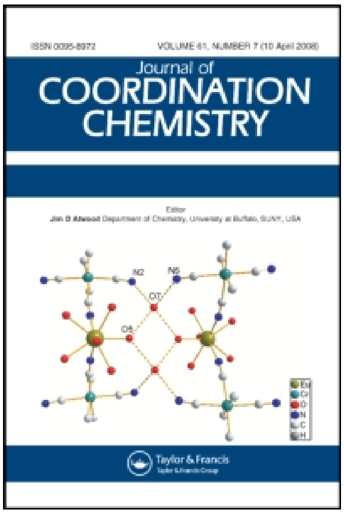

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Reaction of $HRu_3(CO)_{10}(\mu\text{-COMe})$ with bma: NMR and X-ray structural evidence for the formation of the Ph_2PH-substituted cluster $HRu_3(CO)_8(Ph_2PH)[\mu\text{-PPh}_2C{=}CC(O)OC(O)]$

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Me_3NO activation of the methylidyne-bridged cluster $HRu_3(CO)_{10}(\mu\text{-COMe})$ (**1**) in the presence of the unsaturated diphosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride (bma) furnishes the bma-substituted cluster $HRu_3(CO)_8(\text{bma})(\mu\text{-COMe})$ (**2**) and the diphenylphosphine-substituted cluster $HRu_3(CO)_8(Ph_2PH)[\mu\text{-PPh}_2C{=}CC(O)OC(O)]$ (**3**) as the major and minor products, respectively. The ^1H and ^{31}P NMR data indicate that the bma ligand in cluster **2** is chelated to one of the ruthenium atoms that is bridged by the hydride and methylidyne ligands. Cluster **3** has been fully characterized in solution by IR and NMR spectroscopies, and the solid-state structure determined by X-ray crystallography. **3** crystallizes in the monoclinic space $P2_1$, $a = 12.1467(7)$ Å, $b = 19.284(1)$ Å, $c = 16.867(1)$ Å, $\beta = 109.639(6)^\circ$, $V = 3721.0(4)$ Å^3, $Z = 4$, and $d_{calcd} = 1.774\,g\,cm^{-3}$; $R = 0.0325$, $R_w = 0.0383$ for 3518 reflections with $I > 3\sigma(I)$. The X-ray data confirm that one of the P–C(maleic anhydride) bonds of the bma ligand has been cleaved and that cluster **3** contains Ph_2PH and $\mu\text{-PPh}_2C{=}CC(O)OC(O)$ ligands, the latter which functions as a face-capping ligand to all three ruthenium atoms. Control experiments indicate that cluster **2** does not function as a precursor to cluster **3** under the employed reaction conditions.

Keywords: Ruthenium clusters; Ligand substitution; Diphosphine ligand; P–C bond activation

1. Introduction

The reduction of $Ru_3(CO)_{12}$ to the hydride cluster $[HRu_3(CO)_{11}]^-$, followed by methylation, has been reported by the Keister and Lewis groups to give the methylidyne-bridged cluster $HRu_3(CO)_{10}(\mu\text{-COMe})$ (**1**) [1, 2]. Cluster **1** has been extensively investigated as a model system for the study of oxidation/reduction processes at discrete polynuclear ensembles [3], as a platform for the controlled construction of mixed-metal clusters [4], photochemical behaviour related to the

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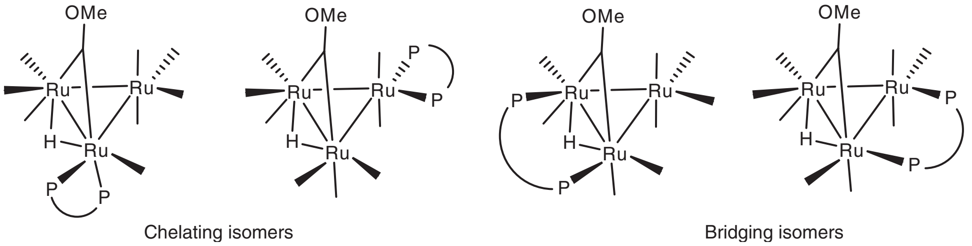
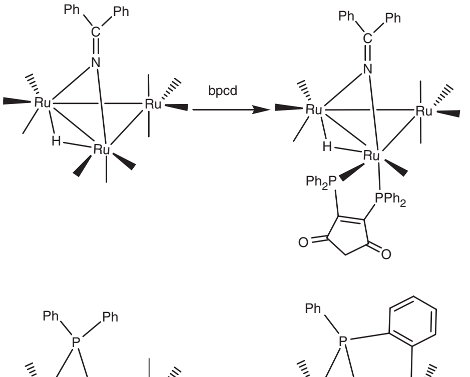


Scheme 1. Possible coordination modes of diphosphine ligand (P–P) at $HRu_3(CO)_8$ (P–P)(μ-COMe).

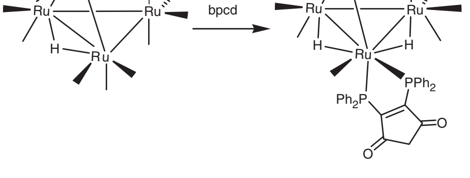
isomerization of the bridging methylidyne ligand [5], and site selectivity in ligand substitution reactions [6].

Our interest in the substitution chemistry of **1** with diphosphine ligands stems from the fact that no such reactions have been reported to date. Moreover, it is not immediately clear what the final diphosphine disposition would be at the cluster polyhedron. Depending on the nature of the diphosphine ligand, bridging and/or chelating coordination modes could be observed. This bonding situation is made more complex by virtue of the inherent asymmetry in the cluster due to the hydride- and methylidyne-bridged ruthenium–ruthenium bond. Scheme 1 shows a few of the coordination possibilities expected for the attachment of a diphosphine ligand (P–P) at cluster **1** [7].

We have previously studied the ligand substitution behaviour of the azavinylidene- and phosphido-bridged ruthenium clusters $HRu_3(CO)_{10}(\mu\text{-}NCPh_2)$ and $HRu_3(CO)_{10}$ (μ-PPh_2) with the unsaturated diphosphine ligands 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) and 2,3-bis(diphenylphosphino)maleic anhydride (bma) [8, 9, 10]. Both clusters react with these particular ligands to give initially the corresponding diphosphine-substituted clusters $HRu_3(CO)_8$(P–P)(μ-$NCPh_2$) and $HRu_3(CO)_8$(P–P) (μ-PPh_2), where the P–P ligands are chelated to one of the hydride-bridged ruthenium atoms. Equations 1 and 2 illustrate these reactions using the bpcd ligand.



(1)



(2)

Given the structural similarity between $HRu_3(CO)_{10}(\mu\text{-COMe})$ and the two pnictogen-bridged clusters $HRu_3(CO)_{10}(\mu\text{-NCPh}_2)$ and $HRu_3(CO)_{10}(\mu\text{-PPh}_2)$, coupled with our interest in metal cluster substitution chemistry using the ligands bpcd and bma [11], we present our results on the reaction of **1** with bma. Activation of cluster **1** by Me_3NO in the presence of bma affords the chelated cluster $HRu_3(CO)_8$(bma) (μ-COMe) (**2**) and the diphenylphosphine-substituted cluster $HRu_3(CO)_8(Ph_2PH)$ [μ-$PPh_2C{=}CC(O)OC(O)$] (**3**) as the major and minor products, respectively. Both product clusters have been isolated and fully characterized in solution by IR and NMR spectroscopies, and the solid-state structure of the minor Ph_2PH-substituted product **3** determined by X-ray diffraction analysis.

2. Experimental section

2.1. *General*

Cluster **1** was prepared from $Ru_3(CO)_{12}$ according to the procedure of Keister and Shapley [12], with the latter starting cluster synthesized from $RuCl_3 \cdot xH_2O$ using the carbonylation procedure of Bruce [13]. The bma ligand used in this study was synthesized from 2,3-dichloromaleic anhydride (Aldrich Chemical Co.) and Ph_2PSiMe_3 [14]. All reaction solvents were distilled from an appropriate drying agent under argon using Schlenk techniques and stored in Schlenk storage vessels equipped with high-vacuum Teflon stopcocks [15]. The IR and NMR solvents were reagent grade and were degassed with argon prior to their use. The reported combustion analysis was performed by Atlantic Microlab, Norcross, GA.

The infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in a 0.1 mm NaCl cell, using PC control and OMNIC software, while the ^1H and ^{31}P NMR spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer and 121 MHz on a Varian 300-VXR spectrometer. The reported ^{31}P chemical shifts, which were recorded in the proton-decoupled mode unless otherwise stated, are referenced to external H_3PO_4 (85%), taken to have $\delta = 0$.

2.2. *Reaction of $HRu_3(CO)_{10}$(μ-COMe) with bma to give clusters 2 and 3*

To 0.10 g (0.15 mmol) of $HRu_3(CO)_{10}(\mu\text{-COMe})$ and 70 mg (0.15 mmol) of bma in 50 mL of CH_2Cl_2 was added 22 mg (0.30 mmol) of Me_3NO, followed by stirring at room temperature for 3 h. TLC analysis at this point revealed the presence of a new yellow-brown spot ($R_f = 0.40$ in CH_2Cl_2) and considerable material at the origin of the plate. Column chromatography over silica gel (−78°C) using hexane afforded a trace amount of unreacted **1** (<10%), after which cluster **2** was isolated by changing the eluent to CH_2Cl_2. After **2** had been fully eluted from the column, cluster **3** was next isolated by flushing the column with CH_2Cl_2 : acetone (10 : 1). Yield of **2** : 0.10 g (66%). IR (CH_2Cl_2) : ν(CO) 2077 (s), 2040 (vs), 2004 (vs), 1985 (sh), 1841 (w, symm anhydride), 1775 (m, antisymm anhydride) cm^{-1}. ^{1}HNMR ($CDCl_3$) : δ 6.80–7.75 (m, 20 H, aryl), 3.76 (s, MeO), −13.16 (t, 1H, $J_{P\text{–}H} = 7$ Hz). ^{31}P NMR ($CDCl_3$; 298 K) : δ 45.45 (s), 24.31 (s). Repeated attempts to secure an acceptable microanalysis for **2** were all unsuccessful due to the oxygen sensitivity of **2**. Yield of **3** : 12 mg (8%). IR (CH_2Cl_2) : ν(CO) 2084 (s), 2047 (vs), 2034 (vs), 1998 (s), 1800 (b, w, symm anhydride), 1738 (m, antisymm anhydride) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.80–7.80 (m, 20 H, aryl), 7.06 (d, 1H, P–H, $J_{P-H} = 388$ Hz), −18.25 (dd, 1 H, hydride, $J_{P-H} = 12$, 17 Hz). ^{31}P NMR (CDCl$_3$; 298 K): δ 5.96 and 30.63 (major isomer; 90%), 21.99 and 28.52 (minor isomer; 10%). Anal. Calcd (found) for $C_{36}H_{22}O_{11}P_2Ru_3$: C, 43.42 (43.04); H, 2.23 (2.80).

2.3. *X-ray diffraction structure for cluster 3*

Single crystals of **3** suitable for X-ray crystallography were grown from a CH$_2$Cl$_2$ solution containing **3** that had been layered with hexane. A suitable crystal was chosen and sealed inside a Lindemann capillary tube, followed by mounting on an Enraf-Nonius CAD-4 diffractometer. After the cell constants were obtained, intensity data in the range of $2° \leq 2\theta \leq 44°$ were collected at 298 K and were corrected for Lorentz, polarization, and absorption (DIFABS). The structure was solved by SIR, and all nonhydrogen atoms were located with difference Fourier maps and full-matrix least-squares refinement. With the exception of the oxygen and carbon atoms, all nonhydrogen atoms (Ru and P) were refined anisotropically. The bridging hydride that spans the Ru(1a)–Ru(2a) and Ru(1b)–Ru(2b) vectors and the hydrogen attached to the Ph$_2$PH ligand [P(2a) and P(2b)] were not located during refinement. The carbon-bound hydrogen atoms were assigned to calculated positions and allowed to ride on the attached heavy atom. Refinement for **3** converged at $R = 0.0325$ and $R_w = 0.0380$ for 3518 independent reflections with $I > 3\sigma(I)$.

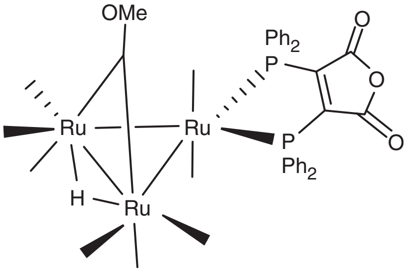
3. Discussion

3.1. *A. Synthesis and spectroscopic data for clusters 2 and 3*

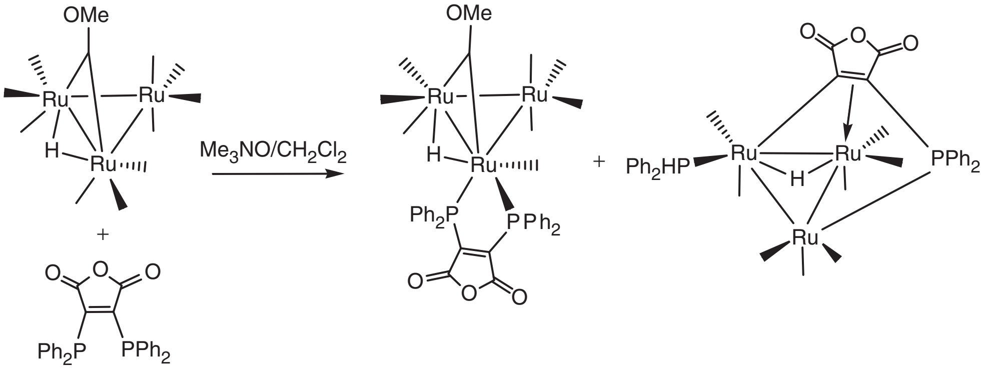
Treatment of HRu$_3$(CO)$_{10}$(μ-COMe) (**1**) and the diphosphine ligand bma in CH$_2$Cl$_2$ with the oxidative-decarbonylation reagent Me$_3$NO (2 equiv.) [16] leads to a rapid reaction and the production of the new clusters HRu$_3$(CO)$_8$(bma)(μ-COMe) (**2**) and HRu$_3$(CO)$_8$(Ph$_2$PH)[μ-PPh$_2$C=CC(O)OC(O)] (**3**). Both clusters exhibited extensive decomposition during chromatographic separation over silica gel at room temperature due to the hydrolysis of the anhydride ring. This complication has been encountered by us in the chromatographic purification of other bma-substituted complexes [17]. Both products could, however, be isolated with minimal material loss by carrying out the chromatography at −78°C under argon. While **2** and **3** appear to be stable in the solid state for a period of at least one week under argon, solutions containing **2** and **3** undergo fairly rapid decomposition upon exposure to the atmosphere. Scheme 2 shows the reaction under consideration and the structures for clusters **2** and **3**.

No reaction between **1** and the diphosphine ligand was observed when stirred at room temperature in the absence of Me$_3$NO, and simply heating a mixture of **1** and bma in either 1,2-dichloroethane or toluene at ca 70–75°C was accompanied by gross material loss and only trace amounts of cluster **2**, as assessed by TLC and IR spectroscopy. The thermolysis reaction between **1** and bma was not investigated further. To confirm that the chelated-bma cluster **2** does not serve as a precursor to cluster **3**, we carried out two control experiments, the first of which involved heating **2** in toluene at 70–75°C. Extensive decomposition was observed and no evidence for the formation of **3** was seen by TLC analysis. Finally, treatment of **2** in CH_2Cl_2 with added Me_3NO at room temperature led only to the slow decomposition of **2**.

The IR spectrum of **2** reveals terminal carbonyl groups at 2077 (s), 2040 (vs), 2004 (vs), 1985 (sh) cm^{-1}, along with a pair of lower energy ν(CO) bands at 1841 and 1775 cm^{-1} belonging to the vibrationally coupled symmetric and antisymmetric anhydride carbonyl groups [18]. The latter IR data support the presence of a bma ligand that is coordinated to the cluster frame by the two phosphorus moieties and not through the C=C π bond of the anhydride ring (*vide infra*). The ^1H NMR spectrum showed characteristic resonances at $\delta -13.16$ and 3.76 that are readily assignable to the high-field hydride and methoxy group, in addition to overlapping aromatic hydrogens at δ6.80–7.75 for the four phenyl groups of the bma ligand. The ^{31}P NMR spectrum of **2** exhibits two down-field singlets at δ 45.45 and 24.31 consistent with the presence of a chelating bma ligand and the proposed structure [19]. The observation of two inequivalent ^{31}P signals for **2** allows us to immediately rule out the below bma-chelated cluster from contention. This particular isomer, with its equatorially disposed diphosphine ligand, would give rise to a single ^{31}P resonance due to the mirror plane of symmetry that bisects the hydride-bridged Ru–Ru bond.



The IR spectrum of cluster **3** displays carbonyl stretching bands for the ruthenium-bound CO ligands at 2084 (s), 2047 (vs), 2034 (vs), and 1998 (s) cm^{-1}, while the two vibrationally coupled carbonyl groups of the anhydride residue appear at 1800 and 1738 cm^{-1}. The symmetric and antisymmetric anhydride carbonyl stretching bands



Scheme 2. Products isolated from the reaction of $HRu_3(CO)_{10}(\mu\text{-COMe})$ with bma.

serve as sensitive indicators for the coordination mode adopted by this ligand. The ca. 36 cm^{-1} shift to lower energy in the anhydride ν(CO) bands of **3** compared to those of cluster **2** confirms that the C=Cπ bond of the anhydride ring is coordinated to one of the ruthenium metals [11a, e, 20]. The ^{1}H NMR spectrum of **3** exhibits a μ_2-hydride resonance centered at δ −18.25 that appears as a doublet-of-doublets due to coupling with two inequivalent phosphorus groups. The doublet centered at δ 7.06 displays a $^1J_{P\text{–}H}$ value of 388 Hz and supports the presence of a Ph_2PH ligand in the coordination sphere of cluster **3**. The magnitude recorded for this geminal P–H coupling in **3** is in good agreement with the $^1J_{P\text{-}H}$ value reported for related Ph_2PH-substituted clusters [21]. The ^{31}P NMR spectrum contains two sets of ^{31}P resonances that support the fact that **3** exists as a ca 9 : 1 isomeric mixture in solution. Here the dominant isomer of **3** exhibits singlets at δ 5.96 and 30.63 for the coordinated Ph_2PH and Ph_2PC(anhydride ring) moieties, respectively, with the minor isomer displaying singlets at 21.99 and 28.52 for its Ph_2PH and Ph_2PC(anhydride ring) groups, respectively. The assignment for the Ph_2PH ligand in the major isomer was ascertained by a gated ^{1}H-decoupling ^{31}P experiment which afforded a geminal $J_{H\text{–}P}$ value identical to that found in the ^{1}H NMR spectrum of 3 (major isomer) [22].

3.2. *B. X-ray diffraction structure for cluster 3*

The solid-state structure of $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)OC(O)]$ (**3**) was determined by X-ray crystallography. Single crystals of **3** were found to exist as two independent molecules in the unit cell with no significant differences in the bond distances and angles between the two molecules. Tables 1 and 2 report the X-ray data

Table 1. X-ray crystallographic data and processing parameters for $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)COC(O)]$.

CCDC entry no.	607261
Space group	Monoclinic, $P2_1$
a (Å)	12.1467(7)
b (Å)	19.284(1)
c (Å)	16.867(1)
β (°)	109.639(6)
V (Å^3)	3721.0(4)
Mol formula	$C_{36}H_{22}O_{11}P_2Ru_3$
Fw	995.71
Formula units per cell (Z)	4
D_{calcd} (g cm^{-3})	1.774
λ (Mo-Kα) (Å)	0.71073
Absorption coeff (cm^{-1})	13.21
R_{merge}	0.013
Abs. corr. factor	0.91/1.08
Total reflections	9946
Independent reflections	4455
Data/res/parameters	4455/0/466
R	0.0325
R_w	0.0380
GOF on F^2	0.99
Weights	$[0.04F^2+(\sigma F)^2]^{-1}$
Largest diff in peak and hole (e Å^{-3})	0.57 near O(2a)

Table 2. Selected bond distances (Å) and angles (deg) for the two independent molecules of $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)OC(O)]$.[a]

Molecule A		Molecule B	
Ru(1a)–Ru(2a)	2.993(1)	Ru(1b)–Ru(2b)	2.988(1)
Ru(1a)–Ru(3a)	2.874(2)	Ru(1b)–Ru(3b)	2.869(2)
Ru(2a)–Ru(3a)	2.771(2)	Ru(2b)–Ru(3b)	2.793(2)
Ru(1a)–P(1a)	2.345(4)	Ru(1b)–P(1b)	2.353(4)
Ru(1a)–C(1a)	1.91(2)	Ru(1b)–C(1b)	1.91(1)
Ru(1a)–C(2a)	1.88(2)	Ru(1b)–C(2b)	1.90(2)
Ru(1a)–C(3a)	1.87(2)	Ru(1b)–C(3b)	1.87(2)
Ru(2a)–P(2a)	2.282(4)	Ru(2b)–P(2b)	2.270(4)
Ru(2a)–C(4a)	1.89(2)	Ru(2b)–C(4b)	1.90(2)
Ru(2a)–C(5a)	1.85(2)	Ru(2b)–C(5b)	1.87(2)
Ru(2a)–C(15a)	2.06(1)	Ru(2b)–C(15b)	2.06(1)
Ru(3a)–C(7a)	1.86(2)	Ru(3b)–C(7b)	1.87(2)
Ru(3a)–C(8a)	1.87(2)	Ru(3b)–C(8b)	1.91(2)
Ru(3a)–C(9a)	1.89(2)	Ru(3b)–C(9b)	1.91(2)
Ru(3a)–C(11a)	2.26(1)	Ru(3b)–C(11b)	2.25(1)
Ru(3a)–C(15a)	2.19(1)	Ru(3b)–C(15b)	2.19(1)
C(11a)–C(15a)	1.45(2)	C(11b)–C(15b)	1.43(2)
P(1a)–Ru(1a)–C(1a)	171.5(5)	P(1b)–Ru(1b)–C(1b)	168.1(5)
P(1a)–Ru(1a)–C(2a)	93.2(5)	P(1b)–Ru(1b)–C(2b)	97.3(5)
P(1a)–Ru(1a)–C(3a)	91.1(5)	P(1b)–Ru(1b)–C(3b)	90.3(5)
C(1a)–Ru(1a)–C(2a)	94.9(7)	C(1b)–Ru(1b)–C(2b)	94.6(7)
C(1a)–Ru(1a)–C(3a)	90.8(7)	C(1b)–Ru(1b)–C(3b)	89.6(7)
C(2a)–Ru(1a)–C(3a)	93.0(7)	C(2b)–Ru(2b)–C(3b)	95.0(7)
P(2a)–Ru(2a)–C(4a)	95.3(5)	P(2b)–Ru(2b)–C(4b)	96.4(5)
P(2a)–Ru(2a)–C(5a)	93.5(5)	P(2b)–Ru(2b)–C(5b)	91.9(5)
P(2a)–Ru(2a)–C(15a)	95.8(4)	P(2b)–Ru(2b)–C(15b)	95.2(4)
C(4a)–Ru(2a)–C(5a)	87.6(7)	C(4b)–Ru(2b)–C(5b)	87.2(7)
C(4a)–Ru(2a)–C(15a)	168.9(6)	C(4b)–Ru(2b)–C(15b)	168.4(6)
C(5a)–Ru(2a)–C(15a)	91.5(6)	C(5b)–Ru(2b)–C(15b)	92.3(6)
C(7a)–Ru(3a)–C(8a)	92.9(8)	C(7b)–Ru(3b)–C(8b)	92.1(7)
C(7a)–Ru(3a)–C(9a)	96.3(7)	C(7b)–Ru(3b)–C(9b)	95.0(7)
C(7a)–Ru(3a)–C(11a)	152.5(7)	C(7b)–Ru(3b)–C(11b)	154.4(7)
C(7a)–Ru(3a)–C(15a)	118.5(6)	C(7b)–Ru(3b)–C(15b)	121.0(6)
C(8a)–Ru(3a)–C(9a)	93.3(8)	C(8b)–Ru(3b)–C(9b)	95.1(7)
C(8a)–Ru(3a)–C(11a)	100.1(6)	C(8b)–Ru(3b)–C(11b)	100.3(6)
C(8a)–Ru(3a)–C(15a)	91.2(6)	C(8b)–Ru(3b)–C(15b)	90.1(6)
C(9a)–Ru(3a)–C(11a)	106.8(6)	C(9b)–Ru(3b)–C(11b)	106.0(6)
C(9a)–Ru(3a)–C(15a)	144.6(6)	C(9b)–Ru(3b)–C(15b)	143.4(7)
C(11a)–Ru(3a)–C(15a)	37.9(5)	C(11b)–Ru(3b)–C(15b)	37.6(5)
Ru(2a)–P(2a)–C(211a)	118.7(4)	Ru(2b)–P(2b)–C(211b)	119.5(4)
Ru(2a)–P(2a)–C(217a)	117.6(5)	Ru(2b)–P(2b)–C(217b)	118.1(5)
C(211a)–P(2a)–C(217a)	104.7(8)	C(211b)–P(2b)–C(217b)	104.0(7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

collection and processing parameters and selected bond distances and angles for **3**, respectively.

The ORTEP diagram of one of the two independent molecules of $HRu_3(CO)_8(Ph_2PH)[\mu\text{-}PPh_2C{=}CC(O)OC(O)]$ is shown in figure 1, where the molecular structure of **3** and the loss of the original bridging methoxymethylidyne ligand in cluster **1** are confirmed. Cluster **3** contains 48-valence electrons and is electron precise. The Ru–Ru bond distances range from 2.771(2) Å [Ru(2a)–Ru(3a)] to 2.993(1) Å [Ru(1a)–Ru(2a)], revealing the presence of a highly asymmetric metallic core in **3**.

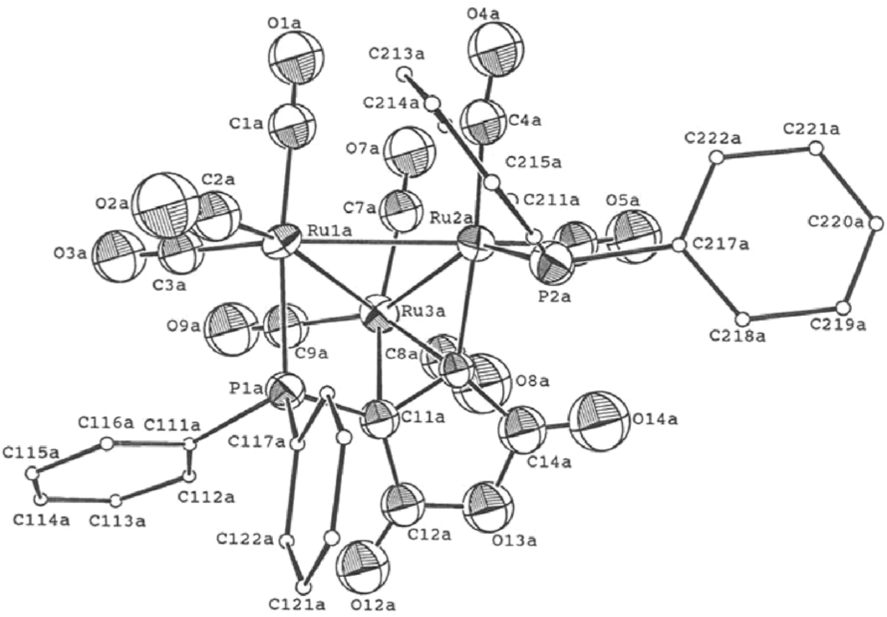


Figure 1. ORTEP diagram of one of the two independent molecules of $HRu_3(CO)_8(Ph_2PH)$ [μ-$PPh_2C{=}CC(O)OC(O)$] showing the thermal ellipsoids at the 30% probability level.

The hydride ligand, although not directly located in the difference maps during refinement, may be confidently assigned to the Ru(1a)–Ru(2a) vector on the basis of the bond-length trends exhibited by the Ru–Ru bond distances in **3** and those bond-length alterations displayed in other hydride-bridged ruthenium clusters [23]. The cleavage of one of the Ph_2P-C(maleic anhydride) bonds in the bma ligand affords the 5-electron, face-capping ligand μ-$PPh_2C{=}CC(O)OC(O)$ that binds one of the two metallic faces through a dative Ru(1a)–P(1a) bond [2.345(4) Å], a Ru–π bond through the anhydride residue [Ru(3a)–C(11a) = 2.26(1) Å; Ru(3a)–C(15a) = 2.19(1) Å], and a Ru(2a)–C(15a) [2.06(1) Å] σ bond; these bond distances are in excellent agreement with those distances reported for other metal cluster compounds possessing such linkages [24]. The Ru(2a)–P(2a) bond length of 2.282(4) Å is consistent with the presence of a coordinated Ph_2PH ligand. Here the angles of 118.7(4), 117.6(5), and 104.7(8)° for the Ru(2a)–P(2a)–C(211a), Ru(2a)–P(2a)–C(217a), and C(211a)–P(2a)–C(217a) linkages, respectively, agree well with those angles found in other Ph_2PH-substituted compounds [25]. The eight terminal carbonyl ligands reveal Ru–CO distances that range from 1.85(2) Å [Ru(2a)–C(5a)] to 1.91(2) Å [Ru(1a)–C(1a)] and collectively display an average distance of 1.88 Å. The remaining bond distances and angles are unremarkable and require no comment.

4. Conclusions

The methylidyne-bridged cluster $HRu_3(CO)_{10}(\mu$-COMe) reacts with bma in the presence of Me_3NO to give the simple substitution product $HRu_3(CO)_8$(bma)

(μ-COMe) and the diphenylphosphine-substituted cluster $HRu_3(CO)_8(Ph_2PH)$ [μ-$PPh_2C{=}CC(O)OC(O)$] as the major and minor products, respectively. The formal cleavage of the Ph_2P-C(maleic anhydride) bond, loss of the carbyne moiety, and formation of the diphenylphosphine ligand in the latter cluster have been verified by spectroscopic methods and single-crystal X-ray diffraction analysis. The mechanism associated with this interesting and facile transformation to **3** will be investigated by our groups in the future.

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