ORGANOMETALLICS

A deceptively simple case of selective hydrogenation of phenylacetylene to styrene catalyzed by a cis-hydrido(.eta.2-dihydrogen)ruthenium(II) complex

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Organometallics, **1992**, 11 (11), 3837-3844• DOI: 10.1021/om00059a056 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

$J_{H_aH_b}$ = 12.8 Hz, $J_{H_aH_N}$ = 3.4 Hz, $J_{H_bH_N}$ = 6.7 Hz), 3.16 (s, 1 H, HC≡C), 1.91 (m, 2 H, CH_2), 1.11 (t, 3 H, CH_3, J_{HH} = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 269.2 (μ_2-C=NH), 187.9, 187.8, 180.6, 178.2, 177.5, 177.3, 175.9, 175.8, 169.6, 169.2 (CO), 156.3 (μ_2-O–CO), 79.9 (CH), 69.8 (C≡CH), 62.5 ($NHCH_2$), 22.1 (CH_2CH_3), 11.4 (CH_2-CH_3). MS (FAB): *m/z* 992 (M^+), 964 (M^+ – CO), 936 (M^+ – 2CO), 922 (M^+ – CNHPr), 908 (M^+ – 3CO).

Complex **5b** was obtained under reaction conditions similar to those of **5a** in 12% using $Os_3(CO)_{11}(CNPr^i)$ as starting material. Data for $Os_3(CO)_{10}(\mu_2$-OCOC≡CH$)(\mu_2$-C=NHPr$^i)$ (**5b**) are as follows. IR (CH_2Cl_2): ν_{CO} = 2100 (w), 2067 (s), 2051 (m), 2014 (s), 1989 (m), 1972 (sh) cm^{-1} [ν_{CO_2} = 1648, 1240 cm^{-1} in KBr]. ^1H NMR ($CDCl_3$): δ 9.08 (d, br 1 H, μ_2-C=NH, J_{HH} = 7.7 Hz), 3.85 (m, 1 H, $CHMe_2$), 3.16 (s, 1 H, HC≡C), 1.49 (d, 3 H, CH_3, J_{HH} = 6.3 Hz), 1.45 (d, 3 H, CH_3, $J_{HH'}$ = 6.7 Hz).

Crystallographic Structure Determination. Crystals of both $Os_3(CO)_{10}(CNPr)(PPh_3)$ (**3a**) and $Os_3(CO)_{10}(\mu_2$-OCOC≡CH$)(\mu_2$-C=NHPr$)$ (**5a**) were grown from CH_2Cl_2/hexane solutions at –5 °C. Specimens of suitable quality were mounted in a glass capillary and used for measurement of precise cell constants and intensity data collection. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.709 30 Å) with θ–2θ scan mode. Unit cells were determined and refined using 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index, and least-squares routines. Space groups were determined from the systematic absences observed during data collection. The centrosymmetric space group was initially assumed and later confirmed by the results of refinement for **3a**. The systematic absences in the diffraction data of **5a** unambiguously established the space group as $P2_12_12_1$. An empirical absorption correction was applied to each of the data sets. The structures were solved by the heavy-atom method. All remaining non-hydrogen atoms ware located from the difference Fourier map, and they were included in the final refinement cycle and refined by full-matrix least squares. All the data processing was carried out on a Microvax 3600 using the NRCC SDP program. Crystallographic data for **3a** and **5a** are shown in Table I. Final atomic coordinates, isotropic thermal parameters, and selected bond distances and bond angles for the two complexes are listed in Tables II–V.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

OM920124N

A Deceptively Simple Case of Selective Hydrogenation of Phenylacetylene to Styrene Catalyzed by a *cis*-Hydrido(η^2-dihydrogen)ruthenium(II) Complex

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Received June 15, 1992

Depending on the substrate to metal complex ratio (2, 3, 4), the reaction of the *cis*-hydrido(η^2-dihydrogen)ruthenium(II) complex $[(PP_3)Ru(H)(H_2)]BPh_4$ (**2**) with HC≡CPh in tetrahydrofuran gives the σ-alkenyl $[(PP_3)Ru\{C(H){=}C(H)Ph\}]^+$ (detected spectroscopically), the σ-alkynyl $[(PP_3)Ru(C{\equiv}CPh)]$-BPh_4·THF (**6**), or the η^3-butenynyl *E*-$[(PP_3)Ru(\eta^3$-$PhC_3CHPh)]BPh_4$ (**3a,b**) [PP_3 = $P(CH_2CH_2PPh_2)_3$]. The latter product is isolated as a 3:1 mixture of geometric isomers displaying a different anchoring mode of the butenynyl ligand to the metal center. The *cis*-hydride(η^2-dihydrogen)ruthenium(II) complex **2** is an active catalyst precursor for the selective hydrogenation of phenylacetylene to styrene. A kinetic study carried out in 1,2-dichloroethane solution shows that the rate of the catalytic hydrogenation reaction is proportional to the initial concentration of the catalyst precursor, second order with respect to dihydrogen pressure, and independent of substrate concentration. At very low concentrations of HC≡CPh (<0.12 M), the order of the catalytic rate with respect to substrate concentration tends to 1. In light of the kinetic study and of the reactivity of **2** toward HC≡CPh, a reaction mechanism is proposed which essentially involves the usual cycle adopted by mono(hydrido)metal catalysts. In fact, unlike the related iron derivative $[(PP_3)Fe(H)(H_2)]BPh_4$ previously investigated, dihydrogen in **2** behaves as a weakly bound ligand which is readily displaced by phenylacetylene. Other ruthenium species, namely the butenynyl complexes **3a,b** and the alkynyl **6**, play a significant role in the catalysis cycle as side intermediates.

Introduction

We have previously reported the synthesis, the characterization, and some chemistry of the *cis*-hydrido(η^2-dihydrogen)ruthenium(II) complexes $[(PP_3)M(H)(H_2)]BPh_4$ [M = Fe (**1**), Ru (**2**); PP_3 = $P(CH_2CH_2PPh_2)_3$].[1–4] The reactivity studies have clearly shown that the solution chemistry of compounds **1** and **2** is dominated by the different metal–dihydrogen bond strengths, which increase

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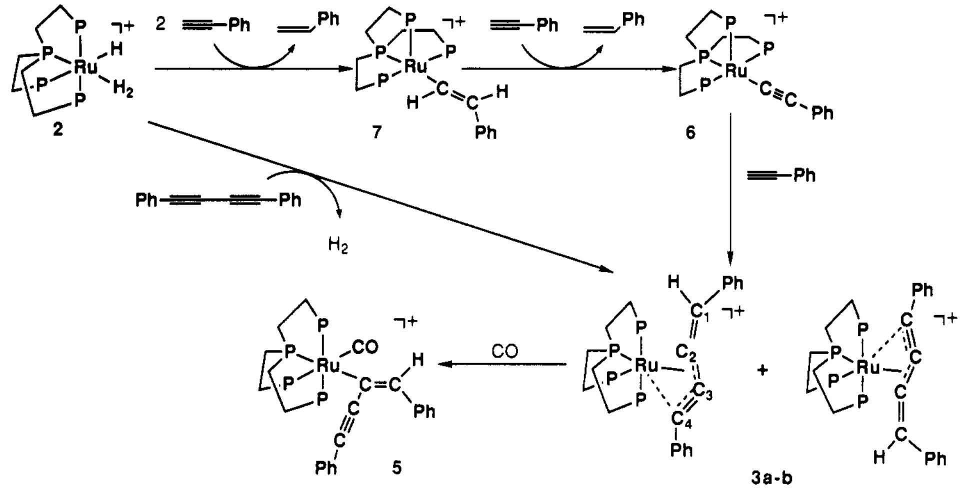
Scheme I



in the order Ru < Fe. Experimental evidence for a larger $d\pi(M)-\sigma^*(H_2)$ back-donation for Fe has recently been obtained by inelastic neutron scattering experiments, which gives a higher barrier to rotation of the dihydrogen ligand in **1**.[5]

The iron compound is the most stable η^2-H_2 complex ever reported in the literature indeed.[6] It does not decompose in refluxing tetrahydrofuran (THF) and does not undergo H/D exchange when treated with D_2 or D_2O for several hours.[1] The dihydrogen ligand is so strongly bound to the iron center that when **1** is used as a homogeneous catalyst for the hydrogenation of 1-alkynes to alkenes, a free coordination site at the metal for an incoming alkyne molecule is provided by unfastening of a phosphine arm of PP_3 rather than by H_2 decoordination.[2b] In contrast, the dihydrogen ligand in the Ru derivative **2** can be readily displaced in room-temperature solutions by a plethora of unidentate ligands, including weak ones such as N_2 or MeCN.[3]

(Trimethylsilyl)acetylene has recently been found to react with **2** yielding a σ-alkenyl complex, which can be isolated only by using a 2-fold excess of 1-alkyne as 1 equiv is hydrogenated to vinyltrimethylsilane.[4] From this result, one might readily infer that H_2 is able somehow to cleave the Ru–C(alkenyl) bond.

Intrigued by the possibility of using **2** as a catalyst for the homogeneous hydrogenation of 1-alkynes, we decided to carry out a mechanistic and kinetic study on the hydrogenation reaction of phenylacetylene. Besides adding confidence to the catalysis cycle proposed for the analogous reaction catalyzed by **1**, the results reported in this paper highlight the different roles that dihydrogen can play in hydrogenation reactions.

Results and Discussion

Reactivity of $[(PP_3)Ru(H)(H_2)]BPh_4$ with Phenylacetylene. Stirring **2** in THF under argon with 4 equiv of HC≡CPh at room temperature for 30 min produces a yellow orange solution. By addition of ethanol, canary yellow crystals analyzing as $[(PP_3)Ru(PhC_3CHPh)]BPh_4$ (**3**) precipitate in quantitative yield. GC-MS analysis reveals the presence of 2 equiv of styrene in the filtrate. The formation of 2 equiv of styrene is confirmed by ^1H NMR spectroscopy when the reaction is carried out in THF-d_8 (ferrocene as internal standard for NMR integration).

The IR spectrum (Nujol mulls) of the yellow crystals contains no band assignable to ν(Ru–H) or ν(RuC≡CPh), while multinuclear NMR spectroscopy shows the product to be a 3:1 mixture of two Ru complexes. Identical product composition is obtained by reacting **2** in THF with a stoichiometric amount of 1,4-diphenylbutadiyne, PhC≡CC≡CPh (Scheme I). In this case, however, H_2 is evolved (^1H NMR). This result is of particular relevance as it strongly suggests that the coupling of two 1-alkyne molecules at ruthenium has occurred in the reaction of **2** with phenylacetylene. In turn, the absence of Ru–H bonds is consistent with the migration of the terminal hydride of **2** to one alkynyl moiety of 1,4-diphenylbutadiyne.

The $^{31}P\{^1H\}$ NMR spectrum of **3** in acetone-d_6 consists of two temperature-invariant AM_2Q spin systems (+50/−88 °C) with parameters which are typical of octahedral complexes of PP_3.[3,7] In particular, the NMR parameters are quite comparable with those of the bis(trimethylsilyl)butenynyl complex *E*-$[(PP_3)Ru\{\eta^3-(SiMe_3)C_3CH(SiMe_3)\}]BPh_4$ (**4**), recently prepared by reaction of **2** with 4 equiv of $HC\equiv CSiMe_3$ and authenticated by an X-ray analysis.[4] The overall geometry about ruthenium in **4** is distorted octahedral with four coordination positions occupied by the donor atoms of the tetraphosphine and the remaining edge taken by the butenynyl ligand. The latter adopts an η^3 bonding mode, the weakest interaction with the metal being that with a carbon atom of the alkynyl moiety.

The presence of an η^3-butenynyl ligand in each of the two complexes constituting **3** is unambiguously demonstrated by the ^1H and $^{13}C\{^1H\}$ NMR spectra. The proton NMR spectrum in CD_2Cl_2 contains a well-resolved doublet of quartets at 6.11 ppm (1H) which is assigned to the vinyl hydrogen of the PhC_3CHPh ligand in the major compound.[4,8] Indeed, a homonuclear correlated 2D-COSY

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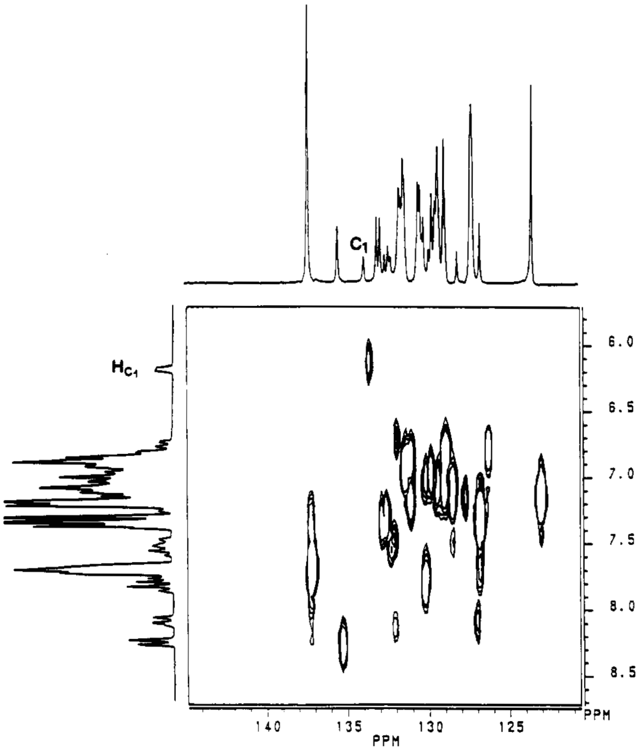


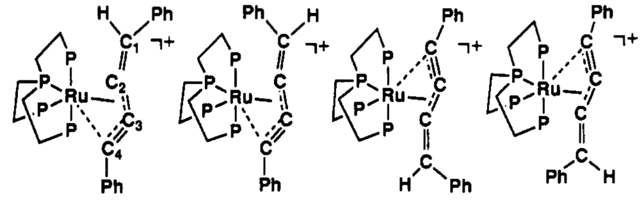
Figure 1. Partial $^{13}C/^{1}H$ 2D-HETCOR NMR spectrum of **3a,b** in acetone-d_6 at 20 °C (^{1}H, 200.13 MHz; ^{13}C, 50.32 MHz).

NMR spectrum shows that the multiplet is not coupled to any other resonance in the spectrum. In keeping with this finding, broad-band decoupling of the PP_3-phosphorus nuclei produces a featureless singlet.

No vinyl proton resonance can directly be observed for the minor isomer as it falls in the aromatic region in the spectrum. From the analysis of the $^{13}C\{^{1}H\}$, ^{13}C-DEPT, and gate decoupling-^{13}C NMR spectra, carbon resonances at δ 147.65, 114.10, and 57.79 ppm are assignable to the C_2, C_4, and C_3 carbons of the butenynyl ligand of the major compound, respectively (Scheme I). These resonances are matched by satellite signals of minor intensity at δ 148.30, 119.48, and 63.90 ppm due to the corresponding carbons of the butenynyl ligand of the other Ru isomer. The resonance of the vinyl carbon (C_1) of the major isomer appears as a narrow singlet at 133.31 ppm in the aromatic carbon region (^{13}C-DEPT NMR spectrum). This assignment is confirmed by a 2D-HETCOR NMR experiment, which provides evidence for a heteronuclear shift correlation between the vinyl proton and the singlet in the aromatic region of the $^{13}C\{^{1}H\}$ spectrum. Part of the 2D-HETCOR NMR spectrum of **3** is shown in Figure 1. Unfortunately, due to the uncertainty in localizing the vinyl hydrogen resonance of the butenynyl ligand of the minor compound, no other reliable information is obtained from the heteronuclear shift correlated experiment.

The isomeric mixture of the η^3-butenynyl complexes reacts in refluxing THF with CO (1 atm) converting quantitatively to pale yellow needles of the air-stable carbonyl E-$[(PP_3)Ru(CO)\{\eta^1\text{-}CH(Ph){=}CC{\equiv}CPh\}]BPh_4$ (**5**) (Scheme I). A strong band at 1964 cm^{-1} in the infrared spectrum of **5** diagnoses the presence of a terminal carbonyl ligand, while a medium-intensity absorption at 2149 cm^{-1} points to the presence of a free $C{\equiv}C$ group. These new IR absorptions indicate that the carbonylation reaction undergone by **3** has caused a change in the bonding mode of the butenynyl ligand (from η^3 to η^1). As a matter of fact, the $^{13}C\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2 shows a low-field doublet of doublets (δ 208.40) which is readily assigned to a terminal carbonyl ligand trans to one of the phosphorus atoms in the equatorial plane of the octahedron [$J(CP_{trans})$ = 79.8 Hz]. The maintenance of an octahedral geometry around ruthenium is further confirmed by the $^{31}P\{^{1}H\}$ NMR spectrum, which still exhibits an AM_2Q splitting pattern. Analysis of the proton NMR spectrum reveals that there is a single vinylic proton (δ 6.59) and that the two phenyl substituents are still hold in the complex. The $^{13}C\{^{1}H\}$ NMR spectrum shows four carbon resonances for the butenynyl backbone at δ 157.16, 140.59, 102.33, and 95.51 ppm. Since only the low-field absorbance at 157.16 ppm is visible in the ^{13}C-DEPT NMR spectrum, one can assign it to the vinylic carbon atom. This assignment is confirmed by a 2D-HETCOR NMR spectrum, which shows the resonance at 157.16 ppm to be correlated with that of the vinylic proton at 6.59 ppm.

In light of the spectroscopic and reactivity data, the two η^3-butenynyl complexes are geometric isomers differing from each other in either the anchoring mode or the stereochemistry of the butenynyl ligands. In principle, four isomeric structures (I–IV) may be drawn out.



I II III IV

Structure I is identical with that of the 1,4-bis(trimethylsilyl)butenynyl derivative **4** and differs from structure II only in the stereochemistry of the butenynyl ligand (*Z* vs *E*). Structures III and IV contain (*Z*)- and (*E*)-butenynyl ligands, respectively, which, however, are anchored to the $(PP_3)Ru$ moiety in a different fashion (the alkenyl carbon C_2 is trans to the bridgehead phosphorus, whereas it is trans to a terminal phosphorus in structures I and II).

Indeed, the formation of a unique carbonyl complex (**5**) is obviously consistent with a single C_1, C_2 stereochemistry within the butenynyl ligands in the starting compounds and suggests the observed isomers are either I, III or II, IV.

A perusal of the NMR parameters allows one to assign the stereochemical arrangement of the butenynyl ligands. In fact, Herberich and Barlage have correlated the value of the long-range $^{3}J(C_3H_{C_1})$ coupling in substituted σ-alkenyl complexes with the configuration of the alkenyl ligand.[9] They have found that the $^{3}J(CH)$ coupling ranges from 14 to 16 Hz for a trans arrangement of H_{C_1} and C_3 while it decreases below 10 Hz for a cis configuration. In the case at hand, long-range coupling constants of 16.3 and 17.1 Hz have been measured for the $^{3}J(C_3H_{C_1})$ coupling, which unequivocally point to a trans arrangement of H_{C_1} and C_3 in both complexes of **3**, as it occurs in sketches I and III.

A further piece of experimental evidence that definitely tips the balance in favor of the I, III couple is provided by the selective production (>92%) of (*Z*)-1,4-diphenylbut-3-en-1-yne when **2** is reacted with $HC{\equiv}CPh$ in catalytic conditions (substrate to catalyst ratio 100, THF, 60 °C, 6 h).[4] In fact, were the II, IV couple the right one, (*E*)-1,4-diphenylbut-3-en-1-yne would have been produced.

In conclusion, we have established that the two Ru butenynyl complexes have the same formula, (*E*)-$[(PP_3)Ru$-

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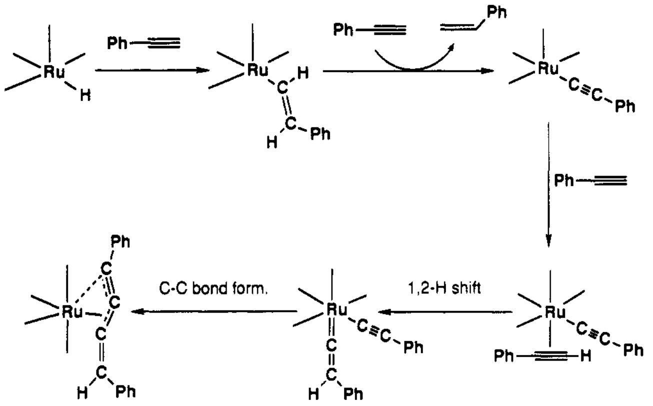
Scheme II



(η^3-PhC_3CHPh)]BPh_4, but exhibit different anchoring modes of the η^3-butenynyl ligand at the $(PP_3)Ru$ moiety. Only X-ray analyses would unambiguously correlate structures with spectroscopic data providing that no isomerization reaction takes place on going from solid state to solution. Actually, the two compounds can be separated by thin-layer chromatography (CH_2Cl_2/C_2H_5OH, 3:1 v/v, as eluent). On the other hand, since this point is not important for the purpose of the present paper, no attempt was made to grow crystals well suited for an X-ray analysis. It is very much likely that the major product has the structure of the trimethylsilyl derivative **4** because of the quite comparable spectroscopic data. However, as previously stated, this point is not of present relevance and, therefore, the two yellow η^3-butenynyl complexes will be considered as a single compound, **3a,b**, hereafter. In contrast, for a better understanding of the chemistry presented in following pages, it is worth spending a few words on the reaction mechanism leading to the formation of **3a,b**.

As recently reported for the reaction of $HC\equiv CSiMe_3$ with **2**,[4] the η^3-butenynyl complex **4** forms via a stepwise path that involves the following: (a) Cis insertion of 1-alkyne across the Ru–H bond to give a σ-alkenyl complex; (b) reaction of the σ-alkenyl compound with a second alkyne molecule to give a σ-alkynyl complex and free alkene, presumably through C–H bond cleavage, followed by the reductive elimination of alkene; (c) coupling of the σ-alkynyl ligand with a third 1-alkyne molecule to give the butenynyl ligand via C–C bond formation at ruthenium between the α-carbons of *cis*-vinylidene and alkynyl ligands (Scheme II).[10]

Monitoring the reactions between **2** and variable amounts of $HC\equiv CPh$ (2, 3, 4 equiv) by ^{31}P NMR spectroscopy shows that an identical sequence of reactions is traversed. In particular, we have been able to intercept the σ-alkynyl $[(PP_3)Ru(C\equiv CPh)]BPh_4\cdot THF$ (**6**) by reaction of **2** with 3 equiv of $HC\equiv CPh$. Complex **6** appears as cherry-red crystals which are air stable in both the solid state and solution. The presence of a σ-alkynyl ligand is shown by the IR spectrum, which exhibits a medium-intensity $\nu(C\equiv C)$ band at 2062 cm^{-1}. The $^{31}P\{^1H\}$ in acetone-d_6 shows **6** to be fluxional in solution. At room temperature the ^{31}P spectrum consists of two broad signals centered at 152.61 and 49.90 ppm with no discernible coupling connection. At -25 °C, a well-resolved AM_2Q spin system is observed. Such a pattern may be due to either square-pyramidal or octahedral geometries of the complex cation. In the latter case, it is conceivable that, at low temperature, a solvent molecule coordinates the 16-electron fragment $[(PP_3)Ru(C\equiv CPh)]^+$ to complete the coordination sphere of the metal center. A similar NMR behavior has previously been observed for the related σ-(trimethylsilyl)alkynyl $[(PP_3)Ru(C\equiv CSiMe_3)]^{+}$[4] as well as several isoelectronic Rh(III) alkynyls of the general formula $[(PP_3)Rh(C\equiv CR)]^{2+}$ (R = Ph, CO_2Et, CHO).[11]

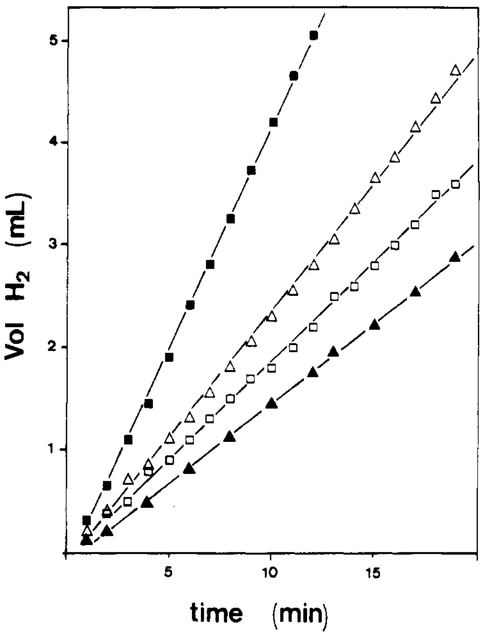


Figure 2. H_2 uptake plots for the $[(PP_3)Ru(H)(\eta^2\text{-}H_2)]BPh_4$-catalyzed hydrogenation of phenylacetylene to styrene in 1,2-dichloroethane at 60 °C: 1 atm of H_2; $[PhC\equiv CH]$ = 0.2 M; $[[(PP_3)Ru(H)(\eta^2\text{-}H_2)]BPh_4]$ = (▲) 0.43×10^{-3} M, (□) 0.63×10^{-3} M, (△) 0.82×10^{-3} M, (■) 1.07×10^{-3} M.

All our attempts to isolate the σ-alkenyl precursor to **6** by reaction of **2** in THF with 2 equiv of phenylacetylene were unsuccessful. However, monitoring the reaction in acetone-d_6 by $^{31}P\{^1H\}$ NMR spectroscopy reveals that an intermediate species, most likely the σ-alkenyl $[(PP_3)Ru\{C(H)=C(H)Ph\}]^+$, forms which then rapidly converts to the alkynyl **6** (see Experimental Section). When all phenylacetylene is consumed, NMR spectroscopy shows that ca. 50% of **2** has disappeared, while ca. 1 equiv of styrene is liberated. Like the reaction of **2** with $HC\equiv CSiMe_3$, this finding suggests that phenylacetylene reacts much faster with the σ-alkenyl intermediate than with **2**.

Hydrogenation of Phenylacetylene Catalyzed by 2. As previously mentioned, the reaction of **2** with 4 equiv of $HC\equiv CPh$ produces 2 equiv of styrene. This indicates that H_2 is able to cleave the Ru–alkenyl bond before the latter bond is cleaved by reaction with a second 1-alkyne molecule to give the σ-alkynyl complex **6** (oxidative addition/reductive elimination path). At this point, a question needs to be answered: does H_2 remain coordinated to ruthenium during the insertion of the first 1-alkyne molecule (as occurs for the iron derivative **1**), or does H_2 reenter the metal coordination sphere after being displaced by the 1-alkyne? The kinetic study reported in the following pages does answer this question and others connected with the role of **2** as catalyst precursor for the hydrogenation of phenylacetylene.

Under a hydrogen atmosphere, $HC\equiv CPh$ is selectively reduced to $PhCH=CH_2$. Neither (*Z*)-1,4-diphenylbut-3-en-1-yne nor ethylbenzene was detected under these conditions.

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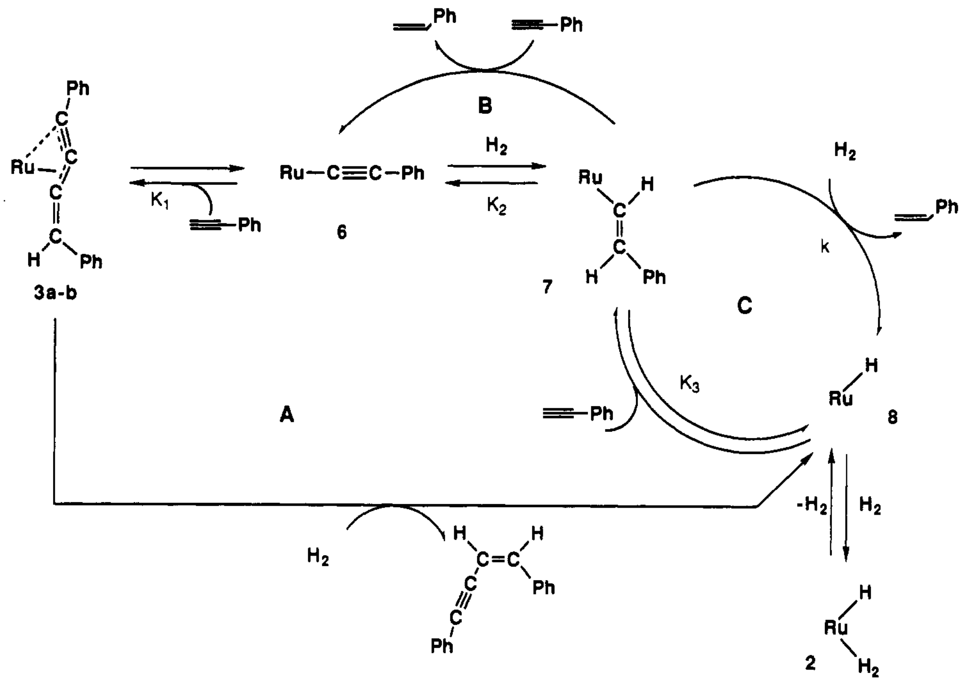
[11] Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, M. F. *Organometallics* **1990**, *9*, 360.

Scheme III



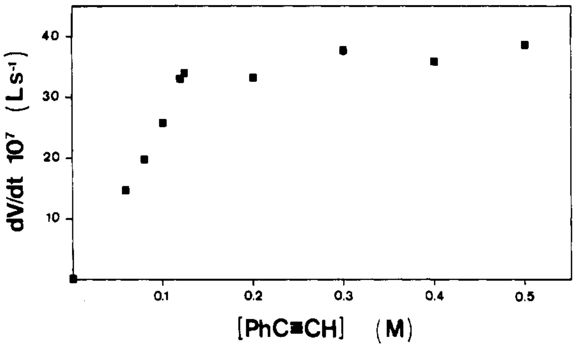


Figure 3. Plot of the variation of the reaction rate on substrate concentration for the hydrogenation of phenylacetylene to styrene catalyzed by $[(PP_3)Ru(H)(\eta^2\text{-}H_2)]BPh_4$.

The hydrogenation of HC≡CPh to PhCH=CH_2 has been studied in 1,2-dichloroethane solution where **2** is quite stable. The reactions were followed by measuring the hydrogen consumption as a function of time. Initial hydrogenation rates were obtained from gas uptake experiments, as shown in Figure 2. In order to determine the dependence of the hydrogen consumption rate on the various reaction components, hydrogenation runs were performed at different catalyst and substrate concentrations and at different hydrogen pressures (Table I). Plots of log ($-dV/dt$) vs log [**2**] and log ($-dV/dt$) vs log (P_{H_2}) yield straight lines of slope 0.94 and 1.98, respectively, showing that the hydrogenation of HC≡CPh is first order in catalyst concentration and second order in hydrogen pressure. The dependence of the initial rate of hydrogen consumption on substrate concentration (Figure 3) is more complicated. At low concentrations of HC≡CPh, the dependence seems to be first order, while at high concentrations a practically zero-order dependence is observed.

Table I. Kinetic Data for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by 2

T (K)	$[Ru/H_2]$ (10^3 M)	[PhC≡CH] (M)	$P(H_2)$ (atm)	dV/dt (10^7 L s^{-1})
333	0.63	0.20	1	33.0
	0.82	0.20	1	41.4
	1.07	0.20	1	62.3
	1.31	0.20	1	72.6
	0.43	0.20	1	26.8
	0.63	0.06	1	14.6
	0.63	0.08	1	19.8
	0.63	0.10	1	25.8
	0.63	0.12	1	33.0
	0.63	0.125	1	34.2
	0.63	0.30	0.76	22.2
	0.63	0.30	0.88	29.8
	0.63	0.30	1	37.5
	0.63	0.40	1	35.8
	0.63	0.50	1	38.7
	0.63	0.10	0.48	5.7
	0.63	0.10	0.67	11.0
	0.63	0.10	0.74	12.7
	0.63	0.10	0.84	15.4
298	1.20	0.20	1	8.2

It has previously been reported that the complexes $[RuH(\eta^2\text{-}H_2)\{P(OR)_3\}_4]BF_4$ catalyze the selective hydrogenation of terminal alkynes to alkenes with an activity which is comparable to that exhibited by **2**.[8a] For these systems, a mechanism has been proposed which involves H_2 decoordination, as a first step, followed by alkyne insertion across the Ru–H bond. A quite similar mechanism has been suggested also for the hydrogenation of HC≡CPh to PhCH=CH_2 in the presence of $OsHCl(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$.[12] In light of the chemical, spectroscopic, and kinetic data reported in this paper, a more complex mechanism may be proposed for the hydrogenation of HC≡CPh to PhCH=CH_2 catalyzed by **2**.

Scheme III illustrates a catalysis mechanism that contains, in equilibrium, the species isolated or spectroscopically detected by the stepwise reaction of **2** with HC≡CPh. According to these observations, under a hydrogen atmosphere, three catalytic cycles might coexist during the catalysis. Cycle A would lead to the formation of (*Z*)-1,4-diphenylbut-3-en-1-yne via **3a,b**, **6**, and **7**. Cycle B would give PhCH=CH_2 by reaction of **7** with HC≡CPh (several examples of reactions between alkenyl complexes and alkynes affording alkenes and alkynyl derivatives have previously been reported).[4,13] Cycle C is the one usually

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(12) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431.

adopted by the hydrogenation catalysts containing an M–H bond.[8a,12,14]

The selectivity in $PhCH{=}CH_2$ calculated by GC analysis and gas uptake experiments was invariably 100%; neither (*Z*)-1,4-diphenylbut-3-en-1-yne nor any other side product was detected. This suggests that cycle A does not work under the reaction conditions. Cycle B could be active but does not contribute significantly to the overall reaction. A significant contribution of cycle B to the overall reaction would involve a dependence of the initial hydrogen consumption rate on H_2 pressure lower than 2, which is in fact not observed. It is noteworthy that isolated **6** reacts with H_2 (1 atm) to give stoichiometric conversion to styrene and **2**. Cycle C is consistent with the data collected in Table I, but these kinetic data further suggest that species **3a,b** and **6** significantly contribute to the overall hydrogenation as side catalytic intermediates.

Since the GC analysis of the reaction products leads to a styrene formation rate practically equal to the hydrogen consumption rate, it is possible to write

$$r_{H_2} = -d[H_2]/dt = -d[HC{\equiv}CPh]/dt = d[PhCH{=}CH_2]/dt \quad (1)$$

The rate of hydrogen consumption via cycle C follows the kinetic law

$$r_{H_2} = -d[H_2]/dt = k[\mathbf{7}]P_{H_2} \quad (2)$$

where the concentration of the key intermediate **7** can be determined as follows:

$$[Ru]_{tot.} = [\mathbf{3a,b}] + [\mathbf{6}] + [\mathbf{8}] + [\mathbf{7}] \quad (3)$$

Thus, $[\mathbf{7}] = [Ru]_{tot.} - [\mathbf{3a,b}] - [\mathbf{6}] - [\mathbf{8}]$. Since $[\mathbf{6}] = [\mathbf{7}]/K_2P_{H_2}$ and $[\mathbf{8}] = [\mathbf{7}]/K_3[HC{\equiv}CPh]$, we have $[\mathbf{3a,b}] = K_1[HC{\equiv}CPh][\mathbf{6}] = K_1[HC{\equiv}CPh][\mathbf{7}]/K_2P_{H_2}$, and finally

$$[\mathbf{7}] = K_2K_3[Ru]_{tot.}[HC{\equiv}CPh]P_{H_2}/[HC{\equiv}CPh] \times (K_1K_3[HC{\equiv}CPh] + K_3 + K_2K_3P_{H_2}) + K_2P_{H_2} \quad (4)$$

Equation 4 transforms into eq 5 if we assume that $K_3[HC{\equiv}CPh] \gg K_1K_3[HC{\equiv}CPh]^2 + P_{H_2}(K_2K_3[HC{\equiv}CPh] + K_2)$.

$$[\mathbf{7}] = K_2[Ru]_{tot.}P_{H_2} \quad (5)$$

Combining eqs 5 and 2, we have eq 6, where $[Ru]_{tot.}$ is the initial concentration of the catalyst precursor.

$$r_{H_2} = -d[H_2]/dt = kK_2[Ru]_{tot.}(P_{H_2})^2 \quad (6)$$

Inspection of eq 6 shows that the rate of the catalytic reaction is proportional to the initial concentration of the catalyst precursor, second order with respect to hydrogen pressure, and independent of substrate concentration, which agrees well with the experimental data, obtained for $P_{H_2} \leq 1$ and for concentrations of $HC{\equiv}CPh$ between 0.1 and 0.5 M.

At very low concentrations of $HC{\equiv}CPh$ (<0.12 M), the contribution of [**3a,b**] to $[Ru]_{tot.}$ (eq 3) decreases and, consequently, the order of the catalytic rate with respect to substrate concentration tends to 1.

At very high $HC{\equiv}CPh$ concentrations (>0.5 M), **3a,b** is expected to be the main ruthenium species in the course of the catalysis. Indeed, it was observed that the hydrogenation activity using **3a,b** as catalyst precursor is essentially identical with the activity of the parent hydride **2**. Furthermore, **3a,b** is the only species spectroscopically detected by ^{31}P NMR in catalytic conditions.

Scheme IV

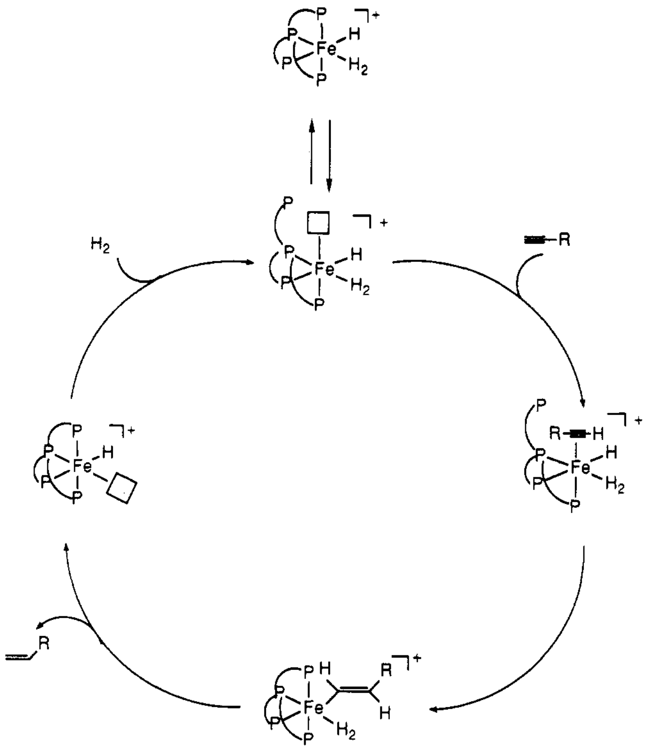

Table II. Influence of the Hydrogen Pressure on the Hydrogenation of Phenylacetylene in the Presence of 2[a]

H_2 pressure (psi)	reacn time (min)	$PhCH_2CH_3$ (%)	$PhCH{=}CH_2$ (%)	$PhC{\equiv}CH$ (%)
76	30	0.8	16.9	82.4
76	60	1.0	52.1	46.9
76	90	1.0	71.1	27.9
76	120	1.5	88.6	9.9
76	150	1.6	94.0	4.4
76	180	1.8	96.8	1.4
437	30	0.1	7.3	92.6
437	60	0.1	12.5	87.3
437	90	0.1	15.8	84.1
437	120	0.1	20.2	79.7
437	150	0.1	23.8	76.1
437	180	0.1	30.2	69.7

[a] Conditions: catalyst, 0.02 mmol; substrate, 20 mmol; tetrahydrofuran, 50 mL; $T = 313$ K; substrate/catalyst = 1000.

The contribution of the starting complex **2** to $[Ru]_{tot.}$ has been considered to be practically zero in the kinetic analysis described above, as the hydrogen ligand of this compound is fairly labile and can be quickly displaced by the substrate.[3] Thus, for the hydrogenation of $HC{\equiv}CPh$ to $PhCH{=}CH_2$ catalyzed by **2**, a free site for the incoming alkyne molecule is provided by dihydrogen decoordination rather than by unfastening of one arm of the PP_3 ligand as it has been found to occur for the iron analog **1**, where the H_2 ligand remains strongly bound to the metal center in the course of the catalysis cycle (Scheme IV).[2b]

The importance of dihydrogen decoordination in providing a vacancy at ruthenium is demonstrated by catalytic experiments carried out at different H_2 pressures. As is shown in Table II, which compares results at 76 and 437 psi, the catalytic activity of **2** is disfavored by a too high H_2 pressure. In our opinion, such a decrease in activity is simply due to the stabilization of the catalyst precursor **2**. In contrast, the hydrogenation of $HC{\equiv}CPh$ catalyzed by the iron derivative **1** is zero order in hydrogen pressure

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[13] (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1991**, *10*, 2371. (b) Echavarren, A. M.; López, J.; Santos, A.; Romero, A.; Hermoso, J. A.; Vegas, A. *Organometallics* **1991**, *10*, 2371.

[14] James, B. R. *Homogeneous Hydrogenation*; John Wiley & Sons: New York, 1973.

(a nondependence that holds in the range from 1 to 105 atm), which is in accord with the catalysis cycle shown in Scheme IV.

Conclusions

The *cis*-hydrido(η^2-dihydrogen)ruthenium(II) complex **2** is an active and selective catalyst precursor for the hydrogenation of $HC{\equiv}CPh$ to $PhCH{=}CH_2$. A kinetic study of the process in 1,2-dichloroethane as solvent suggests that the reaction mechanism essentially involves the cycle usually adopted by monohydrido hydrogenation catalysts, although other Ru species more complex than the usual intermediates significantly contribute to the overall hydrogenation reaction as side catalytic intermediates. The study of the reactivity of **2** toward $HC{\equiv}CPh$ proves these species to be the butenynyl complexes **3a,b** and the σ-alkynyl **6**.

The results herein presented confirm that dihydrogen can play several roles in hydrogenation reactions of unsaturated substrates. As a ligand, H_2 can either easily provide a free coordination site at the metal for the incoming unsaturated substrate (weakly bound H_2)[11,12,15,16] or favor the decoordination of another ligand (strongly bound H_2).[2b] As a reagent, H_2 can hydrogenate the substrate either via an intramolecular acid/base reaction[2b] or via an oxidative addition/reductive elimination path.[11,12,16]

Experimental Section

General Data. Tetrahydrofuran, dichloromethane, 1,2-dichloroethane, and *n*-hexane were purified by distillation over $LiAlH_4$, P_2O_5, and Na, respectively, just prior to use. Phenylacetylene (Aldrich) was distilled prior to use. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. All reactions and manipulations were routinely performed under a dry argon or nitrogen atmosphere by using Schlenk tube techniques. The solid complexes were collected on sintered-glass frits and washed with ethanol and petroleum ether (bp 40–70 °C) before being dried in a stream of nitrogen. Literature methods were used for the preparation of $[(PP_3)Ru(H)(H_2)]BPh_4$ (**2**).[3]

Deuterated solvents for NMR measurements (Janssen) were dried over molecular sieves. Proton NMR spectra were recorded on Varian VXR 300 and Bruker AC 200P instruments operating at 299.94 and 200.13 MHz, respectively. Peak positions are relative to tetramethylsilane as an external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at 121.42 and 81.01 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. $^{13}C\{^1H\}$ NMR spectra were run on the Bruker instrument operating at 50.13 MHz. Peak positions are relative to tetramethylsilane and were calibrated against solvent resonance. The 2D-HETCOR NMR experiments were recorded on the Bruker spectrometer using Bruker's XHCORR pulse program. The 90° ^{13}C pulse was for 5.5 μs, the 90° ^1H pulse from the decoupler was for 8.8 μs, and the acquisition time was 0.5–0.20 s. The number of incremental spectra was determined according to the concentration of the sample and spectral width used for collection of the FIDs. Zero-filling and a 2D Fourier transformation resulted in a spectrum with resolution of ca. 7 and 15 Hz in the proton and carbon dimensions, respectively. Spectra with adequate signal-to-noise ratios were obtained in ca. 12 h. The 2D-COSY NMR experiments were performed with either Varian's and Bruker's pulse sequences on the two instruments. A delay period of 1 s was used between acquisitions. A 2D Fourier transformation gave 2D spectra with adequate signal-to-noise ratios after 4–8 h of data collection, depending on sample concentration and spectral width. Proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. The infrared spectra were recorded on a Perkin-Elmer Series 1600 FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 1×10^{-3} M in nitroethane solutions at room temperature (22 °C).

Synthesis of the Complexes. Preparation of *E*-$[(PP_3)Ru(\eta^3\text{-}PhC_3CHPh)]BPh_4$ (3a,b). Method A. Neat phenylacetylene (0.50 mL, 4.50 mmol) was pipeted into a THF solution (30 mL) of **2** (1.09 g, 1.00 mmol). Stirring the solution for 1 h at room temperature produced a light yellow solution. By addition of ethanol (30 mL) and slow evaporation of the solvent under a stream of nitrogen, canary yellow needles of the butenynyl complexes **3a,b** precipitated, yield 94%. GC analysis of the solution showed total consumption of the alkyne reagent and formation of 2 equiv of styrene as the only organic product.

Method B. The same product was obtained in quantitative yield by reacting **2** (1.09 g, 1.00 mmol) with 1 equiv of 1,4-diphenylbutadiyne (0.21 g, 1.04 mmol) under identical conditions. IR: phenyl-reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{82}H_{73}BP_4Ru$: C, 76.10; H, 5.69; Ru, 7.81. Found: C, 75.92; H, 5.80; Ru, 7.72. NMR analysis of the reaction mixture and of the isolated product invariably shows the presence of two Ru complexes in a ratio ranging from 2.5 to 3.0 regardless of the reaction conditions (large excesses of phenylacetylene, reflux temperature, long reaction times) and the synthesis method as well. Data for the major isomer, **3a**, are as follows: $^{31}P\{^1H\}$ NMR (20 °C, 121.42 MHz, acetone-d_6, H_3PO_4 85% reference): AM_2Q system, $\delta(P_A)$ 153.48, $\delta(P_M)$ 47.88, $\delta(P_Q)$ 74.11; $J(P_AP_M)$ 6.8 Hz, $J(P_AP_Q)$ 9.4 Hz, $J(P_MP_Q)$ 21.2 Hz. ^1H NMR (20 °C, 299.945 MHz, CD_2Cl_2, Me_4Si reference): 6.11 [dq, 1H, J(HP) 3.2 Hz, J(HP) 1.2 Hz, $C{=}C(H)$]. $^{13}C\{^1H\}$ NMR (20 °C, 50.13 MHz, CD_2Cl_2, Me_4Si reference): 147.65 (dtd, $C{=}C(H)Ph$, J(CP) 40.3 Hz, J(CP) 8.7 Hz, J(CP) 3.4 Hz), 133.31 (s, $C{=}C(H)$, assigned by 2D-HETCOR NMR experiment), 114.10 (dq, $PhC{\equiv}C$, J(CP) 28.1 Hz, J(CP) 1.5 Hz), 57.79 (s, $PhC{\equiv}C$, ^3J(CH) 16.3 Hz assigned by gate decoupling ^{13}C NMR experiment). Data for the minor isomer, **3b**, are as follows. $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, H_3PO_4 85% reference): AM_2Q system, $\delta(P_A)$ 150.90, $\delta(P_M)$ 47.02, $\delta(P_Q)$ 79.48; $J(P_AP_M)$ 6.0 Hz, $J(P_AP_Q)$ 5.9 Hz, $J(P_MP_Q)$ 22.1 Hz. ^1H NMR (20 °C, 299.945 MHz, CD_2Cl_2, Me_4Si reference): The vinyl proton resonance was not observed. $^{13}C\{^1H\}$ NMR (50.13 MHz, CD_2Cl_2, Me_4Si reference): 148.30 (dtd, $C{=}C(H)Ph$, partially superimposed on the corresponding carbon resonance of **3a**), 119.48 (dq, $PhC{\equiv}C$, J(CP) 32.5 Hz, J(CP) 3.1 Hz), 63.90 (s, $PhC{\equiv}C$). The resonance due to the vinylic carbon atom of the butenynyl ligand in **3b** could not be assigned as it is obscured by the resonances of the aromatic carbon atoms.

Reaction of 3a,b with Carbon Monoxide. Carbon monoxide was bubbled through a refluxing THF solution (20 mL) of **3a,b** (0.40 g, 0.31 mmol) for 30 min. The solution was then cooled to room temperature, and ethanol (20 mL) was added. Concentration of the resulting pale yellow solution under a brisk current of nitrogen yielded pale yellow crystals of $[(PP_3)Ru(CO)\{\eta^1\text{-}PhC_3CHPh\}]BPh_4$ (**5**), yield 85%. IR: $\nu(C{\equiv}C)$ 2149 cm^{-1} (mw); $\nu(C{=}O)$ 1964 cm^{-1} (s); phenyl reinforced vibration 1579 cm^{-1}. Anal. Calcd for $C_{83}H_{73}BOP_4Ru$: C, 75.39; H, 5.57; Ru, 7.59. Found: C, 75.18; H, 6.02; Ru, 7.46. $^{31}P\{^1H\}$ NMR (20 °C, 81.01 MHz, CD_2Cl_2, H_3PO_4 85% reference): AM_2Q system, $\delta(P_A)$ 139.46, $\delta(P_M)$ 53.51, $\delta(P_Q)$ 56.67 ppm; $J(P_AP_M)$ 12.7 Hz, $J(P_AP_Q)$ 5.6 Hz, $J(P_MP_Q)$ 14.1 Hz. ^1H NMR (20 °C, 200.13 MHz, CD_2Cl_2, Me_4Si reference): 6.59 ppm [dt, 1H, J(HP) 6.4 Hz, J(HP) 2.1 Hz, $C{=}C(H)Ph$]. $^{13}C\{^1H\}$ NMR (20 °C, 50.13 MHz, CD_2Cl_2, Me_4Si reference): 208.40 ppm (dd, $RuCO$, J(CP) 79.8 Hz, J(CP) 9.8 Hz), 157.16 ppm (t, $C{=}C(H)Ph$, J(CP) 4.4 Hz, assigned by DEPT and 2D-HETCOR NMR experiments), 140.59 ppm (t, $C{=}C(H)Ph$, J(CP) 2.0 Hz), 102.33 ppm (s, $PhC{\equiv}C$, J(CP) 3.0 Hz), 95.51 ppm (d, $PhC{\equiv}C$, J(CP) 3 Hz).

Preparation of $[(PP_3)Ru(C{\equiv}CPh)]BPh_4{\cdot}THF$ (6). A 100-mL flask equipped with a magnetic bar was charged with a solution of **2** (0.90 g, 0.80 mmol) in THF (30 mL) and $HC{\equiv}CPh$

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[15] Present work.

[16] (a) Lundquist, E. G.; Huffmann, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. (b) Johnson, T.; Huffmann, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073. (c) Marinelli, G.; Rachidi, I. El-I.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346. (d) Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffmann, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855.

(0.27 mL, 2.41 mmol). The mixture was stirred at 0 °C for 30 min during which time the pale yellow solution became deep red. GC analysis of the solution showed the disappearance of the alkyne and the formation of 2 equiv of styrene. Addition of ethanol and concentration of the solvent afforded cherry-red microcrystals of **6**, yield 65%. IR: ν(C≡C) 2062 cm^{-1} (m); phenyl reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{78}H_{75}BOP_4Ru$: C, 74.11; H, 5.98; Ru, 7.99. Found: C, 74.09; H, 5.80; Ru, 7.86. $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, −60 °C, H_3PO_4 85% reference): AM_2Q system, $\delta(P_A)$ 153.74, $\delta(P_M)$ 50.24, $\delta(P_Q)$ 47.38; $J(P_AP_M)$ 5.2 Hz, $J(P_AP_Q)$ 3.1 Hz, $J(P_MP_Q)$ 21.7 Hz.

Attempted Synthesis of [(PP$_3$)Ru{C(H)=C(H)Ph}]$^+$ (7). When the above reaction was performed by reacting **2** with 2.5 equiv of phenylacetylene, a ca. 1:1 mixture of the starting complex **2** and of the alkynyl complex **6** was obtained. However, variable-temperature ^{31}P NMR analysis of the reaction mixture in acetone-d_6 provides evidence for the formation of an intermediate species **7** which initially forms at the expense of **2** and then rapidly converts to **6**. $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, −60 °C, H_3PO_4 85% reference): AM_2Q system, $\delta(P_A)$ 152.46, $\delta(P_M)$ 46.39, $\delta(P_Q)$ 51.82; $J(P_AP_M)$ 2.8 Hz, $J(P_AP_Q)$ 2.8 Hz, $J(P_MP_Q)$ 21.9 Hz.

Reaction of 6 with HC≡CPh. Neat phenylacetylene (28 μL, 0.25 mmol) was syringed at room temperature into a THF solution (25 mL) of **6** (0.25 g, 0.21 mmol). The solution was stirred under nitrogen for 15 min, during which time the starting red color turns light yellow. $^{31}P\{^1H\}$ NMR analysis of the reaction mixture shows the quantitative formation of **3a,b**.

Reaction of 6 with H$_2$. A THF solution (25 mL) of **6** (0.25 g, 0.21 mmol) under hydrogen (1 atm) was heated at 60 °C for 30 min, during which time the color changed gradually from red to yellow. By addition of ethanol (30 mL) and partial evaporation of the solvent under a stream of nitrogen, yellow crystals of **2** precipitated in 90% yield. GC analysis of the reaction mixture showed the formation of 1 equiv of styrene.

Catalytic Hydrogenation Reactions. Low-Pressure Experiments. The catalytic reactions were followed by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). Analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8500 gas chromatograph with an FFAP on Chromosorb GHP 80/100 mesh (3.6 × $^1/_8$ in.) column at 160 °C.

The catalyst precursors **2** and **3a,b** were carried with a degassed solution of the substrate in 1,2-dichloroethane (8 mL) into a Schlenk manifold. The flask was closed by a silicone septum. The system was evacuated and refilled with hydrogen six times, and the flask was then immersed in a constant-temperature bath. The mixture was vigorously shaken during the run. Plots of the kinetic data were fitted by use of conventional linear regression programs.

High-Pressure Experiments. Air was evacuated from the autoclave; then, the solution containing the catalyst, the substrate, and the solvent, prepared in a Schlenk tube, was introduced by suction. Hydrogen was added up to the desired pressure, and the solution in the autoclave was stirred at the selected temperature. At the end of the reaction, the autoclave was cooled, the gas was vented out, and the solution was collected. The conversion was determined from the crude product by GC analysis with a 2-m packed column containing a fatty acid phase (5%) on Chromosorb G AW-DMCS.

Acknowledgment. Thanks are expressed to the "Progetto Finalizzato Chimica Fine II", CNR, Rome, to the MURST, Rome, and to the DGICYT (Project PB-89-0055, Programa de Promociôn General de Conocimiento) for financial support.

OM920350X

Synthesis and Structure of (Phosphaalkenyl)mercury Compounds

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Received May 8, 1992

The (phosphaalkenyl)mercury compounds (*E*)-Mes*P=CHHgCl [(*E*)-**4**], (*Z*)-Mes*P=CHHgCl [(*Z*)-**4**], (*E*,*E*)-(Mes*P=CH)$_2$Hg [(*E*,*E*)-**5**], and (*Z*,*Z*)-(Mes*P=CH)$_2$Hg [(*Z*,*Z*)-**5**] (Mes* = 2,4,6-tri-*tert*-butylphenyl) were prepared from (*E*/*Z*)-Mes*P=CHLi [(*E*/*Z*)-**3**] or (*Z*)-Mes*P=CHLi [(*Z*)-**3**], respectively, and $HgCl_2$. The *Z* isomers (*Z*)-**4** and (*Z*,*Z*)-**5** were more stable than the corresponding *E* isomers: (*E*,*E*)-**5** decomposed and (*E*)-**4** and (*E*,*E*)-**5** rearranged to the corresponding *Z* isomers. The X-ray crystal structure determination of (*Z*,*Z*)-**5** was carried out; crystals are monoclinic, space group $P2_1/c$ with unit-cell dimensions a = 13.8800 (7), b = 14.4938 (6), c = 19.8504 (5) Å, and β = 104.494 (3)°, final R = 0.0497, and R_w = 0.0313 for 2671 reflections with $I > 2.5\sigma(I)$ and 375 parameters. The results show a double *Z* configuration with the mercury atom sandwiched between the two phenyl rings; the phenyl rings are slightly bent toward the mercury atom, indicating a stabilizing interaction between these groups. When (*Z*,*Z*)-**5** was reacted with *n*-butyllithium, only lithium–mercury exchange was observed.

Introduction

Phosphaalkenes RP=CXY containing a phosphorus–carbon double bond—and therefore not so long ago believed to be uncapable of existence[1]—have in recent years become increasingly known to be stable compounds if properly substituted.[2] Still, several goals wait to be accomplished: one concerns the stereochemistry around the P=C bond, i.e., a convenient way to determine the *E*/*Z*

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