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Reactivity of a coordinatively unsaturated diruthenium hydride: reversible insertion of alkynes

Yuan Gao, Michael C. Jennings and Richard J. Puddephatt *
Department of Chemistry, University of Western Ontario, London, Canada N6A.
E-mail: pudd@uwo.ca

Received 16th October 2002, Accepted 20th November 2002
First published as an Advance Article on the web 11th December 2002

The chemistry of the coordinatively unsaturated hydridodiruthenium complex cation $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}dppm)_2]^+$, **1**, is described. Complex **1** adds CO to give $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]^+$, reacts with hydrogen to give $[Ru_2(\mu\text{-}H)_2(CO)_4(\mu\text{-}dppm)_2]$ and H^+ and, in the presence of Et_3N, is an efficient catalyst for decomposition of formic acid to CO_2 and H_2. Complex **1** reacts easily with acetylene to give $[Ru_2(\mu\text{-}CH{=}CH_2)(CO)_4(\mu\text{-}dppm)_2]^+$, with PhCCH to give the coordinatively unsaturated alkenyl complex $[Ru_2\{C(Ph){=}CH_2\}(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)_2]^+$ which then rearranges to the isomeric, coordinatively saturated complex $[Ru_2(E\text{-}\mu\text{-}CH{=}CHPh)(CO)_4(\mu\text{-}dppm)_2]^+$, and reacts reversibly with PhCCPh to give $[Ru_2\{Z\text{-}C(Ph){=}CHPh\}(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)_2]^+$.

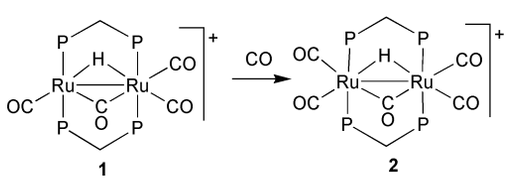
Introduction

Coordinatively unsaturated hydride complexes are of interest because of their important role in homogeneous catalysis.[1] There are still relatively few coordinatively unsaturated binuclear hydrides, though there is clearly potential for interesting chemistry and catalysis with such compounds, as shown for the cationic diruthenium hydride $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}PNP)_2]^+$, PNP=RN{P(OR)$_2$}$_2$.[2] The related dihydrido complex with more robust $Ph_2PCH_2PPh_2$ (dppm) ligands, $[Ru_2(\mu\text{-}H)(H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$, is formed as an intermediate in the interconversion of HCO_2H and H_2/CO_2 using $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ as catalyst,[3] and in the catalytic transfer hydrogenation of internal alkynes using formic acid as the hydrogen source.[4] However, its chemistry has not been studied extensively because it could not be isolated in good yield from these reactions. Recently, the reaction of $MeOSO_2CF_3$ with $[Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2]$ was shown to give ethylene and the coordinatively unsaturated 32-electron complex $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}dppm)_2][O_3SCF_3]$,[5] **1**, in good yield. The chemistry of this coordinatively unsaturated hydridodiruthenium complex is described in this paper.

Results and discussion

The reactions of complex 1 with CO and H_2

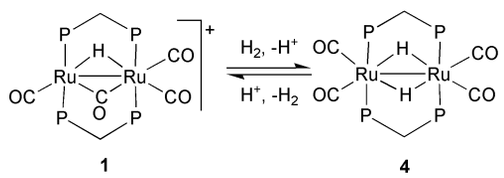
Carbon monoxide reacted rapidly with the coordinatively unsaturated hydride $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}dppm)_2]^+$, **1**, to give the 34-electron complex $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]^+$, **2**, according to eqn. (1). Complex **2** can be formed independently by protonation of the complex $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$, **3**.[3,6]



(1)

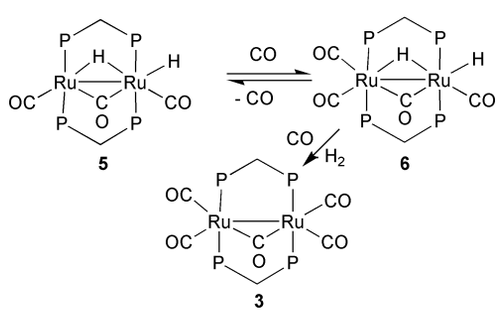
Complex **1** reacted reversibly with hydrogen to give the known dihydride complex $[Ru_2(\mu\text{-}H)_2(CO)_4(\mu\text{-}dppm)_2]$, **4**,[3] according to eqn. (2). The reaction was readily monitored by NMR and it was shown that higher pressure of hydrogen gave faster, more complete reaction, but no intermediates were detected.

Complex **4** is coordinatively saturated and it failed to react with CO under mild conditions. In contrast, the coordinatively



(2)

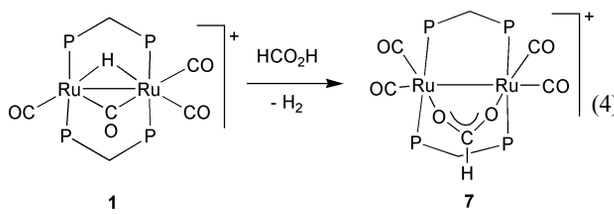
unsaturated dihydride $[Ru_2(\mu\text{-}H)(H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$, **5**, reacts with CO to give hydrogen and complex **3**.[5] It is likely that CO reacts with **5** to give the adduct **6**, which is an isomer of **4**, and which then eliminates hydrogen as shown in eqn. (3).



(3)

The reaction of 1 with formic acid

Complex **1** reacted slowly with HCO_2H in either CD_2Cl_2 or acetone-d_6 solution at room temperature to give the known complex cation $[Ru_2(\mu\text{-}HCO_2)(CO)_4(\mu\text{-}dppm)_2]^+$, **7**,[3] according to eqn. (4). The catalytic decomposition of formic acid did not occur under these conditions.[3]

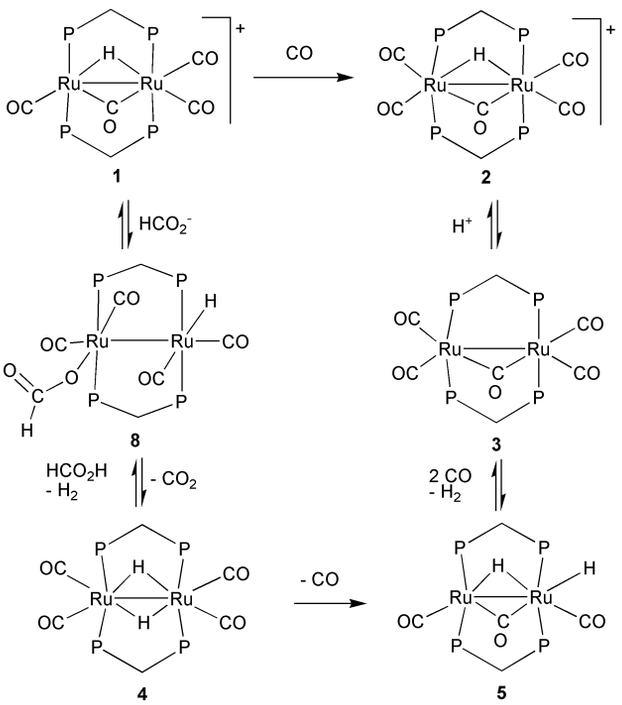


(4)

However, in the presence of the base triethylamine, complex **1** was an excellent catalyst for decomposition of $H^{13}CO_2H$ in acetone-d_6 at room temperature to give H_2 and $^{13}CO_2$ as determined by ^{1}H and ^{13}C NMR. When reaction was complete, the ruthenium products were **1**, **2**, **3**, **4**, **5** and $[Ru_2(HCO_2)(H)(CO)_4(\mu\text{-}dppm)_2]$, **8**,[3] in approximate ratio **1** : **2** : **3** : **4** : **5** : **7** = 1 : 0.4 : 0.5 : 0.25 : 0.2 : 0.6 as determined from integration of the ^{31}P{H} NMR spectrum. The catalyst remained active for decomposition of more formic acid. When monitored by NMR

DOI: 10.1039/b210171h

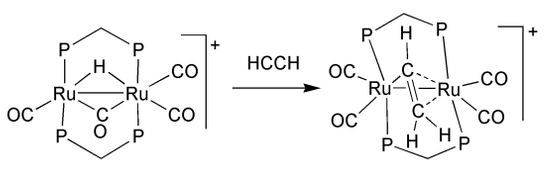
at −25 °C, the above reaction was slow and only traces of complex **4** could be detected along with **1**. At −10 °C, the formation of **4** proceeded faster and $^{13}CO_2$ and hydrogen were detected. At 5 °C, the catalytic decomposition of formic acid proceeded much faster and no formic acid could be detected after 30 minutes. The ruthenium complexes **1**–**5** and **8** were all present at completion of the reaction. The catalysis is known to be retarded by CO and by acid, so the use of a coordinatively unsaturated catalyst under basic conditions is optimal for high catalytic activity. Possible reactions for interconversion of the complexes observed during and after catalysis are shown in Scheme 1.



Scheme 1

Reactions of complex 1 with alkynes

The reaction of complex **1** with the alkynes HCCH, PhCCH and PhCCPh were studied and each gave a different reaction. The reaction of **1**, as the triflate salt, with HCCH in toluene solution occurred with immediate precipitation of a yellow solid, that was characterized as $[Ru_2(\mu\text{-}HC{=}CH_2)(CO)_4(\mu\text{-}dppm)_2][CF_3SO_3]$, **9**$[CF_3SO_3]$, according to eqn. (5).



(5)

The molecular structure of the cation **9** is shown in Fig. 1, and selected bond distances and angles are summarized in Table 1. The structure contains a *trans*,*trans*-$Ru_2(\mu\text{-}dppm)_2$ unit with the $Ru_2P_4C_2$ atoms in the boat conformation. There are four terminal carbonyl ligands which lie roughly in a plane perpendicular to the Ru_2P_4 plane. The vinyl group is σ-bonded to Ru(1) [Ru(1)–C(3) = 2.056(7) Å] and π-bonded to Ru(2) [Ru(2)–C(3) = 2.294(6), Ru(2)–C(4) = 2.289(6) Å]. The bond distance C(3)–C(4) = 1.361(9) Å is close to a normal C=C double bond [1.34 Å] and the angle Ru(1)–C(3)–C(4) = 129.9(5)°. The distance Ru(1)–Ru(2) = 2.8777(7) Å is consistent with a metal–metal single bond.[6] The μ-vinyl group acts as a three-electron ligand and the complex is coordinatively saturated, with structural features similar to those of other μ-alkenyl complexes.[2,4]

Table 1 Selected bond distances (Å) and angles (°) for complex **9**

Ru(1)–C(11)	1.880(6)	Ru(2)–P(4)	2.356(1)
Ru(2)–C(21)	1.897(7)	Ru(1)–C(3)	2.056(7)
Ru(1)–C(10)	1.920(7)	Ru(2)–C(3)	2.294(6)
Ru(2)–C(20)	1.892(8)	Ru(1)–Ru(2)	2.8777(7)
Ru(1)–P(1)	2.353(2)	Ru(2)–C(4)	2.289(6)
Ru(2)–P(2)	2.377(2)	C(3)–C(4)	1.361(9)
Ru(1)–P(3)	2.363(2)		
P(1)–Ru(1)–P(3)	178.79(6)	P(4)–Ru(2)–Ru(1)	93.68(4)
P(2)–Ru(2)–P(4)	173.63(5)	C(4)–C(3)–Ru(1)	129.9(5)
P(1)–Ru(1)–Ru(2)	90.34(4)	C(4)–C(3)–Ru(2)	72.5(4)
P(2)–Ru(2)–Ru(1)	91.10(4)	Ru(1)–C(3)–Ru(2)	82.6(2)
P(3)–Ru(1)–Ru(2)	90.41(4)		

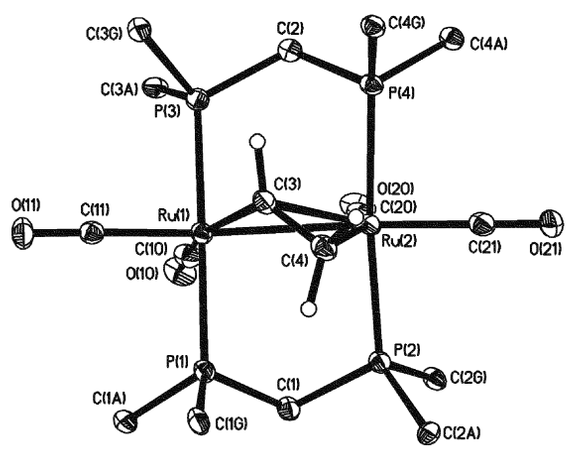


Fig. 1 A view of the structure of the cationic μ-vinyl complex **9**. Only the *ipso* carbon atoms of the phenyl groups are shown for clarity.

The low symmetry of complex **9**, as determined by the solid state structure, is maintained in solution. Thus, the ^{31}P NMR spectrum at room temperature exhibits an ABCD pattern of peaks indicating that all four phosphorus atoms are inequivalent. Four resonances were observed in the ^1H NMR spectrum for the CH_2P_2 protons (one coupled pair at δ 4.70 and 3.92 and the other at δ 3.92 and 2.98). The vinyl protons were observed at δ 7.60 [RuCH] and 3.98 [overlapping peaks for $=CH_2$ protons], consistent with NMR parameters observed in other μ-alkenyl complexes.[2,4]

When the reaction of complex **1** with acetylene was carried out in CD_2Cl_2 at room temperature, a black material, which was insoluble in common organic solvents, was formed slowly and is presumed to be polyacetylene. Complex **9** in CD_2Cl_2 at room temperature also reacted slowly with acetylene to form this black material. A complex mixture of ruthenium-containing products was formed in each case. The precipitation of complex **9** when the reaction of **1** with acetylene is carried out in toluene solution is probably important, since further reaction with acetylene does not then occur.

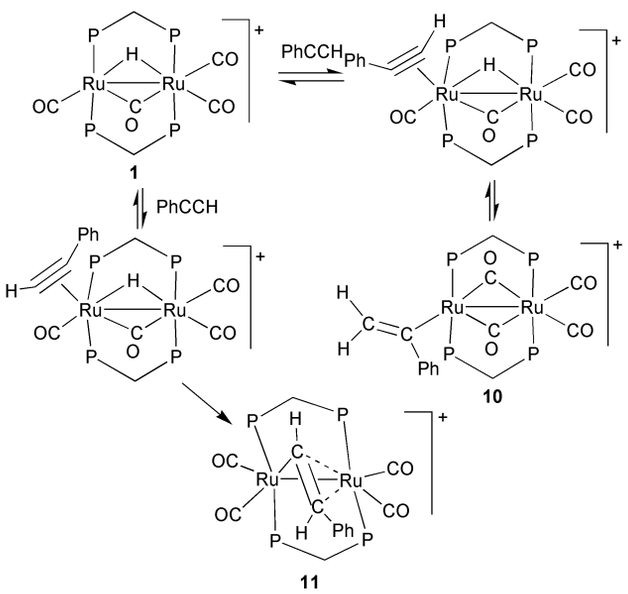
The reaction of phenylacetylene with a solution of **1** in CD_2Cl_2 at room temperature rapidly gave a complex **10** that isomerized to complex **11** over a period of two hours (Scheme 2). These same compounds are formed in the reaction of the coordinatively saturated hydride $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]^+$, **2**, with PhCCH in acetone-d_6 or CD_2Cl_2 but, in this case, the rate of formation of complex **10** is similar to the rate of its rearrangement to **11**. Complex **11** was characterized crystallographically as $[Ru_2(\mu\text{-}CH{=}CHPh)(CO)_4(\mu\text{-}dppm)_2]^+$, and the intermediate complex, **10**, was tentatively (and erroneously) characterized as $[Ru_2(\mu\text{-}CPhCH_2)(CO)_4(\mu\text{-}dppm)_2]^+$.[4] In the present work, the reaction of complex **1** with PhCCH in toluene solution led to precipitation of complex **10** and so it could be isolated in pure form for the first time, and so characterized more completely.

The IR spectrum of **10** exhibited two peaks at 2060 and 2016 cm^{-1} and one strong peak at 1730 cm^{-1}, indicating the presence

Table 2 Selected NMR data for complexes **10** and **12**

Complex	**10**	**12**
$\delta(CH^aH^bP_2)$	3.20, 3.32	3.20, 3.37
δ(RuC=C*H*)	4.72, 5.44	6.02
δ(RuC*Ph*)	6.17(*o*), 6.58(*m*), 6.66(*p*)	6.07(*o*), 6.68(*m*), 6.80(*p*)
$\delta(CH^aH^bP_2)$	26	26
δ(RuC=*C*H)	111.6	127.8
δ(Ru*C*Ph)	185	182
δ(RuC*Ph*)	144(*i*), 126(*o*), 127(*m*), 125(*p*)	144(*i*), 128(*o*), 128(*m*), 125(*p*)
δ(Ru*C*O)	194, 195	194, 195.5
$\delta(Ru_2$–μ-*C*O)	253, 259	253, 260
δ(Ru*P*)	25.0, 26.8	22.9, 24.2

[a] The alkenyl and phenyl carbon assignments were confirmed by the $^1H^{13}C$ correlated gHSQC and gHMBC spectra. [b] Carbonyl resonances were identified by using ^{13}CO enriched samples.



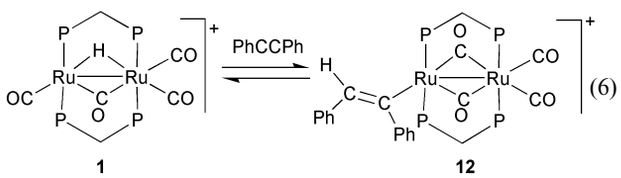
Scheme 2

of both terminal and bridging carbonyl ligands. Furthermore, the $^{13}C\{H\}$ NMR spectrum of a ^{13}CO labeled sample of **10** displayed two multiplets at δ 259.2 and 252.6, in the range for bridging CO, and two multiplets δ 194.8 and 194.4, in the range for terminal CO. Since there are two bridging carbonyl ligands, the styryl group cannot be bridging as previously proposed.[4] The styrenyl protons of the RuC(Ph)=CH_2 group appear as singlets in the ^1H NMR at δ 4.72 and 5.44, and both are directly bonded to an alkenyl carbon at δ = 111.6. The RuC(Ph)= carbon resonance was observed at δ 185, with no directly attached protons. These NMR parameters are consistent with a one-electron, but not with a three-electron, alkenyl group, for which δ(α-C) = 220–300 and δ(β-C) < 80.[7] For comparison, the complex Tp^N(CO)(PhCCH)W(η^1-C(Ph)=CH_2) gives δ(α-C) = 161.8 and δ(β-C) = 119.9 for the W(η^1-CPh=CH_2) group.[7]

The mechanism described in Scheme 2 requires that the formation of the σ-alkenyl complex **10** [RuC(Ph)=CH_2] be reversible in order to allow the rearrangement to the isomeric σ,π-alkenyl complex **11** [*E*-RuCH=CHPh]. It is likely that the α-phenyl substituent in **10** prevents formation of the σ,π-alkenyl because of steric hindrance with the phenyl substituents of the dppm ligands.

The reaction of PhCCPh with a solution of **1** in CD_2Cl_2 was reversible and gave an equilibrium between the starting materials and a new alkenyl complex [Ru_2(η^1-CPh=CHPh)-(μ-CO)$_2$(CO)$_2$(μ-dppm)$_2$]$^+$, **12**, according to eqn. (6).

Solutions containing **12** as the only detectable ruthenium complex could be prepared by using a large excess of PhCCPh, but efforts to isolate pure **12** or to grow crystals from this solution were unsuccessful and always resulted in the regeneration



(6)

of the precursor complex **1**. The structure of **12** was therefore established by comparing its NMR parameters with those of complex **10** (Table 2). The alkenyl hydrogen was located at δ 6.02, while the alkenyl carbon atoms were at δ 182 (α-C) and 127.8 (β-C), in the range expected for η^1-alkenyl groups. Two resonances were observed for the $CH^aH^bP_2$ protons in the ^1H NMR and two signals for the dppm phosphorus atoms in the ^{31}P NMR, indicating that the complex has effective C_s symmetry. There were two bridging and two terminal carbonyl resonances, very similar to those in **10**.

The equilibrium constant was determined as K = 3.8 M^{-1}, from the equilibrium concentrations of **1**, **12** and PhCCPh, which were determined by NMR. Although easy insertion of an alkyne into a Ru–H bond is well-known, the direct observation of an equilibrium between the hydride + alkyne and the alkenyl complex is rare.[2–8] No further rearrangement of **12** to form a bridging alkenyl complex analogous to **11** was observed, presumably because steric effects prevent it.

Discussion

Complex **1** has the properties of a coordinatively unsaturated (32-electron) binuclear compound. It easily adds CO to give the 34-electron complex **2** (eqn. (1)) and reacts with hydrogen to give the neutral dihydridodiruthenium complex **4** (eqn. (2)). In the presence of base, it is an excellent catalyst for decomposition of formic acid. Its reactions with alkynes are particularly interesting as shown in eqns. (5) and (6) and in Scheme 2. The reactivity pattern can be understood in terms of the steric environment created by the *trans*,*trans*-[Ru_2(μ-dppm)$_2$] unit. Other ligands tend to lie in the plane containing the RuRu axis and perpendicular to the Ru_2P_4 plane in order to avoid steric interactions with the phenyl substituents of the dppm ligands. The vinyl group in complex **9** is readily accommodated in the bridging position and no other isomers are observed. Phenylacetylene can approach the vacant site in complex **1** in two orientations as shown in Scheme 2 and, once coordinated, cannot rotate due to steric hindrance. The favored orientation evidently leads to the kinetic product **10**, having a one-electron alkenyl ligand. The α-phenyl substituent is bulky and formation of the three-electron μ-alkenyl group, in which the alkenyl group must lie across the Ru–Ru axis, is prevented by phenyl–phenyl steric repulsions. In principle, it could form a three-electron vinyl group at a single ruthenium center, but the NMR data clearly show that it does not.[7] Complex **10** slowly isomerizes to **11**, in which the β-phenyl substituent can be accommodated in the μ-alkenyl group, and so allows coordinative

saturation. The isomerization must presumably occur by a β-elimination-reinsertion process as shown in Scheme 2. The reversibility of the insertion reaction is shown directly in the reaction of complex **1** with diphenylacetylene, which forms only the one-electron alkenyl derivative **12**. Such easy reversible insertion of alkynes is rare and this appears to be the only known example in ruthenium hydride chemistry.[2–8]

Experimental

All manipulations were carried out under a dry nitrogen atmosphere using either standard Schlenk techniques or a glove box. Toluene was dried by distillation from sodium-benzophenone and CH_2Cl_2 was distilled from CaH_2. $[Ru_2(\mu\text{-}CO)(\mu\text{-}H)(CO)_3(\mu\text{-}dppm)_2][OSO_2CF_3]$, **1**$[OSO_2CF_3]$, was synthesized according to the published procedure.[5] NMR spectra were recorded using Varian INOVA 600 or 400 or a Mercury 400 spectrometer. IR spectra were recorded by using a Perkin-Elmer FTIR 2000 spectrometer.

The reaction of 1 with CO

A stream of CO was passed through a solution of **1** (10 mg, 0.008 mmol) in CD_2Cl_2 (0.5 mL) in a septum-sealed NMR tube for one minute, giving a color change from orange–red to orange–yellow. The product $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$-[OTf], **2**[OTf], was identified by its ^1H and ^{31}P NMR spectra as the only ruthenium complex in solution, by comparison with an authentic sample.[3]

The reaction of 1 with H_2

A stream of H_2 was bubbled through a solution of **1** (10 mg, 0.008 mmol) in CD_2Cl_2 (0.5 mL) in a septum-sealed NMR tube for 5 min. A slow transformation of **1** to $[Ru(\mu\text{-}H)_2(CO)_4$-$(\mu\text{-}dppm)_2]$, **4**, identified by its NMR spectrum,[3] occurred.

The reaction of 1 with HCO_2H

To a solution of **1** (10 mg, 0.008 mmol) in CD_2Cl_2 (0.5 mL) in a septum-sealed NMR tube, was added HCO_2H (1.5 μL, 0.03 mmol) by microsyringe. The color of the solution slowly changed from orange–red to orange–yellow. After 24 h, the product was identified as $[Ru_2(\mu\text{-}HCOO)(CO)_4(dppm)_2]^+$, **7**, by its ^1H and ^{31}P NMR spectra.[3]

The reaction of 1 with HCO_2H/Et_3N

To a solution of **1** (10 mg, 0.008 mmol) in acetone-d_6 (0.5 mL) in a septum-sealed NMR tube was added HCO_2H (4 μL, 0.08 mmol) and Et_3N (3.8 μL, 0.03 mmol). Gas evolution was observed immediately, and no formic acid could be detected after 20 min. The known complexes **2**, **4**, $[Ru(\mu\text{-}H)(H)(\mu\text{-}CO)$-$(CO)_2(\mu\text{-}dppm)_2]$, **5**, $[Ru_2(H)(HCOO)(CO)_4(\mu\text{-}dppm)_2]$, **8**, and $[Ru(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$, **3**, along with unreacted **1**, were identified by their ^{31}P NMR spectra.

$[Ru_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}CH_2)(CO)_4(\mu\text{-}dppm)_2][OTf]$, 9[OTf]

A stream of HCCH was bubbled through a solution of **1** (15 mg, 0.012 mmol) in toluene-d_8 (0.5 mL) in a septum-sealed NMR tube for 20 s, to form the product as a pale-yellow precipitate, which was washed with pentane and dried under vacuum. Yield: 11 mg, 73%. IR (Nujol, cm^{-1}): ν(CO) = 2017, 1988, 1948 and 1938. NMR in CD_2Cl_2 at 20 °C: $\delta(^1H)$ = 7.60 [m, 1H, C*H*=CH_2]; 3.98 [overlapping m, 2H, H_2C=CH]; 4.70 [m, 1H, P–C*H*–P], 3.92 [m, 2H, P–CH–P], 2.98 [m, 1H, P–C*H*–P]; $\delta(^{31}P)$ = 49.85 [ddd, $J(P^aP^b)$ = 247, $J(P^aP^c)$ = 50, $J(P^aP^d)$ = 25 Hz, P^a]; 27.85 [ddd, $J(P^aP^b)$ = 247, $J(P^bP^d)$ = 68, $J(P^bP^c)$ = 28 Hz, P^b]; 35.30 [ddd, $J(P^cP^d)$ = 279, $J(P^aP^c)$ = 50, $J(P^bP^c)$ = 28 Hz, P^c]; 32.30 [ddd, $J(P^cP^d)$ = 279, $J(P^aP^d)$ = 25, $J(P^bP^d)$ = 68 Hz, P^d].

Table 3 Crystal data and structure refinement for **9**[OTf]·1.5CH_2Cl_2

Formula, FW	$C_{58.5}H_{49}Cl_3F_3O_7P_4Ru_2S$, 1385.41
Temperature/K	150(2)
Wavelength/Å	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
a/Å	11.2830(8)
b/Å	15.3642(14)
c/Å	18.1169(16)
α/°	87.153(3)
β/°	75.089(4)
γ/°	73.662(4)
Volume/Å^3, *Z*	2911.5(4)
Density (calc.)/Mg m^{-3}	1.580
Absorption coefficient/mm^{-1}, *F*(000)	0.864, 1396
Crystal size/mm	0.20 × 0.18 × 0.05
Reflections, independent reflections	13897, 11530 [*R*(int) = 0.041]
Absorption correction	Integration
Data/restraints/parameters	11530/0/616
R indices [$I > 2\sigma(I)$]	*R*1 = 0.0659, *wR*2 = 0.1691
R indices (all data)	*R*1 = 0.1000, *wR*2 = 0.1855

Polymerization of HC≡CH in the presence of 1

A stream of HCCH was bubbled through a solution of **1** (10 mg, 0.008 mmol) in CD_2Cl_2 (0.5 mL) in a septum-sealed NMR tube for 5 min. A black solid was observed after 0.5 h and increased with time. The solid was isolated by centrifuging. XPS analysis showed only carbon, with Ru and P absent.

$[Ru_2(\eta^1\text{-}PhC{=}CH_2)(CO)_4(\mu\text{-}dppm)_2][OTf]$, 10[OTf]

To a solution of **1** (20 mg, 0.016 mmol) in toluene-d_8 (0.5 mL) in a septum-sealed NMR tube was added PhCCH (3 μL, 0.027 mmol) by microsyringe to give the product as a pale yellow precipitate, which was washed with pentane and dried under vacuum. Yield: 14 mg, 66%. IR (Nujol, cm^{-1}): ν(CO) = 2060 and 2016 (terminal CO); 1730 (bridging CO). Anal. calc. for $C_{63}H_{51}F_3O_7P_4Ru_2S$: C, 56.67; H, 3.85. Found: C, 56.91; H, 3.46%. NMR in CD_2Cl_2 at −10 °C: see Table 2.

$[Ru_2(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHPh)(CO)_4(\mu\text{-}dppm)_2][OTf]$, 11[OTf]

To a solution of **1** (10 mg, 0.008 mmol) in CD_2Cl_2 (0.5 mL) in a septum-sealed NMR tube at room temperature was added PhCCH (2 μL, 0.018 mmol) by microsyringe. After 3 h, complex **11** was the only ruthenium complex present and was identified by its NMR spectra.[4] The same product was formed from a solution of complex **10** in CD_2Cl_2 after 3 h.

$[Ru_2(\eta^1\text{-}CPh{=}CHPh)(CO)_4(\mu\text{-}dppm)_2][OTf]$, 12[OTf]

To a solution of **1** (10 mg, 0.008 mmol) in CD_2Cl_2(0.5 mL) in an NMR tube was added a large excess PhCCPh (54 mg, 0.2997 mmol). There was an immediate color change and the solution was shown to contain complex **12** along with some of the starting material **1** and excess PhCCPh. NMR in CD_2Cl_2 at 20 °C: see Table 2.

Determination of K_{eq} for the reaction of 1 with PhCCPh

To a solution of **1** (38 mg, 0.0308 mmol) in CD_2Cl_2 (0.034 mL) in an NMR tube was added PhCCPh (36 mg, 0.1998 mmol). The solution was set aside for 6 h to ensure that equilibrium was reached. The relative concentrations of **1** and **12** in the equilibrium mixture were determined by integration of the ^1H NMR spectrum for the CH_2P_2 protons, and the absolute concentrations were then determined to give K_{eq} = 3.7 M^{-1}. The same procedure was repeated with varying concentrations of PhCCPh to give the mean value of K_{eq} = 3.8(2) M^{-1}.

Structure determination for complex 9

Crystals of $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)(CO)_4(\mu\text{-}dppm)_2][OTf]\cdot 1.5CH_2Cl_2$ were grown by slow diffusion of pentane into a dichloromethane solution. A crystal was mounted on a glass fiber. Data were collected at 150 K using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. 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 (Nonius, 1998) and no other absorption corrections were applied. The crystal data and refinement parameters are listed in Table 3.

The SHELXTL 5.1 (G. M. Sheldrick, Madison, WI) program package was used to solve the structure by the Patterson method, followed by successive difference Fouriers. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atom.

CCDC reference number 195497.

See http://www.rsc.org/suppdata/dt/b2/b210171h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the NSERC (Canada) for financial support. R. J. P. thanks the Government of Canada for a Canada Research Chair.

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