Ruthenium-Capping of Di- and Tetraethynylbiphenyls

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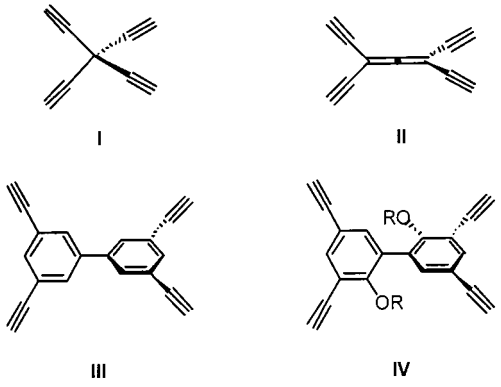
The di- and tetraalkynyl biphenyls **3** and **5** have been synthesized from the tetrabromo derivative **1** by using Pd-catalyzed cross-coupling reactions. The reaction of **3** or **5** with *cis*-[$RuCl_2(dppe)_2$] (**8**) affords vinylidene ruthenium complexes, which were deprotonated with Et_3N to give the terminal σ-alkynylruthenium derivatives **9**–**12**. The reaction of **3** or **5** with [$Ru(CO)ClH(PPh_3)_3$] (**13**) gave the corresponding di-σ-alkenyl ruthenium complexes **14** and **15**.

Introduction

Carbon-rich organometallics containing rigid conjugated branches have attracted great attention, since they are potentially useful for building carbon-rich networks,[1] organometallic polymers[2] and π-conjugated polymetallic systems,[3] which can all find applications in material science. Of special interest are the σ-alkynyl complexes, since they allow electronic communication between coordinated metal centers through the C≡C bonds in the π-conjugated systems. Indeed, a number of alkynyl complexes have been designed for use in nonlinear optics[4] and as liquid crystals.[5] Polyethynylated complexes may form organometallic polymers in which the metal binds two ethynyl groups.[4b,5c,6] Polymetallic compounds with -$(C{\equiv}C)_n$- or polyethynylbenzene bridges have also been studied.[3,4b,4c,5c,7] Other di- or trimetallic alkynyl complexes have been prepared from ethynyl ferrocene.[8] Additionally, alkynyl derivatives have given rise to mixed-valence systems,[9] and organometallic macrocycles[10] have also been prepared.

The assembly of carbon-rich two- or three dimensional nanomaterials from ethynylated scaffolds has also attracted great attention.[11,12] Major achievements in this field are the preparation of tetraethynylmethane (**I**),[13] tetraethynylethene,[14] hexaethynylbenzene,[15] and π-metal complexes of tetraethynylcyclobutadiene,[16] and pentaethynylcyclopentadiene.[17] Tetraethynylallene (**II**), topologically related to the tetraalkyne **I**, still remains an elusive target. The biphenyls **III**[18] and **IV**, which display the four alkynes in a flexible elongated tetrahedral arrangement, could offer a potential alternative to **I** and **II** (Scheme 1).



Scheme 1

Herein we report the synthesis of alkynes **3** and **5** as new potential building blocks for the construction of carbon-rich networks,[19] and their reactions with the ruthenium complexes *cis*-[$RuCl_2(dppe)_2$] (**8**) [dppe = 1,2-bis(diphenyl)-phosphanylethane] and [$Ru(CO)ClH(PPh_3)_3$] (**13**), which afford mono- and di-alkynyl and di-alkenyl ruthenium complexes, respectively, in good yields.[20]

Results and Discussion

Synthesis of Di- and Tetraalkynylbiphenyls

The synthesis of alkynes **3** and **5** was based on palladium-catalyzed transformations as the key steps. The tetrabromo diester **1** was readily obtained from 2,2′-biphenol by bromination with excess bromine in methanol at 23 °C,[21] followed by acylation with pivalic anhydride (95% overall yield). Thus, Sonogashira coupling[22] of tetrabromo dipivalate ester (**1**) with excess trimethylsilylacetylene {[$PdCl_2(PPh_3)_2$] and CuI catalysts (20 mol % each), Et_3N, 70 °C, 48 h] led to **2** (89% yield). No further coupling between **2** and trimethylsilylacetylene took place through the more hindered *o*-bromides by using this coupling procedure, even under severe conditions (Scheme 2).

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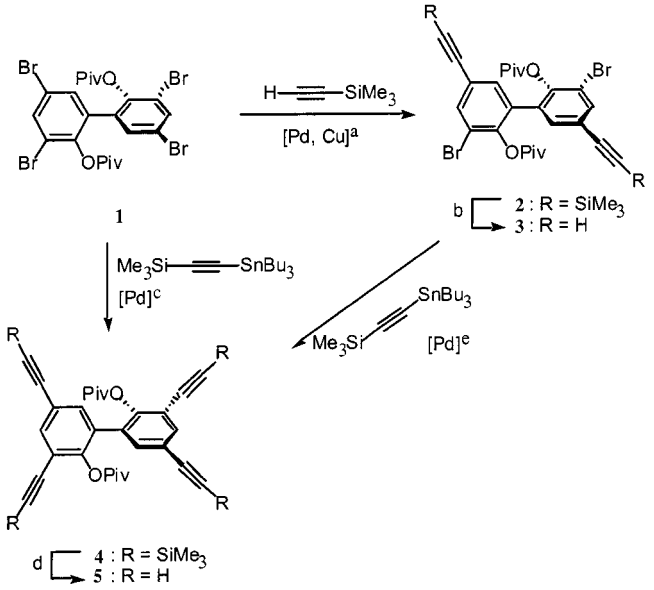
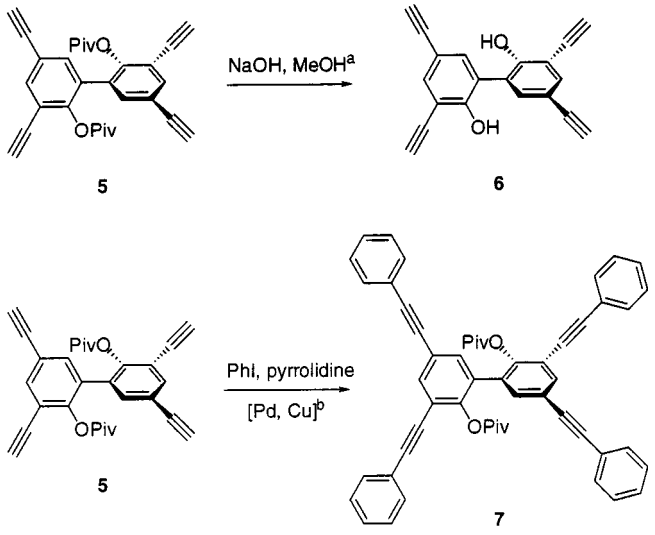


Scheme 2. a: $[PdCl_2(PPh_3)_2]$ (20 mol %), CuI (20 mol %), Et_3N, 70 °C, 48 h (89%); b: K_2CO_3, MeOH, 23 °C, 30 min. (90%); c: $[Pd(PPh_3)_4]$ (20 mol %), toluene, reflux, 4 h (90%); d: K_2CO_3, MeOH, 23 °C, 30 min. (95%); e: $[Pd(PPh_3)_4]$ (20 mol %), toluene, reflux, 4 h (92%)



Scheme 3. a: NaOH, MeOH, 23 °C, 18 h (80%); b: $[Pd(PPh_3)_4]$ (20 mol %), CuI (20 mol %), pyrrolidine, 23 °C, 3 h (83%)

However, by using the Stille coupling[23] the four bromides could be efficiently replaced by alkynyl substituents in a single step. Thus, coupling of **1** with (trimethylsilylethynyl)-tributylstannane[24] in the presence of $[Pd(PPh_3)_4]$ as catalyst gave the tetraalkynyl derivative **4** (90% yield) as a stable colorless oil. The biphenyl **4** was also obtained by the coupling of dibromide **2** with (trimethylsilylethynyl)tributylstannane under the same conditions (92% yield). The terminal alkynes **3** and **5** could be obtained by standard deprotection of the TMS groups with K_2CO_3 in MeOH in 90 and 95% yields, respectively. The pivaloyl groups of **5** could be efficiently removed under stronger basic conditions [NaOH, MeOH, 23 °C, 18 h, 80%] to yield the biphenol **6**. This compound could undergo self-condensation by copper- or palladium-catalyzed alkyne−alkyne coupling to furnish three dimensional polymers bearing hydrophilic cavities.

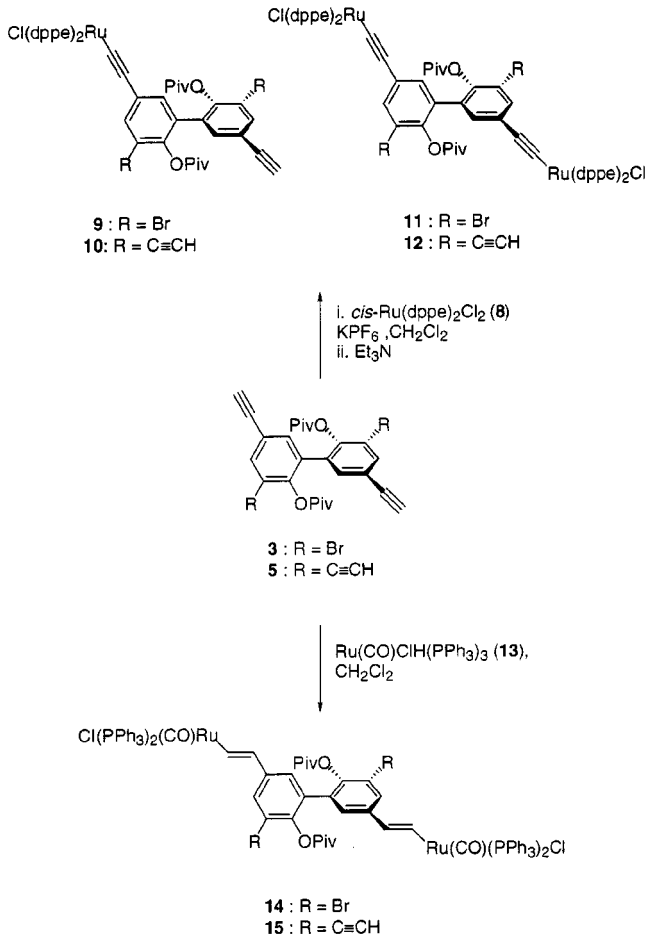
While alkynes **3** and **5** are stable compounds that can be stored under ordinary conditions, alkyne **6** undergoes slow decomposition as a solid. However, it can be easily manipulated and stored in the dark without significant decomposition. The potential utility of these tetraethynylbiphenyls as tectons for the building of more complex structures relies upon their ability to couple with appropriate electrophiles. Thus, the coupling of **5** with iodobenzene (4 equiv.) afforded **7** [$Pd(PPh_3)_4$ and CuI (20 mol % each), pyrrolidine, 23 °C, 3 h, 83%; Scheme 3].

Synthesis of Ruthenium Alkynyl Complexes

The reactions of alkynes **3** and **5** with one equivalent of *cis*-$[RuCl_2(dppe)_2]$ (**8**) and two equivalents of KPF_6 in CH_2Cl_2 at room temperature for four days led to the conversion of the starting alkynes into a mixture of two ruthenium complexes. On the basis of the spectroscopic data and literature precedent,[25−27] these products were tentatively assigned as the monovinylidene and η^2-alkyne ruthenium complexes. Thus, the IR spectra show relatively intense bands in the range 1625−1630 cm^{-1}, characteristic of the vinylidene ruthenium complexes. However, the ^1H NMR spectra were complex, suggesting that isomeric (η^2-alkyne)ruthenium complexes were also present in solution. These complexes decompose readily in the presence of dissolved oxygen or water to furnish the carbonyl complex $[Ru(CO)Cl(dppe)_2]PF_6$ almost quantitatively. This ruthenium(II) complex was characterized by IR and ^1H NMR spectroscopy and by the determination of the crystal structure.[28,29] Similar transformations of vinylidene- or allenylidene complexes into their carbonyl derivatives have been reported previously.[30]

The crude mixtures containing the monovinylidene and η^2-alkyne isomers were readily deprotonated with Et_3N in CH_2Cl_2 at room temperature to give the corresponding monoalkynyl complexes **9** (72%) and **10** (74%), respectively. Similarly, reaction of **3** and **5** with two equivalents of *cis*-$[RuCl_2(dppe)_2]$ (**8**) and four equivalents of KPF_6 for seven days at room temperature, followed by deprotonation, furnished the dialkynyl ruthenium complexes **11** (72%) and **12** (85%) (Scheme 4).

Crystals of complexes **11** and **12** could be obtained, although the crystal structure determination could not be performed due to their decomposition by the X-rays. The IR spectra of all these alkynyl complexes are very similar and show very strong ν(C≡C) bands around 2050 cm^{-1}. In the ^{13}C NMR spectrum of **12** the quintet at δ = 127.9 ($^2J_{PC}$ = 16 Hz) was assigned to the alkynyl carbon which is α to Ru, thus demonstrating a *trans*-configuration of the chloro- and ethynyl ligands.



Scheme 4

A cyclic voltammetric study of complex **12** showed a single quasi-reversible redox wave for both ruthenium systems [$E_{1/2}$ versus Cp_2Fe^+/Cp_2Fe: + 0.72 V (ΔE_p = 63 mV)]. This unique oxidation wave shows that the dialkynyl complex **12** is capable of providing two electrons at the same potential and that the bridge between the ethynylated phenyl rings of the biphenyl system does not allow significant communication between the ruthenium centers.

Synthesis of Ruthenium Alkenyl Complexes

The reaction of alkynes **3** and **5** with two equivalents of [Ru(CO)HCl(PPh_3)$_3$] (**13**) in CH_2Cl_2 at room temperature gave rise to the red dialkenyl complexes **14** (92%) and **15** (91%). As expected,[31] the hydroruthenation proceeds in a cis fashion, as demonstrated by a trans $^3J(^1H\text{-}^1H)$ coupling of 13.7−14 Hz. Although the pentacoordinated Ru centers of these complexes are less sterically hindered than those of **9**−**12**, a tetrametallated derivative could not be obtained by reaction of alkyne **5** with four equivalents of hydride **13**.

Conclusions

We have described the synthesis of the di- and tetraalkynyl biphenyls **3** and **5** from the tetrabromo derivative **1** by using Pd-catalyzed cross-coupling reactions as well as their derivatization with ruthenium complexes to afford stable alkynyl and alkenyl complexes. The reaction of the terminal −C≡CH groups of **3** and **5** with *cis*-[$RuCl_2$(dppe)$_2$] (**8**), followed by deprotonation of these mixtures with Et_3N, leads to the terminal σ-alkynylruthenium derivatives. Reaction of **3** and **5** with the ruthenium hydride [Ru(CO)ClH(PPh_3)$_2$] (**13**) gave the corresponding di-σ-alkenyl complexes. The diruthenium complexes **12** and **15** bear two free terminal alkyne groups, which could be further metallated to form heterometallic complexes. Further work in this area is in progress.

Experimental Section

General: Infrared spectra were recorded at the ICMM on a Nicolet 20 SXC FT-IR spectrophotometer, using KBr disks. The NMR determinations were carried out on a Bruker AC-200 (or a Bruker AMX-300) apparatus at 23 °C. Mass spectra were performed at the SIdI (UAM), using the fast cesium-ion bombardment (liquid secondary ion mass spectrometry, LSIMS) or EI-MS techniques. Only the most significant IR frequencies and MS fragmentations are given. Elemental analyses were performed at the ICMM or SIdI (UAM). Differential thermal analysis (DTA) curves were obtained at the ICMM, using a Stanton STA 781 analyzer. All reactions were performed under a nitrogen atmosphere, using Schlenk techniques and the solvents were deoxygenated and dried by standard methods.

Cyclic voltammetric measurements were carried out at the Universidad Complutense de Madrid (Departamento de Química Inorgánica I, Facultad de Ciencias Químicas) on an Autolab apparatus equipped with a PSTA 10 potentiostat, using a three-electrode cell with platinum wire as working and auxiliary electrodes and Ag/AgCl electrode as a reference with a solution of the complex (10^{-3} mol/dm^3) in dichloromethane containing [Nbu_4][BF_4] (0.2 mol/dm^3) as the base electrolyte, at a scan rate of 200 mV s^{-1}. Values are referred to an Ag/AgCl electrode and ferrocene was used as internal standard.

The complexes [$PdCl_2(PPh_3)_2$], [$Pd(PPh_3)_4$],[32] *cis*-[$RuCl_2$(dppe)$_2$] (**8**),[33] and [RuHCl(CO)(PPh_3)$_3$] (**13**)[34] were prepared by known procedures.

3,5,3′,5′-Tetrabromobiphenyl-2,2′-diyl Dipivalate (1): A solution of 3,3′,5,5′-tetrabromo-2,2′-dihydroxybiphenyl (2.00 g, 4.0 mmol) in pyridine (50 mL) and pivalic anhydride (4.0 mL, 19.7 mmol) was heated under refluxing conditions for 2 h. After being cooled to room temperature, the mixture was diluted with water and extracted with EtOAc. The organic layer was washed with aqueous HCl (10%), dried (Na_2SO_4) and the solvent was evaporated to yield **1** (2.60 g, 97%) as a beige solid: m.p. 115 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.13 (s, 18 H), 7.34 (s, 2 H), 7.78 (s, 1 H), 7.79 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 26.7, 39.1, 118.2, 119.00, 132.5, 132.6, 135.8, 145.5, 174.9. − EI-MS: *m*/*z* (%) = 666 (0.5) [M$^+$], 582 (5), 498 (8), 417 (4), 339 (1), 311 (3), 85 (43), 57 (100). − $C_{22}H_{22}Br_4O_4$ (670.03): calcd. C 39.44, H 3.31; found C 39.40, H 3.15.

3,3′-Dibromo-5,5′-bis(trimethylsilylethynyl)biphenyl-2,2′-diyl Dipivalate (2): A mixture of **1** (500 mg, 0.74 mmol), trimethylsilylacetylene (0.42 mL, 3 mmol), [$PdCl_2(PPh_3)_2$] (103 mg, 0.148 mmol), and CuI (56 mg, 0.30 mmol) in Et_3N (25 mL) was stirred at 23 °C

for 12 h. The mixture was diluted with CH_2Cl_2, washed with H_2O, dried and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 4:1) to give **2** as a colorless oil (466 mg, 89%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.23 (s, 9 H), 0.25 (s, 9 H), 1.12 (s, 18 H), 7.30 (s, 1 H), 7.31 (s, 1 H), 7.70 (s, 1 H), 7.71 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = −0.2, 26.7, 39.1, 96. 6, 102.0, 116.9, 122.4, 133.4, 131.61, 136.2, 146.2, 175.2. − EI-MS: *m*/*z* (%) = 702 (2) [M^+], 618 (14), 534 (13), 519 (5), 439 (8), 179 (7), 85 (11), 73 (12) 57 (100). − $C_{32}H_{40}Br_2O_4Si_2$ (704.64): calcd. C 54.54, H 5.72; found C 54.88, H 6.11.

3,3′-Dibromo-5,5′-diethynylbiphenyl-2,2′-diyl Dipivalate (3): A mixture of **2** (466 mg, 0.66 mmol) and K_2CO_3 (182 mg, 1.3 mmol) in a mixture of CH_2Cl_2 (2 mL), MeOH (10 mL), and H_2O (0.5 mL) was stirred at 23 °C for 30 min. The mixture was diluted with CH_2Cl_2, washed with H_2O, aqueous HCl (10%), dried (Na_2SO_4) and the solvents evaporated to yield **3** as a colorless oil (332 mg, 90%). Recrystallization (Et_2O/hexane, 1:1) gave **3** as a white solid, m.p. 121−123 °C. − IR (KBr): ṽ = 3262 s ν(≡CH), 2104 w ν(C≡C), 1748 vs ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.11 (s, 18 H), 3.12 (s, 2 H), 7.33 (s, 1 H), 7.73 (s, 1 H), 7.74 (s, 1 H), 7.75 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 26.7, 39.0, 79.2, 80.8, 117.1, 121.3, 131.6, 133.5, 136.5, 146.6, 174.7. − EI-MS: *m*/*z* (%) = 558 (0.1) [M^+], 474 (80), 389 (0.1), 309 (0.2), 231 (2), 85 (21), 57 (100). − $C_{26}H_{24}Br_2O_4$ (560.28): calcd. C 55.74, H 4.32; found C 56.58, H 4.77.

3,3′,5,5′-Tetrakis(trimethylsilylethynyl)biphenyl-2,2′-diyl Dipivalate (4): A mixture of **1** (134 mg, 0.2 mmol), [$Pd(PPh_3)_4$] (46 mg, 0.04 mmol) and (trimethylsilyl)ethynyltributylstannane (470 mg, 1.2 mmol) in toluene (10 mL) was heated under refluxing conditions for 4 h. After being cooled to room temperature, the mixture was diluted with CH_2Cl_2, washed with water and a saturated solution of KF, dried (Na_2SO_4) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 9:1) to give **4** as a colorless oil (133 mg, 90%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.21 (s, 18 H), 0.23 (s, 18 H), 1.13 (s, 18 H), 7.30 (s, 1 H), 7.31 (s, 1 H), 7.61 (s, 1 H), 7.62 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = −0.2, 26.8, 38.9, 95.4, 98.7, 99.8, 102.8, 118.5, 120.9, 130.3, 134.3, 136.7, 149.2, 175.2. − EI-MS: *m*/*z* (%) = 738 (36) [M^+], 654 (100), 570 (28), 481 (4), 467 (13), 57 (25). − $C_{42}H_{58}O_4Si_4 \cdot 0.5H_2O$ (748.26): calcd. C 67.42, H 7.95; found C 67.41; 8.18.

3,3′,5,5′-Tetraethynylbiphenyl-2,2′-diyl Dipivalate (5): A mixture of **4** (139 mg, 0.118 mmol) and K_2CO_3 (33 mg, 0.24 mmol) in a mixture of CH_2Cl_2 (1 mL), MeOH (5 mL), and H_2O (0.3 mL) was stirred at 23 °C for 30 min. The mixture was diluted with CH_2Cl_2, washed with H_2O and aqueous HCl (10%), dried (Na_2SO_4) and the solvents evaporated to give **5** (77 mg, 95%) as a white solid: m.p. 125 °C. − IR (KBr): ṽ = 3306 ms, 3279 sh ν(≡CH), 2165 w, 2135 w ν(C≡C), 1750 vs ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.11 (s, 18 H), 3.08 (s, 2 H), 3.21 (s, 2 H), 7.37 (d, *J* = 2.0 Hz, 2 H), 7.66 (d, *J* = 2.0 Hz, 2 H). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 26.7, 38.9, 77.6, 78.5, 81.4, 82.6, 117.7, 120.1, 130.4, 134.8, 136.9, 150.1, 175.3. − FAB-MS: *m*/*z* (%) = 450 (15) [M^+], 366 (47), 282 (87), 253 (11), 224 (15), 85 (9), 57 (100). − $C_{30}H_{26}O_4 \cdot 0.5H_2O$ (459.53): calcd. C 78.41, H 5.92; found C 78.87, H 5.97.

2,2′-Dihydroxy-3,3′,5,5′-tetra(ethynyl)biphenyl (6): A mixture of **5** (10 mg, 0.022 mmol) and NaOH (6 mg, 0.15 mmol) in a mixture of MeOH (2 mL), and H_2O (0.1 mL) was stirred at 23 °C for 18 hours. The mixture was diluted with CH_2Cl_2, washed with H_2O and aqueous HCl (10%), dried (Na_2SO_4) and the solvents evaporated to give **6** (5 mg, 80%) as a white solid: (decomposes without melting; the DTA curve shows two exothermic peaks at 115 °C and 196 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.01 (s, 2 H), 3.49 (2 H), 7.43 (d, *J* = 2.0 Hz, 2 H), 7.59 (d, *J* = 2.0 Hz, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 76.7, 77.4, 82.1, 84.8, 109.9, 114.7, 123.5, 136.0, 136.2, 154.7. − EI-MS: *m*/*z* (%) = 282 (100) [M^+], 253 (23), 224 (32).

3,3′,5,5′-Tetra(phenylethynyl)biphenyl-2,2′-diyl Dipivalate (7): A mixture of **5** (41 mg, 0.1 mmol), [$Pd(PPh_3)_4$] (23 mg, 0.02 mmol), iodobenzene (60 μL, 0.53 mmol), and CuI (4 mg, 0.02 mmol) in pyrrolidine (5 mL) was stirred at 23 °C for 3 h. The mixture was diluted with CH_2Cl_2, washed with H_2O, dried and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 9:1) to give **7** as a colorless oil (62 mg, 83%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.17 (s, 18 H), 7.78 (d, *J* = 2.1 Hz, 2 H), 7.39−7.27 (m, 12 H), 7.55−7.45 (m, 10 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.9, 39.1, 83.7, 87.5, 90.4, 94.2, 118.8, 121.3, 122.7, 122.8, 128.4, 128.5, 128.7, 130.8, 131.6, 131.7, 133.8, 135.9, 148.9, 175.6. − EI-MS: *m*/*z* (%) = 754 (8) [M^+], 670 (25), 586 (62), 57 (100). − HRMS calcd. for $C_{54}H_{42}O_4$: 754.3083; found 754.3054.

Synthesis of the Monosubstituted Alkynyl Complex 9: A solution of alkyne **3** (29 mg, 0.052 mmol), *cis*-[$RuCl_2$(dppe)$_2$] (**8**) (50 mg, 0.052 mmol), and KPF_6 (18.96 mg, 0.103 mmol) in CH_2Cl_2 (5 mL) was stirred for 4 days at room temperature. The intermediate vinylidene complex could be isolated by trituration with hexane as a brown-beige powder (75 mg, 88%). − IR (KBr): ṽ = 3274 w ν(≡CH), 1750 ms ν(C=O), 2110 vw ν(C≡CH), 1620 ms ν(=C=C), 836 vs ν(PF_6). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.07, (s, 9 H), 1.17 (s, 9 H), 2.60−3.05 (m, 8 H), 3.11 (s, 1 H), 3.12 (br. s, 1 H), 6.85−7.55 (m, 43 H), 7.68 (br. s, 1 H) (minor signals of an η^2-alkyne complex were also observed); − $C_{78}H_{72}Br_2ClF_6O_4P_5Ru$ (1638.61): calcd. C 57.17, H 4.43; found C 57.11, H 4.48. An excess of Et_3N (0.05 mL, 0.35 mmol) was added to the brownish-yellow solution containing the vinylidene complex and the resulting solution was stirred for 1 h at 23 °C. After addition of CH_2Cl_2 (15 mL), this yellow solution was washed with water (3 ×). After the usual extractive workup, the solvent was partially evaporated. Addition of hexane led to a yellow precipitate, which was filtered off to give **9** (55 mg, 72%). − IR (KBr): ṽ = 3298 w ν(≡CH), 2110 vw ν(C≡CH), 2054 s ν(C≡C), ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.14 (s, 9 H), 1.16 (s, 9 H), 2.66 (br. s, 8 H), 3.17 (s, 1 H), 6.22 (br. s, 1 H), 6.64 (br. s, 1 H), 6.84−7.49 (m, 33 H), 7.51 (br. s, 8 H), 7.75 (s, 1 H). − ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 49.55 (s). − $C_{78}H_{71}Br_2ClO_4P_4Ru \cdot 0.5H_2O$ (1501.63): calcd. C 62.39, H 4.83; found C 62.44, H 4.89.

Formation of *trans*-[Ru(CO)Cl(dppe)$_2$]PF_6 from Biphenyl 3 and Ruthenium Complex 8: A solution of alkyne **3** (26 mg, 0.05 mmol), *cis*-[$RuCl_2$(dppe)$_2$] (**8**) (89 mg, 0.10 mmol), and KPF_6 (34 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was stirred for 7 days at 23 °C until no free alkyne was detectable by TLC. The mixture was filtered and the filtrate was partially evaporated. Addition of hexane led to precipitation of a solid, which was filtered off and washed with hexane to give a beige powder (140 mg, quantitative yield). This solid was suspended in CH_2Cl_2 (2 mL) and hexane (10 mL), and was then stirred in air at 23 °C for 3 h. The solvents were evaporated and the greenish-brown solid was triturated with Et_2O and filtered off to give a greenish-beige powder. To eliminate residual vinylidene, the crude product was dissolved in CH_2Cl_2 (5 mL) and treated with Et_3N (0.1 mL) at 23 °C. The solution was washed with water (3 ×) and, after the usual extractive workup, the residue was filtered through basic alumina. Partial evaporation of the solvent and addition of hexane gave *trans*-[Ru(CO)Cl(dppe)$_2$]PF_6 as gray-white crystals (98 mg, 59%) and the dialkynyl complex **9** (20 mg,

11%) as yellow crystals, which were separated by fractional crystallization.

***trans*-[Ru(CO)Cl(dppe)$_2$]PF$_6$:** IR (KBr): $\tilde{\nu}$ = 1946 vs ν(C=O), 837 vs ν(PF_6). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.66 (m, 4 H), 2.92 (m, 4 H), 6.95−7.50 (m). − $C_{53}H_{48}ClF_6OP_5Ru$ (1106.3): calcd. C 57.54, H 4.37; found C 57.51, H 4.40.

Synthesis of the Monosubstituted Alkynyl Complex 10: Alkyne **5** (23 mg, 0.052 mmol) was treated as above to give **10** as a yellow powder (52 mg, 74%). − IR (KBr): $\tilde{\nu}$ = 3282 ms ν(≡CH), 2110 vw ν(C≡CH), 2049 s ν(C≡C), 1748 s ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.13 (s, 9 H), 1.15 (s, 9 H), 2.67 (br. s, 8 H), 3.13 (s, 2 H), 3.21 (s, H), 6.22 (br. s, 1 H), 6.60 (br. s, 1 H), 6.89−7.10 (2m, 16 H), 7.10−7.32 (2m, 16 H), 7.37 (br. s, 1 H), 7.46 (br. s, 8 H), 7.67 (s, 1 H). − ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 49.45(s). − $C_{82}H_{73}ClO_4P_4Ru{\cdot}H_2O$ (1400.89): C 70.30, H 5.40; found C 70.40, H 5.34. The intermediate vinylidene complex could be isolated as above to give a brown-beige powder: IR (KBr): $\tilde{\nu}$ = 3273 ms ν(≡CH), 2110 w ν(C≡CH), 1751 ms ν(C=O), 1628 ms ν(=C=C), 843 vs ν(PF_6). − $C_{82}H_{74}ClF_6O_4P_5Ru$ (1528.9): calcd. C 64.42, H 5.18; found C 64.75, H 5.52.

Synthesis of the Disubstituted Alkynyl Complex 11: A solution of alkyne **3** (29 mg, 0.052 mmol), *cis*-[$RuCl_2$(dppe)$_2$] (**8**) (100 mg, 0.10 mmol), and KPF_6 (38 mg, 0.21 mmol) in CH_2Cl_2 (5 mL) was stirred for 7 days at 23 °C. The mixture was filtered and the filtrate was partially evaporated. Addition of hexane led to precipitation of a solid, which was filtered off and washed with hexane to give the divinylidene complex. − IR (KBr): $\tilde{\nu}$ = 1750 ms ν (C=O), 1626 s ν (=C=C), 836 vs ν (PF_6). − $C_{130}H_{120}Br_2Cl_2F_{12}O_4P_{10}Ru_2$ (2716.9): calcd. C 57.47, H 4.45; found C 57.41, H 4.46. An excess of Et_3N (0.71 mmol, 0.1 mL) was added to the solution containing the vinylidene complex, and the resulting solution was stirred for 1 h at 23 °C. The yellow solution, after addition of CH_2Cl_2 (15 mL), was washed with water (3 ×). After the usual workup the solvent was partially evaporated. Addition of hexane led to the formation of a yellow microcrystalline powder, which was filtered off to give **11** (89 mg, 72%). − IR (KBr): $\tilde{\nu}$ = 2050 s ν(C≡C), 1750 s ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (s, 18 H), 2.66 (br. s, 16 H), 6.48 (br. s, 2 H), 6.54 (br. s, 2 H), 6.92 (m, 16 H), 7.02 (m, 20 H), 7.18 (m, 12 H), 7.29 (m, 16 H), 7.40 (m, 16 H). − ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 26.9, 30.6 (m), 39.0, 110.7, 115.4 (br. s, Ru−C≡*C*), 127.0, 127.3 (br. s), 128.1 (quint, $^2J_{PC}$ = 16 Hz, C≡*C*−Ru), 128.9 (br. s), 131.7, 132.6, 133.9, 134.5 (br. s), 134.7, 135.8 (m), 141.5, 175.3. − ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 49.90 (s). − FAB-MS: *m/z* (%) = 2421 (8) [M^+], 2386 (3), 2026 (59), 897 (59), 685 (6), 499 (42), 316 (56), 185 (95), 57 (100). − $C_{130}H_{122}Br_2Cl_2O_6P_8Ru_2{\cdot}2H_2O$ (2461.00): calcd. C 63.45, H 5.00; found C 63.26, H 5.17.

Synthesis of the Disubstituted Alkynyl Complex 12: An excess of Et_3N (0.1 mL, 0.71 mmol) was added to the brownish-yellow solution containing the divinylidene complex prepared from **5** (23 mg, 0.052 mmol), and the resulting solution was stirred for 1 h at 23 °C. The yellow solution, after addition of CH_2Cl_2 (15 mL), was washed with water (3 ×). After the usual extractive workup, the solvent was partially evaporated. Addition of hexane led to a yellow microcrystalline powder of the dialkynyl complex **12** (101 mg, 85%) as a yellow powder. This compound contained traces of the monoalkynyl complex **10**. A pure product was obtained by crystallization from CH_2Cl_2/hexane to yield yellow crystals, which decompose on exposure to X-ray radiation. IR (KBr): $\tilde{\nu}$ = 3282 m ν(≡CH), 2110 w ν(C≡CH), 2049 s ν(C≡C), 1748 s ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (s, 18 H), 2.66 (br. s, 16 H), 3.15 (s, 2 H), 6.48 (br. s, 2 H), 6.58 (br. s, 2 H), 6.88−7.10 (m, 34 H), 7.10−7.22 (m, 16 H), 7.36 (br. s, 32 H). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 26.8, 30.6, 38.8, 79.4 (s, *C*≡CH), 80.0 (s, C≡*C*H, 111.2, 115.5 (s, Ru−C≡*C*), 126.9 (br. s), 127.3 (br. s), 127.9 (quint., $^2J_{PC}$ = 16 Hz, C≡*C*−Ru), 128.4, 128.9 (br. s), 130.5, 131.8, 133.9, 134.5 (br. s), 135.2, 135.8 (q, *J* = 22.7 Hz, dppe), 145.2, 175.5. − ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 49.89 (s). − FAB-MS: *m/z* (%) = 2315.1 (6) [M^+], 1917 (4), 1381 (2), 957 (9), 933 (19), 897 (100), 685 (16.). − $C_{134}H_{120}Cl_2O_4P_8Ru_2{\cdot}1.5H_2O$ (2342.25): calcd. C 68.71, H 5.28; found C 68.69, H 5.30. The intermediate divinylidene could be isolated as above as a beige powder: IR (KBr): $\tilde{\nu}$ = 3285 m ν(≡CH), 2110 vw ν(C≡CH), 1757 ms ν(C=O), 1628 s ν(=C=C), 843 vs ν(PF_6). − $C_{134}H_{122}Cl_2F_{12}O_4P_{10}Ru$ (2607.2): 61.73, H 4.72; found C 62.61, H 5.15.

Synthesis of the Disubstituted Alkenyl Complex 14: A solution of [$RuHCl(CO)(PPh_3)_3$] (**13**; 80 mg, 0.084 mmol) and alkyne **3** (23.5 mg, 0.042 mmol) was stirred at 23 °C in CH_2Cl_2 (10 mL) for 30 min. The orange-red solution was concentrated and hexane was added. after cooling to 0 °C, the mixture was filtered and the filtrate was evaporated. The residue was taken up in CH_2Cl_2/Et_2O and filtered. Hexane was added to the filtrate to give a precipitate, which was filtered off to give **14** (78 mg, 92%) as an orange solid. − IR (KBr): $\tilde{\nu}$ = 1924 vs ν(C≡O), 1736 s ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (s, 18 H), 5.49 (d, $^3J_{HP}$= 13.7 Hz, 2 H), 6.35 (s, 2 H), 6.89 (s, 2 H), 7.20−7.42 (m, 36 H, Ph), 7.45−7.70 (m, 24 H, Ph), 8.38 (d, $^3J_{HP}$ = 13.7 Hz, 2 H). − $C_{100}H_{86}Br_2Cl_2O_6P_4Ru_2{\cdot}CH_2Cl_2$ (2025.43): calcd. C 59.89, H 4.38; found C 59.83, H 4.27.

Synthesis of the Disubstituted Alkenyl Complex 15: Similarly, a solution of [$RuHCl(CO)(PPh_3)_3$] (**13**; 50 mg, 0.0525 mmol) and the alkyne **5** (11.83 mg, 0.0263 mmol) was stirred at 23 °C in CH_2Cl_2 (5 mL) for 1.5 h. After partial evaporation of solvent, addition of Et_2O led to a precipitate, which was filtered off to give **15** (44 mg, 91%). − IR (KBr): $\tilde{\nu}$ = 3288 w ν(≡CH), 2110 vw ν(C≡CH), 1922 vs ν(C≡O), 1740 ν(C=O). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (s, 18 H), 3.11 (s, 2 H), 5.53 (d, $^3J_{HP}$ = 14.0 Hz, 2 H), 6.41 (d, *J* = 2.0 Hz, 2 H), 6.84 (d, *J* = 2.0 Hz, 2 H), 7.42−7.20 (m, 36 H), 7.70−7.45 (m, 24 H, Ph), 8.33 (dm, $^3J_{HP}$ = 14.0 Hz, 2 H); − $C_{104}H_{88}Cl_2O_6P_4Ru_2{\cdot}0.75H_2O$ (1844.26): calcd. C 67.73, H 4.89; found C 67.80, H 4.80.

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