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Isomerization of the diphosphine ligand 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) at a triosmium cluster and P–C bond cleavage in the unsaturated cluster 1,1-$Os_3(CO)_9$(bmf): Synthesis and X-ray diffraction structures of the isomeric $Os_3(CO)_{10}$(bmf) clusters and $HOs_3(CO)_8(\mu\text{-}C_6H_4)[\mu\text{-}PhPC{=}C(Ph_2P)CH(OMe)OC(O)]$

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ABSTRACT

The labile cluster 1,2-$Os_3(CO)_{10}(MeCN)_2$ (**1**) reacts with the chiral diphosphine ligand 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) to furnish 1,2-$Os_3(CO)_{10}$(bmf) (**2a**) in high yield. Heating cluster **2a** over the temperature range 358–383 K under CO leads to isomerization of the bmf ligand and formation of the diphosphine-chelated cluster 1,1-$Os_3(CO)_{10}$(bmf) (**2b**) and an equilibrium mixture consisting of **2a** and **2b** in a 15:85 ratio. Extended thermolysis of an equilibrium mixture of $Os_3(CO)_{10}$(bmf) is accompanied by CO loss and ortho-metalation of an aryl ring to afford an inseparable mixture of three diastereomeric hydride clusters $HOs_3(CO)_9(C_{29}H_{23}O_3P_2)$ (**3a–c**). Thermolysis of $HOs_3(CO)_9(C_{29}H_{23}O_3P_2)$ (**3a–c**) in refluxing toluene leads to P–C bond cleavage and formation of the benzyne-substituted clusters $HOs_3(CO)_8(\mu\text{-}C_6H_4)(\mu\text{-}C_{23}H_{19}O_3P_2)$ (**4a,b**) as a 4:1 mixture of diastereomers. The unequivocal identity of the major benzyne-substituted cluster has been determined by X-ray diffraction analysis, where the activation of one of the phenyl groups situated α to the furanone carbonyl group in the bmf ligand has been established. The isomerization and activation of the bmf ligand are contrasted with other $Os_3(CO)_{10}$(diphosphine) derivatives prepared by our groups.

1. Introduction

Numerous studies dealing with the substitution chemistry of the lightly-activated cluster 1,2-$Os_3(CO)_{10}(MeCN)_2$ with a wide variety of diphosphine ligands have been published [1]. The formal displacement of the MeCN ligands typically proceeds with the formation of either the bridging or chelating diphosphine-substituted cluster, where the observed substitution product has been assumed to be the thermodynamically more stable isomeric form of the cluster. We have recently demonstrated that 1,2-$Os_3(CO)_{10}$ $(MeCN)_2$ undergoes reaction with the rigid, unsaturated diphosphine ligands (Z)-$Ph_2PCH{=}CHPPh_2$ (dppen) [2], 4,5-bis(diphenylphosphino)-4-cyclopentene-1,3-dione (bpcd) [3], 2,3-bis(diphenyl-phosphino)-N-*p*-tolylmaleimide (bmi) [4], and 2-(ferrocenylidene)- 4,5-bis(diphenylphosphino)-4-cyclopentene-1,3-dione (fbpcd) [5], whose structures are shown in Scheme 1, to afford the bridging cluster 1,2-$Os_3(CO)_{10}$(P–P) as the kinetically controlled product of substitution. These particular 1,2-$Os_3(CO)_{10}$(P–P) clusters are not stable and readily undergo isomerization to the diphosphine-chelated clusters 1,1-$Os_3(CO)_{10}$(P–P) when heated at elevated temperature [6]. In the case of the dppen ligand, the rearrangement of the diphosphine ligand about the cluster polyhedron has been studied by our groups, and convincing kinetic evidence has been presented for a reversible, non-dissociative unimolecular process involving a species where one of the phosphorus groups is simultaneously bound to two osmium metals, as depicted below in Eq. (1) [2]. The ability of a phosphine ligand to bind simultaneously to two osmium centers in the triply bridged species $Os_3(CO)_8(\mu_2\text{-}CO)_2(\mu_2,\eta^1\text{-dppen})$ parallels the fluxional behavior of the ubiquitous CO ligand, whose coordinative flexibility is well-established [7]. While we could not eliminate $Os_3(CO)_8(\mu_2\text{-}CO)_2(\mu_2,\eta^1\text{-dppen})$ as a short-lived intermediate or a transition state in the reversible isomerization of the dppen ligand about the triosmium

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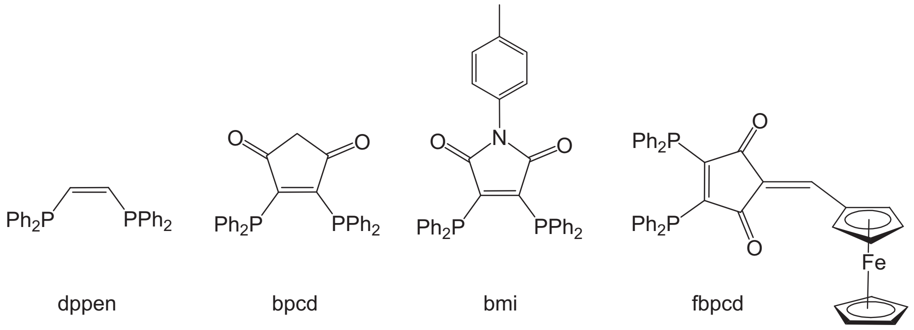
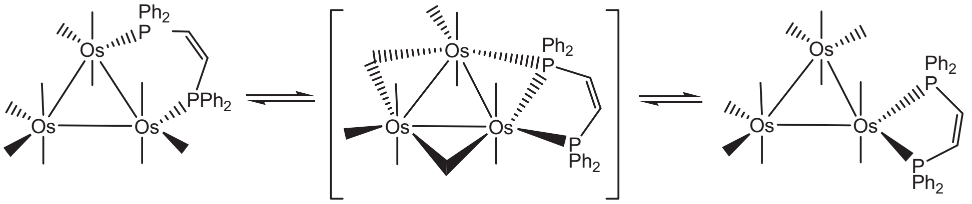


Scheme 1.

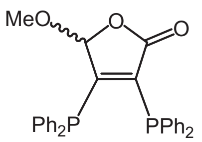
cluster in our earlier report, recently completed DFT calculations indicate that $Os_3(CO)_8$ (μ_2-$CO)_2$(μ_2,η^1-dppen) serves as the transition state connecting the ground-state clusters 1,2-$Os_3(CO)_{10}$(dppen) and 1,1-$Os_3(CO)_{10}$(dppen) [8].



(1)

In the case of the triosmium cluster 1,2-$Os_3(CO)_{10}$(bpcd), the bridge-to-chelate isomerization of the bpcd ligand is irreversible in nature, proceeding quantitatively to 1,1-$Os_3(CO)_{10}$(bpcd) [3]. Thermolysis of 1,1-$Os_3(CO)_{10}$(bpcd) leads to CO loss, followed by the activation of one of the ancillary aryl groups through an ortho-metalation process. The resulting hydride cluster $HOs_3(CO)_9$[μ-$PhP(C_6H_4)C{=}C(PPh_2)C(O)CH_2C(O)$] quantitatively regenerates 1,1-$Os_3(CO)_{10}$(bpcd) when heated under CO, which establishes the reversible nature associated with the reactivity of the C–H bond in terms of oxidative cleavage and reductive coupling sequences. Detailed kinetic and isotopic substitution studies on the reductive coupling step have confirmed that C–H bond formation exhibits an inverse equilibrium isotope effect (EIE). These data signal the involvement of the transient pi complex $Os_3(CO)_9$[μ-$PhP(\mu$-$C_6H_5)C{=}C(PPh_2)C(O)CH_2C(O)$], whose formation precedes the generation of the coordinatively unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd). The right-hand portion of Scheme 2 illustrates the pertinent aspects of the observed ortho-metalation reaction. In the absence of a scavenging ligand (i.e., added CO), the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd) reacts with one of the ancillary aryl rings of the bpcd ligand via an irreversible P–C bond-activation to afford ultimately the benzyne-substituted cluster $HOs_3(CO)_8$(μ_3-C_6H_4)[μ_2,η^1-$PPhC{=}C(PPh_2)C(O)CH_2C(O)$].

To date all of our ligands employed in the above osmium cluster studies have utilized symmetrical diphosphine ligands. The preparation of a 1,1-$Os_3(CO)_{10}$(P–P) cluster bearing a chiral diphosphine would allow us to probe regio- and stereochemical aspects related to the ortho-metalation process [9]. The chiral ligand 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf), whose structure is depicted below, is a close relative to bpcd and is ideally suited as an auxiliary ligand for the investigation of fundamental bond-activation processes at a metal cluster. In fact, the bmf ligand has already been employed by us in studies involving alkyne functionalization and P–C(aryl) bond cleavage at polynuclear compounds [10,11]. Herein we report the synthesis and structural characterization of the isomeric clusters 1,2- and 1,1-$Os_3(CO)_{10}$(bmf), including our data on the thermal and photochemical reactivity of these new clusters.



bmf

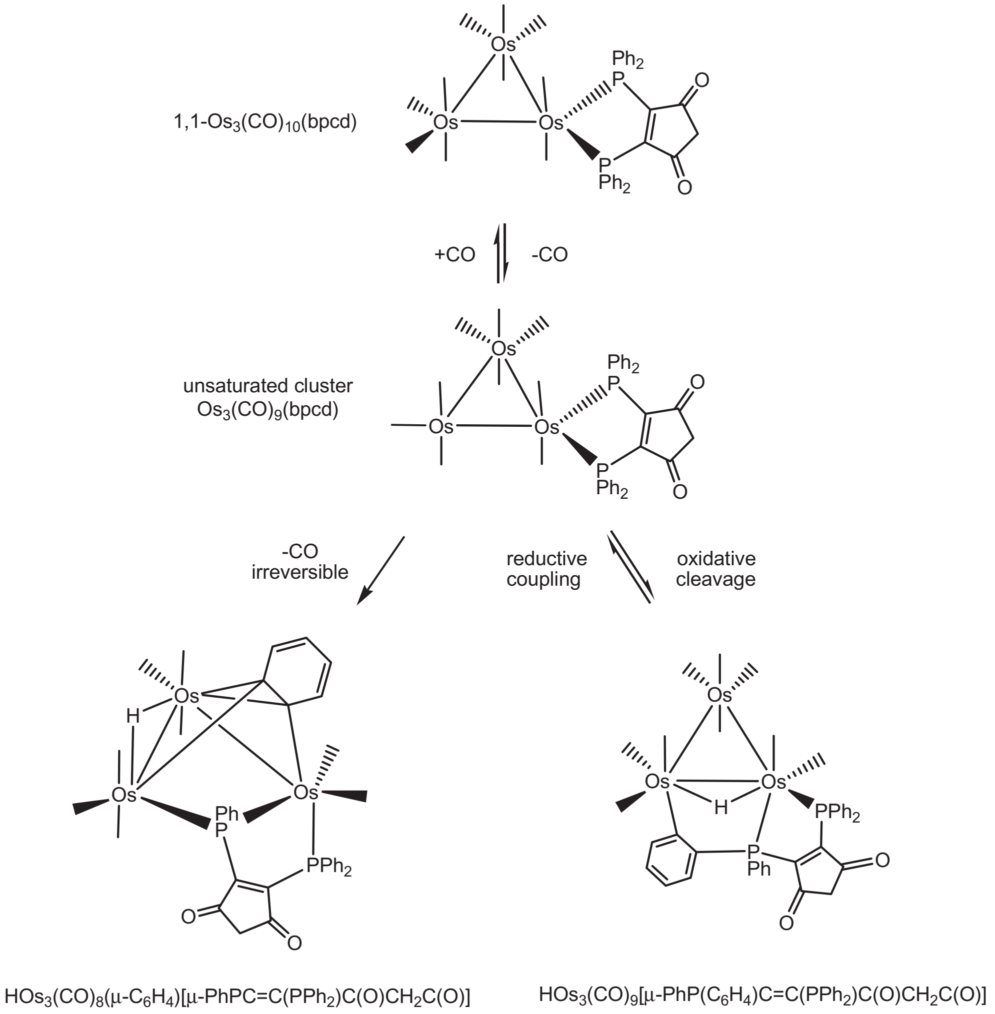
2. Experimental

2.1. General methods

The starting cluster 1,2-$Os_3(CO)_{10}(MeCN)_2$ was prepared from $Os_3(CO)_{12}$, Me_3NO, and MeCN [12], with the parent cluster $Os_3(CO)_{12}$ prepared from OsO_4 and CO [13]. The bmf ligand was synthesized from 3,4-dichloro-5-hydroxy-2(5H)-furanone and Ph_2PSiMe_3 via the procedure described by Fenske and Becher [14]. The OsO_4 was purchased from Engelhard Chemical Co, and the chemicals $Me_3NO{\cdot}xH_2O$, Me_3SiCl, and mucochloric acid were purchased from Aldrich Chemical Co. The anhydrous Me_3NO employed in our studies was obtained from $Me_3NO{\cdot}xH_2O$, after the waters of hydration were azeotropically removed under reflux using benzene as a solvent. All reaction solvents were distilled from a suitable drying agent under argon or obtained from an Innovative Technology (IT) solvent purification system; when not in use, purified solvents were stored in Schlenk storage vessels equipped with high-vacuum Teflon stopcocks [15]. The photochemical studies were conducted with GE Blacklight bulbs having a maximum output at 366 ± 20 nm and a photon flux of ca. 1×10^{-6} Einstein/min. Combustion analyses were performed by Atlantic Microlab, Norcross, GA.

2.2. Instrumentation

The IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in sealed 0.1 mm NaCl cells, while the quoted ^1H NMR data



Scheme 2.

was recorded at either 200 or 500 MHz on Varian Gemini and Varian VXR-500 spectrometers, respectively. The ^{31}P NMR spectra were recorded at 121 and 201 MHz on Varian 300-VXR and Varian VXR-500 spectrometers, respectively. The reported ^{31}P chemical shift data were recorded in the proton-decoupled mode and are referenced to external H_3PO_4 (85%), whose chemical shift was set at $\delta = 0$.

2.3. Synthesis of 1,2-$Os_3(CO)_{10}$(bmf) (**2a**)

To a 250 mL Schlenk flask containing 25 mL of CH_2Cl_2 and 0.25 g (0.27 mmol) of 1,2-$Os_3(CO)_{10}(MeCN)_2$ was added 0.15 g (0.30 mmol) of bmf under argon flush, after which the solution was stirred for 2 h at room temperature. TLC examination using CH_2Cl_2/hexane (3:2) as the eluent confirmed the consumption of the starting cluster and the presence of a large dark orange spot ($R_f = 0.45$), in addition to unreacted bmf and a small amount of material that remained at the origin of the TLC plate. The solvent was removed under vacuum, and the crude residue separated by column chromatography over silica gel using the aforementioned mobile phase to give cluster **2a**, which was subsequently recrystallized from benzene/CH_2Cl_2 to furnish **2a** in 60% yield (0.22 g). IR (CH_2Cl_2): ν(CO) 2090 (vs), 2042 (s), 2011 (vs) 2007 (vs), 1976 (m) 1772 (s, furanone) cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.22 (s, 3H), 4.40 (s, 1H), 6.92–7.20 (m, 17H, aryl), 7.36 (m, 1H, aryl), 7.62 (m, 1H, aryl), 7.97 (m, 1H, aryl). ^{31}P NMR (C_6D_6): δ −18.12 (d, $^3J_{P-P} = 8.0$ Hz), −5.26 (d, $^3J_{P-P} = 8.0$ Hz). *Anal.* Calc. for $C_{39}H_{24}Os_3O_{13}P_2$: C, 35.14; H, 1.81. Found: C, 34.77; H, 1.82%.

2.4. Isomerization of 1,2-$Os_3(CO)_{10}$(bmf) (**2a**) to an equilibrium mixture of **2a** and 1,1-$Os_3(CO)_{10}$(bmf) (**2b**)

A large Schlenk tube was charged with 0.20 g (0.15 mmol) of **2a** and 20 mL of toluene, and the solution was saturated with CO for 15 min. The reaction vessel was then sealed and heated at ca. 90 °C for a period of 72 h, after which time the solvent was removed under vacuum and the residue was separated by column chromatography over silica gel using CH_2Cl_2/hexane (3:2) to give 0.16 g (0.12 mmol) of a 15:85 equilibrium mixture containing clusters **2a** and **2b**, respectively, as assessed by ^{1}H and ^{31}P NMR spectroscopy. Spectroscopic data for **2b**: IR (CH_2Cl_2): ν(CO) 2095 (vs), 2046 (vs), 2014 (vs) 2005 (vs), 1991 (m), 1977 (m) 1771 (s, furanone) cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.79 (s, 3H), 4.83 (s, 1H), 6.86–7.29 (m, 17H, aromatic), 7.70 (dd, 1H, $J = 8.0$, 12.5 Hz), 7.87 (dd, 1H, $J = 7.0$, 11.5 Hz), 8.00 (dd, 1H, $J = 8.5$, 12.5 Hz). ^{31}P NMR (C_6D_6): δ 13.26 (d, $^3J_{P-P} = 8.4$ Hz), 17.22 (d, $^3J_{P-P} = 8.4$ Hz).

2.5. Photolysis of **2a,b** and formation of the hydride clusters $HOs_3(CO)_9(C_{29}H_{23}O_3P_2)$(**3a–c**)

About 0.20 g (0.15 mmol) of a thermally equilibrated mixture of the clusters 1,2-$Os_3(CO)_{10}$(bmf) and 1,1-$Os_3(CO)_{10}$(bmf) was charged to a large Schlenk tube, followed by 40 mL of CH_2Cl_2 via syringe. The solution was then irradiated at 366 nm for 7 days at room temperature. The CO that accompanies the formation of the hydride clusters was periodically removed by multiple freeze–pump–thaw degas cycles, allowing the reaction to be driven to completion. The sample was also briefly heated at 60 °C several times during the photolysis reaction to help drive the bridging isomer to the chelating isomer, the latter which undergoes photochemical reaction to afford the hydride products **3a–c**. At the end of 7 days, the solvent was removed under vacuum and the crude mixture of hydride clusters were separated by column chromatography over silica gel using CH_2Cl_2/hexane (3:2) to give an inseparable, ternary mixture of the hydride clusters $HOs_3(CO)_9(\mu\text{-}C_{29}H_{23}O_3P_2)$ in an overall yield of 90% yield (0.18 g). ^1H NMR (C_6D_6): δ −15.92 (t, μ_2-H, J_{P-H} = 12.4 Hz), −15.99 (dd, μ_2-H, J_{P-H} = 12.4, 14.1 Hz), −16.17 (dd, μ_2-H, J_{P-H} = 12.4, 14.0 Hz), 2.70, 2.71, 2.75 (s, 3H, MeO groups), 4.41, 4.78, 4.93 (s, 1H, methine groups), 6.85–8.77 (m, 19H, aromatic). ^{31}P (C_6D_6): δ 13.63 (s), 17.03 (bs), 23.73 (bs), 24.40 (s). *Anal.* Calc. for $C_{38}H_{24}Os_3O_{12}P_2$: C, 34.97; H, 1.85. Found: C, 34.61; H, 1.86%.

2.6. Synthesis of $HOs_3(CO)_9(\mu_3\text{-}C_6H_4)$ $[\mu\text{-}C_{23}H_{19}O_3P_2]$(**4a,b**)

About 0.10 g (0.07 mmol) of a cluster mixture of 1,2-$Os_3(CO)_{10}$(bmf) and 1,1-$Os_3(CO)_{10}$(bmf) was charged to a Carius tube, followed by 10 mL of toluene. The reaction tube was sealed and then heated at 110 °C in a thermostated bath. The progress of reaction was monitored by ^{31}P NMR spectroscopy through the periodic removal of aliquots for NMR analysis. Upon consumption of the starting cluster mixture of **2a,b**, the solvent was removed under vacuum and the residue was separated by column chromatography over silica gel using CH_2Cl_2/hexane (3:2). Recrystallization of the crude product from a mixture of benzene/hexane afforded 90 mg (95% yield) of **4a,b**. IR (CH_2Cl_2): ν(CO) 2074 (vs), 2040 (vs), 2028 (vs), 2004 (vs), 1988 (m), 1770 (s, furanone) cm^{-1}. ^1H NMR ($CDCl_3$): δ −16.60 (major, dd, μ_2-H, J_{P-H} = 14.0, 5.5 Hz), −16.50 (minor, dd, μ_2-H, J_{P-H} = 12.5, 7.5 Hz), 3.55 (minor, s, MeO), 3.61 (major, s, MeO), 5.87 (major, s, methine), 6.26 (major, s, methine), δ 6.70–9.20 (19H, benzyne and aryl groups). ^{31}P NMR (C_6D_6): δ −70.31, (d, phosphido, J_{P-P} = 8.0 Hz), −66.17 (d, phosphido, J_{P-P} = 6.8 Hz), 7.08 (d, phosphine, J_{P-P} = 6.8 Hz), 7.98 (d, phosphine, J_{P-P} = 8.0 Hz). *Anal.* Calc. for $C_{37}H_{24}O_{11}Os_3P_2 \cdot C_6H_6$: C, 38.11; H, 2.23. Found: C, 37.93; H, 2.41%.

2.7. X-ray crystallography

Single crystals of **2a**, as the benzene solvate, suitable for X-ray diffraction analysis were grown from a dichloromethane solution of **2a** that had been layered with benzene, while single crystals of **2b** were grown from a 15:85 equilibrium mixture containing **2a,b** in toluene and hexane at 5 °C. X-ray quality crystals of the benzyne-substituted cluster **4a** were obtained through repeated recrystallization of a mixture of **4a,b** using hexane and toluene at room temperature. The X-ray diffraction data for **2a** were collected in the variable scan speed mode at 295(1) K on a Bruker SMART APEX II CCD-based diffractometer. The X-ray diffraction for **2b** and **4a** were collected in the variable scan speed mode at 100(2) K on Bruker SMART APEX CCD- and APEX II CCD-based diffractometers, respectively. The frames were integrated with the available SAINT and APEX II software packages using a narrow-frame algorithm [16,17], and each structure was solved and refined using the available SHELXTL program package. An absorption correction was applied to all three clusters using the program SADABS [18], and the molecular structures were checked using PLATON [19]. The bridging hydride ligand spanning the Os(1)–Os(2) vector in **4a** was located during refinement, while all other hydrogen atoms were assigned calculated positions and allowed to ride on the attached carbon atom. In the case of cluster **2b**, the diffraction data revealed a disorder among the six osmium atoms Os(1)–Os(6) and the 10 CO groups associated with the two $Os_3(CO)_{10}$ units. The bmf ligand is not affected in the two structures and the diffraction data give rise to a "Star of David" disorder involving two $Os_3(CO)_{10}$ units, with each cluster containing a single bmf ligand. The occupancy factors for 1,1-$Os_3(CO)_{10}$(bmf) (chelating isomer, **2b**) have been refined to 0.85 and those of 1,2-$Os_3(CO)_{10}$(bmf) (bridging isomer, **2a**) refined to 0.15. The clusters **2a** and **2b** each contained one disordered

Table 1
X-ray crystallographic data and processing parameters for the triosmium clusters **2a**, **2b**, and **4a**.

Compound	**2a**	**2b**	**4a**
CCDC entry No.	730 527	730 529	730 528
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P21/c$	$P\bar{1}$
a (Å)	9.4668(4)	9.3489(6)	10.3986(5)
b (Å)	12.3057(6)	19.736(1)	11.3464(5)
c (Å)	20.776(1)	21.182(1)	17.0559(7)
α (°)	75.473(2)		74.683(1)
β (°)	79.960(2)	92.153(3)	72.592(1)
γ (°)	68.052(1)		84.108(1)
V (Å^3)	2164.4(2)	3905.4(4)	1851.4(1)
Molecular formula	$C_{42}H_{27}O_{13}Os_3P_2$	$C_{39}H_{24}O_{13}Os_3P_2$	$C_{37}H_{24}O_{11}Os_3P_2$
Formula weight	1372.18	1333.12	1277.10
Formula units per cell (Z)	2	4	2
D_{calc} (Mg/m^3)	2.105	2.267	2.291
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	8.921	9.884	10.416
Absorption correction factor	0.6640/0.2685	0.3342/0.2957	0.5738/0.2422
Total reflections	20 403	29 023	23 179
Independent reflections	9515	7132	8182
Data/restraints/parameters	9515/204/542	7132/107/586	8182/0/483
R_1[a] ($I \geqslant 2\sigma(I)$]	0.0242	0.0741	0.0174
wR_2[b]	0.0582	0.1629	0.0433
Goodness-of-fit (GOF) on F^2	1.030	1.183	1.049
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	2.164/−0.685	5.509/−1.551	1.529/−0.962

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$.

[b] $R_2 = \{\Sigma[w(F^2o - F^2c)^2/\Sigma[w(F^2o)^2]]\}^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for the triosmium clusters **2a**, **2b**, and **4a**.

Cluster **2a**			
Bond distances			
Os(1)–Os(2)	2.8611(3)	Os(1)–Os(3)	2.8776 (2)
Os(2)–Os(3)	2.8742(3)	Os(1)–P(1)	2.322(1)
Os(2)–P(2)	2.322(1)	P(1)–C(3)	1.843(4)
P(2)–C(2)	1.841(4)	O(1)–C(1)	1.346(6)
O(1)–C(4)	1.443(5)	O(3)–C(4)	1.365(5)
O(3)–C(5)	1.443(6)	C(1)–C(2)	1.511(6)
C(2)–C(3)	1.333(5)	C(3)–C(4)	1.524(5)
P(1)···P(2)	3.831(4)		
Bond angles			
P(1)–Os(1)–Os(2)	97.07(3)	P(1)–Os(1)–Os(3)	154.82(3)
P(2)–Os(2)–Os(1)	104.09(3)	P(2)–Os(2)–Os(3)	160.44(3)
C(3)–P(1)–Os(1)	118.2(1)	C(2)–P(2)–Os(2)	119.7(1)
C(3)–C(2)–P(2)	132.4(3)	C(2)–C(3)–P(1)	132.9(3)
C(4)–C(3)–P(1)	118.4(3)	C(1)–C(2)–P(2)	119.5(3)
Cluster **2b**			
Bond distances			
Os(4)–Os(6)	2.8905(9)	Os(4)–Os(5)	2.9020(9)
Os(5)–Os(6)	2.8814(9)	Os(4)–P(1)	2.298(4)
Os(4)–P(2)	2.303(4)	P(1)–C(2)	1.87(2)
P(2)–C(1)	1.83(2)	O(2)–C(3)	1.39(2)
O(2)–C(4)	1.42(2)	O(3)–C(4)	1.32(2)
O(3)–C(5)	1.46(2)	C(1)–C(2)	1.35(2)
C(2)–C(3)	1.47(2)	C(1)–C(4)	1.50(2)
P(1)···P(2)	3.22(1)		
Bond angles			
P(1)–Os(4)–Os(5)	106.1(1)	P(1)–Os(4)–Os(6)	163.5(1)
P(2)–Os(4)–Os(5)	163.4(1)	P(2)–Os(4)–Os(6)	106.6(1)
C(2)–P(1)–Os(4)	104.3(5)	C(1)–P(2)–Os(4)	103.7(5)
C(2)–C(1)–P(2)	123(1)	C(1)–C(2)–P(1)	118(1)
P(1)–Os(4)–P(2)	88.8(2)		
Cluster **4a**			
Bond distances			
Os(1)–Os(2)	2.9305(2)	Os(2)–Os(3)	2.8227(2)
Os(1)–P(2)	2.3454(8)	Os(1)–P(1)	2.3789(8)
Os(3)–P(2)	2.3889(8)	Os(1)–C(14)	2.158(3)
Os(1)–H(1)	1.81(4)	Os(2)–C(14)	2.310(3)
Os(2)–C(15)	2.372(3)	Os(2)–H(1)	1.89(4)
Os(3)–C(15)	2.143(3)	C(9)–C(12)	1.500(4)
C(10)–C(13)	1.511(4)	C(12)–C(13)	1.330(4)
Os(1)···Os(3)	3.8137(3)	P(1)···P(2)	3.229(1)
Bond angles			
Os(3)–Os(2)–Os(1)	83.017(6)	C(14)–Os(1)–P(2)	165.23(9)
C(14)–Os(1)–P(1)	81.51(8)	P(1)–Os(1)–P(2)	86.23(3)
C(2)–Os(1)–Os(2)	92.2(1)	P(2)–Os(1)–Os(2)	119.26(2)
P(1)–Os(1)–Os(2)	83.66(2)	C(14)–Os(2)–C(15)	36.1(1)
C(5)–Os(2)–Os(1)	117.2(1)	C(3)–Os(2)–Os(1)	89(1)
Os(1)–P(1)–Os(3)	106.24(3)		

phenyl group involving the atoms C(24)–C(29) and C(111)–C(116), respectively. These phenyl groups were refined using an appropriate disorder model. Table 1 summarizes the pertinent X-ray data collection and processing parameters, with Table 2 providing selected bond distances and angles for the triosmium clusters.

3. Discussion

3.1. Synthesis, spectroscopic data, and solid-state structure for *2a*

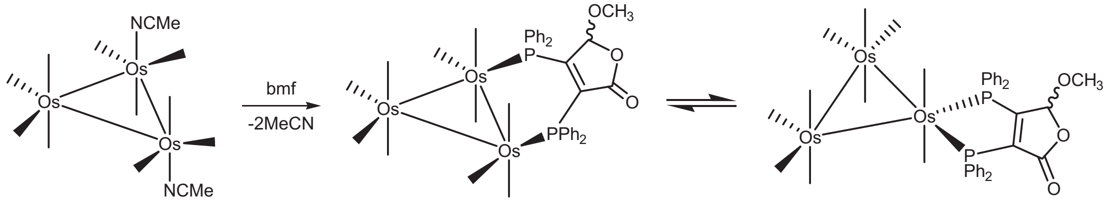
The reaction between the activated cluster 1,2-$Os_3(CO)_{10}(MeCN)_2$ (**1**) and the unsaturated diphosphine ligand bmf proceeds rapidly at room temperature to furnish the ligand-bridged cluster 1,2-$Os_3(CO)_{10}$(bmf) (**2a**) as the major product. Trace amounts of the minor product $Os_3(CO)_{11}(\eta^1$-bmf) have been observed in this reaction and are attributed to the mono(acetonitrile) derivative $Os_3(CO)_{11}$(MeCN) that often accompanies the synthesis of **1**. **2a** was purified by column chromatography over silica gel and characterized in solution by IR and NMR spectroscopy. The observation of a pair of doublets at δ −18.12 and −5.26 in the ^{31}P NMR spectrum of **2a** is consistent with the two inequivalent phosphine groups in the bmf ligand and the presence of a single isomer in solution. The ^{1}H NMR spectrum of **2a** recorded in C_6D_6 showed two singlets at δ 2.22 and 4.40 for the methoxy and methine groups, respectively, associated with the furanone platform, along with 20 aromatic hydrogens appearing at δ 6.92–7.20 (m, 17H), 7.36 (m, 1H), 7.62 (m, 1H), and 7.97 (m, 1H). Scheme 3 summarizes the course of the ligand substitution reaction between **1** and bmf.

The bridging nature of the bmf ligand in **2a** was unequivocally established by X-ray diffraction analysis. The molecular structure of **2a**, as the benzene solvate, is shown in Fig. 1, where the bridging disposition of the bmf ligand and its equatorial coordination to the Os(1) and Os(2) centers are confirmed. The Os–Os bond distances range from 2.8611(3) Å [Os(1)–Os(2)] to 2.8776(2) Å [Os(1)–Os(3)] and display a mean distance of 2.871 Å. The Os–Os bond distances in **2a** are in good agreement with those Os–Os bond distances in the parent cluster $Os_3(CO)_{12}$ and numerous diphosphine-bridged clusters $Os_3(CO)_{10}$(P–P) [1c–e,20,21]. The two Os–P bonds display distances of 2.322(1) Å [Os(1)–P(1)] and 2.322(1) Å [Os(2)–P(2)], while the 10 terminal carbonyl groups exhibit distances and angles consistent with their linear nature. Coordination of the bmf ligand across the Os(1)–Os(2) vector is accompanied by a significant "stretching" of the bmf ligand and an overall ground-state destabilization of cluster **2a** relative to the chelating isomer **2b** (*vide infra*). Here the internuclear P(1)···P(2) distance of 3.831(4) Å found in **2a** is significantly longer (>0.55 Å) than the corresponding P(1)···P(2) distance found in cluster **2b** and the P(1)···P(2) distance in the free diphosphine ligands (Z)-$Ph_2PCH{=}CHPPh_2$ and dppbz [22,23]. The remaining bond distances and angles are unexceptional and require no comment.

3.2. Isomerization of *2a* to an equilibrium mixture of *2a*/*2b*

The thermal stability of **2a** was next probed by NMR spectroscopy in toluene-d_8 at 85 °C. Samples of **2a** that were heated under 1 atm CO, whose presence retards CO loss and formation of the hydride-bridged clusters **3a–c**, were accompanied by a decrease in the intensity of the initial methoxy and methine singlets of **2a** and the growth of two new singlets at δ 2.85 and 4.80 corresponding to the methoxy and C(5) methine groups of the chelating isomer **2b**. The spectral changes in the ^{31}P NMR spectrum of **2a** also corroborate the isomerization of the bmf ligand about the triosmium cluster. Here a new pair of ^{31}P doublets was observed at δ 13.26 and 17.22, coming at the expense of **2a**, and whose large nuclear deshielding is consistent with the formation of the bmf-chelated cluster **2b** [24]. Continued heating of the **2a,b** mixture over the course of several days afforded an equilibrium value of 15:85 in favor of the chelating isomer **2b**, as determined by both ^{1}H and ^{31}P NMR spectroscopy. The K_{eq} value for the isomerization of **2a** to **2b** was found to be constant over the temperature range of 85–110 °C with a magnitude of 5.7 in toluene solvent under 1 atm CO. The magnitude of the K_{eq} value found for **2a,b** is close to the K_{eq} value of 6.9 determined for the reversible isomerization of the dppen ligand at $Os_3(CO)_{10}$(dppen) at 373 K [3,25]. Finally, a preparative isomerization reaction employing **2a** was also examined by TLC, and the single TLC spot exhibited by the isomeric mixture of **2a,b** negated any possible chromatographic separation of these two clusters.

The molecular structure of **2b** was established by X-ray diffraction analysis (Fig. 1), and interestingly enough, the two independent structures found in the solid state consisted of an isomeric mixture of clusters **2a,b** whose ratio coincidently is identical with the K_{eq} value determined by NMR spectroscopy. The observed solid-state disorder is best described as that arising from a "Star



cluster **1** cluster **2a** cluster **2b**

Scheme 3.

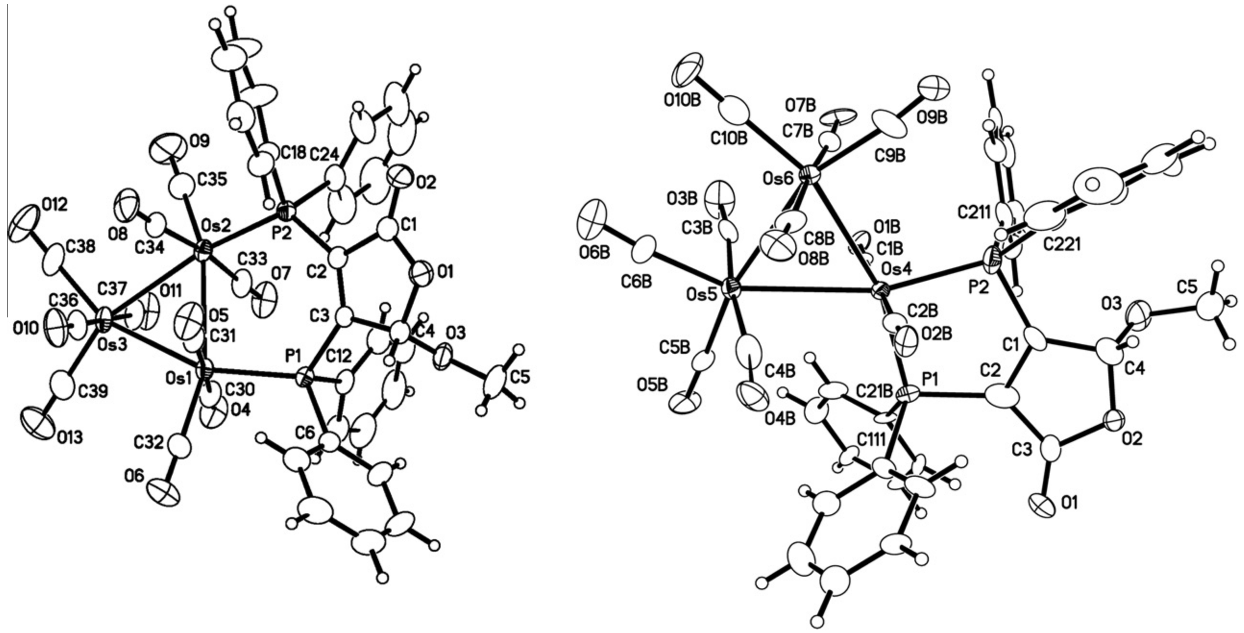
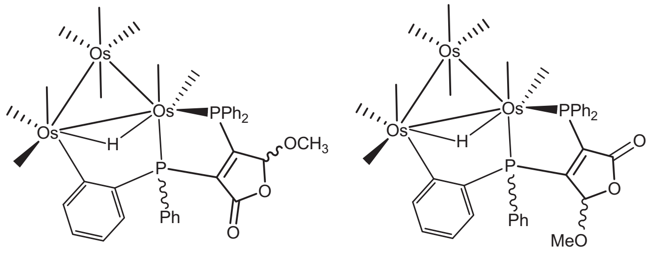


Fig. 1. Molecular structures and numbering schemes of **2a** (left) and **2b** (right) at the 30% and 50% probability level, respectively. The benzene solvent in the former structure has been omitted for clarity and hydrogen atoms drawn as spheres of arbitrary radii.

of David" involving two locally disordered $Os_3(CO)_{10}$ moieties relative to the bmf ligand [26]. The bmf ligand in **2b** coordinates the Os(1) atom and resides in the equatorial plane defined by the three osmium atoms. The Os–Os bond distances range from 2.9020(9) Å [Os(4)–Os(5)] to 2.8814(9) Å [Os(5)–Os(6)] and the two Os–P bonds exhibit distances of 2.303(4) Å [Os(4)–P(2)] and 2.298(4) Å [Os(4)–P(1)]. The observed bond angle of 88.8(2)° for the P(1)–Os(4)–P(2) atoms and the internuclear P(1)···P(2) distance of 3.22(1) Å mirror those values reported by us for other bmf-substituted cluster compounds [10,11,27].

3.3. Thermal and photochemical preparation of the hydride clusters $HOs_3(CO)_9(C_{29}H_{23}O_3P_2)$ (*3a–c*) from *2a,b*

The thermal and photochemical reactivity of the equilibrium mixture of clusters **2a,b** was next examined due to our previous reports of efficient CO loss and C–H bond-activation of an ancillary aryl ligand in numerous diphosphine-chelated $Os_3(CO)_{10}$(P–P) clusters. Controlled thermolysis of **2a,b** in a sealed NMR tube in benzene-d_6 at 353 K in the absence of added CO furnished a ternary mixture of hydride diastereomers through the loss of CO and rapid ortho-metalation of one of the aryl groups attached to the bmf ligand. ^{1}H NMR analysis of the reaction revealed the growth of three hydride resonances at δ −15.92, −15.99, and −16.17 in roughly equal amounts for clusters **3a–c**. The splitting patterns and J_{P-H} values for these bridging hydrides are reported in the experimental section. Three sets of methoxy (δ 2.70, 2.71, 2.75) and methine (δ 4.41, 4.78, 4.93) singlets are also observed and are consistent with the formation of the three new hydride clusters. The 19 aryl hydrogens belonging to **3a–c** appear as a complex set of overlapping resonances from δ 6.85–8.77. Unfortunately, the extensive overlap of these aryl hydrogens precluded any definitive spectral assignments. The ^{31}P NMR spectrum showed four new resonances at δ 13.63, 17.03, 23.73, and 24.40, of which the two resonances centered at δ 17.03 and 23.73 actually derive from the overlap of two of the three new hydride species. Careful integration of these resonances relative to the remaining pair of ^{31}P resonances provided additional support for this premise. Assignment of the likely hydride-based products is problematic given the presence of two different PPh_2 groups and the C-5 chiral center, which give rise to a maximum of eight theoretical diastereomers [28]. Depicted below are the likely candidates that arise from the ortho-metalation that takes place upon CO loss in **2b**, the nature of which draws from our earlier work where the crystallographic structure of the hydride cluster obtained from the ortho-metalation of the diphosphine ligand 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (fbpcd) in 1,1-$Os_3(CO)_{10}$(fbpcd) was determined [5]. There it was shown that the phenyl group involved in the ortho-metalation process must occupy an axial site relative the metallic frame. Suffice it to say, the three hydride diastereomers resulting from the thermolysis of **2a,b** indicate a modicum of selectivity for the ortho-metalation that occurs at the putative intermediate 1,1-$Os_3(CO)_9(bmf)$.



possible diastereomeric hydride clusters

Examination of preparative thermolysis reactions using **2a,b** by TLC showed a single spot for **3a–c** that prevented any physical separation of this ternary product mixture. The hydride clusters **3a**–c are sensitive to the presence of CO, and this particular reaction may be reversed through the addition of CO and continued heating, as previously demonstrated by us for related diphosphine-chelated clusters $HOs_3(CO)_9[\mu\text{-}(Ph_2P)HC{=}CH\{PPh(C_6H_4)\}]$ and $HOs_3(CO)_9[\mu\text{-}(Ph_2P)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ [2,3]. Control reactions involving samples of **3a–c** that were heated in benzene at 358 K under CO (1 atm) regenerated the equilibrium mixture of **2a,b** in quantitative yield.

Photolysis of **2a,b** at room temperature using 366 nm light proceeds selectively with the consumption of the chelating isomer **2b** to furnish the hydride clusters **3a–c**. In fact, photolysis of **2a,b** with periodic removal of the liberated CO ultimately furnished **2a** (15%) and **3a–c** (85%). The observed reactivity data, namely diastereoselective ortho-metalation of **2b**, parallel the isomer dependency exhibited by the bridging and chelating isomers of $Os_3(CO)_{10}$[(Z)-dppen] [2]. The clusters **2a,b** could be driven to **3a–c** in essentially quantitative yield through photolysis with intermittent heating of the sample at 358 K, followed by resumption of irradiation. Utilization of this irradiation/thermolysis protocol ultimately allowed the equilibrium mixture of **2a** and **2b** to be driven completely to the hydride clusters **3a–c**.

*3.4. Preparation of the benzyne-substituted clusters **4a,b** and X-ray diffraction structure of $HOs_3(CO)_8(\mu\text{-}C_6H_4)(\mu\text{-}C_{23}H_{19}O_3P_2)$*

The thermal stability of the hydride clusters **3a–c** was next explored for their propensity to undergo P–C(aryl) bond cleavage of an aryl group from the diphosphine ligand, leading to the formation of a benzyne-substituted cluster. Degradation of a phosphine ligand via this manifold represents one of the chief modes by which a phosphine-modified catalyst is rendered catalytically inactive [29]. Heating samples of **2a,b** above 383 K in toluene in a Carius tube led to the consumption of **3a–c** and the appearance of a new spot by TLC ascribed to the phosphido-bridged clusters **4a,b**. The ^{31}P NMR data for the crude reaction mixture also supported the presence two phosphido-bridged clusters based on the presence of two pairs of new resonances recorded at δ −70.31 and 7.98 (major) and δ −66.17 and 7.08 (minor) in a 4:1 ratio. The upfield ^{31}P resonance in these products is consistent with the presence of a bridging phosphido moiety that spans non-bonded osmium centers [30]. The two products could not be separated by column chromatography and were consequently isolated as a mixture of diastereomers. The ^1H NMR spectrum of **4a,b** revealed a pair of hydrides at −16.60 (major) and −16.50 (minor), along with resonances at δ 3.55 (minor) and 3.61 (major) and δ 5.87 (major) and 6.26 (major) for the methoxy and methine hydrogens, respectively. The nineteen hydrogens associated with the benzyne and aryl moieties were observed from δ 6.70–9.20.

The cleavage of one of the phenyl groups from the bmf ligand and stereochemical disposition of the bmf ligand relative to the triosmium frame were unequivocally established by X-ray crystallography in the case of the major diastereomer, which we have arbitrarily labeled as **4a** for discussion purposes. While difficult and time consuming, **4a** could be isolated, albeit with considerable material loss, through repeated recrystallization [31]. The molecular structure of **4a** is shown in Fig. 2, where the presence of a face-capping benzyne ligand and phosphido moiety is confirmed. **4a** contains $50e^-$, which is two electrons in excess of the electron-precise count of 48 valence electrons for saturated triangular Os_3 clusters, accounting for the observed polyhedral opening of the metallic frame across the initial Os(1)–Os(3) bond. The two Os–Os vectors in **4a** display distances of 2.8227(2) Å [Os(2)–Os(3)] and 2.9305(2) Å [Os(1)–Os(2)], with the longer of the two bond distances serving as the site for the ancillary hydride H(1) that resides on the metallic face opposite the benzyne ligand. The observed lengthening of the hydride-bridged Os(1)–Os(2) vector is in keeping with the trend found in numerous hydride-bridged clusters [32]. The internuclear Os(1)···Os(3) distance of 3.8137(3) Å far exceeds the van der Waals radii of the two metal atoms and precludes any direct bonding. The P(1) phosphido moiety and the three osmium atoms give rise to a near planar butterfly arrangement of atoms based on a σ_p value of 0.092 Å. The origin of the benzyne ligand, which is defined by the atoms C(14)–C(19), is traced to the P(1) atom that spans the Os(1) and Os(3) centers. The benzyne ligand functions as a typical four-electron, face-capping ligand by way of two Os–C σ bonds [Os(1)–C(14) 2.158(3) Å and (Os(3)–C(15) 2.143(3) Å] and an Os–C π bond defined by the Os(2)–C(14) [2.310(3) Å] and Os(2)–C(15) [2.372(3) Å] vectors. The methoxy group bound to C(10) of the furanone ring is distally oriented away from the cluster core and the C(26)–C(31) phenyl carbons. The stereoselective binding of the bmf ligand to polynuclear clusters is strongly influenced by the steric environment about the cluster polyhedron, and we have

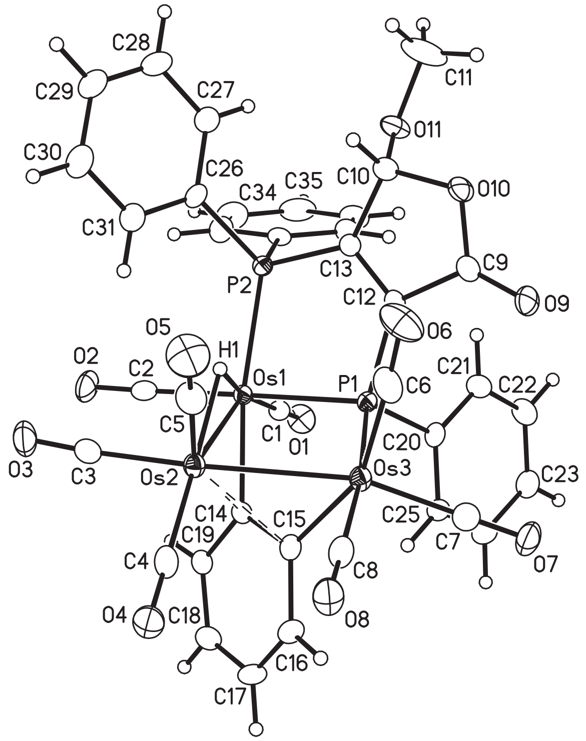


Fig. 2. Molecular structure and numbering scheme of **4a** at the 50% probability level, with hydrogen atoms drawn as spheres of arbitrary radii.

documented this phenomenon in the reaction of bmf with the cluster compounds $PhCCo_2NiCp(CO)_6$, $PhCCo_2MoCp(CO)_8$, and $Ru_6(\mu_6\text{-}C)(CO)_{17}$ [11,33]. The bond distances and angles exhibited by the benzyne ligand in **4a** are similar to those distances and angles found in other benzyne-substituted osmium clusters [34]. The remaining bond distances and angles are unexceptional and require no comment.

4. Conclusions

Substitution of the MeCN ligands in 1,2-$Os_3(CO)_{10}(MeCN)_2$ by the chiral diphosphine bmf affords the ligand-bridged cluster 1,2-$Os_3(CO)_{10}$(bmf) as the kinetic product of ligand substitution. The bmf ligand in 1,2-$Os_3(CO)_{10}$(bmf) is coordinatively flexible and readily isomerizes under CO (1 atm) over the temperature range of 358–373 K to furnish an equilibrium mixture of 1,2- and 1,1-$Os_3(CO)_{10}$(bmf) in favor of the latter isomer ($K_{eq} = 5.7$). The isomeric decacarbonyls undergo CO loss upon thermolysis or optical excitation using near-UV light to afford a mixture of hydride clusters (**3a–c**) through ortho metalation of one of the ancillary phenyl groups. Thermolysis of **3a–c** at elevated temperatures leads, ultimately, to the release of one of the aryl groups and the formation of a pair of benzyne-substituted Os_3 clusters, which have been characterized spectroscopically in solution and by X-ray diffraction analysis in the case of one of the diastereomers. Future studies will probe the coordination chemistry of different chiral ligands at Os_3 and other metal clusters, and we hope to achieve high regio- and diastereoselectivity in the activation of the ancillary C–H and P–C bonds of the chiral auxiliary, which then can serve as a starting point for the more elaborate functionalization of the initial ligand system.

5. Supplementary data

CCDC 730527, 730529, and 730528 contains the supplementary crystallographic data for **2a**, **2b**, and **4a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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