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Synthesis and reactivity studies of the diphosphine ligand 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (fbpcd): Bridge-to-chelate ligand isomerization kinetics in Os₃(CO)₁₀(fbpcd) and X-ray diffraction structure of the *ortho*-metalated cluster HOs₃(CO)₉[µ-PhP(C₆H₄)-C=C(PPh₂)C(O)C=CH(C₅H₄FeCp)C(O)]

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Abstract

Knoevenagel condensation of ferrocenecarboxaldehyde with 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) yields the new diphosphine ligand 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (fbpcd) in near quantitative yield. The reaction of fbpcd with the activated cluster 1,2-Os₃(CO)₁₀(MeCN)₂ has been examined, with the diphosphine-bridged cluster 1,2-Os₃(CO)₁₀(fbpcd) (**2b**) observed as the major product. Cluster **2b** is unstable and transforms into the corresponding chelating isomer 1,1-Os₃(CO)₁₀(fbpcd) (**2c**) on heating. The kinetics associated with the conversion of **2b** \rightarrow **2c** have been studied over the temperature range of 313-343 K by ¹H NMR and UV–vis spectroscopies. On the basis of the observed activation parameters, a nondissociative isomer erization process that involves a transient μ_2 -bridged phosphine moiety is presented. Near-UV irradiation of cluster **2c** leads to CO loss and *ortho*-metalation of the one of the ancillary phenyl groups to give the hydride cluster HOs₃(CO)₉[μ -PhP(C₆H₄)C=C(PPh₂)-C(O)C=CH(C₅H₄FeCp)C(O)] (**3**) as a 45:55 mixture of diastereomers. The fbpcd ligand and clusters **2b**, **2c**, and **3** have been isolated and characterized in solution by IR and NMR (¹H and ³¹P) spectroscopies, and by X-ray diffraction analysis in the case of the hydride-bridged cluster **3**.

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1. Introduction

The coordination chemistry and redox reactivity of the rigid, unsaturated diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma), 2,3-bis(diphenylphosphino)-*N*-*p*-tolylmaleimide (bmi), and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) at polynuclear metal clusters have remained under active investigation by our groups [1–3]. These particular diphosphine ligands have provided crucial insight into the thermally and photochemically promoted C–H and P–C bond activation manifolds exhibited by such diphosphines at polynuclear metal clusters. Moreover, the same ligands have also been shown to undergo nondissociative isomerization about various cluster polyhedra via μ_2 -phosphine moieties in a

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manner analogous to that displayed by CO ligands [4]. The structures of these three diphosphine ligands are shown below.



Wishing to explore further the chemistry of organometallic compounds with structurally more diverse diphosphine ligands that possess highly conjugated π arrays and welldefined redox and photochemically sensitive moieties, we have instituted studies on the modification of the bpcd ligand. The successful synthesis of such second-generation diphosphine ligands would allow us the opportunity to study heretofore novel cluster-ligand systems as redox relays, energy-storage devices, and photochemical and/or redox sensing components [5,6]. Early results using bpcd as a platform for the construction of new diphosphine ligands have been encouraging, and significant structural modifications of the parent diphosphine with the aldehydes 9-anthracenecarboxaldehyde and thiophene-2-carboxaldehyde have produced the new ligands 2-(anthracenyl-9-ylidene)-4.5-bis(diphenylphosphino)-4-cyclopenten-1.3-dione and 2-(2-thienylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione, respectively, through a Knoevenagel condensation route [7,8]. Scheme 1 depicts the synthetic protocol and structures of these new diphosphine ligands.

Herein we present our results on the condensation of bpcd with ferrocenecarboxaldehyde to give the new diphosphine ligand 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (fbpcd). The reactivity of the fbpcd ligand with the triosmium cluster $1,2-Os_3(CO)_{10}$ -(MeCN)₂ has been examined, and the kinetics for the isomerization of the fbpcd ligand in $1,2-Os_3(CO)_{10}$ (fbpcd) (**2b**) to $1,1-Os_3(CO)_{10}$ (fbpcd) (**2c**) are discussed. Near-UV irradiation of cluster **2c** leads to CO loss and production of the hydride-bridged cluster HOs₃(CO)₉[μ -PhP(C₆H₄)-C=C(PPh₂)C(O)C=CH(C₅H₄FeCp)C(O)] (**3**). The *ortho*-metalation of one of the aryl groups of the fbpcd ligand in **3** has been structurally confirmed.

2. Experimental

2.1. General

The starting cluster 1,2-Os₃(CO)₁₀(MeCN)₂ was prepared from Os₃(CO)₁₂ [9], which was in turn was obtained from the carbonylation of OsO₄ using a 450 mL Parr Series 4560 bench-top mini reactor [10]. The bpcd ligand was synthesized from hexachlorocyclopentadiene [11]. The chemicals hexachlorocyclopentadiene, ferrocenecarboxaldehyde, and Me₃NO \cdot 2H₂O were purchased from Aldrich Chemical Co. The latter chemical was dried by azeotropic distillation from benzene and stored under argon when not in use. 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 [12]. The combustion analysis was performed by Atlantic Microlab, Norcross, GA.

All IR spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in sealed 0.1 mm NaCl cells, while the



Scheme 1.

¹H spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer. The ³¹P NMR spectra were collected in the proton-decoupled mode on a Varian 300-VXR spectrometer at 121 MHz, with the reported chemical shifts referenced to external H₃PO₄ (85%), taken to have $\delta = 0$. The MALDI-TOF mass spectra for the fbpcd ligand and cluster **3** were recorded at the University of the Pacific in the positive ion mode.

2.2. Synthesis of the diphosphine ligand fbpcd

To a Schlenk tube containing 0.20 g (0.43 mmol) of bpcd dissolved in 30 mL of CH₂Cl₂ at room temperature was added 92 mg of ferrocenecarboxaldehyde (0.43 mmol) and ca. 5 g of 4 Å molecular sieves. The introduction of the molecular sieves was accompanied by an immediate color change from the orange-yellow color of the two starting reagents to that of purple, signifying the presence of the desired product. The vessel was sealed and stirring was continued overnight. TLC examination of the reaction solution the following day revealed the complete consumption of the starting materials and the presence of a single purple spot at $R_f = 0.50$ using CH₂Cl₂/hexane (1:1) as a mobile phase. The crude reaction was filtered to remove the molecular sieves and the solvent concentrated down to ca. 0.5 mL, after which the product was run across a short column of silica gel using a 40:60 mixture of CH₂Cl₂/hexane as the eluent. Yield of purple fbpcd: 0.28 g (97%). IR (CH₂Cl₂): v(CO) 1717 (w, symm dione), 1671 (vs. antisymm dione) cm⁻¹. ¹H NMR (CDCl₃): δ 4.13 (s, 5H, Cp), 4.67 (br, 2H, Cp), 5.16 (br, 2H, Cp), 7.27–7.44 (m, 21H, aryls and alkenyl). ³¹P NMR (CDCl₃): δ -23.49 (AB quartet, ${}^{3}J_{P-P} = 60$ Hz). MALDI-TOF MS (m/z): 660.7 [fbpcd]⁺.

2.3. Preparation of $1,2-Os_3(CO)_{10}(fbpcd)$ (2b) from $1,2-Os_3(CO)_{10}(MeCN)_2$ and fbpcd

To 0.25 g (0.27 mmol) of 1,2-Os₃(CO)₁₀(MeCN)₂ in 30 mL of CH₂Cl₂ was added 0.18 g (0.27 mmol) of fbpcd under argon. The solution was stirred at room temperature, and the progress of the reaction was monitored by TLC analysis, which confirmed the consumption of both starting materials after 3 h and the presence of a new dark blue spot corresponding to the clusters **2b**, **2c**, and **3**. The solvent was evaporated under vacuum and the residue passed over a short column of silica gel using a 70:30 mixture of hexane/CH₂Cl₂ to furnish 0.30 g of a dark blue solid. The composition of the isolated cluster mixture was analyzed by using ¹H and ³¹P NMR spectroscopies, which revealed the product distribution: **2b** (80%), **2c** (19%), and **3** (1%).

NMR spectroscopic data for **2b**: ¹H NMR (toluene-*d*₈): δ 3.54 (s, 5H, Cp), 4.20 (br, 2H, Cp), 4.64 (br, 2H, Cp), 6.95–7.25 (m, 12H, aryl), 7.55 (s, 1H, vinyl), 7.70–7.95 (m, 8H, aryl). ³¹P NMR (toluene-*d*₈): δ –18.0 (AB quartet, $J_{P-P} = 17$ Hz).

2.4. Thermal isomerization of 2b to 2c

To a Schlenk vessel under argon was charged 0.10 g of the previous cluster mixture, followed by 25 mL of toluene via cannula. The solution was next saturated with CO. after which the vessel was sealed and removed from the vacuum line and placed in a thermostated bath at 315 K. The solution was heated for several days and the progress of the reaction was periodically checked by NMR spectroscopy, which revealed the complete consumption of 2b and a concomitant increase in the amount of cluster 2c and only a trace amount of cluster 3. Heating the same sample for an additional 45 days showed only the presence of cluster 2c. The solvent was removed and cluster 2c was run across a short column of silica gel and then recrystallized from benzene/CH₂Cl₂. Yield: 95 mg (95%). IR (CH₂Cl₂): v(CO) 2095 (s), 2046 (s), 2010 (vs), 1975 (s), 1961 (m), 1926 (m), 1719 (w, symm dione), 1675 (m, antisymm dione) cm^{-1} . ¹H NMR (toluene- d_8): δ 3.71 (s. 5H, Cp), 4.26 (br, 2H, Cp), 4.95 (br, 2H, Cp), 7.05-7.29 (m, 12H, aryl), 7.63 (s, 1H, vinyl), 7.83-8.00 (m, 8H, aryl). ³¹P NMR (toluene- d_8): δ 19.8 (AB quartet, $J_{P-P} = 21$ Hz). Anal. Calc. for C₅₀H₃₀FeO₁₂Os₃P₂ · CH₂Cl₂: C, 38.38; H, 2.02. Found: C, 37.99; H, 1.95%.

2.5. Photochemical preparation of 3 from 2c

To 50 mg (0.033 mmol) of 2c in a Schlenk tube was added 20 mL of toluene, after which the vessel was freeze-pump-thaw degassed three times and sealed. The solution was irradiated at room temperature using two GE Blacklights having a maximum output of 366 ± 20 nm for an extended period of time, with periodic removal of the liberated CO through additional freeze-pump-degas cycles. Depending on the thickness of the Schlenk tube, near quantitative conversion to the desired hydride-bridged cluster 3 was typically achieved after two weeks of continuous irradiation. The sample of 3 was passed across a short column of silica gel using CH₂Cl₂ and then recrystallized from benzene/CH₂Cl₂. Yield: 40 mg (82%). IR (CH₂Cl₂): v(CO) 2085 (vs), 2041 (vs), 2015 (vs), 1986 (vs), 1967 (sh), 1720 (w, symm dione), 1676 (m, antisymm dione) cm^{-1} . ¹H NMR (toluene- d_8): δ -15.87 (t, hydride, $J_{P-H} = 14$ Hz), 3.61 and 3.65 (s, 5H each, Cp), 4.19 and 4.32 (br, 2H each, Cp), 4.56 and 4.85 (br, 1H each, Cp), 4.93 and 4.91 (br, 1H each, Cp), 6.90–8.30 (overlapping m, aryls and vinyl). ³¹P NMR (toluene- d_8): δ 21.40 (d, $J_{P-P} = 13$ Hz), 22.11 (d, $J_{P-P} = 13$ Hz), 30.64 (t, $J_{P-P} = 13$ Hz). MALDI-TOF MS (m/z): 1457.7 $[M-CO]^+$.

2.6. X-ray diffraction data for cluster 3

Tables 1 and 2 contain the X-ray data and processing parameters and selected bond distances and angles, respectively, for cluster **3**. Single crystals of **3** suitable for X-ray diffraction analysis were grown at room temperature from a CH_2Cl_2 solution containing **3** that had been layered with Table 1

X-ray crystallographic data and processing parameters for cluster 3

CCDC Entry no.	628577
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.275(3)
b (Å)	14.681(4)
c (Å)	16.557(4)
α (°)	100.085(4)
β(°)	91.507(4)
γ (°)	101.870(4)
$V(\text{\AA})^3$	2635(1)
Molecular formula	$C_{49}H_{30}FeO_{11}Os_3P_2 + disordered C_5H_{12}$
Fw	1555.26
Formula units per cell (Z)	2
$D_{\text{calc}} (\text{Mg/m}^3)$	1.959
λ (Mo Kα) (Å)	0.71073
$\mu (mm^{-1})$	7.598
R _{merge}	0.0603
Absorption correction	empirical
Absorption correction factor	0.9223/0.2490
Total reflections	21587
Independent reflections	11383
Data/restraints/parameters	11383/0/617
R	0.0455
$R_{ m w}$	0.0992
Goodness-of-fit on F^2	0.959
$\Delta \rho(\text{max}), \Delta \rho(\text{min}) (e/Å^3)$	2.503, -1.662

Table 2

Selected bond distances (Å) and angles (°) in cluster 3

Bond distances			
Os(1)-Os(3)	2.9132(7)	Os(1)-Os(2)	2.9441(8)
Os(2)–Os(3)	2.8666(8)	Os(1)-P(1)	2.365(2)
Os(1)–P(2)	2.305(2)	$P(1) \cdot \cdot \cdot P(2)$	3.184(3)
Os(2)-C(24)	2.165(9)	C(1) - C(2)	1.32(1)
C(1)–C(5)	1.54(1)	C(2)–C(3)	1.50(1)
C(3)-C(4)	1.47(1)	C(4)–C(6)	1.37(1)
C(4)-C(5)	1.45(1)	C(6) - C(7)	1.44(1)
Cp(centroid)-Fe ^a	1.646(4)	Cp'(centroid)-Fe ^b	1.655(6)
Bond angles			
C(41)-Os(1)-C(42)	92.4(4)	C(41)-Os(1)-P(2)	87.0(3)
C(42)–Os(1)–P(2)	94.7(3)	C(41)-Os(1)-P(1)	168.9(3)
C(42)–Os(1)–P(1)	96.7(3)	P(2)-Os(1)-P(1)	85.95(7)
C(42)-Os(1)-Os(3)	86.5(3)	P(2)-Os(1)-Os(3)	172.47(6)
P(1)-Os(1)-Os(3)	86.52(5)	P(2)-Os(1)-Os(2)	120.63(5)
P(1)-Os(1)-Os(2)	86.66(5)	C(44)-Os(2)-Os(3)	87.1(3)
C(43)-Os(2)-Os(1)	117.2(3)	C(23)-P(1)-Os(1)	115.0(3)
C(1)-P(1)-Os(1)	105.1(3)	C(2)-P(2)-Os(1)	107.3(3)
C(6)-C(4)-C(5)	121.0(7)	C(6)-C(4)-C(3)	131.2(7)
C(5)-C(4)-C(3)	107.8(6)	C(4)-C(6)-C(7)	133.0(8)
C(24)-C(23)-P(1)	119.7(6)		

^a Cp centroid defined by the atoms C(7)-C(11).

^b Cp' centroid defined by the atoms C(12)-C(16).

pentane. The reported X-ray data were collected on a Bruker SMART[™] 1000 CCD-based diffractometer at 211 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm, [13] and the structure was solved and refined using the SHELXTL program package. [14] The molecular structure was checked by using PLATON [15] and solved by direct methods with all nonhydrogen atoms refined anisotropically. All carbonbound hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom, unless otherwise noted. The hydride ligand that bridges the Os(1)–Os(2) vector could not be located and the presence of a disordered pentane solvent molecule that resisted refinement was also noted. Convergence for **3** was achieved at R = 0.0455 and $R_w = 0.0992$ for 11383 independent reflections with $I > 2\sigma(I)$.

2.7. Kinetic studies

The UV-vis studies were carried out using a mixture of clusters **2b** and **2c** at a concentration of ca. 10^{-4} M using 1.0 cm quartz UV-vis cells that were equipped with a high-vacuum Teflon stopcock to facilitate handling on the vacuum line. Solutions containing the isomeric mixture of clusters 2b and 2c were prepared under 1 atm CO and used immediately before each kinetic measurement. The role of CO is to suppress the formation of the hydride-bridged cluster 3 from cluster 2c at elevated temperature. The Hewlett-Packard 8452A diode array spectrometer employed in our studies was configured with a variable-temperature cell holder and was connected to a VWR constant temperature circulator, allowing for the quoted temperatures to be maintained within ± 0.5 K. The UV-vis kinetics for the transformation of $2b \rightarrow 2c$ were monitored by following the increase of the 360 nm absorbance band as a function of time typically for 4-6 half-lifes. The rate constants quoted in Table 3 were determined by non-linear regression analysis using the single exponential function¹:

$A(t) = A_{\infty} + \Delta A * e^{(-kt)}$

The ¹H NMR kinetic experiment was conducted under CO (1 atm) in a 5 mm NMR tube possessing a J. Young valve and was monitored for slightly over 2 half-lifes. The concentration of the initial ca. 70/30 mixture of **2b**/**2c** was ca. 10^{-2} M and the solvent used was toluene-*d*₈. The extent of the reaction was determined by following the decrease in the intensity of the Cp singlet of **2b** at δ 3.54, as quantified against the methoxy resonance of the internal standard *p*-dimethoxybenzene.

The activation parameters for the isomerization of **2b** to **2c** were calculated from a plot of $\ln(k/T)$ versus T^{-1} [16], with the error limits representing deviation of the data points about the least-squares line of the Eyring plot.

¹ The rate calculations were performed by using the Agilent ChemStation software package configured to the spectrometer or the commercially available program ORIGIN6.0. Here the initial (A_0) and final (A_{∞}) absorbances and the rate constant (k) were floated to give the quoted least-squares value for first-order rate constant k.

Table 3 Experimental rate constants for the isomerization of 2b to $2c^a$

Entry number	Temperature (K)	Solvent	$10^{5}k (s^{-1})$
1	313.0	toluene	2.07 ± 0.04
2	318.0	toluene	3.21 ± 0.08
3	323.0	toluene	4.90 ± 0.09
4	323.0	toluene	5.9 ± 0.1^{b}
5	323.0	toluene-d ₈	$7.0\pm0.5^{\rm c}$
6	328.0	toluene	9.8 ± 0.1
7	333.0	toluene	18.5 ± 0.4
8	338.0	toluene	29 ± 1
9	343.0	toluene	54.1 ± 0.2

^a The UV-vis kinetic data were collected in ca. 10^{-4} M solution containing a ca. 70/30 mixture of clusters **2b** and **2c** under 1 atm CO by following the increase in the absorbance of the 360 nm band.

^b Reaction performed in the presence of PPh₃ (25 equivalents).

^c Reaction analyzed by ¹H NMR spectroscopy using ca. 10^{-2} M solution containing a ca. 70/30 mixture of **2b/2c**.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of the diphosphine ligand fbpcd

Knoevenagel condensation of ferrocenecarboxaldehdye with the diphosphine ligand bpcd proceeds rapidly in CH₂Cl₂ at room temperature in the presence of added molecular sieves (4 Å) to afford the new diphosphine ligand 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (fbpcd) in 97% yield. The role of the molecular sieves is to drive the condensation reaction to completion through the removal of the accompanying H₂O. This latter aspect was verified by a control experiment where the ferrocenecarboxaldehdye and bpcd reagents were stirred for a period of several days in the absence of molecular sieves. No fbpcd ligand was observed, as assessed by TLC and IR analyses. However, the addition of the molecular sieves to this solution led to the immediate formation of the desired ligand. The fbpcd ligand was subsequently isolated as an air-sensitive purple solid after chromatographic separation over silica using CH₂Cl₂/ petroleum ether (3:2) as the eluent. The following equation illustrates the reaction leading to the fbpcd ligand.

The fbpcd ligand was fully characterized in solution by IR and NMR spectroscopies, and by MALDI-TOF mass spectrometry. The IR spectrum showed the vibrationally coupled symmetric and antisymmetric v(CO) bands belong-

ing to the dione moiety at 1717 and 1671 cm^{-1} [17]. These carbonyl stretching bands are 25 and 34 cm^{-1} lower in energy, respectively, relative to the v(CO) bands of the starting bpcd ligand [11,18], supporting the fact that the fbpcd ligand is more electron rich than the parent diphosphine ligand. The ¹H NMR spectrum confirmed the loss of the methylene hydrogens of the bpcd ligand and the formyl hydrogen of the ferrocenecarboxaldehyde substrate. A singlet at δ 4.13 (5H) and two broadened resonances at δ 4.67 and 5.16, each of which integrates for 2H, are readily assigned to the intact ferrocene Cp ring and the functionalized Cp ring that is attached to the dione platform. The vinyl hydrogen associated with the ferrocenylidene moiety and the aromatic hydrogens from the four phenyl groups appear as a multiplet from δ 7.27–7.44. The two inequivalent ³¹P groups in the fbpcd ligand appear as a classic AB quartet centered at $\delta - 23.49$ with a $J/\overline{\Delta v}$ value of 0.30 [19]. The MALDI-TOF mass spectrum of the diphosphine ligand revealed a strong m/z peak at 660.7 for the singly charged parent $[fbpcd]^+$ ion consistent with the proposed formulation of the fbpcd ligand.

3.2. Reaction of $1,2-Os_3(CO)_{10}(MeCN)_2$ with the ligand fbpcd

Treatment of the activated cluster 1,2-Os₃(CO)₁₀- $(MeCN)_2$ (1) with an equimolar amount of the fbpcd ligand at 293 K in CH₂Cl₂ leads to the rapid consumption of 1 and the fbpcd ligand (≤ 1 h) and formation of a new dark blue spot ($R_f = 0.60$ using a 1:1 mixture of CH₂Cl₂/hexane as the eluent), as determined by TLC analysis. NMR analysis (¹H and ³¹P) of the reaction solution before a formal work-up revealed the presence of three species assignable to $1,2-Os_3(CO)_{10}(fbcpd)$ (2b), $1,1-Os_3(CO)_{10}(fbpcd)$ (2c), and $HOs_3(CO)_9[\mu-PhP(C_6H_4)C=C(PPh_2)C(O)C=CH (C_5H_4FeCp)C(O)$](3). These three products showed no discernable separation on silica gel and neutral alumina when analyzed with sundry different mobile phases. The diphosphine-bridged cluster 2b is formed as the major product in ca. 80% yield, with cluster 2c present in ca. 18–19% and the hydride-bridged cluster 3 accounting for the reminder of the ternary mixture. The observed product distribution is reminiscent of that found by us in the reaction between cluster 1 and the related diphosphine ligand bmi [2a]. These data are in accord with cluster 1 serving as an independent platform for the formation of clusters 2b and 2c and not a process involving the isomerization of 2b to 2c since our extrapolated rate data for such an isomerization at 293 K would occur with a half-life on the order of 42 h (vide infra). The bimodal substitution behavior exhibited in the reaction of cluster 1 and fbpcd is not without precedent, as we have found that the reaction of cluster 1 with the diphosphine ligand 1,2-bis(dimethylphosphino)ethane (dmpe) affords the isomeric clusters $1,2-Os_3(CO)_{10}(dmpe)$ and $1,1-Os_3(CO)_{10}(dmpe)$ as a noninterconverting mixture [20]. Scheme 2 illustrates the course of this substitution reaction using the fbpcd ligand.



Scheme 2.

Given the nature of the product mixture and the fact that both 2b and 2c possess overlapping carbonyl bands, the IR spectral data for pure 2b cannot be reported with certainty.² Fortunately, the NMR data for 2b could be extracted from the crude reaction mixture due to sufficient resolution of the two major components. The ¹H NMR spectrum of **2b** recorded in toluene- d_8 exhibits three distinct sets of cyclopentadienyl resonances at δ 3.54 (5H), 4.20 (2H), and 4.64 (2H) that are similar to the pattern displayed by the free fbpcd ligand. The aromatic hydrogens appear as two sets of multiplets from δ 6.95–7.25 (m, 12H, aryl) and 7.70-7.95 (m, 8H, aryl), with a vinyl singlet for the ferrocenylidene moiety appearing at δ 7.55. The ³¹P NMR spectrum of 2b reveals the presence of an AB quartet centered at δ -18.0 with $J_{P-P} = 17$ Hz. The high-field location of the bridging fbpcd ligand in 2b is in keeping with the general trend found in other diphosphine-bridged clusters vis-á-vis the corresponding chelating isomer (vide infra) [21].

3.3. Synthesis of 2c and isomerization kinetics

The thermally promoted isomerization of the fbpcd ligand about the triosmium frame in **2b** was next explored

as part of our interest in the coordinative flexibility exhibited by rigid unsaturated diphosphine ligands [2a,3c,22]. Heating the initially formed cluster mixture under 1 atm CO produced clear spectroscopic changes in the ¹H and ³¹P NMR spectra in concert with the conversion of **2b** and **3** to the chelating cluster **2c**. Provided these reactions were conducted in the dark or under red-light conditions, the formation of **2c** from **2b** was found to be quantitative. Pure **2c** was subsequently isolated via recrystallization and characterized in solution by traditional spectroscopic methods and combustion analysis.

The IR spectrum of 2c recorded in CH₂Cl₂ revealed terminal Os-CO carbonyl stretching bands at 2095 (s), 2046 (s), 2010 (vs), 1975 (s), 1961 (m), and 1926 (m) cm^{-1} , with the two dione carbonyl bands appearing at 1719 (w) and 1675 (m) cm^{-1} . The symmetry and frequencies of the terminal carbonyl stretching bands closely match those IR data reported by us for the diphosphine-chelated clusters 1,1- $Os_3(CO)_{10}(bpcd)$ and $1,1-Os_3(CO)_{10}(bmi)$ [2a,3c]. The chelation of the fbpcd ligand in 2c is accompanied by a down-field shift of the signature cyclopentadienyl ¹H resonances relative to **2b** and appear at δ 3.71 (5H), 4.26 (2H), and 4.95 (2H). The resonances belonging to the aromatic hydrogens [δ 7.05–7.29 (12H) and 7.83–8.00 (8H)] and the lone ferrocenylidene hydrogen (δ 7.63) are relatively unchanged from that of cluster **2b**. Finally, the ³¹P NMR spectrum displays an AB quartet at δ 19.8 for the diphosphine ligand. The large nuclear deshielding exhibited by

 $^{^2}$ The spectral contributions from the hydride cluster **3** (<1%) did not offer significant interference in comparison to the carbonyl frequencies from cluster **2c**.



Fig. 1. ¹H NMR kinetic data for the isomerization of $2b \rightarrow 2c$ in toluene- d_8 at 323 K in the cyclopentadienyl region at (A) 0 h, (B) 3 h, and (C) 20 h.

the fbpcd ligand in 2c relative to the bridging analogue is consistent with the adoption of a chelating coordination mode [21].

The isomerization kinetics for $2b \rightarrow 2c$ were initially examined by ¹H NMR spectroscopy in toluene- d_8 at 323 K. Here a cluster mixture that contained ca. a 70/30 composition of **2b** to **2c** was employed.³ Representative spectral changes in the cyclopentadienvl region from δ 3.00-5.20 are illustrated in Fig. 1. Here the growth of the three cyclopentadienyl resonances belonging to the chelating isomer was found to be proportional to the rate of consumption of the Cp resonances belonging to 2b. A traditional plot of ln [2b] versus time furnished the first-order rate constant quoted in Table 3 (entry 5), which agrees nicely with the two other rate constants measured by UV-vis spectroscopy at the same temperature (entries 3 and 4). The clean conversion to 2c found by NMR spectroscopy underscores the fact that the isomerization is not accompanied by the formation of extraneous material(s) and is unidirectional unlike the isomerization reactions in the diphosphine-substituted clusters $Os_3(CO)_{10}$ - $[(Z)PPh_2CH=CHPPh_2]$ and $H_4Ru_4(CO)_{10}(dppe)$ that give rise to an equilibrium mixture of bridging and chelating isomers [22,23].

The kinetics for the isomerization of $2b \rightarrow 2c$ were also investigated by UV-vis spectroscopy in toluene solution over the temperature range 313-343 K. The first-order rate constants for these reactions are reported in Table 3, while Fig. 2a shows the spectral changes that accompany the isomerization at 323 K. The rate of the reaction was easily assessed by following the increase in the absorbance of the 360 nm belonging to 2c. The isomerization was judged to be free from kinetic complications and negligible material loss based on the isosbestic point at 390 nm that is maintained throughout the course of the reaction. Fig. 2b shows the fit between the absorbance data and the least-squares regression curve that affords the quoted rate constant in Table 3. The effect of added PPh₃ on the reaction at 323 K was also examined (Table 3, entry 4), yielding a rate constant of $5.9 \pm 0.1 \text{ s}^{-1}$ that is essentially indistinguishable with the rate constant measured under CO (entry 3). These data argue against a rate-limiting dissociative process that yields a long-lived unsaturated intermediate. The kinetic data for the conversion of $2b \rightarrow 2c$ strongly support the involvement of a unimolecular process whereby one of the phosphine moieties and two CO groups undergo an equatorial permutation about the cluster polyhedron via a μ -phosphine/ μ -CO intermediate. The Eyring plot of $\ln(k/$ T) versus T^{-1} shown in Fig. 3 afforded activation parameters $(\Delta H^{\ddagger} = 23.1 \pm 0.3 \text{ kcal/mol} \text{ and } \Delta S^{\ddagger} = -7 \pm 1 \text{ eu})$ consistent with the structural rearrangement exemplified by the "merry-go-process" that is depicted in the following equation [2a,3c,22]:

 $^{^3}$ The trace amount of cluster 3, which is initially present and ultimately converted to 2c under CO, can be ignored as it does not adversely affect the data analysis.



Fig. 2. UV-vis spectral changes for the isomerization of $2b \rightarrow 2c$ in toluene at 323 K (left) and the absorbance changes at 360 nm versus time curve for the experimental data (**I**) and the least-squares fit of k (**—**, right).



Fig. 3. Eyring plot for the conversion of $2b \rightarrow 2c$ in toluene over the temperature range of 313–343 K.

3.4. Synthesis of the hydride-bridged cluster 3 from 2c

The photochemical reactivity of 2c was examined given our interest in diphosphine ligand activation at metal clusters through ortho-metalation [2a,3c,22]. We have previously demonstrated the photoefficient CO loss and C-H bond activation of an ancillary aryl ligand in the diphosphine-chelated clusters $Os_3(CO)_{10}(bpcd)$ and $Os_3(CO)_{10}(bmi)$ to give the hydride-bridged clusters HOs_3 - $(CO)_9[\mu-Ph_2PC=C(PhP\{C_6H_4\})C(O)CH_2C(O)]$ and HOs₃- $(CO)_{9}[\mu-Ph_{2}PC=C(PhP\{C_{6}H_{4}\})C(O)N(p-tolyl)C(O)],$ respectively. Irradiation of cluster 2c using 366 nm light leads to the slow loss of CO and ortho-metalation of one of the phenyl ligands to give the cluster HOs₃(CO)₉- $[\mu-PhP(C_6H_4)C=C(PPh_2)C(O)C=CH(C_5H_4FeCp)C(O)] (3).$ In comparison to our earlier studies on $Os_3(CO)_{10}(bpcd)$ and $Os_3(CO)_{10}(bmi)$, the photochemically promoted orthometalation of 2c is exceeding slow, as assessed by NMR analvsis. Depending upon the amount of 2c employed, good yields of 3 could be achieved by prolonged photolysis for several weeks with frequent removal of the liberated CO. Optical excitation of $Os_3(CO)_{10}(bpcd)$ has been shown to furnish the unsaturated cluster $Os_3(CO)_9(bpcd)$, followed by an intermediate π -aryl complex that precedes the formal *ortho*-metalation step. The π -aryl complex is sensitive to extraneous CO, which upon capture regenerates the starting cluster $Os_3(CO)_{10}(bpcd)$ [3c]. The same scenario is assumed to be operative in the case of cluster 2c, which accounts of the observed sensitivity to CO. Photolysis of a CO-saturated solution of 2c shows no evidence for the formation of the desired hydride-bridged cluster 3. Controlled thermolysis of 3 with CO (1 atm) regenerates 2c in quantitative yield, as determined by NMR spectroscopy. Cluster 3 was isolated by column chromatography, followed by recrystallization, as an air-sensitive, blue solid. Eq. (3) illustrates the reaction of 2c to 3:



Fig. 4. Thermal ellipsoid plot of cluster **3** showing the thermal ellipsoids at the 50% probability level. The pentane solvent molecule has been omitted for clarity.



Cluster 3 was characterized in solution by IR and NMR spectroscopies. The ortho-metalation attendant on photolysis was confirmed by ¹H NMR spectroscopy. The observation of a high-field triplet at δ -15.87 provides unequivocal evidence for the presence of an edge-bridged cluster hydride. Particularly informative were the NMR data that revealed the existence of a 45:55 mixture diastereomers for 3, whose origin derives from the proximal and distal orientations of the ferrocene moiety relative to the ortho-metalated aryl group. The nonfunctionalized Cp ring in the ¹H NMR spectrum of **3** appears as two singlets at δ 3.61 and 3.65, while the other Cp ring exhibits three sets of broadened multiplets at δ 4.19 and 4.32 (br, 2H each), 4.56 and 4.85 (br, 1H each), and 4.93 and 4.91 (br, 1H each). The essentially equimolar composition of diastereomers was corroborated by ³¹P NMR spectroscopy. The presence of two distinct high-field doublets recorded at δ 21.40 and 22.11 and one triplet at δ 30.64, which results from overlapping doublets, is consistent with this formulation. No attempts have been made to assign these resonances to specific phosphine moieties. The MALDI-TOF mass spectrum showed a weak peak centered on m/e 1457.7 for the loss of one CO group from of **3**, as well as ions for the loss of seven additional CO groups.

The molecular composition of one of the diastereomers of 3 was established by X-ray diffraction analysis. Fig. 4 shows the thermal ellipsoid plot 3 and ascertains the activation of one of the aryl rings via ortho-metalation. The Os–Os bond distances range from 2.866(8) Å [Os(2)– Os(3)] to 2.9441(8) Å [Os(1)-Os(2)], with an mean distance of 2.908 Å that parallels those Os–Os single-bond distances reported for other Os₃ clusters. Despite the fact that the bridging hydride was not located during the crystallographic refinement, its location may be confidently assigned to the Os(1)-Os(2) vector [24]. Here the formation of an edge-bridging hydride leads to an elongation of the Os(1)–Os(2) bond length relative to the other two Os–Os bonds in 3. Both phosphorus atoms of the fbpcd ligand coordinate to the Os(1) center in a chelating fashion and exhibit distinct axial [P(1)] and equatorial [P(2)] dispositions. This represents a change in the phosphine disposition from 2c where both phosphine moieties were initially situated at equatorial sites. Presumably, the stereochemical change facilitates the ensuing ortho-metalation. The P(1)-Os(1)-P(2) angle of 85.95(7)° and the two Os-P distances of 2.305(2) Å [Os(1)-P(2)] and 2.365(2) Å [Os(1)-P(1)]exhibit values unremarkable to those angles and distance found by us in related compounds [1-3]. The Os(2)–C(24) bond distance of 2.165(9) Å is in excellent agreement with those metal-carbon sigma bond distances found in di- and trinuclear osmium compounds containing an ortho-metalated aryl ligand [25]. The nine CO groups are

linear and exhibit distances and angles consistent with such linkages. The ferrocene and dione ring moieties are unexceptional and require no comment.

4. Conclusions

The synthesis and properties of the new diphosphine ligand fbpcd are described. The kinetics for the bridge-to-chelate isomerization of the fbpcd ligand in $Os_3(CO)_{10}$ -(fbpcd) have been measured, with a sequence involving a nondissociative "merry-go-round" migration of the ancillary fbpcd ligand and two CO groups supported by a moderately negative entropy of activation. The chelating isomer of $Os_3(CO)_{10}$ (fbpcd) losses CO upon 366 nm irradiation, leading to the *ortho*-metalation of the one of the aryl groups and formation of the hydride-bridged cluster HOs_3(CO)_9[\mu-PhP(C_6H_4)C=C(PPh_2)C(O)C=CH(C_5H_4Fe-Cp)C(O)], whose molecular structure has been crystallographically determined.

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Appendix A. Supplementary material

CCDC 628577 contains the supplementary crystallographic data for **3**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.03.057.

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