1182 *Organometallics* 1992, *11*, 1182–1186

Cluster Chemistry. 79.[1] Formation of Unusual Phosphine Ligands by Three-Component Condensation Reactions on a Ruthenium Cluster. X-ray Structures of $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ and $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$

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Three-component cyclization reactions between ethene or 1,3-butadiene, CO, and the C_2PPh_2 ligand present in $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ have given the complexes $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (**2**) and $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (**3**), respectively. X-ray crystallographic studies showed that these complexes contain metalated diphenylphosphinocyclopentenone and -benzoyl ligands, respectively. Crystals of **2** are orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 19.512$ (15) Å, $b = 18.700$ (11) Å, $c = 11.048$ (4) Å, $V = 4031$ Å^3, $R = 0.036$, $R_w = 0.036$, based on 4465 reflections with $I > 3\sigma(I)$. Crystals of **3** are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 17.800$ (2) Å, $b = 11.502$ (5) Å, $c = 11.283$ (2) Å, $\alpha = 93.83$ (2)°, $\beta = 91.65$ (1)°, $\gamma = 99.30$ (2)°, $V = 2273$ Å^3, $R = 0.037$, $R_w = 0.048$, based on 7097 reflections with $I > 3\sigma(I)$.

Introduction

We have described the synthesis and structure of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**)[2] and some of its reactions with dihydrogen or CO,[3] aurating agents,[4] tertiary phosphines,[1,5] and phosphites.[5] In these reactions both the open Ru_5 skeleton and the $\mu_5\text{-}C_2PPh_2$ ligand may be altered. In extending these reactions to unsaturated hydrocarbons, we have discovered a series of three-component condensations which give unusual cluster-bridging functional tertiary phosphine ligands. This paper describes complexes containing such ligands obtained from reactions between **1** and ethene or 1,3-butadiene.[6]

Results

Product from 1 and Ethene. Reactions involving the addition of ethene to **1** have been investigated under a variety of conditions. A red tetraruthenium cluster $Ru_4\{\mu^4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (**2**) (Scheme I), fully characterized by an X-ray study, was obtained from the thermal reaction of **1** and ethene under pressure. A reaction performed in an autoclave was incomplete after 5 h, but higher yields of **2** (27%) were obtained from reactions carried out in Carius tubes, a small amount of $Ru_3(CO)_{12}$ also being isolated. Two other complexes have also been isolated, which contain ligands formed by combination of two or three molecules of the olefin with a C_2 unit released by cleavage of the P–C(sp) bond in **1**; they will be described elsewhere.

Table I. Selected Bond Distances (Å) and Angles (deg) in $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (2)

Ru(1)–Ru(2)	2.787 (1)	Ru(2)–C(1)	2.301 (7)
Ru(1)–Ru(3)	2.899 (2)	Ru(2)–C(2)	2.202 (7)
Ru(1)–Ru(4)	2.868 (2)	C(3)–O(3)	1.247 (9)
Ru(2)–Ru(3)	2.865 (2)	C(1)–C(2)	1.43 (1)
Ru(1)–P(1)	2.282 (2)	C(1)–C(5)	1.53 (1)
Ru(4)–P(1)	2.306 (2)	C(2)–C(3)	1.44 (1)
Ru(3)–P(3)	2.360 (2)	C(3)–C(4)	1.50 (1)
Ru(4)–O(3)	2.141 (5)	C(4)–C(5)	1.54 (1)
Ru(1)–C(2)	2.072 (7)		
Ru(2)–Ru(1)–Ru(4)	96.31 (2)	Ru(3)–Ru(1)–Ru(4)	156.47 (3)

Molecular Structure of $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (2). A plot of a molecule of **2** is shown in Figure 1, and selected bond distances and angles are given in Table I. The metal core in **2** is a spiked triangle; the spike is bridged by a phosphido group while the Ru_3 triangle is capped by a diphenylphosphinocyclopentenonato ligand. The metal core is related to that in **1** by loss of an "$Ru(CO)_2$" fragment [which appears as $Ru_3(CO)_{12}$]. The "spike" atom Ru(4) lies 0.197 (2) Å above the least-squares plane through Ru(1)Ru(2)Ru(3) and at a distance of 2.868 (2) Å from Ru(1). The Ru(3)–Ru(1)–Ru(4) sequence is bent [Ru(3)–Ru(1)–Ru(4) 156.47 (3)°]. Within the Ru_3 triangle, the two Ru–Ru separations Ru(1)–Ru(3) [2.899 (2) Å], Ru(2)–Ru(3) [2.865 (2) Å] are normal, while Ru(1)–Ru(2) [2.787 (1) Å] is shorter. The $\mu\text{-}PPh_2$ group bridges the Ru(1)–Ru(4) vector [Ru(1)–P(1) 2.282 (2), Ru(4)–P(1) 2.306 (2) Å] and is unexceptional. The P–Ru distances [2.282 (2)–2.306 (2) Å] are within the normal range. Three carbonyl ligands are attached to each of Ru(2), Ru(3) and Ru(4), while two are attached to Ru(1).

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(6) For a recent article on cluster-assisted ligand transformations see: Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: Weinheim, 1990; pp 201–302.

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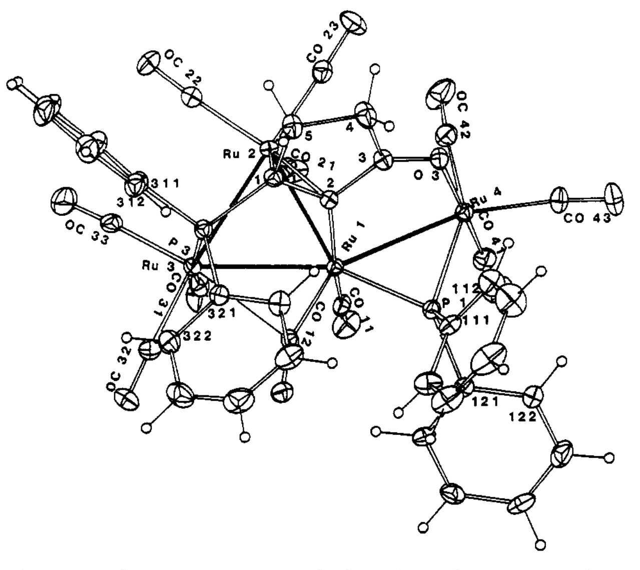
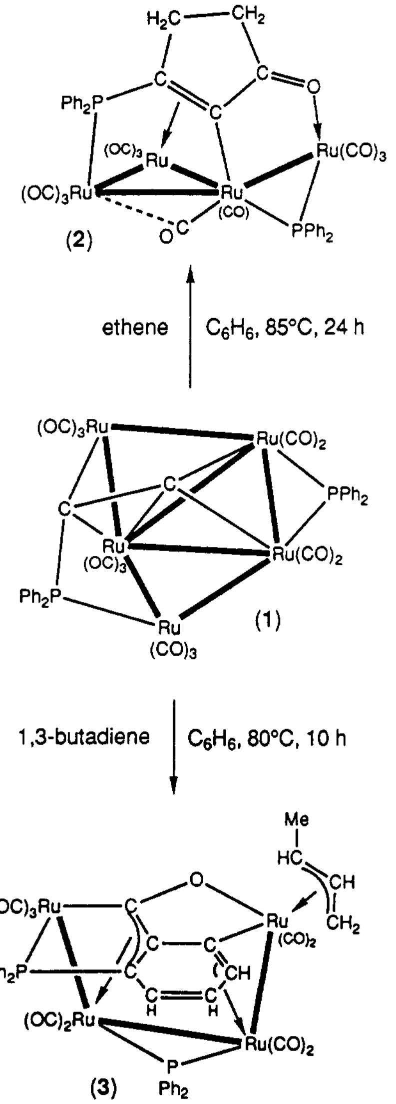


Figure 1. Computer-generated plot of a molecule of $Ru_4\{\mu_4\text{-}\sigma\text{-}(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (**2**).

Scheme I



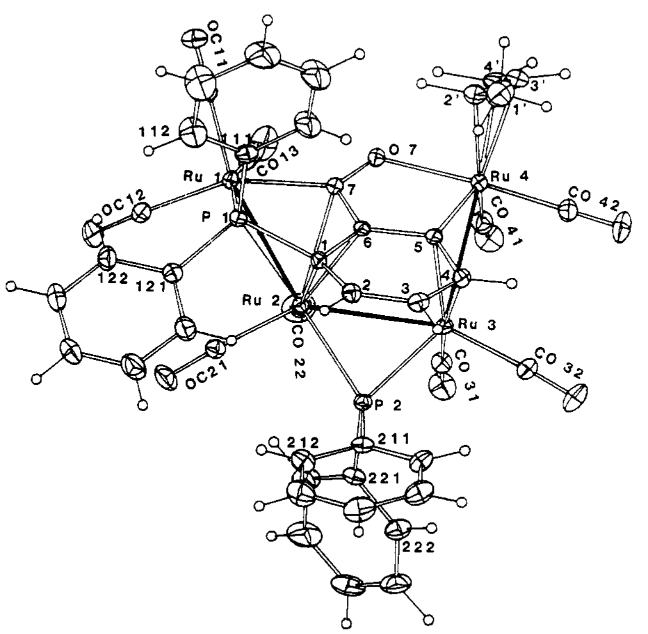


Figure 2. Computer-generated plot of a molecule of $Ru_4\{\mu_4\text{-}\sigma\text{-}(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (**3**).

A semibridging carbonyl interaction is found between Ru(1) and Ru(3), with a Ru(1)C(12)O(12) angle of 157.6 (6)° and Ru(3)–C(12) contact of 2.552 (8) Å. As there is no obvious electronic imbalance at Ru(1) or Ru(3), the reason for this mode of bonding appears to lie with the steric interactions of the phosphido group attached to Ru(1).

The organic ligand is best described as a metalated diphenylphosphinocyclopentenone. It is attached to Ru(3) via the PPh_2 group [Ru(3)–P(3) 2.360 (2) Å], to Ru(4) by the ketonic carbonyl group [Ru(4)–O(3) 2.141 (5) Å; Ru(4)–O(3)–C(3) 121.9 (4)°] and to Ru(1) and Ru(2) by a σ,π-vinyl interaction with two of the ring carbons [Ru(1)–C(2) 2.072 (7), Ru(2)–C(1) 2.301 (7), Ru(2)–C(2) 2.200 (7) Å]. Within the organic ligand, delocalized double bonds were found for C(1)–C(2) and C(2)–C(3) [1.43 (1), 1.44 (1) Å] and localized C–C single bonds for C(1)–C(5), C(3)–C(4), and C(4)–C(5) [1.53 (1), 1.50 (1), 1.54 (1) Å, respectively], confirming the σ-vinyl interaction of the cyclopentenone ligand with the cluster. The five-membered ring and associated carbonyl oxygen are significantly but only trivially nonplanar ($\chi^2{}_{C(5)O}$ 159, δ_{max} 0.06 Å); the mean plane is inclined at 48.0 (2)° to the Ru(1)–Ru(2)–Ru(3) plane. Each ruthenium achieves an 18-electron configuration; as a whole, the cluster is a 64-electron, 8 SEP species.

The spectroscopic properties of **2** in solution are consistent with the solid-state structure. The IR spectrum has nine terminal ν(CO) bands between 2082 and 1958 cm^{-1}, a bridging carbonyl absorption at 1820 cm^{-1}, and a weak band assigned to the ketonic carbonyl absorption at 1588 cm^{-1}. No molecular ion was found in the positive-ion spectrum of **2**; the negative-ion spectrum, however, contained $[M]^-$ at m/z 1163. The proton NMR spectrum of this complex contained phenyl resonances between δ 8.1 and 6.2 and four signals at δ 2.83, 2.73, 2.20, and 1.47 which were assigned to the protons on the cyclopentenone group.

Product from 1 and 1,3-Butadiene. A similar reaction between **1** and 1,3-butadiene afforded a mixture of products from which yellow $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (**3**) (Scheme I) was separated; this complex was also characterized by a single-crystal X-ray study.

Molecular Structure of $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (3). A plot of a molecule of **3** is given in Figure 2, and important bond distances and angles are listed in Table II. The molecule consists of a chain of four Ru atoms; the Ru–Ru separa-

Table II. Selected Bond Distances (Å) and Angles (deg) in $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (3)

Ru(1)–Ru(2)	2.848 (1)	Ru(3)–C(4)	2.468 (5)
Ru(2)–Ru(3)	2.906 (1)	Ru(3)–C(5)	2.181 (4)
Ru(3)–Ru(4)	2.936 (1)	Ru(4)–C(5)	2.068 (5)
Ru(1)–P(1)	2.349 (1)	C(7)–O(7)	1.279 (6)
Ru(2)···P(1)	3.018 (1)	C(1)–C(2)	1.448 (6)
Ru(2)–P(2)	2.321 (2)	C(1)–C(6)	1.452 (6)
Ru(3)–P(2)	2.272 (1)	C(2)–C(3)	1.347 (8)
Ru(4)–O(7)	2.119 (4)	C(3)–C(4)	1.443 (7)
Ru(1)–C(7)	2.072 (5)	C(4)–C(5)	1.413 (6)
Ru(2)–C(1)	2.290 (4)	C(5)–C(6)	1.444 (7)
Ru(2)–C(6)	2.251 (4)	C(6)–C(7)	1.439 (6)
Ru(2)–C(7)	2.465 (4)		
Ru(1)–Ru(2)–Ru(3)	126.91 (2)	τ(1,2,3,4)[a]	−1.57 (2)
Ru(2)–Ru(3)–Ru(4)	95.62 (3)		

[a] Torsion angle about Ru(2)–Ru(3).

Table III. Crystal Data and Refinement Details for 2 and 3[a]

compd	2	3
formula	$C_{40}H_{24}O_{12}P_2Ru_4$	$C_{44}H_{30}O_{10}P_2Ru_4\cdot0.5C_7H_8$
MW	1162.9	1231.0
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$ (D_2^4, No. 19)	$P\bar{1}$ (C_i^1, No. 2)
a, Å	19.512 (15)	17.800 (2)
b, Å	18.700 (11)	11.502 (5)
c, Å	11.048 (4)	11.283 (2)
α, deg		93.83 (2)
β, deg		91.65 (1)
γ, deg		99.30 (2)
V, $Å^3$	4031	2272.8
Z	4	2
D_c, g cm^{-3}	1.92	1.80
F(000)	2264	1210
cryst size, mm	0.11 × 0.15 × 0.50	0.58 × 0.21 × 0.55
μ, cm^{-1}	14.6	12.9
$2\theta_{max}$, deg	60	50
*A** min, max	1.16, 1.20	1.32, 1.43
N	5648	7988
N_o	4465	7097
R	0.036	0.037
R_w	0.036	0.048

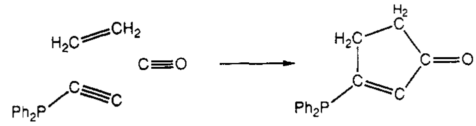
[a] *Abnormal features/variations in procedure.* All organic ligand hydrogen atoms were resolved as difference map residues. In 3, difference map artifacts were modeled as a fully populated toluene molecule disordered through an inversion center.

tions are 2.848 (1), 2.906 (1), and 2.936 (1) Å, the central one being bridged by the PPh_2 group [Ru(2)–P(2) 2.321 (2), Ru(3)–P(2) 2.272 (1) Å]. The chain is cis bent at Ru(2) and Ru(3) [Ru(1)–Ru(2)–Ru(3) 126.91 (2), Ru(2)–Ru(3)–Ru(4) 95.62 (3)°]. The four metal atoms are also bridged by a cyclic $C_6H_3(CO)(PPh_2)$ unit, which may be described as a metalated diphenylphosphinobenzoyl ligand. This is attached to Ru(1) by P(1) [2.349 (1) Å], to Ru(2) by an η^2 interaction with C(1)–C(6), and to Ru(3) and Ru(4) by a σ,π-vinyl interaction with C(4)–C(5) [Ru(4)–C(5) 2.068 (5), Ru(3)–C(4) 2.468 (5), Ru(3)–C(5) 2.181 (4) Å]. The latter is similar to that found in **2**. However, the corresponding Ru–Ru separation is much longer [2.936 (1) Å]. There is a weak interaction between C(7) of the carbonyl group and Ru(2) [2.465 (4) Å], while the Ru(4)–O(7) separation is 2.119 (4) Å, also similar to that found in **2**, with Ru(4)–O(7)–C(7) 115.7 (3)°. There is also a bond between the carbonyl carbon C(7), and Ru(1) [2.072 (5) Å]. Within the C_6 ring, only C(2)–C(3) [1.347 (8) Å] is a localized C=C double bond; the others range from 1.413 to 1.452 (8) Å, the two extremes being the two C—C bonds attached to Ru(3) and Ru(2), respectively; the latter value indicates a strong attachment to the electron-deficient metal atom. The C_7O plane is significantly, but again only trivially, nonplanar (χ^2 1275; δ_{max} 0.1 Å), with P(1) being 0.483 (6) Å out of the plane, and the dihedral angle with the Ru_4 plane is 102.72 (6)°. An almost planar (χ^2 15.8; δ_{max} 0.025 Å) η^3-$CH_2CHCHMe$ ligand is attached to Ru(4). Coordination about the metal atoms is completed by nine CO groups, three on Ru(1), and two on each of the other Ru atoms. Each ruthenium atom has an 18-electron configuration; as expected for an open-chain geometry, the "cluster" is a 68-electron, 7 SEP species.

Spectroscopic data in solution are consistent with the solid-state molecular structure: there are seven terminal ν(CO) absorptions between 2073 and 1948 cm^{-1}, but no bridging carbonyl bands. The ^1H NMR spectrum shows that the η^3-methallyl group is fluxional, broad resonances at δ 1.73, 2.26, 2.68 and 4.34, and 5.11 being assigned to the Me, CHMe, the two CH_2, and central CH protons, respectively. Within the C_6 ligand, resonances at δ 5.20, 5.44, and 6.85 are assigned to H(3), H(2), and H(4), respectively; only H(2) and H(4) show couplings to ^{31}P, as expected. The ^{13}C NMR spectrum also contained broad signals at δ 20.2, 58.9, 85.8, and 106.3 arising from the methallyl group; the only resonance of the C_6 ligand that could be assigned unambiguously was at δ 119.5, from C(4), the others being contained within the phenyl multiplet. The CO carbons (including C(7)) appeared as nine resonances between δ 191.6 and 206.4. The FAB mass spectrum contains a parent ion at *m/z* 1186, ions formed by the loss of up to nine CO groups, and also shows loss of C_2H_4 and C_4H_7 from the carbonyl-free ion at *m/z* 906.

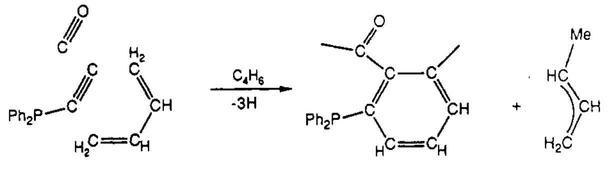
Discussion

The structures determined demonstrate that incorporation of the olefin or diene, CO, and the C_2PPh_2 group via C–C coupling reactions has occurred in each instance. In the formation of **2**, we see the cycloaddition of CO and ethene to a η^2-coordinated acetylide moiety to form the C_5 ring without cleavage of the C–P bond (eq 1), whereas



(1)

with **3**, considerable dehydrogenation of the butadiene has also occurred, partly by a second molecule of the diene to form the η^3-C_4H_7 group found on Ru(4) (eq 2).



(2)

Carty et al.[7] have reported the synthesis of the tetranuclear cyclopentadienyl complex $\{Ru_2[\mu\text{-}\sigma(C,O),\eta^7\text{-}C_5MePh_2(C_6H_4)(O)](\mu\text{-}PPh_2)(CO)_8\}_2$, obtained by coupling of coordinated phenylallene with CO and diphenylethyne. The mechanism proposed for the formation of the cyclopentadienyl ligand involves the addition of alkyne and CO to the η^2-coordinated double bond of the allenyl ligand. Related reactions involving coupling of CO and alkynes on bi- or trimetallic systems include the formation of 3,5-diethyl-1-osmacyclohexa-2,5-dien-4-one from HC_2Et

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[7] Randall, S. M.; Taylor, N. J.; Carty, A. J.; Haddah, T. B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1988**, 870.

Table IV. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters for $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (2)

atom	x	y	z	U(eq), Å^2
Ru(1)	0.94462 (3)	0.05008 (3)	0.93039 (5)	0.0286 (3)
Ru(2)	0.92872 (3)	0.08963 (3)	0.68877 (5)	0.0309 (3)
Ru(3)	0.80804 (3)	0.06893 (3)	0.83220 (5)	0.0326 (3)
Ru(4)	1.09100 (3)	0.03704 (3)	0.92398 (5)	0.0325 (3)
P(1)	1.0210 (1)	0.0683 (1)	1.0837 (2)	0.037 (1)
P(3)	0.8316 (1)	0.1927 (1)	0.8296 (2)	0.040 (1)
C(11)	0.9370 (4)	−0.0492 (4)	0.9584 (7)	0.045 (5)
O(11)	0.9350 (3)	−0.1108 (3)	0.9681 (6)	0.068 (4)
C(12)	0.8715 (4)	0.0752 (4)	1.0338 (7)	0.045 (5)
O(12)	0.8437 (3)	0.0877 (3)	1.1248 (5)	0.057 (4)
C(21)	0.9381 (4)	−0.0119 (4)	0.6913 (7)	0.045 (4)
O(21)	0.9449 (3)	−0.0721 (3)	0.6760 (5)	0.061 (4)
C(22)	0.8754 (4)	0.0980 (5)	0.5462 (7)	0.057 (6)
O(22)	0.8474 (3)	0.0983 (4)	0.4544 (5)	0.089 (5)
C(23)	1.0095 (4)	0.1089 (4)	0.6026 (7)	0.051 (5)
O(23)	1.0586 (3)	0.1183 (4)	0.5462 (6)	0.081 (5)
C(31)	0.8087 (4)	−0.0349 (4)	0.8219 (7)	0.051 (5)
O(31)	0.8043 (3)	−0.0950 (3)	0.8176 (6)	0.075 (4)
C(32)	0.7340 (4)	0.0714 (5)	0.9452 (7)	0.055 (5)
O(32)	0.6915 (3)	0.0736 (4)	1.0154 (6)	0.072 (4)
C(33)	0.7478 (4)	0.0715 (4)	0.6972 (7)	0.050 (5)
O(33)	0.7108 (4)	0.0683 (4)	0.6209 (6)	0.095 (5)
C(41)	1.0926 (5)	−0.0571 (4)	0.9795 (7)	0.054 (5)
O(41)	1.0935 (4)	−0.1139 (3)	1.0165 (6)	0.078 (5)
C(42)	1.1058 (4)	0.0010 (5)	0.7583 (8)	0.055 (5)
O(42)	1.1171 (4)	−0.0257 (4)	0.6691 (6)	0.104 (6)
C(43)	1.1839 (4)	0.0491 (4)	0.9755 (8)	0.053 (5)
O(43)	1.2371 (3)	0.0518 (4)	1.0161 (7)	0.086 (5)
C(111)	1.0315 (4)	0.1535 (4)	1.1614 (7)	0.044 (4)
C(112)	1.0864 (5)	0.1973 (5)	1.1371 (8)	0.064 (6)
C(113)	1.0971 (6)	0.2581 (5)	1.209 (1)	0.090 (8)
C(114)	1.0529 (6)	0.2746 (5)	1.3009 (9)	0.092 (8)
C(115)	0.9988 (6)	0.2320 (5)	1.3234 (9)	0.080 (7)
C(116)	0.9871 (5)	0.1708 (4)	1.2546 (8)	0.063 (6)
C(121)	1.0217 (4)	0.0102 (4)	1.2160 (6)	0.040 (4)
C(122)	1.0828 (4)	0.0027 (5)	1.2796 (8)	0.060 (6)
C(123)	1.0873 (5)	−0.0384 (5)	1.3818 (8)	0.069 (6)
C(124)	1.0300 (5)	−0.0701 (5)	1.4260 (7)	0.064 (6)
C(125)	0.9694 (5)	−0.0633 (5)	1.3617 (8)	0.064 (6)
C(126)	0.9645 (4)	−0.0227 (5)	1.2593 (8)	0.056 (5)
C(1)	0.9194 (4)	0.1966 (4)	0.7907 (7)	0.039 (4)
C(2)	0.9648 (4)	0.1477 (3)	0.8497 (6)	0.035 (4)
C(3)	1.0330 (4)	0.1747 (3)	0.8311 (7)	0.040 (4)
O(3)	1.0880 (3)	0.1446 (3)	0.8577 (5)	0.044 (3)
C(4)	1.0332 (4)	0.2471 (4)	0.7726 (9)	0.062 (6)
C(5)	0.9572 (4)	0.2630 (4)	0.7446 (8)	0.049 (5)
C(311)	0.7885 (4)	0.2557 (4)	0.7254 (8)	0.049 (5)
C(312)	0.7828 (4)	0.3274 (4)	0.7590 (8)	0.054 (5)
C(313)	0.7513 (5)	0.3766 (5)	0.681 (1)	0.076 (7)
C(314)	0.7246 (5)	0.3543 (5)	0.572 (1)	0.080 (7)
C(315)	0.7309 (6)	0.2851 (5)	0.5398 (9)	0.080 (7)
C(316)	0.7633 (5)	0.2349 (5)	0.6166 (9)	0.064 (6)
C(321)	0.8206 (4)	0.2373 (4)	0.9755 (7)	0.041 (5)
C(322)	0.7534 (5)	0.2429 (5)	1.0216 (9)	0.060 (6)
C(323)	0.7423 (5)	0.2725 (5)	1.135 (1)	0.077 (7)
C(324)	0.7963 (6)	0.2971 (6)	1.1997 (9)	0.086 (8)
C(325)	0.8621 (5)	0.2923 (5)	1.1579 (8)	0.070 (6)
C(326)	0.8740 (4)	0.2614 (5)	1.0444 (8)	0.056 (6)

and $Os_3(\mu\text{-}H)_2(CO)_{10}$ and its subsequent conversion to a substituted alkyl(oxy)cyclopentadienyl derivative[8] and $\sigma,\eta^3\text{-}C_5HBu^t(CF_3)_2$ and 2-η^2-2,3-bis(trifluoromethyl)-5-*tert*-butylcyclopentadienone ligands formed from $Rh_2(\mu\text{-}CO)\{\mu\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2$ and HC_2Bu^t.[9]

The three-component CO–alkene–acetylide coupling reactions examined here are without precedent in cluster chemistry and are therefore of considerable interest. Reactions of ethene with clusters have generally given η^2-bonded complexes.[10-12] The reactions of $Ru_3(CO)_{12}$ with

Table V. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters for $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (3)

atom	x	y	z	U(eq), Å^2
Ru(1)	0.78684 (2)	0.47803 (3)	0.18678 (3)	0.0307 (2)
Ru(2)	0.77366 (2)	0.23766 (3)	0.09786 (3)	0.0270 (2)
Ru(3)	0.87258 (2)	0.07092 (3)	0.15850 (3)	0.0284 (2)
Ru(4)	0.97659 (2)	0.23880 (3)	0.31896 (4)	0.0338 (2)
C(11)	0.7941 (3)	0.6066 (5)	0.3030 (5)	0.041 (3)
O(11)	0.7952 (3)	0.6810 (4)	0.3755 (4)	0.066 (3)
C(12)	0.7240 (3)	0.5340 (5)	0.0669 (5)	0.045 (3)
O(12)	0.6910 (3)	0.5637 (4)	−0.0101 (4)	0.073 (3)
C(13)	0.8786 (4)	0.5389 (5)	0.1080 (5)	0.050 (3)
O(13)	0.9346 (3)	0.5721 (4)	0.0672 (5)	0.085 (3)
C(21)	0.6881 (3)	0.2595 (5)	0.0034 (5)	0.040 (3)
O(21)	0.6393 (2)	0.2696 (4)	−0.0604 (4)	0.065 (2)
C(22)	0.8424 (3)	0.2836 (5)	−0.0207 (5)	0.042 (3)
O(22)	0.8824 (3)	0.3157 (4)	−0.0929 (4)	0.076 (3)
C(31)	0.9169 (3)	0.0695 (5)	0.0090 (5)	0.041 (3)
O(31)	0.9441 (2)	0.0641 (4)	−0.0804 (4)	0.061 (2)
C(32)	0.8962 (3)	−0.0781 (4)	0.1873 (5)	0.040 (3)
O(32)	0.9070 (3)	−0.1706 (3)	0.2019 (4)	0.066 (3)
C(41)	1.0244 (3)	0.2280 (5)	0.1691 (5)	0.048 (3)
O(41)	1.0626 (3)	0.2300 (4)	0.0881 (4)	0.068 (3)
C(42)	1.0148 (3)	0.1069 (5)	0.3631 (5)	0.044 (3)
O(42)	1.0396 (3)	0.0266 (4)	0.3896 (4)	0.071 (3)
C(1)	0.7325 (3)	0.2261 (4)	0.2878 (4)	0.030 (2)
C(2)	0.6994 (3)	0.1201 (4)	0.3420 (4)	0.034 (2)
C(3)	0.7434 (3)	0.0414 (4)	0.3736 (4)	0.037 (2)
C(4)	0.8248 (3)	0.0599 (4)	0.3613 (4)	0.035 (2)
C(5)	0.8623 (3)	0.1698 (4)	0.3274 (4)	0.030 (2)
C(6)	0.8151 (3)	0.2526 (4)	0.2895 (4)	0.028 (2)
C(7)	0.8535 (3)	0.3639 (4)	0.2539 (4)	0.031 (2)
O(7)	0.9263 (2)	0.3821 (3)	0.2634 (3)	0.038 (2)
C(1′)	0.9289 (5)	0.2639 (6)	0.6058 (6)	0.081 (5)
C(2′)	0.9627 (4)	0.3248 (5)	0.5017 (5)	0.057 (3)
C(3′)	1.0403 (4)	0.3334 (6)	0.4789 (6)	0.065 (4)
C(4′)	1.0722 (4)	0.3837 (6)	0.3795 (7)	0.068 (4)
P(1)	0.69237 (7)	0.3607 (1)	0.2874 (1)	0.0309 (6)
C(111)	0.6802 (3)	0.4047 (5)	0.4449 (4)	0.042 (3)
C(112)	0.6249 (5)	0.4669 (8)	0.4805 (6)	0.087 (5)
C(113)	0.6179 (6)	0.501 (1)	0.6000 (7)	0.119 (7)
C(114)	0.6671 (5)	0.4709 (8)	0.6832 (6)	0.094 (5)
C(115)	0.7231 (5)	0.4120 (8)	0.6486 (6)	0.094 (5)
C(116)	0.7293 (4)	0.3785 (7)	0.5297 (5)	0.075 (4)
C(121)	0.5945 (3)	0.3331 (4)	0.2274 (4)	0.035 (2)
C(122)	0.5645 (3)	0.4263 (5)	0.1832 (5)	0.051 (3)
C(123)	0.4901 (4)	0.4116 (6)	0.1376 (5)	0.059 (3)
C(124)	0.4449 (3)	0.3022 (6)	0.1371 (6)	0.058 (3)
C(125)	0.4737 (4)	0.2113 (6)	0.1788 (7)	0.072 (4)
C(126)	0.5479 (3)	0.2245 (5)	0.2227 (6)	0.057 (3)
P(2)	0.75866 (7)	0.0348 (1)	0.0556 (1)	0.0307 (6)
C(211)	0.6784 (3)	−0.0652 (4)	0.1097 (4)	0.037 (2)
C(212)	0.6060 (3)	−0.0434 (5)	0.0904 (5)	0.052 (3)
C(213)	0.5437 (4)	−0.1176 (7)	0.1309 (6)	0.070 (4)
C(214)	0.5549 (4)	−0.2139 (6)	0.1900 (6)	0.070 (4)
C(215)	0.6267 (4)	−0.2355 (5)	0.2109 (6)	0.066 (4)
C(216)	0.6889 (3)	−0.1625 (5)	0.1697 (5)	0.049 (3)
C(221)	0.7580 (3)	−0.0270 (5)	−0.0980 (4)	0.039 (2)
C(222)	0.7605 (4)	−0.1450 (5)	−0.1218 (5)	0.055 (3)
C(223)	0.7653 (4)	−0.1927 (6)	−0.2369 (7)	0.074 (4)
C(224)	0.7658 (4)	−0.1223 (7)	−0.3293 (6)	0.079 (4)
C(225)	0.7629 (5)	−0.0069 (8)	−0.3100 (6)	0.087 (5)
C(226)	0.7583 (4)	0.0429 (6)	−0.1936 (5)	0.065 (4)
C(101)	0.474 (3)	0.092 (5)	0.489 (5)	0.21 (3)
C(1011)[a]	0.452 (3)	0.207 (5)	0.496 (3)	0.31 (5)
C(102)	0.442 (1)	−0.014 (8)	0.440 (2)	0.22 (3)
C(103)	0.457 (5)	−0.113 (5)	0.432 (5)	0.31 (5)

[a] Population parameter = 0.5.

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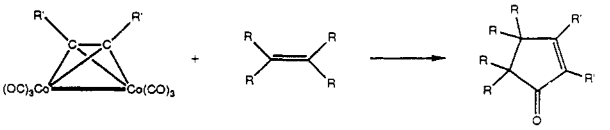
ethene have been shown to give C–C coupled products such as $Ru_4(\mu_4\text{-}\eta^2\text{-}C_2Me_2)(CO)_{12}$ and $Ru_6C(\mu\text{-}\eta^4\text{-}MeCH{=}CHCH{=}CHMe)(CO)_{15}$ through oligomerization of the olefin.[13] The closest analogy is the Pauson–Khand reaction,[14] in which alkyne–$Co_2(CO)_6$ complexes react with alkenes to give cyclopentenones (eq 3). Clusters **2** and



(3)

3 may also be seen as model compounds for C–C bond-forming reactions which occur at metal surfaces.[15] The ready formation of complexes **2** and **3** from **1** shows that acetylide–alkene–CO coupling is also a facile process for transition-metal cluster complexes.

This work has described novel three-component cyclization reactions occurring on metal clusters, but in order for such transformations to be useful for organic synthesis, a facile method of liberating the organic molecule is required.

Experimental Section

General reaction conditions and the synthesis of **1** have been described previously.[2] Ethene (Commonwealth Industrial Gases) and 1,3-butadiene (Matheson) were used as received.

Synthesis of $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ (2). A solution of **1** (150 mg, 0.12 mmol) in benzene (20 mL) was placed in a Carius tube (40 mL internal volume), and ethene (1.0 g, 35.7 mmol) was added. After heating at 85 °C for 24 h, the solution was cooled and the excess ethene vented. The solvent was removed under reduced pressure and the residue purified by preparative TLC (petroleum ether/acetone 9/1). Four bands separated: a yellow band (R_f 0.85) near the solvent front was identified (IR, spot TLC) as $Ru_3(CO)_{12}$ (4 mg, 0.006 mmol, 5%); the fourth, red band (R_f 0.33) was removed from the silica quickly and crystallized (CH_2Cl_2/MeOH) by slow evaporation to give small red needles of $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}\cdot 0.5CH_2Cl_2$ (**2**) (37 mg, 0.032 mmol, 27%), mp >280 °C. Anal. Calcd for $C_{40}H_{24}O_{12}P_2Ru_4\cdot 0.5CH_2Cl_2$: C, 40.36; H, 2.09; M, 1163. Found: C, 40.76; H, 2.06; M (mass spectrometry), 1163. IR (cyclohexane): ν(CO) 2082 (m), 2064 (m), 2025 (s), 2019 (sh), 2002 (sh), 1998 (m), 1976 (w), 1968 (m), 1958 (sh), 1820 (w) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1588 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 240 K): δ 1.47 (1 H, ddd, J = 14.6, 9.8, 3.5 Hz, CH_2), 2.20 (1 H, dd, J = 20.2, 6.7 Hz, CH_2), 2.73 (1 H, dd, J = 14.8, 4.7 Hz, CH_2), 2.83 (1 H, m, CH_2), 7.8–6.7 (20 H, m, Ph). FAB MS (negative ion): 1163–967, $[M - nCO]^-$ (n = 0–7); 942–830, $[\{M - 8CO) + 3\,H\} - nCO, C_2H_4]^-$ (n = 0–3). FAB MS (positive ion): 1135–855, $[M - nCO]^+$ (n = 1–11). This compound was unstable in solution and apparently reacted with MeOH to form larger clusters (by FAB MS analysis of the products).

Synthesis of $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (3). A solution of **1** (150 mg, 0.12 mmol) and 1,3-butadiene (2.0 g, 37 mmol) in benzene (15 mL) in a Carius tube was heated for 10 h at 80 °C (tube oven). After cooling to room temperature, the solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 10/3) to give six bands. A yellow band (R_f 0.50) was recrystallized from (CH_2Cl_2/MeOH) to yield $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)\cdot CH_2Cl_2$ (**3**) (24 mg, 17%), mp >300 °C dec. Anal. Calcd for $C_{44}H_{30}O_{10}P_2Ru_4\cdot CH_2Cl_2$: C, 42.57; H, 2.54; M, 1186. Found: C, 42.82; H, 2.61; M (mass spectrometry), 1186. IR (cyclohexane): ν(CO) 2073 (s), 2042 (vs), 2018 (s), 2009 (m), 1991 (s), 1982 (s), 1948 (m) cm^{-1}. ^1H NMR: δ($CDCl_3$) 1.73 (3 H, s (br), Me), 2.27 (1 H, s (br), H(2′)), 2.68 (1 H, d (br), J = 7 Hz, H(4′a)), 4.34 (1 H, d (br), J = 7.3 Hz, H(4′b)), 5.11 (1 H, s (br), H(3′)), 5.20 (1 H, dd, J = 5.7, 8.9 Hz, H(3)), 5.44 (1 H, dd, J(HH) = 8.7, J(PH) = 6.6 Hz, H(2)), 6.85 (1 H, dd, J(HH) = 5.4, J(PH) = 2.5 Hz, H(4)), 6.93–7.74 (20 H, m, Ph). ^{13}C NMR: δ($CDCl_3$) 20.19 (s, Me), 58.96 (s (br), C(4′)), 85.85 (s (br), C(3′)), 106.32 (s (br), C(2′)), 119.49 (d, J(CP) = 6.4 Hz, C(3)), 126.08–133.90 (m, Ph + C_6), 140.67–142.91 (m, ipso C), 191.59 (d), 191.61 (d), 195.45 (m), 196.79 (s), 198.06 (s), 199.30 (d), 201.37 (m), 202.05 (s), 206.38 (t) (10 CO). FAB MS (m/z): 1186, $[M]^+$; 1158–906, $[M - nCO]^+$ (n = 1–10); 879, $[M - 10CO - C_2H_4]^+$; 851, $[M - 10CO - C_4H_7]^+$.

Crystallography

Unique data sets were measured at ca. 295 K within the specified $2\theta_{max}$ limits using an Enraf-Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U_{iso})_H$ were included, constrained at estimate values. Conventional residuals R,R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system[16] implemented by S. R. Hall; neutral-atom complex scattering factors were employed.[17] The crystal data and refinement details for **2** and **3** are summarized in Table III. Non-hydrogen positional and equivalent isotropic displacement parameters for **2** and **3** are listed in Tables IV and V, respectively.

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Supplementary Material Available: Tables of hydrogen coordinates and isotropic thermal parameters, anisotropic thermal displacement parameters, and bond lengths and angles for **2** (Tables SUP 1–4) and **3** (Tables SUP 5–8) (13 pages); listings of observed and calculated structure factor amplitudes for **2** (Table SUP-9) and **3** (Table SUP-10) (21 pages). Ordering information is given on any current masthead page.

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