1972 *Organometallics* **1991**, *10*, 1972-1980

Reactions of [RuCl(PMe$_3$)$_2$(Cp)] with Aliphatic Alkynols Leading to Cationic Vinylvinylidene and Neutral Enynyl Complexes and Reactions of the Enynyls with Heteroallenes

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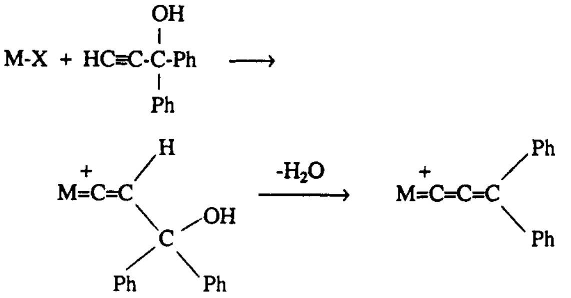
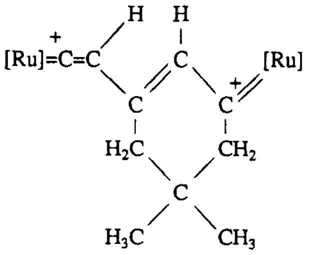
Reactions of [RuCl(PMe$_3$)$_2$(Cp)] with 1-ethynylcyclohexanol or 1-ethynylcyclopentanol and NH$_4$PF$_6$ lead to cationic cycloalkenyl vinylidene complexes [Ru(C=CHR)(PMe$_3$)$_2$(Cp)][PF$_6$] (**1**, R = cyclohexenyl, and **2**, R = cyclopentenyl) in ca. 80% yield. Similarly, 3-isopropyl-4-methyl-1-pentyn-3-ol (HC≡CC(OH)(CHMe$_2$)$_2$) produces [Ru[C=CHC(CHMe$_2$)(=CMe$_2$)](PMe$_3$)$_2$(Cp)][PF$_6$] (**3**) in 77% yield. The structure of the 1-ethynylcyclohexanol product **1** was determined by X-ray diffraction ($R = 6.3\%$, $R_w = 9.3\%$). The molecule contains a cyclohexenylvinylidene ligand bonded to the ruthenium atom by a short Ru–C bond (1.843 (7) Å). Complexes **1**–**3** are reversibly deprotonated by sodium methoxide to yield the corresponding enynyl complexes [Ru(C≡CR)(PMe$_3$)$_2$(Cp)] (**4**, R = cyclohexenyl, and **5**, R = cyclopentenyl) and [Ru[C≡CC(CHMe$_2$)(=CMe$_2$)](PMe$_3$)$_2$(Cp)] (**6**). The reaction of enynyl **4** with carbon disulfide gave a [2 + 2] cycloadduct via nucleophilic attack of the enynyl β-carbon on CS$_2$. The reaction of **4** with methyl isocyanate gave only isocyanate polymers. Attempted reactions with other heteroallenes were not successful.

Introduction

The formation of vinylidene complexes from reactions of 1-alkynes with certain unsaturated or labile transition-metal complexes is now a well-established method.[1] We have reported that reactions of 1-alkyn-3-ols with [RuCl(PR$_3$)$_2$(Cp)] in polar media lead to hydroxyvinylidene intermediates, which spontaneously dehydrate in situ.[2,3] In the case of 1,1-diphenyl-2-propyn-1-ol, allenylidene complexes are formed exclusively (reaction 1).[2] However, when there are hydrogen atoms adjacent to the hydroxy group, dehydration can occur in two different directions (Scheme I) to give either allenylidene (path a) or vinylvinylidene (path b) products. We suggested that concurrent formation of both types of products could explain the formation of [Ru$_2$(μ-C$_{10}$H$_{12}$)(PPh$_3$)$_4$(Cp)$_2$][PF$_6$]$_2$ (**7**) from the reaction of [RuCl(PPh$_3$)$_2$(Cp)] with 2-methyl-3-butyn-2-ol.[3] We report here the formation of stable vinylvinylidene complexes from reactions of [RuCl(PMe$_3$)$_2$(Cp)] with alkyn-1-ols, supporting this suggestion.[4]



(1)



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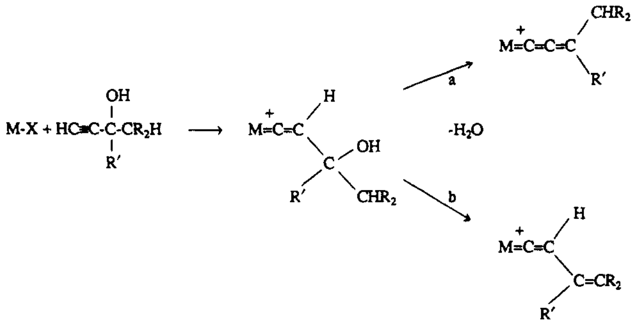
[Ru] = [Ru(PPh$_3$)$_2$(Cp)]

Scheme I



Experimental Section

General Considerations. All procedures were carried out under an atmosphere of dry, oxygen-free nitrogen by using Schlenk or glovebox techniques. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. Pentane, hexane, toluene, ethyl ether, and THF were dried over sodium benzophenone ketyl. Methanol and ethanol were dried over magnesium, and methylene chloride was dried over phosphorus pentoxide. Column chromatography was carried out under positive nitrogen pressure by using activity III alumina (6% H$_2$O) and dry, oxygen-free solvents. Samples were "dry-loaded" by evaporating concentrated solutions or suspensions directly onto a few grams of alumina. Fractions were collected in Schlenk flasks against a vigorous nitrogen purge. Melting points were measured in sealed capillaries under vacuum by using a Mel-Temp apparatus. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN) or Atlantic Microlab (Atlanta, GA).

Infrared spectra were recorded as CH$_2$Cl$_2$ solutions or KBr pellets by using a Perkin-Elmer 1420 double-beam spectrometer or a Perkin-Elmer 1710 FTIR spectrometer. ^{1}H NMR spectra were recorded by using Varian Gemini 200 and Varian XL-200 spectrometers; ^{13}C NMR spectra were recorded by using the same instruments (50 MHz) or a Varian VXR-400 (100 MHz) spectrometer. Both ^{1}H and ^{13}C spectra were referenced internally to the solvent peak, and chemical shifts are reported in ppm downfield from tetramethylsilane. ^{31}P NMR spectra were recorded with proton decoupling by using a Varian XL-200 (81 MHz),

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VXR-400 (162 MHz), or FT-80 (32 MHz) spectrometer; chemical shifts (δ_P) are reported in ppm downfield from external H_3PO_4. NMR coupling constants are reported as absolute values. Deuterated solvents were purchased from Cambridge Isotope Laboratories in sealed ampules and used as received. Mass spectra were obtained on a VG ZAB-2F spectrometer by using electron impact ionization at 70 eV. Molecular ion peaks were confirmed by comparison to calculated isotope patterns.

The reagents 1-ethynylcyclohexanol (Aldrich), 1-ethynylcyclopentanol (Farchan), 3-isopropyl-4-methyl-1-pentyn-3-ol (Farchan), dicyclopentadiene (J. T. Baker), carbon dioxide (Air Products), triphenylphosphine (M & T Chemicals), and ruthenium trichloride hydrate (Johnson-Matthey, Engelhard, Colonial Metals) were obtained from commercial sources as indicated and used without further purification. Methyl isothiocyanate (Aldrich), methyl isocyanate (Aldrich), carbon disulfide (Mallinckrodt), and MeI (Aldrich) were distilled prior to use. [RuCl(PPh$_3$)$_2$(Cp)],[5] [RuCl(PMe$_3$)$_2$(Cp)],[6] and trimethylphosphine[7] were prepared as cited.

[Ru(C=CHC$_6$H$_9$)(PMe$_3$)$_2$(Cp)][PF$_6$] (1). A mixture of [RuCl(PMe$_3$)$_2$(Cp)] (0.817 g, 2.31 mmol), 1-ethynylcyclohexanol (0.727 g, 5.85 mmol) and NH_4PF_6 (0.763 g, 4.69 mmol) in 50 mL of dry methanol was refluxed for 3.5 h under nitrogen. The reaction mixture was reduced to dryness in vacuo, and the pink residue was extracted with 40 mL of dichloromethane. The mixture was filtered to remove NH_4Cl and excess NH_4PF_6, the volume was reduced to 5 mL, and the product was precipitated with 25 mL of ethyl ether. This was washed with pentane (2 × 20 mL) and dried in vacuo to yield 1.13 g (86%) of 1 as a red solid. Mp: 165–170 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ_H 5.44 (s, 5 H, Cp), 5.34 (br m, 1 H, Ru=C=C*H*), 4.97 (unresolved t, 1 H, $\overline{\mathrm{C{=}C}\mathit{H}\mathrm{(C}}\mathrm{H_2)_4}$), 2.15 (br m, 4 H, allylic CH$_2$), 1.92 (br m, 4 H, alkyl CH$_2$), 1.61 (virtual t, $|^2J_{PH} + {}^4J_{PH}| = 10$ Hz, 18 H, PMe). ^{13}C{^{1}H} NMR (50 MHz, $(CD_3)_2CO$): δ_C 355.8 (t, $^2J_{PC} = 15$ Hz, C_α), 125.2 (s, =CH—*C*=CH), 120.0 (s, =CH—C=*C*H), 116.9 (s, C_β), 92.2 (s, Cp), 29.7 (s, C=C—*C*H$_2$), 26.1 (s, C=CH—*C*H$_2$), 23.5, 22.9 (s, CH$_2$), 22.2 (virtual t, $|^1J_{PC} + {}^3J_{PC}| = 37$ Hz, PMe$_3$). ^{31}P NMR (32 MHz, $(CD_3)_2CO$): δ_P 12.27 (s, PMe). IR (KBr): 3936 (w), 3436 (m), 3111 (m), 2921 (vs), 2340 (w), 2028 (w), 1973 (m), 1647 (s, C=C), 1423 (vs), 1373 (s), 1340 (s), 1311 (s), 1294 (vs), 1241 (m), 1188 (s), 1147 (s), 1081 (m), 923 (vs), 850 (s, PF_6^-), 741 (vs), 704 (s), 678 (vs), 651 (vs), 553 (vs), 512 (w), 489 (m), 465 (m), 449 (m), 408 (s) cm^{-1}.

[Ru(C=CHC$_5$H$_7$)(PMe$_3$)$_2$(Cp)][PF$_6$] (2). A mixture of [RuCl(PMe$_3$)$_2$(Cp)] (0.273 g, 0.77 mmol) and NH_4PF_6 (0.263 g, 1.61 mmol) was dissolved in 20 mL of dry methanol. An excess of 1-ethynylcyclopentanol (0.50 mL, 4.37 mmol) was injected via syringe, and the solution was stirred at room temperature for 1.5 h, after which time NH_4Cl had precipitated. The reaction mixture was reduced to dryness in vacuo, and the residue was extracted with 40 mL of dichloromethane. Filtration, evaporation to a volume of 5 mL, and dropwise addition of 20 mL of ethyl ether produced 0.313 g (73%) of 2 as a pink powder. Mp: 178–181 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ_H 5.44 (s, 5 H, Cp), 5.37 (br s, 1 H, Ru=C=C*H*), 5.25 (br s, 1 H, =C*H*CH$_2$), 2.49, 2.19 (br m, 2 H each, allylic CH$_2$), 1.94 (m, 2 H, alkyl CH$_2$), 1.62 (virtual t, $|^2J_{PH} + {}^4J_{PH}| = 10$ Hz, 18 H, PMe). ^{13}C{^{1}H} NMR (50 MHz, $(CD_3)_2CO$): δ_C 356.0 (br s, C_α), 129.3 (s, =CH—*C*=CH), 123.6 (s, =CH—C=*C*H), 110.8 (s, C_β), 92.3 (s, Cp), 35.2 (s, C=C—*C*H$_2$), 32.5 (s, C=CH—*C*H$_2$), 24.3 (s, CH$_2$), 22.2 (virtual t, $|^1J_{PC} + {}^3J_{PC}| = 36$ Hz, PMe$_3$). ^{31}P NMR (32 MHz, $(CD_3)_2CO$): δ_P 9.78 (s, PMe). IR (KBr): 3435 (w), 3113 (m), 2965 (s), 2833 (s), 2340 (w), 1971 (w), 1626 (s, C=C), 1601 (s), 1467 (w), 1426 (s), 1341 (m), 1311 (m), 1294 (vs), 1261 (w), 1148 (m), 1043 (w), 938 (vs), 877 (vs, PF_6^-), 735 (vs), 704 (w), 679 (s), 616 (w), 559 (vs), 465 (w), 426 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{31}F_6P_3Ru$: C, 38.93; H, 5.63; P, 16.73. Found: C, 39.14; H, 5.63; P, 16.57.

[Ru[C=CHC(CHMe$_2$)(=CMe$_2$)](PMe$_3$)$_2$(Cp)][PF$_6$] (3). A mixture of [RuCl(PMe$_3$)$_2$(Cp)] (0.258 g, 0.73 mmol) and NH_4PF_6 (0.236 g, 1.45 mmol) was dissolved in 25 mL of dry methanol. A large excess (1.0 mL) of 3-isopropyl-4-methyl-1-pentyn-3-ol was injected via syringe, and the solution was refluxed for 2 h. The reaction mixture was reduced to dryness in vacuo, and the residue was extracted with 40 mL of dichloromethane. After filtration and evaporation to a volume of 5 mL, 20 mL of ethyl ether was added to precipitate the product. This was recrystallized from CH_2Cl_2/ether, washed successively with ether (2 × 20 mL) and pentane (2 × 20 mL) to yield 0.320 g (75%) of a tan microcrystalline solid, which was dried in vacuo. Mp: 118–124 °C dec. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 5.40 (s, 5 H, Cp), 4.46 (br s, 1 H, Ru=C=C*H*), 2.81 (sep, $^3J_{HH} = 7$ Hz, 1 H, C*H*Me$_2$), 1.80, 1.76 (s, 3 H each, C=CMe$_2$), 1.56 (virtual t, $|^2J_{PH} + {}^4J_{PH}| = 10$ Hz, 18 H, PMe), 0.89 (d, $^3J_{HH} = 7$ Hz, 6 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ_C 345.6 (t, $^2J_{PC} = 30$ Hz, C_α), 129.0 (s, C=*C*Me$_2$), 125.3 (s, *C*=CMe$_2$), 106.4 (s, C_β), 91.1 (s, Cp), 29.7 (s, *C*HMe$_2$), 24.2 (s, C=C*Me*$_2$), 21.6 (virtual t, $|^1J_{PC} + {}^3J_{PC}| = 37$ Hz, PMe$_3$), 21.0 (s, CH*Me*$_2$), 19.6 (s, C=C*Me*$_2$). ^{31}P NMR (32 MHz, $(CD_3)_2CO$): δ_P 10.35 (s, PMe). IR (KBr): 3415 (m), 2980 (vs), 2940 (s), 1713 (s, C=C), 1640 (m), 1461 (s), 1417 (s), 1367 (vs), 1258 (w), 1173 (s), 1087 (w), 996 (w), 946 (m), 761 (w), 590 (m), 428 (vs) cm^{-1}. Anal. Calcd for $C_{20}H_{37}F_6P_3Ru$: C, 40.96; H, 6.53. Found: C, 40.50; H, 6.24.

[Ru(C≡CC$_6$H$_9$)(PMe$_3$)$_2$(Cp)] (4). Compound 1 (0.212 g, 0.372 mmol) was placed in a Schlenk flask, and 50 mL of pentane was added. An excess (0.5 mL) of freshly prepared sodium methoxide (ca. 25% in MeOH) was injected via syringe, and the mixture was stirred at room temperature for 2 min. The pale yellow, air-sensitive solution was decanted away from a small amount of oil left in the flask, and the solvent was stripped. Recrystallization from pentane at −78 °C yielded 4 (0.112 g, 71%) as a bright yellow powder. Mp: 96–97 °C. ^{1}H NMR (200 MHz, C_6D_6): δ_H 5.97 (br s, 1 H, $\overline{\mathrm{C{=}C}\mathit{H}\mathrm{(C}}\mathrm{H_2)_4}$), 4.52 (s, 5 H, Cp), 2.43, 2.14, 1.63 (br m, 8 H, ring protons), 1.22 (virtual t, $|^2J_{PH} + {}^4J_{PH}| = 8.8$ Hz, 18 H, PMe). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C 126.8 (s, C=*C*H), 122.8 (s, ≡C—*C*=CH), 111.4 (t, $^2J_{PC} = 27$ Hz, C_α), 109.8 (s, C_β), 80.8 (s, Cp), 32.7 (s, ≡C—C—*C*H$_2$), 26.1 (s, C=CH—*C*H$_2$), 23.8 (s, CH$_2$), 23.1 (virtual t, $|^1J_{PC} + {}^3J_{PC}| = 30$ Hz, PMe$_3$), 23.0 (s, CH$_2$). ^{31}P NMR (162 MHz, C_6D_6): δ_P 12.81 (s, PMe). IR (CH_2Cl_2): 3435 (s), 2053 (m, C≡C), 1636 (m), 1422 (w), 1273 (vs), 940 (m), 772 (vs), 671 (w), 461 (w), 455 (w) cm^{-1}. Mass spec: $m/z = 424$ (M$^+$). Anal. Calcd for $C_{19}H_{32}P_2Ru$: C, 53.89; H, 7.62. Found: C, 53.25; H, 8.00.

[Ru(C≡CC$_5$H$_7$)(PMe$_3$)$_2$(Cp)] (5). Compound 2 (0.206 g, 0.371 mmol) was placed in a Schlenk flask, and 50 mL of pentane was added. An excess (0.5 mL) of freshly prepared sodium methoxide (ca. 25% in MeOH) was injected via syringe, and the mixture was stirred at room temperature for 2 min. The pale yellow, air-sensitive solution was decanted away from a small amount of oil left in the flask, and the solvent was stripped. Recrystallization from pentane at −78 °C yielded 5 (0.095 g, 63%) as a bright yellow powder. Mp: 126–128 °C. ^{1}H NMR (200 MHz, C_6D_6): δ_H 5.76 (t, $^3J_{HH} = 2.1$ Hz, 1 H, =C*H*), 4.51 (s, 5 H, Cp), 2.65 (td, $^3J_{HH} = 2.1$ Hz, $^3J_{HH} = 7.4$ Hz, 2 H, =CHC*H*$_2$), 2.47 (br t, 2 H, =CC*H*$_2$), 1.86 (pentet, $^3J_{HH} = 7.4$ Hz, 2 H, CH$_2$C*H*$_2$CH$_2$), 1.21 (virtual t, $|^2J_{PH} + {}^4J_{PH}| = 8.9$ Hz, 18 H, PMe). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C 131.8 (s, C=*C*H), 124.1 (s, ≡C—*C*=CH), 118.3 (t, $^2J_{PC} = 28$ Hz, C_α), 104.8 (s, C_β), 80.9 (s, Cp), 38.9 (s, ≡C—C—*C*H$_2$), 32.9 (s, C=CH—*C*H$_2$), 24.0 (s, CH$_2$), 23.1 (virtual t, $|^1J_{PC} + {}^3J_{PC}| = 31$ Hz, PMe$_3$). ^{31}P NMR (162 MHz, C_6D_6): δ_P 12.67 (s, PMe). IR (CH_2Cl_2): 2907 (w), 2055 (m, C≡C), 1422 (w), 1273 (vs), 941 (m), 797 (w), 736 (vs), 671 (m), 469 (m), 464 (m), 453 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{30}P_2Ru$: C, 52.80; H, 7.38. Found: C, 52.24; H, 7.51.

Preparation of [Ru[C≡CC(CHMe$_2$)(=CMe$_2$)](PMe$_3$)$_2$(Cp)] (6). Compound 3 (0.168 g, 0.287 mmol) was placed in a Schlenk flask, and 50 mL of pentane was added. An excess (0.5 mL) of freshly prepared sodium methoxide (ca. 25% in MeOH) was injected via syringe, and the mixture was stirred at room temperature for 2 min. The pale yellow, air-sensitive solution was decanted away from a small amount of oil left in the flask, and

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the solvent was stripped. Recrystallization from pentane at −78 °C yielded **6** (0.071 g, 56%) as a bright yellow microcrystalline solid. Mp: 69–70 °C. ^{1}H NMR (200 MHz, C_6D_6): δ_H 4.56 (s, 5 H, Cp), 3.04 (sep, $^3J_{HH}$ = 7 Hz, 1 H, C*H*Me$_2$), 2.30, 1.87 (s, 3 H each, $C{=}CMe_2$), 1.38 (d, $^3J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.22 (virtual t, $|^2J_{PH} + {}^4J_{PH}|$ = 9 Hz, 18 H, PMe). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C 128.8 (s, C=*C*Me$_2$), 124.4 (s, *C*=CMe$_2$), 115.6 (t, $^2J_{PC}$ = 23 Hz, C_α), 105.3 (s, C_β), 80.9 (s, Cp), 30.3 (s, *C*HMe$_2$), 24.4 (s, C=C*Me*$_2$), 23.5 (virtual t, $|^1J_{PC} + {}^3J_{PC}|$ = 30 Hz, PMe_3), 22.8 (s, CH*Me*$_2$), 19.4 (s, C=C*Me*$_2$). ^{31}P NMR (162 MHz, C_6D_6): δ_P 13.27 (s, PMe). IR (CH_2Cl_2): 2967 (m), 2906 (m), 2047 (m, C≡C), 1423 (w), 1279 (w), 1273 (vs), 958 (m), 940 (m), 793 (m), 731 (vs), 671 (m), 470 (w), 462 (w), 454 (w) cm^{-1}. Anal. Calcd for $C_{20}H_{36}P_2Ru$: C, 54.66; H, 8.26. Found: C, 50.63; H, 7.58.

Reaction of 4 with CS$_2$. Compound **4** (125 mg, 0.295 mmol) was dissolved in pentane, and 1 mL of N_2-purged CS_2 was added via syringe. The solution was stirred at room temperature for 12 h, after which time a purple solid had precipitated. The solvent was decanted, and the solid was washed with ether and pentane and dried in vacuo to yield 122 mg (83%) of the crude adduct **4**·CS_2. The compound could not be obtained analytically pure. Mp: 400 °C. ^{1}H NMR (90 MHz, $(CD_3)_2CO$): δ_H 5.53 (s, 1 H, vinyl), 4.80 (s, 5 H, Cp), 1.78 (virtual t, $|^2J_{PH} + {}^4J_{PH}|$ = 10 Hz, 18 H, PMe), 1.63 (unresolved multiplet, 8 H, ring alkyls). IR (CH_2Cl_2): 1975 (w), 1610 (m, br), 1415 (m, ring C=C), 1250 (s, C=S), 978 (w), 935 (m), 893 (s), 843 (s) cm^{-1}. MS: m/z = 244; no M$^+$ found at 499. UV/vis: 368 nm (ϵ = 9378 L mol^{-1} cm^{-1}), 536 nm (ϵ = 3777 L mol^{-1} cm^{-1}).

Reaction of 4 with MeNCO. Compound **4** (54 mg, 0.13 mmol) was dissolved in 10 mL of THF, and MeNCO (0.5 mL, 8 mmol) was added via syringe. The solution was refluxed for 18 h, after which time an off-white solid had precipitated. The solid was washed with ether and pentane and dried in vacuo. Sublimation at 85 °C yielded trimethyl isocyanurate (118 mg, 26%) as colorless crystals. Mp: 163–167 °C. ^{1}H NMR (90 MHz, $(CD_3)_2CO$): δ_H 3.17 (s, Me). IR (CH_2Cl_2): 1685 (s, C=O), 1470 (s, C—N), 1385 (m), 1245 (s), 1052 (s), 937 (m) cm^{-1}. MS: m/z = 171 (M$^+$). Analysis of the residue remaining after sublimation suggested a higher polymer of methyl isocyanate (92 mg). Mp: 178–184 °C dec. ^{1}H NMR (90 MHz, $(CD_3)_2CO$): δ_H 3.23 (s, 3 H, NMe), 2.87 (s, 3 H, NMe). IR (CH_2Cl_2): 1640 (s, C=O), 1505 (w, C—N), 1245 (s), 1095 (s, br), 1050 (vs), 935 (w), 885 (m) cm^{-1}. MS: m/z = 342 ($(MeNCO)_6$).

Crystal Structure Analysis of 1. A deep red crystal was obtained by diffusion of ethyl ether-saturated nitrogen into a concentrated CH_2Cl_2 solution of **1**. The crystal was mounted in air on the tip of a glass fiber by using quick-setting epoxy cement, with which the crystal was coated. Crystallographic data were obtained on an Enraf-Nonius CAD-4 diffractometer as summarized in Table I. The unit cell was determined from 25 reflections, which were recentered to obtain refined cell dimensions. Data were corrected for Lorentz and polarization effects. Three intensity standards, collected every 60 min, showed less than 7% fluctuation during data collection. The ruthenium atom was located by using Patterson methods, and remaining non-hydrogen atoms by using successive difference Fourier methods. Subsequent refinement of the structure was carried out with local versions of Ibers' NUCLS least-squares program (based on the Busing–Levy ORFLS) and Zalkin's FORDAP Fourier program. Anomalous dispersion corrections were included for the scattering of Ru, P, and F. The disordered cyclopentadienyl ring was modeled as two independent, rigid five-membered rings with C–C distances of 1.44 Å, C–C–C angles of 108°, and independent isotropic thermal parameters on each carbon atom. Nongroup atoms were refined with anisotropic thermal parameters. Least-squares refinements minimized the function $\sum_{hkl} w(F_oF_c)_2$ where the weighting factor was $w = 1/\sigma(F_o)^2$. Hydrogen atoms on the vinylidene ligand were placed in calculated positions with isotropic thermal parameters equal to B(attached carbon) + 1.0 and were not refined but were adjusted after each least-squares cycle. Full-matrix least-squares refinement with 239 variables led to R = 6.3%, R_w = 9.3%. Additional details of refinement are presented in Table I.

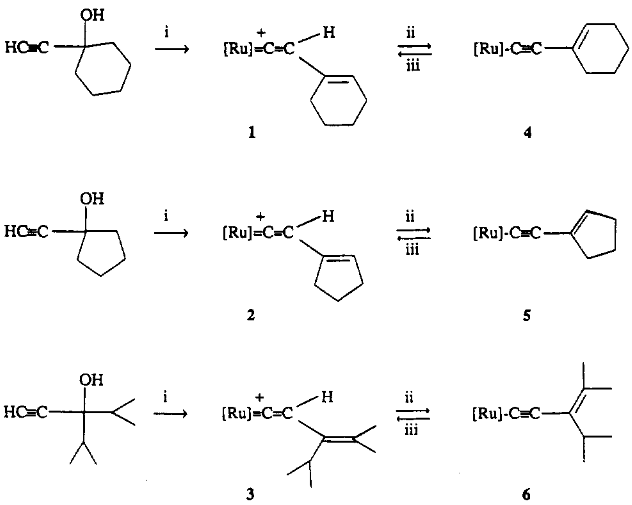
Results

Syntheses. Reactions of $[RuCl(PMe_3)_2(Cp)]$ with 1-ethynylcyclohexanol or 1-ethynylcyclopentanol and NH_4PF_6 in methanol produced cationic vinylvinylidene complexes $[Ru(C{=}CHR)(PMe_3)_2(Cp)][PF_6]$ (Scheme II; **1**, R = cyclohexenyl, and **2**, R = cyclopentenyl). Compound **1** is formed in 86% yield after a 2–3-h reflux, al-

Table I. Summary of Crystal Data and Details of Intensity Collection and Refinement for $[Ru[C{=}CH\overline{C{=}CH(C}H_2)_4](PMe_3)_2(Cp)[PF_6]$ (1)

Crystal Data	
color habit	red prism
size, mm^3	0.60 × 0.60 × 0.45
formula	$C_{19}H_{33}F_6P_3Ru$
fw	569.45
ρ_{calcd}, g·cm^{-3}	1.521
a, Å	8.411 (1)
b, Å	15.948 (3)
c, Å	18.548 (3)
β, deg	91.32 (1)
V, Å^3	2487.37
F(000)	1160
F(000) corrected	1155.773
Data Collection	
radiation	Mo Kα
λ, Å	0.71073
temp, °C	23
no. of sets of setting angles refined	25
θ range for cell, deg	9.7–13.8
max counting time, s	90
θ limits for data, deg	2–25
hkl ranges	0–10, 0–19, −22 to +22
scan type	ω–2θ
scan range, deg	0.80 + 0.35 tan θ
no. of stds	3
max variation, %	7
no. of unique data	4832
no. of data with $I \geq 3\sigma(I)$	3487
Structure Solution and Refinement	
space group	$P2_1/n$ (No. 14)
Z	4
final no. of variables	239
p factor for calculation of $\sigma(I)$	0.02
max shift/error in last cycle	−1.70 (β_{33} of C16)
R, %	6.3
R_w, %	9.3
error in obsn of unit weight	5.51
major peaks in final difference Fourier, e·Å^{-3}	0.097 (near Ru) 0.095 (near PF_6)
μ, cm^{-1}	8.551
abs corrcn	none
extinction corrcn	none

Scheme II[a]



[a] [Ru] = $[Ru(PMe_3)_2(Cp)]$; i = $[RuCl(PMe_3)_2(Cp)]$, NH_4PF_6, MeOH; ii = NaOMe, pentane; iii = HBF_4·Et_2O.

Table II. Selected Spectroscopic Data[a] for Vinylvinylidenes 1–3 and Enynyls 4–6

	R	δ_H(Cp)	δ_H(=C*H*R)	δ_C(Cp)	δ_C(C$_\alpha$)	δ_C(C$_\beta$)	δ_P(PMe$_3$)	ν(C=C)	ν(C≡C)
				[Ru(C=CHR)(PMe$_3$)$_2$(Cp)]PF$_6$					
1	cyclohexenyl	5.44	5.34	92.2	355.8	116.9	12.27	1647	
2	cyclopentenyl	5.44	5.37	92.3	356.0	110.8	9.78	1626	
3	C(=CMe$_2$)(CHMe$_2$)	5.40	4.46	91.1	345.6	106.4	10.35	1640	
				[Ru(C≡CR)(PMe$_3$)$_2$(Cp)]					
4	cyclohexenyl	4.52		80.8	111.4	109.8	12.81		2053
5	cyclopentenyl	4.51		80.9	118.3	104.8	12.67		2055
6	C(=CMe$_2$)(CHMe$_2$)	4.56		81.0	115.6	105.3	13.27		2047

[a] NMR chemical shifts (ppm) vs TMS or 85% H_3PO_4; IR frequencies in cm^{-1}.

though the reaction may continue for 4–6 h without detrimental effects. Compound **2** forms even more easily, requiring only 1.5 h at room temperature to obtain a 73% yield. A 4-h reflux decreased the yield of **2** to 50%.

Similarly, the reaction of [RuCl(PMe$_3$)$_2$(Cp)] with 3-isopropyl-4-methyl-1-pentyn-3-ol (HC≡CC(OH)(CHMe$_2$)$_2$) and NH$_4$PF$_6$ in refluxing methanol produced [Ru[C=CHC(CHMe$_2$)(=CMe$_2$)](PMe$_3$)$_2$(Cp)][PF$_6$] (**3**) in 77% yield. The formation of **3** was much more sensitive to reaction conditions than either **1** or **2**. A mixture consisting of two major products resulted after 20 h at room temperature, while refluxing for 3–4 h led to extensive decomposition. Thermolysis of the mixture formed at room temperature also gave decomposition rather than a single product. Pure **3** is obtained reproducibly by using a 2-h reflux in methanol.

Deprotonation of cationic complexes **1–3** by using sodium methoxide produced enynyl complexes [Ru(C≡CR)(PMe$_3$)$_2$(Cp)] (Scheme II; **4**, R = cyclohexenyl, and **5**, R = cyclopentenyl) and [Ru[C≡CC(CHMe$_2$)(=CMe$_2$)](PMe$_3$)$_2$(Cp)] (**6**). Optimal yields (50–70%) were obtained by adding freshly generated sodium methoxide to a suspension of the vinylvinylidene salt in pentane so that the enynyl product dissolved in the pentane as it was formed, thus avoiding separation problems. In all cases, the enynyl complexes are formed rapidly at room temperature. These deprotonations are reversible; the enynyl complexes can be reprotonated by the addition of 1 equiv of HBF$_4$·Et$_2$O in CDCl$_3$ at room temperature to give exclusively the parent vinylvinylidene compounds, as monitored by ^{1}H NMR spectroscopy.

Numerous attempts were made to obtain similar products by reacting [RuCl(PPh$_3$)$_2$(Cp)] or [RuCl(dppe)(Cp)] (dppe = 1,2-bis(diphenylphosphino)ethane, Ph$_2$PCH$_2$CH$_2$PPh$_2$) with the three hydroxyalkynes. Various reaction times, temperature, and workups were tried, but in no case were tractable products obtained. For example, reactions of [RuCl(PPh$_3$)$_2$(Cp)] with the three alkynols gave mixtures of products either at room temperature or in refluxing methanol. In the case of 1-ethynylcyclopentanol, infrared evidence (ν(C=C=C) at 1953 cm^{-1})[1,2] suggested that allenylidene [Ru[C=C=C(CH$_2$)$_4$](PPh$_3$)$_2$(Cp)][PF$_6$] was a major product. Unfortunately, of six products isolated by column chromatography, five were decomposition products without cyclopentadienyl ligands (by ^{1}H NMR spectroscopy), and the sixth could not be sufficiently purified for further characterization. Direct deprotonation of the [RuCl(PR$_3$)$_2$(Cp)]/alkynol reaction mixtures by using sodium methoxide led rapidly to the crude enynyl complexes, which precipitated from methanol as yellow powders.[8] These reactions were not clean, and protonation of the putative enynyls by using HPF$_6$ gave oily product mixtures that were not fully characterized.

Alkynyl complex **4** reacted with the electrophile CS$_2$ to give a 1:1 adduct. Optimal yields were obtained by stirring **4** in pentane containing excess CS$_2$ for 8 h at room temperature. The resulting deep purple precipitate was insoluble in common organic solvents. Refluxing a mixture of **4** and MeNCO yielded the cyclic trimer trimethylisocyanurate[9] and a polymer,[10] which contained at least six MeNCO units according to the mass spectrum. No tractable metal-containing products were isolated. Reaction of **4** with MeNCS gave a mixture of products that could not be separated and characterized. Compound **4** did not react with CO$_2$.

Spectroscopic Properties. Spectroscopic evidence (Table II), particularly ν(C=C) infrared absorptions between 1600 and 1650 cm^{-1}[11] and the absence of ν(C=C=C) bands at ca. 1950 cm^{-1},[1,2] indicated that products **1–3** are vinylvinylidene, rather than allenylidene, complexes. The chemical shifts of the cyclopentadienyl and vinylidene protons (Ru=C=C*H*) show no obvious dependence on the vinylidene ligand. The vinylidene signals appeared as a triplet of doublets for **1** in (CD$_3$)$_2$CO ($^4J_{PH}$ = 8 Hz, $^4J_{HH}$ = 6 Hz) but as unresolved multiplets for **2** and **3**. The ^{13}C NMR shifts of **1–3** show little variation, with narrow shift ranges for Cp, C$_\alpha$, and C$_\beta$. The C$_\alpha$ resonances were characteristically weak triplets ($^2J_{PC}$ = 16 Hz) in the alkylidene region, ca. 350 ppm.[11] The ^{31}P NMR shifts for the PMe$_3$ ligands did not vary systematically with the vinylidene substituents.

Spectroscopic evidence (Table II) also supports enynyl structures for the deprotonation products **4–6**. Their ^{1}H NMR Cp shifts fall about 1 ppm upfield, and ^{13}C NMR Cp shifts fall about 10 ppm upfield, from those of the corresponding cationic vinylvinylidene complexes, reflecting the increased electron density at the metal center.[2,6] Alkynyl C$_\alpha$ and C$_\beta$ chemical shifts fall in the typical δ_C 100–125 range of alkynyls,[12] with characteristic P–C$_\alpha$ coupling. The ^{31}P NMR chemical shifts did not change appreciably from the vinylvinylidenes. The infrared-active alkynyl stretches were all found at about 2050 cm^{-1}.

Molecular Structure of [Ru(C=CHC$_6$H$_9$)(PMe$_3$)$_2$(Cp)][PF$_6$] (1). The X-ray crystal structure of **1** confirmed the proposed vinylvinylidene formulation. ORTEP[13] plots are shown in Figure 1; crystal data, positional and equivalent isotropic thermal parameters, bond distances, and bond angles are presented in Tables I and III–V. The most important structural feature is the geometry of the

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Table III. Positional Parameters and Equivalent *B* Values[a] for the Atoms of 1

atom	*x*	*y*	*z*	B_{eq}, Å^2
Ru	0.21970 (7)	0.04866 (3)	0.25569 (3)	3.2
P1	0.4185 (3)	−0.0098 (1)	0.1898 (2)	5.2
P2	0.3087 (4)	−0.0109 (2)	0.3616 (1)	7.2
P3	0.1702 (4)	0.2369 (2)	0.5616 (2)	7.0
F1	0.272 (2)	0.203 (1)	0.5069 (8)	26.3
F2	0.211 (2)	0.1537 (9)	0.5948 (8)	19.4
F3	0.068 (3)	0.262 (1)	0.618 (1)	35.9
F4	0.114 (3)	0.3134 (8)	0.5271 (8)	22.0
F5	0.318 (2)	0.278 (1)	0.5778 (8)	25.8
F6	0.033 (2)	0.1894 (9)	0.528 (1)	21.8
C1	0.0937 (9)	−0.0448 (5)	0.2421 (4)	3.7
C2	−0.0062 (9)	−0.1065 (5)	0.2339 (4)	4.0
C3	−0.0675 (8)	−0.1453 (5)	0.1658 (4)	3.8
C4	−0.1648 (9)	−0.2085 (5)	0.1662 (5)	5.0
C5	−0.234 (1)	−0.2510 (7)	0.0995 (6)	6.7
C6	−0.160 (2)	−0.226 (1)	0.0344 (8)	9.9
C7	−0.122 (2)	−0.136 (1)	0.0350 (6)	8.6
C8	−0.020 (1)	−0.1029 (7)	0.0975 (5)	6.3
C11	0.406 (2)	0.021 (1)	0.0954 (8)	10.8
C12	0.431 (2)	−0.1228 (7)	0.1836 (9)	10.5
C13	0.618 (1)	0.0259 (9)	0.2130 (9)	9.0
C14	0.373 (2)	−0.118 (1)	0.365 (1)	14.5
C15	0.477 (2)	0.045 (1)	0.4046 (7)	11.6
C16	0.168 (3)	−0.011 (2)	0.433 (1)	17.2

[a] The equivalent displacement parameter is defined as (4/3)Tr(βG), where $\beta_{ij} = 2\pi^2 a_i{}^* a_j{}^* U_{ij}$.

Table IV. Selected Bond Distances (Å) with Esd's for the Structure of 1

Ru–C1	1.843 (7)	C1–C2	1.30 (1)
Ru–P1	2.292 (2)	C2–H2	0.973 (7)
Ru–P2	2.292 (3)	C2–C3	1.49 (1)
Ru–Cp0[a]	1.920	C3–C4	1.30 (1)
P1–C12	1.81 (1)	C3–C8	1.50 (1)
P1–C13	1.82 (1)	C4–H4	0.98 (1)
P1–C11	1.82 (2)	C4–C5	1.52 (1)
P2–C14	1.79 (2)	C5–C6	1.43 (2)
P2–C16	1.80 (2)	C6–C7	1.46 (2)
P2–C15	1.84 (1)	C7–C8	1.52 (1)
P3–F(ave)	1.46 (3)	C8–C3	1.50 (1)

[a] Cp0 is the averaged centroid of the two rigid group cyclopentadienyl rings, Cp1–Cp5 and Cp1A–Cp5A.

vinylidene ligand. The Ru–C1–C2 angle is nearly linear (174.8 (6)°), while the C1–C2–C3 angle is bent (128.5 (7)°). Bond lengths indicate clearly that the C1–C2 and C3–C4 bonds are double, while C2–C3 is single. The C1–C2 and C3–C4 double bonds are oriented *S*-trans about C2–C3, with a C1–C2–C3–C4 torsional angle of 178.2°. The vinylidene ligand (C1–C2–C3 plane) lies nearly perpendicular to the pseudomirror plane of the [Ru(PMe$_3$)$_2$(Cp)] group (Cp centroid-Ru–C1), with a dihedral angle of 98.2°. The vinylidene plane and the attached alkene are nearly coplanar; deviations from this plane for atoms Ru, C1, C2, C3, C4, C5 and C8 are 0.029, −0.046, 0.016, −0.020, 0.020, 0.002, and 0.001 Å, respectively. Atoms C6 and C7 are −0.320 and 0.297 Å from this plane. The cyclopentadienyl ring is disordered in two equally occupied orientations. The PMe$_3$ carbons and PF$_6^-$ ion are highly anisotropic. The cation is well-separated from the PF$_6^-$ anion, with the closest approach being 3.22 Å from F3 to Cp1A.

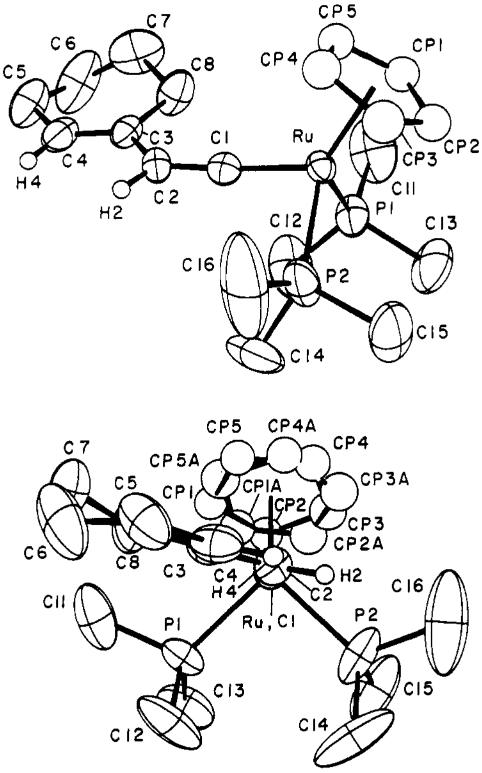


Figure 1. Two ORTEP[13] views of the cation of 1 showing 50% probability ellipsoids. (a, top) Side view. (b, bottom) View down the Ru–C1 bond, showing the disordered cyclopentadienyl ring.

Table V. Selected Bond Angles (deg) with Esd's for the Structure of 1

C1–Ru–P1	91.3 (2)	Ru–C1–C2	174.8 (6)
C1–Ru–P2	87.6 (2)	H2–C2–C1	116.5 (7)
P1–Ru–P2	93.5 (1)	H2–C2–C3	115.0 (7)
Cp0[a]–Ru–C1	129.4	C1–C2–C3	128.5 (7)
Cp0[a]–Ru–P1	123.3	C2–C3–C4	121.6 (8)
Cp0[a]–Ru–P2	121.4	C8–C3–C4	122.3 (8)
C12–P1–C13	105.8 (7)	C2–C3–C8	115.9 (7)
C12–P1–C11	102.2 (8)	H4–C4–C3	117.5 (8)
C12–P1–Ru	119.0 (4)	H4–C4–C5	117.5 (8)
C13–P1–C11	100.0 (7)	C3–C4–C5	124.9 (9)
C13–P1–Ru	115.4 (5)	C4–C5–C6	113.3 (9)
C11–P1–Ru	112.1 (5)	C5–C6–C7	112 (1)
C14–P2–C16	100 (1)	C6–C7–C8	118 (1)
C14–P2–C15	102.5 (8)	C7–C8–C3	109.5 (9)
C14–P2–Ru	121.4 (6)	F5–P3–F3	104 (1)
C16–P2–C15	101.1 (8)	F–P3–F(ave trans)	90 (8)
C16–P2–Ru	115.2 (9)	F–P3–F(ave cis)	172 (4)
C15–P2–Ru	113.8 (4)		

[a] Cp0 is the averaged centroid of the two rigid group cyclopentadienyl rings, Cp1–Cp5 and Cp1A–Cp5A.

Discussion

Vinylvinylidene Formation. [RuCl(PMe$_3$)$_2$(Cp)] reacts smoothly with certain aliphatic alkyn-1-ols to give cationic vinylvinylidene complexes in good yield. This system is interesting in that vinylvinylidene products are obtained exclusively; there is no evidence for either allenylidene complexes or dimeric vinylidene/alkylidene complexes such as [Ru$_2$(μ-C$_{10}$H$_{12}$)(PPh$_3$)$_4$(Cp)$_2$][PF$_6$]$_2$ (7).[3] Since conjugated double bonds are typically more stable than cumulated double bonds, the failure to form allenylidenes is perhaps not surprising. Evidently, the vinylvinylidene isomer is favored when protons are available on the δ carbon atom of the complex, in the absence of complications due to steric requirements of the various ligands.

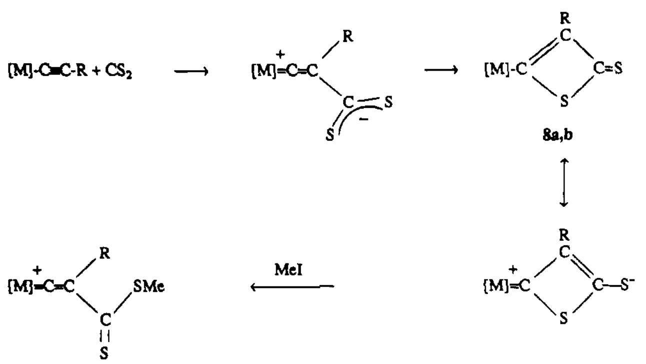
Since only [RuCl(PMe$_3$)$_2$(Cp)] gave tractable products in this reaction, little insight can be gained into the effects of the ancillary phosphine ligands on the direction of the dehydration in Scheme I. The electron-rich fragment [Ru(PMe$_3$)$_2$(Cp)]$^+$ can support either vinylvinylidene (compounds 1–3) or allenylidene[2] ligands. Since the less electron-rich [RuCl[P(OMe)$_3$]$_2$(Cp)] also reacts with HC≡CC(OH)Ph$_2$ in the presence of NH$_4$PF$_6$ to yield [Ru(C=C=CPh$_2$)[P(OMe)$_3$]$_2$(Cp)][PF$_6$],[14] an extremely electron-rich metal center is not required to form a stable allenylidene complex. The failure of bulkier PPh_3 and dppe complexes to give tractable products may be due to an electronic preference for vinylvinylidene products, combined with an opposing steric preference for allenylidene ligands. In the PMe_3 (cone angle 118°)[15] system, vinylvinylidenes are clearly preferred. Steric conflicts between bent vinylvinylidenes and the bulkier phosphines PPh_3 (cone angle 145°) and dppe (cone angle 125° per phosphorus) are likely, whereas linear allenylidenes are not likely to bump into ancillary phosphines. It is possible that cationic arene-bonded PPh_3 complexes[16-18] or methanol adducts of the desired allenylidene and vinylvinylidene complexes[1,8] are also competitively formed.

The structure of the alkynol influences the course of the reaction. Compounds **1** and **2** form readily without interference from side products, perhaps partly because the alkyl rings in these complexes prevent dimerization. Dimers like **7** formed from 1-ethynylcyclohexanol or 1-ethynylcyclopentanol would have strained bicyclic structures with doubly bonded bridgehead carbons. Vinylvinylidene compound **3** is obtained exclusively from 3-isopropyl-4-methyl-1-pentyn-3-ol, since the proton transfers required for dimerization are impossible. Its formation was much more sensitive to reaction conditions than either **1** or **2**. A 2-h reflux in methanol is required to obtain a significant yield of **3**, with extensive decomposition occurring after 3 h. In contrast, compound **1** is stable in refluxing methanol for at least 6 h.

Dixneuf has studied closely related reactions of alkynols with $[RuCl_2(PMe_3)(\eta\text{-}C_6Me_6)]$ in $MeOH/NH_4PF_6$. For $HC{\equiv}CCPh_2OH$, an intermediate allenylidene $[Ru(C{=}C{=}CPh_2)Cl(PMe_3)(\eta\text{-}C_6Me_6)][PF_6]$ was isolated, whereas for $HC{\equiv}CCMe_2OH$ and 1-ethynylcyclohexanol, methoxycarbenes $[Ru[C(OMe)CH{=}CR_2]Cl(PMe_3)(\eta\text{-}C_6Me_6)][PF_6]$ ($R = Me$; $R_2 = C_5H_{10}$) were obtained exclusively.[17] This suggests that hydroxyvinylidene dehydration gives allenylidene, not vinylvinylidene, intermediates, since the latter ought to lead instead to isomeric $[Ru[C(OMe)CH_2CMe{=}CH_2]Cl(PMe_3)(\eta\text{-}C_6Me_6)][PF_6]$ and $[Ru[C(OMe)CH_2\overline{C{=}CH(CH_2)_4}]Cl(PMe_3)(\eta\text{-}C_6Me_6)][PF_6]$. The higher reactivity toward methanol and the different direction of dehydration, compared to the $[Ru(PMe_3)_2(Cp)]$ system, are remarkable for such similar metal centers.

Acid-promoted dehydration of hydroxyvinylidene complexes has been studied in a related manganese system. Kolobova and co-workers reported that the action of mineral acids, SiO_2, or Al_2O_3 on hydroxyvinylidenes $[Mn[C{=}CHC(OH)RR'](CO)_2(Cp)]$ ($R = R' = Ph$; $R = R' = Me$; $R = Me$, $R' = Ph$) caused their dehydration to allenylidenes $[Mn(C{=}C{=}CRR')(CO)_2(Cp)]$, but never to vinylvinylidenes $[Mn[C{=}CHC({=}CH_2)R'](CO)_2(Cp)]$.[19] In contrast, hydroxyvinylidenes $[Mn[C{=}CHC(OH)RR'](CO)_2(Cp)]$ ($R = R' = CMe_3$;[20] $R = R' = H$;[21] $R = H$, $R' = Me$[19]) are not dehydrated by HCl or Al_2O_3. Berke has reported that deoxygenation of $Li_2[L_nM(C{\equiv}CCR_2O)]$ ($L_nM = (CO)_5Cr$, $(CO)_5W$, $R = CHMe_2$; $L_nM = (Cp)(CO)_2Mn$, $R = C_6H_{11}$, CH_2Ph) by using phosgene or HCl leads to allenylidene complexes $[M(C{=}C{=}CR_2)(CO)_5]$ rather than hypothetical vinylvinylidene isomers similar to **3**.[26,27]

Scheme III[a]



[a] **8a**: [M] = $[Ru(PMe_3)_2(Cp)]$, R = 1-cyclohexenyl. **8b**: [M] = $[Fe(dppe)(Cp)]$, R = Me.

Numerous γ-hydroxyalkynyls of divalent palladium and platinum, *trans*-$[M[C{\equiv}CC(OH)R_2]_2L_2]$ and *trans*-$[MX[C{\equiv}CC(OH)R_2]L_2]$ ($R = H$, Me, Et, Ph, CF_3 or $R_2 = c\text{-}(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$; $L = PPh_3$, PMe_2Ph, $AsMe_2Ph$; $X = Cl$, H, $C{\equiv}CC(OH)R_2$), have been reported.[22-25] Some of the platinum(II) alkynyls with tertiary hydroxyl groups were dehydrated to enynyls such as *trans*-$[Pt[C{\equiv}CC(Me){=}CH_2]_2L_2]$ by using pyridine in acetic anhydride or simply by heating.[22,23] A crystal structure of the ethyl ether of the ethynyl cyclohexanol product *trans*-$[PtCl[C{\equiv}C\overline{C(OEt)(CH_2)_5}](PPh_3)_2]$ was reported.[23b] Attempts to isolate cationic allenylidene or vinylvinylidene complexes were unsuccessful in this system, although their intermediacy in etherification reactions with alcohols was implicated.[23]

It is not clear why hydroxyvinylidenes in the $[Ru(PMe_3)_2(Cp)]^+$ system dehydrate to give vinylvinylidenes (path a, Scheme I), whereas the isolobal, d^6 $[RuCl(PMe_3)(\eta\text{-arene})]^+$ and $[Mn(CO)_2(Cp)]$ systems give allenylidenes. The $[Ru(PMe_3)_2(Cp)]^+$ center with its two phosphine ligands is likely the most electron-rich and the strongest π-donor center.[1,8,18] Vinylidenes are among the best π-acceptor ligands, comparable to CO and CS ligands and better than allenylidenes.[1] We suggest that the electron-rich $[Ru(PMe_3)_2(Cp)]^+$ center therefore favors better π-acceptor vinylvinylidene ligands over their allenylidene isomers. Results from our laboratory and briefly

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noted by Davies[8] suggest that the less electron-rich and bulkier $[Ru(PPh_3)_2(Cp)]^+$ center favors allenylidenes over vinylvinylidenes.

Deprotonation. Deprotonations of cationic allenylidenes **1**–**3** by NaOMe to give the enynyls **4**–**6** occur rapidly at room temperature. The moderate yields are most likely due to problems in isolating the alkane-soluble, air-sensitive compounds. The deprotonations occur so rapidly that methoxide does not add to the vinylidenes even though nucleophilic addition to the α carbon is well-known for other cationic vinylidene complexes.[1]

Heteroallene Reactions. Reactions of enynyl **4** with the heteroallenes CS_2, CO_2, MeNCS, and MeNCO were examined. Propynyl $[Fe(C{\equiv}CMe)(dppe)(Cp)]$ reacts with CS_2 at C_β to form a β-dithiolactone (2*H*-thiete-2-thione) complex **8b**, which undergoes ring-opening when methylated at sulfur by using iodomethane (Scheme III, [M] = [Fe(dppe)(Cp)], R = Me).[28] We were curious whether the conjugated alkene of enynyl **4** would become involved in the reaction with heteroallenes, perhaps by adding to CS_2 at C_δ rather than C_β or by inducing a [4 + 2] cycloaddition.

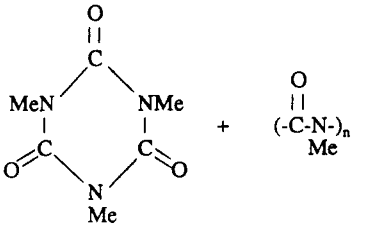
Enynyl **4** reacts with CS_2 in pentane to form a deep purple solid (**8a**, Scheme III), which was very poorly soluble in all common organic solvents. Although the purple color formed after a few minutes, an overnight reaction was required for the product to precipitate from the pentane solution. The resulting solid demonstrated remarkable thermal stability, showing no sign of melting or decomposition in an evacuated capillary at 400 °C. The poor solubility of the CS_2 adduct precluded purification by recrystallization, and attempted sublimation at 135 °C in dynamic vacuum led to slow decomposition. Attempts to grow single crystals by slow diffusion of CS_2-saturated nitrogen over a pentane solution of **4** yields only soft needle-like crystals, which were unsuitable for X-ray diffraction. Reaction of **8a** with MeI did not give the expected cationic vinylidene complex (Scheme III).

The electronic spectrum of **8a** showed absorption bands at 368 nm (ϵ = 9378 L mol^{-1} cm^{-1}) and 536 nm (ϵ = 3777 L mol^{-1} cm^{-1}), typical of a transition-metal complex of this color.[29] These bands are similar to those observed at 402 and 564 nm for **8b** but higher in energy than those of α-dithiopyrone (S=CSCH=CHCH=CH, λ = 436, 587 nm).[30] A strong IR absorption at 1250 cm^{-1} due to the thiocarbonyl group is at the high end of the range found for most thiones and thioesters (1190–1250 cm^{-1})[31] yet lower than that of the similar iron complex (1275 cm^{-1}). An absorption near 1050 cm^{-1} would be expected for the open-chain dithiocarboxylate form shown in Scheme III,[32] but none was found in this region. The Cp signal in the ^{1}H NMR spectrum of **8a** is at 4.8 ppm, at slightly lower field than the neutral parent enynyl **4** (4.5 ppm) but at much higher field than the corresponding cationic vinylidene **1** (6.0 ppm). This suggests that the metal center bears only a slight positive charge, more consistent with the closed 2*H*-thiete-2-thione structure **8a** and its contributing resonance form than with the open dithiocarboxylate form in which the metal bears a full formal positive charge. Thus, spectroscopic evidence suggests that the closed form **8a** is the best description of $4{\cdot}CS_2$, just as it was for $[Fe(C{\equiv}CMe)(dppe)(Cp)]{\cdot}CS_2$ (**8b**), so the pendant alkene of **4** is not involved in electrophilic addition to CS_2. We are not aware of any additional organometallic 2*H*-thiete-2-thiones in the literature, although Templeton has mentioned that alkynyls $Li[W(C{\equiv}CR)(CO)_3(dppe)]$ (R = Me, Bu^n) do not react cleanly with CS_2.[33]

Reactions of **4** with MeNCS gave mixtures of intractable products. Enynyl **4** did not react with CO_2 even under ultraviolet photolysis, consistent with the lack of reactivity of $[Fe(C{\equiv}CMe)(dppe)(Cp)]$.[28] Only the very nucleophilic alkynyls $Li[W(C{\equiv}CR)(CO)_3(dppe)]$ (R = Me, Bu^n) react with CO_2, and only when the lithium counterion is present to interact with the resulting carboxylate oxygen.[33]

Enynyl **4** did not undergo a cycloaddition reaction with MeNCO but instead showed a completely different mode of reactivity. Two major organic products were isolated after refluxing in THF (eq 2). The first was a cyclic trimer of MeNCO, trimethylisocyanurate,[9] which was sublimed from the reaction mixture and identified by ^{1}H NMR, IR, and mass spectroscopy. The sublimation residue contained a polymer whose ^{1}H NMR spectrum consisted of two singlets (3.23, 2.87 ppm) in an approximate 1:1 ratio. Mass spectrometry was consistent with the formula $(MeNCO)_n$ with *n* ranging up to at least 6. Methyl isocyanate polymerization is a well-known process, catalyzed by a variety of bases including cyanide, tertiary amines, and tertiary phosphines. The two ^{1}H NMR signals may be due to differing helical conformations (rodlike and random coil) of the typical nylon structure of the polymer backbone.[10] We were unable to characterize the metal-containing products. The metal complex (or a trace of dissociated PMe_3) apparently catalyzes the polymerization, since no polymer was formed by merely refluxing MeNCO in THF.

$$[M]\text{-}C{\equiv}C\text{-}R + MeN{=}C{=}O \longrightarrow$$



(2)

A few related reactions of metal complexes with isocyanates are known. Aryl isocyanates are trimerized by $[Ni(C{\equiv}CH)(PPh_3)(Cp)]$, but substituted alkynyls are inactive.[34] Related [2 + 2] cycloaddition reactions of nickel[35] and iron[36] alkynyls with ketenes and similar dipolar electrophiles have also been reported. Electron-rich, binuclear nickel isocyanide complexes convert methyl isocyanate or carbon dioxide to poly(dimethylcarbodiimide).[37] Hydrogenated dimers (RNHCONRCHO) are formed during the ruthenium-cluster-catalyzed hydrogenation of alkyl isocyanates (120 °C, 50 atm of H_2).[38]

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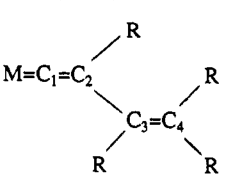
Table VI. Vinylvinylidene Geometries

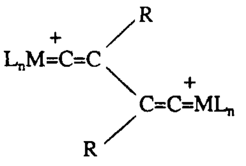


compd	M	M═C	C_1—C_2	C_2—C_3	C_3—C_4	M—C_1—C_2	C_1—C_2—C_3	C_2—C_3—C_4	C_1—C_2—C_3—C_4	ref
1	Ru	1.843 (7)	1.30 (1)	1.49 (1)	1.30 (1)	174.8 (6)	128.5 (7)	121.6 (8)	178.2	
7	Ru	1.83 (2)	1.29 (2)	1.45 (2)	1.37 (2)	166 (1)	127 (2)	120 (1)	174.6	3
9	Fe	1.746 (9)	1.33 (1)	1.50 (1)	1.32 (1)	174.9 (7)	120.4 (9)	123.7 (8)	−150.7	44
		1.766 (9)	1.32 (1)	1.50 (1)	1.33 (1)	170.0 (8)	123.7 (8)	120.4 (9)	−150.7	
10	Mo	1.951 (5)	1.353 (7)	1.47 (1)	1.353 (7)	177.9 (4)	123.8 (9)	123.8 (9)	180.0	45
11	Os	1.90 (1)	1.33 (1)	1.49 (1)	1.33 (2)	169 (3)	*a*	*a*	*a*	46
				1.46 (1)	1.31 (2)		*a*			
12	Re	1.90 (2)	1.33 (3)	1.46 (3)	1.41 (3)	179 (3)	116 (2)	119 (2)	29.7	47
13	W	1.899 (6)	1.376 (7)	1.482 (8)	1.345 (9)	174.4 (5)	120.1 (6)	121.9 (6)	43.5	48

[a] Coordinates not available.

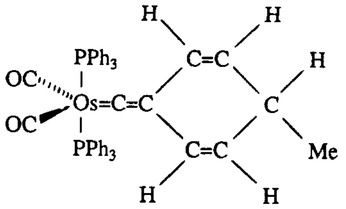
Molecular Structure of Vinylvinylidene Complex 1. The Ru–C1(vinylidene) bond length in 1 (1.843 (7) Å) falls at the short end of the range of formally double Ru–C bonds in similar $[RuL_2(Cp)]$ complexes,[8,18,39] from 1.823 (9) Å for $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(Cp)][BF_4]$[40] to 1.98 (2) Å for the alkylidene bond of $[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(Cp)_2][PF_6]_2$.[41] The Ru–C1 bond length in 1 is approximately equal to the 1.848 (9) Å Ru–C bond length in vinylidene $[Ru(C{=}CHMe)(PMe_3)_2(Cp)][PF_6]$[42] but slightly shorter than that of the allenylidene complex $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$[2] (1.884 (5) Å), consistent with significant metal to ligand π-backbonding in 1. Like most vinylidene complexes, the Ru–C1–C2 linkage is nearly linear and the C1–C2 and C3–C4 bond orders are clearly double.

Very few vinylvinylidene complexes have been previously reported, and only six structures were found in the Cambridge file.[43] Vinylvinylidene/alkylidene complex 7 was prepared by reacting $[RuCl(PPh_3)_2(Cp)]$ with $HC{\equiv}CC(OH)Me_2$.[3] Two divinylidene dications 9[44] and 10[45] were obtained by oxidative coupling of alkynyl or vinylidene $[L_nM(C{=}CHR)]^+$ complexes. Nucleophilic addition of $LiBHEt_3$ to $[Os(C\text{-}p\text{-}C_6H_4Me)(CO_2)(PPh_3)_2]^+[L_nM(C{\equiv}CR)]$ led to 11.[46] Complex 12, in which the vinyl substituent is η^2-bonded to a second rhenium center, was one of several products of the reaction of $[Re(thf)(CO_2)(Cp)]$ with $PhC{\equiv}CH$.[47] Vinylvinylidene complexes of zero valent tungsten (13)[48] and chromium (14)[26] have been prepared by alkyne cycloaddition to a vinylidene complex followed by ring opening. Relevant structural parameters are collected in Table VI. All of the complexes display short metal–carbon bonds, a definite alternation of double and single bond lengths in the vinylidene chain, and nearly linear M–C_1–C_2 linkages. The structures fall into two distinct groups with respect to the C_1–C_2–C_3–C_4 torsional angle; compounds 12 and 13 are *S*-cis at the C_2–C_3 single bond, and the others are *S*-trans. In complexes 1, 7, 9, and 10, *S*-trans geometry evidently minimizes steric interactions within the molecules. For osmium complex 11, *S*-trans geometry is obviously enforced by the cyclohexadienyl ring. In dirhenium complex 12, the *S*-cis ge-



9, L_nM = $[Ru(PPh_3)_2(Cp)]$, R = Me

10, L_nM = $[Mo(dppe)(C_7H_7)]$, R = Ph



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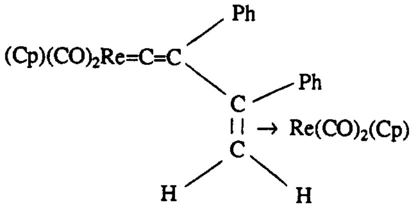

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(41) The 2.30 (2) Å Ru–alkylidene bond length reported for $[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(Cp)_2][PF_6]_2$ in ref 3 is incorrect.

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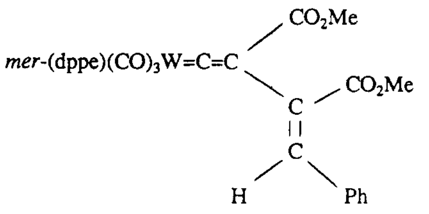

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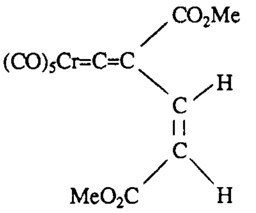

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ometry appears to minimize contacts between the $[Re(CO)_2(Cp)]$ groups at each end of the vinylvinylidene bridge. The reason for *S*-cis geometry in tungsten complex **13** is not obvious, but it may be a means of maximizing aromatic stacking between the phenyl substituent on the vinylvinylidene ligand and one of the dppe phenyl rings.

Conclusions. These results clearly indicate a preference for dehydration of hydroxyvinylidene intermediates to give vinylvinylidene, rather than allenylidene, products when protons are available on the δ-carbon atom in the $[Ru(PMe_3)_2(Cp)]^+$ system. This supports the intermediacy of a vinylvinylidene complex, presumably $[Ru[C{=}CHC(Me){=}CH_2](PPh_3)_2(Cp)]^+$, in the formation of dimer **7**.[3] Evidently, similar dimerization of **1** and **2** is prevented by the ring strain and the bridgehead double bonds, which would be present in similar dimers. Likewise, dimerization of **3** is prevented by the four additional methyl substituents, which interfere sterically and preclude the proton transfers from δ-carbons that accompany C—C bond making during the formation of **7**. Deprotonations of the cationic vinylvinylidene complexes straightforwardly lead to enynyls. Cycloaddition of enynyl **4** with CS_2 takes place in a [2 + 2] rather than a [4 + 2] fashion.

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Supplementary Material Available: Listings of positional and thermal parameters, bond distances, torsion angles, and least-squares planes (4 pages); a table of experimental and calculated structure factors for the structure of 1 (22 pages). Ordering information is available on any current masthead page.

Catalytic Oligomerization of Terminal Alkynes by Lanthanide Carbyls $(\eta^5\text{-}C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, La, Ce)

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Lanthanide and group 3 carbyls $Cp^*_2LnCH(SiMe_3)_2$ (**1**, Ln = Y; **2**, Ln = La; **3**, Ln = Ce) are active catalyst precursors for the oligomerization of terminal alkynes $HC{\equiv}CR$ (R = alkyl, aryl, $SiMe_3$). The regioselectivity and the extent of oligomerization depend strongly on the lanthanide applied as well as on the alkyne substituent R. For yttrium, alkyl-substituted alkynes are dimerized selectively to 2,4-disubstituted 1-buten-3-ynes whereas mixtures of two enyne isomers, i.e. 2,4-disubstituted 1-buten-3-ynes and 1,4-disubstituted 1-buten-3-ynes, are found for phenylacetylene and (trimethylsilyl)acetylene. The reactions with lanthanum and cerium produce, besides dimers, higher oligomers (trimers, tetramers) of various sorts (allenes and diynes). NMR studies indicate that lanthanide acetylides $[Cp^*_2LnC{\equiv}CR]_n$, formed by σ-bond metathesis between the carbyls and the alkyne CH bond, are the active species in the catalytic cycle. Two oligomeric cerium acetylides $[Cp^*_2CeC{\equiv}CR]_n$ (**7**, R = *t*-Bu; **20**, R = Me) have been synthesized on a preparative scale. Spectroscopic data for these compounds suggest a significant contribution of the CC triple bond in the bonding of the acetylide unit.

Introduction

Linear and cyclooligomerization of terminal alkynes by various transition metals has been studied extensively.[1,2] However, only a few catalyst systems, mainly based on Pd, Rh, Ru, Cu, or Cr, are known for the dimerization of terminal alkynes.[3] The coupling reactions are not very selective, and in general, mixtures of various dimers are produced: 1,4-disubstituted butatrienes, 2,4-disubstituted enynes, or 1,4-disubstituted enynes (Figure 1).

The first step in the catalytic cycle is believed to be an alkyne CH bond activation, which produces the active metal acetylide, $L_nMC{\equiv}CR$. However, detailed mecha-

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(1) The following abbreviations are used in this article: Ln = lanthanide or group 3 element; Cp* = η^5-pentamethylcyclopentadienyl ring; lw = linewidths of NMR resonances at half maximum.

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