Synthesis of Butenynylruthenium Complexes from Hydrido, Alkenyl, or Alkynyl Complexes

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Summary: The reaction of $Ru(CO)ClH(PPh_3)_3$ with 1-alkynes in 1,2-dichloroethane under reflux conditions provides the coordinatively unsaturated butenynyl complexes $[Ru\{C(C{\equiv}CR){=}CHR\}(CO)Cl(PPh_3)_2]$ in good yield. These and related butenynyl complexes were also prepared by starting from the corresponding alkenyl- or alkynylruthenium complexes. Hydrogenolysis of $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)Cl(PPh_3)_2]$ in the presence of pyridine gave (Z)-1,4-diphenylbutenyne and $Ru(CO)ClH(py)(PPh_3)_2$.

The reaction of ruthenium hydrides, such as $Ru(CO)ClH(PPh_3)_3$ (1), with alkynes usually results in the formation of σ-alkenyl derivatives by insertion of the alkyne into the Ru–H bond (hydroruthenation).[1] However, the cationic hydrides $[Ru(CO)H(py)_2(PPh_3)_2]A$ (A = ClO_4, BF_4, PF_6) react with 1-alkynes to give (σ-alkynyl)-ruthenium derivatives.[2] In this process, labile alkenyl complexes were formed first, which react with another molecule of alkyne to give alkynyl complexes and 1-alkenes.[2] On the other hand, phenylacetylene reacts in the presence of a catalytic amount of these hydrides to give (Z)-1,4-diphenyl-1-buten-3-yne as the major product.[3] These results, as well as related work reported in the literature,[4] suggest that σ-alkynyl complexes are intermediates in the formation of σ-butenynyl complexes (Scheme I).[5] The last step in this scheme probably involves an insertion of a σ-alkynyl group into a *cis*-vinylidene ligand.[4f,g,k] Related complexes are formed by metal-catalyzed dimerization of alkynes[4] or by reaction between butadiynes and hydrides.[4l,m,6] Butenynyl complexes are likely intermediates in the potentially useful dimerization of alkynes leading to butenynes[3,4f,g] or butatrienes.[4l,m] Here we report a simple synthesis of coordinatively unsaturated butenynylruthenium complexes from the readily available hydride 1[6] and 1-alkynes. Furthermore, we have found that butenynyl complexes can also be prepared directly by starting from the corresponding alkenyl- or alkynylruthenium complexes.

Ruthenium hydride 1 reacts with 1-alkynes in dichloromethane to give σ-alkenyl derivatives.[1] More reactive substrates, such as methyl propiolate, lead also to butenynyl complexes in the presence of excess alkyne.[7] However, when hydride 1 was heated in 1,2-dichloroethane under reflux in the presence of excess 1-alkyne, butenynyl complexes **3–6** were cleanly obtained in good yield as the only isolated products (Scheme II). Similar results were obtained for hydride **2** with a quinoline ligand. However, the related isoquinoline hydride, similarly prepared from 1,[8] gave no butenynyl complexes under these reaction conditions. The stereochemistry of hydride **2** was assigned by analogy with that of the related (pyrazole)ruthenium hydride.[9] Complexes **3** and **5** have been prepared before by hydroruthenation of 1,4-di-*tert*-butylbutadiyne[4l,m] and 1,4-diphenylbutadiyne,[6] respectively. The structures of **4** and **6** were established by spectroscopic methods and by comparison with the structures of **3** and **5**. Alkenyl complex **7**, prepared by hydroruthenation of phenylacetylene with hydride 1,[1] reacts with excess phenylacetylene to give **5** as the only isolated product (Scheme II), probably by first forming a σ-alkynyl complexes. Alkynyl complexes derived from hydride 1 were indeed detected by IR analysis of the crude reaction mixtures, although they could not be isolated pure.

Treatment of butenynyl complex **5** with 1 atm of H_2 in dichloromethane in the presence of 1 equiv of pyridine at room temperature for 22 h led smoothly to (Z)-1,4-

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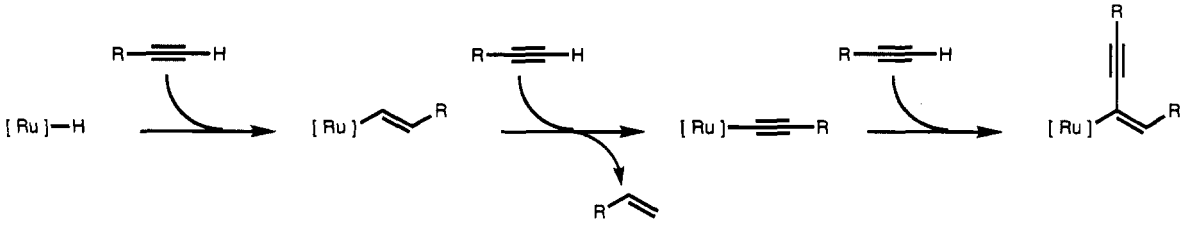
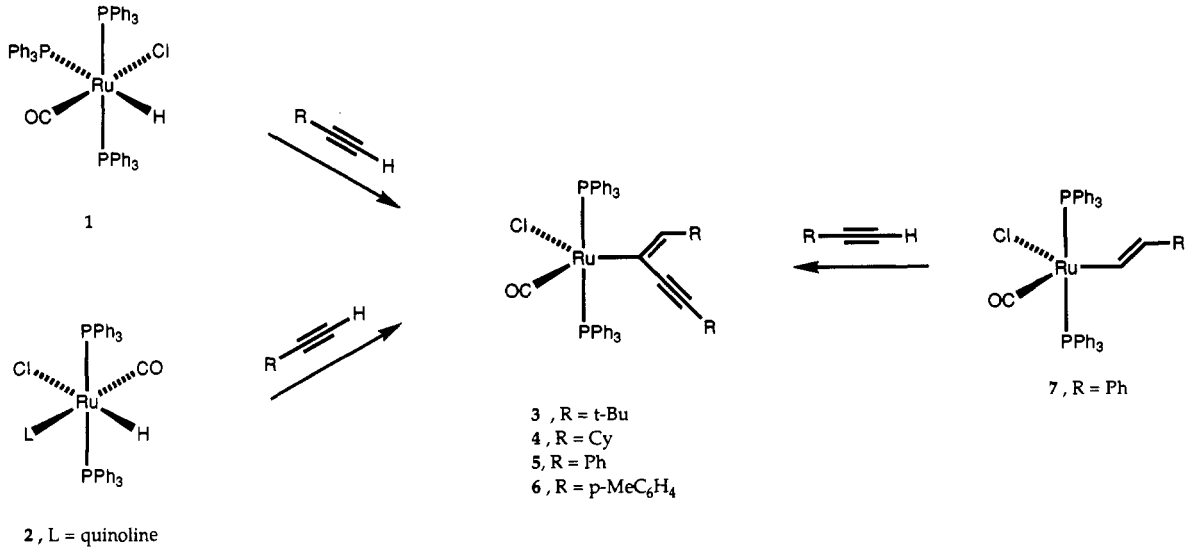
Scheme I



Scheme II



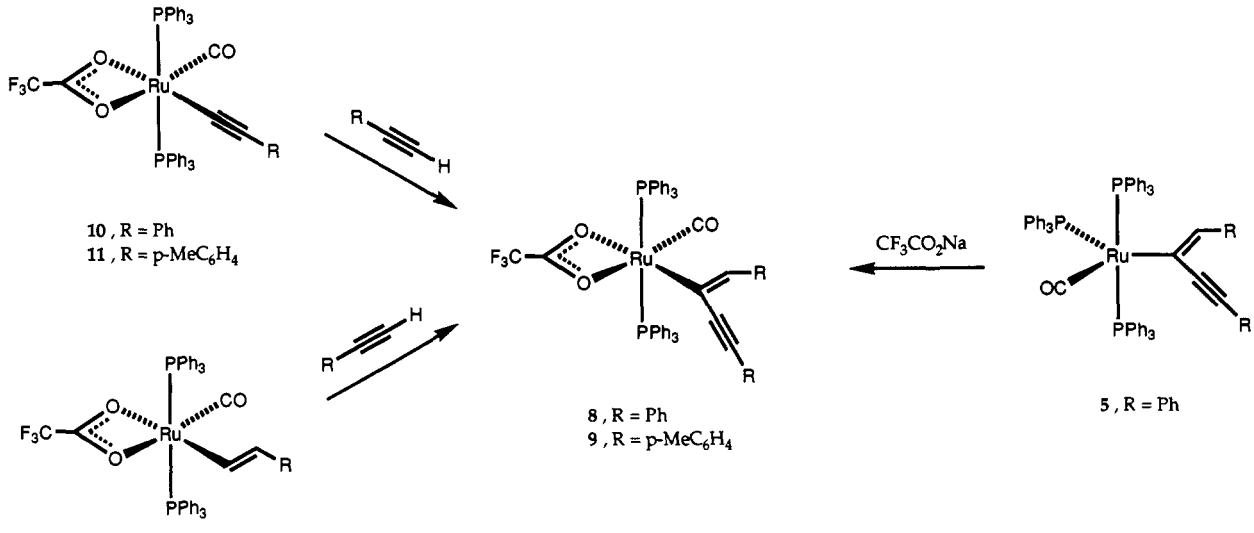
1

2, L = quinoline

3, R = t-Bu
4, R = Cy
5, R = Ph
6, R = p-MeC$_6$H$_4$

7, R = Ph

Scheme III



10, R = Ph
11, R = p-MeC$_6$H$_4$

8, R = Ph
9, R = p-MeC$_6$H$_4$

5, R = Ph

12, R = t-Bu
13, R = Ph

diphenyl-1-buten-3-yne in almost quantitative yield, along with the corresponding hydride Ru(CO)ClH(py)(PPh$_3$)$_2$.[10]

Butenynyl complexes **8** and **9**[4a-c] were prepared from alkynyl complexes **10** and **11** or alkenyl complexes **12** and **13** in good yield (Scheme III). In agreement with the formation of free 1-alkenes by reaction of alkenyl complexes with 1-alkynes,[2] formation of 3,3-dimethyl-1-butene in quantitative yield was observed in the formation of **9** from alkenyl complex **12**. Reaction of **13** with phenylacetylene gave **8** and free styrene. Alkynyl ligand exchange is a fast reaction under these reaction conditions. Thus, phenylacetylene complex **10** leads to butenynyl species **9** when treated with excess *p*-tolylacetylene. Additionally, (*Z*)-1,4-diphenyl-1-buten-3-yne was also obtained in low yield in the preparation of **8** from alkenyl compound **13**. In contrast with the reactivity of **10** and **11**, alkynyl complex **20** was recovered unchanged when treated with excess alkynes in 1,2-dichloroethane under reflux conditions. The starting alkenyl or alkynyl complexes were synthesized as shown in Scheme IV from the corresponding neutral[1] or cationic[2] alkenyl (**14–17**) and alkynyl complexes (**18** and **19**)[3] by ligand-exchange reactions. Complex **8** was also

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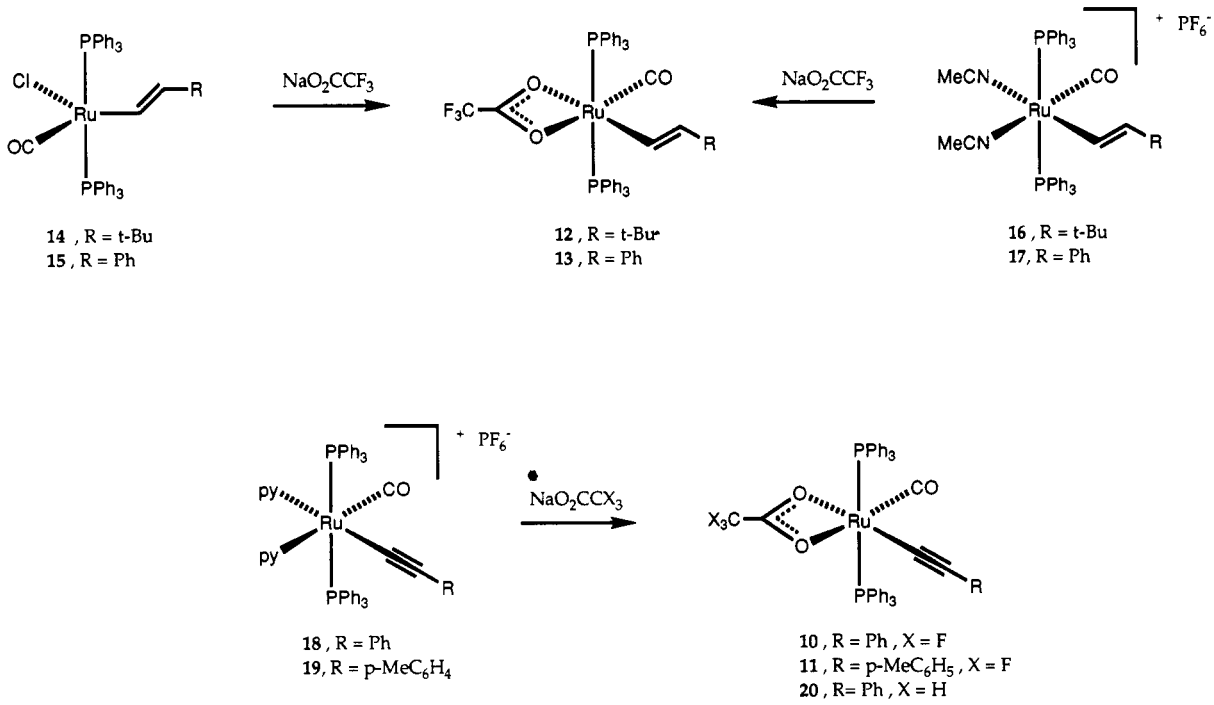
Scheme IV



14, R = t-Bu
15, R = Ph

12, R = t-Bu
13, R = Ph

16, R = t-Bu
17, R = Ph

18, R = Ph
19, R = p-MeC_6H_4

10, R = Ph, X = F
11, R = p-MeC_6H_5, X = F
20, R = Ph, X = H

prepared from **5** by treatment with sodium trifluoroacetate. Monitoring the reaction of alkenyl complex **13** with phenylacetylene by ^1H NMR in benzene-d_6 showed formation of styrene and **9**, in accordance with the reaction pathway outlined in Scheme I.

In summary, η^1-butenynyl complexes **3–6**, **8**, and **9** have been prepared from readily available starting materials. The formation of butenynyl complexes **8** and **9** from **10–13** supports the intermediacy of alkenyl and alkynyl complexes in these transformations.

Experimental Section

^1H NMR spectra were recorded on a Bruker AM 200 (200 MHz) or a Varian XL-300 (300 MHz) spectrometer in $CDCl_3$. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM 200 (50 MHz) instrument in $CDCl_3$. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300 (121 MHz) spectrometer. IR spectra were recorded on a Pye Unicam SP-3-300S spectrophotometer using KBr disks. Elemental analyses were performed at the Instituto de Química Orgánica. 1,2-Dichloroethane was distilled from calcium hydride. All reactions were performed under a N_2 atmosphere.

Ru(CO)ClH(quin)(PPh_3)$_2$ (2). To a suspension of hydride **1** (300 mg, 0.31 mmol) in ethanol (30 mL) was added quinoline (1.0 mL, 8.46 mmol), and the resulting mixture was heated under reflux conditions for 8 h. After being cooled to room temperature, the mixture was filtered off and washed with ethanol, Et_2O, and hexane to give **2** as a white solid (228 mg, 90%): IR (cm^{-1}) ν(Ru–H) 2040 m, ν(C≡O) 1905 s; ^1H NMR (200 MHz) δ 9.80–9.55 (m, 1 H, quin), 9.22–8.96 (m, 1 H, quin), 7.83–6.90 (m, 34 H, 2 PPh_3 + 4 H, quin), 6.68–6.49 (m, 1 H, quin), −13.05 (t, J = 19.5 Hz, 1 H, Ru–H). Anal. Calcd for $C_{46}H_{38}ClNOP_2Ru$: C, 67.44; H, 4.67; N, 1.71. Found: C, 67.06; H, 4.61; N, 1.54.

Synthesis of (σ-Butenynyl)ruthenium Complexes 3–6. General Procedure. To a suspension of hydride **1**[7] (310 mg, 0.33 mmol) in 1,2-dichloroethane (3 mL) was added the corresponding 1-alkyne (2.5–3.5 mmol). The resulting mixture was heated under reflux conditions for 2–3 h. After being cooled to room temperature, the solvent was evaporated and the resulting residue was triturated with Et_2O to give the butenynyl complexes in the stated yields. Complex **6** was similarly prepared from hydride **2** by following the same procedure (5 h of heating under reflux conditions). Complex **5** was prepared from alkenyl complex **7** under the same reaction conditions (1.5 h under reflux conditions).

3[4l,m] (90%): IR (cm^{-1}) ν(C≡C) 2150 vw, ν(C≡O) 1910 vs; ^1H NMR (300 MHz) δ 7.75–7.62 (m, 12 H, PPh_3), 7.41–7.26 (m, 18 H, PPh_3), 4.64 (t, J = 1.9 Hz, HC≡C), 1.04 (s, 9 H, t-Bu), 0.63 (s, 9 H, t-Bu). Anal. Calcd for $C_{49}H_{49}ClOP_2Ru$: C, 69.04; H, 5.79. Found: C, 69.16; H, 5.51.

4 (70%): IR (cm^{-1}) ν(C≡C) 2050 m, ν(C≡O) 1915 vs; ^1H NMR (300 MHz) δ 7.67–7.62 (m, 12 H, PPh_3), 7.37–7.30 (m, 18 H, PPh_3), 4.41 (dt, J = 7.7, 1.4 Hz, HC≡C), 2.10–2.00 (m, 1 H, Cy), 1.92–1.86 (m, 1 H, Cy), 1.53–1.43 (m, 8 H, Cy), 1.27–0.98 (m, 10 H, Cy), 0.60–0.49 (m, 2 H, Cy); ^{13}C NMR (50 MHz) δ 208.43 (t, J = 14.6 Hz, CO), 143.63, 134.72 (t, J = 5.7 Hz, PPh_3), 132.66 (t, J = 21.9 Hz, PPh_3), 121.67 (s, PPh_3), 127.84 (t, J = 4.8 Hz, PPh_3), 117.71, 70.78, 44.03, 32.75, 31.55, 26.15, 25.89, 24.92 (three carbon signals were not observed). Anal. Calcd for $C_{53}H_{53}ClOP_2Ru$: C, 70.38; H, 5.91. Found: C, 70.15; H, 5.77.

5[6] (77% from hydride **1** and 67% from alkenyl **7**[1]): IR (cm^{-1}) ν(C≡C) 2090 vw, ν(C≡O) 1925 vs; ^1H NMR (300 MHz) δ 7.68–7.59 (m, 12 H, PPh_3), 7.23–7.07 (m, 23 H, PPh_3 + Ph), 5.29 (t, J = 1.5 Hz, HC≡C).

6 (77% from hydride **1** and 58% from hydride **2**): IR (cm^{-1}) ν(C≡C) 2100 vw, ν(C≡O) 1920 vs; ^1H NMR (300 MHz) δ 7.68–7.55 (m, 12 H, PPh_3), 7.27–7.09 (m, 18 H, PPh_3), 7.06–6.95 (m, 8 H, C_6H_4), 5.23 (t, J = 1.5 Hz, HC≡C), 2.34 (s, 3 H, Me), 2.28 (s, 3 H, Me); ^{31}P NMR (121 MHz) δ 33.89. Anal. Calcd for $C_{55}H_{44}ClOP_2Ru$: C, 71.85; H, 4.82. Found: C, 71.68; H, 4.60.

Hydrogenolysis of Complex 5. A mixture of complex **5** (303 mg, 0.34 mmol) and pyridine (0.028 mL, 0.35 mmol) in dichloromethane (20 mL) was stirred under H_2 (1 atm) at 23 °C for 22 h. The solvent was evaporated, and the residue was triturated with Et_2O to give Ru(CO)ClH(py)(PPh_3)$_2$ (190 mg, 73%). Evaporation of the filtrate and chromatography gave (*Z*)-1,4-diphenyl-1-buten-3-yne (68 mg, 98%).[3]

Synthesis of (σ-Butenynyl)ruthenium Complexes 8 and 9. (a) Synthesis of Complex 8 from Alkynyl Complex 10. To a suspension of complex **10** (213 mg, 0.24 mmol) in ethanol (15 mL) was added phenylacetylene (0.20 mL, 1.82 mmol), and the resulting mixture was heated under reflux conditions for 1 h. After being cooled to room temperature, the mixture was filtered off to yield complex **10** as a bright yellow solid (170 mg, 71%) identical with the compound previously prepared from the

corresponding hydride:[4a,b] ^{1}H NMR (300 MHz) δ 7.53–7.46 (m, 12 H, PPh_3), 7.36–7.22 (m, 24 H, 18 H PPh_3 + 6 H Ph), 7.06–7.00 (m, 2 H, Ph), 6.98–6.88 (m, 2 H, Ph), 5.78 (br s, 1 H).

(b) Synthesis of Complex 8 from Alkenyl Complex 13. To a suspension of **13** (101 mg, 0.1 mmol) in toluene (4 mL) was added phenylacetylene (0.10 mL, 0.91 mmol), and the resulting mixture was heated under reflux conditions for 1.5 h. After being cooled to room temperature, the solvent was evaporated and the residue was triturated with Et_2O to give **8** (70 mg, 60%). Flash chromatography (silica gel, hexanes as eluent) of the filtrate gave (*Z*)-1,4-diphenyl-1-buten-3-yne in low yield (*ca.* 5%).[3] When the same reaction was performed in benzene-d_6 in an NMR tube, styrene was detected as the major alkene product after 11 h at 23 °C. After additional stirring at 50 °C for 30 min, a 1:2.4 ratio of styrene to complex **8** was determined.

(c) Synthesis of Complex 8 from Butenynyl Complex 5. To a solution of **5** (225 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was added NaO_2CCF_3 (142 mg, 1.04 mmol). The resulting suspension was stirred at 23 °C for 21 h. The mixture was filtered and evaporated. The residue was triturated with hexane to give **8** (210 mg, 88%).

(d) Synthesis of Complex 9 from Alkynyl Complex 11. To a suspension of complex **11** (91 mg, 0.10 mmol) in ethanol (6 mL) was added tolylacetylene (0.10 mL, 0.79 mmol), and the resulting mixture was heated under reflux conditions for 1.5 h. After being cooled to room temperature, the mixture was filtered off to yield complex **10** as a yellow solid (70 mg, 70%) identical with the compound previously prepared from the corresponding hydride:[4l,m] ^{1}H NMR (200 MHz) δ 7.51–7.48 (m, 12 H, PPh_3), 7.33–7.24 (m, 22 H, 18 H PPh_3 + 4 H C_6H_4), 6.90–6.75 (m, 4 H, C_6H_4), 5.74 (br s, 1 H, C=CH), 2.41 (s, 3 H, Me), 2.24 (s, 3 H, Me).

(e) Synthesis of Complex 9 from Alkynyl Complex 10. To a suspension of complex **10** (336 mg, 0.39 mmol) in ethanol (15 mL) was added tolylacetylene (0.40 mL, 3.15 mmol), and the resulting mixture was heated under reflux conditions for 1.5 h. After being cooled to room temperature, the mixture was filtered off to yield complex **9** as a yellow solid (170 mg, 44%).

(f) Synthesis of Complex 9 from Alkenyl Complex 12. A solution of complex **12** (177 mg, 0.21 mmol) and tolylacetylene (0.21 mL, 1.67 mmol) in toluene (5 mL) was heated under reflux conditions for 1.5 h. After being cooled to room temperature, the solvent was evaporated and the residue was triturated with hexane to yield **9** (127 mg, 61%). A reaction in a sealed tube ($CDCl_3$ solution) was monitored by ^{1}H NMR. Identical integrations were obtained by recording the spectra at 30, 0, or −20 °C. After 30 min at 50 °C, the yield of 3,3-dimethyl-1-butene was 16%. Quantitative formation (by NMR) of the alkene was obtained after additional 3.5 h at 80 °C.

Synthesis of Alkenyl Complexes 12 and 13. General Procedure. To a suspension of alkenyl complex in toluene was added NaO_2CCF_3 (1.5 equiv) and the mixture was stirred at 23 °C for 12–13 h. Faster reactions, but lower yields, were obtained when the reactions were heated under reflux conditions. The mixture was filtered, and the solvent was evaporated. The residue was triturated with hexane to give the alkenyl complexes as yellow solids in the stated yields.

12 (77% from **14**[1b] and 41% from **16**[1c]): IR (cm^{-1}) ν(C≡O) 1950 vs, ν(OCO) 1650 m; ^{1}H NMR (200 MHz) δ 7.45–7.32 (m, 30 H, PPh_3), 6.28 (dt, *J* = 14.5, 2.2 Hz, HC=C), 4.95 (dt, *J* = 14.5, 2.0 Hz, C=CH), 0.35 (s, 9 H, *t*-Bu); ^{31}P NMR (121 MHz) δ 37.16. Anal. Calcd for $C_{45}H_{41}F_3O_3P_2Ru$: C, 63.60; H, 4.86. Found: C, 63.53; H, 5.09.

13 (70% from **15**[1a] and 72% from **17**[1c]): IR (cm^{-1}) ν(C≡O) 1925 vs, ν(OCO) 1610 m; ^{1}H NMR (200 MHz) δ 7.71 (dt, *J* = 14.9, 2.7 Hz, HC=C), 7.47–7.24 (m, 30 H, PPh_3), 7.02–6.86 (m, 3 H, Ph), 6.39–6.35 (m, 2 H, Ph), 5.72 (d, *J* = 14.5 Hz, C=CH); ^{31}P NMR (121 MHz) δ 36.97. Anal. Calcd for $C_{47}H_{37}F_3O_3P_2Ru{\cdot}H_2O$: C, 63.58; H, 4.43. Found: C, 63.80; H, 4.52.

Alkynyl Complex 19. This complex was prepared from $[Ru(CO)H(py)_2(PPh_3)_2]^+PF_6^-$ (845 mg, 0.88 mmol) and tolylacetylene (0.25 mL, 1.97 mmol) in CH_2Cl_2 (30 mL).[2] After being stirred at 23 °C for 23 h, the solvent was evaporated. The resulting residue was triturated with Et_2O to yield **19** as a white solid (900 mg, 95%): IR (cm^{-1}) ν(C≡C) 2100 w, ν(C≡O) 1945 vs, ν(PF_6^-) 840 vs; ^{1}H NMR (300 MHz) δ 8.10 (d, *J* = 5.1 Hz, 2 H, py), 7.56–7.38 (m, 12 H, PPh_3), 7.37–7.25 (m, 10 H, PPh_3 + 4 H py), 7.21–7.16 (m, 12 H, PPh_3), 6.98 (d, *J* = 8.0 Hz, 2 H, C_6H_4), 6.82 (d, *J* = 8.0 Hz, 2 H, C_6H_4), 6.75–6.72 (m, 4 H, py), 2.30 (s, 3 H, Me). Anal. Calcd for $C_{56}H_{47}F_6N_2OP_3Ru$: C, 62.75; H, 4.42; N, 2.61. Found: C, 62.55; H, 4.40; N, 2.53.

Synthesis of Alkynyl Complexes 10, 11, and 20. General Procedure. To a suspension of the alkynyl complex in toluene was added NaO_2CCF_3 (2 equiv), and the mixture was heated at 90 °C for 2 h. Complex **20** was similarly prepared in ethanol under reflux conditions for 1 h with NaO_2CCH_3 (1.7 equiv). The mixture was filtered and the solvent was evaporated. The residue was triturated with Et_2O to give the alkynyl complexes as yellow solids in the stated yields.

10 (76% from **18**[3]): IR (cm^{-1}) ν(C≡C) 2090 m, ν(C≡O) 1950 vs, ν(OCO) 1685 m; ^{1}H NMR (300 MHz) δ 7.66–7.59 (m, 12 H, PPh_3), 7.37–7.20 (m, 21 H, 15 H PPh_3 + 6 H Ph), 6.90 (d, *J* = 7.5 Hz, 2 H, Ph). Anal. Calcd for $C_{47}H_{35}F_3O_3P_2Ru$: C, 65.05; H, 4.06. Found: C, 65.08; H, 4.14.

11 (70% from **19**): IR (cm^{-1}) ν(C≡C) 2110 m, ν(C≡O) 1960 vs, ν(OCO) 1685 m; ^{1}H NMR (300 MHz) δ 7.57–7.49 (m, 12 H, PPh_3), 7.35–7.14 (m, 18 H, PPh_3), 6.95 (d, *J* = 8.0 Hz, 2 H, C_6H_4), 6.81 (d, *J* = 8.0 Hz, 2 H, C_6H_4), 2.29 (s, 3 H); ^{31}P NMR (121 MHz) δ 33.67. Anal. Calcd for $C_{48}H_{37}F_3O_3P_2Ru$: C, 65.38; H, 4.23. Found: C, 65.18; H, 4.51.

20 (80% from **18**[2]): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1940 vs, ν(OCO) 1510 m; ^{1}H NMR (300 MHz) δ 7.63–7.57 (m, 12 H, PPh_3), 7.41–7.36 (m, 18 H, PPh_3), 6.91–6.88 (m, 3 H, Ph), 6.26–6.23 (m, 2 H, Ph), 0.55 (s, 3 H); ^{13}C NMR (50 MHz) δ 204.45 (t, *J* = 13.6 H, C≡O), 185.06 (t, *J* = 1.3 Hz, C=O), 134.70 (t, *J* = 5.8 Hz, PPh_3), 131.27 (t, *J* = 22.3 Hz, PPh_3), 130.73 (s, Ph), 129.93 (s, PPh_3), 129.06 (s, Ph), 128.03 (t, *J* = 4.8 Hz, PPh_3), 127.14 (s, Ph), 123.89 (s, Ph), 115.33 (t, *J* = 1.4 Hz, C≡), 107.41 (t, *J* = 16.6 Hz, ≡C), 22.39 (s, Me). Anal. Calcd for $C_{47}H_{38}O_3P_2Ru$: C, 69.36; H, 4.71. Found: C, 69.10; H, 4.95.

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