Insertion Reactions of Alkynes into the Ru−H Bond of Indenylruthenium(II) Hydride Complexes. Mechanism of the Reaction of Phenylacetylene with [RuH(η^5-C_9H_7)(dppm)] (dppm = Bis(diphenylphosphino)methane)

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The indenyl complexes [RuX(η^5-C_9H_7)(dppm)] (dppm = bis(diphenylphosphino)methane, X = H, D) react with phenylacetylene to give the products of *syn* addition [Ru{(*E*)-CH=CXPh}(η^5-C_9H_7)(dppm)] in toluene, in the temperature range 40−80 °C. The indenyl complexes [RuH(η^5-C_9H_7)LL′] (L = L′ = PMe_2Ph; L = PPh_3, L′ = PMe_2Ph; L = PPh_3, L′ = PMe_3; LL′ = dppe) and [RuH(η^5-$Me_3C_9H_4$)(CO)(PPh_3)] and the cyclopentadienyl complex [RuH(η^5-C_5H_5)(dppm)] do not react with PhC≡CH, even under more forcing conditions. The complexes [RuH(η^5-C_9H_7)LL′] (LL′ = dppe; LL′ = dppm; L = L′ = PMe_2Ph; L = PPh_3, L′ = PMe_3; L = PPh_3, L′ = PMe_2Ph) and the indenyl-substituted complexes [RuH(η^5-$Me_3C_9H_4$)(CO)(PR_3)] (PR_3 = PPh_3, P^iPr_3) react with dimethyl acetylenedicarboxylate to give the alkenyl derivatives [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)LL′] and [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-$Me_3C_9H_4$)(CO)(PR_3)], respectively, in diethyl ether under reflux. The reaction of [RuH(η^5-C_9H_7)LL′] with methyl propiolate yields the α-metalated alkenyl complexes [Ru{C(CO_2Me)=CH_2}(η^5-C_9H_7)LL′] (LL′ = dppe, dppm; L = L′ = PMe_2Ph; L = PPh_3, L′ = PMe_3) in refluxing diethyl ether. A kinetic study has been carried out for the reaction of the complexes [RuX(η^5-C_9H_7)(dppm)] with phenylacetylene in toluene, by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The reactions are first order with respect to the ruthenium complex and to the alkyne. The hydride and the deuteride complexes react at the same rate; intermediates are not detectable neither by kinetic studies nor by spectroscopy. The activation parameters, from rate measurements in the range 40−60 °C, are as follows: $\Delta H^{\ddagger} = 17 \pm 2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -21 \pm 4$ cal mol^{-1} K^{-1}. An associative mechanism is proposed for the reaction, which involves the formation of an intermediate from the ruthenium complex and the alkyne under rate-determining steady-state conditions, followed by fast hydride migration and product formation. Due to the lack of reactivity of the analogous cyclopentadienyl complex [RuH(η^5-C_5H_5)(dppm)], the reaction represents a case of *indenyl effect*. On the other hand, the indenyl and the cyclopentadienyl complexes react at comparable rates with the activated alkyne methyl propiolate.

Introduction

The insertion of acetylenes into metal−hydrogen bonds represents a key step in many processes of homogeneous catalysis.[1] In this respect, the formation of σ-vinyl complexes from alkynes and transition-metal hydrides, which are involved in the reduction of a wide variety of organic functional groups, has been studied in detail, in particular with regard to the regio- and stereochemistry of addition.[2] When terminal alkynes react with metal hydrides, the outcome of the reaction is hardly predictable, due to the polyfunctional nature of both the alkyne and the metal complex. The σ-vinyl product can react further with the alkyne to give a variety of organometallic and organic species.[3] For these reasons, the mechanistic features of the simple addition step (eq 1) to the triple bond have not been described in depth.

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(1)

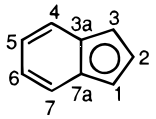
Continuing our interest in the activation of alkynes, in this work we report on the reactions of the indenyl complexes [RuH(η^5-C_9H_7)LL′] (LL′ = 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm); L = L′ = PMe_2Ph; L = PPh_3, L′ = PMe_3; L = PPh_3, L′ = PMe_2Ph) and [RuH(η^5-$Me_3C_9H_4$)(CO)(PR_3)] (PR_3 = PPh_3, P^iPr_3) with dimethyl acetylenedicarboxylate, methyl propiolate, and phenylacetylene to give the corresponding σ-vinyl derivatives. A mechanistic study is described for the reaction of [RuX(η^5-C_9H_7)(dppm)] (X = H, D) and [RuH(η^5-C_5H_5)(dppm)] with phenylacetylene and methyl propiolate. We have recently reported on the reactions of indenylruthenium complexes with propargylic alcohols, forming very stable allenylidene complexes.[4] The reactions of cyclopentadienylruthenium complexes [RuX(η^5-C_5H_5)(PPh_3)$_2$] (X = H, Me, CH_2Ph) with activated alkynes have been described.[5] In particular, the cyclopentadienyl hydride complex reacts with methyl propiolate or pentafluorophenylacetylene to yield the acetylide complex and products resulting from interaction of one, two, or three alkyne molecules. It is also known that ruthenium hydride complexes are catalysts for the dimerization of alkynes, which provides a highly attractive route to C_4 unsaturated units.[6]

There is a general interest in studying indenyl (Ind, C_9H_7) complexes which exhibit reactivity or stereochemical features different from those of the corresponding cyclopentadienyl complexes.[7] Although it is well-known that indenyl complexes may react at faster rates in ligand substitution reactions,[8] evidence of higher reactivity for other reactions is still scarce.[9] In this respect, and in the context of this work, rhodium complexes [Rh(η^5-C_9H_7)L_2] (L = ethylene, cyclooctene; L_2 = 1,5-cyclooctadiene) have been described as very efficient catalysts for the cyclotrimerization of alkynes to benzene derivatives in comparison with the isostructural cyclopentadienyl complexes.[10] A kinetic and mechanistic investigation of the alkyne insertion reaction in the iridium complex [IrH(Me)(η^5-C_9H_7)(PMe_3)] has revealed the existence of a low barrier pathway for the coordination of the alkyne to the metal center.[11]

Experimental Section

The reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. Dimethyl acetylenedicarboxylate, methyl propiolate, and phenylacetylene were used as received. The hydrides [RuH(η^5-$R_3C_9H_4$)LL′] and the deuteride [RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)] have been prepared by following the conventional method.[12]

Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer (incomplete combustion was observed for complexes **7** and **11**). NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standard. The following atom labels have been used for the ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic data:



Selected ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data for the complexes **1**−**11** are collected in Tables 1 and 2.

Synthesis of [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)LL′] (LL′ = dppe (1), dppm (2); L = L′ = PMe_2Ph (3); L = PPh_3, L′ = PMe_3 (4); L = PPh_3, L′ = PMe_2Ph (5). A mixture of [RuH(η^5-C_9H_7)LL′] (0.41 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (0.41 mmol) in diethyl ether (50 mL) was heated under reflux. After the reaction was completed, the solvent was evaporated and the solid obtained was washed with hexane (2 × 20 mL) and dried under vacuum. In order to obtain satisfactory elementary analysis, the products were purified by means of column chromatography in Florisil. The products were eluted with a mixture of diethyl ether and ethyl acetate (5/1). In the case of complex **2**, the reaction takes place at room temperature and the product precipitates in the mixture. **1, LL′ = dppe:** reaction time, 2 h; color, yellow; yield, 60%. Anal. Calcd for $RuC_{41}H_{38}O_4P_2$: C, 64.99; H, 5.02. Found: C, 64.55; H, 5.50. IR (KBr, 2 CO_2Me, cm^{-1}): 1697. ^{1}H NMR (δ, ppm): 2.27 and 2.86 (m, 2H each, $P(CH_2)_2P$), 4.90 (s, b, 2H, H-1,3), 5.24 (s, b, 1H, H-2), 7.00−7.47 (m, 24H, H-4,5,6,7, PPh_2). $^{13}C\{^1H\}$ NMR (δ, ppm): 27.50 (m, $P(CH_2)_2P$), 50.58 ($2CO_2$*Me*), 71.45 (C-1,3), 92.75 (C-2), 109.96 (C-3a,7a), 124.30 and 124.93 (C-4,7 and C-5,6), 127.28−135.67 (m, PPh_2), 162.05 (*C*O_2Me), 180.54 (*C*O_2Me). **2, LL′ = dppm:** color, yellow; yield, 70%. Anal. Calcd for $RuC_{40}H_{36}O_4P_2$: C, 64.60; H, 4.80. Found: C, 64.81; H, 4.77. IR (KBr, 2 CO_2Me, cm^{-1}): 1696, 1709. ^{1}H NMR (δ, ppm): 4.57 (dt, 1H, J_{HH} = 13.7 Hz, $^2J_{HP}$ = 10.3 Hz, PC*H*$_a$H$_b$P), 5.13 (dt, 1H, J_{HH} = 13.7 Hz, $^2J_{HP}$ = 10.3 Hz, PCH$_a$*H*$_b$P), 5.31 (t, 1H, J_{HH} = 2.5 Hz, H-2), 5.44 (d, 2H, J_{HH} = 2.5 Hz, H-1,3), 7.17−7.60 (m, 24H, H-4,5,6,7, PPh_2). $^{13}C\{^1H\}$ NMR (δ, ppm): 47.66 (t, J_{CP} = 21.2 Hz, PCH_2P), 49.75 and 49.93 ($2CO_2$*Me*), 65.05 (C-1,3), 88.33 (C-2), 109.61 (C-3a,7a), 123.89 and 123.98 (C-4,7 and C-5,6), 126.50−138.80 (m, PPh_2), 161.44 (*C*O_2Me), 179.58 (*C*O_2Me). **3, L = L′ = PMe_2Ph:** reaction time, 0.5 h;

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(12) (a) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, 37, 1747. (b) Experimental procedure for the synthesis of [RuH(η^5-$R_3C_9H_4$)LL′]: excess NaOMe (*ca.* 5:1) was added to a suspension of [RuX(η^5-$R_3C_9H_4$)LL′] (R = H, X = Cl; R = Me, X = Br) (1 mmol) in MeOH (100 mL). The mixture was stirred at room temperature or heated under reflux, depending on the complex. When the reaction was complete, the solvent was evaporated and the residue was recrystallized from diethyl ether. The deuteride complex [RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)] precipitates in the reaction mixture. The complexes obtained were yellow solids or oils. (c) The complexes have been characterized by IR, ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, and elemental analysis (see Supporting Information). The crystal structure of [RuH(η^5-C_9H_7)(PPh_3)$_2$] was determined by X-ray diffraction methods (García-Granda, S.; Borge, J. Unpublished Results). (d) A subsequent paper about the protonation of these hydride complexes and the structural characterization of neutral hydride and cationic dihydride derivatives is being prepared.

Table 1. Selected NMR Data[a] for the Alkenyl Complexes 1−7

compd	$^{31}P\{^1H\}$	^1H[r]		$^{13}C\{^1H\}$[r]	
		CO_2Me	H_β	C_α	C_β
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)(dppe)] (**1**)	90.93 s	2.91 s 3.30 s	3.95 s	184.21 t[b]	126.50
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)(dppm)] (**2**)	21.43 s	3.30 s 3.54 s	4.48 s	183.53 t[c]	125.67 t[d]
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)(PMe_2Ph)$_2$] (**3**)	21.79 s	3.64 s 4.15 s	5.88 s	188.50 t[e]	124.58 t[f]
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)(PPh_3)(PMe_3)] (**4**)	4.45 d[g] (PMe_3) 57.90 d[h]	3.44 s 3.82 s	5.00 s	189.10 vt[i]	*j*
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-C_9H_7)(PPh_3)(PMe_2Ph)] (**5**)	16.95 d[k] (PMe_2Ph) 58.54 d[l]	3.28 s 3.80 s	4.81 s	186.36 vt[m]	*j*
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-$Me_3C_9H_4$)(CO)(PPh_3)] (**6**)	51.65 s	3.32 s 3.37 s	5.87 s	182.54 d[n]	124.47 d[o]
[Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-$Me_3C_9H_4$)(CO)(P^iPr_3)] (**7**)	55.37 s	3.49 s 3.86 s	5.97 s	183.86 d[p]	124.34 d[q]

[a] δ in ppm. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Spectra recorded in C_6D_6. [b] $^2J_{CP}$ = 13.3 Hz. [c] $^2J_{CP}$ = 13.0 Hz. [d] $^3J_{CP}$ = 4.2 Hz. [e] $^2J_{CP}$ = 14.4 Hz. [f] $^3J_{CP}$ = 6.8 Hz. [g] $^2J_{PP}$ = 33.9 Hz. [h] $^2J_{PP}$ = 33.9 Hz. [i] $^2J_{CP} = {}^2J_{C'P'}$ = 14.2 Hz. [j] Signal overlapped by aromatic signals. [k] $^2J_{PP}$ = 33.3 Hz. [l] $^2J_{PP}$ = 33.3 Hz. [m] $^2J_{CP} = {}^2J_{C'P'}$ = 14.9 Hz. [n] $^2J_{CP}$ = 11.7 Hz. [o] $^3J_{CP}$ = 4.5 Hz. [p] $^2J_{CP}$ = 12.0 Hz. [q] $^3J_{CP}$ = 4.5 Hz. [r] The following atom labels are used for the ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data:

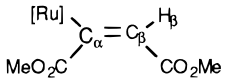
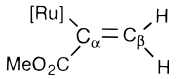


Table 2. Selected NMR Data[a] for Complexes 8−11

compd	$^{31}P\{^1H\}$	^1H[h]		$^{13}C\{^1H\}$[h]	
		CO_2Me	$=CH_2$	C_α	C_β
[Ru{C(CO_2Me)=CH_2}(η^5-C_9H_7)(dppe)] (**8**)	94.45 s	3.04 s	4.23 s, b 5.99 s, b	152.30 t[b]	*c*
[Ru{C(CO_2Me)=CH_2}(η^5-C_9H_7)(dppm)] (**9**)	21.50 s	2.93 s	4.13 s, b 5.34 s, b	152.57 m	*c*
[Ru{C(CO_2Me)=CH_2}(η^5-C_9H_7)(PMe_2Ph)$_2$] (**10**)	23.08 s	3.81 s	5.03 s 6.39 s, b	157.65 t[d]	126.13 t[e]
[Ru{C(CO_2Me)=CH_2}(η^5-C_9H_7)(PPh_3)(PMe_3)] (**11**)	5.14 d[f] (PMe_3) 57.25 d[g]	3.56 s	5.27 s, b 6.48 s, b	153.60 m	*c*

[a] δ in ppm. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad signal. Spectra recorded in C_6D_6. [b] $^2J_{CP}$ = 14.6 Hz. [c] Signal overlapped by aromatic signals. [d] $^2J_{CP}$ = 15.9 Hz. [e] $^3J_{CP}$ = 5.4 Hz. [f] $^2J_{PP}$ = 33.8 Hz. [g] $^2J_{PP}$ = 33.8 Hz. [h] The following atom labels are used for the ^1H and $^{13}C\{^1H\}$ spectroscopic data:



color, yellow; yield, 70%. Anal. Calcd for $RuC_{31}H_{36}O_4P_2$: C, 58.57; H, 5.71. Found: C, 58.87; H, 5.65. IR (KBr, 2 CO_2Me, cm^{-1}): 1700, 1742. ^1H NMR (δ, ppm): 1.49 (vt, 6H, $|^2J_{HP} + {}^4J_{HP'}| = 8.3$ Hz, PMe_a, $PMe_{a'}$), 1.67 (vt, 6H, $|^2J_{HP} + {}^4J_{HP'}| = 7.8$ Hz, PMe_b, $PMe_{b'}$), 5.10 (d, 2H, J_{HH} = 2.5 Hz, H-1,3), 5.94 (t, 1H, J_{HH} = 2.5 Hz, H-2), 7.01−7.26 (m, 14H, H-4,5,6,7, PPh). $^{13}C\{^1H\}$ NMR (δ, ppm): 17.60 (vt, $|J_{CP} + {}^3J_{CP'}| = 30.1$ Hz, PMe_a, $PMe_{a'}$), 19.70 (vt, $|J_{CP} + {}^3J_{CP'}| = 28.2$ Hz, PMe_b, $PMe_{b'}$), 49.60 and 50.08 ($2CO_2$*Me*), 72.09 (vt, $^2J_{CP} = {}^2J_{C'P'}$ = 3.5 Hz, C-1,3), 96.90 (C-2), 109.76 (C-3a,7a), 123.63 and 124.21 (C-4,7 and C-5,6), 124.44−141.34 (m, PPh), 161.51 (*C*O_2Me), 179.70 (*C*O_2Me). **4, L = PPh_3, L′ = PMe_3:** reaction time, 1 h; color, yellow; yield, 75%. Anal. Calcd for $RuC_{36}H_{38}O_4P_2$: C, 61.97; H, 5.50. Found: C, 60.98; H, 5.77. IR (KBr, 2 CO_2Me, cm^{-1}): 1699. ^1H NMR (δ, ppm): 1.10 (d, 9H, $^2J_{HP}$ = 8.9 Hz, PMe_3), 4.59, 4.86, and 5.34 (s, b, 1H each, H-1,2,3), 5.97, 6.76, and 6.90 (m, 1H each, H-4,5,6,7), 7.01−7.30 (m, 16H, H-4,5,6,7, PPh_3). $^{13}C\{^1H\}$ NMR (δ, ppm): 21.00 (d, J_{CP} = 28.1 Hz, PMe_3), 50.71 and 51.10 ($2CO_2$*Me*), 71.78 (d, $^2J_{CP}$ = 8.0 Hz) and 73.63 (d, $^2J_{CP}$ = 8.3 Hz) (C-1,3), 99.56 (C-2), 107.71 and 111.34 (C-3a,7a), 124.05, 124.11, 124.92, and 125.82 (C-4,5,6,7), 126.08−137.30 (m, PPh_3), 162.44 (*C*O_2Me), 181.25 (*C*O_2Me). **5, L = PPh_3, L′ = PMe_2Ph:** reaction time, 1 h; color, yellow; yield, 65%. Anal. Calcd for $RuC_{41}H_{40}O_4P_2$: C: 64.81; H: 5.30. Found: C, 63.62; H, 5.31. IR (KBr, 2 CO_2Me, cm^{-1}): 1684, 1705. ^1H NMR (δ, ppm): 1.44 (d, 3H, $^2J_{HP}$ = 8.9 Hz, PMe_a), 1.73 (d, 3H, $^2J_{HP}$ = 8.7 Hz, PMe_b), 4.51, 4.84, and 5.45 (s, b, 1H each, H-1,2,3), 5.70 (m, 1H, H-4,5,6 or 7), 6.30-7.30 (m, 23H, H-4,5,6,7, Ph, PPh_3). $^{13}C\{^1H\}$ NMR (δ, ppm): 17.93 (d, J_{CP} = 27.0 Hz, PMe_a), 20.50 (d, J_{CP} = 29.7 Hz, PMe_b), 49.89 and 50.54 ($2CO_2$*Me*), 72.85 (d, $^2J_{CP}$ = 7.5 Hz), and 74.47 (d, $^2J_{CP}$ = 7.5 Hz) (C-1,3), 98.68 (C-2), 111.71 (m, C-3a,7a), 122.62, 123.90, 124.70, and 126.05 (C-4,5,6,7), 127.13−143.07 (m, Ph, PPh_3), 162.26 (*C*O_2Me), 181.00 (*C*O_2Me).

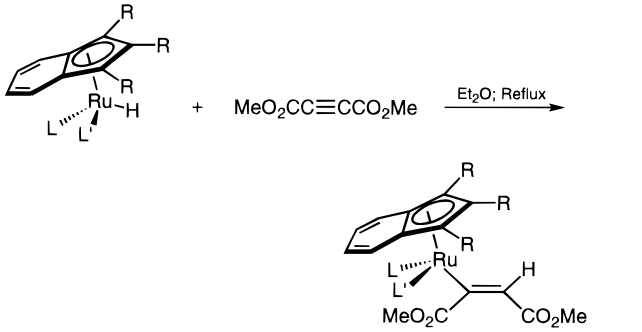
Synthesis of [Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(η^5-$Me_3C_9H_4$)(CO)(PR_3)] (PR_3 = PPh_3 (6), P^iPr_3 (7)). A mixture of [RuH(η^5-$Me_3C_9H_4$)(CO)(PR_3)] (0.5 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (2.5 mmol) in diethyl ether (75 mL) was heated under reflux. After the reaction was completed, the solvent was evaporated and the products were purified by means of column chromatography in Florisil. The products were eluted with a mixture of diethyl ether and ethyl acetate (5/1). In the case of complex **7**, toluene is used instead of diethyl ether, the reaction takes place at 65 °C, and the product obtained is an oil. **6, PR_3 = PPh_3:** reaction time, 2 h 45 min; color, yellow; yield, 50%. Anal. Calcd for $RuC_{37}H_{35}O_5P$: C, 64.25; H, 5.10. Found: C, 63.32; H, 4.77. IR (CH_2Cl_2, CO, cm^{-1}): 1924. IR (KBr, 2 CO_2Me, cm^{-1}): 1703, 1740. ^1H NMR (δ, ppm): 1.42 (d, 3H, $^4J_{PH}$ = 1.5 Hz), 1.85 (d, 3H, $^4J_{PH}$ = 1.0 Hz), and 2.13 (d, 3H, $^4J_{PH}$ = 2.5 Hz) (*Me*$_3$$C_9H_4$), 6.52−7.55 (m, 19H, H-4,5,6,7, PPh_3). $^{13}C\{^1H\}$ NMR (δ, ppm): 7.94, 9.42, and 10.77 (*Me*$_3$$C_9H_4$), 50.26 and 50.44 ($2CO_2$*Me*), 83.22 and 84.53 (d, $^2J_{CP}$ = 7.2 Hz) (C-1,3), 105.39, 110.32, and 116.27 (C-2,3a,7a), 120.84, 122.73, 124.72 and 126.72 (C-4,5,6,7), 127.71−134.51 (m, PPh_3), 161.94 (*C*O_2Me), 177.67 (*C*O_2Me), 207.46 (d, $^2J_{CP}$ = 17.1 Hz, CO). **7, PR_3 = P^iPr_3:** reaction time, 1 h 45 min; color, yellow. IR (CH_2-

Cl_2, CO, cm^{-1}): 1925. IR (KBr, 2 CO_2Me, cm^{-1}): 1697. ^1H NMR (δ, ppm): 0.75−0.93 (m, 18H, P([CH(CH_3)$_2$]$_3$), 1.83−1.94 (m, 3H, P([CH(CH$_3$)$_2$]$_3$), 1.81 (s, 3H), 2.01 (d, 3H, $^4J_{PH}$ = 1.2 Hz) and 2.04 (d, 3H, $^4J_{PH}$ = 1.2 Hz) (*Me*$_3$C$_9$H$_4$), 6.80−7.16 (m, 4H, H-4,5,6,7). $^{13}C\{^1H\}$ NMR (δ, ppm): 10.68 (Me-1,3), 11.48 (Me-2), 20.15 and 20.49 (3Me each, P([CH(*C*H$_3$)$_2$]$_3$), 28.13 (d, $^2J_{CP}$ = 20.7 Hz, P([*C*H(CH$_3$)$_2$]$_3$), 51.03 and 51.07 (2CO_2*Me*), 82.74 (d, $^2J_{CP}$ = 3.3 Hz) and 84.15 (C-1,3), 109.41, 111.78, and 114.48 (C-2,3a,7a), 122.86, 122.99, 125.14, and 125.40 (C-4,5,6,7), 162.45 (*C*O_2Me), 178.98 (*C*O_2Me), 211.14 (d, $^2J_{CP}$ = 17.4 Hz, CO).

Synthesis of [Ru{C(CO$_2$Me)=CH$_2$}(η⁵-C₉H₇)LL′] (LL′ = dppe (8), dppm (9); L = L′ = PMe$_2$Ph (10); L = PPh$_3$, L′ = PMe$_3$ (11). A mixture of [RuH(η⁵-C₉H₇)LL′] (0.41 mmol) and HC≡CCO$_2$Me (1.25 mmol) in diethyl ether (50 mL) was heated under reflux. After the reaction was completed, the solvent was evaporated and the products were purified by means of column chromatography in Florisil. The products were eluted with a mixture of diethyl ether and ethyl acetate (5/1). **8, LL′ = dppe:** reaction time, 3 h; color, brown; yield, 70%. Anal. Calcd for $RuC_{39}H_{36}O_2P_2$: C, 66.95; H, 5.15. Found: C, 66.78; H, 5.41. IR (KBr, CO_2Me, cm^{-1}): 1697. ^1H NMR (δ, ppm): 2.18 and 2.90 (m, 2H each, P(CH$_2$)$_2$P), 5.06 (d, 2H, J_{HH} = 2.4 Hz, H-1,3), 5.51 (t, 1H, J_{HH} = 2.4 Hz, H-2), 7.07−7.87 (m, 24H, H-4,5,6,7, PPh$_2$). $^{13}C\{^1H\}$ NMR (δ, ppm): 27.41 (m, P(CH$_2$)$_2$P), 50.48 (CO_2Me), 71.52 (vt, $^2J_{CP}$ = $^2J_{C'P'}$ = 1.5 Hz, C-1,3), 93.04 (C-2), 109.60 (vt, $^2J_{CP}$ = $^2J_{C'P'}$ = 1.8 Hz, C-3a,7a), 124.30 and 124.45 (C-4,7 and C-5,6), 128.00−143.31 (m, PPh$_2$), 181.20 (*C*O_2Me). **9, LL′ = dppm:** reaction time, 1 h; color, orange; yield, 80%. Anal. Calcd for $RuC_{38}H_{34}O_2P_2$: C, 66.57; H, 4.96. Found: C, 65.82; H, 4.87. IR (KBr, CO_2Me, cm^{-1}): 1691. ^1H NMR (δ, ppm): 4.56 (m, 1H, PCH_aH$_b$P), 4.80 (m, 1H, PCH$_a$*H*$_b$P), 5.34 (s, b, 1H, H-2), 5.45 (s, b, 2H, H-1,3), 7.06−7.51 (m, 24H, H-4,5,6,7, PPh$_2$). $^{13}C\{^1H\}$ NMR (δ, ppm): 48.70 (m, PCH$_2$P), 50.42 (CO_2*Me*), 68.09 (C-1,3), 89.28 (C-2), 110.10 (C-3a,7a), 123.97 and 124.72 (C-4,7 and C-5,6), 125.09−135.58 (m, PPh$_2$), 181.06 (*C*O_2Me). **10, L = L′ = PMe$_2$Ph:** reaction time, 2 h; color, yellow; yield, 80%. Anal. Calcd for $RuC_{29}H_{34}O_2P_2$: C, 60.30; H, 5.93. Found: C, 59.38; H, 5.89. IR (KBr, CO_2Me, cm^{-1}): 1681. ^1H NMR (δ, ppm): 1.62 (vt, 6H, $|^2J_{HP} + {}^4J_{HP'}|$ = 9.9 Hz, PMe$_a$, PMe$_{a'}$), 1.73 (vt, 6H, $|^2J_{HP} + {}^4J_{HP'}|$ = 8.0 Hz, PMe$_b$, PMe$_{b'}$), 5.18 (d, 2H, J_{HH} = 2.5 Hz, H-1,3), 5.91 (t, 1H, J_{HH} = 2.5 Hz, H-2), 7.05 (m, 2H, H-4,7 or H-5,6), 7.18−7.26 (m, 12H, PPh, H-4,7 or H-5,6). $^{13}C\{^1H\}$ NMR (δ, ppm): 20.42 (vt, $|J_{CP} + {}^3J_{CP'}|$ = 29.3 Hz, PMe$_a$, PMe$_{a'}$), 22.84 (vt, $|J_{CP} + {}^3J_{CP'}|$ = 28.1 Hz, PMe$_b$, PMe$_{b'}$), 51.92 (CO_2*Me*), 73.30 (vt, $^2J_{CP}$ = $^2J_{C'P'}$ = 3.7 Hz, C-1,3), 98.59 (C-2), 111.69 (C-3a, C-7a), 125.79 (C-4,5,6,7), 130.61−144.54 (m, PPh, C-4,5,6,7), 182.53 (*C*O_2Me). **11, L = PPh$_3$, L′ = PMe$_3$:** reaction time, 1.5 h; color, yellow; yield, 70%. Anal. Calcd for $RuC_{34}H_{36}O_2P_2$: C, 63.85; H, 5.63. Found: C, 62.53; H, 5.63. IR (KBr, CO_2Me, cm^{-1}): 1698. ^1H NMR (δ, ppm): 1.09 (d, 9H, $^2J_{HP}$ = 8.3 Hz, PMe$_3$), 5.10 (s, b, 2H, H-1,3), 5.77 (s, b, 1H, H-2), 6.74 (m, 1H, H-4,5,6 or 7), 7.16−7.91 (m, 18H, H-4,5,6,7, PPh$_3$). $^{13}C\{^1H\}$ NMR (δ, ppm): 20.45 (d, J_{CP} = 27.4 Hz, PMe$_3$), 50.32 (CO_2*Me*), 70.28 (d, $^2J_{CP}$ = 7.8 Hz) and 71.08 (d, $^2J_{CP}$ = 7.0 Hz) (C-1,3), 98.98 (C-2), 106.88 and 109.86 (C-3a,7a), 122.63, 123.04, 123.20 and 124.45 (C-4,5,6,7), 127.08−138.69 (m, PPh$_3$), 180.46 (*C*O_2Me).

Synthesis of [Ru{(*E*)-CH=CHPh}(η⁵-C₉H₇)(dppm)] (12). A mixture of [RuH(η⁵-C₉H₇)(dppm)] (0.41 mmol) and HC≡CPh (0.41 mmol) in toluene (30 mL) was heated at 80 °C for 3 h, the color of the solution changing from yellow to dark orange. The solvent was evaporated, and the product obtained was washed with hexane (2 × 10 mL) and dried under vacuum: reaction time, 3 h; color, orange; yield, 70%. Anal. Calcd for $RuC_{42}H_{36}P_2$: C, 71.70; H, 5.12. Found: C, 71.61; H, 5.14. ^1H NMR (δ, ppm): 3.92 (dt, 1H, J_{HH} = 13.7 Hz, $^2J_{HP}$ = 11.2 Hz, PCH_aH$_b$P), 4.53 (dt, 1H, J_{HH} = 13.7 Hz, $^2J_{HP}$ = 9.8 Hz, PCH$_a$*H*$_b$P), 5.16 (t, 1H, J_{HH} = 2.6 Hz, H-2), 5.35 (d, 2H, J_{HH} = 2.6 Hz, H-1,3), 5.38 (d, 1H, J_{HH} = 16.4 Hz, H$_\beta$), 6.35−6.91 (m, 5H, =CPh), 7.01 (m, 2H, H-4,7 or H-5,6), 7.10−7.50 (m, 22H, PPh$_2$, H-4,7 or H-5,6), 7.64 (dt, 1H, J_{HH} = 16.4 Hz, $^3J_{HP}$ = 5.0 Hz, H$_\alpha$). $^{13}C\{^1H\}$ NMR (δ, ppm): 49.29 (t, J_{CP} = 21.1 Hz, PCH$_2$P), 68.63 (vt, $^2J_{CP}$ = $^2J_{C'P'}$ = 3.3 Hz, C-1,3), 90.68 (C-2), 108.63 (t, $^2J_{CP}$ = $^2J_{C'P'}$ = 2.0 Hz, C-3a,7a), 122.98 and 124.33 (C-4,7 and C-5,6), 127.90−140.08 (m, Ph, PPh$_2$), 140.33 (t, $^3J_{CP}$ = 5.0 Hz, C$_\beta$), 151.27 (t, $^2J_{CP}$ = 15.3 Hz, Ru−C$_\alpha$).

Scheme 1. Insertion of Dimethyl Acetylenedicarboxylate in the Ru−H Bond



(1) R= H, L-L'= dppe
(2) R= H, L-L'= dppm
(3) R= H, L= L'= PMe$_2$Ph
(4) R= H, L= PPh$_3$, L'= PMe$_3$
(5) R= H, L= PPh$_3$, L'= PMe$_2$Ph
(6) R= Me, L= CO, L'= PPh$_3$
(7) R= Me, L= CO, L'= P^{i}Pr$_3$

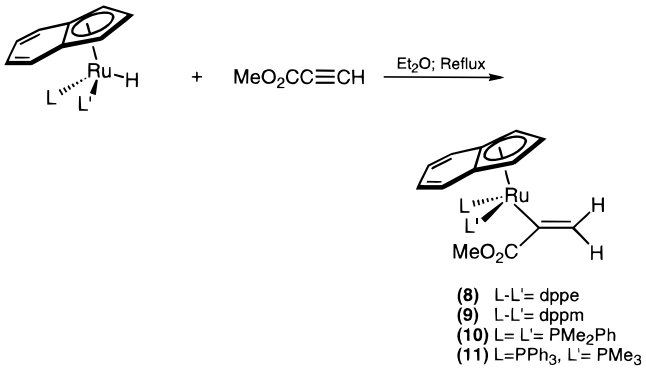
Kinetic Measurements. Toluene was distilled over potassium/benzophenone; phenylacetylene was distilled under argon. Kinetic experiments were carried out under pseudo-first-order conditions, using a large excess of the alkyne, and followed by NMR spectroscopy. The alkyne (24−60 μL) was added by syringe in a 5 mm NMR tube to solutions of the ruthenium complex (6−20 mg) in 700 μL of toluene-d_8 (^1H NMR) or 500 μL of toluene and 200 μL of toluene-d_8 (^{31}P NMR) using 1,3,5 tri-*tert*-butylbenzene (0.1−0.2 mg), triphenylphosphine, or tri-*o*-tolylphosphine (6−10 mg) as internal standard, respectively. The tube was kept in the NMR probe and thermostated at the appropriate temperature (±1 °C) throughout all the experiment. The rate of disappearance of the hydride complex was followed by integration of the Ru−H resonance or the phosphorus resonance versus the corresponding internal standards. Pseudo-first-order rate constants (k_{obs}) were obtained by exponential fitting of the ratio of the integrated resonances *vs* time, using a nonlinear least-squares regression program. Duplications of single kinetic runs were reproducible to within 12%. Measurements by ^1H NMR were in agreement with those by ^{31}P NMR. Activation parameters were obtained by linear least-squares analysis of the dependence of ln(k_2/T) on 1/T. Blank experiments on solutions of the ruthenium complex in the absence of phenylacetylene showed no significant decomposition during the time required for the kinetic runs.

Results

Reactions with Activated Alkynes. Complexes of the type [RuH(η⁵-C₉H₇)LL′] and [RuH(η⁵-Me$_3$C$_9$H$_4$)(CO)(L′)] react with an equimolar amount of dimethyl acetylenedicarboxylate in refluxing diethyl ether to give the (*E*)-alkenyl complexes **1**−**7** (50−75% yield) (Scheme 1). However, no reaction occurs for the complex [RuH(η⁵-C₉H₇)(PPh$_3$)(PMePh$_2$)].

Complexes **1**−**7** have been isolated as yellow air-stable solids. IR spectra show one or two ν(C=O) absorptions in the range 1684−1742 cm^{-1}, typical of uncoordinated CO_2Me groups.[2c] Selected NMR data are reported in Table 1. $^{31}P\{^1H\}$ NMR spectra displaying

Scheme 2. Insertion of Methyl Propiolate in the Ru−H Bond



(8) L-L'= dppe
(9) L-L'= dppm
(10) L= L'= PMe_2Ph
(11) L=PPh_3, L'= PMe_3

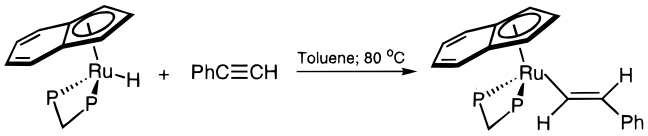
singlet resonances (complexes **1**−**3**, **6**, and **7**) and the expected AX pattern (complexes **4** and **5**) are in agreement with the proposed structures. $^{13}C\{^1H\}$ and ^1H NMR spectra show carbon and proton resonances of the alkenyl group which can be compared to those of similar (*E*)-alkenyl ruthenium(II) complexes formed in analogous insertion reactions with dimethyl acetylenedicarboxylate. In particular, the ^{13}C NMR spectrum of complex **5** shows that the coupling constant ($^3J_{CH}$) for H_β and the carbon atom of the carboxylate group in the trans position (on the C_α atom) is 13.8 Hz. Similar values are characteristic for other *E* isomers ($^3J_{CH}$ = 14−16 Hz), while significantly lower values correspond to *Z* isomers ($^3J_{CH}$ = 8.5−10 Hz).[5a,13] Characteristic resonances of these complexes are (i) a singlet in the range δ 3.95−5.97 ppm of the alkenyl proton (ii) a triplet in the range δ 183.53−189.1 ppm ($^2J_{CP}$ = 12.4−14.9 Hz) of the alkenyl C_α atom, and (iii) a singlet or triplet signal in the range δ 124.58−126.5 ppm of the C_β atom.

The terminal alkyne methyl propiolate reacts with the indenyl complexes [RuH(η^5-C_9H_7)LL′] (LL′ = dppm, dppe; L = L′ = PMe_2Ph; L = PPh_3, L′ = PMe_3) to give vinyl complexes **8**−**11** (70−80% yield) (Scheme 2). However, no insertion product is obtained when the complexes [RuH(η^5-C_9H_7)(PPh_3)(PMe_2Ph)] and [RuH(η^5-$Me_3C_9H_4$)(CO)(PR_3)] (PR_3 = PPh_3, P^iPr_3) are used.

Spectroscopic data for complexes **8**−**11** are reported in Table 2. ^1H NMR spectra show two unresolved multiplets at δ 4.13−5.27 and 5.99−6.48 ppm assigned to the unequivalent vinyl protons. The relatively small J_{HH} indicates the *cis* (geminal) arrangement consistent with an α-metalation insertion. Characteristic signals in the $^{13}C\{^1H\}$ NMR spectra (δ 152.3−157.65 ppm, t, J_{CP} = 15.5 Hz, Ru−*C* CO_2Me, and 122.73 ppm, t, J_{CP} = 1.4 Hz, =*C*H_2) are also in agreement with this alkenyl configuration. Similar vinyl groups have also been generated from insertion reactions of methyl propiolate in ruthenium(II) and osmium(II) hydride complexes.[14]

Reactions with Phenylacetylene. The reaction of an equimolar mixture of the complex [RuH(η^5-C_9H_7)(dppm)] and phenylacetylene in toluene at 80 °C leads to an orange solution from which the styryl complex [Ru{(*E*)-CH=CHPh}(η^5-C_9H_7)(dppm)] (**12**) is obtained as a yellow-orange air-stable solid (Scheme 3).

Scheme 3. Insertion of Phenylacetylene in the Ru−H Bond



(12)

$^{13}C\{^1H\}$ and ^1H NMR spectra for complex **12** show typical alkenyl resonances in the *E* configuration. Proton resonances at δ 5.38 (d) and 7.64 (dt, $^3J_{HP}$ = 5.0 Hz) ppm show a large proton coupling constant (J_{HH} = 16.4 Hz), in agreement with the mutually *trans* arrangement. The α-alkenyl proton is also coupled to the equivalent phosphorus atoms of dppm (δ 22.59 ppm). The regioselectivity of the insertion process is confirmed by the reactions of deuterated species. The ruthenium deuteride complex [RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)] reacts with PhC≡CH to give [Ru{(*E*)-CH=CDPh}(η^5-C_9H_7)(Ph_2-PCD_2PPh_2)] (^1H NMR: t, δ 7.88 ppm, $^3J_{HP}$ = 5.4 Hz, RuCH=). The reaction of [RuH(η^5-C_9H_7)(dppm)] with phenylacetylene-*d* affords the complex [Ru{(*E*)-CD=CHPh}(η^5-C_9H_7)(dppm)] (^1H NMR: s, δ 5.70 ppm, =CHPh, toluene-d_8), as indicated by the disappearance of the double triplet of RuCH= observed in **12** at 7.86 ppm (toluene-d_8).

When the reaction is carried out in the presence of excess phenylacetylene, the alkenyl complex **12** is formed as the major product, along with traces of the alkynyl complex [Ru(C≡CPh)(η^5-C_9H_7)(dppm)], as observed by FT-IR spectroscopy (2085 cm^{-1}, toluene), and traces of styrene. Consistent formation of the coupling products of phenylacetylene, as a mixture of *trans* and *cis* isomers of PhC≡CCH=CHPh, occurs during 4−5 days (50 °C) and is accompanied by decomposition of all organometallic species, as a black precipitate. The reaction is moderately catalytic, since 4 mol of enynes/mol of hydride complex is obtained. Studies to determine the reaction conditions and efficiency of the catalytic dimerization of alkynes by indenylruthenium complexes are in progress.[15] This process has been described for other ruthenium complexes as well.[6]

The effect of structural features on the insertion reaction has been exploited in a variety of complexes having different ancillary ligands. In contrast to the reactivity of the complex [RuH(η^5-C_9H_7)(dppm)], the analogous complexes [RuH(η^5-C_9H_7)LL′] (L = L′ = PMe_2-Ph; L = PPh_3, L′ = PMe_2Ph; L = PPh_3, L′ = PMe_3; LL′ = dppe), [RuH(η^5-$Me_3C_9H_4$)(CO)(PPh_3)] and the cyclopentadienyl complex [RuH(η^5-C_5H_5)(dppm)] do not react with PhC≡CH, neither under stoichiometric conditions nor with excess alkyne, after several days in toluene at 80 °C.

Kinetics. A kinetic study for the reaction between [RuH(η^5-C_9H_7)(dppm)] and phenylacetylene has been carried out using ^1H and ^{31}P NMR spectroscopy, in solutions of toluene-d_8. Phenylacetylene has been used in large excess, in the concentration range 0.26−0.72 M with respect to the ruthenium complex, 0.04−0.01 M, in order to ensure pseudo-first-order conditions. ^1H NMR allows us to detect the disappearance of the hydride signal, as a triplet of doublets at −13.5 ppm,

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(14) (a) Werner, H.; Meyer, U.; Peters, K; von Schnering, H. G. *Chem. Ber.* **1989**, 122, 2097. (b) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schulünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, 11, 2034.

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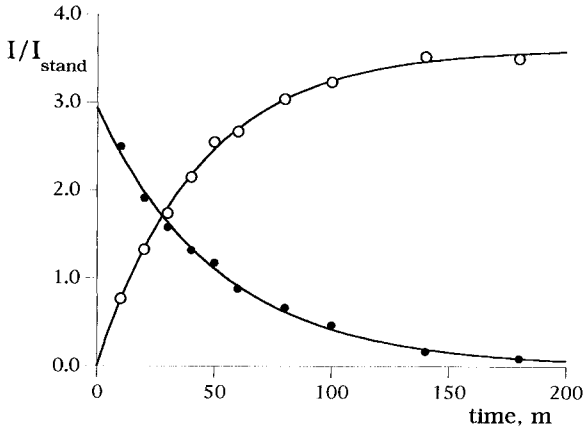

Figure 1. Plot of ^{31}P NMR integrals (I/I_{stand})) *versus* time for the disappearance of the complex [RuH(η^5-C_9H_7)(dppm)] and for the formation of the complex [Ru{(*E*)-CH=CHPh}-(η^5-C_9H_7)(dppm)], in the reaction with phenylacetylene (0.719 M, 50 °C) in toluene/toluene-d^8. [Ru] = Ru(η^5-C_9H_7)-(dppm).

Table 3. Observed Rate Constants, k_{obs}, for the Reaction of [RuH(η^5-C_9H_7)(dppm)] with Phenylacetylene in Toluene, at 50 °C[a]

T (°C)	[PhC≡CH], (M)	method[b]	k_{obs} (s^{-1})[c,d]	k_{obs} (s^{-1})[d,e]	k_1 (M^{-1} s^{-1})
50	0.265	^{31}P{^{1}H}	9.7×10^{-5}	1.2×10^{-4}	
50	0.265	^{1}H		1.3×10^{-4}	
50	0.386	^{31}P{^{1}H}	1.5×10^{-4}		
40	0.504	^{31}P{^{1}H}	9.2×10^{-5}		1.8×10^{-4}
50	0.504	^{31}P{^{1}H}	2.0×10^{-4}		4.0×10^{-4}
60	0.504	^{31}P{^{1}H}	5.3×10^{-4}		1.1×10^{-3}
50	0.719	^{31}P{^{1}H}	3.2×10^{-4}		

[a] [RuH(η^5-C_9H_7)(dppm)] = 0.01−0.04 M. [b] Internal integration standards are tris-*tert*-butylbenzene for ^{1}H NMR and P(*o*-tolyl)$_3$ for ^{31}P{^{1}H} NMR spectroscopy. [c] −d[RuH(η^5-C_9H_7)(dppm)]/d*t*. [d] All values ±12%. [e] (d[**12**]/d*t*).

and the appearance of the doublet of the vinylic product at 5.75 ppm (J_{HH} = 16.3 Hz). The presence of the starting material and that of the product are conveniently followed with time by ^{31}P NMR (δ 18.65 and 20.84 ppm, respectively). The latter method allows more precise integration of the resonances with respect to the internal standard triphenylphosphine or tri-*o*-tolylphosphine and has therefore been used in most experiments. The reactions are cleanly first order with respect to the hydride complex for 3−4 half-lives. Figure 1 shows a plot of integrals *vs* time for both the disappearance of the hydride complex [RuH(η^5-C_9H_7)-(dppm)] and the formation of the alkenyl complex **12**.

Observed rate constants, k_{obs} (s^{-1}), obtained at different concentrations of PhC≡CH and temperatures are reported in Table 3. Figure 2 shows a plot of k_{obs} vs the concentration of phenylacetylene for the disappearance of the hydride complex.

The linear dependence on [PhC≡CH] indicates that the reaction is first order in the alkyne as well, therefore second order overall, and that intermediates are not kinetically detectable (eq 2).

$$k_{obs} = k_1[\text{PhC}{\equiv}\text{CH}] \qquad (2)$$

The second-order rate constants k_1 (M^{-1} s^{-1}), are reported in Table 3. The enthalpy and the entropy of activation, calculated from the experiments in the range 40−60 °C, are $\Delta H^{\ddagger} = 17 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -21 \pm 4$ cal mol^{-1} K^{-1}, respectively. The kinetics for the reaction of the deuteride complex [RuD(η^5-C_9H_7)(PPh_2-CD_2PPh_2)] with phenylacetylene have been obtained by following the disappearance of the phosphorus peak at 18.12 ppm with time by ^{31}P NMR or the appearance of the product [Ru{(*E*)-CH=CDPh}(η^5-C_9H_7)(PPh_2CD_2-PPh_2)] by ^{1}H NMR spectroscopy. The values of the observed rate constants are reported in Table 4.

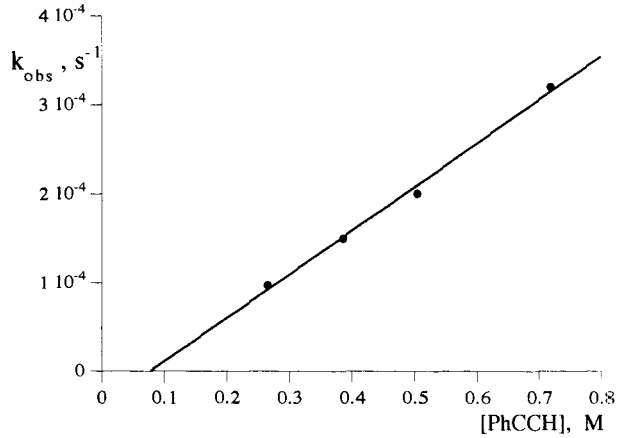

Figure 2. Plot of k_{obs} *vs* phenylacetylene concentration for the reaction of [RuH(η^5-C_9H_7)(dppm)] in toluene, at 50 °C.

Table 4. Observed Rate Constants, k_{obs}, for the Reaction of [RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)] with Phenylacetylene in Toluene, at 50 °C[a,b]

[PhC≡CH], (M)	k_{obs} (s^{-1})[c]	k_{obs} (s^{-1})[d]
0.265	1.1×10^{-4}	
0.504	2.7×10^{-4}	2.4×10^{-4}
0.503		2.2×10^{-4} [e]

[a] [RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)] = 0.020−0.025 M. [b] ^{31}P{^{1}H} NMR. [c] (−d[RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)]/d*t*). [d] d[Ru{(*E*)-CH=CDPh}(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)]/d*t*. [e] ^{1}H NMR (t, J_{HH} = 2.7 Hz, indenyl H-2).

The reactions of the indenyl and cyclopentadienyl complexes [RuH(η^5-L)(dppm)] (L = C_5H_5, C_9H_7) with methyl propiolate have been followed by ^{31}P{^{1}H} NMR, in toluene at 40 °C. The two complexes react at similar rates ([RuH(η^5-C_5H_5)(dppm)], k_{obs} = 7.8×10^{-4} s^{-1}, [HC≡CCO_2Me] = 0.48 M; [RuH(η^5-C_9H_7)(dppm)], k_{obs} = 6.8×10^{-4} s^{-1}, [HC≡CCO_2Me] = 0.24 M).

Discussion

Reactions. The reaction of the ruthenium(II) hydride complex [RuH(η^5-C_9H_7)(dppm)] with phenylacetylene proceeds smoothly in toluene to form essentially the product of insertion, [Ru{(*E*)-CH=CHPh}(η^5-C_9H_7)-(dppm)] (Scheme 3). The reactions with deuterium-labeled species, [RuD(η^5-C_9H_7)($Ph_2PCD_2PPh_2$)] or PhC≡CD, confirm that the insertion is regio- and stereoselective and proceeds in a cis fashion, as has been found in a number of reactions of phenylacetylene with the ruthenium hydride complexes.[14a,16]

The alkynes bearing electron-withdrawing substituents react readily with the indenylruthenium(II) hydride complexes to give the expected alkenyl derivatives. Thus, complexes **1**−**7** are obtained from the cis insertion of the symmetric dimethyl acetylenedicarboxylate, while the reactions with the asymmetric alkyne methyl propiolate yield the α-metalated complexes **8**−**11**. The

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stereo- and regiochemistry of these reactions can be compared with that reported for analogous ruthenium(II) and osmium(II) alkenyl complexes. The complex $[Ru\{(Z)\text{-}MeO_2CC{=}C(H)CO_2Me\}(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ is formed from the isomerization of the corresponding *E* stereoisomer.[5a] β-Metalation-type insertions have been reported in the reactions of 16e$^-$ complexes $[MHCl(CO)(PR_3)_2]$ (M = Ru, Os)[14a] and $[OsHCl(CO)_2(OCMe_2)(P^iPr_3)_2]$[14b] with HC≡CCO$_2$Me. It is worth noting the steric influence of the ancillary phosphine ligands. In contrast to the reactivity of $[RuH(\eta^5\text{-}C_9H_7)(PMe_2Ph)_2]$, which yields the vinyl complex **10**, the insertion reaction with methyl propiolate does not proceed for the complexes $[RuH(\eta^5\text{-}C_9H_7)(PMe_2Ph)(PPh_3)]$ and $[RuH(\eta^5\text{-}Me_3C_9H_4)(CO)(PR_3)]$ (PR_3 = PPh_3, P^iPr_3).

Kinetics. The relevant results of the kinetic study for the reaction of $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ with phenylacetylene are the following: first-order dependence on both hydride complex and alkyne, negative entropy of activation, absence of primary kinetic isotopic effect, intermediates not observable by either spectroscopic or kinetic means, and *indenyl effect*. This picture is indicative of an associative process, in which both the hydride complex and phenylacetylene participate in the rate-limiting step. The lack of isotopic effect suggests that the overall transformation from hydride to vinyl complex is not a single concerted process and that breaking of the Ru−H bond occurs rapidly after the rate-limiting step. An associative mechanism consistent with the experiments is represented in Scheme 4. The

Scheme 4

$$[RuH(\eta^5\text{-}C_9H_7)(dppm)] + PhC{\equiv}CH \underset{k_{-1}}{\overset{k_1\ (slow)}{\rightleftharpoons}} \{intermediate\}$$

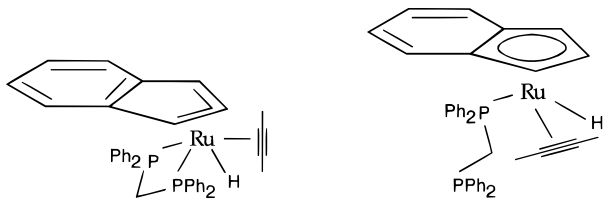
$$\{intermediate\} \xrightarrow{k_2\ (fast)} [Ru(CH{=}CHPh)(\eta^5\text{-}C_9H_7)(dppm)]$$

first step (k_1) is rate-determining and forms a transient intermediate, under steady-state conditions, which rapidly converts into the product (k_2). In such a case, the bimolecular intermediate would not be detectable. This situation is described by eq 3. The forward transformation of the intermediate is much faster than its reversal to the starting material ($k_2 \gg k_{-1}$), resulting in a linear dependence of k_{obs} on [PhC≡CH] (eq 2, Figure 2).

$$k_{obs} = \frac{k_1 k_2 [PhC{\equiv}CH]}{k_{-1} + k_2} \qquad (3)$$

The reaction with phenylacetylene is dependent upon the structure of the hydride complex, with regard to both the phosphine and the η^5 ligands. A role of the four-membered ring of dppm is indicated by the fact that exchange of dppm in $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ for either dppe or monodentate phosphine ligands inhibits the process. The small P−Ru−P "bite" angle in the dppm complex leaves larger space for an incoming molecule to attack at the metal center, with respect to more crowded complexes. Relevant as well may be a ring-opening process through Ru−P bond breaking, as an effect of ring strain, to produce a temporarily free coordination site. In fact, the tendency of dppm to act as a bridging system for bimetallic complexes rather than to act as a chelating ligand for monometallic species is well-known.[17] Monodentate dppm complexes generated from precursors in which chelating dppm is acting as a chelate ligand have been reported.[18] Exchange of the indenyl ligand for the cyclopentadienyl ring also completely inhibits the process. Therefore, this reaction represents another case of the indenyl effect, in a process different from the classical cases of ligand substitution reactions.[7,8] However, the effect vanishes in the reaction with the activated alkyne methyl propiolate. In fact, by taking into consideration the different concentrations of alkyne in the two experiments (k_{obs}/[HC≡CCO$_2$Me]), the indenyl complex appears less than twice as reactive as the cyclopentadienyl analogue. A relevant precedent for indenyl effect in reactions of alkynes has been described for the trimerization process catalyzed by indenylrhodium complexes.[10]

Chart 1



(**A**) (**B**)

Analogous experimental features, *e.g.* linear dependence on alkyne concentration, negative entropy of activation, and lack of kinetic isotopic effect, were observed by Bergman and Foo for the insertion reaction of the iridium complex $[IrH(Me)(\eta^5\text{-}C_9H_7)(PMe_3)]$ with *tert*-butylacetylene, and the data were interpreted according to the same kinetic analysis shown in Scheme 4 and eq 3.[11] Reaction rates of the iridium complex (*e.g.* second-order rate constant: 1.1×10^{-4} M^{-1} s^{-1} at 35 °C) and of the ruthenium complex of this study are also similar. Although a direct rate comparison with an analogous iridium cyclopentadienyl complex is not available, the importance of ring-slipped pathways was proposed to explain the facile insertion process. In fact, the role of the indenyl ligand in providing low-energy pathways through changes of hapticity is well-documented for the two metals of group 9, rhodium[8,10] and iridium.[19]

With regard to the structure of the intermediate indicated in Scheme 4, it is possible that the indenyl ligand is induced to ring slippage from η^5 to η^3 coordination by the incoming alkyne (Chart 1, A), to form an Ru−alkyne π-bond, as in $[RuH(\eta^2\text{-}PhC{\equiv}CH)(\eta^3\text{-}C_9H_7)(dppm)]$. An alternative pathway may arise from strain in the four-membered ring of the Ru−dppm bite. The push from the entering phenylacetylene may in fact induce ring opening and formation of the transient species $[RuH(\eta^2\text{-}PhC{\equiv}CH)(\eta^5\text{-}C_9H_7)(dppm\text{-}kP)]$, in which dppm is monodentate (Chart 1, B), more efficiently than

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in the analogous cyclopentadienyl complex [RuH(η^5-C_5H_5)(dppm)]. In this respect, it has been observed that the exchange of triphenylphosphine with alkylarylphosphines in [RuCl(η^5-ligand)(PPh_3)$_2$] (ligand = C_9H_7, C_5H_5) occurs through a dissociative mechanism not involving ring-slipped intermediates. The reaction of the indenyl complex is 1 order of magnitude faster than that of the cyclopentadienyl analogue, implying a weaker Ru−P bond in the indenyl species and easier bond rupture in the transition state of the rate-determining step.[20]

Conclusions

Different ruthenium hydride indenyl complexes react easily with activated alkynes, such as methyl propiolate and dimethyl acetylenedicarboxylate, leading to regio- and stereoselective insertion products. The reactions are strongly dependent on the ancillary ligands, since only those complexes containing the less sterically demanding systems are reactive. Moreover, the reaction with phenylacetylene has peculiar structural requirements for the metal complex. Only the indenyl complex [RuH(η^5-C_9H_7)(dppm)], coordinated by the short-bite bis(diphenylphosphino)methane ligand, undergoes insertion of PhC≡CH to form the corresponding σ-vinyl derivative, whereas the cyclopentadienyl analog [RuH(η^5-C_5H_5)(dppm)] does not react, thus representing another case of the indenyl effect. The mechanism is associative, and formation of a reactive intermediate between the hydride complex and alkyne occurs slowly and precedes fast hydride transfer from ruthenium to the triple bond.

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Supporting Information Available: Text giving spectroscopic and elemental analysis data for the neutral hydride complexes (2 pages). Ordering information is given on any current masthead page.

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