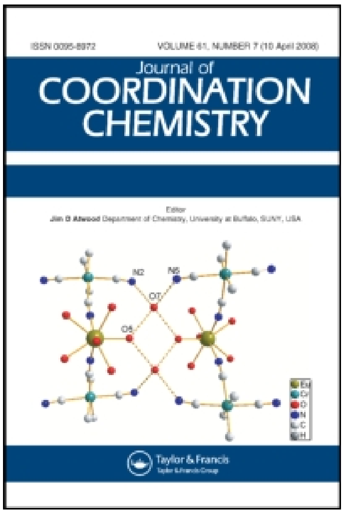

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Photochemically promoted regiospecific P–C bond cleavage in the diruthenium compound $Ru_2(CO)_2$(bmf): X-ray diffraction structure of $Ru_2(CO)_6$ [μ-C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2)

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The ruthenium cluster $Ru_3(CO)_{12}$ reacts with the diphosphine ligand 3,4-*bis*(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) in refluxing toluene to furnish the donor–acceptor compound $Ru_2(CO)_2$(bmf) as a 1 : 1 mixture of diastereomers. Photolysis of $Ru_2(CO)_2$(bmf) using 366 nm light leads to the oxidative cleavage of a P–C bond and formation of the phosphido-bridged complex $Ru_2(CO)_6$[μ-C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2). The regioselective Ph_2P–C(furanone ring) bond activation attendant upon optical excitation is traced to the phosphine group that was β to the furanone carbonyl group, as established by X-ray analysis of one of the diastereomers of $Ru_2(CO)_6$[μ-C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2). Both diruthenium products have been fully characterized in solution by IR and NMR (^1H and ^{31}P) spectroscopies and elemental analyses. The observed regioselectivity associated with the P–C bond activation in $Ru_2(CO)_2$(bmf) is discussed with respect to the chemistry of other bmf-substituted compounds prepared by our groups.

Keywords: Ruthenium; Diphosphine ligand; P–C bond oxidative cleavage; Photochemistry

1. Introduction

The exploration of the chemical reactivity of the unsaturated diphosphine ligands 2,3-*bis*(diphenylphosphino)maleic anhydride (bma), 4,5-*bis*(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd), and 3,4-*bis*(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) stills commands the attention of our groups [1]. Our interest in these rigid diphosphine ligands, the structures of which are depicted below, stems, in large part, from the nondissociative diphosphine ligand bridge-to-chelate isomerization and facile P–C and C–H bond activation exhibited by numerous di- and trinuclear metal compounds containing these ligands [2]. Studies dealing with the degradation pathways exhibited by diphosphine ligands are important to the greater scientific community given the numerous catalytic processes that are promoted by diphosphine-substituted metal complexes [3]. Knowledge of such reactions can guide researchers in the design of

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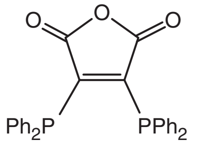
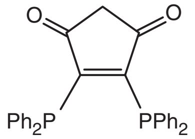
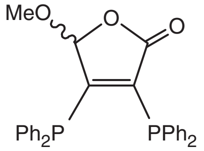
more robust catalyst systems that do not undergo deleterious ortho metalation of the aryl substituents and P–C bond cleavage reactions of the ancillary diphosphine ligand. Earlier we reported our results on the near-UV photolysis of the diruthenium compound $Ru_2(CO)_6$(bpcd), where the oxidative cleavage of the Ph_2P–C(dione) bond of the bpcd ligand and formation of the phosphido-bridged compound $Ru_2(CO)_6$ [μ-C=C(PPh_2)C(O)CH_2C(O)](μ-PPh_2) was demonstrated, as shown in equation (1) [4].



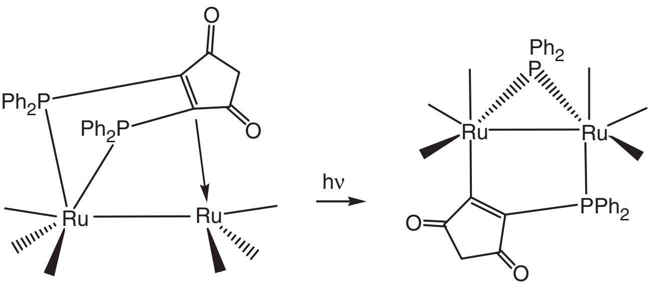
bma



bpcd

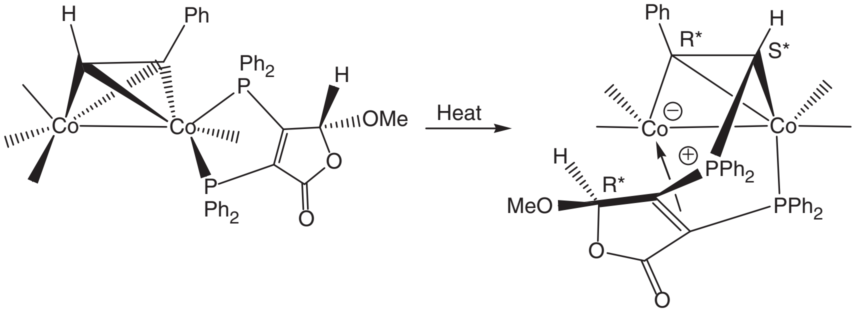


bmf



Equation (1)

While the reaction chemistry displayed by metal complexes substituted with bma and bpcd ligands is typically similar, the chiral bmf ligand often reveals different reactivity vis-á-vis the aforementioned diphosphine ligands due to the presence of inequivalent phosphine groups. The bmf ligand is thus ideally suited as a probe ligand for investigation of the regioselectivity and diastereoselectivity that may accompany any activation experienced by this ligand. One such reaction that illustrates this concept involves the intramolecular attack on the coordinated alkyne by the bmf ligand in $Co_2(CO)_4$(bmf)(μ-PhCCH) to produce the hydrocarbyl compound $Co_2(CO)_4$ [μ-PhC=CHPPh_2C=C(PPh_2)C(O)OCH(OMe)], as depicted in equation (2) [5, 6]. The observed product is interesting because it involves the formal attack of a phosphine group on the terminal alkyne carbon. Release of the least basic phosphine group in the bmf ligand, which also happens to be the one that was conjugated with the 2-carbonyl group of the furanone ring, readily accounts for the observed regiochemistry.



Equation (2)

Besides the above example that demonstrates the coordinative flexibility of the bmf ligand with respect to phosphine migration and alkyne attack, we have also observed the regioselective P–C bond cleavage and diastereoselective product formation in the thermolysis of mixed-metal tetrahedrane Co_2Ni and Co_2Mo clusters containing the bmf ligand [7, 8]. Examples of these reactions are shown in scheme 1, where the initially formed phosphido ligand in each of the phosphido-bridged clusters can be traced back to the phosphine moiety that was conjugated with the C(2) carbonyl group of the furanone ring. In the case of the Co_2Ni cluster, ^1H and ^{31}P NMR measurements on $PhCCo_2NiCp(CO)_4$(bmf) revealed the presence of two diastereomers in a 70 : 30 ratio that upon heating transform exclusively to the phosphido-bridged diastereomer depicted in the scheme. The reaction of the Co_2Mo cluster is more interesting in that the bmf-bridged cluster $PhCCo_2MoCp(CO)_6$(bmf), which is formed from the reaction of $PhCCo_2MoCp(CO)_8$ and bmf in refluxing CH_2Cl_2, is not stable and immediately fragments by an analogous P–C bond cleavage route to afford the diastereomerically pure phosphido-bridged compound $Co_2MoCp(CO)_5[\mu_2,\eta^2,\eta^1\text{-}C(Ph)C{=}C(PPh_2)C(O)OC(O)](\mu\text{-}PPh_2)$. The mono-phosphido Co_2Mo cluster competitively decomposes through a second P–C bond cleavage to produce the *bis*(phosphido) cluster $Co_2MoCp(CO)_5[\mu_2,\eta^2,\eta^1\text{-}C(Ph)C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$.

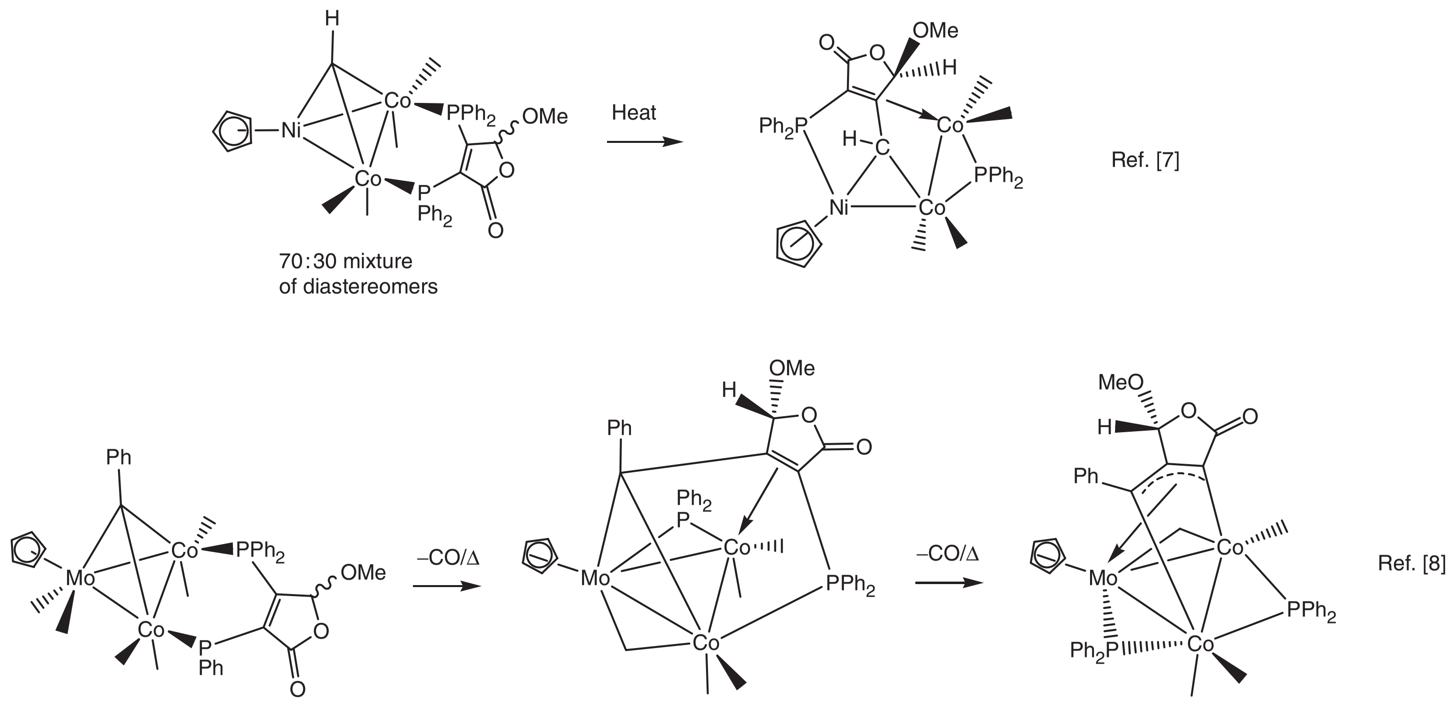
Herein we present our data on the ligand substitution in $Ru_3(CO)_{12}$ with the ligand bmf, which affords the diruthenium compound $Ru_2(CO)_6$(bmf). Photolysis of $Ru_2(CO)_6$(bmf) by near-UV light leads to regioselective activation of one of the two Ph_2P-C(furanone ring) and formation of the phosphido-bridged compound $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$, which is shown by NMR measurements to exist as a 1 : 1 mixture of diastereomers. The solid-state structure of one of the diastereomers of $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ has been determined by X-ray diffraction analysis.

2. Experimental section

2.1. *General*

The $Ru_3(CO)_{12}$ used in our studies was prepared from hydrated $RuCl_3$ using the carbonylation procedure of Bruce [9], while the bmf ligand was synthesized from 3,4-dichloro-5-hydroxy-2(5H)-furanone and Ph_2PLi [10]. All reaction and NMR solvents were distilled from an appropriate drying agent using Schlenk techniques and stored under argon in storage vessels equipped with high-vacuum Teflon stopcocks [11]. The near-UV photolyses were conducted with GE blacklights, having a maximum output of 366 ± 20 nm and a photon flux of ca 1×10^{-6} einstein min^{-1}. The reported quantum yield for the conversion of $Ru_2(CO)_6$(bmf) to $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ was determined by ferrioxalate actinometry [12]. The combustion analyses were 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 were recorded in



Scheme 1. Bmf ligand reactivity at mixed-metal tetrahedrane clusters.

the proton-decoupled mode and referenced to external H_3PO_4 (85%), taken to have $\delta = 0$.

2.2. *Preparation of $Ru_2(CO)_6$(bmf)*

To a large Schlenk vessel under argon was added 1.00 g (1.56 mmol) of $Ru_3(CO)_{12}$, 0.75 g (1.56 mmol) of bmf, and 50 mL of toluene, after which the vessel was heated overnight at 85°C. TLC examination of the cooled reaction solution revealed the presence of the desired compound as the major product as a light yellow spot ($R_f = 0.40$ in CH_2Cl_2/hexane 1 : 1 v/v). The solvent was removed under vacuum and the product purified by column chromatography using CH_2Cl_2/hexane 1 : 1 v/v. The isolated $Ru_2(CO)_6$(bmf) was recrystallized from CH_2Cl_2/hexane at 0°C. Yield of $Ru_2(CO)_6$(bmf): 0.53 g (40% based on bmf consumed). IR (CH_2Cl_2): v(CO) 2074 (s), 2039 (vs), 2016 (s), 1998 (s), 1975 (s), 1732 (m, ester) cm^{-1}. ^1H NMR (C_7D_8): δ 3.01 (s, OMe), 3.29 (s, OMe), 5.67–5.71 [b, overlapping CH(OMe)] 6.50–8.40 (m, 20H, aryl). ^{31}P NMR (C_7D_8): δ 22.77 (d, $J_{P-P} = 24$ Hz), 24.16 (d, $J_{P-P} = 24$ Hz), 25.56 (d, $J_{P-P} = 24$ Hz), 27.15 (d, $J_{P-P} = 24$ Hz). Anal. Calcd (found) for $C_{35}H_{24}O_9P_2Ru_2$: C, 49.30 (49.16); H, 2.84 (2.90).

2.3. *Photochemical preparation of $Ru_2(CO)_6$ [μ-C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2)*

To 0.20 g (0.23 mmol) of $Ru_2(CO)_6$(bmf) in a small Schlenk tube under argon was added 20 mL of CH_2Cl_2, after which the vessel was sealed and irradiated at 366 nm at 20°C. The sample was periodically monitored by IR spectroscopy until all of the starting material was consumed (ca three days). The solvent was next concentrated to ca 0.5 mL and subjected to a preliminary chromatographic purification over silica gel using CH_2Cl_2/hexane 1 : 1. The crude product was recrystallized from benzene/hexane to afford $Ru_2(CO)_6[\mu\text{-C=C(PPh}_2\text{)C(O)OCH(OMe)}](\mu\text{-PPh}_2)$ as a pale yellow solid in 71% yield (0.14 g). IR (CH_2Cl_2): v(CO) 2080 (vs), 2046 (vs), 2021 (s), 1991 (m), 1976 (m), 1746 (m, ester) cm^{-1}. ^1H NMR (C_7D_8): δ 3.57 (s, OMe), 3.59 (s, OMe), 5.58 [s, CH(OMe)], 5.99 [d, CH(OMe), $J_{P-H} = 1$ Hz], 6.85–7.90 (m, 20H, aryl). ^{31}P NMR (C_7D_8): δ 21.05 (d, $J_{P-P} = 29$ Hz), 21.64 (d, $J_{P-P} = 29$ Hz), 169.96 (d, phosphido, $J_{P-P} = 29$ Hz), 170.43 (d, phosphido, $J_{P-P} = 29$ Hz). Anal. Calcd (found) for $C_{35}H_{24}O_9P_2Ru_2$: C, 49.30 (49.14); H, 2.84 (2.86).

2.4. *X-ray diffraction structure for $Ru_2(CO)_6$ [μ-C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2)*

Single crystals of $Ru_2(CO)_6[\mu\text{-C=C(PPh}_2\text{)C(O)OCH(OMe)}](\mu\text{-PPh}_2)$ suitable for X-ray diffraction analysis were grown from a solution of the title compound in CH_2Cl_2 that had been layered with hexane. The chosen crystal was 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 $2^\circ \leq 2\theta \leq 44^\circ$ were collected at 298 K and were corrected for Lorentz, polarization, and absorption (DIFABS). The structure was solved by SHELX-86, and all nonhydrogen atoms were located with difference Fourier maps and full-matrix least-squares refinement and refined anisotropically. The carbon-bound hydrogen atoms were assigned to calculated positions and allowed to ride on the attached heavy atom. Refinement for $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ converged at $R = 0.0233$ and $R_w = 0.0237$ for 3271 independent reflections with $I > 3\sigma(I)$. Tables 1 and 2 summarize the pertinent X-ray data.

Table 1. X-ray crystallographic data and processing parameters for $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$.

CCDC entry no.	616940
Space group	Orthorhombic, Fdd2
a (Å)	37.982(2)
b (Å)	38.352(4)
c (Å)	9.445(1)
V (Å^3)	13,758(2)
Mol. formula	$C_{35}H_{24}O_9P_2Ru_2$
FW	852.66
Formula units per cell (Z)	16
D_{Calcd} (g cm^{-3})	1.646
λ (Mo-Kα) (Å)	0.71073
absorption coeff. (μ, cm^{-1})	10.04
R_{merge}	0.020
Absorption correction	Empirical
Abs. corr. factor	0.87/1.03
Total reflections	8396
Independent reflections	3271
Data/res./parameters	3271/0/432
R	0.0233
R_w	0.0237
GOF on F^2	0.98

Table 2. Selected bond distances (Å) and angles (°) in $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$.[a]

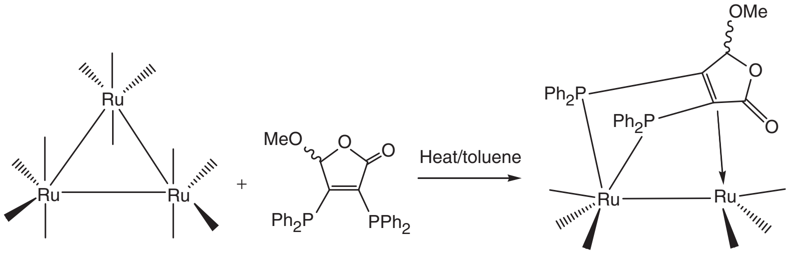
Ru(1)–Ru(2)	2.8755(6)	Ru(1)–P(1)	2.397(2)
Ru(1)–P(2)	2.330(1)	Ru(1)–C(1)	1.946(6)
Ru(1)–C(2)	1.936(6)	Ru(1)–C(3)	1.913(6)
Ru(2)–P(2)	2.326(1)	Ru(2)–C(4)	1.948(6)
Ru(2)–C(5)	1.993(7)	Ru(2)–C(6)	1.877(6)
Ru(2)–C(11)	1.783(5)	Ru(2)–C(15)	2.082(6)
C(11)–C(12)	1.499(8)	C(11)–C(15)	1.332(7)
C(14)–C(15)	1.524(8)	O(13)–C(12)	1.361(7)
O(13)–C(14)	1.440(7)		
Ru(2)–P(2)–Ru(1)	76.28(5)	P(2)–Ru(1)–P(1)	94.68(6)
P(2)–Ru(2)–C(15)	90.0(1)	P(2)–Ru(2)–C(4)	152.6(2)
P(2)–Ru(2)–C(5)	92.4(2)	P(2)–Ru(2)–C(6)	104.4(2)
C(15)–Ru(2)–C(4)	85.8(2)	C(15)–Ru(2)–C(5)	175.4(2)
C(15)–Ru(2)–C(6)	91.6(3)	Ru(1)–Ru(2)–C(6)	156.3(2)
Ru(2)–Ru(1)–C(3)	161.6(2)	P(2)–Ru(1)–C(3)	110.2(2)
P(2)–Ru(1)–C(2)	140.1(2)	P(2)–Ru(1)–C(1)	89.2(2)
P(1)–Ru(1)–C(3)	89.8(2)	P(1)–Ru(1)–C(2)	88.4(2)
P(1)–Ru(1)–C(1)	175.8(2)	P(1)–C(11)–C(15)	122.6(4)
O(14)–C(14)–C(15)	110.3(5)	O(14)–C(14)–O(13)	110.2(5)
C(111)–P(1)–C(117)	102.3(2)	C(211)–P(2)–C(217)	99.0(2)

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

3. Results and discussion

3.1. *Synthesis and characterization of Ru$_2$(CO)$_6$(bmf)*

Thermolysis of Ru$_3$(CO)$_{12}$ with the diphosphine ligand bmf in toluene solvent at 85°C furnishes the dinuclear compound Ru$_2$(CO)$_6$(bmf) as the dominant reaction product, as shown in equation (3). The fact that Ru$_2$(CO)$_6$(bmf) is formed as the major product and not the bmf-substituted cluster Ru$_3$(CO)$_{10}$(bmf) is attributed to the instability of this latter cluster that undoubtedly forms but fragments to the observed diruthenium compound. Accompanying the decomposition of the putative cluster Ru$_3$(CO)$_{10}$(bmf) is the formation of "Ru(CO)$_4$", which trimerizes to regenerate Ru$_3$(CO)$_{12}$. The generality of this scenario has been confirmed in the reaction of Ru$_3$(CO)$_{12}$ with the unsaturated diphosphine ligands (Z)-Ph$_2$PCH=CHPPh$_2$ and bpcd [4, 13]. TLC examination of the reaction solution revealed the presence of the starting cluster and Ru$_2$(CO)$_6$(bmf), along with two other minor products, the IR spectra of which did not display any evidence for a coordinated bmf ligand. The decomposed material observed at the origin of the plate did not exhibit any mobility in common solvents and its identity was not pursued. The Ru$_2$(CO)$_6$(bmf) was subsequently isolated by column chromatography over silica gel as a light yellow, air-stable solid. Ru$_2$(CO)$_6$(bmf) was characterized in solution by IR and NMR spectroscopies and by combustion analysis.

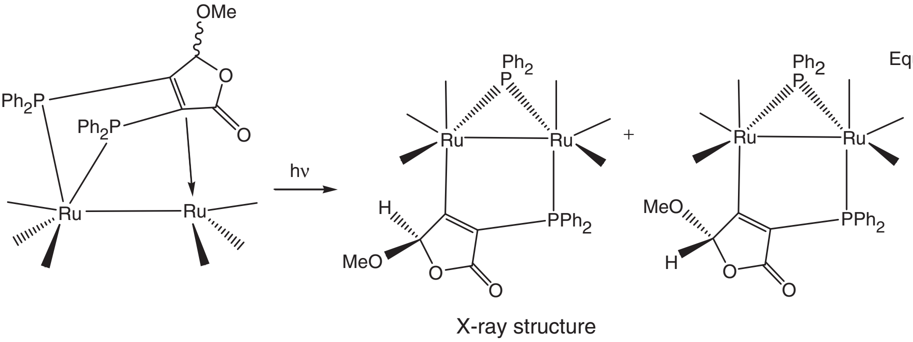


Equation (3)

The IR spectrum of Ru$_2$(CO)$_6$(bmf) in CH$_2$Cl$_2$ exhibits terminal carbonyl stretching bands at 2074 (s), 2039 (vs), 2016 (s), 1998 (s), and 1975 (s) cm^{-1} that closely match the reported IR data for the related diruthenium compounds Ru$_2$(CO)$_6$[(Z)-Ph$_2$PCH = CHPPh$_2$] [13a], Ru$_2$(CO)$_6$(bpcd) [3], and Ru$_2$(CO)$_6$(bma) [14]. The signature v(CO) band of the furanone moiety was found at 1732 (m) cm^{-1}, which is shifted by ca 20 cm^{-1} to lower energy relative to free bmf [10b] due to coordination of the alkene π bond of the furanone ring to one of the ruthenium atoms in Ru$_2$(CO)$_6$(bmf). The NMR data provided crucial insight into the diastereomeric composition of Ru$_2$(CO)$_6$(bmf). The ^{1}H NMR spectrum in toluene-d$_8$ revealed the presence of a pair of methoxy resonances at δ 3.01 and 3.29 in a 46 : 54 ratio, respectively, supporting the existence of an essentially equimolar mixture of diastereomers in solution. The observation of a 1 : 1 mixture of diastereomers suggests that minimal steric congestion exists between the alkene-bound Ru(CO)$_3$ moiety and the proximal and distal methoxy groups in Ru$_2$(CO)$_6$(bmf). The two methine hydrogens in Ru$_2$(CO)$_6$(bmf) could not be correlated with the distinct methoxy groups since they appeared as overlapping resonances centered at δ 5.69. Finally, the aryl hydrogens appeared as a multiplet at δ 6.50–8.40. Examination of the same sample by ^{31}P NMR spectroscopy corroborated the ^{1}H NMR data. Here four equal intensity doublets at δ 22.77, 24.16, 25.56, and 27.15 were recorded in agreement with the proposed mixture of diastereomers.

3.2. *Photochemical activation of Ru$_2$(CO)$_6$(bmf) and X-ray structure for Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$)*

The thermal and photochemical reactivity of Ru$_2$(CO)$_6$(bmf) parallels that of the related diphosphine-substituted complex Ru$_2$(CO)$_6$(bpcd) [4]. Heating a sealed NMR tube containing Ru$_2$(CO)$_6$(bmf) in toluene-d$_8$ at 100°C for 24 hrs revealed only unreacted starting material, which is in agreement with Ru$_2$(CO)$_6$(bpcd) and its reported stability up to ca 140°C. Ru$_2$(CO)$_6$(bmf) is photosensitive and upon exposure to near-UV light cleanly transforms into the phosphido-bridged compound Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) (see equation (4)). The measured quantum efficiency (Φ) of 0.005 for the conversion of Ru$_2$(CO)$_6$(bmf) to Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$), while low, compares favorably with those values determined by us in other systems exhibiting P–C bond activation [2d, 4, 15]. That the nature of the ancillary diphosphine ligand is important in the photochemically promoted P–C bond activation sequence is verified by the fact that Ru$_2$(CO)$_6$[(Z)-Ph$_2$PCH=CHPPh$_2$] is inert under comparable conditions [4]. Having established a convenient protocol for the synthesis of Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$), the compound was isolated by column chromatography and characterized in solution by IR and NMR spectroscopies and the molecular structure determined by X-ray crystallography.



Equation (4)

The IR spectrum for Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) exhibits v(CO) bands at 2080 (vs), 2046 (vs), 2021 (s), 1991 (m), and 1976 (m) cm^{-1} for the terminal Ru-CO groups. The furanone carbonyl moiety appears at 1746 (m) cm^{-1} as a well-behaved Gaussian band, reinforcing the cleavage of only one of the two Ph$_2$P–C (furanone ring) bonds. Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) exists in solution as a 1 : 1 mixture of diastereomers based on the two sets of methoxy (δ 3.57 and 3.59) and methine (δ 5.58 and 5.99) resonances recorded in the ^{1}H NMR spectrum. In concert with the ^{1}H NMR data, the ^{31}P NMR spectrum showed a set of down-field doublets (δ 169.96 and 170.43) for the two phosphido moieties and two up-field doublets (δ 21.05 and 21.64) assignable to the tertiary phosphine ligand in each diastereomer [16].

The solid-state structure of Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) was established by X-ray crystallography. Single crystals of Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) were found to exist as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. The ORTEP diagram of Ru$_2$(CO)$_6$[μ-C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) is shown in figure 1,

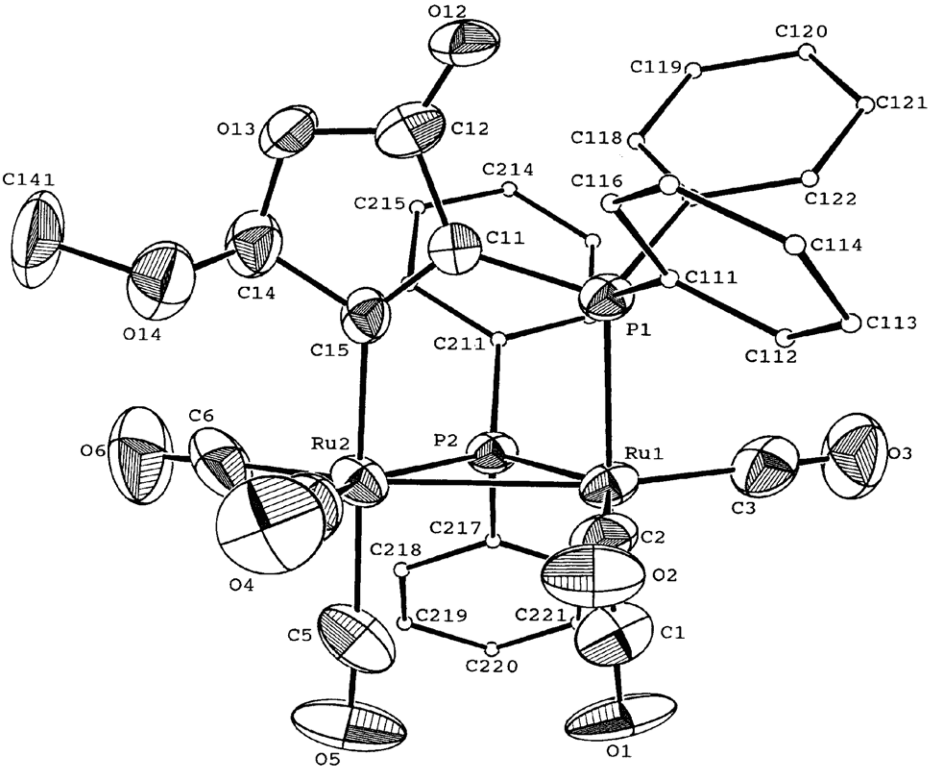


Figure 1. ORTEP diagram of $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ showing the thermal ellipsoids at the 30% probability level.

where the regiochemistry for the P–C bond activation is unequivocally traced to the phosphine moiety in the bmf ligand that was located β to the furanone carbonyl group [i.e. C(12) in the ORTEP diagram]. Each ruthenium atom is formally six-coordinate and displays a distorted-octahedral geometry. The Ru(1)–Ru(2) bond length of 2.8755(6) Å agrees well with its single-bond designation and those bond distances found in other di- and polynuclear ruthenium compounds [2a, 4, 12, 17]. The Ru(1)–P(2) [2.330(1) Å] and Ru(2)–P(2) [2.326(1) Å] bond distances and the Ru(1)–P(2)–Ru(2) bond angle of 76.28(5)° are unremarkable with respect to those distances and angles in related phosphido-bridged diruthenium compounds structurally characterized by us [4, 13, 18]. The phosphido ligand and the furanone moiety are orthogonally situated based on the 94.68(6)° and 90.0(1)° bond angles for the P(2)–Ru(1)–P(1) and P(2)–Ru(2)–C(15) linkages, respectively. The diastereomer depicted in the ORTEP diagram contains a distal or *trans* methoxy group relative to the bridging the phosphido ligand. The other diastereomer of $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ containing a proximal or *cis* methoxy group with respect to the μ_2-PPh_2 is not expected to experience any major steric perturbations based on the X-ray structural data of the distal isomer in agreement with the recorded NMR data that reveal an equimolar mixture of diastereomers. The remaining bond distances and angles require no comment.

4. Conclusions

Heating the diphosphine ligand bmf with $Ru_3(CO)_{12}$ is accompanied by cluster fragmentation and formation of the diruthenium compound $Ru_2(CO)_6$(bmf), which exists as a 1 : 1 mixture of diastereomers by NMR. Photolysis of $Ru_2(CO)_6$(bmf) with 366 nm light promotes the regioselective activation of the Ph_2P–C(furanone ring) bond that is situated β to the carbonyl moiety in the furanone ring. The resulting phosphido-bridged compound $Ru_2(CO)_6[\mu\text{-}C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$, which exists as an equimolar mixture of diastereomers, has been fully characterized in solution by IR and NMR spectroscopies. The solid-state structure of the distal diastereomer explored has been established by X-ray crystallography. Future studies employing transient photochemical techniques are planned in order to fully elucidate the nature of the excited state species involved in the P–C bond cleavage reaction.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/Cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: +44 1223 336033.

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