Hydrogen transfer from formic acid to alkynes catalyzed by a diruthenium complex

Yuan Gao, Michael C. Jennings, and Richard J. Puddephatt

Abstract: The diruthenium(0) complex $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$), is a catalyst for the transfer hydrogenation, using formic acid as hydrogen donor, of the alkynes PhC≡CPh, PhC≡CMe, EtC≡CEt, and PrC≡CPr but not of the terminal alkynes HC≡CH, PhC≡CH, BuC≡CH, or the alkynes containing one or two electron-withdrawing substituents PhC≡CCO_2Me and MeO_2CC≡CCO_2Me. In the successful reactions, the formic acid is first decomposed to carbon dioxide and hydrogen, which then hydrogenates the alkynes in a slower reaction. In the unsuccessful reactions, the decomposition of formic acid is strongly retarded by the alkyne. In the case with the alkyne PhC≡CH, it is shown that the alkyne reacts with protonated **1** to give first $[Ru_2(\mu\text{-}CPh{=}CH_2)(CO)_4(\mu\text{-}dppm)_2][HCO_2]$, which then isomerizes to give the catalytically inactive, stable complex $[Ru_2(\mu\text{-}CH{=}CHPh)(CO)_4(\mu\text{-}dppm)_2][HCO_2]$. This complex has been structurally characterized and both of the μ-styrenyl complexes are shown to be fluxional in solution.

Key words: ruthenium, hydrogenation, catalysis, binuclear.

Résumé : Le complexe de diruthénium(0) $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) est un catalyseur pour l'hydrogénation par transfert dans laquelle l'acide formique est utilisé comme source d'hydrogène; cette réaction est efficace pour les alcynes tels que PhC≡CPh, PhC≡CMe, EtC≡CEt et PrC≡CPr, mais elle ne fonctionne pas avec les alcynes terminaux, tels que HC≡CH, PhC≡CH, BuC≡CH, ou avec les alcynes comportant un ou deux substituants électroaffinitaires, tels que PhC≡CCO_2Me et MeO_2CC≡CCO_2Me. Dans les réactions qui donnent les résultats espérés, l'acide formique est initialement décomposé en bioxyde de carbone et en hydrogène qui provoque l'hydrogénation des alcynes dans une réaction plus lente. Dans les réactions qui ne donnent pas les résultats espérés, la décomposition de l'acide formique est fortement ralentie par l'alcyne. Dans le cas de l'alcyne PhC≡CH, on a démontré que l'alcyne réagit avec le complexe **1** protoné pour donner dans une première étape le $[Ru_2(\mu\text{-}CPh{=}CH_2)(CO)_4(\mu\text{-}dppm)_2][HCO_2]$ qui s'isomérise alors pour donner le complexe stable et inactif $[Ru_2(\mu\text{-}CH{=}CHPh)(CO)_4(\mu\text{-}dppm)_2][HCO_2]$. On a caractérisé la structure de ce complexe et on a démontré que, en solution, les deux complexes μ-styrényles sont en état de fluxion.

Mots clés : ruthénium, hydrogénation, catalyseur, binucléaire.

[Traduit par la Rédaction]

Introduction

There has been increasing interest in using formic acid in catalytic transfer hydrogenation of multiple bonds, as an alternative to the traditional hydrogenation using hydrogen gas (1–3). Several active catalysts for this transfer hydrogenation have been identified, and all such catalysts are also active in the decomposition of formic acid to CO_2 and H_2 (1–4). All the catalysts studied so far have been mononuclear, and only a few of these have been studied in terms of reaction mechanisms (3, 4). Since the binuclear complex $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) has been shown to have high activity toward the decomposition of formic acid (5), and also to react easily with terminal alkynes (6), it was considered likely that it might also be active for the catalytic transfer hydrogenation of alkynes using formic acid. This article reports that the desired catalysis is successful and also describes studies of the reaction mechanism.

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Dedicated to Professor B.R. James, in recognition of his distinguished contributions to homogeneous catalysis, on the occasion of his 65th birthday.

Y. Gao, M.C. Jennings, and R.J. Puddephatt.[1] Department of Chemistry, University of Western Ontario, London, ON N6A 5B7, Canada.
[1]Corresponding author (telephone: (519) 679-2111; fax: (519) 850-2371; e-mail: pudd@uwo.ca).

Results

Hydrogen transfer from formic acid to internal alkynes

In the presence of $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (**1**) the reaction of HCOOH with internal alkynes, containing either phenyl or alkyl substituents (diphenylacetylene, 1-phenyl-1-propyne, 3-hexyne, or 4-octyne), in acetone at room temperature gave the pure *cis*-alkene as shown in eq. [1]. No trace of *trans*-alkene, and no further hydrogenation of alkene to alkane, was detected when the reactions were monitored by ^{1}H NMR. Using a 20:10:1 ratio of formic acid to diphenylacetylene to complex **1**, the reaction to give *cis*-stilbene was complete in 1 day. Incomplete conversion of about 40% was observed when using equimolar amounts of formic acid and diphenylacetylene under similar conditions. The conversion rate of alkyne to alkene was found to follow

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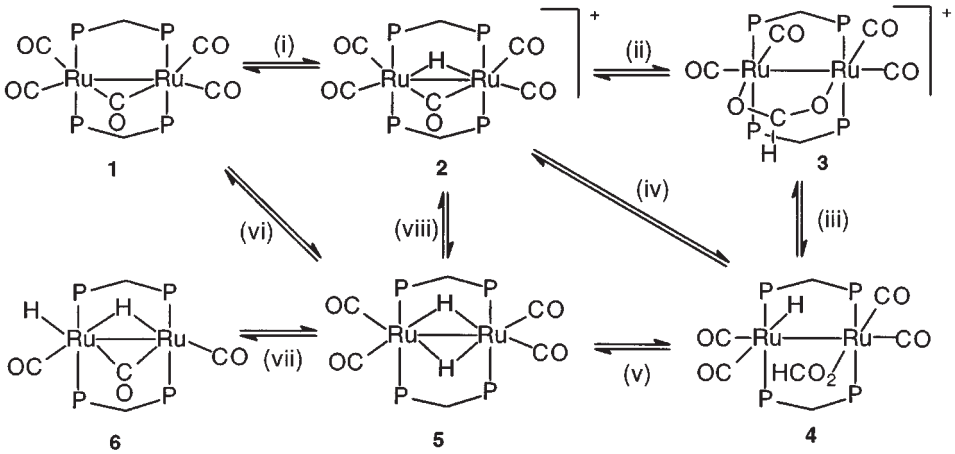
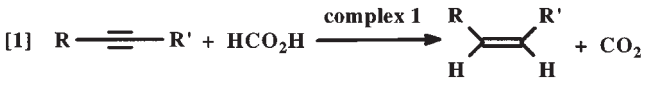
Scheme 1. Reagents: (*i*) H^+; (*ii*) HCO_2H, H_2; (*iii*) H_2, H^+; (*iv*) HCO_2^-, CO; (*v*) CO_2; (*vi*) CO, H_2; (*vii*) CO; (*viii*) H^+, CO, H_2.



the sequence: diphenylacetylene > > 1-phenyl-1-propyne > 3-hexyne ≈ 4-octyne. For example, using a 10:10:1 molar ratio of HCO_2H:PhCCMe:complex **1**, the conversion was



about 15% after 1 day.

These catalytic hydrogenation reactions were all slower than the catalytic decomposition of formic acid by complex **1** (5). This reaction could be monitored independently by ^1H NMR and it was complete in about 20 min under the above conditions, to give CO_2 and H_2. It is therefore clear that the catalytic transfer hydrogenations occur in two steps. First, the formic acid is decomposed to give hydrogen and then, in a much slower reaction, catalytic hydrogenation of the alkyne occurs. Excess formic acid is required because excess hydrogen is needed for the slow second step. A similar reaction sequence has been proposed for catalytic transfer hydrogenation using formic acid and the mononuclear catalyst $[RuCl_2(PPh_3)_3]$, either alone or in combination with the heterogeneous hydrogenation catalyst Pd/C (7). Complex **1** was shown to be a catalyst for hydrogenation of diphenylacetylene using hydrogen gas at 1 atm (1 atm = 101.325 kPa) pressure, consistent with the above mechanism, and the hydrogenation is not affected by the presence or absence of free carbon dioxide.

The reactions were monitored at low temperature (–5 to –10°C) by NMR using $H^{13}COOH$. The catalytic decomposition of formic acid occurred by way of the intermediates shown in Scheme 1, and occurred at a similar rate as in the absence of alkyne (5). No new intermediates were observed and complex **1** was regenerated once the catalytic decomposition of formic acid was complete (5). No alkene was detected until the formic acid was completely decomposed to CO_2 and H_2. During the subsequent slow hydrogenation step, the only complex present in detectable quantity was complex **1**. This result is not unexpected since these internal alkynes without electronegative substituents (eq. [1]) do not react with complex **1**, but it does show that all reaction intermediates are short-lived (6).

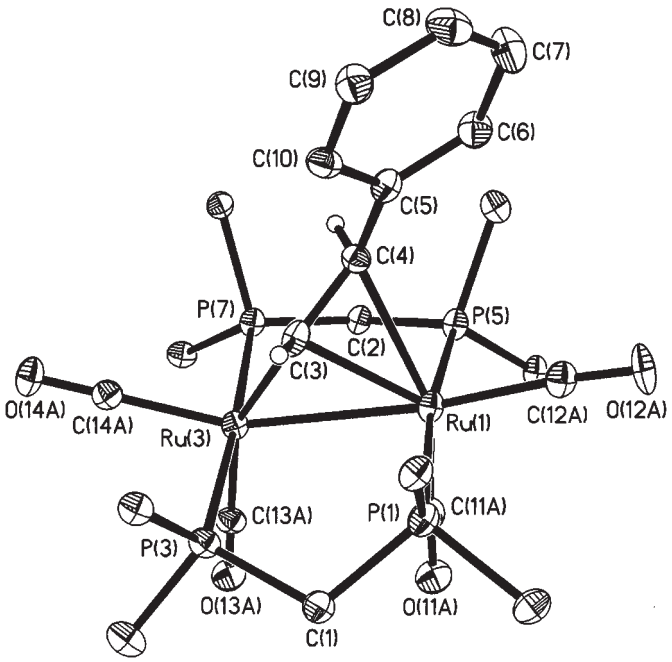
Hydrogen transfer from formic acid to terminal alkynes and to internal alkynes with electron-withdrawing substituents

The terminal alkynes (PhCCH, HCCH, 1-hexyne) or internal alkynes with electron-withdrawing substituents ($PhCCCO_2Me$, MeO_2CCCCO_2Me) strongly inhibited the decomposition of formic acid to carbon dioxide and hydrogen. Thus, using $H^{13}CO_2H$ to allow detection of $^{13}CO_2$ by ^{13}C NMR, no CO_2 was detected at room temperature and only a trace was detected on warming the sample to 50°C. In terms of the ruthenium complexes present, in each case complexes **2** and **3** were formed first, in the same way as in the absence of the alkyne. This is consistent with the faster reaction of **1** with formic acid than with the alkynes (5, 6). However, the other intermediates of Scheme 1, including the important intermediate **4**, were not observed. Instead, products arising from reactions of **2** or **3** with the alkynes were observed. In the cases with the alkynes $PhC{\equiv}CCO_2Me$ or $MeO_2CC{\equiv}CCO_2Me$, the reactions gave complex mixtures that could not be identified but the terminal alkynes reacted more selectively, as described below.

The reaction of $PhC{\equiv}CH$ with complex **2** was relatively slow and thus was chosen for detailed study. At room temperature, the reaction occurred through several steps, as monitored by ^1H and ^{31}P NMR, to finally give a single product after 1 day at room temperature. This compound was characterized crystallographically as $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHPh)(CO)_4(\mu\text{-}dppm)_2][HCOO]$ (**7**) and it is logical to suggest that it is formed from **2** by *cis*-insertion of phenylacetylene into the ruthenium hydride bond, with loss of a carbonyl ligand.

The molecular structure of the cation **7** is shown in Fig. 1 and selected interatomic distances and angles are listed in Table 1. The unit cell contains two independent cations **7** as well as formate anions and solvent molecules. Table 1 shows equivalent bond parameters for the two cations **7** in each row, and there are no major differences. The discussion will focus on the cation containing atoms Ru(1) and Ru(3) shown in Fig. 1. Each cation **7** contains a $Ru_2(\mu\text{-dppm})_2$ group in which the $Ru_2P_4C_2$ atoms adopt a slightly twisted, extended boat conformation. In addition each ruthenium is bound to two terminal carbonyl ligands and to the bridging styrenyl group. The α-carbon (C(3)) of the styrenyl group is σ-

Fig. 1. A view of the structure of the cation $[Ru_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHPh)(\mu\text{-}dppm)_2]^+$. Only the ipso carbon atoms of the phenyl substituents of the dppm ligands are shown for clarity.



bonded to Ru(3) (Ru(3)C(3) = 2.09(1) Å) and the C=C unit is π-bonded to Ru(1) (Ru(1)C(3) = 2.27(1) Å, Ru(1)C(4) = 2.39(1) Å). Both C(3) and C(4) are chiral centers and the unit cell contains equal numbers of the *R,S* and *S,R* enantiomers: Fig. 1 shows the *S,R* enantiomer and the molecule containing Ru(2)Ru(4) is *R,S*. The distance C(3)—C(4) = 1.38(1) Å is slightly longer than a free double bond (1.34 Å) but significantly shorter than a single bond (1.53 Å), indicating relatively weak back-bonding to the C=C π*-orbital. The phenyl substituent of the styrenyl group is positioned between a sheath of phenyl substituents of the dppm ligands. The angles Ru(3)-C(3)-C(4) = 129.4(7) and C(3)-C(4)-C(5) = 123(1)° are each somewhat greater than the ideal angles of 120° for a double bond and, of course, significantly greater than the tetrahedral angle. Again this suggests that the carbon—carbon bond of the μ-styrenyl group is close to a double bond. The distortion of the angle Ru(3)-C(3)-C(4) is probably to maximize the Ru(1)-C(3-)C(4) π-bonding interaction. The distance Ru(1)—Ru(3) = 2.855(1) Å is consistent with a metal—metal single bond. Each ruthenium then has an 18-electron configuration if Ru(1) carries the positive charge. The structural features are consistent with those of other μ-alkenyl complexes (8).

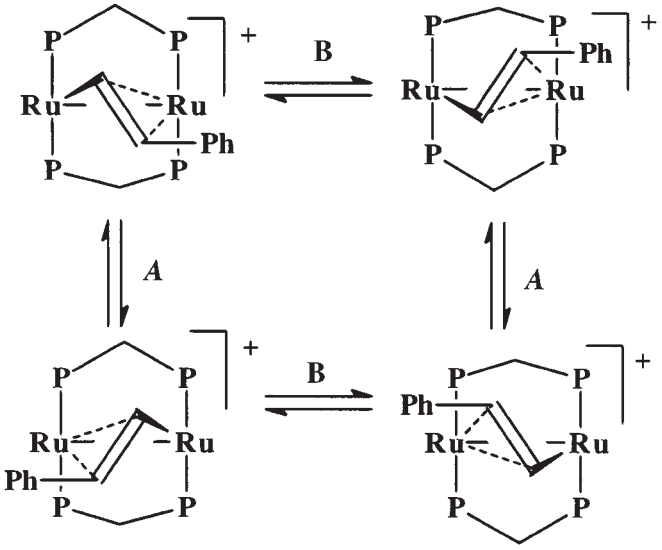
The ^{31}P NMR spectrum of **7** contained only a very broad singlet at δ = 33 at room temperature and so **7** is clearly fluxional. The ^{1}H NMR spectrum at room temperature contained two vinyl resonances, each as a doublet of quintets, at δ = 8.4 and δ = 5.5, assigned to the hydrogen atoms on the α- and β-carbons [C(3) and C(4) in Fig. 1], respectively, (9). The magnitude of the doublet coupling constants ^3J (H-H) = 14 Hz confirm that these protons are *trans* within the vinyl group, and so confirms the stereochemistry shown crystallographically. Both vinyl hydrogen resonances show effectively equal coupling to the four phosphorus atoms, with J $(P\text{-}H)_{obs}$ = 7 and 3 Hz for the α- and β-protons, respectively. The phenyl protons of the bridging styrenyl ligand were observed δ = 6.9 (*para*), δ = 6.5 (*meta*), and at δ = 5.7 (*ortho*). These unusual chemical shifts for aryl protons are probably due to shielding by the surrounding four phenyl groups of the dppm ligands. Two broad, unresolved resonances were observed for the $CH^aH^bP_2$ protons at δ = 4.2 and 3.7 ppm.

Table 1. Selected bond lengths (Å) and bond angles (°) for complex **7**.

Bond lengths (Å)			
Ru(1)—C(11A)	1.87(1)	Ru(4)—C(23B)	1.89(1)
Ru(1)—C(12A)	1.90(1)	Ru(4)—C(24B)	1.90(1)
Ru(1)—C(3)	2.27(1)	Ru(4)—C(13)	2.25(1)
Ru(1)—P(1)	2.378(3)	Ru(4)—P(8)	2.349(3)
Ru(1)—P(5)	2.387(3)	Ru(4)—P(4)	2.382(3)
Ru(1)—C(4)	2.39(1)	Ru(4)—C(14)	2.41(1)
Ru(1)—Ru(3)	2.855(1)	Ru(2)—Ru(4)	2.867(1)
Ru(3)—C(14A)	1.88(1)	Ru(2)—C(22B)	1.87(1)
Ru(3)—C(13A)	1.92(1)	Ru(2)—C(21B)	1.96(1)
Ru(3)—C(3)	2.09(1)	Ru(2)—C(13)	2.09(1)
Ru(3)—P(3)	2.347(3)	Ru(2)—P(6)	2.368(3)
Ru(3)—P(7)	2.363(2)	Ru(2)—P(2)	2.372(3)
C(3)—C(4)	1.38(1)	C(13)—C(14)	1.40(1)
C(4)—C(5)	1.49(1)	C(14)—C(15)	1.48(1)
Bond angles (°)			
C(4)-C(3)-Ru(3)	129.4(7)	C(14)-C(13)-Ru(2)	131.1(9)
C(4)-C(3)-Ru(1)	77.8(6)	C(14)-C(13)-Ru(4)	79.1(6)
Ru(3)-C(3)-Ru(1)	81.6(3)	Ru(2)-C(13)-Ru(4)	82.8(4)
C(3)-C(4)-C(5)	123(1)	C(13)-C(14)-C(15)	122(1)

At –50°C, complex **7** exhibits an ABCD pattern of peaks in the ^{31}P NMR spectrum, consistent with the structure established in the solid state by X-ray crystallography. The fluxional process that leads to the equivalence of phosphorus atoms must include not only the process A (Scheme 2), which can be considered to arise from an intermediate in which the plane of the vinyl group is perpendicular to the metal—metal bond (10–12), but also process B (Scheme 2), which requires an intermediate in which the plane of the vinyl group is parallel with the metal—metal bond. Process A is thought to occur through a $\mu\text{-}\eta^1$-vinyl intermediate (10–12), but it is likely that process B occurs by way of an intermediate with a terminal σ-vinyl group. Certainly the conventional ruthenium—alkene π-bond will be lost in the transition state in which the vinyl group and Ru—Ru bond are coplanar. At low temperature, four resonances were observed for the CH_2P_2 protons (one coupled pair at δ = 4.7 and 4.3 and the other at δ = 4.4 and 3.2), indicating that all are inequivalent. The chemical shifts of the vinyl protons did not change significantly but the appearance did. In particu-

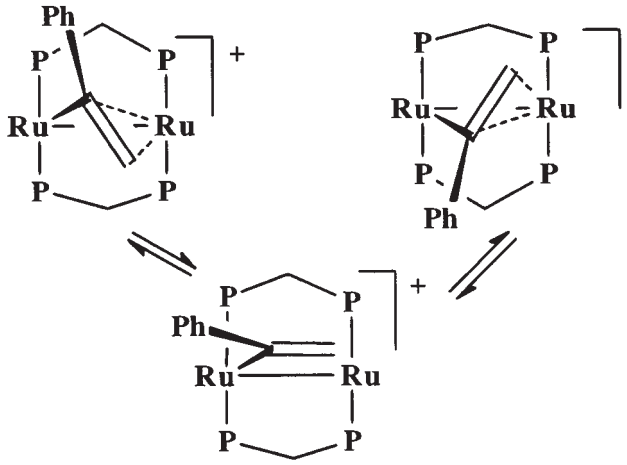
Scheme 2.



lar, the β-H resonance now appeared as a doublet of doublets with ^3J (H-H) = 14 Hz and J (P-H) = 10 Hz, thus showing coupling to only one phosphorus atom. The α-H resonance gave a complex unresolved multiplet, indicating nonequivalent couplings to several phosphorus atoms. These data are all easily rationalized in terms of the static structure determined crystallographically.

When the reaction of **1** with formic acid and phenylacetylene was monitored by NMR, a reaction intermediate was detected and characterized as $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CPhCH_2)(CO)_4(\mu\text{-dppm})_2][HCOO]$ (**8**). Complex **8** displays an AA′BB′ pattern of peaks in the ^{31}P NMR spectrum with δ (P) = 25.0 and 26.8 ppm. The vinyl protons appeared as broad singlets in the ^1H NMR spectrum at δ 4.8 and 5.5; the absence of resolved coupling between them indicates that these are geminal protons and this was confirmed by a $^1H^{13}C$ HSQC experiment which showed that both vinyl protons are attached to the same carbon atom at δ (C) = 111.5. The phenyl protons of the styrenyl group appeared at δ = 6.3 (ortho), 6.6 (*meta*), and 6.8 (*para*). The ^{31}P NMR spectrum broadened but did not split further at –90°C. Since the static structure is expected to give an ABCD pattern of peaks in the ^{31}P NMR spectrum, it is clear that the fluxionality differs from that of complex **7**. In particular, the two processes analogous to A and B of Scheme 2 must have different rates, one being fast and the other slow on the NMR time scale; it is likely that B is rapid but that A is slow. The distinction can be made on the basis of the CH_2P_2 resonances in the ^1H NMR spectrum. In each process, the styrenyl group stays on the same side of the $Ru_2(\mu\text{-dppm})_2$ unit, so each CH_2 group will have nonequivalent protons CH^aH^b. However, process A does not lead to equivalent dppm ligands, whereas process B does. Hence, if it is process A that is fast, four resonances (each 1H) are expected whereas, if process B is fast, two resonances (each 2H) are expected for the CH_2P_2 protons. The spectrum contains two resonances for the CH_2P_2 protons at δ = 3.2 (2H) and 3.4 (2H), indicating that it is process B that is fast. It is likely that steric hindrance in complex **8** prevents process A, which requires the phenyl substituent of the styrenyl group to swing by the phenyl substituents of the

Scheme 3.



dppm ligands. A much smaller motion of the α-phenyl substituent is required in process B. Following this line of reasoning, it is likely that process B is also fast for complex **7** (Scheme 2) and that process A is rate-determining. The proposed fluxionality of **8** is shown in Scheme 3.

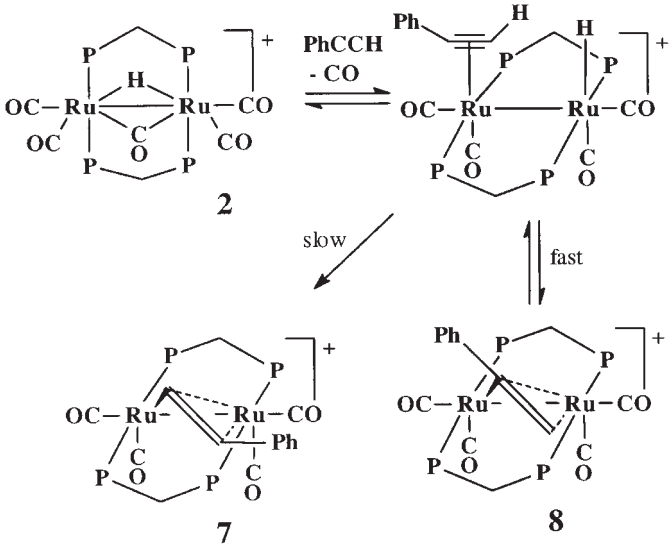
The complex **8** was formed rapidly and isomerized to **7** slowly over a period of several hours at room temperature. Clearly then, **8** is the kinetic product arising from reaction of PhCCH with **2**, and it isomerizes slowly to the thermodynamic product **7**. The isomerization is suggested to occur by a β-elimination–reinsertion sequence (Scheme 4). The stereochemistry of the intermediate is uncertain, as is the mechanism of insertion and β-elimination, which could occur at one or across both metal centers.

It is noteworthy that complex **7** is stable in solution in the presence of excess PhCCH, hydrogen gas, acids (HBF_4, HCO_2H), or bases (Et_3N, potassium *t*-butoxide). The strong inhibition of the catalytic decomposition of formic acid by phenylacetylene, and absence of catalytic transfer hydrogenation of phenylacetylene, can therefore be attributed to formation of the stable complex **7**, which is not an active catalyst. It has not been possible to characterize the products obtained when using the alkynes HCCH, BuCCH, MeO_2CCCCO_2Me, or $PhCCCO_2Me$, since intractable mixtures were obtained, but it is likely that they also give stable alkenyl or alkyne complexes that are not active catalysts.

Discussion

In catalytic transfer hydrogenation using formic acid, the donor must transfer two hydrogen atoms to the metal center (with loss of CO_2) to give metal hydride bonds, and the substrate must coordinate to the metal and accept the hydrogen atoms, typically by insertion followed by reductive elimination. However, within this framework there are many possible reaction sequences (1–3). One important classification is based on whether the hydrides react rapidly with substrate as they are formed, as is implied by the term transfer hydrogenation, or are first eliminated as free dihydrogen. The second case is then equivalent to hydrogenation with hydrogen gas, but with the hydrogen generated in situ from the formic acid (13). There is evidence for both cases in catalytic transfer hydrogenation using formic acid and mononuclear catalysts

Scheme 4.

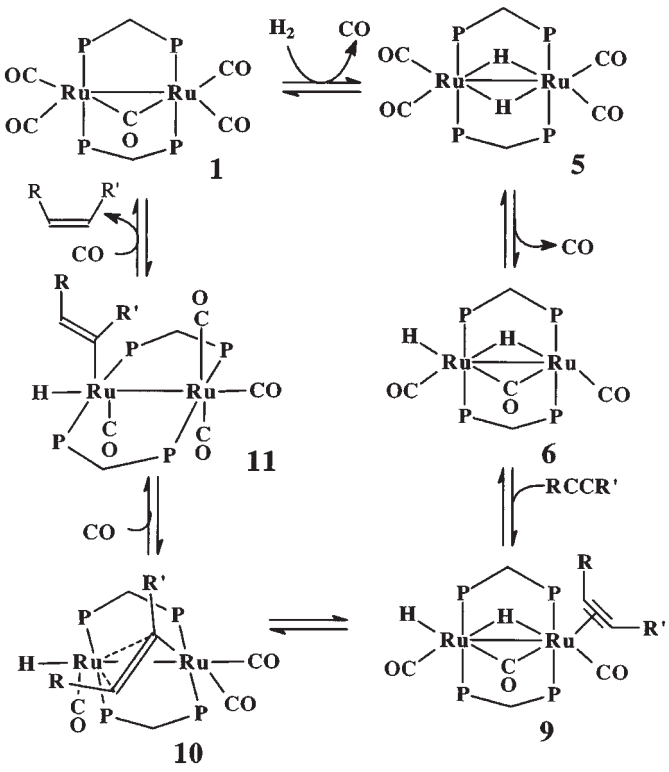


(1–3, 7). In the present case, the successful hydrogenations all occur by the mechanism in which formic acid is catalytically decomposed to carbon dioxide and hydrogen, followed by the slower catalytic hydrogenation of the alkyne.

In the successful catalytic reactions, no intermediates were detected in which the alkyne or its hydrogenation products were coordinated to ruthenium. This was the case when using any of HCOOH, HCOOH:Et_3N (5:2), or H_2 as the hydrogen source. It is likely that weak binding of the alkyne to the diruthenium complex is a prerequisite to successful catalysis, since those alkynes known to bind strongly (6) were not hydrogenated. On the other hand, alkenes are not hydrogenated by this catalyst system and they do not coordinate either. It seems there is a balance such that both substrates that bind strongly (terminal alkynes, alkynes with electon-withdrawing substituents) and those that cannot coordinate at all (alkenes) are not hydrogenated, and that substrates that are hydrogenated can probably bind transiently to the diruthenium center (internal alkynes without electron-withdrawing groups).

The mechanism of hydrogenation is necessarily speculative. The only difference in observed intermediates, compared to those observed in the catalytic decomposition of formic acid in the absence of alkynes, was that the hydride derivatives **5** and **6** were not observed. It is easy to understand how the coordinatively unsaturated hydride **6** might react with alkynes, and one possible mechanism based on this observation is shown in Scheme 5. Since none of the possible intermediates **9**–**11** of Scheme 5 is directly observed, the structures are very tentative. However, the overall mechanism involving oxidative addition of hydrogen with CO loss to give **5** and **6**, followed by rapid alkyne coordination (complex **9**), *cis*-insertion to give a vinyl derivative (complexes **10**, **11**), and reductive elimination of alkene with CO addition to regenerate the resting state complex **1**, is consistent with the observations. There are numerous instances of related mechanistic proposals with mononuclear ruthenium complexes, but the extension to binuclear catalysts is new (13, 14).

Scheme 5.



Experimental

All manipulations were operated under a dry nitrogen atmosphere using either standard Schlenk techniques or a glove box. Acetone was dried over 3 Å molecular sieves, toluene was dried by distillation from sodium benzophenone, and CH_2Cl_2 was distilled before use from CaH_2. The HCOOH (96%) and $H^{13}COOH$ (95%, 99 C^{13} atom%) contained 4 to 5% water and were used as purchased. [Ru_2(μ-CO)$(CO)_4$(μ-dppm)$_2$] (**1**) was synthesized according to literature procedure (15). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using Varian Inova 400 or Gemini 300 spectrometers.

Hydrogen transfer studies from HCOOH to alkynes

To a saturated solution of [Ru_2(μ-CO)$(CO)_4$(μ-dppm)$_2$] (**1**) (1.1×10^{-3} mmol) in acetone-d_6 (0.5 mL, 2.2 mM) in an NMR tube was added PhCCPh (1.98 mg, 1.1×10^{-2} mmol) and the tube was sealed with a septum. HCOOH (1.00 μL, 2.2×10^{-2} mmol) was then injected through the septum by syringe. The decay of formic acid and formation of *cis*-stilbene were monitored as a function of time by comparing the integrals of the formyl and vinyl hydrogen resonances with the integral of the CH_2P_2 resonance of **1** in the ^1H NMR spectrum. The decomposition of HCO_2H to H_2 and CO_2 was complete in 20 min, while the hydrogenation of PhCCPh to *cis*-stilbene was complete in 24 h at 20°C.

Reactions with diphenylacetylene, 1-phenyl-1-propyne, 3-hexyne, and 4-octyne were carried out in a similar way. For comparison of rates, the ratio of alkyne:formic acid:**1** was maintained at 10:10:1. Alkene products were characterized by their ^1H NMR spectra in acetone-d_6 as follows: *cis*-stilbene (16): δ (^1H) = 6.6 (s, =CH); *cis*-1-phenylpropene

(17): δ (^{1}H) = 7.3 (m, 5H, Ph), 6.42 (dq, *J* (H-H) = 13 Hz, *J* (H-H) = 2 Hz, PhCH=), 5.77 (dq, *J* (H-H) = 13 Hz, *J* (H-H) = 7 Hz, MeCH=), 1.85 (dd, *J* (H-H) = 7 Hz, *J* (H-H) = 2 Hz, Me); *cis*-3-hexene (18): δ (^{1}H) = 5.3 (m, =CH0, 2.03 (m, CH_2), 0.9 (t, *J* (H-H) = 6 Hz, Me); *cis*-4-octene (19): δ (^{1}H) = 5.3 (m, =CH), 2.03 (m, CH2)], 1.38 (m, CH_2), 0.9 (t, *J* (H-H) = 6 Hz, Me).

In the similar reaction using PhCCH (3 μL, 0.027 mmol), the complete decomposition of HCOOH (6.5 μL, 0.130 mmol) took 2 weeks to reach completion and no hydrogenation product (styrene) was detected. The only ruthenium complex present at the final stage was complex **7**. The alkynes HCCH, BuCCH, $PhCCCO_2Me$, and MeO_2CCCCO_2Me also retarded the decomposition of formic acid by complex **1** and failed to give the alkenes expected to be formed by catalytic hydrogenation.

Synthesis of $[Ru_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHPh)(\mu\text{-}dppm)_2][HCOO]$ 7

To a saturated solution of $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ in acetone-d_6 (0.5 mL, 2.2 mM) in a septum-sealed NMR tube was added PhCCH (3 μL, 0.027 mmol) and HCOOH (6.5 μL, 0.130 mmol) by syringe. The solution was set aside for 18 h at room temperature to give complex **7** as the only product as determined by NMR. The same product was formed by heating to 45°C for 3 h, and using CD_2Cl_2 as solvent. Crystals were obtained from CD_2Cl_2 by slow diffusion of pentane. The crystals were formed with solvent occluded (see structure determination), which was partially lost on drying, thus making it difficult to obtain good analytical data. ^{1}H NMR (acetone-d_6, 20°C) δ: 8.4 (s, 1H, *H*COO], 8.2 (m, 1H, PhCH-C*H*), 5.4 (d quin, 1H, ^3J (H-H) = 14 Hz, *J* (P-H) = 3 Hz, PhC*H*-CH), 5.7 (d, 2H, ^3J (H-H) = 8 Hz, *Ph*CHCH), 6.5 (t, 2H, *J* (H-H) = 8 Hz, *Ph*CHCH), 6.8 (t, 1H, *J* (H-H) = 8 Hz, *Ph*CHCH), 5.05 (br s, 2H, P-C*H*-P), 3.65 (br s, P-C*H*-P). ^{31}P NMR δ: 33 (br s, dppm). ^{1}H NMR (acetone-d_6, –50°C) δ: 8.6 (s, 1H, *H*COO), 8.4 (m, 1H, PhC*H*-CH), 5.4 (dd, 1H, ^3J (H-H) = 14 Hz, ^3J (P-H) = 10 Hz, PhCH-C*H*), 5.6 (d, 2H, *J* (H-H) = 7 Hz, *Ph*CHCH), 6.44 (t, 2H, *J* (H-H) = 7 Hz, *Ph*CHCH), 6.8 (t, 1H, *J* (H-H) = 7 Hz, *Ph*CHCH), 4.7, 4.4, 4.3, 3.2 (m, each 1H, P-C*H*-P). ^{31}P NMR δ: 49.3 (ddd, *J* (P^a-P^b) = 56 Hz, *J* (P^a-P^c) = 237 Hz, *J* (P^a-P^d) = 30 Hz, P^a), 35.1 (ddd, *J* (P^a-P^b) = 56 Hz, *J* (P^b-P^c) = 38 Hz, *J* (P^b-P^d) = 267 Hz, P^b), 32.6 (ddd, *J* (P^a-P^c) = 237 Hz, *J* (P^b-P^c) = 30 Hz, *J* (P^c-P^d) = 73 Hz, P^c), 30.9 (ddd, *J* (P^a-P^d) = 30 Hz, *J* (P^b-P^d) = 267 Hz, *J* (P^c-P^d) = 73 Hz, P^d).

Structure determination

Crystals of $[(CO)_2Ru(\mu\text{-}dppm)_2(\mu\text{-}CHCHPh)Ru(CO)_2]\text{-}[HCOO]\cdot 1.5CH_2Cl_2\cdot 0.5C_5H_{12}\cdot 0.5H_2O$ were grown from CH_2Cl_2–pentane. A yellow block was mounted on a glass fibre at dry ice temperature. Data were collected at 200 K using a Nonius Kappa-CCD diffractometer using COLLECT software (20). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (21) and no other absorption corrections were applied. The SHELXTL 5.101 (22) program package was used to solve the structure by direct methods and refinement was by successive difference Fouriers. All non-hydrogen atoms were refined with anisotropic thermal parameters. One formate anion was poorly behaved and the C—O bond distances were fixed. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. There were several disordered solvent molecules in the lattice, and these were modeled isotropically and with partial occupancies. The crystal data and refinement parameters are listed in Table 2. The crystal was of poor quality, with disordered anion and solvent molecules, but the structure of the cations was well-defined.

Table 2. Crystal data and structure refinement for **7**$[HCO_2]\cdot 1.5CH_2Cl_2\cdot 0.5C_5H_{12}\cdot 0.5\ H_2O$.

Empirical formula	$C_{67}H_{60.75}Cl_3O_{6.50}P_4Ru_2$
Formula weight	1403.78
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Cell dimensions	
a (Å)	14.8925(9)
b (Å)	21.6229(15)
c (Å)	23.2355(14)
α (°)	109.723(3)
β (°)	101.557(3)
γ (°)	100.677(3)
Volume (Å^3)	6636.0(7)
Z	4
Density (calculated) (mg m^{-3})	1.405
Absorption coefficient (mm^{-1})	0.722
F(000)	2858
Crystal size (mm^3)	0.46 × 0.14 × 0.11
θ range for data collection (°)	2.58–30.15
Refl., ind. refl.	72 876, 34 486 (*R*(int) = 0.0980)
Absorption correction	Scalepack
Max and min transmission	0.9248 and 0.7324
Data / restraints / parameters	34 486 / 22 / 1493
Goodness-of-fit on F^2	1.014
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.1131, *wR*2 = 0.2807
Largest diff. peak and hole (e Å^{-3})	1.591 and –0.769

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