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Rates and Mechanism of Rhodium-Catalyzed [2+2+2] Cycloaddition of Bisalkynes and a Monoalkyne

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The mechanism of $RhCl(PPh_3)_3$-catalyzed [2+2+2] cycloaddition of alkynes is investigated in the case of the reaction of symmetrical diynes **1a** and **1b** with the monoalkyne **3** ($HOCH_2-C\equiv C-CH_2OH$), leading to highly substituted benzene derivatives in dichloromethane at 25 °C. The two main steps of the catalytic cycle are characterized. The intermediate rhodacyclopentadiene Rh^{III} complexes **2a** and **2b** (formed by oxidative coupling after the coordination of the diynes **1a** and **1b** to $RhCl(PPh_3)_2$) are characterized by cyclic voltammetry, conductivity measurements, ^{31}P NMR, and ESI-MS. The formation of complexes **2a** and **2b** (step A) and their further reactions with the monoalkyne **3**, which deliver $RhCl(PPh_3)_3$ and the final product (step B), are followed by means of electrochemical techniques that deliver kinetic data for the two successive separately investigated steps. From the relative values of the half-reaction times of step A ($t_{A1/2}$ = 650 and 75 s for **1a** and **1b**, respectively) and step B ($t_{B1/2}$ = 130 and 680 s for **2a** and **2b**, respectively) determined under stoichiometric conditions, it emerges that step A (coordination of the two C≡C bonds of **1**, followed by oxidative coupling) is rate-determining in the reaction involving **2a**, whereas step B (reaction of the intermediate complexes **2** with the monoalkyne **3**) is rate-determining in the reaction involving **1b**. Kinetic data for the catalytic cycle of a $RhCl(PPh_3)_3$-catalyzed [2+2+2] cycloaddition of alkynes are thus presented for the first time.

Introduction

Transition-metal-catalyzed [2+2+2] cycloaddition reactions of three alkynes is one of the most elegant methods for the construction of three new bonds in a one-step process to generate polysubstituted benzene derivatives.[1] Various transition-metal complexes, including those of Ni, Co, Rh, Ru, Mo, Ir, Pd, and Fe, have been shown to be efficient catalysts in this type of process.[1] Our group has recently demonstrated[2] that the [2+2+2] cycloisomerization of aza-macrocyclic triynes can be achieved in the presence of catalytic amounts of the Wilkinson catalyst ($RhCl(PPh_3)_3$), affording efficiently fused tetracycles with a benzene core.

In order to comprehensively establish this methodology, it is necessary to elucidate the mechanistic aspects of the [2+2+2] cycloadditions of alkynes. Recent progress in computational chemistry over the past decade has advanced our understanding of the mechanism of the transition-metal-catalyzed [2+2+2] cycloadditions of three acetylenes.[3] In the particular case of rhodium(I) complexes, which is the transition metal that our group is particularly interested in, only one DFT study has been published using CpRh and InRh.[3m] More recently our group has investigated the Wilkinson catalyst in a theoretical study of cycloisomerization reactions of macrocyclic systems.[4] Scheme 1 shows the

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(3) For a pioneering semiempirical study, see: (a) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M. −L; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010–2023. For DFT studies of the reaction mechanism of the [2+2+2] cycloadditions involving three acetylene molecules catalyzed by Co, see: (b) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055–6067. (c) Dahy, A. A.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 781–791. (d) Dahy, A. A.; Suresh, C. H.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 792–803. (e) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860–8871. (f) Varela, J. A.; Saá, C. *J. Organomet. Chem.* **2009**, *694*, 143–149. Catalyzed by Ru, see: (g) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721–11729. (h) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143–12160. (i) Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **2004**, 2609–2626. (j) Dazinger, G.; Torres-Rodrigues, M.; Kirchner, K.; Calhorda, M. J.; Costa, P. J. *J. Organomet. Chem.* **2006**, *691*, 4434–4445. (k) Ref [3f]. (l) Kirchner, K. *Monatsch. Chem.* **2008**, *139*, 337–348. Catalyzed by CpRh and InRh, see: (m) Orian, L.; van Stralen, J. N. P.; Bickelhaupt, F. M. *Organometallics* **2007**, *26*, 3816–3830.

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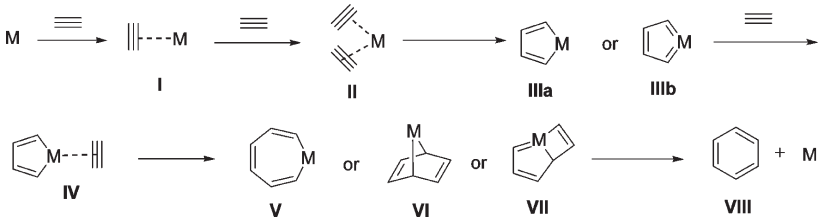
Scheme 1. Schematic [2+2+2] Cycloaddition Reaction Mechanism with M = Transition Metal

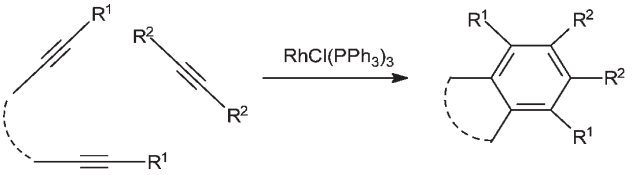


general mechanism proposed for the transition-metal-catalyzed [2+2+2] cycloaddition reaction. The reaction begins via a pair of ligand−alkyne substitution reactions. Then the oxidative coupling of the two alkyne ligands generates a metallacyclopentadiene **IIIa** or a metallacyclopentatriene **IIIb** with a biscarbene structure. This has been found to be the rate-determining step. Intermediate **IIIa** when M = Rh is supported by the isolation and characterization of several derivatives.[5] Subsequent coordination of a third alkyne ligand to the metallacyclopentadiene or **IIIb** intermediate is followed by either alkyne insertion to form a metallacycloheptatriene **V** (the so-called Schore's mechanism)[6] or metal-mediated [4+2] cycloaddition to yield the metallanorbornadiene **VI** or cycloaddition to give a metallabicyclo-[3.2.0]heptatriene **VII**. Finally, the arene **VIII** is formed by the reductive elimination of the metal.

To the best of our knowledge, only one kinetic study has been published regarding the cyclo-oligomerization of alkynes catalyzed by $RhCl_3$ under phase transfer conditions.[7] The initial reaction rates of the catalytic reactions have been determined. Kinetic data on each step of the catalytic cycle are not provided.

Our objective is to study the main steps of a catalytic cycle (kinetics and characterization of the catalytic species) using electrochemical techniques, NMR, and electrospray ionization mass spectrometry (ESI-MS). A cycloaddition between a symmetric diyne and a symmetric monoalkyne catalyzed by the Wilkinson catalyst $RhCl(PPh_3)_3$ was chosen as a model reaction to obtain the greatest amount of mechanistic information (Scheme 2).

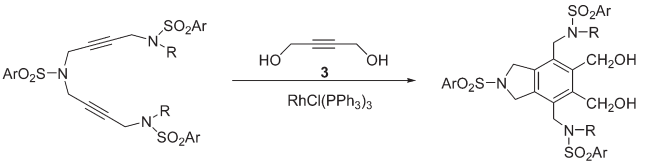
Scheme 2. Rh^I-Catalyzed [2+2+2] Cycloaddition of Alkynes



Results and Discussion

Rh^I-Catalyzed [2+2+2] Cycloadditions of Diynes (1) and 2-Butyn-1,4-diol (3). The specific reaction investigated is shown in Table 1. Our group has been interested in the study of propargylic sulfonamide derivatives **1** as part of our broader research interest in [2+2+2] cycloaddition of this kind of substrate.[2] **1a** and **1b** can be differentiated by the fact that, unlike **1b**, the two terminal nitrogen sulfonamides in **1a** are protected with a *tert*-butyloxycarbonyl group (BOC). In a first step the best conditions for the reaction of diynes **1** with commercially available 2-butyn-1,4-diol, **3**, were tested (Table 1).

Table 1. Rh^I-Catalyzed [2+2+2] Cycloaddition Reactions between Diynes (1) and 2-Butyn-1,4-diol (3)



1a (R = BOC, Ar = 2,4,6-triisopropylphenyl)
1b (R = H, Ar = 2,4,6-triisopropylphenyl)

4a (R = BOC, Ar = 2,4,6-triisopropylphenyl)
4b (R = H, Ar = 2,4,6-triisopropylphenyl)

entry	diyne	solvent	catalyst % molar	*T* (°C)	product (yield, %)
1	**1a**	toluene	5	65	**4a** (32)
2	**1b**	toluene	5	65	**4b** (43)
3	**1a**	CH_2Cl_2	10	reflux	**4a** (20)[a]

[a] The reaction has not been optimized.

Using toluene as the solvent and 5% molar Wilkinson catalyst, cyclotrimerized compounds **4a** and **4b** are obtained in moderate yields (Table 1, entries 1 and 2). A more conducting solvent such as CH_2Cl_2 was tested in order to look for a reaction medium suitable for electrochemical experiments (Table 1, entry 3).

[2+2+2] Cycloaddition of Alkynes in the Presence of $RhCl(PPh_3)_3$ as Monitored by Cyclic Voltammetry, ^{31}P NMR, and ESI-MS. The reaction of dialkynes **1** with $RhCl(PPh_3)_3$ in dichoromethane was followed by means of cyclic voltammetry (CV), taking advantage of the fact that oxidation (or reduction) currents are proportional to the concentration of electroactive species.[8] Cyclic voltammetry has been associated with ^{31}P NMR spectroscopy and ESI-MS (Scheme 3).

The Rh^I complex $RhCl(PPh_3)_3$ (1.5 mM) in dichloromethane (containing n-Bu_4NBF_4, 0.3 M, as the supporting electrolyte) was first examined. It exhibited two successive irreversible oxidation peaks at a steady gold disk electrode (Figure 1a) at the scan rate of 0.5 V s^{-1}. The oxidation peak current of the major peak (E^p_{O2} = +0.633 V versus SCE)

(5) Selected references: (a) Müller, E. *Synthesis* **1974**, 761–774. (b) Mague, J. T. *Inorg. Chem.* **1970**, *9*, 1610–1618. (c) Mague, J. T. *Inorg. Chem.* **1973**, *12*, 2649–1654. (d) Gastinger, R. G.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Organomet. Chem.* **1976**, *117*, 355–364. (e) Iglesias, M.; del Pino, C.; Ros, J.; García Blanco, S.; Carrera, S. M. *J. Organomet. Chem.* **1988**, *338*, 89–102. (f) Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127–5129. (g) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vacca, A. *Organometallics* **1991**, *10*, 636–645. (h) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 645–651. (i) Rourke, J. P.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Chem. Commun.* **2001**, 2626–2627. (j) Nishiyama, H.; Niwa, E.; Inoue, T.; Ishima, Y.; Aoki, K. *Organometallics* **2002**, *21*, 2572–2574. (k) Xue, P.; Sung, H. S. Y.; Williams, I. D.; Jia, G. *J. Organomet. Chem.* **2006**, *691*, 1945–1953.

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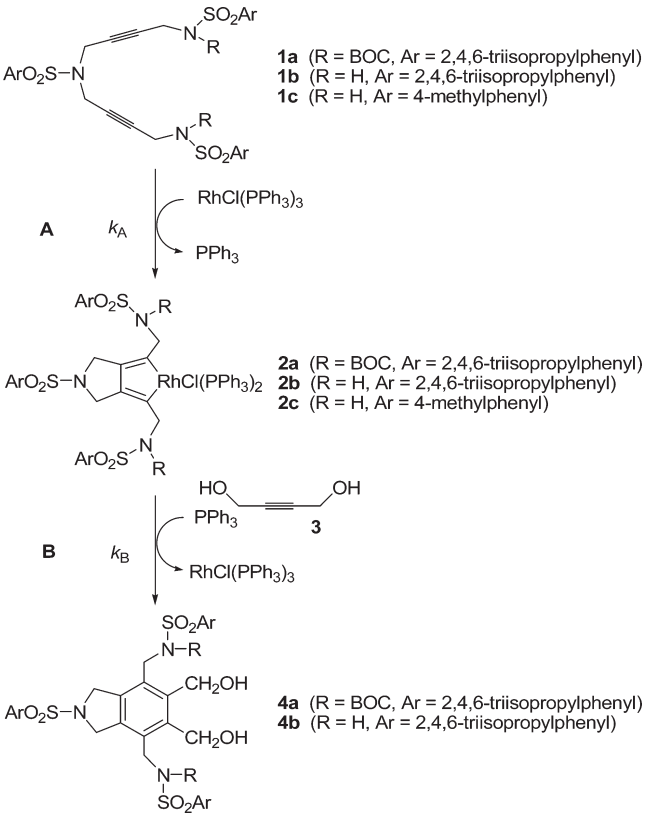
Scheme 3. [2+2+2] Cycloaddition Reactions Studied by CV, ^{31}P NMR, and ESI-MS



increased at the expense of the oxidation peak current of the minor and broader oxidation peak ($E^{p}_{O1} = +0.483$ V) upon addition of $RhCl(PPh_3)_3$ (0.5 equiv) or PPh_3 (1 equiv). O_2 was the only oxidation peak observed in the presence of 10 equiv of PPh_3. This proves that $RhCl(PPh_3)_3$ (oxidized at O_2)[9] is involved in an equilibrium with $RhCl(PPh_3)_2$ (oxidized at O_1) and PPh_3 (eq 1).[10]

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$

The ^{31}P NMR spectrum of $RhCl(PPh_3)_3$ (11 mM) in CD_2Cl_2 exhibited signals characteristic of the phosphines in a square-planar environment around the Rh atom in agreement with reported data.[11] The presence of signals having a narrow line width for $RhCl(PPh_3)_3$ indicates that this complex was not significantly dissociated in dichloromethane at the NMR concentration, at 22 °C. The detection of the oxidation peak of $RhCl(PPh_3)_2$ in the cyclic voltammogram performed at a scan rate of 0.5 V s^{-1} was due to a shift of the equilibrium in eq 1 toward $RhCl(PPh_3)_2$ as a consequence of its consumption by its oxidation in the diffusion layer (CE mechanism).[12a]

After addition of the dialkyne **1a** (1 equiv), the oxidation peaks of $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_2$ disappeared with time (Figure 1a), while the color of the solution turned from orange-red to yellow. Concomitantly, a reversible oxidation peak was observed at more positive potentials. After total

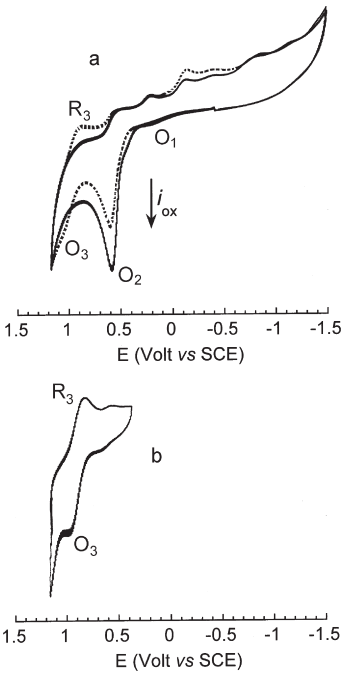


Figure 1. Cyclic voltammetry performed in CH_2Cl_2 containing nBu$_4$NBF$_4$ (0.3 M) at a steady gold disk electrode (d = 2 mm) at the scan rate of 0.5 V s^{-1} at 25 °C. (a) (—) $RhCl(PPh_3)_3$ (1.5 mM) oxidation first; (----) $RhCl(PPh_3)_3$ (1.5 mM) in the presence of **1a** (1.5 mM) after 15 min. (b) After full reaction with **1a**. The current scale has been amplified by a factor of 2 when compared to part a.

Table 2. Characterization of the Rhodacyclopentadiene Complexes 2a–c and 5 in Dichloromethane

		^{31}P NMR (101 MHz, H_3PO_4)	
complex	standard oxidation potential, E^0 V vs SCE[a]	J_{RhP} (Hz)	δ (ppm)
2a	+0.935	185	38.8
2c	+0.951	119	22.9
2b	+0.915	119	19.6
5	+0.911[b]	124	29.9

[a] Potentials measured at a steady gold disk electrode (d = 2 mm) at a scan rate of 0.5 V s^{-1}. [b] E^{p}_{ox} of an irreversible process.

conversion of $RhCl(PPh_3)_3$, the reversible oxidation peak was fully developed and observed at $E^{p}_{O3} = +0.997$ V ($E^{p}_{R3} = +0.874$ V, $E^0 = +0.935$ V) (Figure 1b).[12b] The reaction of $RhCl(PPh_3)_3$ with **1a** (1 equiv) was also followed by ^{31}P NMR spectroscopy. A new doublet was observed centered at 38.8 ppm (J_{RhP} = 185 Hz), which characterized a complex containing two magnetically equivalent PPh_3. A reversible oxidation peak ($E^0 = +0.951$ V) associated to a ^{31}P NMR doublet at 22.9 ppm was also observed for an isolated sample of the related rhodacyclopentadiene complex **2c**[13] (Scheme 3) in CH_2Cl_2 with, however, a lower J_{RhP} coupling constant, J_{RhP} = 119 Hz, (Table 2). Consequently, the oxidation peak

(9) For the CV of $RhCl(PPh_3)_3$ at a glassy-carbon disk see: Barrière, F.; Geiger, W. E. *Organometallics* **2001**, *20*, 2133–2135.

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(12) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001. (b) According to Barrière and Geiger, the oxidation of $RhCl(PPh_3)_3$ involves one electron.[9] Consequently, the oxidation process at O_1 (irreversible) and O_3 (reversible) involves one electron each.

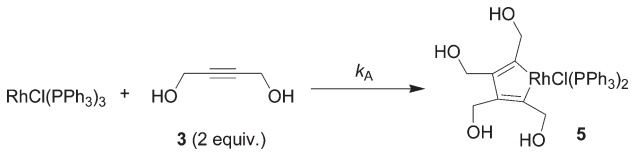
(13) Diyne **1c** has three *p*-tolylsulfonyl units instead of 2,4,6-triisopropylsulfonyl units. The *p*-tolylsulfonyl units, as well as giving crystallinity to the compounds, simplify the ^{1}H and ^{13}C NMR spectra when characterizing the resulting products.

Table 3. ESI Mass Spectrometry Study of the [2+2+2] Cycloaddition of Alkynes Catalyzed by the Wilkinson Complex

entry	sample	MS (m/z)[a]/identified species	MS/MS (m/z)[a]/identified species
1	$RhCl(PPh_3)_3$	889.1 $[Rh(PPh_3)_3]^+$ 709.2 $[Rh(PPh_3)_2(CH_3CN)_2]^+$ 627.0 $[Rh(PPh_3)_2]^+$ 587.4 $[RhCl(PPh_3)(CH_3CN)_4+Na]^+$	627.0 $[Rh(PPh_3)_2]^+$ 627.0 $[Rh(PPh_3)_2]^+$
2	**1a** + $RhCl(PPh_3)_3$	1514.6 [**2a**−Cl−PPh_3]$^+$ 1172.7 [**1a**+Na]$^+$	nonidentified species
3	**1b** + $RhCl(PPh_3)_3$	1314.3 [**2b**−Cl−PPh_3]$^+$ 972.5 [**1b**+Na]$^+$	784.0 [**2b**−Cl−2PPh_3 −(2,4,6-^{i}Pr$C_6H_2SO_2$)−H]$^+$
4	**1c** + $RhCl(PPh_3)_3$	1239.8 [**2c**-Cl]$^+$ 978.0 [**2c**−Cl−PPh_3]$^+$ 636.1 [**1c**+Na]$^+$	977.9 [**2c**−Cl−PPh_3]$^+$ 715.9 [**2c**−Cl−2PPh_3]$^+$
5	**3** + $RhCl(PPh_3)_3$	537.2 [**5**−Cl−PPh_3]$^+$	nonidentified species

[a] Reported m/z values correspond to the most abundant peak.

Scheme 4



O_3 and the ^{31}P NMR doublet, observed by reacting $RhCl(PPh_3)_3$ with stoichiometric **1a**, were assigned to complex **2a** (Scheme 3). The latter could not be isolated but was also characterized *in situ* by ESI-MS (*vide infra*).

The reversible oxidation peak of the rhodacyclopentadiene complex **2a** at O_3 disappeared after addition of the monoalkyne **3** (1 equiv), while the oxidation peak of $RhCl(PPh_3)_3$ at O_2 was partly restored. The oxidation peak current and consequently the concentration of the recovered $RhCl(PPh_3)_3$ were higher when the reaction was performed in the presence of 2 equiv of PPh_3 added before the monoalkyne **3**. Such experiments establish that **2a** reacts with the monoalkyne **3** (reaction B in Scheme 3) to deliver the final product **4a** (characterized by TLC by comparison to the authentic sample) and the initial $RhCl(PPh_3)_3$ complex.

Similar experiments were performed from dialkyne **1b**, synthesized and isolated in the reaction of **1a** with TFA in dichloromethane.[2a] The stoichiometric reaction of $RhCl(PPh_3)_3$ with **1b** was followed by ^{31}P NMR in CD_2Cl_2 (step A in Scheme 3). Besides the signals of $RhCl(PPh_3)_3$, one doublet centered at 19.6 ppm was observed for complex **2b** with J_{RhP} = 119 Hz, the same coupling constant as for the isolated complex **2c** (Table 2). The higher J_{RhP} constant found for complex **2a** (Table 2) was probably due to a difference of geometry induced by the bulky protecting groups BOC. The reaction was also followed by cyclic voltammetry as for **1a**. The oxidation peak of the Wilkinson catalyst disappeared with time, while a reversible oxidation peak appeared at more positive potential (Table 2), which characterizes complex **2b** (step A in Scheme 3). The monoalkyne **3** (1 equiv) was added to complex **2b** generated *in situ*, just after addition of PPh_3 (2 equiv). The Wilkinson catalyst was recovered, and the final product **4b** was formed and identified by comparison of its TLC with that of an authentic sample.

To gain further structural information on the intermediates of the [2+2+2] cycloaddition of alkynes catalyzed by the Wilkinson complex, we conducted an electrospray ionization mass spectrometry study. Electrospray ionization mass spectrometry (ESI-MS)[14] is a technique that has become increasingly popular as a mechanistic tool for studying transient intermediates involved in organometallic catalytic reactions.[15] Our investigation began with the characterization of the Wilkinson complex (entry 1, Table 3). A solution of the complex dissolved in degassed dichloromethane and diluted in acetonitrile was injected into the mass spectrometer. Two peaks, identified as $[Rh(PPh_3)_3]^+$ and $[Rh(PPh_3)_2]^+$ species, formed by dissociation of chloride and triphenylphosphine, respectively, from the Wilkinson complex, were identified among other adducts, which corresponded to related species such as $[Rh(PPh_3)_2(CH_3CN)_2]^+$ and $[RhCl(PPh_3)(CH_3CN)_4+Na]^+$ (see Figures SI1 and SI2 in SI).

The oxidative cyclization of dialkynes with the Wilkinson complex (step A in Scheme 3) was then studied. The three different dialkynes, **1a**, **1b**, and **1c**, were respectively mixed with stoichiometric amounts of the Wilkinson catalyst in either dichloromethane or toluene solution. Upon color change from orange-red to yellow, an aliquot was diluted in degassed acetonitrile and injected into the mass spectrometer for analysis. The reactant sodium adducts of the dialkyne product together with ionic species corresponding to the rhodacyclopentadiene intermediate of type **2**, which had lost the chlorine atom and adducts corresponding to the Wilkinson catalyst, could be detected in all cases (Table 3). Two different species with one or two triphenylphosphines were detected for rhodacyclopentadiene **2c** (entry 4, Table 3), which contained the less sterically demanding arylsulfonamide (4-methylphenyl). On the other hand, the other two rhodacyclopentadienes, **2a** and **2b**, which contain the 1,3,5-triisopropylphenyl as the aryl unit in the sulfonamide moiety, showed only ionic adducts containing one triphenylphosphine coordinated to the Rh^{III} atom.[16] All these

(14) *Electrospray Ionization Mass Spectrometry, Fundamentals, Instrumentation and Applications*; Cole, R. B., Ed.; Wiley-Interscience: New York, 1997.

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(16) Neutral species **2** containing chlorine and two triphenylphosphines as ligands coordinated to the rhodium(III) center are proposed instead of cationic ones (after release of one chloride). Indeed, conductimetry measurements conducted on a dichloromethane solution of **2b** (2 mM) showed only a very low increase of conductimetry when compared to the solvent alone (from 9.3 to 13.3 μS cm^{-1}, respectively, at 20 °C). The same measurements conducted in a dissociative and more coordinating solvent such as DMF exhibited a much higher increase in conductivitity (from 2.6 to 23.3 μS cm^{-1}). However, this value is still too low to assume that **2b** was fully dissociated to the cationic complex in DMF.[17] Evidence for the formation of neutral complexes **2** in dichloromethane as confirmed by conductivity measurements might seem to contrast with the ESI-MS results. However, this is not the case, as the ionic species detected by means of ESI-MSI could be formed by in-source dissociation (i.e., chlorine and/or triphenylphosphine dissociation) from undetectable neutral species present in the solution.

rhodacyclopentadiene intermediates were then mass-selected for MS/MS structural characterization. The behavior was different for each substrate but allowed the proposed rhodacyclopentadienes **2b** and **2c** (entries 3 and 4, Table 3) to be confirmed. Fragmentation of rhodacyclopentadiene **2a** occurred to give nonidentified species that had a lower mass than that of the ligand.

Also, isolated rhodacyclopentadiene species **2b** and **2c** were dissolved in acetonitrile and injected into the mass spectrometer. The same ionic species as in entries 3 and 4 (Table 3) were again detected, excluding those corresponding to the Wilkinson complex (see Figures SI3−SI7 in SI).

2-Butyn-1,4-diol (**3**) was added to the mixtures containing the rhodacyclopentadiene intermediates **2**. No peak related to a more advanced intermediate could be detected (step B, Scheme 3). Neither the addition of triphenylphosphine *prior* to the addition of 2-butyn-1,4-diol (**3**) nor the monitoring of the whole reaction mixture allowed us to detect any other intermediate. After the addition of the monoalkyne, the composition of the cationic species changed gradually over time: the intensity of the rhodacyclopentadiene species faded, the cycloaddition product was observed and increased in intensity over time, and triphenylphosphine oxide-related peaks appeared.

For the purpose of comparison, the reaction of $RhCl(PPh_3)_3$ (1.5 mM) with the monoalkyne **3** (2 equiv) was also followed by cyclic voltammetry, as done for the reaction of **1a** and **1b**. The oxidation peak of $RhCl(PPh_3)_3$ disappeared with time while a new irreversible oxidation peak appeared at more positive potential (Table 2), which was assigned to complex **5** (Scheme 4). The latter was also characterized by ^{31}P NMR (Table 2).

The formation of rhodacyclopentadiene **5** was confirmed again by injecting a 2:1 molar mixture of 2-butyn-1,4-diol, **3**, and the Wilkinson catalyst in dichloromethane into the mass spectrometer (entry 5, Table 3). Apart from the signals corresponding to the Wilkinson catalyst, a new peak emerged, which was identified as rhodacyclopentadiene **5**, which had lost the chlorine atom and one triphenylphosphine ligand (see Figure SI8 in SI).

In summary, the two main steps of the catalytic cycle (steps A and B in Scheme 3) have been followed by cyclic voltammetry and ^{31}P NMR. The formation of rhodacyclopentadiene species **2** (step A in Scheme 3) was confirmed by ESI-MS. Kinetic data on those two steps were also obtained using electrochemical techniques,[8] as will be illustrated below.

Rate and Mechanism of the Stoichiometric Oxidative Cyclization of Dialkynes with the Wilkinson Complex $RhCl(PPh_3)_3$ (step A in Scheme 3). The kinetics of the reaction of the Wilkinson catalyst (C_0 = 1.5 mM) with **1a** in CH_2Cl_2 (containing n-Bu_4NBF_4, 0.3 M) (step A in Scheme 3) was monitored by recording the decay of the oxidation plateau current i_{ox} of $RhCl(PPh_3)_3$ (proportional to its concentration)[8] measured at a rotating gold disk electrode polarized at +1 V, on the plateau of the oxidation wave of $RhCl(PPh_3)_3$, after addition of **1a** (C_0 = 1.5 mM) in stoichiometric amount at 25 °C (Figure 2). Stoichiometric conditions were used to avoid further reactions. The reaction of **1a** was slower in the presence of added PPh_3 (2 equiv) (Figure 2), establishing that the reactive species was $RhCl(PPh_3)_2$ involved in an equilibrium with $RhCl(PPh_3)_3$ and PPh_3. There is clearly a competition between PPh_3 and the C≡C bonds of the dialkyne for the coordination of the Rh^I center.

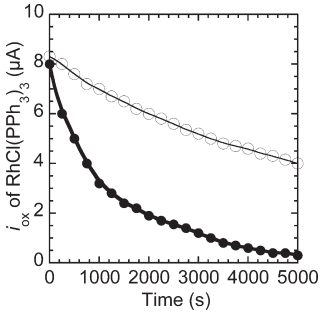

Figure 2. Kinetics of the reaction of the dialkyne **1a** (1.5 mM) with $RhCl(PPh_3)_3$ (1.5 mM) in CH_2Cl_2 containing n-Bu_4NBF_4 (0.3M) at 25 °C, as monitored by chronoamperometry at a rotating gold disk electrode (d = 2 mm) polarized at +1 V. Decrease of the oxidation plateau current of $RhCl(PPh_3)_3$ (proportional to its concentration) with time: (●) in the absence of PPh_3; (○) in the presence of PPh_3 (3 mM).

Table 4. Half-Reaction Times, $t_{A1/2}$, for the Formation of the Rhodacyclopentadiene Complexes 2a,b and 5 from $RhCl(PPh_3)_3$ (1.5 mM) and 1a,b (1.5 mM) or 3 (3 mM) Respectively in Dichloromethane at 25 °C (step A in Scheme 3 or 4)

entry	complex	additive	$t_{A1/2}$ (s)
1	**2a**	no	650
2	**2a**	PPh_3 (2 equiv)	4750
3	**2b**	no	75
4	**5**	no	1360

The reaction of $RhCl(PPh_3)_3$ (1.5 mM) with the diakyne **1b** (1 equiv) was found to be faster by ca. a factor of 10 when compared to that of the more bulky dialkyne **1a** (entries 1 and 3 in Table 4, Figure SI9 in SI), which shows that the reaction is sensitive to steric factors around the C≡C bonds, which affect their coordination to the Rh^I center prior to oxidative coupling. A precoordination of the Rh^I center by the NH group of **1b** would also favor step A when compared to **1a**.

The kinetics of the reaction of $RhCl(PPh_3)_3$ (1.5 mM) with the monoakyne **3** (2 equiv) (Scheme 4) was also investigated in dichloromethane by means of the electrochemical techniques, as performed above for the reaction of **1a** and **1b** (see Figure SI10 in SI). The complex $RhCl(PPh_3)_3$ was fully consumed. From the value of $t_{A1/2}$ observed for the formation of the rhodacyclopentadiene (**5**), it emerges that the oxidative cyclization from the dialkyne **2a** was ca. twice as fast as that of the monoalkyne **3** (compare entries 1 and 4 in Table 4). The complex $RhCl(PPh_3)_2$ had to undergo two successive C≡C coordinations to cause the oxidative coupling that generates the rhodacyclopentadiene complex **2a** or **5**. The kinetic results suggest that the second reversible coordination of dialkyne **1a** to $RhCl(PPh_3)_2$ was more favored than that of the monoalkyne **3** due to intramolecular coordination.

Rate and Mechanism of the Reaction of a Monalkyne with the Rhodacyclopentadiene Complexes 2a,b (step B in Scheme 3). As observed above, the amount of $RhCl(PPh_3)_3$ recovered in the reaction of complex **2a** with **3** was much higher when the reaction was performed in the presence of extra PPh_3. This suggests that the monoalkyne **3** reacts with $RhCl(PPh_3)_3$ (formed in the reaction of **2a** with **3**) to deliver the rhodacyclopentadiene complex **5** (as evidenced in Table 4 and Scheme 4). The latter reaction might be at the origin of the lack of $RhCl(PPh_3)_3$ observed in the reaction of complex

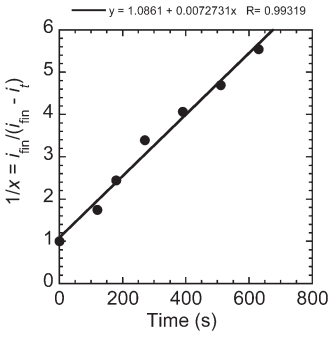

Figure 3. Kinetics of the reaction of the rhodacyclopentadiene complex **2a** with the monoalkyne **3** (1.5 mM). **2a** was generated *in situ* from $RhCl(PPh_3)_3$ (1.5 mM) and **1a** (1.5 mM) in CH_2Cl_2 containing nBu_4NBF_4 (0.3 M) at 25 °C. The reaction was monitored by cyclic voltammetry performed with time at a steady gold disk electrode (d = 2 mm). Plot of $1/x$ versus time ($x = (i_{fin} - i_t)/i_{fin}$); i_t = oxidation peak current of $RhCl(PPh_3)_3$ at t; i_{fin} = final oxidation peak current of $RhCl(PPh_3)_3$).

2a with the monoalkyne **3** (1 equiv). In the presence of added PPh_3, the reaction of **3** with $RhCl(PPh_3)_3$ was inhibited and $RhCl(PPh_3)_3$ could be fully recovered. Consequently the kinetics of the reaction of complex **2a** with **3** was investigated under stoichiometric conditions and in the presence of excess PPh_3.

Once the rhodacyclopentadiene complex **2a** was formed *in situ* by reacting the Wilkinson catalyst (C_0 = 1.5 mM) with **1a** (C_0 = 1.5 mM) in CH_2Cl_2 at 25 °C, 2 equiv of PPh_3 was added, followed by the monoalkyne **3** (1 equiv). The kinetics of step **B** in Scheme 3 was followed by monitoring the rate of formation of one of the final products, $RhCl(PPh_3)_3$, i.e., by recording the increase with time of the oxidation plateau current of $RhCl(PPh_3)_3$ measured at the rotating gold disk electrode. We had however to face severe problems of passivation at the rotating disk electrode, at the very beginning of the reaction, preventing any accurate determination of the oxidation current of $RhCl(PPh_3)_3$. The kinetics of the reaction of **2a** with **3** was thus followed by periodically recording cyclic voltammetry at the steady gold disk electrode until the oxidation peak current of $RhCl(PPh_3)_3$ reached a constant final value. Meanwhile, the reversible oxidation peak of complex **2a** disappeared with time. The plot of $1/x$ versus time was linear ($x = (i_{fin} - i_t)/i_{fin}$, i_t = oxidation peak current of $RhCl(PPh_3)_3$ at t; i_{fin} = final oxidation peak current of $RhCl(PPh_3)_3$) (Figure 3).

This characterizes a second-order reaction, i.e., the reaction of **2a** with **3** under stoichiometric conditions, showing that $RhCl(PPh_3)_3$ was generated in a step (reductive elimination that also generated the final benzene product **4a**) that was considerably faster[18] than the complexation of **2a** by **3** followed by cycloaddition, which was therefore rate-determining for the overall step B. The apparent rate constant k_B of step B was determined from the slope of the straight line: $1/x = 1 + k_B C_0 t$ (Table 5).

(17) For reviews on the characterization of ionic coordination compounds by conductivity measurements, see: (a) Geary, W. J. *Coord. Chem. Rew.* **1971**, *7*, 81–122. (b) Jutand, A. *Eur. J. Inorg. Chem.* **2003**, 2017–2040.

(18) If the reaction of **2a** with **3** was much faster than the reductive elimination that generates $RhCl(PPh_3)_3$, then an intermediate complex would accumulate. The formation of $RhCl(PPh_3)_3$ from the intermediate complex (which would be rate-determining) would be thus a first-order reaction with a kinetic law $\ln x = -k^{elim}t$.

Table 5. Kinetics of the Reaction of the Monoalkyne 3 (1.5 mM) with the Rhodacyclopentadiene Complexes 2a,b Generated *in Situ* from $RhCl(PPh_3)_3$ (1.5 mM) and 1a,b (1.5 mM), Respectively, in Dichloromethane at 25 °C

complex	$t_{B1/2}$ (s)[a]	k_B (M^{-1} s^{-1})[b,c]
2a	130	4.7
2b	680	1.1

[a] $t_{B1/2}$ is the half-reaction time of step B in Scheme 3. [b] k_B is the apparent rate constant of step B. [c] 2 equiv of PPh_3 was added to the Rh^{III} complexes **2a**,**b** before **3**.

The reaction of **2b** (C_0 = 1.5 mM) with **3** (1 equiv) was also followed by cyclic voltammetry at the steady electrode (Figure SI11a in SI). The apparent rate constant k_B of step B was estimated from the slope of the straight line obtained in the plot of $1/x$ versus time (Figure SI11b in SI). $1/x = 1 + k_B C_0 t$ (Table 5).

From the values of the half-reaction times found for step A (Table 4) and step B (Table 5), it emerges that at identical concentrations of **1a**, **1b**, **3**, and $RhCl(PPh_3)_3$ the formation of the rhodacyclopentadiene complex was rate-determining in the reaction of **1a**, whereas step B was rate-determining for the reaction involving **1b**. When comparing the relative values of the half-reaction times $t_{B1/2}$ measured for the reaction of complexes **2a** and **2b** with **3** (130 versus 680 s, respectively, Table 5) to the values of the half-reaction times $t_{A1/2}$ measured for the formation of complexes **2a** and **2b** (650 versus 75 s, respectively, Table 4), it emerges that the first step, A, is affected by the substitution on the N atoms (NH versus NBOC): the more hindered, the less reactive. It is clear that the bis-coordination of two alkynes to the Rh^I center before the oxidative coupling must be strongly affected by the bulk around the two C≡C bonds. In addition to steric hindrance, a precomplexation of NH on the Rh^I center could favor the reaction of **1b** compared to **1a** in step A. Step B is also affected by the substitution on the N atoms, but the more substituted **2a** is found to be more reactive than the less substituted **2b**. The second step, B, consists in the reaction of the Rh^{III} complex **2a** or **2b** with **3** (coordination of **3** followed by cycloaddition (see Scheme 1)). No internal complexation took place in complexes **2a** and **2b** because the two PPh_3 were found to be equivalent (only one singlet in ^{31}P NMR). In contrast to step A, steric hindrance might be beneficial in step B by favoring the release of one PPh_3 by steric decompression to facilitate the coordination of the C≡C bond of **3** onto the Rh^{III} center. In other words, one phosphine would be more labile in the bulky **2a** than in the less bulky **2b**.

Conclusion

The two main steps of the catalytic cycle of the $RhCl(PPh_3)_3$-catalyzed [2+2+2] cycloaddition of the symmetrical diynes **1a** and **1b** with the monoalkyne **3** were characterized in dichloromethane at room temperature. The reactions of the diynes **1a** and **1b** with $RhCl(PPh_3)_3$ were followed by cyclic voltammetry, ^{31}P NMR, and ESI-MS (step A). The rhodacyclopentadiene Rh^{III} complexes **2a** and **2b** formed in these reactions were characterized by the same techniques. The reaction of complexes **2a** and **2b** with the monoalkyne **3**, which delivers the final product together with $RhCl(PPh_3)_3$ (step B), was followed by electrochemical techniques. Kinetic data on the two main steps of the catalytic cycle for a $RhCl(PPh_3)_3$-catalyzed [2+2+2] cycloaddition of alkynes were thus available for the first time. From the values of

the half-reaction times $t_{A1/2}$ and $t_{B1/2}$ of steps A and B, respectively, it was found that step A (coordination of the two C≡C bonds of **1a**, followed by oxidative coupling) was rate-determining for the reaction of the bulky **1a**. In contrast, step B, reaction of **2b** (generated from the nonprotected and thus less bulky diyne **1b**) with the monoalkyne **3** with subsequent recovery of the Wilkinson catalyst, was rate-determining. We conclude that the first or second step may be rate-determining according to the structure of the starting reagents.

Experimental Part

All experiments were performed under an argon atmosphere. ^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) with H_3PO_4 as an external reference. ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers (200 and 400 MHz) with TMS as an internal reference. Cyclic voltammetry and chronoamperometry were performed at a gold disk electrode (d = 2 mm) with a homemade potentiostat and a waveform generator EGG model 175. Voltammograms were recorded on a Nicolet 301 oscilloscope. Conductivity measurements were performed on a Tacussel CDM210 conductivity meter (cell constant = 1 cm^{-1}).

Chemicals. Dichloromethane was distilled from calcium hydride and kept under argon. The monoalkyne **3** and the Wilkinson catalyst $RhCl(PPh_3)_3$ were commercially available. The diynes **1a**, **1b**, and **1c** were prepared as previously described by us.[2a,b]

General Procedure for the [2+2+2] Cycloadditions of Diynes 1 and Monoalkyne 3. A degassed solution of diyne **1b** (0.10 g, 0.10 mmol), 2-butyn-1,4-diol, **3** (0.011 g, 0.13 mmol), and chlorotris(triphenylphosphine)rhodium(I) (0.0046 g, 0.005 mmol, 5% molar) in anhydrous toluene (15 mL) was heated at 65 °C for 7 h (TLC monitoring). The solvent was then evaporated and the residue was chromatographed through silica gel with hexanes/ethyl acetate (polarity from 7:3 to 6:4) to afford **4b** (0.047 g, 43%) as a colorless solid. A sample specially purified for elemental analysis was obtain by digestion from diethyl ether: mp 210−212 °C (dec); IR (ATR) 3288, 2958, 2928, 2868, 2163, 1319, 1149 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17−1.30 (m, 54H), 2.91 (sept, J = 6.8 Hz, 3H), 3.37 (br s, 2H), 3.98−4.22 (m, 10H), 4.60 (s, 4H), 4.78 (s, 4H), 5.40−5.45 (m, 2H), 7.16 (s, 4H), 7.17 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2, 25.5, 25.6, 30.2, 30.4, 34.8, 42.4, 52.7, 59.0, 124.6, 124.7, 131.5, 131.8, 132.5, 137.8, 140.4, 151.1, 152.1, 153.8, 154.0; ESI-MS (m/z) 1036 [M + H]$^+$, 1053 [M + NH_4]$^+$, 1058 [M + Na]$^+$; HRMS calcd. for $[C_{57}H_{86}N_3O_8S_3]^+$ 1036.5572, found 1036.5546. Anal. Calcd for $C_{57}H_{85}N_3O_8S_3\cdot Et_2O$ (1110.631): C, 65.97; H, 8.62; N, 3.78; S, 8.66. Found: C, 66.46 and 66.04; H, 8.75 and 8.86; N, 3.81 and 3.77; S, 8.26 and 8.20.

Spectroscopic data for **4a**: mp 92−94 °C; IR (ATR) 3512, 2960, 2930, 2871, 1725, 1317, 1149, 1130 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12 (s, 18H), 1.18−1.45 (m, 54H), 2.92 (sept, J = 7 Hz, 3H), 3.58 (br s, 2H), 3.89 (sept, J = 6.6 Hz, 4H), 4.29 (sept, J = 6.7 Hz, 2H), 4.85 (s, 4H), 4.85 (s, 4H), 5.02 (s, 4H), 7.15 (s, 4H), 7.16 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2, 25.5, 25.6, 28.3, 30.1, 34.8, 34.9, 45.2, 52.7, 58.9, 85.6, 124.2, 124.4, 131.1, 132.4, 134.5, 138.0, 140.7, 151.2, 151.4, 152.1, 153.4, 154.3; ESI-MS (m/z) 1236 [M + H]$^+$, 1253 [M + NH_4]$^+$, 1258 [M + Na]$^+$, 1274 [M + K]$^+$. A sample specially purified for elemental analysis was obtain by digestion from *n*-pentane: HRMS calcd for $[C_{67}H_{101}N_3O_{12}S_3Na]^+$ 1258.6440, found 1258.6435. Anal. Calcd for $C_{67}H_{101}N_3O_{12}S_3\cdot C_5H_{12}$ (1308.882): C, 66.07; H, 8.70; N, 3.21; S, 7.35. Found: C, 65.80 and 65.83; H, 8.55 and 8.57; N, 3.25 and 3.27; S, 6.69 and 6.95.

General Procedure for the Synthesis of Rhodacyclopentadiene Rh^{III}, 2. A degassed solution of diyne **1b** (0.040 g, 0.042 mmol) and chlorotris(triphenylphosphine)rhodium(I) (0.039 g, 0.042 mmol) in degassed dichloromethane (4 mL) was stirred at room temperature for 5 h. Then, degassed diethyl ether (6 mL) was added to the reaction mixture and a solid was precipitated. The solvents were evaporated to afford **2b** (0.048 g, 87%) as a red solid: mp 96−99 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (d, J = 6.7 Hz, 18H), 1.10−1.28 (m, 36H), 2.81 (sept, J = 6.7 Hz, 4H), 3.00−3.04 (m, 4H), 3.30 (br s, 4H), 3.40−3.65 (m, 4H), 3.90−4.20 (m, 3H), 6.80−7.70 (m, 36H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2, 25.7, 25.8, 30.2, 30.6, 34.8, 46.5, 48.6, 124.2, 124.7, 127.7, 128.8, 128.9, 129.0, 129.1, 130.3, 130.8, 131.2, 131.7, 133.1, 134.9, 135.0, 135.1, 149.0, 150.7, 151.6, 152.8, 153.4; ^{31}P NMR (101 MHz, CD_2Cl_2) δ 19.6 (d, J = 119 Hz); ESI-MS (m/z) 1314 [M − Cl − PPh_3]$^+$; HRMS calcd. for $[C_{71}H_{94}N_3O_6PRhS_3]^+$ 1314.5092, found 1314.5119. Conductivity measurements were done on a solution of **2b** in CH_2Cl_2 or DMF (5 mL) to determine whether the complex was cationic or neutral. At 20 °C, in CH_2Cl_2, the conductivity increased from 9.3 μS cm^{-1} (residual conductivity of CH_2Cl_2) to 13.3 μS cm^{-1} after addition of **2b** (17 mg, 0.01 mmol, 2 mM) and to 17 μS cm^{-1} for **2b** (4 mM). In DMF, a strongly more dissociative solvent than CH_2Cl_2, the conductivity increased from 2.6 μS cm^{-1} (residual conductivity of DMF) to 23.3 μS cm^{-1} after addition of **2b** (17 mg, 0.01 mmol, 2 mM). From these low values of conductivities, we assume that complex **2b** was not significantly dissociated to the cationic complex and chloride anion.[16,17]

Spectroscopic data for 2c: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 6H), 2.54 (s, 3H), 3.00−3.34 (m, 4H + 4H + 2H), 7.16−7.67 (m, 42 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.3, 46.9, 48.9, 127.7, 128.6, 128.8, 128.9, 129.0, 130.0, 130.2, 130.3, 130.5, 130.9, 131.4, 134.6, 134.7, 134.9, 134.9, 136.8, 143.9, 144.1, 149.6, 149.7, 152.9, 153.6; ^{31}P NMR (101 MHz, CD_2Cl_2) δ 22.9 (d, J = 119 Hz); ESI-MS (m/z) 1240 [M − Cl]$^+$, 978 [M − Cl − PPh_3]$^+$; HRMS calcd for $[C_{47}H_{46}N_3O_6PRhS_3]^+$ 978.1336, found 978.1377.

Spectroscopic data for 2a: ^{31}P NMR (101 MHz, CD_2Cl_2) δ 38.8 (d, J = 185 Hz); ESI-MS (m/z) 1514 [M − Cl − PPh_3]$^+$.

General Procedure for Cyclic Voltammetry. Experiments were carried out in a three-electrode thermostated cell (25 °C) connected to a Schlenk line. The reference was a saturated calomel electrode separated from the solution by a bridge filled with 1.5 mL of CH_2Cl_2 containing nBu$_4$NBF$_4$ (0.3 M). The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area. Eighteen milliliters of CH_2Cl_2 containing nBu$_4$NBF$_4$ (0.3 M) were introduced into the cell followed by 25 mg (0.027 mmol) of $RhCl(PPh_3)_3$. Cyclic voltammetry was performed at a steady gold disk electrode (d = 2 mm) at the scan rate of 0.5 V s^{-1}. Then 31 mg (0.027 mmol) of **1a** was added to the cell. Cyclic voltammetry was performed with time. Similar experiments were performed from 26 mg (0.027 mmol) of **1b** or 4.7 mg (0.054 mmol) of the monoalkyne **3**.

In a second step, 2.3 mg (0.027 mmol) of the monoalkyne **3** was added to either **2a** or **2b** generated as reported just above. The cyclic voltammetry was performed at fixed time intervals at the scan rate of 0.5 V s^{-1}.

General Procedure for the Investigation of the Kinetics of the Reaction of $RhCl(PPh_3)_3$ with 1a or 1b or 3 (step A in Scheme 3 or 4). Kinetic experiments were performed in the same cell as used for cyclic voltammetry (*vide supra*). Eighteen milliliters of CH_2Cl_2 containing nBu$_4$NBF$_4$ (0.3 M) was introduced into the cell followed by 25 mg (0.027 mmol) of $RhCl(PPh_3)_3$. The rotating gold disk electrode (Radiometer, EDI 65109, d = 2 mm, angular velocity: ω = 105 rad s^{-1}) was polarized at +1 V versus SCE. The decrease of the oxidation current of the $RhCl(PPh_3)_3$ was recorded with time after addition of 31 mg (0.027 mmol) of **1a** until total conversion. Similar experiments were done in the presence of 40 mg (0.054 mmol) of PPh_3.

Similar experiments were done with 26 mg (0.027 mmol) of **1b** and 4.7 mg (0.054 mmol) of **3**.

General Procedure for the Investigation of the Kinetics of the Reaction of 2a or 2b with the Monoalkyne 3 (step B in Scheme 3). The kinetics of the reaction of 2.35 mg (0.027 mmol) of **3** with the

complexes **2a** and **2b** was monitored by cyclic voltammetry at the steady gold disk electrode performed randomly at a scan rate of 0.5 V s^{-1}. The complexes **2a** and **2b** were generated *in situ*, as reported just above, by reacting 25 mg (0.027 mmol) of $RhCl(PPh_3)_3$ with 31 mg (0.027 mmol) of **1a** or 26 mg (0.027 mmol) of **1b**.

General Procedure for ^{31}P NMR Experiments (101.3 MHz, H_3PO_4). To an NMR tube containing 0.5 mL of CD_2Cl_2 was added 10 mg (0.01 mmol) of $RhCl(PPh_3)_3$, followed by 12 mg (0.01 mmol) of **1a**. The ^{31}P NMR was performed with time to observe the formation of **2a**. Similar experiments were performed with 10 mg (0.01 mmol) of **1b**.

General Procedure for ESI Mass Spectrometry Studies. Electrospray mass spectrometry analyses were recorded on an Esquire 6000 ion trap mass spectrometer (Bruker) equipped with an electrospray ion source. The instrument was operated in the positive ESI(+) ion mode. The samples (5 μL) were introduced into the mass spectrometer ion source through an Agilent HPLC with a mobile phase flow of 100 μL/min (80/20 v/v CH_3CN/H_2O).

Degassed dichloromethane (0.5 mL) was added to a 5 mL flask containing $RhCl(PPh_3)_3$ (0.003 g, 6.5 mmol) and dialkyne **1c** (0.002 g, 6.5 mmol) under a nitrogen atmosphere. Upon color change from red-orange to yellow, aliquots were taken at fixed time intervals, diluted in degassed acetonitrile, and injected into the HPLC. 2-Butyn-1,4-diol (0.0005 g, 6.5 mmol) dissolved in dichloromethane was then added, and aliquots were taken following the methodology described above until completion of the reaction. Similar experiments were performed with **1a**, **1b**, and **3**.

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Supporting Information Available: ESI-MS spectra and kinetic data. These materials are available free of charge via the Internet http://pubs.acs.org.