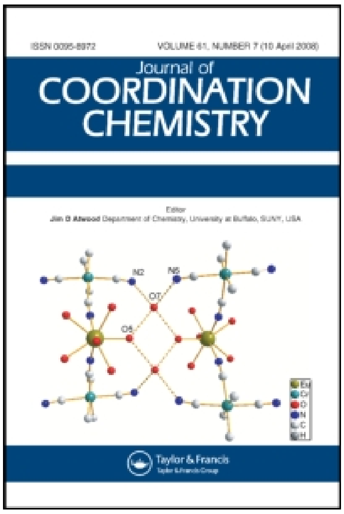

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A BINUCLEAR ALKYNE COMPLEX OF RUTHENIUM

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To cite this Article Mirza, Hameed A. , Vittal, Jagadese J. and Puddephatt, Richard J.(1996) 'A BINUCLEAR ALKYNE COMPLEX OF RUTHENIUM', Journal of Coordination Chemistry, 37: 1, 131 — 139

To link to this Article: DOI: 10.1080/00958979608023546

URL: http://dx.doi.org/10.1080/00958979608023546

J. Coord. Chem., 1996, Vol 37, pp. 131–139
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A BINUCLEAR ALKYNE COMPLEX OF RUTHENIUM

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(Recieved February 20, 1995; in final form June 13, 1995)

The reaction of $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, dppm = $Ph_2PCH_2PPh_2$, with the alkyne $MeO_2CC{\equiv}CCO_2Me$ gives only the dimetallacyclobutene derivative $[Ru_2(CO)_4(\mu\text{-}MeO_2CC{=}CCO_2Me)(\mu\text{-}dppm)_2]$, **5b**, which has been characterized spectroscopically and by an X-ray structure determination [$C_{60}H_{72}O_8P_4Ru_2$, monoclinic, $P2_1/c$, a = 12.534(2), b = 16.236(3), c = 27.094(6) Å, β = 99.93(1)°, Z = 4, R_f, R_w = 0.054, 0.046]. The reaction is particularly simple compared to the complex reaction of $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dmpm)_2]$, dmpm = $Me_2PCH_2PMe_2$, and possible reasons for this are discussed.

KEYWORDS: ruthenium, alkynes, dimetallocyclobutene, dimetallic

INTRODUCTION

The chemistry of alkynes with metal-metal bonded complexes is interesting and often complex.[1] It remains a very active field of research, especially with respect to the reactions of binuclear and cluster complexes of ruthenium with alkynes.[2–11] Some intriguing chemistry has been discovered on reaction of the complexes $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PXP)_2]$, where PXP = $R_2PCH_2PR_2$ or $(RO)_2PNEtP(OR)_2]$ with alkynes.[6,9,12] The reactions of $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dmpm)_2]$, **1a**, with $MeO_2CC{\equiv}CCO_2Me$ are shown in Scheme (1) [PP = dmpm = $Me_2PCH_2PMe_2$, R = CO_2Me], and are of particular interest because the alkyne adds without loss of CO.[9] The initial reaction occurs rapidly to give an adduct tentatively characterized as **2**, which then reacts with more alkyne to give **3**. A slower reaction occurs in which alkyne is lost and **4** is formed, presumably by isomerization of **2**. Finally, when heated to 90°C, **4** loses CO to give **5a**. In contrast, the complexes $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PXP)_2]$, where PXP = dppm = $Ph_2PCH_2PPh_2$ or $(RO)_2PNEtP(OR)_2]$ react with $HC{\equiv}CH$ with loss of CO to give **6** (Scheme 2) and, when PXP = dppm, a *subsequent* reaction with CO may occur to give **7**.[6,12] Heating **7** caused loss of CO with formation of **6**, when PP = dppm (Scheme 2).[12] Thus, although similar products may be formed in Schemes (1) and (2), the mechanisms of reactions are clearly different. From this work, it is not clear if the above differences are caused primarily by the different diphosphine ligands or by the different alkynes used. Therefore a study of the reaction of $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}$

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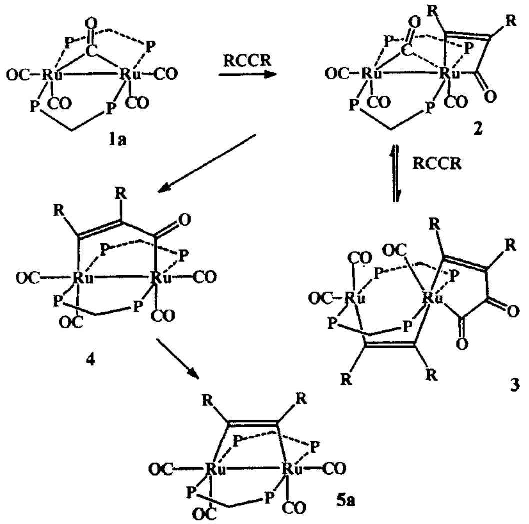
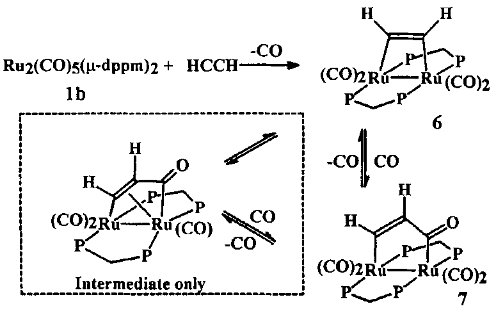
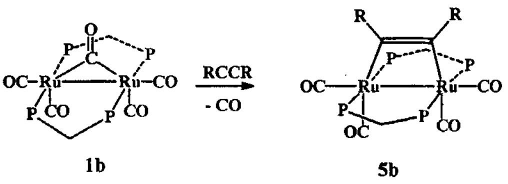


(1)



(2)



(3)

dppm)$_2$], **1b**,[13,14] with the alkyne $MeO_2CC{\equiv}CCO_2Me$ has been carried out to provide a more direct comparison of the reactivity as a function only of the supporting diphosphine ligand. The reaction is particularly simple and is summarized in Scheme (3), PP = dppm.

EXPERIMENTAL

General methods and the synthesis of [$Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$] have been reported elsewhere.[12,13]

Synthesis of $[Ru_2(CO)_4(\mu\text{-}MeO_2CCCCO_2Me)(\mu\text{-}dppm)_2]$

To a solution of $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$(0.28 g) in CH_2Cl_2 (10 cm^{-3}) was added $MeO_2CC{\equiv}CCO_2Me$ (0.043 cm^3) in CH_2Cl_2 (2 cm^3). The mixture was stirred for 18 h at room temperature, the solvent was evaporated and the yellow product was recrystallized from CH_2Cl_2/EtOH and dried under vacuum. Yield 85%. MP 174–176°C (decomp.) *Anal.* Calc. for $C_{60}H_{50}O_8P_4Ru_2$: C, 58.8; H, 4.1. Found: C, 58.1; H, 4.4%. IR: $\upsilon_{C\equiv O}$ = 2000(s), 1955(vs), 1940(vs), 1909(s); $\upsilon_{C=O}$ = 1696(m), 1666(m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.36 (m, 2H, CH_2), 4.76 (m, 2H, CH_2), 2.68 [s, 6H, CH_3]. ^{31}P NMR (CD_2Cl_2): δ 25.5 (s, dppm). FAB-MS: M/Z 1227 (*P*), 1199 (*P*-CO), 1171 (*P*-2CO), 1143 (*P*-3CO).

X-ray Structure Determination

Single crystals were formed by diffusion of *n*-hexane into a solution of **5b** in CH_2Cl_2/C_6H_6. A crystal (with dimensions 0.23×0.24×0.45 mm) was wedged into a Lindemann capillary tube and flame sealed. The data collection was carried out using an Enraf-Nonius CAD4F diffractometer with graphite monochromated Mo Kα radiation[15] at 23°C. Photo and automatic indexing routines, followed by least squares fits of 21 accurately centered reflections ($24.0 \leq 2\theta \leq 29.5°$), gave cell constants and an orientation matrix. Intensity data were recorded in ω mode, at variable scan speeds (1.18 to 4.12 $deg.min^{-1}$) and a scan width of $0.75 + 0.35\tan\theta$, with a maximum time per datum of 60 s. Three standard reflections were monitored every 120 min. of X-ray exposure time. In all 7733 reflections in the 2θ range 2–45° ($-13 \leq h \leq 13$, $-1 \leq k \leq 17$, $-29 \leq l \leq 1$) were recorded. The data were processed using the NRCVAX crystal structure programs.[16] An empirical absorption correction[17] was applied to the data based on *psi* scans (ψ = 0→360° every 10°) for χ values near 90°. Seven sets of reflections with σ ranging from 5.5 to 11.0° gave an absorption profile with maximum and minimum tranmission values 0.8513 and 0.7913. The Niggli matrix, and symmetry equivalent reflec-

Table 1 Crystal Data and Experimental Details

compound, formula weight	$C_{60}H_{72}O_8P_4Ru_2$, 1247.26
crystal system, space group	Monoclinic, *P*2$_1$/*c* (No. 14)
temperature	23°C
cell dimensions	*a* = 12.534(2), Å *b* = 16.236(3), Å *c* = 27.094(6), Å β = 99.93(1)°
cell volume (Å^3), *Z*	5431(2), 4
density, $g.cm^{-3}$ obs., calc.	1.49(3), 1.524
F(000)	2576
diffractometer, monochromator	Enraf Nonius CAD4F; graphite
radiation, wavelength (Å)	Mo Kα, 0.71073
abs coeff (cm^{-1})	7.2
no. of observ., variables	4580($I \geq 2.5\sigma(I)$), 332
final model; R_f and R_w	0.054, 0.046
GOF	2.88

$R_f = (\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)$

$R_w = [\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

GOF,S = $\Sigma w(|Fo|-|Fc|)^2$/(no. of reflections - no. of parameters)]$^{1/2}$

tions indicated the Laue symmetry 2/m and the systematic absences[18] suggested that the space group was $P2_1/c$. The correctness of the choice of the space group was confirmed by successful solution and refinement of the structure. The equivalent reflections were averaged leaving 7094 independent reflections. The structure solution and the refinements were done by full-matrix least-squares techniques on F. Anisotropic thermal parameters were assigned and refined for all the non-benzene ring atoms. All the hydrogen atoms were placed in ideal positions (C-H = 1.08 Å) and their thermal parameters were allowed to ride 10% more on the attached carbon atoms. In the final cycles, the refinement of 332 parameters and 4580 ($I \leq 2.5\sigma(I)$) observations, the model converged at R_f = 0.054, R_w = 0.046 and GOF = 2.88 using a weighting scheme based on counting statistics. In the final difference Fourier synthesis, peaks ranged from 0.881 to −1.07 e.Å^{-3}. The maximum shift/sigma ratio was 0.027. The secondary extinction was refined (0.79(2)). Experimental and crystal data are summarized in Table 1, while atomic coordinates are given in Table 2.

RESULTS AND DISCUSSION

The reaction of $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-dppm})_2]$,**1b**,[13] with the alkyne $MeO_2CC{\equiv}CCO_2Me$ is shown in scheme (3) in which PP = dppm and R = CO_2Me. The reaction occurs within a few minutes at room temperature and no intermediates were detected when the reaction was monitored by ^1H and ^{31}P NMR. The product **5b** did not react with CO under mild conditions. Complex **5b** was also formed in high yield by reaction of either $[Ru_2(CO)_4(\mu\text{-}HCCH)(\mu\text{-dppm})_2]$, **6**, or $[Ru_2(CO)_4(\mu\text{-}HCCHCO)(\mu\text{-dppm})_2]$, **7**, with $MeO_2CC{\equiv}CCO_2Me$. The reaction with **6** or **7** occurs with displacement of $HC{\equiv}CH$ or a mixture of $HC{\equiv}CH$ and CO respectively. Since **7** is already known to convert to **6** and CO,[12] these reactions prove that one alkyne can displace another in these complexes. The electron withdrawing CO_2Me substituents lead to greater thermal stability and lower reactivity of **5b** compared to **6**. The mechanism of displacement of $HC{\equiv}CH$ from **6** is not clear, but it is presumed to be associative since the reaction occurs much faster than decomposition of **6**.

Complex **5b** is an air stable, yellow solid. It was characterized spectroscopically and by an X-ray structure determination. In the IR, the values of $\nu(C{\equiv}O)$ are in the range 2000–1909 cm^{-1} compared to 1995–1879 cm^{-1} for **6** and 1996–1883 cm^{-1} for **1b**. The somewhat higher frequencies for **5b** are presumably a reflection of the greater electron withdrawing ability of the $\mu\text{-}C_2(CO_2Me)_2$ ligand compared to $\mu\text{-}C_2H_2$ or μ-CO. The ^1H NMR spectrum contains a single resonance for the MeO protons but two resonances for the $P_2CH^aH^b$ protons, while the ^{31}P NMR spectrum contains only a singlet due to the phosphorus atoms of dppm. The FAB-MS contained an envelope of peaks of low intensity at M/Z 1227 due to the parent ion of **5b** and intense peaks centred at 1199 (*P-CO*), 1171 (*P*-2CO) and 1143 (*P*-3CO), due to sequential loss of carbonyl ligands. These spectra clearly support the proposed structure of **5b**.[6,9,12]

The structure of **5b** is illustrated in Figure 1, and is characterized by the bond distances and angles in Table 3. The core contains a *trans, trans*-$Ru_2(\mu\text{-dppm})_2$ unit, with each Ru_2P_2C ring in the envelope conformation with the CH_2 flaps directed towards the μ-alkyne ligand. In this conformation, the steric effects of the phenyl substituents are minimized on the side of the $Ru_2(\mu\text{-dppm})_2$ unit where the bulkier

Table 2 Atomic Positional and Thermal Parameters.

Atom	*x*	*y*	*z*	B_{iso}
Ru(1)	0.17396(6)	0.21015(5)	0.41753(3)	2.30(4)
Ru(2)	0.15665(7)	0.32414(6)	0.33102(3)	3.15(4)
P(1)	0.31236(2)	0.29324(17)	0.46150(10)	2.58(12)
P(2)	0.03505(20)	0.13187(17)	0.36989(10)	2.59(12)
P(3)	0.05328(20)	0.22915(17)	0.27780(10)	2.63(12)
P(4)	0.30250(19)	0.40125(17)	0.37100(10)	2.53(13)
C(1)	0.0792(8)	0.2460(6)	0.4595(4)	3.3(5)
C(2)	0.2243(8)	0.1194(7)	0.4558(4)	3.4(5)
C(3)	0.1543(8)	0.3958(7)	0.2767(4)	3.4(5)
C(4)	0.0472(8)	0.3697(7)	0.3627(4)	3.2(5)
C(5)	0.5114(8)	0.0527(8)	0.4142(5)	6.0(7)
C(6)	0.3483(8)	0.1089(7)	0.3703(4)	3.4(6)
C(7)	0.2791(7)	0.1818(6)	0.3646(4)	2.7(5)
C(8)	0.2769(7)	0.2334(6)	0.3273(4)	2.5(5)
C(9)	0.3465(8)	0.2248(7)	0.2881(4)	3.0(5)
C(10)	0.3981(9)	0.2773(8)	0.2149(4)	5.9(7)
C(11)	0.0470(7)	0.1264(6)	0.3045(3)	2.7(5)
C(12)	0.3905(7)	0.3456(6)	0.4208(4)	2.7(5)
O(1)	0.0260(6)	0.2650(5)	0.4883(3)	5.7(5)
O(2)	0.2540(6)	0.0616(5)	0.4799(3)	5.6(5)
O(3)	0.1465(7)	0.4438(5)	0.2464(3)	6.4(5)
O(4)	-0.0193(6)	0.4017(5)	0.3793(3)	4.9(4)
O(5)	0.4428(5)	0.1223(4)	0.4010(3)	4.3(4)
O(6)	0.3243(6)	0.0409(5)	0.3530(3)	5.3(5)
O(7)	0.3303(5)	0.2823(5)	0.2530(3)	4.4(4)
O(8)	0.4151(5)	0.1733(5)	0.2891(3)	5.2(4)
C(111)	0.2810(5)	0.3780(3)	0.5020(2)	2.6(2)
C(112)	0.3605(4)	0.4035(4)	0.5416(2)	3.1(2)
C(113)	0.3414(4)	0.4707(4)	0.5709(2)	4.2(3)
C(114)	0.2428(5)	0.5125(3)	0.5606(2)	4.4(3)
C(115)	0.1634(4)	0.4871(4)	0.5210(2)	4.1(3)
C(116)	0.1825(4)	0.4198(4)	0.4917(2)	3.5(2)
C(121)	0.4142(5)	0.2365(4)	0.5047(2)	2.9(2)
C(122)	0.5162(5)	0.2191(4)	0.4934(2)	4.0(2)
C(123)	0.5910(4)	0.1743(4)	0.5271(3)	5.6(3)
C(124)	0.5638(5)	0.1469(4)	0.5721(2)	5.7(3)
C(125)	0.4617(6)	0.1643(4)	0.5834(2)	5.6(3)
C(126)	0.3869(4)	0.2091(4)	0.5497(3)	4.8(3)
C(211)	-0.1083(4)	0.1553(4)	0.3654(2)	3.2(2)
C(212)	-0.1460(5)	0.2283(4)	0.3835(2)	4.1(3)
C(213)	-0.2570(6)	0.2437(4)	0.3771(3)	6.4(3)
C(214)	-0.3303(4)	0.1863(5)	0.3526(3)	6.3(3)
C(215)	-0.2926(5)	0.1133(4)	0.3345(2)	5.9(3)
C(216)	-0.1816(6)	0.0978(3)	0.3409(2)	4.4(3)
C(221)	0.0381(5)	0.0249(3)	0.3899(2)	2.6(2)
C(222)	0.1066(4)	-0.0317(4)	0.3725(2)	3.1(2)
C(223)	0.1197(4)	-0.1103(4)	0.3935(2)	4.1(3)
C(224)	0.0642(5)	-0.1322(3)	0.4320(2)	4.6(3)
C(225)	-0.0043(5)	-0.0756(4)	0.4494(2)	4.8(3)
C(226)	-0.0174(4)	0.0030(4)	0.4284(2)	4.0(2)
C(311)	0.0993(5)	0.2037(4)	0.2182(2)	3.0(2)
C(312)	0.1428(5)	0.1268(4)	0.2100(2)	5.1(3)
C(313)	0.1779(5)	0.1103(3)	0.1649(3)	6.1(3)
C(314)	0.1695(5)	0.1708(5)	0.1279(2)	5.3(3)
C(315)	0.1261(5)	0.2477(4)	0.1360(2)	4.4(3)

Table 2 (Continued)

C(316)	0.0909(4)	0.2642(3)	0.1811(3)	3.7(2)
C(321)	-0.0857(4)	0.2593(4)	0.2523(2)	2.7(2)
C(322)	-0.1156(4)	0.3418(3)	0.2543(2)	3.2(2)
C(323)	-0.2178(5)	0.3675(3)	0.2306(2)	4.1(2)
C(324)	-0.2903(4)	0.3106(4)	0.2048(2)	4.0(2)
C(325)	-0.2604(5)	0.2281(4)	0.2028(2)	4.9(3)
C(326)	-0.1582(5)	0.2024(3)	0.2265(2)	4.2(2)
C(411)	0.4029(4)	0.4352(4)	0.3328(2)	2.7(2)
C(412)	0.4946(5)	0.3882(3)	0.3294(2)	3.5(2)
C(413)	0.5708(4)	0.4171(4)	0.3016(2)	4.2(3)
C(414)	0.5553(5)	0.4929(4)	0.2772(2)	4.7(3)
C(415)	0.4636(5)	0.5399(3)	0.2806(2)	5.0(3)
C(416)	0.3874(4)	0.5110(4)	0.3084(2)	4.2(3)
C(421)	0.2738(5)	0.5001(3)	0.3982(2)	2.7(2)
C(422)	0.1753(4)	0.5390(4)	0.3806(2)	3.4(2)
C(423)	0.1521(4)	0.6150(4)	0.4004(3)	4.8(3)
C(424)	0.2273(6)	0.6520(3)	0.4377(3)	5.6(3)
C(425)	0.3258(5)	0.6132(4)	0.4553(2)	4.9(3)
C(426)	0.3491(4)	0.5372(4)	0.4355(2)	3.6(2)

μ-alkyne unit is situated. The stereochemistry about each ruthenium atom is roughly octahedral, with $RuP_2(CO)_2(C)(Ru)$ coordination. The Ru-Ru distance of 2.965(1) Å is indicative of a single bond. Structures have now been determined for three complexes $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu\text{-L})]$, where L = μ-CO, **1b**,[13] μ-

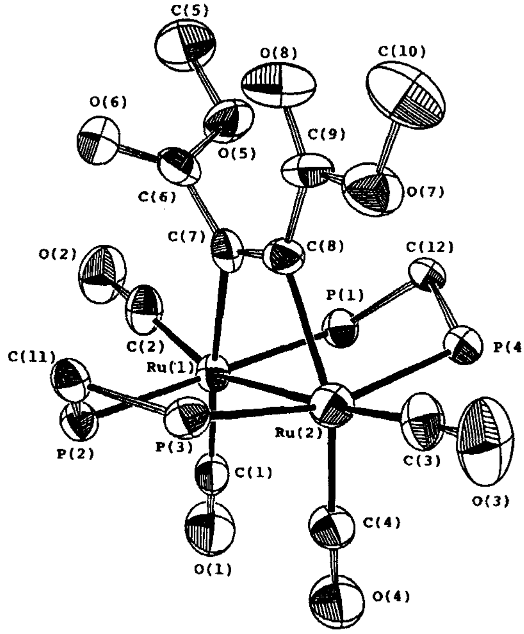


Figure 1 A view of the structure of complex **5b**, showing 50% probability ellipsoids. The phenyl groups and hydrogen atoms are omitted for clarity.

Table 3 Bond Distances (Å) and Angles (°).

Ru(1)-Ru(2)	2.9650(13)	Ru(1)-P(1)	2.353(3)
Ru(1)-P(2)	2.353(3)	Ru(1)-C(1)	1.874(11)
Ru(1)-C(2)	1.849(11)	Ru(1)-C(7)	2.157(10)
Ru(2)-P(3)	2.344(3)	Ru(2)-P(4)	2.324(3)
Ru(2)-C(3)	1.871(11)	Ru(2)-C(4)	1.889(10)
Ru(2)-C(8)	2.122(9)	C(1)-O(1)	1.151(13)
C(2)-O(2)	1.168(14)	C(3)-O(3)	1.124(14)
C(4)-O(4)	1.139(12)	C(5)-O(5)	1.428(13)
C(6)-C(7)	1.460(15)	C(6)-O(5)	1.343(13)
C(6)-O(6)	1.216(14)	C(7)-C(8)	1.311(14)
C(8)-C(9)	1.493(14)	C(9)-O(7)	1.324(14)
C(9)-O(8)	1.197(13)	C(10)-O(7)	1.446(12)
P(1)-C(12)	1.808(9)	P(1)-C(111)	1.845(6)
P(1)-C(121)	1.825(6)	P(2)-C(11)	1.807(10)
P(2)-C(211)	1.820(5)	P(2)-C(221)	1.818(6)
P(3)-C(11)	1.826(10)	P(3)-C(311)	1.854(6)
P(3)-C(321)	1.827(5)	P(4)-C(12)	1.828(9)
P(4)-C(411)	1.846(7)	P(4)-C(421)	1.828(6)
Ru(2)-Ru(1)-P(1)	89.39(7)	Ru(2)-Ru(1)-P(2)	87.54(7)
Ru(2)-Ru(1)-C(1)	108.6(3)	Ru(2)-Ru(1)-C(2)	155.8(3)
Ru(2)-Ru(1)-C(7)	65.0(3)	P(1)-Ru(1)-P(2)	176.9(1)
P(1)-Ru(1)-C(1)	90.2(3)	P(1)-Ru(1)-C(2)	91.3(3)
P(1)-Ru(1)-C(7)	88.7(3)	P(2)-Ru(1)-C(1)	90.8(3)
P(2)-Ru(1)-C(2)	91.5(3)	P(2)-Ru(1)-C(7)	89.9(3)
C(1)-Ru(1)-C(2)	95.6(5)	C(1)-Ru(1)-C(7)	173.5(4)
C(2)-Ru(1)-C(7)	90.8(4)	Ru(1)-Ru(2)-P(3)	91.89(7)
Ru(1)-Ru(2)-P(4)	91.33(8)	Ru(1)-Ru(2)-C(3)	176.7(3)
Ru(1)-Ru(2)-C(4)	81.1(3)	Ru(1)-Ru(2)-C(8)	69.4(3)
P(3)-Ru(2)-P(4)	161.5(1)	P(3)-Ru(2)-C(3)	89.6(3)
P(3)-Ru(2)-C(4)	99.7(3)	P(3)-Ru(2)-C(8)	80.5(2)
P(4)-Ru(2)-C(3)	86.3(3)	P(4)-Ru(2)-C(4)	98.7(3)
P(4)-Ru(2)-C(8)	83.6(3)	C(3)-Ru(2)-C(4)	101.5(5)
C(3)-Ru(2)-C(8)	108.0(4)	C(4)-Ru(2)-C(8)	150.5(4)
Ru(1)-P(1)-C(12)	113.0(3)	Ru(1)-P(1)-C(111)	121.0(2)
Ru(1)-P(1)-C(121)	114.1(2)	C(12)-P(1)-C(111)	101.8(4)
C(12)-P(1)-C(121)	103.7(4)	C(111)-P(1)-C(121)	101.1(3)
Ru(1)-P(2)-C(11)	112.7(3)	Ru(1)-P(2)-C(211)	123.5(3)
Ru(1)-P(2)-C(221)	112.1(2)	C(11)-P(2)-C(211)	101.1(4)
C(11)-P(2)-C(221)	104.2(4)	C(211)-P(2)-C(221)	100.9(3)
Ru(2)-P(3)-C(11)	114.5(3)	Ru(2)-P(3)-C(311)	117.5(2)
Ru(2)-P(3)-C(321)	116.5(2)	C(11)-P(3)-C(311)	100.5(4)
C(11)-P(3)-C(321)	106.9(3)	C(311)-P(3)-C(321)	98.6(3)
Ru(2)-P(4)-C(12)	113.8(3)	Ru(2)-P(4)-C(411)	117.2(2)
Ru(2)-P(4)-C(421)	117.9(2)	C(12)-P(4)-C(411)	100.3(3)
C(12)-P(4)-C(421)	105.8(4)	C(411)-P(4)-C(421)	99.5(3)
Ru(1)-C(1)-O(1)	174.8(9)	Ru(1)-C(2)-O(2)	178.6(9)
Ru(2)-C(3)-O(3)	173.0(10)	Ru(2)-C(4)-O(4)	175.0(9)
C(7)-C(6)-O(5)	112.2(9)	C(7)-C(6)-O(6)	126.3(9)
O(5)-C(6)-O(6)	121.3(10)	Ru(1)-C(7)-C(6)	121.5(7)
Ru(1)-C(7)-C(8)	116.2(7)	C(6)-C(7)-C(8)	122.2(9)
Ru(2)-C(8)-C(7)	109.2(7)	Ru(2)-C(8)-C(9)	127.3(7)
C(7)-C(8)-C(9)	123.5(9)	C(8)-C(9)-O(7)	114.2(8)
C(8)-C(9)-O(8)	123.7(10)	O(7)-C(9)-O(8)	122.0(9)
P(2)-C(11)-P(3)	111.1(5)	P(1)-C(12)-P(4)	111.2(4)
C(5)-O(5)-C(6)	117.1(9)	C(9)-O(7)-C(10)	115.9(8)
P(1)-C(111)-C(112)	118.8(4)		

$MeO_2CC = CCO_2Me$, **5b**, and μ-CH = CH-C(O),**7**.[12] The Ru_2(μ-L) unit contains three-, four- and five-membered rings in **1b**, **5b** and **7** and the Ru-Ru distances are 2.903(2), 2.965(1) and 2.988(1) respectively, giving a clear trend of increasing Ru-Ru distance with increasing ring size. Within the Ru_2C_2 ring, the C = C distance is 1.31(1) Å, indicating a double bond, while the Ru-C distances of 2.12(1) and 2.16(1) Å are typical of single bonds. Hence this unit can be considered as a dimetallacyclobutene.[6,9,12] The ideal bond angles for trigonal carbon and octahedral ruthenium are 120 and 90° respectively and the strain in the four-membered Ru_2C_2 ring leads to lower angles of 116.2(7), 109.2(7) and 65.0(3), 69.4(3)° respectively; the distortions are greater at ruthenium than at carbon. In the complex $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}MeO_2CC = CCO_2Me)(\mu\text{-}dppm)_2]$, which contains a dimetallated alkene with no metal-metal bond, the analogous angles at carbon are 120.3(2)°, very close to the ideal value. Each of the $C\{CO_2C(Me)\}$ units is approximately planar, with one lying in, and the other perpendicular to, the Ru_2C_2 plane. Thus the dihedral angles between the Ru(1)Ru(2)C(7)C(8) plane and the C(8)C(9)O(8)O(7)C(10) and C(7)C(6)O(6)O(5)C(5) planes are 2.2(3) and 94.8(3)°, respectively. Steric effects prevent both groups from being coplanar with the Ru_2C_2 plane, the conformation in which conjugation between unsaturated units is possible; the trends in bond distances do not indicate significant conjugation with either group.

How can the different reactions of schemes (1)[9] and (3) be rationalized? We suggest that reaction of the 34-electron $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PP)_2]$ with an alkyne L is probably associative, giving an initial 36-electron adduct $[Ru_2(CO)_5(L)(\mu\text{-}PP)_2]$ or $[Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}L)(PP)_2]$, with cleavage of the Ru-Ru bond. This reaction could be a simple ligand addition or it could be initiated by ruthenium to alkyne electron transfer. If steric hindrance in the adduct is severe, then CO loss occurs rapidly and leads directly to $[Ru_2(CO)_4(\mu\text{-}L)(PP)_2]$, **5**, as in the case with PP = dppm shown in scheme (3). However, if steric hindrance is less severe, the adduct may be sufficiently long-lived to undergo intramolecular insertion of CO leading to the more complex system of scheme (1).[9]

Acknowledgements

We thank the NSERC (Canada) for financial support and Dr. N.C. Payne for access to X-ray facilities.

SUPPLEMENTARY MATERIAL

Tables of thermal parameters, hydrogen atom positions, torsion angles and structure factors are available from the authors.

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