New Ruthenium Complexes in the Catalytic Hydrogenation of Alkynes. Study of Structure and Mechanism

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Received June 11, 1996[⊗]

The reaction of [(η^5-$Ph_4C_4COHOCC_4Ph_4$-η^5)(μ-H)[$(CO)_4Ru_2$] (**1**) with several alkynes was studied. Two new types of Ru complexes, [(η^5-Ph_4C_4CO)$(CO)_2$RuC(Ph)=CPh] (**6**) and [(η^5-Ph_4C_4COH)$(CO)_2$ $RuC(CO_2Me)$=$CHCO_2Me$] (**7**), were isolated and structurally characterized by single-crystal X-ray crystallography. These complexes were found to be implicated in the hydrogenation of alkynes with **1** as a catalyst precursor. While complex **7** was found to function as a catalyst in the hydrogenation cycle, complex **6** acts as a catalysis poison by virtue of its stability and irreversible formation. A catalytic cycle has been proposed.

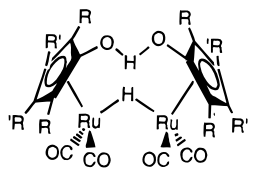
Introduction

Mechanisms of organometallic reactions, and those related to catalytic reactions in particular, pose an ongoing scientific challenge to organometallic chemists. Kinetic studies, spectral detection of reaction intermediates, and isolation and charaterization of reaction intermediates are the methods of choice in tackling such mechanism problems.

In the present study we have investigated a mechanistic problem related to the hydrogenation of alkynes with complex **1** as a precatalyst. Our ultimate goal was to unravel, on the basis of experimental results, the catalytic cycle that governs the above process. Two principle problems had to be addressed: (a) What is the molecular structure of a complex which was formed (isolated) in the hydrogenation reaction of alkynes with **1**, and what role does it play in the catalytic hydrogenation cycle, in particular in view of its total catalytic inertness (vide infra)? (b) How does an alkyne substrate interact with a metal complex, in particular since the known chemistry of **1** (vide infra) does not provide a complex with an empty coordination site?

Results and Discussion

We have previously reported that complex **1** is a precatalyst for a variety of reactions,[1] such as hydrogenation of various carbonyl groups, alkenes, and alkynes[2] at moderate hydrogen pressures and various water-gas-shift type reductions (CO + H_2O),[3] as well as extremely efficient reduction of carbonyl groups by H transfer from formic acid.[4] While, with alkenes and ketones, hydrogenation turnover numbers in the range of ca. 2000 were recorded, alkynes performed poorly with only few hundred turnovers.[5]



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We have found now that TLC of the hydrogenation reaction mixture of diphenylacetylene revealed the presence of **1** and a new spot of a nonpolar complex, not detected in the hydrogenation reaction mixture of alkenes or ketones.

It was inferred that alkynes gradually poison the catalytic hydrogenation process of alkynes by reacting irreversibly with either **1** or other catalytic species to generate a stable nonreactive complex. This hypothesis has now been tested by reacting **1** with diphenylacetylene (molar ratio 1:6.5, respectively) in refluxing toluene till all of **1** had disappeared (10 h). Chromatographic purification gave a yellow solid having a TLC spot identical with that of the hydrogenation reaction mixture of diphenylacetylene. The following chemical observations have been made on the above yellow compound:[6] (a) It was found to be unreactive in hydrogenation of alkynes. (b) It was recovered unchanged when heated under CO pressure (34 atm). (c) It was not affected by dihydrogen (15 atm).

The above results attest to the chemical stability of the said yellow compound, thus identifying the chemical species the formation of which is responsible for quenching the catalytic hydrogenation of alkynes when complex **1** is the loaded catalyst.

Elemental analysis of the yellow compound points out to a molecular formula of (Ph_4C_4CO)$(CO)_2$(diphenylacetylene)Ru (**2**). Its spectral properties are listed in Tables 1 and 2. The two infrared CO stretching bands (Table 1) are indicative of two coordinated CO groups. The rather low infrared C=O stretching frequency (below 1600 cm^{-1}) indicates a cyclopentadienol struc-

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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(2) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics*. **1984**, *4*, 1459.

(3) Shvo, Y.; Czarkie, D. *J. Organomet. Chem*. **1986**, *315*, C25; **1989**, *368*, 357.

(4) Menashe, N.; Salant, E.; Shvo, Y. *J. Organomet. Chem*. **1996**, *514*, 97.

(5) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400.

(6) Blum, Y. Ph.D. Thesis.

S0276-7333(96)00469-4 CCC: $14.00

Table 1. Infrared Spectral Data

no.	R	R′	alkyne	solvent	ν(CO), cm^{-1}	ν(C═O), cm^{-1}
2	Ph	Ph	PhC≡CPh	CH_2Cl_2	2019, 1964	1595
3	Ph	Ph	PhC≡CH	CH_2Cl_2	2020, 1972	1600
4	Ph	*p*-Cl-C_6H_4	PhC≡CPh	KBr	2025, 1970	1575
5	Ph	*p*-Cl-C_6H_4	PhC≡CH	KBr	2025, 1970	1585
6	Ph	Ph	C_2(4-Cl-Ph)$_2$	CH_2Cl_2	2020, 1967	1600
7[a]	Ph	Ph	$C_2(CO_2Me)_2$	CH_2Cl_2	2034, 1983	1579

[a] Additional bands were recorded at ν = 1709 (ester) and 1657 (C═C) cm^{-1}.

Table 2. NMR Spectral Data

		^{13}C-NMR					
no.	^{1}H-NMR	CO	C1	C2 + C5	C3 + C4	phenyls	**C**═C
2[a]	7.59 (m, 4H); 7.35−6.78 m	201.5	170.6	89.8	106.0	132.5−124.6	149.2 143.8
3[b]	7.40−6.98 m; 5.81 (s,1H)	199.4	177.6	87.8	105.9	133.5−123.0	151.5 141.3
4[b]	7.55 (m, 4H); 7.32−6.76 m	200.5	170.7	90.1	104.5	134.2−124.7	148.9 143.6
5[a]	7.43 (m, 4H); 7.35 (d,7Hz,2H); 5.84 (s,1H)	199.9	179.1	96.3	106.2	134.2−124.2	154.4 138.5
6[c]	7.55−6.64 (m)	200.6	168.9	89.9	105.9	132.4−126.0	147.4 142.8
7[c,d]	9.03 (b, 1H); 7.0−7.3 m, 6.16 (s, 1H); 3.62 (s, 3H); 3.20 (s,3H)	199.2	179.6	89.0	104.3	132.2−127.8	136.6

[a] Measured in benzene-d_6. [b] Measured in methylene chloride. [c] Measured in $CDCl_3$; ^{13}C-NMR showed additional signals for COOMe at 164.5, 162.8 and 52.0, 51.3 ppm.

ture, i.e. η^5-coordination of the ring. A cyclopentadienone structure (η^4-coordination) exhibits a C═O stretching frequency at about 1650 cm^{-1}. However, the C═O ^{13}C-NMR resonance signal (Table 2) of **2** (170.6 ppm) is closer to that of η^4 (173.7 ppm) than to η^5-ring coordination (154.3 ppm).

Significantly, the ^{13}C-NMR signals of the acetylene sp carbon atoms are chemically shifted (Table 2). Thus the alkyne must be nonsymmetrically bound to the Ru atom. The rather low chemical shift values of these signals (149.2, 143.8 ppm) rule out π-coordination and support σ-bonding of the alkyne C atoms; i.e. the alkyne C atoms must have a substantial sp^2 character.

Complex **2** failed to yield X-ray-quality crystals. In the quest for such crystals, a series of complexes, isostructural with **2**, have been prepared (Tables 1 and 2). It is clear that the reaction of complexes of type **1** with a variety of alkynes is a general one. The similarity of the spectral data of Table 2 supports the isostructural nature of compounds **2**−**6**. Significantly, the two phenylacetylene complexes, **3** and **5**, give rise to an ^{1}H-NMR signal at 5.8 ppm (singlet) (Table 2) which is related to the original acetylene-bound H atom. This large downfield shift relative to the chemical shift of the same protons in free phenylacetylenes (3.05 ppm) implies that the sp carbon atoms of the original alkynes were transformed into sp^2 carbon atoms in the complexes listed in Table 1.

X-ray diffraction analysis was carried out on a single crystal of **6** and is presented in Figure 1. Selected structural parameters are given in Table 3. The most important structural feature is the bonding of the diphenylacetylene ligand via two σ-bonds: C−Ru (2.114 Å) and C−O (1.409 Å). Evidently, the original triple bond was transformed into a double bond (C36−C44 = 1.351 Å).

Two structural features support a η^5−Cp ring system: (a) The C6 atom is located 0.014(10) Å exo to the plane defined by the four carbon atoms C7, C8, C9, and C10 of the Cp ring, indicating a planarity of the five-membered ring. (b) The five C atoms of the Cp ring are all within bonding distance to the Ru atom, 2.175(11)−2.321(9) Å, with the longest distance for Ru−C9.

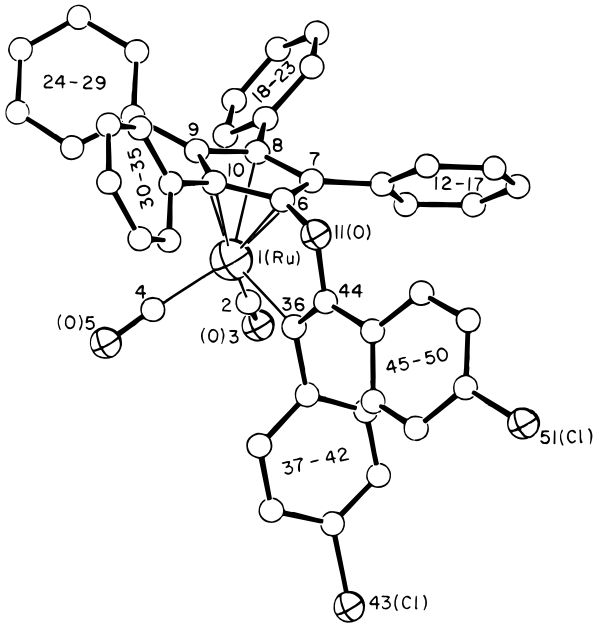

Figure 1. ORTEP diagram of complex **6**.

For comparison, a Ru−C6 distance of 2.530(3) Å was found[7] for the tetrahaptocomplex [η^4-(Ph_4C_4C═O)$(CO)_3$-Ru] with the C6 atom displaced 0.33 Å exo to the plane defined by C7−C8−C9−C10. Thus, the five-membered ring of **6** constitutes an η^5-ligand with the Ru(II) atom acquiring an 18e coordinately saturated configuration.

The four atoms bound to C36 and C44 are essentially coplanar. However the dihedral angle defined by C36−C44−C45−C46 is 30.0°, pointing to the nonplanarity of

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Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in 6

(a) Bond Distances

Ru1−C2	1.901(15)	Ru1−C4	1.861(11)
Ru1−C6	2.175(11)	Ru1−C7	2.250(9)
Ru1−C8	2.286(8)	Ru1−C9	2.321(9)
Ru1−C10	2.244(10)	Ru1−C36	2.114(11)
C2−O3	1.111(20)	C4−O5	1.164(13)
C6−C7	1.441(11)	C6−C10	1.383(13)
C6−O11	1.392(13)	C7−C8	1.440(16)
C8−C9	1.422(11)	C9−C10	1.487(14)
O11−C44	1.409(11)	C36−C37	1.467(14)
C36−C44	1.351(17)	C44−C45	1.452(17)

(b) Bond Angles

C2−Ru1−C4	89.9(6)	C2−Ru1−C36	93.2(5)
C4−Ru1−C36	95.1(4)	C6−O11−C44	111.6(7)
Ru1−C2−O3	177.9(12)	Ru1−C4−O5	176.5(11)
Ru1−C36−C44	116.1(7)	Ru1−C36−C37	121.3(7)
C6−C7−C8	105.7(8)	C7−C8−C9	109.4(8)
C8−C9−C10	106.9(8)	C9−C10−C6	106.6(8)
C37−C36−C44	122.1(9)	C36−C44−C45	131.5(9)

(c) Torsion Angles

C37−C36−C44−C45	−3.41(18)	C6−O11−C44−C36	−11.3(12)

the cis-substituted phenyl rings system, thereby introducing a molecular axial chirality.

It may be safely concluded that complexes **2**−**5** are isostructural with **6**. However, complexes **3** and **5**, which have a nonsymmetrically substituted alkyne ligand, may have two regio isomers with partial structures: RuC(H)═C(Ph)O− (I) and RuC(Ph)═C(H)O− (II). The NMR chemical shift (5.8 ppm) of the vinylic proton of **3** and **5** supports structure I.

Dahl et al.[8] isolated an iron complex of similar gross structure (X-ray crystallography) from the reaction of methyl propargylate and $Fe(CO)_5$.

The reaction of **1** with another alkyne, dimethyl acetylenedicarboxylate (DMA), gave complex **7** with infrared spectral properties very similar to those of complexes **2**−**6** (Table 1). However its ^{1}H-NMR spectrum (Table 2) shows a broad signal at 9.03 ppm and a singlet at 6.16 ppm, each integrating for 1H, inconsistent with the structure assigned to complexes **2**−**6**. The ^{1}H- and the ^{13}C-NMR spectra of **7** show nonequivalence of the two carbomethoxy groups. The elemental analysis indicate a molecular formula of $(Ph_4C_4CO)(CO)_2(DMA)H_2Ru$.

X-ray diffraction analysis was carried out on a single crystal of **7** and is presented in Figure 2. Selected structural parameters are given in Table 4. The central X-ray structural feature of **7** is a ruthenium−carbon σ bond (2.096 Å) and a new proton bound to C41. Carbon atoms 36 and 41 must be sp^2 hybridized in view of the distance of 1.324(10) Å between them, i.e. a double bond. The dihedral angle for C37−C36−C41−C42 is 1.2° indicating a planar OCC═CCO structural element. However, while the C42−O43 carbonyl group is essentially coplanar with the C36−C41 double bond (dihedral angle 9.4°), the latter makes an angle of 94.5° with the C37−C38 carbonyl, thus disrupting the π-conjugation in the fumarate system. This must be due to a steric constraint, and the loss of π-conjugation is partly compensated for by hydrogen bonding of the twisted carbonyl, with an observed distance of 2.762(7) Å for O38−O11, (O38---H11 = 1.96 Å).

(8) Dahl, L. F.; Doedens, R. J.; Hubel, W.; Nielsen, J. *J. Am. Chem. Soc.* **1966**, *88*, 446.

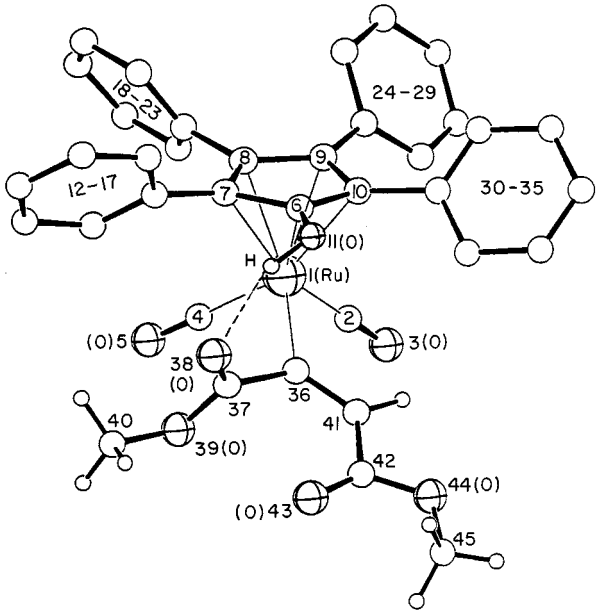


Figure 2. ORTEP diagram of complex **7**.

Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in 7

(a) Bond Distances

Ru1−C2	1.876(7)	Ru1−C4	1.869(7)
Ru1−C6	2.316(5)	Ru1−C7	2.273(6)
Ru1−C8	2.214(6)	Ru1−C9	2.263(6)
Ru1−C10	2.269(5)	Ru1−C36	2.096(7)
C2−O3	1.145(9)	C4−O5	1.145(9)
C6−C7	1.447(7)	C6−C10	1.405(8)
C6−O11	1.355(6)	C7−C8	1.446(7)
C8−C9	1.403(8)	C9−C10	1.475(6)
C36−C41	1.324(10)	C36−C37	1.469(10)
C37−O38	1.212(8)	C41−C42	1.492(10)

(b) Bond Angles

C2−Ru1−C4	89.9(3)	C2−Ru1−C36	87.7(3)
C4−Ru1−C36	89.6(3)	Ru1−C2−O3	179.6(7)
Ru1−C4−O5	177.5(7)	Ru1−C36−C41	127.0(6)
Ru1−C36−C37	112.1(5)	C6−C7−C8	104.4(5)
C7−C8−C9	111.7(5)	C8−C9−C10	105.8(5)
C9−C10−C6	107.7(5)	C36−C37−O39	112.7(6)
C37−C36−C41	120.6(7)	C36−C41−C42	122.5(7)

(c) Torsion Angles

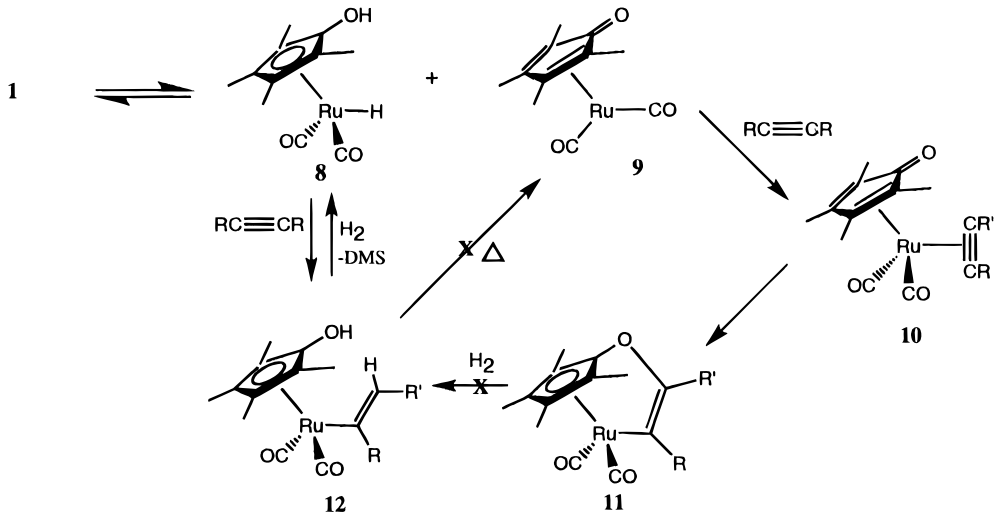
C37−C36−C41−C42	−1.2(11)	C41−C36−C37−O39	94.5(10)

Structural features similar to those pointed out for **6** also support a pentahapto Cp ring system in **7**. Thus, the distances between the Ru atom to the five carbon atoms of the Cp ring are in the range 2.214(6)−2.316(5) Å, all within bonding distance. The longest distance is to C6, which lies 0.06 Å exo to the plane defined by the other four C atoms. Therefore, with the η^5-Cp ligand, the Ru(II) atom acquires an 18e coordinately saturated configuration.

Complex **7** showed the following chemical behavior: (a) Under dihydrogen pressure (15 atm) at 110 °C it gave back the starting complex **1** accompanied by dimethyl succinate. (b) Surprisingly, it was thermally stable at 140 °C for several hours in toluene.

Scheme 1 presents structural information and experimental chemical data acquired for the purpose of analyzing the catalytic hydrogenation cycle of alkynes, using **1** as the loaded catalyst. All structures except for **9** and **10** were experimentally identified. The equilibrium **1** ⇌ **8** + **9** has been previously determined,[5] finding that the forward reaction becomes significant at 80 °C. Under hydrogen pressure at 110 °C **1** is

Scheme 1



Ring substituents were omitted for clarity

quantitatively converted to **8**, probably via oxidative addition of H_2 to **9**, which has been inferred but never detected.[5] The formation of the thermodynamically stable **11** may take place by coordination of an alkyne with **9** (16e) and subsequent rearrangement of the resulting complex **10**. Complex **7** (represented by stucture **12**; Scheme 1) may be viewed as a cis addition product of Ru−H to the triple bond of an alkyne (DMA). The following important observations are summarized: (a) Complex **2**, represented by structure **11** (Scheme 1), could not be converted to **12** by hydrogenation (15 atm/140 °C), as it was recovered back. (b) Complex **7**, represented by structure **12** (Scheme 1), is thermally stable (140 °C in toluene for 10 h); it does not eliminate an alkene. (c) Complex **7**, represented by structure **12** (Scheme 1), is quantitatively converted by hydrogenation (15 atm) in THF into dimethyl succinate (DMS) and **1** (via **8**). (d) Spectral observations reveal the presence of **1** and **8** during hydrogenation of alkynes, with **11** slowly growing in.

On the basis of Scheme 1 and the accompanying experimental observations, it is possible now to propose a catalytic cycle for the hydrogenation of alkynes with **1** as the loaded catalyst (Scheme 2).

As mentioned previously, complex **11** is stable under hydrogenation conditions. Thus, the sequence **9** → **10** → **11** represents an irreversible side reaction path which depletes the catalyst pool, thus eventually quenching the main hydrogenation cycle and accounting for the isolation of **11**. Substantial hydrogenation of alkynes still does take place due to the competitive transformation **9** → **8** (oxidative addition of H_2).

Scheme 2

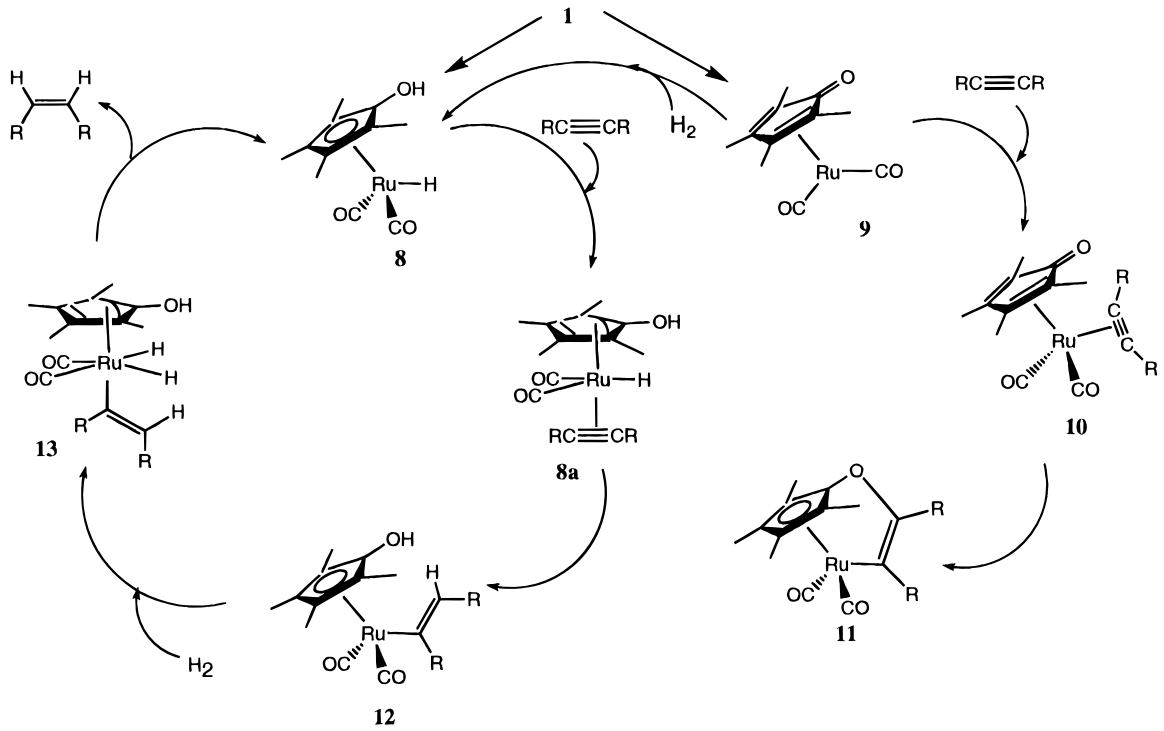


Table 5. Analytical Data

compd no.	mp, °C (dec)	color	empirical formula	calcd, % C	calcd, % H	found, % C	found, % H
2	242	yellow	$C_{45}H_{30}O_3Ru$	75.10	4.17	75.02	4.41
3	160	yellow	$C_{39}H_{26}O_3Ru$	72.55	4.18	73.10	4.61
4	235	yellow	$C_{45}H_{28}Cl_2O_3Ru$	68.70	3.56	69.17	3.78
5		yellow					
6	256	yellow	$C_{45}H_{28}Cl_2O_3Ru$	68.70	3.56	67.95	3.43
7	204−5	beige	$C_{37}H_{28}O_7Ru$	64.81	4.11	64.68	4.18

The left-hand cycle (Scheme 2) represents the viable hydrogenation cycle which transforms alkynes to alkenes and subsequently to alkanes. The identifiable complexes **8** and **12** must function as intermediates in this cycle. Since **8** persists during hydrogenation, it is reasonable that the rate-limiting step is its interaction with an alkyne (**8a**). Complex **8**, is an 18e coordinately saturated complex; therefore a reasonable proposition that may account for alkyne complexation is an $\eta^5 \rightarrow \eta^3$ rearrangement of the cyclopentadienol system, as described by **8a**, followed by Ru−H cis addition to the triple bond to generate **12**. This sequence of structural events may in fact be considered as the known associative ligand substitution reaction of an 18 electron complex.[9] In essence, ring slippage provides an empty coordination site. The η^3 species (**8a**) has been assigned an arbitrary electronic arrangement of the cyclopentadienol ring. We are unaware of previous mentioning of such a slippage mechnism of a Cp ring in conjunction with catalysis.

Our previous notion that **12** can reductively eliminate an alkene, and generate **9**, which may then continue the cycle (Scheme 2), is apparently incorrect. As stated previously, **12** is an extremely stable complex. In fact we have experimentally demonstrated (vide supra) that it does release a reduced substrate but only *in the presence of dihydrogen* (Scheme 1). In order to explain the interaction of **12**, an 18e complex, with dihydrogen, we must again invoke an associative type mechanism resulting in **13**. Reductive elimination of a reduced substrate from **13** would generate **8**, thus completing the catalytic hydrogenation cycle.

In practice, an alkane (dimethyl succinate) rather than alkene (dimethyl maleate) has been isolated. A completely analogous hydrogenation cycle may be considered for the hydrogenation of alkenes to alkanes. It is also plausible that the alkene does not depart from the metal after the reductive elimination from **13**.

An alternative route for the formation of **8a** via oxidative addition of H_2 to **10** (Scheme 2) is unlikely, since it would in fact require thermal loss of dihydrogen from **8** to generate **9** *under H_2 pressure*. However it can not be strictly ruled out.

The above analysis (Scheme 2) is based on the isolation and X-ray structural characterization of two complexes **6** and **7** which are represented by **11** and **12** (Scheme 2). Admittedly, they have not been isolated from the same reaction. It appears that complexes of type **12** are unstable with most alkynes as they could not be isolated but in the case of DMA. Thus, the Ru−C bond in the DMA complex **7** (2.096 Å) is stronger than that in **6** (2.114 Å). Possibly, the two carbomethoxy groups in **7** provide a lower π^* energy level for Ru back-donation. The infrared spectral data (Table 1) support this argument as well, in as much as the CO stretching frequencies of **7** are higher than those of **6** indicative of better back donation in **7**.

(9) Basolo, F. *Isr. J. Chem.* **1986**, *27*, 233.

Conclusions

Hydrogenation of alkynes with complex **1** (or with its ring-substituted derivatives) as a precatalyst generates a new complex in which the alkyne substrate is bound, via two sp^2-C atoms, to the Ru atom as well as to the oxygen atom of the cyclopentadienol ring system. Such complexes can be prepared independent of the hydrogenation reaction by a simple thermal reaction of alkynes and complexes of the general structure **1**. They are extremely stable both thermally and chemically, and when formed during hydrogenation reaction of alkynes, they slowly poison the hydrogenation process by virtue of their catalytic inertness. Their mode of formation is described in Scheme 2.

Complexes of type **7** (isolated and characterized in the case of dimethyl acetylenedicarboxylate), which are the formal addition products of Ru−H to a triple bond, are the viable hydrogenation intermediates. A complex of type **8a**, with η^3-coordination of the cyclopentadienol ring system, is a logical precursor for **7**. Being thermally stable, the mode of decomposition of **7** to products requires dihydrogen as described in Scheme 2.

Experimental Section

General Procedure for the Preparation of Complexes 1−7. Dimer (0.8 mmol) and an alkyne (1.6 mmol) in toluene (10 mL) were heated under a nitrogen blanket in a closed reactor at 140 °C for 24 h. The toluene was evaporated in vacuum and the residue taken in methylene chloride and chromatographed on Silica 60. Elution of the column with methylene chloride−petroleum ether mixture (1:1) gave microcrystalline yellow solids which were further purified by crystallization from a methylene chloride−hexane mixture (1:1).

Hydrogenation of 7. A solution of complex **7** (27.2 mg) in THF (10 mL) was heated is a closed SS reactor in a glass sleeve under dihydrogen (500 psi) at 140 °C for 6 h. Infrared spectrum of the colorless solution: 2013, 1954, 1743 cm^{-1}. The first two bands are identical with those of **8,** obtained by hydrogenation of **1** under the above conditions. TLC of the two solutions gave the same spot for **8**. The last band was found to be identical with that of dimethyl succinate measured in THF.

Crystal Structure Analyses. The X-ray diffraction measurements were carried out at room temperature (ca. 298K) on an automated CAD4 diffractometer equipped with a graphite monochromator, using Mo Kα ($\lambda = 0.7107$ Å) radiation. Intensity data were collected out to $2\theta = 46°$ by the $\omega-2\theta$ scan mode with a constant scan speed of 4 deg/min for **6** and 2 deg/min for **7**. Possible deterioration of the analyzed crystals was tested by detecting periodically the intensities of three standard reflections from different zones of the reciprocal space and was found negligible during the experiment. A total of

3163 and 3859 unique reflections with positive intensities were recorded for **6** and **7**, respectively. The data were corrected for absorption by an empirical method,[10] but no corrections for secondary extinction effects were applied.

Crystal data for 6: $C_{45}H_{28}Cl_2O_3Ru$, fw 788.69, trigonal, space group $P3_2$, $a = 9.902(4)$ Å, $b = 9.902(4)$ Å, $c = 32.488(7)$ Å, $V = 2758.7$ Å^3, $Z = 3$, $D_{calc} = 1.424$ g·cm^{-3}, $F(000) = 1200$, μ(Mo Kα) = 6.02 cm^{-1}.

The structure was solved by Patterson and direct methods (SHELXS-86),[10] and refined by full-matrix least squares (SHELXL-93),[13] including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The final refinement, based on F^2, converged smoothly at $R = 0.044$ for 2827 observations above the intensity threshold of $2\sigma(I)$. The hydrogen atoms were introduced in calculated positions. At convergence, the peaks and troughs of the final difference density map did not exceed 0.46 and −0.45 e·Å^{-3}, respectively.

Crystal data for 7: $C_{37}H_{28}O_7Ru$, fw 685.69, monoclinic, space group $P2_1/c$, $a = 14.417(2)$ Å, $b = 8.988(6)$ Å, $c = 24.724(4)$ Å, $\beta = 100.98(1)°$, $V = 3145.1$ Å^3, $Z = 4$, $D_{calc} = 1.448$ g·cm^{-3}, $F(000) = 1400$, μ(Mo Kα) = 5.35 cm^{-1}.

The structure was solved by Patterson and direct methods (SHELXS-86),[11] and refined by full-matrix least squares (SHELX-76),[12] including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The final refinement, based on F, converged smoothly at $R = 0.045$ and w$R = 0.045$ for 2794 observations above the intensity threshold of $3\sigma(I)$. The hydrogen atoms attached to carbon were introduced in calculated positions, the methyls being treated as rigid groups. That of the hydroxyl group was located by difference Fourier. At convergence, the peaks and troughs of the final difference density map did not exceed 0.53 and −0.54 e·Å^{-3}, respectively.

Supporting Information Available: Tables of full bond lengths and angles, atomic coordinates and equivalent isotropic thermal parameters, and anisotropic thermal parameters for **6** and **7** (13 pages). Ordering information is given on any current masthead page.

OM960469W

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