Synthesis of the chiral tetrahedral clusters RCCo$_2$NiCp(CO)$_4$(bmf) (R = H, Ph) and thermally promoted diphosphine ligand activation: Regiospecific P–C bond scission and X-ray diffraction structure of Co$_2$NiCp(CO)$_4$-[μ_2,η^2,η^1-C(H)C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$)

Simon G. Bott [a,*], Kaiyuan Yang [b], Michael G. Richmond [b,*]

[a] *Department of Chemistry, University of Houston, Houston, TX 77004, United States*
[b] *Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, TX 76203-5070, United States*

Abstract

Controlled thermolysis of the mixed-metal clusters RCCo$_2$NiCp(CO)$_6$ (R = H, Ph) with the chiral diphosphine ligand 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) leads to CO substitution and formation of the corresponding bmf-bridged clusters RCCo$_2$NiCp(CO)$_4$ (bmf) (R = H, Ph). These clusters exist in solution as a non-interconverting mixture of diastereomers, as determined by NMR spectroscopy. Whereas the benzylidyne-capped cluster PhCCo$_2$NiCp(CO)$_4$(bmf) decomposes in 1,2-dichloroethane (DCE) during prolonged heating at 83 °C, thermolysis of HCCo$_2$NiCp(CO)$_4$(bmf) affords the new phosphido-bridged cluster Co$_2$NiCp-(CO)$_4$[μ_2,η^2,η^1-C(H)C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) under the same conditions. This latter cluster has been isolated and characterized in solution by IR and NMR spectroscopies and the solid-state structure determined by X-ray diffraction analysis. The structural highlights for Co$_2$NiCp(CO)$_4$[μ_2,η^2,η^1-C(H)C=C(PPh$_2$)C(O)OCH(OMe)](μ-PPh$_2$) include the regioselective cleavage of the P–C(furanone ring) bond, coupled with polyhedral opening of the Co$_2$Ni core and attack on the CpNi center by the other phosphine moiety of the bmf ligand. The diastereoselectivity accompanying the formation of cluster Co$_2$NiCp(CO)$_4$[μ_2,η^2,η^1-C(H)C=C(PPh$_2$)C(O)OCH-(OMe)](μ-PPh$_2$) is discussed relative to steric effects within the cluster polyhedron.

1. Introduction

The ligand substitution behavior of the mixed-metal clusters RCCo$_2$NiCp(CO)$_6$ (R = Ph, H) with the rigid diphosphine ligands (Z)-Ph$_2$PCH=CHPPh$_2$ and 2,3-bis(diphenylphosphino)maleic anhydride (bma) has been recently studied by our groups [1–3]. While the former archetypal diphosphine reacts with PhCCo$_2$NiCp(CO)$_6$ to furnish the stable cobalt–cobalt bridged cluster PhCCo$_2$NiCp(CO)$_4$-[(Z)-Ph$_2$PCH=CHPPh$_2$], the latter diphosphine, with its electron-withdrawing maleic anhydride moiety, displays more diverse reaction chemistry. The bma ligand in PhCCo$_2$-NiCp(CO)$_4$(bma) is labile in solution at sub-ambient temperatures and yields spectroscopically observable quantities of the bridged and chelated cluster isomers. Thermolysis of PhCCo$_2$NiCp(CO)$_4$(bma) leads to bma/cluster activation and formation of the opened cluster Co$_2$NiCp-(CO)$_4$[μ_2,η^2,η^1-C(Ph)C=C(PPh$_2$)C(O)OC(O)](μ_2-PPh$_2$).

* Corresponding authors. Tel.: +1 713 743 2771 (S.G. Bott), +1 940 565 3548 (M.G. Richmond); fax: +1 940 565 4318 (M.G. Richmond).

E-mail addresses: sbott@uh.edu (S.G. Bott), cobalt@unt.edu (M.G. Richmond).

In contrast to the chemistry exhibited by the phenyl-capped cluster, the reaction of $HCCo_2NiCp(CO)_6$ with bma proceeds quite differently and with no direct evidence for the formation of the simple substitution product $HCCo_2$-$NiCp(CO)_4(bma)$. Here the bma ligand attacks the capping methylidyne carbon and the nickel center to furnish the 50e-cluster $Co_2NiCp(CO)_4(\mu_2\text{-}CO)[\mu_2,\eta^2,\eta^1\text{-}C(H)PPh_2C=C(PPh_2)C(O)OC(O)]$, which upon continued heating yields the phosphido-bridged cluster $Co_2NiCp(CO)_4[\mu_2,\eta^2,\sigma\text{-}C\text{-}(H)PPh_2C=CC(O)OC(O)](\mu_2\text{-}PPh_2)$. We believe that both steric and electronic effects within the cluster control the course of these reactions with bma [1,2], and our data clearly demonstrate the participation of the capping alkylidyne ligand in these reactions. Scheme 1 illustrates the divergent bma reactivity with the two different tetrahedrane clusters.

In comparison to the aforementioned diphosphine ligands the reactivity of the related chiral diphosphine 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone(bmf) has not been explored, to our knowledge, with polynuclear systems [4]. The bmf ligand is of interest as it will allow us to test for any preference in regioselectivity between the inequivalent PPh_2 moieties associated with the furanone platform, should the bmf ligand undergo analogous ligand activation upon cluster coordination. The electronic environments of these two PPh_2 moieties are sufficiently different, with the phosphine group at C-4 of the furanone ring being considerably less basic due to conjugation with the 2-carbonyl group. In an earlier study on the bmf-substituted cobalt compound $Co_2(CO)_4(bmf)(PhCCH)$, high diastereoselectivity and regioselectivity accompanied phosphine attack on the coordinated alkyne ligand, with the least basic phosphine group of the bmf ligand involved in this reaction, as shown in Eq. (1) [5–7].

chelating bmf ligand

$$(1)$$
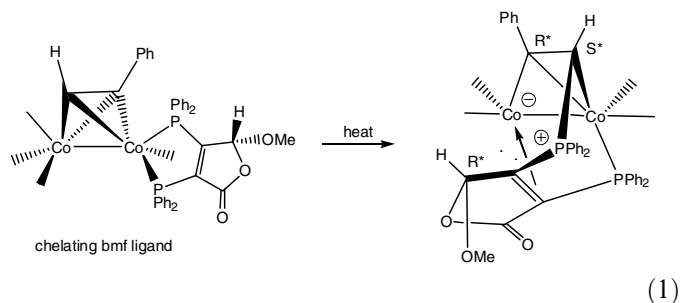
Herein we present our data on the ligand substitution in the mixed-metal tetrahedrane clusters $RCCo_2NiCp(CO)_6$ (R = Ph, H) with the diphosphine ligand bmf. The replacement of two CO groups by the bmf ligand affords the bridged cluster compounds $RCCo_2NiCp(CO)_4(bmf)$ as a non-equilibrating mixture of diastereomers [8], whose identities have been established by IR and NMR spectroscopies and elemental analyses. The thermolysis reactivity of these diastereomers has been studied, and in the case of $HCCo_2NiCp(CO)_4(bmf)$, the new cluster $Co_2NiCp(CO)_4$-$[\mu_2,\eta^2,\eta^1\text{-}C(H)C=C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ has been isolated as the exclusive diastereomer and fully characterized in solution and by X-ray crystallography. The X-ray structure of $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1\text{-}C(H)C=C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ confirms the regiospecific cleavage of the PPh_2 moiety associated with the bmf ligand and the subsequent coupling of the furanone ring with the μ_3-methylidyne capping ligand. The subtle but important role played by the furanone ring through its electronic perturbation of the two PPh_2 moieties in the bmf ligand is briefly discussed in the context of P–C bond cleavage reactivity.
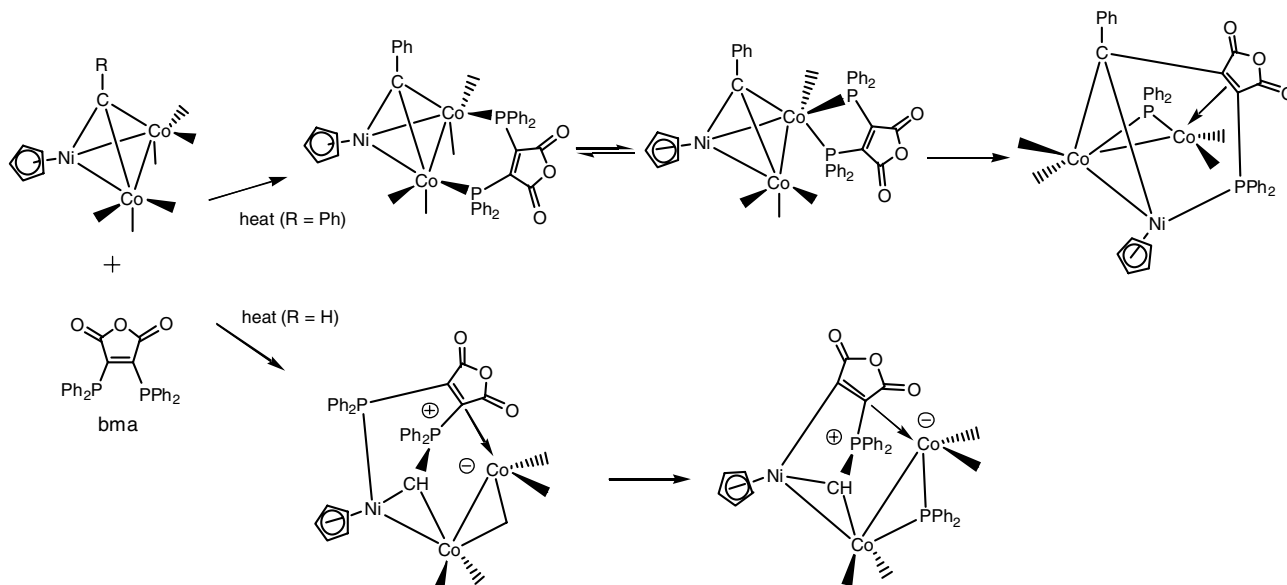
Scheme 1.

2. Experimental

2.1. General methods

The starting mixed-metal clusters $HCCo_2NiCp(CO)_6$ and $PhCCo_2NiCp(CO)$ were prepared from the corresponding tricobalt clusters $RCCo_3(CO)_9$ (R = H, Ph) and nickelocene according to the published procedures [9], and the bmf ligand was synthesized from 3,4-dichloro-5-hydroxy-2(5H)-furanone and Ph_2PK [4,10]. All reaction and NMR solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels [11]. The combustion analyses were performed by Atlantic Microlab, Norcross, GA.

The reported infrared data were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm amalgamated NaCl cells, using PC control and OMNIC software, while the ^1H NMR spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer and the ^{31}P NMR spectra were recorded at 121 MHz on a Varian 300-VXR spectrometer.

2.2. Synthesis of $RCCo_2NiCp(CO)_4(bmf)$

A. $HCCo_2NiCp(CO)_4(bmf)$. To a large Schlenk tube containing 0.40 g (0.95 mmol) of $HCCo_2NiCp(CO)_6$ and 0.45 g (0.93 mmol) of bmf was added 25 mL of 1,2-dichloroethane (DCE) via syringe. The reaction was then gently heated at 45–50 °C for 3 h, after which TLC examination of the solution revealed the complete consumption of the starting cluster and the formation of a new green–black spot ascribed to $HCCo_2NiCp(CO)_4(bmf)$. The product cluster was subsequently isolated by column chromatography over silica gel using CH_2Cl_2 as the eluent and recrystallized from CH_2Cl_2/hexane to afford $HCCo_2NiCp(CO)_4(bmf)$ in 81% yield (0.65 g). IR (CH_2Cl_2): v(CO) 2011 (s), 1983 (vs), 1964 (s), 1767 (m, furanone C=O) cm^{-1}. ^1H NMR (C_6D_6; 298 K): 2.24 (OMe, major), 2.34 (OMe, minor), 4.26 (CHOMe, major), 4.78 (CHOMe, minor), 5.19 (b, Cp), 6.80–7.90 (m, phenyl groups), 12.54 (μ_3-CH, major), 12.64 (μ_3-CH, minor). ^{31}P NMR (CH_2Cl_2; 183 K): 30.75 (minor), 32.33 (major), 34.75 (minor), 36.36 (major). Anal. Calc. (found) for $C_{39}H_{30}Co_2NiO_7P_2 \cdot 1/2CH_2Cl_2$: C, 53.19 (53.08); H, 3.48 (3.60).

B. $PhCCo_2NiCp(CO)_4(bmf)$. To 0.15 g (0.30 mmol) of $PhCCo_2NiCp(CO)_6$ and 0.15 g (0.31 mmol) of bmf in a large Schlenk tube was added ca. 30 mL of DCE. The reaction was refluxed for 1 h and then checked by TLC analysis, which confirmed the formation of a new black spot, some unreacted starting cluster and decomposition material at the origin of the TLC plate. The DCE was removed under vacuum and the residue was extracted with hexane to remove the unreacted $PhCCo_2NiCp(CO)_6$. The product was purified by column chromatography, as described above, to afford $PhCCo_2NiCp(CO)_4(bmf)$ as a black solid. Recrystallization from CH_2Cl_2/hexane gave $PhCCo_2NiCp(CO)_4(bmf)$ in 54% yield (0.15 g). IR (CH_2Cl_2): v(CO) 2008 (m), 1983 (vs), 1962 (s), 1767 (m, furanone

C=O) cm^{-1}. ^1H NMR (C_6D_6; 298 K): 2.13 (OMe, minor), 2.32 (OMe, major), 3.98 (CHOMe, minor), 4.40 (CHOMe, major), 4.78 (Cp, minor), 4.93 (Cp, major), 6.60–7.80 (m, phenyl groups). ^{31}P NMR (CH_2Cl_2; 183 K): 26.20 (major), 27.52 (minor), 34.95 (major), 36.58 (minor). Anal. Calc. (found) for $C_{45}H_{34}Co_2NiO_7P_2 \cdot 1/4CH_2Cl_2$: C, 57.43 (57.26); H, 3.65 (3.46).

2.3. Thermolysis of $HCCo_2NiCp(CO)_4(bmf)$

Heating a DCE solution (ca. 20 mL) containing 0.20 g (0.24 mmol) of $HCCo_2NiCp(CO)_4(bmf)$ under argon at 83 °C for 6 h led to the consumption of nearly all of the starting cluster (>95%) and production of a dark brown–black colored material, as judged by TLC analysis. The new material was isolated by column chromatography and recrystallized from CH_2Cl_2/hexane to furnish 0.11 g (55% yield) of $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-C(H)C=C(PPh_2)C(O)OCH(O-Me)](μ-PPh_2). IR (CH_2Cl_2): v(CO) 2020 (s), 1989 (vs), 1967 (s), 1951 (m), 1738 (m, furanone C=O) cm^{-1}. ^1H NMR (C_6D_6; 298 K): 3.29 (OMe), 4.84 (Cp), 4.95 (CHOMe), 6.80–8.45 (m, phenyl groups), 9.73 (μ_2-CH). ^{31}P NMR (CH_2Cl_2; 183 K): 71.22 (s, phosphine), 170.70 (s, phosphido). Anal. Calc. (found) for $C_{45}H_{34}Co_2NiO_7P_2$: C, 55.16 (54.68); H, 3.56 (3.32).

2.4. X-ray structural determination

A suitable black crystal of $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-C(H)C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2), which was grown from a CH_2Cl_2 solution of the cluster that had been layered with hexane, for X-ray diffraction analysis was selected and sealed inside a Lindemann capillary, followed by mounting on an Enraf-Nonius CAD-4 diffractometer. After the cell constants were obtained, intensity data in the range of $2 \leqslant 22 \leqslant 40°$ were collected at 298 K and were corrected for Lorentz, polarization, and absorption (DIFABS). The structure of $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-C(H)C=C(PPh_2)C(O)OCH(OMe)](μ-PPh_2) was solved by using Mo1EN. All non-hydrogen atoms were located with difference Fourier maps and full-matrix least-squares refinement and were refined isotropically due to weak crystal scattering. All hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom. Refinement converged at $R = 0.0509$ and $R_w = 0.0562$ for 962 unique reflections with $I > 3\sigma(I)$.

3. Results and discussion

3.1. Synthesis and spectroscopic data for $RCCo_2NiCp(CO)_4(bmf)$

Thermolysis of the clusters $RCCo_2NiCp(CO)_6$ (R = H, Ph) with bmf in 1,2-dichloroethane leads to the replacement of two CO ligands by the bmf ligand and formation of the new clusters $RCCo_2NiCp(CO)_4(bmf)$ in good yields. Both products were isolated by column chromatography

over silica gel and characterized in solution by IR and NMR spectroscopies. Solutions of $HCCo_2NiCp(CO)_4$-(bmf) and $PhCCo_2NiCp(CO)_4$(bmf) under argon appear to be indefinitely stable at room temperature, with slow decomposition being observed in solution upon exposure to oxygen.

The IR spectral data for the two $RCCo_2NiCp$-$(CO)_4$(bmf) clusters are essentially identical and exhibit three terminal $v(CO)$ bands for the cobalt-bound CO groups at 2011 (s), 1983 (vs), 1964 (s) cm^{-1} for $HCCo_2$-$NiCp(CO)_4$(bmf) and 2008 (m), 1983 (vs), 1962 (s) cm^{-1} for $PhCCo_2NiCp(CO)_4$(bmf). The IR spectral data for the terminal Co–CO bands in $RCCo_2NiCp(CO)_4$(bmf) are in excellent agreement with those data reported for $PhCCo_2$-$NiCp(CO)_4[(Z)-Ph_2PCH=CHPPh_2]$, whose diphosphine ligand bridges the two cobalt centers [3]. The carbonyl stretching band belonging to the ester moiety of the bmf ring in both products is found at 1767 cm^{-1} and is insensitive to the nature of the μ_3-hydrocarbyl capping ligand in each cluster [12].

The ^{1}H and ^{31}P NMR data provided valuable and unequivocal evidence for the presence of diastereomeric clusters from each reaction. The ^{1}H spectrum of $HCCo_2$-$NiCp(CO)_4$(bmf) in C_6D_6 solvent displayed diastereotopic resonances at δ 2.24 (major) and 2.34 (minor) belonging to the methoxy group and at δ 4.26 (major) and 4.78 (minor) for the methine hydrogen of the furanone carbocyclic ring. The relative ratio of these diastereomers based on the methoxy and methine hydrogens was ca. 2.7:1, a value also mirrored by the two distinct μ_3-CH capping ligand resonances at δ 12.54 (major) and 12.64 (minor). The Cp ligand and the phenyl groups appeared as a broadened singlet (δ 5.19) and a multiplet (δ 6.80–7.90), respectively. Consistent

with the determined ^{1}H NMR ratio of diastereomers was the ^{31}P NMR spectrum for $HCCo_2NiCp$-$(CO)_4$(bmf). Here two pairs of ^{31}P resonances at δ 36.36 and 32.33 (major) and δ 34.75 and 30.75 (minor) in a 2.7:1 ratio were found in CH_2Cl_2 and room temperature. The two different ^{31}P resonances found in each diastereomer result from the local bmf environment that renders the two phosphine groups inequivalent. That the observed broadness in the ^{31}P resonances (ca. 50–65 Hz full-width at half height) was due to ^{59}Co quadrupolar effects and not a fluxional process involving the equilibration of the diastereomers was ascertained by recording the ^{31}P NMR spectrum at 183 K [13]. A slight sharpening of the ^{31}P resonances was found with no significant change in the relative populations or chemical shifts of the two diastereomers, reinforcing the static or frozen coordination of the bmf ligand at the cluster polyhedron. The top portion of Scheme 2 depicts the two diastereomers of $HCCo_2NiCp(CO)_4$(bmf). Unfortunately, no definitive assignment can be made concerning the exact disposition or make-up of the major and minor diastereomers of $HCCo_2NiCp(CO)_4$(bmf) displayed in Scheme 2, on the basis of the data at hand. Attempts to grow crystals of $HCCo_2NiCp(CO)_4$(bmf) for X-ray analysis were not successful.

The NMR data for the related benzylidyne-capped cluster $PhCCo_2NiCp(CO)_4$(bmf) parallel those of $HCCo_2$-$NiCp(CO)_4$(bmf). Here a pair of methoxy [δ 2.13 (minor) and 2.32 (major)], methine [δ 3.98 (minor) and 4.40 (major)], and Cp [δ 4.78 (minor) and 4.93 (major)] signals support the presence of diastereomers, whose ratio of ca. 2.7:1 is similar to that found for the methylidyne-capped analogue (vide supra). The ^{31}P NMR spectrum recorded at 183 K exhibited two pairs of slightly broadened resonances
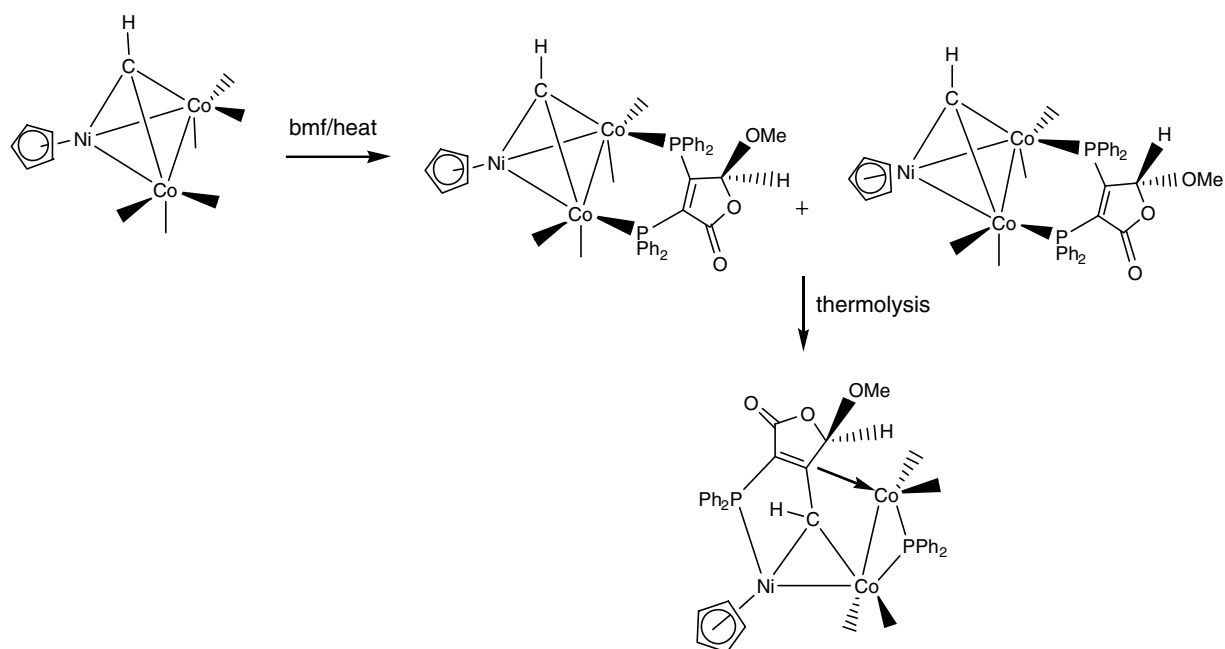
Scheme 2.

[δ 26.20 and 34.95 (major); 27.52 and 36.58 (minor)] fully consistent with the proposed nature of these diastereomers. Recording the ^{31}P NMR spectrum at room temperature did not lead to any substantial change in the diastereomer ratio.

3.2. Thermolysis reactivity of HCCo₂NiCp(CO)₄(bmf) and PhCCo₂NiCp(CO)₄(bmf)

Routine thermolysis studies were next conducted with HCCo₂NiCp(CO)₄(bmf) and PhCCo₂NiCp(CO)₄(bmf) in order to examine the stability of these clusters towards ligand/cluster activation. Refluxing both clusters in DCE solution under argon leads to a noticeable reaction as judged by TLC analysis, but whereas PhCCo₂NiCp(CO)₄(bmf) decomposes, HCCo₂NiCp(CO)₄(bmf) transforms into the new phosphido-bridged cluster Co₂NiCp(CO)₄[μ_2,η^2,η^1-C(H)C=C(PPh₂)C(O)OCH(OMe)](μ-PPh₂). This cluster could be isolated by column chromatography as a mildly air-sensitive brown–black solid. The IR spectrum exhibited five carbonyl stretching bands at 2020 (s), 1989 (vs), 1967 (s), 1951 (m), and 1738 (m) cm⁻¹, of which the former four represent terminal carbonyl groups associated with the two cobalt atoms. The low-energy ν(CO) band at 1738 cm⁻¹ is readily ascribed to the C=O moiety of the furanone ring, and the 29 cm⁻¹ shift to lower energy relative to the same carbonyl group in HCCo₂NiCp(CO)₄(bmf) and PhCCo₂-NiCp(CO)₄(bmf) supports the coordination of the C=C π bond of the furanone ring to one of three metal atoms in the product [5,14]. ^{1}H NMR signals at δ 3.29 (OMe), 4.84 (Cp), 4.95 (CHOMe), 6.80–8.45 (phenyls), and 9.73 (μ_2-CH) indicate that only a single diastereomer is present [15]. The observation of a low-field ^{31}P resonance at δ 170.70 supports the formation of a phosphido moiety [16], and the sharp ^{31}P resonance at δ 71.22 rules out a cobalt-bound phosphine moiety and suggests that the CpNi center has been attacked by one of the two PPh₂ groups of the original bmf ligand. A similar transformation has recently been reported by us in the thermolysis of PhCCo₂NiCp(CO)₄(bma) [2]. While the ^{31}P NMR data reveal an activation of the bmf ligand with respect to a P–C bond cleavage, the data do not shed light on which phosphine moiety has participated in the cleavage reaction.

3.3. X-ray diffraction structure of Co₂NiCp(CO)₄ [μ_2,η^2,η^1-C(H)C=C(PPh₂)C(O)OCH(OMe)](μ-PPh₂)

The molecular structure and the source of the phosphido moiety in Co₂NiCp(CO)₄[μ_2,η^2,η^1-C(H)C=C(PPh₂)C(O)O-CH(OMe)](μ-PPh₂) were established by X-ray crystallography. Single crystals of Co₂NiCp(CO)₄[μ_2,η^2,η^1-C(H)C=C(PPh₂)C(O)OCH(OMe)](μ-PPh₂) crystallize in the unit cell as independent molecules with no unusually short inter- or intramolecular contacts. Tables 1 and 2 report the X-ray data collection and processing parameters and selected bond distances and angles, respectively.

Table 1

X-ray crystallographic data and processing parameters for Co₂NiCp-(CO)₄[μ_2,η^2,η^1-C(H)C=C(PPh₂)C(O)OCH(OMe)](μ-PPh₂)

CCDC entry no.	274192
Space group	Orthorhombic, $Pac2_1$
a (Å)	20.864(8)
b (Å)	9.528(3)
c (Å)	17.923(5)
V (Å³)	3563(2)
Molecular formula	C₃₉H₃₀Co₂NiO₇P₂
Fw	849.19
Formula units per cell (Z)	4
D_{calcd} (g/cm³)	1.583
λ (Mo Kα) (Å)	0.71073
Absorption coefficient (cm⁻¹)	15.82
Max/min trans.	0.94/1.18
Total reflections	1936
Independent reflections	962
Data/res/parameters	962/0/204
R	0.0509
R_w	0.0562
Goodness-of-Fit on F^2	1.12
Weights	$[0.04F^2 + (\sigma F^2)]^{-1}$

Table 2

Selected bond distances (Å) and angles (°) for Co₂NiCp(CO)₄[μ_2,η^2,η^1-C(H)C=C(PPh₂)C(O)OCH(OMe)](μ-PPh₂)[a]

Bond distances (Å)	
Ni–Co(1)	2.463(5)
Ni–P(1)	2.145(7)
Ni–C(16)	2.03(2)
Co(1)–C(16)	1.93(2)
Co(2)–C(11)	1.98(3)
C(11)–C(12)	1.43(4)
C(14)–C(15)	1.62(3)
O(14)–C(14)	1.41(3)
Co(1)–Co(2)	2.612(5)
Ni–Cp(centroid)	1.77(2)
Co(1)–P(2)	2.120(7)
Co(2)–P(2)	2.145(7)
Co(2)–C(15)	2.10(2)
C(11)–C(15)	1.46(3)
C(15)–C(16)	1.34(4)
O(14)–C(141)	1.45(3)
Bond angles (°)	
Co(1)–Ni–P(1)	96.9(3)
P(1)–Ni–C(16)	88.2(7)
Ni–Co(1)–P(2)	147.7(3)
Co(2)–Co(1)–P(2)	52.7(2)
Co(2)–Co(1)–C(2)	144(1)
P(2)–Co(1)–C(16)	99.1(7)
Co(1)–P(2)–Co(2)	75.5(2)
C(11)–Co(2)–C(15)	41.9(9)
Co(1)–Ni–C(16)	49.8(7)
Ni–Co(1)–Co(2)	98.7(1)
Ni–Co(1)–C(16)	53.3(6)
Co(2)–Co(1)–C(1)	99.2(9)
Co(2)–Co(1)–C(16)	73.0(7)
Co(1)–Co(2)–P(2)	51.8(2)
Ni–C(16)–Co(1)	76.9(8)

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

The ORTEP diagram of $Co_2NiCp(CO_4[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)C(O)OCH(OMe)](\mu$-$PPh_2)$ is shown in Fig. 1. One of the important structural features associated with this 50-valence electron cluster includes the *nido → hypho* polyhedral cluster opening in going from $HCCo_2NiCp(CO)_4(bmf)$ to $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)C(O)OCH(O$-$Me)](\mu$-$PPh_2)$ [17]. The Co(1)–Co(2) and Ni–Co(1) bond distances of 2.612(5) and 2.463(5) Å, respectively, are unremarkable relative to other structurally characterized Co and Ni containing clusters of this genre [1–3,18]. and the internuclear distance of 3.85(2) Å between the Ni···Co(2) centers rules out any direct bonding between these atoms, consistent with Polyhedral Skeletal Electron Pair (PSEP) theory that guides the polyhedral opening in Co_2NiCp-$(CO)_4[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)C(O)OCH(OMe)](\mu$-$PPh_2)$ [17]. The unequivocal origin of the phosphido ligand that spans the Co(1)–Co(2) vector in $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)C(O)OCH(OMe)](\mu$-$PPh_2)$ is traced to the Ph_2P moiety that was conjugated to the carbonyl group of the bmf ligand in $HCCo_2NiCp(CO)_4(bmf)$. This supports our contention concerning the regioselectivity for P–C bond cleavage reactions in the case of the non-symmetrical bmf ligand. Here the less basic phosphine group is expected to dissociate more readily from a metal center in comparison to other more basic and strongly bound PPh_2 moiety, facilitating the subsequent P–C bond cleavage. Complicating matters with respect to the order or timing for phosphine dissociation in the thermal activation of $HCCo_2NiCp$-$(CO)_4(bmf)$ is the accompanying attack of the CpNi center

by the other phosphine moiety. The preferential dissociation of the less basic phosphine moiety in a coordinated bmf ligand at a related Co_2Mo tetrahedral cluster has been confirmed by us in keeping with our postulate [19]. The 6e-donor ligand μ_2,η^2,η^1-$C(H)C=C(PPh_2)C(O)OCH(OMe)$ binds the metallic frame in a manner identical to that found by us in the bma-activated ligand in $Co_2NiCp(CO)_4$-$[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)C(O)OC(O)](\mu$-$PPh_2)$ [2]. The Co(1)–P(2) [2.120(7) Å] and Co(2)–P(2) [2.145(7) Å] bond distances and the 75.5(2)° angle for the Co(1)–P(2)–Co(2) linkage are consistent with other phosphido ligands that span a Co–Co bond [20]. The four carbonyl groups associated with the two cobalt centers are linear with normal distances.

The 1.46(3) Å distance found for the C(11)–C(15) π bond of the furanone ring is lengthened by ca. 0.11 Å in comparison to a simple alkene unit as a result of coordination to the Co(2) center. The corresponding Co(2)–C(11) and Co(2)–C(15) bond lengths of 1.98(3) and 2.10(2) Å, respectively, and the C(11)–Co(2)–C(15) bond angle of 41.9(9)° are similar to values reported for other cobalt-bound alkene compounds. The observed stereoisomeric control in the reaction that furnishes $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)$-$C(O)OCH(OMe)](\mu$-$PPh_2)$ is strongly influenced by the ancillary methoxy group attached to C(14) and its interaction with the bridging phosphido moiety. Here the methoxy group can adopt one of two positions relative to the phosphido ligand, being either proximal (syn) or distal (anti) to P(2) and its phenyl substituents. In the case of

Fig. 1. ORTEP diagram of $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1$-$C(H)C=C(PPh_2)C(O)OCH(OMe)](\mu$-$PPh_2)$ showing the thermal ellipsoids at the 30% probability level.

$Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1\text{-}C(H)C{=}C(PPh_2)C(O)OCH(OMe)]\text{-}$ (μ-PPh$_2$), a distal relationship exists, and this allows the methoxy moiety to avoid close, unfavorable intramolecular contacts with the phenyl group composed by the C(217) through C(222) atoms.

4. Conclusions

The ligand substitution in the mixed-metal clusters $RCCo_2NiCp(CO)_6$ (R = H, Ph) with the chiral diphosphine ligand bmf has been found to give a diastereomeric mixture of the bmf-bridged clusters $RCCo_2NiCp(CO)_4(bmf)$. Whereas heating $PhCCo_2NiCp(CO)_4(bmf)$ leads to complete destruction of the cluster, thermolysis of $HCCo_2NiCp(CO)_4(bmf)$ yields the new phosphido-bridged cluster Co_2NiCp-$(CO)_4[\mu_2,\eta^2,\eta^1\text{-}C(H)C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$ as a result of regiospecific Ph$_2$P–C(furanone ring) bond cleavage. The participation of the less basic phosphine moiety in the bmf ligand in the P–C bond activation was ascertained by X-ray crystallography.

5. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 274192 for $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1\text{-}C(H)C{=}C(PPh_2)C(O)OCH(OMe)](\mu\text{-}PPh_2)$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; email: deposit@ccdc.ac.uk or http://www:ccdc.cam.ac.uk].

References

[1] S.G. Bott, K. Yang, K.A. Talafuse, M.G. Richmond, Organometallics 22 (2003) 1383.
[2] S.G. Bott, K. Yang, M.G. Richmond, J. Organomet. Chem. 690 (2005) 3067.
[3] S.G. Bott, K. Yang, S.-H. Huang, M.G. Richmond, J. Chem. Crystallogr. 34 (2004) 883.
[4] D. Fenske, H.J. Becher, Chem. Ber. 108 (1975) 2115.
[5] K. Yang, S.G. Bott, M.G. Richmond, Organometallics 14 (1995) 4977.
[6] (a) Only one of the four chiral chelating isomers of $Co_2(CO)_4(bmf)(\mu$-HCCPh) is shown in Eq. (1);
(b) The X-ray strucucture of $Co_2(CO)_4[\mu\text{-}\eta^2,\eta^2,\eta^1,\eta^1\text{-}PhC{=}C(H)$-$PPh_2C{=}C(PPh_2)(C(O)OCH(OMe)]$ consists of a racemic mixture of the R,S,R and S,R,S enantiomers (Ref. [5]), with Eq. (1) showing only the latter enantiomer for simplicity.

[7] For a report on the only other known dinuclear bmf-substituted compound, see S.G. Bott, K. Yang, M.G. Richmond, J. Chem. Crystallogr. 35 (2005) 719.
[8] (a) The existence of diastereomers in our bmf-substituted clusters stems from the C-5 stereocenter in the furanone ring of the bmf ligand and the inherent chirality associated with the tetrahedron of the Co_2Ni cluster upon coordination of the bmf ligand. For other reports on chiral tetrahedrane clusters, see F. Richter, H. Vahrenkamp, Angew. Chem. Int. Ed. Engl. 17 (1978) 864;
F. Richter, H. Vahrenkamp, Angew. Chem. Int. Ed. Engl. 19 (1980) 65;
(b) C.U. Pittman Jr., M.G. Richmond, M. Absi-Halabi, H. Beurich, F. Richter, H. Vahrenkamp, Angew. Chem. Int. Ed. Engl. 21 (1982) 786;
(c) D. Mani, H.-T. Schacht, A. Powell, H. Vahrenkamp, Organometallics 6 (1987) 1360;
(d) K.A. Sutin, J.W. Kolis, M. Mlekuz, P. Bougeard, B.G. Sayer, M.A. Quilliam, R. Faggiani, C.J.L. Lock, M.J. McGlinchey, G. Jaouen, Organometallics 6 (1987) 439;
(e) M.F. D'Agostino, M.J. McGlinchey, Polyhedron 7 (1988) 807;
(f) Q.-Y. Zhao, W.-Q. Zhang, Y.-H. Zhang, B. Hu, Y.-Q. Yin, C.-G. Xia, Organometallics 23 (2004) 817.
[9] (a) H. Beurich, R. Blumhofer, H. Vahrenkamp, Chem. Ber. 115 (1982) 2409;
(b) R. Blumhofer, K. Fischer, H. Vahrenkamp, Chem. Ber. 119 (1986) 194.
[10] D.T. Mowry, Am. Chem. Soc. 72 (1950) 2535.
[11] D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.
[12] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, third ed., Academic Press, New York, 1990.
[13] (a) For reports on the effects of ^{59}Co quadrupolar broadening on ^{31}P and ^{13}C NMR resonances, see M.G. Richmond, J.K. Kochi, J. Organomet. Chem. 6 (1987) 254;
(b) P. Yuan, M.G. Richmond, M. Schwartz, Inorg. Chem. 30 (1990) 679;
(c) W.H. Watson, A. Nagl, S. Hwang, M.G. Richmond, J. Organomet. Chem. 445 (1993) 163.
[14] (a) For related examples, see: K. Yang, J.M. Smith, S.G. Bott, M.G. Richmond, Organometallics 12 (1993) 4779;
(b) K. Yang, S.G. Bott, M.G. Richmond, Organometallics 13 (1994) 3788;
(c) S.G. Bott, H. Shen, M.G. Richmond, Struct. Chem. 12 (2001) 225.
[15] The two stereocenters in $Co_2NiCp(CO)_4[\mu_2,\eta^2,\eta^1\text{-}C(H)C{=}C(PPh_2)$-$C(O)OCH(OMe)](\mu\text{-}PPh_2)$ are defined by the original carbon stereocenter in the furanone ring and the methylidene carbon atom that tethers the Ni and Co(1) centers.
[16] (a) P.E. Garrou, Chem. Rev. 81 (1981) 229;
(b) A.J. Carty, S.A. MacLaughlin, D. Nucciarone, in: J.G. Verkade, L.D. Quin (Eds.), Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes, VCH Publishers, New York, 1987 (Chapter 16).
[17] D.M.P. Mingos, D.J. Wales, Introduction to Cluster Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1990.
[18] (a) H. Beurich, R. Blumhofer, H. Vahrenkamp, Chem. Ber. 115 (1982) 2409;
(b) R. Blumhofer, K. Fischer, H. Vahrenkamp, Chem. Ber. 119 (1986) 194.
[19] Unpublished results.
[20] (a) A.D. Harley, R.R. Whittle, G.L. Geoffroy, Organometallics 2 (1983) 60;
(b) S. Onaka, H. Muto, Y. Katsukawa, S. Takagi, J. Organomet. Chem. 543 (1997) 241.