The Effect of N-Donor Ligands on the Reaction of Ruthenium Hydrides with 1-Alkynes

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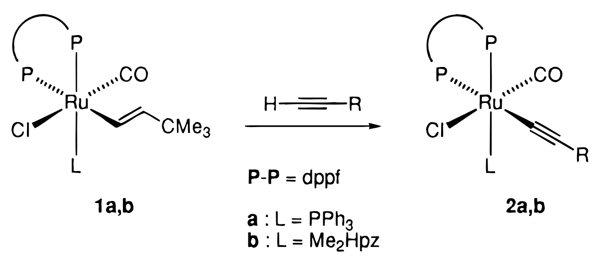
Neutral ruthenium hydrides $Ru(CO)ClH(L)(PPh_3)_2$ bearing one N-donor ligand react with 1-alkynes at 23 °C to yield neutral alkenyl complexes $Ru(CO)Cl(CH{=}CHR)(L)(PPh_3)_2$. Under similar conditions, cationic hydrido complexes $[Ru(CO)H(L)_2(PPh_3)_2]PF_6$ with pyridine-type N-donor ligands yield alkynyl complexes $[Ru(CO)(CH{\equiv}CHR)(L)_2(PPh_3)_2]PF_6$ as a result of the reaction of the intermediate labile alkenyl with a second molecule of alkyne. Under more forcing conditions, 1-alkynyl complexes could also be prepared from the neutral ruthenium hydrides. Cationic ruthenium hydrides with bidentate N-donor ligands are unreactive toward 1-alkynes. Neutral alkenyl complexes $Ru(CO)Cl(CH{=}CHR)(L)(PPh_3)_2$ (R = *p*-MeC_6H_4, CMe_3; L = pyridine, isoquinoline) reacted smoothly with 1-alkynes to afford the corresponding σ-alkynyl ruthenium derivatives $Ru(CO)Cl(C{\equiv}CR)(L)(PPh_3)_2$.

Introduction

The hydroruthenation of alkynes with ruthenium hydrides usually leads to the selective formation of *E*-alkenylruthenium complexes.[1,2] Under certain conditions, the resulting σ-alkenylruthenium complexes may undergo metathesis with the CH bond of a second molecule of alkyne to furnish σ-alkynylruthenium complexes with concomitant formation of the 1-alkene corresponding to the starting alkenyl derivative.[3,4] These alkynyl complexes may further react with a third molecule of alkyne under more forcing conditions to give butenynylruthenium complexes.[5] This last process involves isomerization of the alkynyl ligand to a vinylidene, followed by insertion of the cis-coordinated η^2-alkyne into the ruthenium−carbon double bond.[6]

Ruthenium-catalyzed transformations of alkynes into useful organic products have great synthetic potential.[7] Additionally, construction of organometallic frameworks based on alkynyl−metal bonds has attracted great interest.[8] We have recently synthesized ruthenium alkenyl complexes **1a**,**b** which were able to react smoothly with 1-alkynes at room temperature to furnish the required σ-alkynylruthenium complexes **2a**,**b** (eq 1).[4]



(1)

With the purpose of developping less sterically-congested alkenyl complexes for the selective capping of alkyne-containing molecules with a ruthenium complex, we decided to examine in detail the effect of nitrogen donor ligands on the reactivity of two series of ruthenium hydrides, namely neutral $Ru(CO)ClH(L)(PPh_3)_2$ and cationic $[Ru(CO)H(L)_2(PPh_3)_2]PF_6$, toward 1-alkynes to determine the factors that control the reactivity of the primary σ-alkenylruthenium complexes with 1-alkynes to give σ-alkynylruthenium complexes. Our aim was to synthesize new alkenyl derivatives that were isolable and storable under ordinary laboratory conditions yet sufficiently reactive in the metathesis reaction with 1-alkynes. Herein, we report the results of this study.

Results and Discussion

Ruthenium Hydrides. Neutral (**3**−**6**) and cationic ruthenium hydrides (**7**−**13**) were readily prepared according to known or an extension of known methods.

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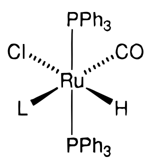
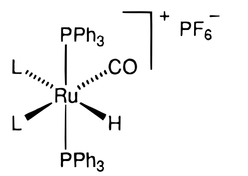
Table 1. Spectroscopic and Analytical Data for New Ruthenium Hydrides

hydride complex	IR (KBr cm^{-1}) ν(Ru−H)	IR (KBr cm^{-1}) ν(C≡O)	^{1}H NMR (CDCl$_3$, 23 °C) hydride	^{1}H NMR (CDCl$_3$, 23 °C) other signals	formula	anal. calcd (found) C	anal. calcd (found) H	anal. calcd (found) N
5	1995 (s)	1905 (vs)	−13.66 (t, J = 19.6 Hz)	7.68−7.56 (m, 12H), 7.32−7.19 (m, 18H) 7.01 (s, 1H), 6.31 (s, 1H), 5.98 (t, J = 1.4 Hz, 1H), 3.03 (s, 3H)	$C_{41}H_{37}ClN_2OP_2Ru$	63.77 (63.47)	4.83 (4.84)	3.63 (3.58)
6	2000 (m)	1920 (vs)	−13.39 (t, J = 19.5 Hz)	9.35−9.17 (m, 1H), 8.00−7.78 (m, 1H), 7.75−7.26 (m, 19H), 7.24−7.05 (m, 15H), 6.75−6.58 (m, 1H)	$C_{46}H_{38}ClNOP_2Ru$	67.44 (67.08)	4.68 (4.66)	1.71 (1.74)
7	1990 (w)	1910 (vs)	−12.49 (t, J = 20.3 Hz)	7.37−7.22 (m, 30H), 6.68 (br s, 1H), 6.56 (br s, 1H), 6.36 (br s, 1H), 6.30 (br s, 1H), 6.18 (br s, 1H), 6.12 (br s, 1H), 3.36 (s, 3H), 3.12 (s, 3H)	$C_{45}H_{43}F_6N_4OP_3Ru$	56.08 (55.81)	4.50 (4.45)	5.81 (5.85)
9	*a*	1920 (vs)	−12.89 (t, J = 20.6 Hz)	7.36−7.19 (m, 34H), 5.99 (d, J = 7.1 Hz, 4H), 2.91 (s, 6H), 2.80 (s, 6H)	$C_{51}H_{51}F_6N_4OP_3Ru$	58.68 (58.96)	4.92 (5.02)	5.37 (5.40)
10[b]	*a*	1920 (vs)	−12.85 (t, J = 20.3 Hz)	8.23 (s, 1H), 8.20 (s, 1H), 7.81−7.36 (m, 10H), 7.35−7.20 (m, 14H), 7.19−7.04 (m, 18H)	$C_{55}H_{45}F_6N_2OP_3Ru$	62.44 (62.20)	4.29 (4.40)	2.65 (2.60)
13	2000 (w)	1950 (vs)	−11.10 (t, J = 20.6 Hz)	8.12 (d, J = 7.4 Hz, 2H), 7.90−7.60 (m, 40H), 6.74 (d, J = 7.4 Hz, 2H), 6.23 (d, J = 7.4 Hz, 2H)	$C_{61}H_{47}F_6N_2OP_3Ru{\cdot}H_2O$	63.71 (63.38)	4.29 (4.27)	2.44 (2.00)

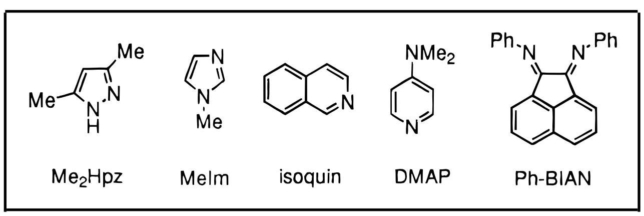
[a] Not observed. [b] A NOEDIFF experiment showed a 10% enhancement of H-1 of isoquinoline ligands after irradiation of the hydride resonance.



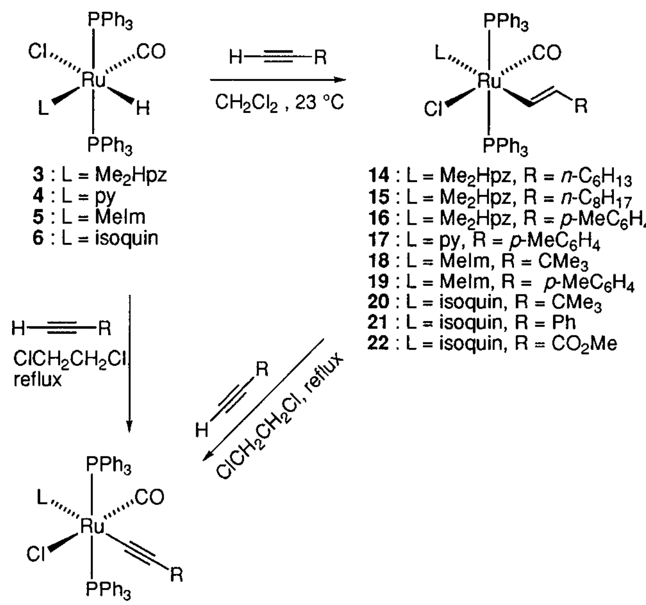
3 : L = Me$_2$Hpz
4 : L = py
5 : L = MeIm
6 : L = isoquin



7 : L = MeIm
8 : L = py
9 : L = DMAP
10 : L = isoquin
11 : L$_2$ = bpy
12 : L$_2$ = phen
13 : L$_2$ = Ph-BIAN



Scheme 1



23 : L = py, R = n-C_8H_{17}
24 : L = py, R = p-MeC_6H_4
25 : L = isoquin, R = Ph
26 : L = isoquin, R = p-MeC_6H_4

However, preparation of analogous complexes with one or two quinoline ligands failed. The spectroscopic and analytical data of new hydride complexes are summarized in Table 1. The stereochemistry of new neutral hydrides **5** and **6** was assigned by comparison of the IR and NMR data with those of known hydrides **3**[9] and **4**.[10] Cationic hydrides showed two mutually *trans*-PPh_3 ligands and *cis*-L ligands.

Alkenyl- and Alkynylruthenium Complexes. Reactions of neutral ruthenium hydrides **3**−**6** with 1-alkynes proceeded at room temperature in CH_2Cl_2 to give *E*-alkenyl complexes[1] Ru(CO)Cl(CH=CHR)L(PPh_3)$_2$ (**14**−**22**) (Scheme 1). The stereochemistry around the metal was assigned, as shown, by comparison with analogous complexes (Table 2).[9b] In the reaction of hydride **5** with *p*-tolylacetylene, besides complex **19** a minor alkenyl isomer was also isolated, which probably differs in the stereochemistry around ruthenium. The hydroruthenation of alkynes most likely proceeds by formation of a coordinatively unsaturated ruthenium hydride Ru(CO)ClH(PPh_3)$_2$ which then coordinates with the alkyne and undergoes migratory insertion to form pentacoordinated Ru(CO)Cl(CH=CHR)(PPh_3)$_2$.[1,2] Final coordination of the basic L ligand afforded the expected product. Hydrido complex **6** with a labile isoquinoline ligand showed the highest reactivity toward the 1-alkynes, yielding alkenyl derivatives **20**−**22** in high yield within 1 h at room temperature.

Alkynyl complexes could also be obtained from neutral ruthenium hydrides by performing the reaction under more forcing conditions. Thus, hydride **4**, which had been previously demonstrated to give alkenyl complexes like **17**,[9] reacted with 1-decyne and *p*-tolylacetylene in 1,2-dichloroethane under reflux to afford complexes **23** and **24** in 50 and 85% yield, respectively. Similarly, hydride **6** gave alkynyl derivatives **25** and **26** (71 and 84%, respectively) under these conditions (Table 3). The arrangement of ligands around the metal in these complexes was assigned tentatively, as shown, by

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Table 2. Spectroscopic and Analytical Data for New Ruthenium Alkenyl Complexes

complex	IR (KBr, cm^{-1}) ν(C≡O)	^{1}H NMR ($CDCl_3$, 23 °C) −HC=HC−	^{1}H NMR other signals	formula	anal. calcd (found) C	H	N
14	1920 (vs)	7.46−7.18 (overlapping, 1H), 4.80 (dm, J = 16.7 Hz, 1H)	11.03 (s, 1H), 7.46−7.18 (m, 30 H), 5.42 (s, 1H), 1.88 (s, 3H), 1.73 (br s, 3H), 1.30−0.95 (m, 10H), 0.85 (t, J = 6.8 Hz, 3H)	$C_{50}H_{53}ClN_2OP_2Ru$	66.99 (66.85)	5.96 (6.01)	3.12 (3.09)
15	1920 (vs)	4.80 (dm, J = 16.7, 1H)	11.03 (s, 1H), 7.46−7.18 (m, 31H), 5.42 (s, 1H), 1.88 (s, 3H), 1.73 (s, 3H), 1.30−0.95 (m, 14H), 0.86 (t, J = 6.1 Hz, 3H)	$C_{52}H_{57}ClN_2OP_2Ru$	67.56 (67.49)	6.21 (6.29)	3.03 (3.01)
16	1940 (vs)	8.60 (dt, J = 16.8, 3.2 Hz, 1H), 5.68 (d, J = 16.8 Hz, 1H)	11.15 (s, 1H), 7.43−7.12 (m, 12H), 7.13−7.11 (m, 18H), 6.88 (d, J = 6.9 Hz, 2H), 6.66 (d, J = 6.9 Hz, 2H), 5.08 (s, 1H), 2.23 (s, 3H), 1.93 (s, 3H), 1.76 (s, 3H)	$C_{51}H_{47}ClN_2OP_2Ru$	67.88 (67.70)	5.25 (5.32)	3.10 (3.08)
17	1930 (vs)	8.67 (dt, J = 16.9, 3.2 Hz, 1H), 5.70 (br d, J = 16.8 Hz, 1H)	8.53−8.51 (m, 2H), 7.52−7.46 (m, 12H), 7.25−7.09 (m, 19H), 6.93 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 6.58 (t, J = 6.8Hz, 2H), 2.25 (s, 3H)	$C_{51}H_{44}ClNOP_2Ru$	69.19 (68.85)	5.01 (4.99)	1.58 (1.70)
18	1910 (vs)	7.15 (m, overlapping), 4.92 (dt, J = 16.4 Hz, 1H)	7.63−7.54 (m, 12H), 7.53−7.15 (m, 19H), 7.05 (s, 1H), 6.70 (s, 1H), 6.28 (s, 1H), 3.17(s, 3H), 0.62 (s, 9H)	$C_{47}H_{47}ClN_2OP_2Ru$	66.07 (65.90)	5.54 (5.47)	3.28 (5.40)
19[a]	1920 (vs)	8.76 (dt, J = 15.8, 3.0 Hz, 1H), 5.86 (d, J = 15.8 Hz, 1H)	7.70−7.45 (m, 12H), 7.46−7.08 (m, 18H), 7.05 (s, 1H), 6.92 (d, J = 7.9 Hz, 2H), 6.78 (d, J = 7.9 Hz, 2H), 6.67 (s, 1H), 6.23 (s, 1H), 3.18 (s, 3H), 2.25 (s, 3H)	$C_{50}H_{45}ClN_2OP_2Ru$	67.60 (67.45)	5.11 (5.23)	3.15 (3.23)
20	1930 (vs)	7.31 (dt, J = 16.1, 3.0 Hz, 1H), 4.90 (dt, J = 16.1, 1.7 Hz, 1H)	9.15 (s, 1H), 8.23 (d, J = 5.8 Hz, 1H), 7.65−7.50 (m, 12H), 7.44 (m, 2H), 7.17−7.05 (m, 20H), 6.99 (br d, J = 6.2 Hz, 1H), 0.68(s, 9H)	$C_{52}H_{48}ClNOP_2Ru$	69.29 (68.98)	5.37 (5.26)	1.55 (1.51
21	1928 (vs)	8.83 (dt, J = 17.7, 3.1 Hz, 1H), 5.86 (br d, J = 16.7 Hz, 1H)	9.15 (s, 1H), 8.34 (d, J = 6.3Hz, 1H), 7.60 (m, 2H), 7.53−7.34 (m, 15H), 7.18−7.03 (m, 18H), 7.00−6.93 (m, 3H), 6.89 (d, J = 7.4 Hz, 2H)	$C_{54}H_{44}ClNOP_2Ru$	70.39 (70.12)	4.81 (4.71)	1.52 (1.48)
22	1945 (vs)	10.53 (br d, J = 16.8 Hz, 1H), 5.67 (br d, J = 16.8 Hz, 1H)	9.06 (s, 1H), 8.28 (d, J = 6.0 Hz, 1H), 7.66−7.53 (m, 2H), 7.52−7.29 (m, 15H), 7.24−6.98 (m, 18H), 3.52 (s, 3H)	$C_{50}H_{42}ClNO_3P_2Ru$	66.48 (66.21)	4.69 (4.66)	1.55 (1.52)
27	1915 (vs)	7.38−7.12 (overlapping, 1H), 4.95 (dt, J = 16.4, 4.0 Hz, 1H)	7.55−7.48 (m, 12H), 7.38−7.12 (m, 18H), 6.73 (s, 1H), 6.59 (s, 1H), 6.55 (s, 1H), 6.47 (s, 2H), 6.44 (s, 1H), 3.30 (s, 3H), 3.24 (s, 3H), 2.10−1.90 (m, 2H), 1.24−1.15 (m, 12H), 0.90 (t, J = 6.6 Hz, 3H)	$C_{55}H_{61}F_6N_4OP_3Ru$[b]			
28	1915 (vs)	7.72 (dt, J = 16.6, 4.0 Hz, 1H), 5.93 (d, J = 16.6 Hz, 1H)	7.38−7.27 (m, 12H), 7.24−7.06 (m, 19H), 7.01 (t, J = 7.2 Hz, 2H), 6.80 (s, 1H), 6.75 (d, J = 7.6 Hz, 2H), 6.69 (br s, 3H), 6.53 (br s, 2H), 3.36 (s, 3H), 3.29 (s, 3H)	$C_{53}H_{49}F_6N_4OP_3Ru$[c]			
29	1940 (vs)	6.51 (dt, J = 16.0, 6.5 Hz, 1H), 5.34 (dt, J = 16.0, 4.5 Hz, 1H)	8.39 (d, J = 7.9 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 5.4 Hz, 1H), 7.97 (t, J = 6.2 Hz, 1H), 7.84 (d, J = 6.2 Hz, 1H), 7.70 (t, J = 7.9 Hz, 1H), 7.33−7.04 (m, 31 H), 6.84 (t, J = 6.4 Hz, 1H), 2.09−1.97 (m, 2H), 1.24−1.15 (m, 12H), 0.89 (t, J = 6.6 Hz, 3H)	$C_{57}H_{57}F_6N_2OP_3Ru$	62.58 (62.33)	5.25 (5.30)	2.56 (2.51)
30	1940 (vs)	7.74 (dt, J = 17.0, 4.6 Hz, 1H), 6.35 (d, J = 17.0 Hz, 1H)	8.30 (s, 1H), 8.13 (s, 1H), 7.59 (d, J = 5.6 Hz, 1H), 7.62 (d, J = 5.7 Hz, 1H), 7.30−7.04 (m, 33H), 6.86 (d, J = 7.2 Hz, 2H), 6.62 (d, J = 5.6 Hz, 1H), 6.56 (d, J = 5.6 Hz, 1H), 2.54 (s, 3H), 2.43 (s, 3H)	$C_{57}H_{49}F_6N_2OP_3Ru$	63.04 (63.33)	4.55 (4.50)	2.58 (2.53)
31[d]	1915 (vs)	6.54 (dt, J = 16.5, 4.7 Hz, 1H), 5.48 (d, J = 16.5 Hz, 1H)	8.60 (d, J = 7.8 Hz,1H), 8.49 (d, J = 4.9 Hz, 1H), 8.24 (dd, J = 8.2, 1.2 Hz, 1H), 8.17(d, J = 8.8 Hz, 1H), 8.12 (dd, J = 5.4, 1.2 Hz, 1H), 8.01(d, J = 8.8 Hz, 1H), 7.28 (dd, J = 8.2, 5.2 Hz, 1H), 7.27−7.22 (m, 6H), 7.15 (dd, J 8.2, 5.1 Hz, 1H), 7.09−7.03 (m, 12H), 6.92−6.85 (m,12H), 0.82 (s, 9H)	$C_{55}H_{49}F_6N_2OP_3Ru$	62.20 (62.71)	4.65 (4.52)	2.64 (2.58)
32[e]	1940 (vs)	7.89 (dt, J = 16.9, 4.7 Hz, 1H), 6.44 (d, J = 16.9 Hz, 1H)	8.63 (d, J = 5.8 Hz, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.30 (dd, J = 8.5, 1.2 Hz, 1H), 8.25 (dd, J = 5.3, 1.4 Hz, 1H), 8.14 (d, J = 8.9 Hz, 1H), 8.08 (d, J = 8.9 Hz, 1H), 7.35 (dd, J = 8.1, 5.2 Hz, 1H), 7.26−7.19 (m, 8H), 7.17−6.96 (m, 14H), 6.95−6.81 (m, 14H)	$C_{57}H_{45}F_6N_2OP_3Ru$	63.28 (63.11)	4.19 (4.02)	2.59 (2.58)

[a] A minor isomer showed the following significative ^{1}H NMR signals: 5.25 (d, J = 16.0 Hz, 1H), 3.12 (s, 3H), 2.27 (s, 3H). [b] This alkenyl complex could not be separated from alkynyl complex **33**. [c] This alkenyl complex could not be separated from alkynyl complex **34**. [d] $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 33.11 (s). [e] $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 32.10 (s).

Table 3. Spectroscopic and Analytical Data for New Ruthenium Alkynyl Complexes

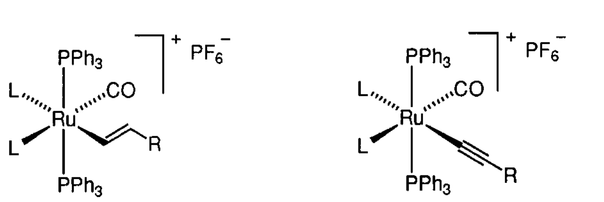
complex	IR (KBr; cm^{-1}) ν(C≡C)	IR (KBr; cm^{-1}) ν(C≡O)	^{1}H NMR ($CDCl_3$, 23 °C)	formula	anal. calcd (found) C	anal. calcd (found) H	anal. calcd (found) N
23	2100 (m)	1945 (vs)	8.90 (br m, 1H), 7.90−7.88 (m, 3H), 7.63−7.47 (m, 12H), 7.22−7.07 (m, 18H), 6.43 (t, *J* = 7.5 Hz, 1H), 1.93−1.42 (m, 2H), 1.36−1.00 (m, 12H), 0.91 (t, *J* = 6.6 Hz, 3H)	$C_{52}H_{52}ClNOP_2Ru$	68.98 (68.79)	5.79 (5.85)	1.55 (1.53)
24[a]	2100 (s)	1948 (vs)	8.95−8.88 (m, 1H), 7.97−7.87 (m, 3H), 7.70−7.60 (m, 12H), 7.32−7.04 (m, 18H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.47 (br m, 1H), 2.30 (s, 3H)	$C_{51}H_{42}ClNOP_2Ru$	69.34 (69.60)	4.79 (4.92)	1.59 (1.66)
25	2100 (s)	1960 (vs)	9.38 (m, 1H), 8.91 (d, *J* = 6.5 Hz, 1H), 7.91−7.84 (m, 4H), 7.67−7.48 (m, 12H), 7.42−7.31 (m, 2H), 7.18−7.04 (m, 22H)	$C_{54}H_{42}ClNOP_2Ru{\cdot}H_2O$	69.19 (69.03)	4.73 (4.45)	1.49 (1.51)
26	2100 (s)	1960 (vs)	9.40 (br s 1H), 8.93 (d, *J* = 6.4 Hz, 1H), 7.91−7.85 (m, 4H), 7.77−7.49 (m, 12H), 7.42−7.30 (m, 1H), 7.13−7.01 (m, 22H), 2.27 (s, 3H)	$C_{55}H_{44}ClNOP_2Ru{\cdot}H_2O$	69.43 (69.50)	4.87 (4.62)	1.47 (1.49)
33[b]	2120 (m)	1940 (vs)	7.54−7.47 (m, 12H), 7.34−7.19 (m, 18H), 6.84 (br s, 1H), 6.61 (br s, 1H), 6.42 (br s, 1H), 6.34 (br s, 1H), 6.22 (br s, 1H), 5.92 (br s, 1H), 3.19 (s, 3H), 3.13 (s, 3H), 2.02−2.16 (m, 2H), 1.30−1.20 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H)	$C_{55}H_{59}F_6N_4OP_3Ru$	60.05 (60.06)	5.41 (5.38)	5.09 (5.12)
34	2090 (m)	1935 (vs)	7.56−7.47 (m, 12H), 7.36−7.11 (m, 21H), 6.94−6.90 (m, 2H), 6.81 (br s, 1H), 6.63 (br s, 1H), 6.48 (br s, 1H), 6.33 (br s, 1H), 6.23 (br s, 1H), 5.97 (br s, 1H), 3.21 (s, 3H), 3.12 (s, 3H)	$C_{53}H_{47}F_6N_4OP_3Ru$	59.83 (59.43)	4.45 (4.39)	5.27 (5.25)
35	2120 (m)	1945 (vs)	8.05 (d, *J* = 5.7 Hz, 2H), 7.50−7.41 (m, 12H), 7.35−7.15 (m, 22H), 6.78−6.79 (m, 4H), 3.38 (t, *J* = 6.6 Hz, 2H), 2.39 (tt, *J* = 6.6, 1.8 Hz, 2H), 1.71 (q, *J* = 6.6 Hz, 2H)	$C_{52}H_{46}ClF_6N_2OP_3Ru$	59.01 (59.34)	4.38 (4.20)	2.65 (2.55)
36	2100 (m)	1945 (vs)	8.10 (d, *J* = 5.7 Hz, 2H), 7.56−7.38 (m, 12H), 7.35−7.25 (m, 8H), 7.21−7.18 (m, 14H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.75−6.72 (m, 4H), 2.30 (s, 3H)	$C_{56}H_{47}F_6N_2OP_3Ru$	62.75 (62.55)	4.42 (4.40)	2.61 (2.53)
37	2100 (m)	1930 (vs)	7.57−7.51 (m, 12H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.31−7.25 (m, 6H), 7.20−7.15 (m, 12H), 6.92 (d, *J* = 7.1 Hz, 2H), 5.75−5.71 (m, 4H), 2.82 (s, 6H), 2.81 (s, 6H), 0.97 (s, 9H)	$C_{57}H_{59}F_6N_4OP_3Ru$	60.90 (60.75)	5.29 (4.99)	4.98 (4.76)
38	2090 (m)	1930 (vs)	7.57−7.49 (m, 14H), 7.32−7.24 (m, 6H), 7.23−7.04 (m, 15H), 7.01 (d, *J* = 7.1 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 5.88−5.77 (m, 4H), 2.84 (s, 6H), 2.82 (s, 6H)	$C_{59}H_{55}F_6N_4OP_3Ru$	61.94 (61.23)	4.85 (4.75)	4.90 (4.88)
39	2090 (m)	1940 (vs)	7.57−7.31 (m, 14H), 7.29− 7.21 (m, 6H), 7.21−7.16 (m, 12H), 7.00 (d, *J* = 6.9 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 5.81−5.77 (m, 4H), 2.84 (s, 6H), 2.82 (s, 6H), 2.29 (s, 3H)	$C_{60}H_{57}F_6N_4OP_3Ru$	62.23 (61.99)	4.96 (5.02)	4.84 (4.58)
40	2100 (m)	1943 (vs)	8.86 (s, 1H), 7.97 (s, 1H), 7.85 (d, *J* = 6.5 Hz, 1H), 7.70−7.59 (m, 6H), 7.58−7.47 (m, 14H),t7.22−7.10 (m, 9H), 7.09−6.99 (m, 12H), 1.05 (s, 9H)	$C_{61}H_{53}F_6N_2OP_3Ru$	64.38 (64.26)	4.69 (4.62)	2.46 (2.62)
41	2095 (m)	1945 (vs)	8.83 (s, 1H), 8.03 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 1H), 7.66−6.98 (m, 46H)	$C_{63}H_{49}F_6N_2OP_3Ru$	65.34 (65.28)	4.26 (4.12)	2.42 (2.52)
42	2100 (m)	1950 (vs)	8.38−8.35 (m, 2H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.86 (br t, *J* = 7.6 Hz, 1H), 7.72 (br t, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.36−7.29 (m, 18H), 7.24−7.14 (m, 12H), 6.68 (br t, *J* = 6.7 Hz, 1H), 6.55 (br t, *J* = 6.8 Hz, 1H), 3.51 (t, *J* = 6.5 Hz, 2H), 2.45 (tt, *J* = 6.6, 1.8 Hz, 2H), 1.81 (q, *J* = 6.5 Hz, 2H)	$C_{52}H_{44}ClF_6N_2OP_3Ru$	59.12 (58.90)	4.20 (4.12)	2.65 (2.42)
44[c,d]	2090 (m)	1950 (vs)	9.52 (s, 1H), 8.76−8.69 (m, 2H), 8.28 (br s, 3H), 8.09−8.07 (m, 3H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.66−7.52 (m, 6H), 7.46−7.40 (m, 5H), 7.37−7.27 (m, 2H), 7.19−7.03 (m, 11H), 7.01−6.83 (m, 6H), 6.59 (br s, 2H), 5.63 (s, 1H), 4.97 (s, 1H), 4.56 (s, 1H), 4.43 (s, 1H), 4.26 (s, 1H), 4.20 (s, 1H), 4.16 (s, 1H), 3.69 (s, 1H), 3.49 (s, 1H)	$C_{71}H_{52}ClFeOP_3Ru{\cdot}CH_2Cl_2{\cdot}H_2O$[d]	66.04 (66.06)	4.31 (4.27)	0.00 (0.10)
45	2080	1927, 1947 (vs)	10.24 (s, 1H), 8.36 (s, 1H), 7.99−6.95 (m, 80H)	$C_{110}H_{82}Cl_2N_2O_2P_4Ru_2$	71.00 (70.59)	4.44 (4.53)	1.51 (1.33)

[a] A minor isomer showed the following significative ^{1}H NMR signals: 8.75 (m, py) and 2.36 (s, Me) ppm. [b] ^{13}C{^{1}H}NMR (50 MHz, $CDCl_3$): δ 204.7 (t, *J* = 13.5 Hz), 141.7 (s), 141.44 (s), 134.0 (t, *J* = 5.2 Hz, PPh_3), 131.9 (t, *J* = 21.7 Hz, PPh_3), 131.4 (s), 129.7 (s), 129.7 (s, PPh_3), 127.7 (t, *J* = 4.6 Hz, PPh_3), 120.5 (s), 114.5 (s), 90.2 (t, *J* = 18 Hz), 39.9 (s), 34.6 (s), 34.2 (s), 30.3 (s), 29.4 (s), 29.3 (s, 2C), 22.7 (s), 22.1 (s), 14.1 (s). [c] A weak (C≡C−H) absorption at 3316 cm^{-1} was observed in the IR. ^{31}P{^{1}H}NMR (121 MHz, $CDCl_3$): δ 19.52 (d, *J* = 20.7 Hz, 2P), −2.46 (t, *J* = 20.7 Hz, 1P). [d] See the Supporting Information for a copy of the ^{1}H NMR spectrum of **44** which demonstrates the presence of CH_2Cl_2 and H_2O.

analogy with the alkenyl complexes and related alkynyl complexes bearing three donor phosphine ligands.[4]

The preparation of alkynylruthenium complexes by metathesis of the neutral alkenyl complexes with the alkyne was attempted in 1,2-dichloroethane under reflux. The desired transformation was indeed demonstrated from alkenyls **17** and **20**. Thus, complex **17** reacted with *p*-tolylacetylene to afford **24** cleanly, which was isolated in 58% yield. Furthermore, the synthesis of an alkynyl from the alkenylruthenium complex with a different R group could also be realized as shown in the transformation of **20** into **26** (56% isolated yield) (Scheme 1).

Among the cationic hydrides studied, only **7** with two *cis*-*N*-methylimidazole ligands gave alkenyl complexes. Thus, reaction of **7** with 1-decyne and phenylacetylene in CH_2Cl_2 at room temperature gave **27** and **28**, respectively. However, these reactions were rather slow and



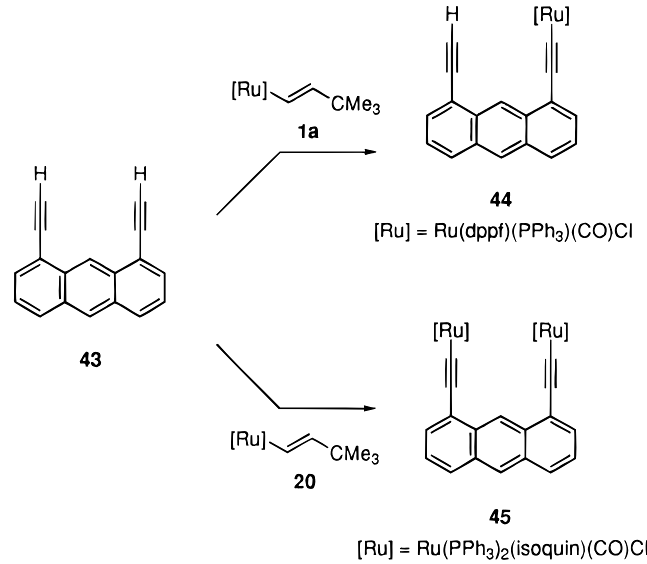
27 : L = MeIm, R = n-C_8H_{17}
28 : L = MeIm, R = Ph
29 : L_2 = bpy, R = n-C_8H_{17}
30 : L_2 = 4,4'-Me_2bpy, R = Ph
31 : L_2 = phen, R = CMe_3
32 : L_2 = phen, R = Ph

33 : L = MeIm, R = n-C_8H_{17}
34 : L = MeIm, R = Ph
35 : L = py, R = $(CH_2)_2CH_2Cl$
36 : L = py, R = p-MeC_6H_4
37 : L = DMAP, R = CMe_3
38 : L = DMAP, R = Ph
39 : L = DMAP, R = p-MeC_6H_4
40 : L = isoquin, R = CMe_3
41 : L = isoquin, R = Ph
42 : L_2 = bpy, R = $(CH_2)_2CH_2Cl$

were accompanied by the formation of the corresponding alkynyl derivatives **33** and **34** as minor products. Complexes **11**−**13** failed to react with 1-alkynes even under forcing conditions. The corresponding alkenyl derivatives (i.e., **29**−**32**) could be obtained by ligand substitution from Ru(CO)Cl(CH=CHR)$(PPh_3)_2$[1] or [Ru(CO)(CH=CHR)$(MeCN)_2(PPh_3)_2$]PF_6[1c] using the appropriate bidentate ligands. The lack of reactivity of the ruthenium hydrides with bidentate chelating ligands toward 1-alkynes indicates that a coordinatively unsaturated intermediate is not attainable under ordinary conditions.[4]

Alkynyl derivatives **33** and **34**, obtained above as minor products, could be prepared in good yields from **7** by performing the reaction with the 1-alkynes in CH_2Cl_2 under refluxing conditions (Table 3). As previously reported,[3] hydride **8** reacted with 1-alkynes under mild conditions to afford alkynylruthenium complexes. Two further examples (**35** and **36**) are included in Scheme 2. Hydrides **9** and **10** with pyridine-type donor ligands gave selectively alkynyl complexes **37**−**41** in high isolated yields.[3] Despite the differences in donor ability of the three pyridine-type ligands (py, DMAP, isoquinoline), no significant differences in reactivity were observed toward the 1-alkynes in CH_2Cl_2 at room temperature. As expected, no alkynyl complexes could be obtained from the ruthenium hydrides with bidentate ligands even under harsh conditions. Again, ligand substitution, illustrated by the preparation of **42** from **35**, provided an indirect entry into this class of complexes.[11]

Scheme 2



Alkenyl ruthenium complex **20**, readily available from new ruthenium hydride **6** and *tert*-butylacetylene allows for the preparation of alkynylruthenium complexes bearing the weakly coordinating isoquinoline ligand. The utility of the new alkenylruthenium(II) complexes for the end-capping of alkynes is illustrated in Scheme 2. Thus, while ruthenium alkenyl **1a**[4] reacted with 1,8-diethynylanthracene (**43**)[12] to form exclusively a mono(alkynyl)ruthenium complex, **44**, under all the conditions examined, reaction between **43** and alkenyl complex **20** lead to diruthenium derivative **45**.[13]

Conclusions

Neutral ruthenium hydride complexes bearing one N-donor ligand lead to alkenyl complexes which are considerably less reactive than their cationic analogues toward a second molecule of alkyne to form alkynyl complexes. However, under more forcing conditions, the 1-alkynyl complexes could be prepared from the neutral hydrides. The higher reactivity of cationic alkenyls is probably due to the ready elimination of the L ligand trans to the carbonyl group leading to five-coordinate intermediates, which can react with a second molecule of alkyne. Cationic hydrides with bidentate N-donor ligands (**11**−**13**) are unreactive toward 1-alkynes. On the other hand, cationic hydride complex **7** with two *N*-methylimidazole ligands was shown to give mixtures of alkenyl and alkynyl complexes at room temperature.

(11) Alkynyl complexes with pyridine-type donor ligands undergo ligand substitution with CO to afford [$Ru(CO)_2(C{\equiv}CR)L(PPh_3)_2$]$PF_6$. See the Supporting Information for details.

(12) Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179.

(13) Complex **45** is probably a mixture of isomers. However, the ratio of these isomers could not be determined by ^1H NMR because of the extremely low solubility of **45.** Its $^{31}P\{^1H\}$ NMR spectrum (121 MHz, $CDCl_3$, 26 060 scans, 27 °C) showed three singlets at δ 30.3, 29.6, and 22.8 in approximately a 1:1:1 ratio. This spectrum may correspond to a 2:1 ratio of two diastereomeric complexes (assuming that the two phosphines on each Ru are mutually trans): the major asymmetrical isomer with a different arrangement of ligands around Ru and the minor symmetrical isomer. The $^{31}P\{^1H\}$ CP MAS spectrum (162 MHz, 2000 scans, 12 000 c/s) of **45** in saccharose showed pair of broad doublets centered at 34.3 (asymmetric doublet) and δ 24.4 (2:1 ratio) ratio. The appearance of doublets is probably due to the ^{14}N nuclear quadrupole moment of the isoquinoline ligands interfering with the magic angle averaging out of the $^{31}P-^{14}N$ interactions, are: McDowell, C. A. *In Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, 1996; Vol. 5, p 2901.

Under more forcing conditions, alkynyl derivatives were obtained. Hydride complexes **8**−**10** with pyridine-type ligands were very reactive, leading directly, at room temperature, to alkynyl complexes in good yields. These are the most reactive hydrides toward alkynes among the series possessing the fragment [Ru(CO)H(PPh_3)$_2$].

Intermediate alkenyl complexes like **17** and **20** reacted smoothly with 1-alkynes to afford σ-alkynylruthenium derivatives. Complexes prepared from **20** posses a weakly coordinating isoquinoline ligand, which could be substituted in a subsequent transformation with stronger donor ligands. Additionally, substitution of the chloride of neutral alkynyl complexes by a second alkynyl group should allow for the stepwise construction of large arrays connected through ruthenium(II) centers.

Experimental Section

Only the most significant IR frequencies are given. Elemental analyses were performed at the Instituto de Química Orgánica (CSIC) or the UAM (SIdI). All reactions were carried out under an atmosphere of Ar. Solvents were purified and dried by standard methods.

The following ruthenium hydrido and alkenyl complexes were prepared by the described procedures: Ru(CO)ClH(PPh_3)$_3$,[14] Ru(CO)ClH(Me_2Hpz)(PPh_3)$_2$ (**3**),[15] Ru(CO)ClH(py)(PPh_3)$_2$ (**4**),[10] [Ru(CO)H($MeCN$)$_2$(PPh_3)$_2$]PF_6,[1d] [Ru(CO)H(py)$_2$(PPh_3)$_2$]PF_6 (**8**),[15b] [Ru(CO)H(bpy)(PPh_3)$_2$]PF_6 (**11**),[15a] [Ru(CO)H(phen)(PPh_3)$_2$]PF_6 (**12**),[15a] Ru(CO)(CH=CHCMe$_3$)Cl(PPh_3)$_2$, and [Ru(CO)(CH=CHCMe$_3$)($MeCN$)$_2$(PPh_3)$_2$]PF_6 (where bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline).[1d] Dialkyne **43** was prepared according to the described procedure.[12]

Ru(CO)ClH(L)(PPh_3)$_2$ (L = MeIm, 5; L = isoquinoline, 6). General Procedure. A mixture of Ru(CO)ClH(PPh_3)$_3$ and the basic ligand (9−20 mol equiv) in EtOH (50−100 mL/mmol of ruthenium hydride) was heated under reflux for 0.5−3 h. The mixture was partially evaporated, and Et_2O was added. The white precipitate was filtered off and washed with Et_2O and hexane to give the ruthenium hydrides: **5** (75%), **6** (86%).

[Ru(CO)H(L)$_2$(PPh_3)$_2$]PF_6 (L = MeIm, 7; L = DMAP, 9; L = Ph-BIAN,[16] 13). General Procedure. A mixture of Ru(CO)ClH(PPh_3)$_3$ and the basic ligand (9−20 mol equiv) was heated in EtOH (50−100 mL/mmol of ruthenium hydride) under refluxing conditions for 30 min. The resulting solution was filtered and partially evaporated, and a solution of NH_4PF_6 or $NaPF_6$ (1.1−2.5 mol equiv) in EtOH (10 mL) was added. A precipitate appeared, which was filtered off and washed with EtOH, Et_2O, and hexane to give the ruthenium hydrides: **7**, white solid (80%); **9**, white solid (89%); **13**, purple solid (85%).

[Ru(CO)H(isoquinoline)$_2$(PPh_3)$_2$]PF_6 (10). A solution of [Ru(CO)H($MeCN$)$_2$(PPh_3)$_2$]PF_6 (500 mg, 0.57 mmol) and isoquinoline (0.5 mL, 4.3 mmol) in a mixture of CH_2Cl_2 (25 mL) and EtOH (25 mL) was heated under refluxing conditions for 4 days. The solution was concentrated, and the resulting white solid was filtered off, washed with EtOH, redissolved in CH_2Cl_2 (25 mL) and EtOH (20 mL), and treated again with isoquinoline (0.2 mL, 1.72 mmol) under refluxing conditions for 2 days. This operation was repeated again to obtain **10** free of the starting hydride. Final concentration, filtration, and washing with EtOH, Et_2O, and hexane provided **10** as a white solid (425 mg, 70%).

Ru(CO)Cl(CH=CHR)(L)(PPh_3)$_2$ (R = *n*-C_6H_{13}, L = Me_2Hpz, 14; R = *n*-C_8H_{17}, L = Me_2Hpz, 15; R = *p*-$CH_3C_6H_4$, L = Me_2Hpz, 16; R = *p*-$CH_3C_6H_4$, L = py, 17; R = CMe_3, L = MeIm, 18; R = *p*-$CH_3C_6H_4$, L = MeIm, 19; R = CMe_3, L = isoquinoline, 20; R = Ph, L = isoquinoline, 21; R = CO_2Me, L = isoquinoline, 22). General Procedure. A solution of hydride **3**−**6** (0.15 mmol) in CH_2Cl_2 (10 mL) and the corresponding alkyne (1 mol equiv) was stirred at 23 °C (reaction time for **3** = 2 h; reaction time for **4** = 1.5 h; reaction time for **5** = 48 h; reaction time for **6** = 1 h). After elimination of the solvent, the residue was triturated with hexane, filtered off, and washed with hexane to give **14** (65%), **15** (60%), **16** (80%), **17** (90%), **18** (94%), **19** (80%), **20** (87%), **21** (72%), and **22** (93%) as yellow solids. The ^1H NMR of crude **19** showed the presence of a minor isomer.

[Ru(CO)(HC=CHC$_8H_{17}$)(MeIm)$_2$(PPh_3)$_2$]PF_6 (27). A solution of hydride **7** (160 mg, 0.17 mmol) and 1-decyne (0.30 mL, 0.17 mmol) in CH_2Cl_2 (10 mL) was stirred at 23 °C for 24 h. After evaporation of the solvent, the residue was triturated with Et_2O to give a mixture of **27** and alkynyl **33** (*ca.* 1:1 mixture) and unreacted hydride (*ca*. 30%). Complex **27** could not be obtained pure by recrystallization.

[Ru(CO)(HC=CHPh)(MeIm)$_2$(PPh_3)$_2$]PF_6 (28). A solution of hydride **7** (80 mg, 0.08 mmol) and phenylacetylene (0.01 mL, 0.09 mmol) in CH_2Cl_2 (5 mL) was stirred at 23 °C for 18 h. After evaporation of the solvent, the residue was triturated with Et_2O to give a mixture of **28** and alkynyl **34** (72 mg, *ca.* 2.8:1 mixture). Complex **28** could not be obtained pure by recrystallization.

[Ru(CO)(HC=CHC$_8H_{17}$)(bpy)(PPh_3)$_2$]PF_6 (29). Method A: Complex **29** was prepared from hydride Ru(CO)ClH(PPh_3)$_3$ (362 mg, 0.38 mmol) and 1-decyne (0.1 mL, 0.55 mmol) in CH_2Cl_2 by stirring at 23 °C for 30 min. The solvent was evaporated and the residue was washed with hexane and redissolved in CH_2Cl_2. To this solution an excess of bpy (200 mg, 1.28 mmol) was added, and the mixture was heated under refluxing conditions. After 30 min, NH_4PF_6 (120 mg, 0.74 mmol) was added and the mixture was heated for 1 h. The resulting suspension was filtered and evaporated, and the residue was triturated with Et_2O and washed with hexane to give **29** (340 mg, 82%) as a yellow solid.

Method B: A solution of **27** (152 mg, 0.15 mmol) and bpy (97 mg, 0.62 mmol) in CH_2Cl_2 (10 mL) was heated under refluxing conditions for 1.5 h. The solvent was partially evaporated, and Et_2O was added to give a yellow precipitate, which was filtered off and washed with hexane to give **29** (100 mg, 60%).

[Ru(CO)(HC=CHPh)(4,4′-Me$_2$bpy)(PPh_3)$_2$]PF_6 (30). Method A: A solution of Ru(CO)Cl(HC=CHPh)(PPh_3)$_2$ (205 mg, 0.21 mmol) and 4,4′-Me$_2$bpy (95 mg, 0.52 mmol) in 1,2-dichloroethane (10 mL) was heated under refluxing conditions. After 45 min, NH_4PF_6 (70 mg, 0.43 mmol) was added and the mixture refluxed for 45 min. After filtration and evaporation of the solvent, the residue was triturated with Et_2O, filtered, and washed with Et_2O and hexane to give **30** as an orange solid (210 mg, 90%).

Method B: A solution of [Ru(CO)(HC=CHPh)($MeCN$)$_2$(PPh_3)$_2$]PF_6 (156 mg, 0.16 mmol) and 4,4′-Me$_2$bpy (60 mg, 0.32 mmol) in 1,2-dichloroethane (10 mL) was heated under refluxing conditions for 2 h. After evaporation of the solvent, the residue was triturated with Et_2O, filtered off, and washed with Et_2O and hexane to give **30** (155 mg, 90%).

[Ru(CO)(HC=CHCMe$_3$)(phen)(PPh_3)$_2$]PF_6 (31). Method A: A mixture of Ru(CO)Cl(HC=CHCMe$_3$)(PPh_3)$_2$ (260 mg, 0.33 mmol), phen (135 mg, 0.75 mmol), and NH_4PF_6 (112 mg, 0.69 mmol) in 1,2-dichloroethane (10 mL) was heated under refluxing conditions for 2 h. The solvent was evaporated, and the residue was triturated with Et_2O, filtered off, and washed with Et_2O and hexane to give **31** (340 mg, 95%).

Method B: A solution of [Ru(CO)(HC=CHCMe$_3$)($MeCN$)$_2$(PPh_3)$_2$]PF_6 (168 mg, 0.17 mmol) and phen (76 mg, 0.42 mmol) in 1,2-dichloroethane (15 mL) was heated under refluxing conditions for 2 h. The solvent was evaporated, and the

(14) Ahmed, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.
(15) (a) Romero, A.; Santos, A.; Vegas, A.; Cuadro, A. *J. Chem. Soc., Dalton Trans.* **1987**, 183. (b) Romero, A.; Vegas, A.; Santos, A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1987**, *319*, 103.
(16) Ph-BIAN: acenaphthenequinone bisphenylimine, see: van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

residue was triturated with Et_2O, filtered off, and washed with Et_2O and hexane to give **31** (150 mg, 81%).

[Ru(CO)(HC=CHPh)(phen)(PPh_3)$_2$]PF_6 (32). A solution of Ru(CO)Cl(HC=CHPh)(PPh_3)$_2$ (317 mg, 0.42 mmol) and an excess of phen (325 mg, 1.8 mmol) in CH_2Cl_2 (10 mL) was heated under refluxing conditions. After 30 min, NH_4PF_6 (130 mg, 0.8 mmol) was added and the mixture was heated for an additional 1 h. After filtration and evaporation of the solvent, the residue was triturated with Et_2O and washed with Et_2O and hexane to give **32** as an orange solid (450 mg, 98%).

Ru(CO)Cl(C≡CC_8H_{17})(py)(PPh_3)$_2$ (23). A solution of hydride **4** (255 mg, 0.33 mmol) and 1-decyne (0.3 mL, 1.7 mmol) was heated under refluxing conditions in 1,2-dichloroethane (20 mL) for 8 h. The solvent was evaporated, and the residue was triturated with hexane, filtered off, and washed with hexane to give **23** as a yellow solid (150 mg, 50%).

Ru(CO)Cl(C≡CC_6H_4Me)(py)(PPh_3)$_2$ (24). Method A: A solution of hydride **4** (381 mg, 0.5 mmol) and *p*-tolylacetylene (0.15 mL, 1.2 mmol) was heated under refluxing conditions in 1,2-dichloroethane (20 mL) for 6 h. The solvent was evaporated, and the residue was triturated with hexane, filtered off, and washed with hexane to give an orange solid, which was recrystallized several times from CH_2Cl_2/hexane to give **24** mixed with a minor isomer (370 mg, 85%).

Method B: A mixture of alkenyl complex **17** (120 mg, 0.15 mmol) and *p*-tolylacetylene (60 mg, 0.5 mmol) was heated under refluxing conditions in 1,2-dichloroethane (7 mL) for 6 h. After partial evaporation of the solvent, addition of hexane gave a solid, which was filtered off and washed with hexane to give **24** as an orange solid (70 mg, 58%).

Ru(CO)Cl(C≡CPh)(isoquinoline)(PPh_3)$_2$ (25). A solution of hydride **6** (240 mg, 0.29 mmol) and phenylacetylene (0.35 mL, 29 mmol) was heated under refluxing conditions in 1,2-dichloroethane (15 mL) for 4 h. The solvent was evaporated, and the residue was triturated with CH_2Cl_2−Et_2O, filtered off, and washed with Et_2O and hexane to give **25** as a brownish solid (190 mg, 71%).

Ru(CO)Cl(C≡CC_6H_4Me)(isoquinoline)(PPh_3)$_2$ (26). Method A: A solution of hydride **6** (240 mg, 0.29 mmol) and *p*-tolylacetylene (0.3 mL, 2.4 mmol) was heated under refluxing conditions in 1,2-dichloroethane (15 mL) for 24 h. After partial evaporation of the solvent, addition of Et_2O gave a solid, which was filtered off and washed with Et_2O and hexane to give **26** as a pale yellow solid (230 mg, 84%).

Method B: A mixture of alkenyl complex **20** (80 mg, 0.11 mmol) and *p*-tolylacetylene (35 mg, 0.3 mmol) was heated under refluxing conditions in 1,2-dichloroethane (5 mL) for 5 h. After partial evaporation of the solvent, addition of Et_2O gave a solid, which was filtered off and washed with Et_2O to give **26** as a pale yellow solid (45 mg, 56%).

[Ru(CO)(C≡CR)(L_2)(PPh_3)$_2$]PF_6 (33−41). General Procedure. A solution of the hydrides **7**−**10** (0.1 mmol) and the alkyne (0.2 mmol) was stirred at 23 °C (for **35**−**41**) or under refluxing conditions (for **33**−**34**) in CH_2Cl_2 (10 mL) (reaction time for **7** = 5 h; reaction time for **8**−**10** = 24 h). The solvent was evaporated, and the residue was triturated with Et_2O, filtered off, and washed with Et_2O and hexane to yield the alkynyl complexes as yellow-orange powders: **33** (76%), **34** (93%), **35** (86%), **36** (95%), **37** (78%), **38** (90%), **39** (95%), **40** (92%), and **41** (88%).

[Ru(CO)(C≡C(CH_2)$_2$$CH_2$Cl)(bpy)($PPh_3$)$_2$]$PF_6$ (42). A solution of alkynyl complex **35** (146 mg, 0.14 mmol) and bpy (51 mg, 0.33 mmol) was heated under refluxing conditions in 1,2-dichloroethane (15 mL) for 2 h. The solvent was evaporated, and the residue was triturated with Et_2O, filtered off, and washed with Et_2O to yield **42** as an orange powder (130 mg, 89%).

Complex 44. A solution of **1a** (300 mg, 0.28 mmol) and dialkyne **43** (64 mg, 0.28 mmol) in CH_2Cl_2 (4.5 mL) was stirred at 23 °C for 3 h. The solvent was partially evaporated, and the residue was triturated with Et_2O to give **44** as a yellow-green solid (211 mg, 62%).

Complex 45. A solution of **20** (80 mg, 0.08 mmol) and dialkyne **43** (10 mg, 0.04 mmol) in 1,2-dichloroethane (4 mL) was heated under refluxing conditions for 6 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **45** as a pale yellow-green solid (31 mg, 42%).

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Supporting Information Available: Text giving the experimental details and characterization data for [Ru(CO)$_2$-(C≡CR)py(PPh_3)$_2$]PF_6 (R = CMe_3, Ph) and NMR and IR spectra for complex **44** (4 pages). Ordering information is given on any current masthead page.

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