Unprecedented Rhodium-Mediated Trimerization of Alkynes HC≡CR (R = Ph, *p*-Tolyl) Leading to (η^4-Cyclobutadiene)rhodium Complexes

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The α-amino acidate complex [(η^5-C_5Me_5)Rh(L-alaninate)Cl] (**1**) reacts with HC≡CR (R = Ph, *p*-tolyl), in methanol, in the presence of NEt_3, to form the new cyclobutadiene compounds [(η^5-C_5Me_5)Rh(η^4-C_4HR_2C≡CR)] (R = Ph (**2a**), *p*-tolyl (**2b**)) as the major products. The X-ray molecular structure determination of complex **2a** has been carried out. The complex exhibits a sandwichlike structure with the rhodium metal located between a η^4-phenylethynyl cyclobutadiene ligand and a η^5-pentamethylcyclopentadienyl group. A possible pathway for the formation of **2** from **1** is proposed.

Introduction

Transition-metal-mediated oligomerization reactions of alkynes have been known for many years[1] and have proved to be a source of a large variety of complexes containing ligands formed from alkynes.[2] Among them, one interesting type is the cyclobutadiene complexes. These complexes open the possibility of studying the reactivity of the carbocyclic ring with interesting implications from both mechanistic and synthetic points of view.[3]

Although there are many synthetic routes now available to transition-metal cyclobutadiene complexes,[3] rhodium derivatives of this type are quite rare. In some instances, their synthesis have been achieved by cyclodimerization of two disubstituted acetylenes[4] or by cyclization of one diacetylene[5] precursor. It has been also reported that the reaction of [{(η^5-C_5Me_5)RhCl}$_2$-(μ-Cl)$_2$] with phenylacetylene yields two rhodium compounds containing a tetramer or a pentamer of the starting terminal acetylene η^4-coordinated through cyclobutadiene-moieties,[6] but as far as we know, transition-metal cyclobutadiene containing complexes have never been the result of an alkyne trimerization process. The most common trimerization process that alkynes undergo is the cycloaddition reaction of three alkyne molecules to render arenes,[7] and very recently, it was reported that the transition-metal-induced stepwise trimerization of the terminal alkynes HC≡CPh[8] and HC≡CCO_2Me[9] does not lead to the expected benzene derivatives but to the linear hexadienynes PhC≡CC(Ph)=CHCH=CHPh and MeO_2CC≡CC(=CHCO_2Me)-CH=CHCO_2Me, respectively.

In the course of our studies on transition-metal complexes with chiral metal centers,[10] we have attempted the preparation of metal−acetylide compounds, and in fact, we have recently reported the synthesis, separation, characterization, and epimerization studies of the R_{Ir},S_N,S_C and S_{Ir},S_N,S_C diastereomers of the iridium acetylide [(η^5-C_5Me_5)Ir(L-prolinate)-(C≡CCMe_3)].[10b] These compounds have been prepared by treating in methanol the chloride precursor [(η^5-C_5Me_5)Ir(L-prolinate)Cl] with HC≡CCMe_3 and NEt_3 in a 1/1/1 molar ratio. Following a similar synthetic strat-

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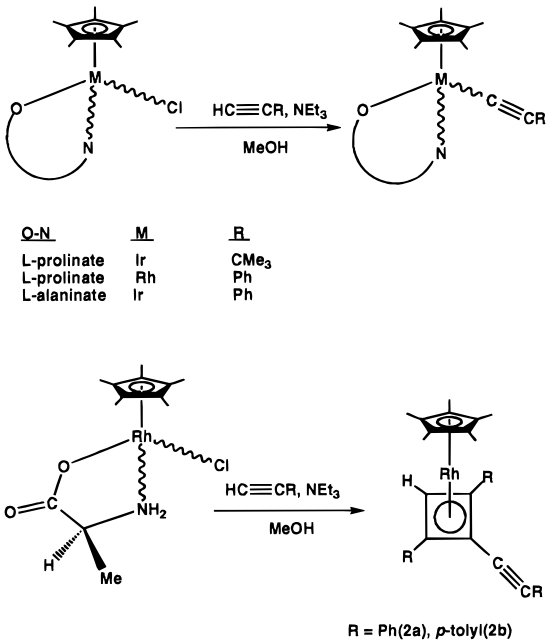
Chart 1



egy, we have succeeded in preparing homologous iridium, rhodium, or (η^6-*p*-cymene)ruthenium acetylide compounds with several α-amino acidates and terminal acetylenes.[10f] However, the reaction of the α-alaninate rhodium chloride [(η^5-C_5Me_5)Rh(L-alaninate)Cl] (**1**) with the monosubstituted alkynes HC≡CR (R = Ph, *p*-tolyl) takes a completely different course. From the reaction medium the alkynylcyclobutadiene complexes [(η^5-C_5Me_5)Rh(η^4-C_4HR_2C≡CR)] (R = Ph (**2a**), *p*-tolyl (**2b**)) can be isolated (Chart 1). Their formation implies a novel type of rhodium-mediated trimerization reaction. Here we report the preparation of complexes **2a** and **2b** as well as their characterization, which includes the determination of the molecular structure of **2a** by diffractometric means. The stepwise course of the unique trimerization process that affords **2** is also discussed.

Results and Discussion

Addition of HC≡CR (R = Ph, *p*-tolyl) and NEt_3 to a methanolic solution of complex [(η^5-C_5Me_5)Rh(L-alaninate)Cl] (**1**)[10a] (molar ratio 1/1/1) caused the intensification of the initial orange color of the solution and the subsequent precipitation of the complexes [(η^5-C_5Me_5)Rh(η^4-C_4HR_2C≡CR)] (R = Ph (**2a**), *p*-tolyl (**2b**)) as orange-yellow solids in moderate isolated yield (~22%). This yield did not change significantly by adding stoichiometric amounts of alkyne, but in this case, spectroscopic analysis of the filtrate showed that the formation yield of **2a** was at least 75%, although we have not been able to separate further fractions of analytically pure product.

Complexes **2** were shown by mass spectrometry to contain, along with the Rh(C_5Me_5) unit, a trimer of the corresponding alkyne less two hydrogens. The isotopic distributions of the molecular ions matched those expected for the mentioned stoichiometry. The presence of an alkynyl group was inferred from a weak ν(C≡C) absorption at 2180 (**2a**) or 2185 cm^{-1} (**2b**). The ^1H and $^{13}C\{^1H\}$ NMR data of these complexes agree with the proposed formulation and are collected in the Experimental Section. Besides the resonances for the protons of the C_5Me_5 and the arene resonances, the ^1H NMR spectra showed a doublet at 4.73 ppm, J = 1.9 Hz (**2a**) or 4.65 ppm, J = 1.7 Hz (**2b**) arising from coupling to ^{103}Rh. The chemical shifts fall in the region of the resonances due to the ring protons in a variety of unsubstituted or partially substituted cyclobutadienemetal complexes (3.50−5.50 ppm),[3] and the coupling constants present values similar to those previously reported for related cyclobutadienerhodium compounds.[6,11] As the most representative data, the carbon NMR spectra showed three doublets from 50 to 80 ppm ($^1J_{RhC}$ = 10.5−11.3 Hz) corresponding to the four carbons of the cyclobutadiene ring. Again, the spectroscopic data are in good agreement with those reported for cyclobutadienerhodium compounds.[6,12] Additionally, we attributed two resonances in the 85−92 ppm region to the α- and β-carbons of the alkynyl group.

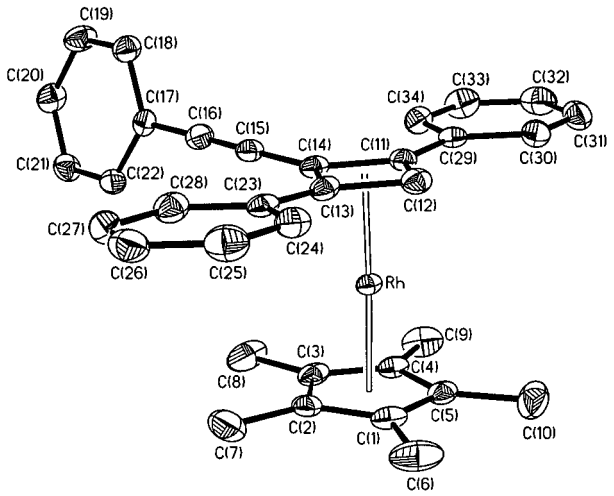


Figure 1. ORTEP view of [(η^5-C_5Me_5)Rh(η^4-C_4HPh_2C≡CPh)] (**2a**) showing the atom-labeling scheme.

In order to provide conclusive evidence for the unusual structure of these products, single crystals of complex **2a** were grown by slow diffusion of hexane into a chloroform solution and its structure was determined by a X-ray diffraction study. Figure 1 displays the molecular structure of the complex, and the most relevant bond lengths and angles are given in Table 1. The rhodium, η^5-bonded on one side to the C_5Me_5 ligand, is η^4-linked on the other to a trisubstituted cyclobutadiene. Two of the substituents are phenyls, in an opposite disposition, while the third is a phenylethynyl group. The Rh−C (C_5Me_5 ring) distances (mean 2.207(2) Å) are comparable to those found in the related complex [(η^5-C_5Me_5)Rh(η^4-C_4Ph_2HCPh=$C_5Ph_2H_2$)] (mean 2.211(14) Å) and in the tetraphenylbenzocyclobutadiene compound [(η^5-C_5Me_5)Rh(η^4-$C_4Ph_2C_4Ph_2H_2$)] (means 2.231(14) and 2.233(5) Å).[6] The rhodium atom is almost equidistant from both carbocyclic rings. It lies 1.842(2) and 1.849(2) Å apart from the plane through the five- and four-membered rings, respectively. The methyl substituents are bent away from the rhodium atom; displacements for C(6), C(7), C(8), C(9), and C(10) from the mean plane throught the C_5 ring are 0.034(3), 0.021-

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Table 1. Selected Bond Distances (Å) and Angles (deg) for [η^5-C_5Me_5)Rh(η^4-$C_4HPh_2C{\equiv}CPh$] (2a)

Rh−C(1)	2.203(3)	C(3)−C(4)	1.419(4)
Rh−C(2)	2.203(2)	C(4)−C(5)	1.430(3)
Rh−C(3)	2.205(2)	C(1)−C(5)	1.437(3)
Rh−C(4)	2.213(2)	C(11)−C(12)	1.458(3)
Rh−C(5)	2.211(2)	C(12)−C(13)	1.452(4)
Rh−G(1)[a]	1.842(2)	C(13)−C(14)	1.472(3)
Rh−C(11)	2.118(3)	C(11)−C(14)	1.470(4)
Rh−C(12)	2.117(2)	C(11)−C(29)	1.458(3)
Rh−C(13)	2.125(2)	C(13)−C(23)	1.454(3)
Rh−C(14)	2.114(2)	C(14)−C(15)	1.420(4)
Rh−G(2)[a]	1.849(2)	C(15)−C(16)	1.199(4)
C(1)−C(2)	1.424(4)	C(16)−C(17)	1.443(4)
C(2)−C(3)	1.433(3)		

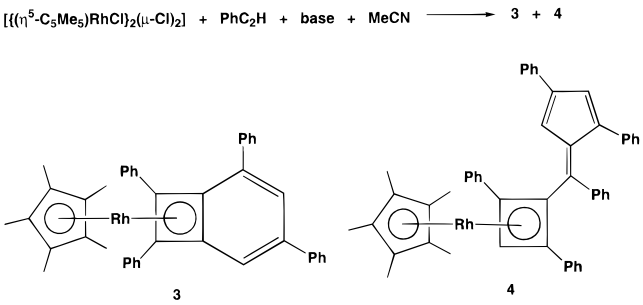
G(1)[a]−Rh−G(2)[a]	177.7(1)	C(14)−C(13)−C(23)	133.9(2)
C(12)−C(11)−C(14)	89.7(2)	C(11)−C(14)−C(13)	89.6(2)
C(12)−C(11)−C(29)	136.2(2)	C(11)−C(14)−C(15)	133.8(2)
C(14)−C(11)−C(29)	134.0(2)	C(13)−C(14)−C(15)	136.2(2)
C(11)−C(12)−C(13)	90.9(2)	C(14)−C(15)−C(16)	177.4(3)
C(12)−C(13)−C(14)	89.9(2)	C(15)−C(16)−C(17)	177.9(3)
C(12)−C(13)−C(23)	136.1(2)		

[a] G(1) and G(2) represent the centroids of the cyclopentadienyl and cyclobutadiene ligands, respectively.

(3), 0.003(3), 0.042(3), and 0.107(3) Å, respectively. The Rh−C (C_4 ring) distances (mean 2.118(2) Å) are in the range of those found in related cyclobutadiene rhodium complexes (2.102(2)−2.152(14) Å).[4a,5e,6] The cyclobutadiene ring is strictly planar and almost parallel to the pentamethylcyclopentadineyl ligand, the angle between them being 2.6(1)°. The cyclobutadiene ring is slightly distorted from a square geometry, with the two C−C bond distances involving the CH moiety (C(12) labeled, 1.458(3) and 1.452(4) Å) being shorter by ∼0.02 Å than the other two cyclic C−C bonds (1.472(3) and 1.470(4) Å). The mean C−C distance (1.464(4) Å) is comparable to the corresponding distances reported for cyclobutadienerhodium complexes[4a,5e,6] (means 1.470(9)−1.482(19) Å). The phenyls and the ethynyl group are subtly bent away from the metal atom by small amounts (0.074(2) Å for C(29), 0.069(2) Å for C(23), and 0.107(2) Å for C(15) from the mean plane through the C_4 ring). The phenyl substituents attached to C(11) and C(13) are almost coplanar with the cyclobutadiene ring (1.7(1) and 3.0(1)°, respectively), but the phenyl ethynyl group is twisted away from coplanarity with the coordinate cyclobutadiene by 78.9(1)°. The C(15)−C(16) bond distance of 1.199(4) Å is a normal carbon−carbon triple bond distance.

In order to gain some insight into the mechanism of formation of complexes **2**, we carried out the reaction of the solvate complex[13] [(η^5-C_5Me_5)Rh($MeOH)_3$]$^{2+}$ with phenylacetylene in the presence of NEt_3. A mixture of unidentified products was obtained, but it is interesting to point out that, according to spectroscopic measurements, complex **2a** was not present in the mixture. In a related reaction (Scheme 1), Maitlis *et al.* reported the preparation of complexes **3** and **4**, which contain cyclobutadiene derivatives, formed by oligomerization of phenylacetylene, as ligands. The authors proposed that the reaction proceeds *via* intermediates such as [(η^5-C_5Me_5)Rh($C_2Ph)_2$(NCMe)] and [(η^5-C_5Me_5)Rh($C_2Ph)_2$(HC_2Ph)].[6] We have not detected either by NMR spectroscopy or by mass spectrometry the formation of either

Scheme 1



3 or **4** in the preparation of the cyclobutadiene compound **2a**.

When, in the absence of NEt_3, **1** was allowed to react with 3 equiv of HC≡CPh, in methanol, the precipitation of a mixture, identified by ^{1}H NMR spectroscopy as **2a** and α-alanine, was observed. This result could be accounted for by assuming the formal abstraction of the phenylacetylene proton by the α-alaninato ligand.

Interestingly, the formation of the cyclobutadiene compounds **2** was only observed for the rhodium alaninate derivative **1** and for the terminal alkynes phenyl- and *p*-tolylacetylene. Thus, for example, the iridium analogue of **1**, [(η^5-C_5Me_5)Ir(L-alaninate)Cl],[10a] or the rhodium prolinate [(η^5-C_5Me_5)Rh(L-prolinate)Cl][10a] reacted with HC≡CPh in the presence of NEt_3, rendering the corresponding alkynyl compounds [(η^5-C_5Me_5)M(L-amino acidate)(C≡CPh)][10f] (Chart 1). On the other hand, under the same conditions, complex **1** did not react with the terminal alkyne HC≡$CCMe_3$, and from the reaction of **1** with HC≡CCO_2Me, only organic compounds derived from the alkyne could be recovered.[10f]

We have also monitored, by ^{1}H NMR spectroscopy, the reaction of **1** with HC≡CPh and NEt_3 (1/3/2 molar ratio) in $CDCl_3$. The reaction mixture remained homogeneous and after 27 h a 52% of conversion to **2a** was measured showing that, in a solvent with lower coordination tendency, such as chloroform, complex **2a** is also formed.

On the basis of these observations it is not possible to unequivocally establish the mechanistic steps for the formation of compounds **2**, and no intermediates have been detected to elucidate this problem. Nevertheless, the structure of the organic ligand indicates that the formation of these complexes must involve both oligomerization and cyclization steps, and in accord with previously reported alkyne oligomerization processes, the pathway shown in Scheme 2 could be suggested. The reaction could start with the protonation of the α-alaninate ligand by one alkyne molecule, the resulting α-alanine remaining η^1-coordinate to the metal. Support for this proposal stems from the formation of **2a** and α-alanine in the reaction of **1** with HC≡CPh in the absence of NEt_3 (see above) and, indirectly, from the observations that **1** reacts with LiC≡CPh but does not afford **2a** and that the reaction of the alkynylrhodium compound [(η^5-C_5Me_5)Rh(L-prolinate)(C≡$CCMe_3$)][10f] with HC≡CPh and NEt_3 proceeds with substitution of the coordinated alkynyl ligand rendering [(η^5-C_5Me_5)Rh(L-prolinate)(C≡CPh)]. Subsequently, one second alkyne molecule could methatetically substitute the chloride anion that will be eliminated as $HNEt_3Cl$. In this way, the neutral species **i**, related to the Maitlis intermediate [(η^5-C_5Me_5)Rh($C_2Ph)_2$(NCMe)], could be formed. At this

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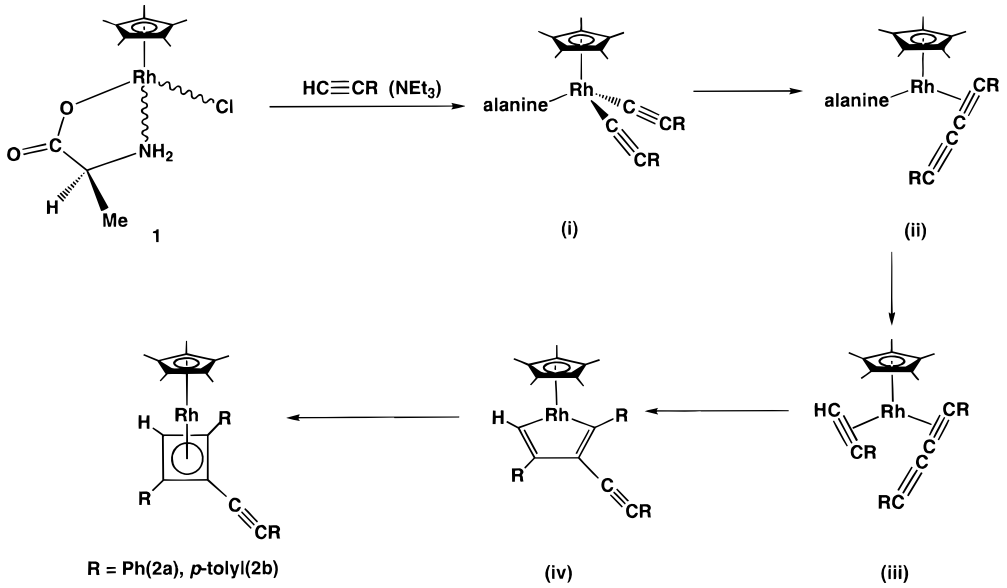
Scheme 2



point, the reductive tail-to-tail coupling of the two alkynyl ligands at rhodium could take place rendering intermediate **ii**. This reductive coupling is a key step since it has been proposed that, in the absence of the amino acid ligand, $[(\eta^5\text{-}C_5Me_5)Rh(C_2Ph)_2(NCMe)]$ inserts acetylenes into the rhodium acetylide bond in a series of stepwise *cis* insertions which ultimately yields **3** and **4**.[6,14] Linear dimerization is rare for alkynes[2] but it is interesting to point out that an essencial step in the linear dimerization of terminal alkynes by copper salts is the formation of $M(C{\equiv}CR)_2$ moieties usually facilitated by the addition of bases.[15,16] The substitution of the α-amino acid by an alkyne molecule in **ii** followed by the oxidative coupling of the two alkyne ligands in **iii** may occur to give the coordinatively unsaturated metallacyclopentadiene **iv**, in which the metal has adopted the formal oxidation state +3. The coupling would proceed to preferentially give the isomer of **iv** in which the bulkier substituents C≡CR and R are apart from the metal atom. The transformation of two coordinated acetylenes into metallacyclopentadienes has been previously reported,[2,3,5b,7,17,18] and in particular, a series of rhodacyclopentadienes have been isolated.[5b,18] Probably, coordination of the amino acid on **iv** avoids the formation of an alkyne−metallacyclopentadiene complex and precludes the formation of benzene derivatives. Finally, compound **iv** could, through a reductive elimination, give the cyclobutadiene complexes **2**, as has been previously proposed for the preparation of related η^4-cyclobutadienerhodium compounds.[3,6]

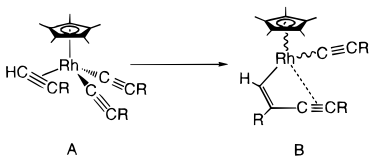
In summary, the reaction of $[(\eta^5\text{-}C_5Me_5)Rh(\text{L-alaninate})Cl]$ (**1**) with HC≡CR (R = Ph, *p*-tolyl), in basic media, affords the transition-metal trisubstituted cyclobutadiene complexes **2a** and **2b**. The process involves an unique type of alkyne trimerization that only in the case of complex **1** and the aforementioned alkynes has been observed. The iridium analogue or related pentamethylcyclopentadienyl rhodium or iridium amino acidates do not promote this type of oligomerization. Although the mechanistic route leading to these compounds has not been elucidated, a possible path with the reductive coupling key step **i** → **ii** is discussed.

Experimental Section

General Comments. Solvents were dried over appropriate drying agents, distilled under N_2, and degassed prior to use. The reactions were carried out under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. The C and H analyses were carried out with a Perkin-Elmer 240B microanalyzer. NMR data were recorded on a Varian Unity 300 spectrometer. Chemical shifts (^1H and $^{13}C\{^1H\}$ NMR spectra) are expressed in ppm upfield from $SiMe_4$. Coupling constants *J* are given in hertz. Mass spectra were measured on a VG Autospec spectrometer. The starting complex $[(\eta^5\text{-}C_5Me_5)Rh(\text{L-alaninate})Cl]$ was prepared by a published method.[10a]

Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4HPh_2C{\equiv}CPh)]$ (2a). To a solution of **1** (167.0 mg, 0.461 mmol) in 20 mL of methanol, phenylacetylene (50.6 μL, 0.461 mmol) and NEt_3 (64.5 μL, 0.461 mmol) were added. After 5 min, the color of the solution changed from orange to dark orange. The mixture was stirred for 20 h, and the orange-yellow solid which precipitated was filtered off, washed with methanol, and vacum-dried. Yield: 54 mg (22%). Anal. Calcd for $C_{34}H_{31}Rh$: C, 75.27; H, 5.75. Found: C, 74.97; H, 5.92. ^1H NMR ($CDCl_3$): δ 1.55 (s, 15H, C_5Me_5), 4.73 (d, 1H, $^2J_{RhH}$ = 1.9, η^4-

(14) A referee suggested an alternative mechanism based on alkyne insertion steps mediated by Rh intermediates. According to this suggestion, the alanine ligand could be substituted in **i** by a third alkyne molecule rendering **A**. Two alkyne insertion steps will afford **iv** from **A** through the intermediate **B**.



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(16) The transient formation of PhC≡CC≡CPh as a result of the oligomerization of two PhC≡C groups has been recently suggested by Koridze *et al.* in the formation of the dirhenium compound $[Re_2(CO)_7(C_2Ph)_4]$: Koridze, A. A.; Zdanovich, V. I.; Kizas, O. A.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1994**, *464*, 197.

(17) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(18) See, for example: 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.

Table 2. Summary of Crystallographic Data for [(η^5-C_5Me_5)-Rh(η^4-$C_4HPh_2C{\equiv}CPh$)] (2a)

formula	$C_{34}H_{31}Rh$
fw	542.52
symmetry	monoclinic, $P2_1/c$
a, Å	11.0287(8)
b, Å	16.5073(9)
c, Å	14.5030(8)
β, deg	99.507(6)
V, Å^3	2604.1(3)
Z	4
radiation	Mo Kα (λ = 0.710 73 Å)
μ, cm^{-1}	6.76
method of collcn	$\omega/2\theta$ scan
scan range, deg	$3 \le 2\theta \le 52$
no. of indep rflns	8971 (h, −13 to +13; k, −20 to +10; l, 0−17)
no. of unique rflns	5160 (R_{merg} = 0.0160)
no. of obsd rflns	4282 ($F_o \ge 4.0\sigma(F_o)$)
R	0.0265
R_w	0.0259
S, goodness of fit	1.37
data-to-param ratio	13.5/1
largest diff peak, e/Å^3	0.39

C_4H), 7.0−7.6 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.93 (s, C_5Me_5), 54.03 (d, $^1J_{RhC}$ = 11.3, $C_3CC{\equiv}CPh$), 57.33 (d, $^1J_{RhC}$ = 11.0, η^4-C_3CH), 79.11 (d, $^1J_{RhC}$ = 10.5, η^4-$C_2C_2Ph_2$), 85.92 (d, $^2J_{RhC}$ = 1.4, $C{\equiv}CPh$), 91.20 (s, $C{\equiv}CPh$), 94.00 (d, $^1J_{RhC}$ = 6.9, C_5Me_5), 123.00 (s) and 128.28 (s) (*o*-C and *m*-C of η^4-C_4Ph_2), 124.79 (s, *p*-C of η^4-C_4Ph_2), 127.45 (s, *p*-C of $C{\equiv}CPh$), 128.39 (s) and 131.12 (s) (*o*-C and *m*-C of $C{\equiv}CPh$). IR (Nujol, cm^{-1}): ν(C≡C) 2180 (w), ν(C=C) 1595 (s) cm^{-1}. MS (FAB$^+$) m/z 542 (M$^+$, 100).

Complex **2b** was similarly prepared. Yield: 22%. Anal. Calcd for $C_{37}H_{37}Rh$: C, 76.02; H, 6.37. Found: C, 75.65; H, 6.02. ^{1}H NMR ($CDCl_3$): δ 1.57 (s, 15H, C_5Me_5), 2.27 (s, 6H, η^4-C_4-*p*-C_6H_4Me), 2.38 (s, 3H, $C{\equiv}C$-*p*-C_6H_4Me), 4.65 (d, 1H, $^2J_{RhH}$ = 1.7, η^4-C_4H), 7.11, 7.05 (AB system, 8H, J_{AB} = 8.2, η^4-C_4-*p*-C_6H_4Me), 7.43, 7.18 (AB system, 4H, J_{AB} = 8.1, $C{\equiv}C$-*p*-C_6H_4Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.01 (s, C_5Me_5), 21.32 (s, η^4-C_4-*p*-C_6H_4Me), 21.53 (s, $C{\equiv}C$-*p*-C_6H_4Me), 53.77 (d, $^1J_{RhC}$ = 10.5, *C*-$C{\equiv}C$-*p*-C_6H_4Me), 56.78 (d, $^1J_{RhC}$ = 10.5, η^4-C_3CH), 79.24 (d, $^1J_{RhC}$ = 10.1, η^4-C_2C_2-(*p*-$C_6H_4Me)_2$), 85.32 (s, $C{\equiv}C$-*p*-C_6H_4Me), 91.03 (s, $C{\equiv}C$-*p*-C_6H_4Me), 93.74 (d, $^1J_{RhC}$ = 6.9, C_5Me_5), 121.88 (s) and 137.40 (s) (*ipso*-C or *p*-C of $C{\equiv}C$-*p*-C_6H_4-Me), 123.06 (s) and 128.93 (s) (*o*-C and *m*-C of η^4-C_4-*p*-C_6H_4-Me), 129.10 (s) and 130.99 (s) (*o*-C and *m*-C of $C{\equiv}C$-*p*-C_6H_4Me), 133.28 (s) and 134.20 (s) (*ipso*-C or *p*-C of η^4-C_4-*p*-C_6H_4Me)). IR (Nujol, cm^{-1}): ν(C≡C) 2185 (m), ν(C=C) 1620 (s), cm^{-1}. MS (FAB$^+$) m/z 584 (M$^+$, 100).

Crystal Structure Determination of [(η^5-C_5Me_5)Rh(η^4-$C_4HPh_2C{\equiv}CPh$)] (2a). A summary of crystal data and refinement parameters are reported in Table 2. A yellow crystalline needle of approximate dimensions 0.194 × 0.190 × 0.741 mm grown by slow diffusion of hexane into a chloroform solution of **2a** was used for the analysis. The selected crystal was glued onto the tip of a glass fiber. A set of randomly searched reflections was indexed to the corresponding crystal symmetry, and accurate unit cell dimensions were determined by least-squares refinement of 59 carefully centered reflections ($20 \le 2\theta \le 50°$). Data were collected on a Stoe AED diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) by the $\omega/2\theta$ scan method. Three orientation and intensity standards were monitored throughout data collection; no variation was observed. All data were corrected for absorption using a semiempirical method (ψ scan).[19] The structure was solved by Patterson methods (SHELXTL PLUS)[20] and conventional Fourier techniques. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms included in the last cycles of refinement in observed positions and refined riding on their carbon atoms. The structure was refined by full-matrix least squares. The function minimized was $\sum[w(F_o - F_c)^2]$ with the weight defined as $\omega^{-1} = [\sigma^2(F_o) + gF_o^2]$. Atomic scattering factors, corrected for anomalous dispersion for rhodium, were used as implemented in the refinement program.[20]

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Supporting Information Available: Refined atomic coordinates, anisotropic displacement parameters, hydrogen positional parameters, all crystallographic and experimental data, and all bond distances and angles for **2a** (Tables S1−S5) (16 pages). Ordering information is given on any current masthead page.

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