.1 (d, *J*(PC) = 10.5 Hz, PCH_2), 26.6 (d, *J*(PC) = 20.3 Hz, P*C*HCH_3), 20.0 (d, *J*(PC) = 3.3 Hz, PCH*C*H_3), 18.5 (d, *J*(PC) = 4.7 Hz, PCH*C*H_3), 16.8 (d, *J*(PC) = 6.5 Hz, PCH*C*H_3), 10.8 (s, C_5*Me*$_5$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 63.4 (s).

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