Diphosphine Isomerization and C−H and P−C Bond Cleavage Reactivity in the Triosmium Cluster $Os_3(CO)_{10}$(bpcd): Kinetic and Isotope Data for Reversible Ortho Metalation and X-ray Structures of the Bridging and Chelating Isomers of $Os_3(CO)_{10}$(bpcd) and the Benzyne-Substituted Cluster $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$[†]

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The coordination and reactivity of the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopentene-1,3-dione (bpcd) with $Os_3(CO)_{10}(MeCN)_2$ (**1**) has been explored. The initial substitution product 1,2-$Os_3(CO)_{10}$(bpcd) (**2b**) undergoes a nondissociative, intramolecular isomerization to furnish the bpcd-chelated cluster 1,1-$Os_3(CO)_{10}$(bpcd) (**2c**) over the temperature range of 323−343 K. The isomerization reaction is unaffected by trapping ligands, yielding the activation parameters $\Delta H^{\ddagger} = 25.0(0.7)$ kcal/mol and $\Delta S^{\ddagger} = -2(2)$ eu. Thermolysis of **2c** in refluxing toluene gives the hydrido cluster $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (**3**) and the benzyne cluster $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$ (**4**). Time−concentration profiles obtained from sealed-tube NMR experiments starting with either **2c** or **3** suggest that both clusters are in equilibrium with the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd) and that the latter cluster serves as the precursor to the benzyne-substituted cluster **4**. The product composition in these reactions is extremely sensitive to CO, with the putative cluster 1,1-$Os_3(CO)_9$(bpcd) being effectively scavenged by CO to regenerate **2c**. Photolysis of cluster **2c** using near-UV light affords **3** as the sole product. These new clusters have been fully characterized in solution by IR and NMR spectroscopy, and the molecular structures of clusters **2b**,**c**, and **4** have been determined by X-ray crystallography. Reversible C−H bond formation in cluster **3** is demonstrated by ligand trapping studies to give 1,1-$Os_3(CO)_9L$(bpcd) (where L = CO, phosphine) via the unsaturated intermediate 1,1-$Os_3(CO)_9$(bpcd). The kinetics for reductive coupling in $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ and $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$ in the presence of PPh_3 give rise to a k_H/k_D value of 0.88, a value that supports the existence of a preequilibrium involving the hydride (deuteride) cluster and a transient arene-bound Os_3 species that precedes the rate-limiting formation of 1,1-$Os_3(CO)_9$(bpcd). Strong proof for the proposed hydride (deuteride)/arene preequilibrium has been obtained from photochemical studies employing the isotopically labeled cluster 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$), whose bpcd phenyl groups each contain one ortho hydrogen and deuterium atom. Generation of 1,1-$Os_3(CO)_9$(bpcd-$d_{4,ortho}$) at 0 °C gives rise to a 55:45 mixture of the corresponding hydride and deuteride clusters, respectively, from which a normal KIE of 1.22 is computed for oxidative coupling of the C−H(D) bond in the ortho metalation step. Photolysis of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) at elevated temperature and thermolysis of the low-temperature photolysis hydride/deuteride mixture afford an equilibrium mixture of hydride (67%) and deuteride (33%), yielding a K_{eq} value of 0.49, which in conjunction with the k_H/k_D ratio from the C−H(D) ortho-metalation step allows us to establish a k_H/k_D value of 0.60 for the reductive coupling from the participant hydride/deuteride clusters. These data, which represent the first isotope study on ortho metalation in a polynuclear system, are discussed relative to published work on benzene activation at mononuclear rhodium systems. UV−vis kinetic data on the transformation **3** → **4** provide activation parameters consistent with the rate-limiting formation of the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd), preceding the irreversible P−C cleavage manifold. The ortho metalation of the bpcd ligand in **3** and formation of the benzyne moiety **4** are discussed relative to ligand degradation reactions in this genre of cluster.

Introduction

The use of ancillary phosphine ligands for the stabilization and reactivity modification of organometallic compounds is a well-documented phenomenon. Mono- and bidentate phosphine ligands continue to receive extensive attention with respect to Heck, Suzuki, and Sonogashira carbon−carbon bond forming reactions,[1] asymmetric catalysis and transformations,[2] and construction of dimensionally defined supramolecular complexes.[3] Of concern to researchers in these fields is the long-term integrity of the ancillary phosphine ligand(s) that is bound to the metal template during catalytic reactions and synthetic

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manipulations, as deleterious cyclometalation of the alkyl substituents, ortho metalation of the aryl substituents,[4] and P−C bond cleavage reactions can lead to diminished catalytic efficiency and serve as an entry point for the complete destruction of the phosphine ligand.[5]

Numerous studies of phosphine-substituted polynuclear clusters have provided unambiguous evidence and conclusively dispelled the early assumptions concerning the inert and spectator nature of such ligands.[6,7] The relative ease and outcome associated with the stepwise activation and bond cleavage reactions exhibited by cluster-bound phosphines have largely been elucidated by solution spectroscopic and crystallographic methods.[8] In the case of the dppm-substituted clusters $Ru_3(CO)_{10}$(dppm) and $Os_3(CO)_{10}$(dppm), valuable insight into the reactivity of the dppm ligand as a result of multisite activation at the cluster polyhedron through ortho metalation of an aryl group(s) and P−C bond activation has been achieved.[9] Mild thermolysis of the triruthenium cluster promotes ortho metalation at an aryl ring on each phosphorus atom with concomitant loss of benzene to initially furnish the phosphido-bridged cluster $Ru_3(CO)_9[\mu\text{-PhPCH}_2\text{PPh}(C_6H_4)]$, which upon subsequent reaction with adventitious CO, followed by reductive coupling, gives the cyclic diphosphine-substituted cluster $Ru_3(CO)_{10}[\mu\text{-PhP}(CH_2)(C_6H_4)\text{PPh}]$.[10] A slightly different outcome is found for the dppm ligand during the thermolysis of $Os_3(CO)_{10}$(dppm). Here the ortho metalation of one of the aryl groups is triggered by the formal loss of CO to ultimately yield the unsaturated cluster $HOs_3(CO)_8[Ph_2PCH_2PPh(C_6H_4)]$.[11] The kinetic stabilization of $HOs_3(CO)_8[Ph_2PCH_2PPh(C_6H_4)]$ can be traced to the capping of one of the Os_3 faces by the two phosphorus atoms and an edge-bridging aryl carbon, the latter resulting from the ortho-metalation sequence. This particular triosmium cluster has proven to be a pivotal precursor for the synthesis of a variety of osmium-substituted clusters under mild conditions because of the highly reversible ortho metalation, which in turns opens up an accessible coordination site within the cluster.[12] Scheme 1 illustrates the course of the dppm activation observed in these two clusters.

The impetus for this report is based, in part, on our earlier studies, where the reactions of the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopentene-1,3-dione (bpcd) with the clusters $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ were investigated. Whereas complete cluster fragmentation and formation of the simple mononuclear complex $Fe(CO)_3$(bpcd) was found in the reaction with the iron cluster,[13] reaction of the ruthenium cluster produced the bpcd-chelated cluster $Ru_3(CO)_{10}$(bpcd), which was found to be unstable at ambient temperature, decomposing to $Ru_3(CO)_{12}$ and the donor−acceptor complex $Ru_2(CO)_6$(bpcd).[14] Emerging from this work was the unexpected ease by which $Ru_2(CO)_6$(bpcd) furnished the phosphido compound $Ru_2(CO)_6[\mu\text{-C}{=}\text{C}(PPh_2)\text{C(O)CH}_2\text{C(O)}](\mu_2\text{-PPh}_2)$ upon near-UV optical excitation through a transient zwitterionic biradical intermediate.

Wishing to complete our diphosphine substitution studies with all three group 8 trimetal clusters, we have explored the reactivity of the bpcd ligand with $Os_3(CO)_{10}(MeCN)_2$. Herein we present our results on the reaction of the activated osmium cluster with bpcd that initially gives the ligand-bridged cluster 1,2-$Os_3(CO)_{10}$(bpcd) (**2b**). The stepwise conversion of cluster **2b** to the chelated cluster 1,1-$Os_3(CO)_{10}$(bpcd) (**2c**) and then to the hydrido cluster $HOs_3(CO)_9[\mu\text{-}(PPh_2)\text{C}{=}\text{C}\{\text{PPh}(C_6H_4)\}\text{C(O)CH}_2\text{C(O)}]$ (**3**) and the benzyne cluster $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-PPhC}{=}\text{C}(PPh_2)\text{C(O)CH}_2\text{C(O)}]$ (**4**) has been established, with the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd) functioning as the bifurcation point for clusters **3** and **4**. All new clusters have

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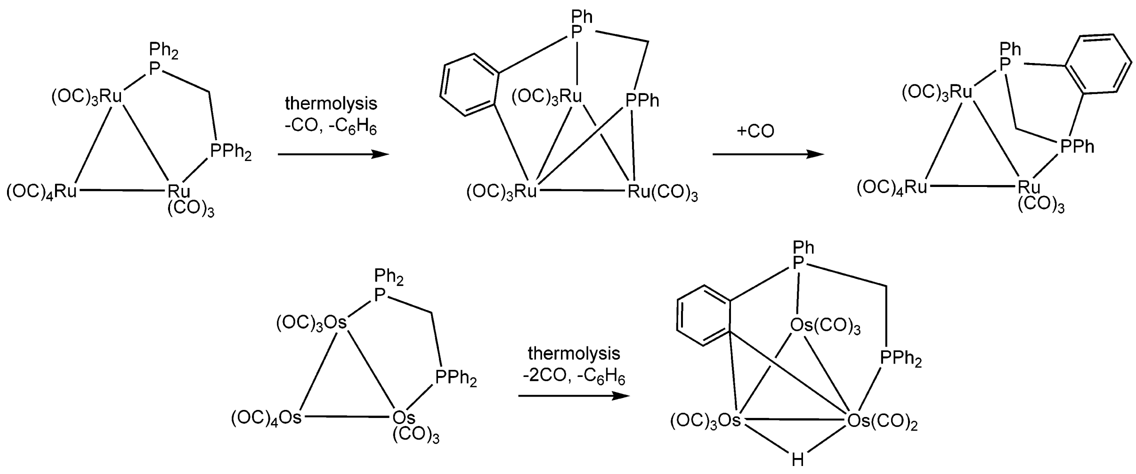
Scheme 1



been isolated and fully characterized in solution; in addition, X-ray analyses have been performed for the clusters **2b**,**c**, and **4**. The ortho-metalation reaction that gives **3** is shown to be reversible and has been probed using deuterated bpcd isotopomers. Kinetic and thermodynamic isotope data are presented that support the existence of an intermediate aryl π complex in the ortho-metalation reaction.

Experimental Section

General Methods. The $Os_3(CO)_{10}(MeCN)_2$ used in our studies was prepared from $Os_3(CO)_{12}$,[15] which in turn was obtained from the high-pressure carbonylation of OsO_4.[16] The bpcd ligand used in these studies was synthesized from 4,5-dichloro-4-cyclopentene-1,3-dione and Ph_2PTMS according to the known procedure.[17] PPh_3-d_{15} was prepared from bromobenzene-d_5 and PCl_3 according to the published procedure,[18] and PPh_3-$d_{3,ortho}$ was synthesized by the method of Noyce et al.[19] 1,2-Bromochlorobenzene and $Me_3NO\cdot 2H_2O$ were purchased from Aldrich Chemical Co., with the former used as received and the latter used after the water was removed by azeotropic distillation from benzene. The ^{13}CO (>99%) employed in the enrichment of $Os_3(CO)_{12}$ and the C_6D_6 (>99.5%) and D_2O (>99.8%) used in the preparation of the isotopically substituted bpcd ligands were all purchased from Isotec, Inc., and used directly as received. All reaction and NMR solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels,[20] and with the exception of chromatographic separations, all reactions were conducted under argon, employing standard Schlenk techniques. Routine photolyses were conducted with GE blacklight bulbs, having a maximum output of 366 ± 20 nm and a photon flux of ca. 1×10^{-6} einstein/min, while the low-temperature NMR tube photochemical experiments were carried out with a 200 W Oriel Hg(Xe) arc lamp. The reported quantum yield for the conversion **2c** → **3** was determined by ferrioxalate actinometry.[21] All C and H 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 NaCl cells, using PC control and OMNIC software. The ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Varian Gemini 200 spectrometer, and the ^{31}P NMR spectra were recorded at 121 MHz on a Varian 300-VXR spectrometer. The reported ^{31}P chemical shifts are referenced to external H_3PO_4 (85%), taken to have δ 0.0. Here positive chemical shifts are to low field of the external standard. All ^{13}C and ^{31}P NMR spectra were run in the proton-decoupled mode. The high-resolution FAB mass spectra were obtained at the Mass Spectrometry facility at the University of California at San Diego using 3-nitrobenzyl alcohol as the sample matrix and polypropylene glycol as a reference.

Preparation of 1,2-$Os_3(CO)_{10}$(bpcd). To the activated cluster $Os_3(CO)_{10}(MeCN)_2$, prepared from 0.80 g (0.88 mmol) of $Os_3(CO)_{12}$ and 0.14 g (1.92 mmol) of Me_3NO, was added 100 mL of benzene, followed by 0.41 g (0.89 mmol) of bpcd. The solution was stirred for 4.0 h at room temperature, after which time TLC analysis (R_f = 0.77 in CH_2Cl_2) confirmed the presence of a green spot belonging to the desired product. The bpcd-bridged cluster was subsequently isolated by column chromatography over silica gel using CH_2Cl_2/hexane (2:3) as the eluent and recrystallized from CH_2Cl_2/hexane (1:1) to give spectroscopically pure 1,2-$Os_3(CO)_{10}$(bpcd) in 48% yield (0.60 g). IR (CH_2Cl_2): ν(CO) 2091 (m), 2030 (m, sh), 2008 (vs, b), 1975 (m, b), 1958 (m, b), 1761 (w, sym dione carbonyl), 1724 (m, antisym dione carbonyl) cm^{-1}. ^1H NMR ($CDCl_3$; 298 K): δ 7.25−7.70 (m, 20H, aryl), 3.06 (s, 2H, dione CH_2). ^{13}C NMR (C_7D_8; 233 K): δ 193.07 (s, 4C, axial), 184.78 (s, 2C, axial), 178.17 (s, 2C, equatorial), 173.12 (s, 2C, equatorial). ^{31}P NMR ($CDCl_3$, 298 K): δ −17.55 (s).

Isomerization of 1,2-$Os_3(CO)_{10}$(bpcd) to 1,1-$Os_3(CO)_{10}$(bpcd). In a large Schlenk tube was charged 0.56 g (0.43 mmol) of 1,2-$Os_3(CO)_{10}$(bpcd) and 40 mL of benzene by syringe, after which the solution was saturated with CO for several minutes in order to suppress the formation of cluster **3** (vide infra). At this point the vessel was sealed and heated for 20 h at 50−60 °C, at which time the solution gradually changed from green to brown. TLC examination of the crude reaction solution showed that the chelating isomer possessed the same R_f value as the bridging isomer in all solvents explored, rendering this mode of analysis useless. The solvent was next removed under vacuum and the crude product was purified by chromatography, as described above, to give 0.42 g (74%) of 1,1-$Os_3(CO)_{10}$(bpcd) as a brown solid. Recrystallization from CH_2Cl_2/hexane furnished the analytical sample. IR (CH_2Cl_2): ν(CO) 2096 (m), 2047 (vs), 2010 (vs, b), 1992 (m), 1977 (m), 1964 (w, b), 1925 (m, b), 1749 (w, sym dione carbonyl), 1717 (m, antisym dione carbonyl) cm^{-1}. ^1H NMR ($CDCl_3$; 298 K): δ 7.25−7.70 (m, 20H, aryl), 3.74 (s, 2H, dione CH_2). ^{13}C NMR (C_7D_8; 233 K): δ 198.59 (t, 2C, axial, J_{P-C} = 8 Hz), 185.03 (s, 4C, axial), 177.02 (s, 2C, equatorial), 171.02 (s, 2C, equatorial). ^{31}P NMR ($CDCl_3$, 298

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K): δ 17.97 (s). Anal. Calcd (found) for $C_{39}H_{22}O_{12}Os_3P_2$: C, 35.62 (35.56); H, 1.69 (1.74).

Preparation of $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$. To a Schlenk vessel was added $Os_3(CO)_{10}(MeCN)_2$, prepared from 0.25 g (0.28 mmol) of $Os_3(CO)_{12}$ and 60 mg (0.80 mmol) of Me_3NO in MeCN, 0.13 g (0.28 mmol) of bpcd, and 50 mL of benzene. The reaction solution was stirred for 3 days at ca. 45−50 °C with periodic removal of the liberated CO by argon purge. TLC inspection of the reaction solution showed two very close moving spots in CH_2Cl_2 assigned to the hydride cluster $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ ($R_f = 0.80$) and the chelating cluster **2c** ($R_f = 0.77$). The presence of these two clusters was also verified by IR and NMR analyses, the latter method indicating a 7:1 ratio of **2c** to **3**. Both clusters were subjected to an initial purification by column chromatography over silica gel using a 2:3 mixture of CH_2Cl_2/hexane. The cluster mixture comprised of **2c** and **3** was dissolved in ca. 40 mL of CH_2Cl_2 and irradiated between two parallel blacklight bulbs for 7 days at room temperature. During this time the CO was periodically removed by argon purge. The crude reaction mixture was filtered through silica gel using CH_2Cl_2 to afford spectroscopically pure $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ as a brown solid in 23% yield (82 mg). The analytical sample was obtained from the slow evaporation of a benzene solution containing cluster **3**. IR (CH_2Cl_2): ν(CO) 2084 (s), 2042 (s), 2019 (vs), 2003 (m), 1751 (w, sym dione carbonyl), 1719 (m, antisym dione carbonyl) cm^{-1}. ^1H NMR ($CDCl_3$; 298 K): δ 6.90−8.30 (m, 19H, aryl), 3.54 (s, 2H, dione CH_2), −16.28 (t, 1H, $J_{P-H} = 13$ Hz). ^1H NMR (C_6D_6; 298 K): δ 6.85−8.50 (m, 19H, aryl), 2.07 (AB quartet, 2H, dione CH_2, $J_{H-H} = 22$ Hz), −15.91 (t, 1H, $J_{P-H} = 13$ Hz). ^{13}C NMR (C_7D_8; 223 K): δ 185.32−184.00 (m, 3C), 179.02 (s, 1C), 178.24 (d, 1C, $J_{P-C} = 9$ Hz), 176.88 (s, broad, 1C), 176.09 (s, broad, 1C), 175.31 (s, 1C), 173.79 (s, 1C). ^{31}P NMR ($CDCl_3$, 298 K): δ 26.71 (d, $J_{P-P} = 15$ Hz), 19.18 (d, $J_{P-P} = 15$ Hz). Anal. Calcd (found) for $C_{38}H_{22}O_{11}Os_3P_2{\cdot}0.5C_6H_6$: C, 37.13 (37.07); H, 1.90 (2.08).

Preparation of $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$. A 0.16 g (0.12 mmol) portion of 1,1-$Os_3(CO)_{10}$(bpcd) and 0.70 mL of toluene-d_8 were charged into a screw-capped NMR tube and heated at 110 °C overnight, with monitoring by ^1H NMR spectroscopy. NMR analysis showed the complete consumption of the cluster **2c** and formation of the hydride cluster **3** and the desired benzyne cluster **4**. The solvent was stripped under vacuum, and the crude residue was purified by column chromatography using a 1:1 mixture of CH_2Cl_2 and hexane. Cluster **4** was isolated as a brown solid in 40% yield (62 mg). The combustion sample of **4** was obtained by slow evaporation of a benzene solution containing **4**. IR (CH_2Cl_2): ν(CO) 2077 (s), 2042 (vs), 2030 (m), 1999 (m), 1990 (m), 1977 (m), 1748 (w, sym dione carbonyl), 1715 (m, antisym dione carbonyl) cm^{-1}. ^1H NMR ($CDCl_3$; 298 K): δ 6.50−9.20 (m, 19H, aryl and benzyne), 3.66 (AB quartet, 2H, dione CH_2, $J_{H-H} = 22$ Hz), −16.68 (dd, 1H, $J_{P-H} = 14$, 7 Hz). ^{13}C NMR (C_7D_8; 223 K): δ 184.41 (d, 1C, $J_{P-C} = 7$ Hz), 182.42 (s, 1C), 180.86 (d, 1C, $J_{P-C} = 74$ Hz), 179.98 (d, 1C, $J_{P-C} = 74$ Hz), 175.64 (s, broad, 1C), 175.10 (d, 1C, $J_{P-C} = 7$ Hz), 174.70 (s, 1C), 171.44 (s, 1C). ^{31}P NMR ($CDCl_3$, 298 K): δ 10.96 (d, phosphine, $J_{P-P} = 12$ Hz), −72.18 (d, phosphido, $J_{P-P} = 12$ Hz). Anal. Calcd (found) for $C_{37}H_{22}O_{10}Os_3P_2{\cdot}0.5C_6H_6$: C, 37.01 (36.58); H, 1.94 (1.90).

Preparation of bpcd-d_{20}. To 1.30 g (4.70 mmol) of $P(C_6D_5)_3$ in a Schlenk flask was added 150 mL of THF via cannula, followed by 0.55 g (14.1 mmol) of freshly cut potassium. The reaction mixture was stirred overnight at room temperature and filtered through a sintered-glass funnel under argon to remove the unreacted potassium. The filtrate containing the $[P(C_6D_5)_2][K]$ and $[C_6D_5][K]$ was next cooled to 0 °C with an ice/water bath and treated with 2.5 mL (18.8 mmol) of trimethylsilyl chloride (TMSCl) dropwise via syringe to furnish $(C_6D_5)_2PTMS$ and C_6D_5TMS. The reaction mixture was stirred for 1 h at 0 °C and for an additional 2 h with warming to room temperature. The solvent, unreacted TMSCl, and C_6D_5TMS were removed under vacuum, and the residue containing $(C_6D_5)_2PTMS$ was dissolved in 5.0 mL of Et_2O, transferred to a clean Schlenk vessel, and cooled to 0 °C. To this solution was added 0.33 g (2.00 mmol) of 4,5-dichloro-4-cyclopentene-1,3-dione dissolved in 20 mL of Et_2O and 3.0 mL of THF dropwise over the course of 0.5 h by the means of a pressure-equilibrated addition funnel, with stirring continued overnight. The solvents were removed the following day, and the crude ligand was isolated by column chromatography over silica gel using a 1:1 mixture of CH_2Cl_2 and hexanes to furnish 0.31 g (32% based on dione consumed) of bpcd-d_{20} as a yellow solid. ^1H NMR ($CDCl_3$; 298 K): δ 2.92 (s, 2H, dione). ^{31}P NMR ($CDCl_3$, 298 K): δ −22.76 (s). FAB-MS (*m*/*z*): 484.2344 (calcd for $C_{29}H_2D_{20}O_2P_2$ 484.2345).

Preparation of 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}) and $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$. Since the overall procedure employed for the synthesis of 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}) and $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$ is identical with that described for 1,1-$Os_3(CO)_{10}$(bpcd) and $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$, only the highlights will be given. To $Os_3(CO)_{10}(MeCN)_2$, prepared from 0.28 g (0.31 mmol) of $Os_3(CO)_{12}$ and 53 mg (0.71 mmol) of Me_3NO in MeCN, in 50 mL of CH_2Cl_2 was added 0.15 g (0.31 mmol) of bpcd-d_{20} in 15 mL of CH_2Cl_2 by cannula, after which the reaction mixture was stirred for 6 h at 40 °C to produce a mixture of 1,2- and 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}). Both clusters were isolated by chromatography, dissolved in CO-saturated CH_2Cl_2, and heated at ca. 45−50 °C for 3 days. At this point the solution contained the desired cluster 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}), which was obtained in 58% yield (0.24 g) after chromatographic separation from the trace amount of unreacted bpcd-d_{20}. The entire amount of 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}) was next dissolved in 12 mL of a 1:2 mixture of toluene-d_8 and benzene-d_6 in a small Schlenk tube and then irradiated for 10 days at room temperature with monitoring by ^1H NMR spectroscopy. The reaction was driven to completion by periodically releasing the liberated CO by either freeze−pump−thaw degas cycles or by argon purge. When all of the 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}) had been consumed, the irradiation was terminated and the solvents were removed under vacuum, affording 0.20 g (83%) of $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$ after chromatographic separation (note: there was no loss of deuterium after chromatography over silica gel, on the basis of the ^1H NMR data). 1,1-$Os_3(CO)_{10}$(bpcd-d_{20}) data are as follows. IR (CH_2Cl_2): ν(CO) 2096 (m), 2047 (vs), 2011 (vs, b), 1992 (m), 1977 (m), 1963 (w, b), 1926 (m, b), 1749 (w, sym dione carbonyl), 1717 (m, antisym dione carbonyl) cm^{-1}. ^1H NMR ($CDCl_3$; 298 K): δ 3.73 (s, 2H, dione). ^{31}P NMR ($CDCl_3$, 298 K): δ 17.03 (s). $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$ data are as follows. ^1H NMR ($CDCl_3$; 298 K): δ 3.55 (s, 2H, dione). ^{31}P NMR ($CDCl_3$, 298 K): δ 26.21 (d, $J_{P-P} = 14$ Hz), 18.92 (d, $J_{P-P} = 14$ Hz).

Preparation of bpcd-$d_{4,ortho}$. To a THF solution (150 mL) containing 1.40 g (5.30 mmol) of $PPh_3\text{-}d_{3,ortho}$[22] was added 0.62 g (16.0 mmol) of freshly cut potassium. The reaction mixture was stirred overnight at room temperature and then filtered under argon to remove the excess potassium. The filtered solution of $[P(Ph\text{-}d_{ortho})_2][K]$ and $[Ph\text{-}d_{ortho}][K]$ was cooled to 0 °C with an ice/water bath and treated with 3.5 mL (27.0 mmol) of trimethylsilyl chloride (TMSCl) dropwise via syringe, followed by warming of the reaction solution to room temperature and continued stirring for an additional 2 h. All volatiles were removed under vacuum, and the crude $(Ph\text{-}d_{ortho})_2PTMS$ was dissolved in 5.0 mL of Et_2O and cooled to 0 °C. To this ether solution was added 0.26 g (1.60 mmol) of 4,5-dichloro-

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[22] The purity of the $PPh_3\text{-}d_{3,ortho}$ employed in the synthesis of bpcd-$d_{4,ortho}$ was ascertained by high-resolution FAB mass spectrometry. Here the $PPh_3\text{-}d_{3,ortho}$ sample exhibited an *m*/*z* value of 265.1099 (calcd for $C_{18}H_{12}D_3P$ 265.1094).

4-cyclopentene-1,3-dione dissolved in 20 mL of Et_2O and 3.0 mL of THF, as described above for the synthesis of bpcd-d_{20}. The solution was stirred overnight with warming and the bpcd-$d_{4,ortho}$ was isolated by column chromatography over silica gel using a 1:1 mixture of CH_2Cl_2 and hexanes as the eluent to give 0.16 g (22%) of bpcd-$d_{4,ortho}$ as a yellow solid. ^{1}H NMR ($CDCl_3$; 298 K): δ 7.15−7.45 (m, 16 H, aryl), 2.93 (s, 2H, dione). ^{31}P NMR ($CDCl_3$, 298 K): δ −22.48 (s). FAB-MS (*m*/*z*): 468.1341 (calcd for $C_{29}H_2D_{20}O_2P_2$ 468.1341).

Preparation of 1,1-$Os_3(CO)_{10}$(bpcd-d_{4ortho}). To $Os_3(CO)_{10}(MeCN)_2$, prepared in situ from 0.25 g (0.28 mmol) of $Os_3(CO)_{12}$ and 53 mg (0.71 mmol) of Me_3NO in MeCN, in 50 mL of CH_2Cl_2 was added 0.16 g (0.34 mmol) of bpcd-$d_{4,ortho}$ in 15 mL of CH_2Cl_2, after which time the reaction mixture was stirred for 6 h at 40 °C. The mixture of 1,2- and 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) was then dissolved in 40 mL of CO-saturated CH_2Cl_2 and heated in a closed Schlenk vessel for 2 days at ca. 55 °C. The desired chelating isomer of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) was isolated by chromatography to furnish 0.22 g (48% yield based on bpcd-$d_{4,ortho}$ consumed) of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) as a brown solid. IR (CH_2Cl_2): ν(CO) 2096 (m), 2047 (vs), 2010 (vs, b), 1992 (m), 1977 (m), 1964 (w, b), 1926 (m, b), 1749 (w, sym dione carbonyl), 1717 (m, antisym dione carbonyl) cm^{-1}. ^{1}H NMR ($CDCl_3$; 298 K): δ 7.35−7.70 (m, 16 H, aryl), 3.75 (s, 2H, dione). ^{31}P NMR ($CDCl_3$, 298 K): δ 17.32.

Determination of the KIE for C−H(D) Oxidative Coupling and the EIE in 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$). (a) KIE Experiment. A 0.020 g (0.015 mmol) portion of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) in 0.50 mL of toluene-d_8 was added to a 5 mm NMR tube equipped with a J. Young value. The solution was freeze−pump−thaw degassed three times and then cooled to 0 °C in a quartz Dewar, after which the sample was irradiated with a 200 W Oriel Hg(Xe) arc lamp until ca. 5% of the starting cluster remained. The amount of hydride, $HOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{2,ortho})C{=}C\{P(Ph\text{-}d_{ortho})(C_6H_3D)\}C(O)CH_2C(O)]$, versus the amount of deuteride, $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{2,ortho})C{=}C\{P(Ph\text{-}d_{ortho})(C_6H_4)\}C(O)CH_2C(O)]$, was then determined by measuring the area under the hydride resonance and the methylene group associated with the bpcd ring of both isotopomers.[23] Under these conditions the amount of hydride to deuteride cluster was found to be 55:45.

(b) EIE Experiment. These experiments were set up analogously, using either benzene-d_6 or toluene-d_8 as the solvent, and the samples were irradiated with two GE blacklights at an ambient temperature of ca. 40 °C. Under these conditions the amount of hydride to deuteride cluster was found to be 67:33.

X-ray Structural Determinations. Single crystals of the cluster 1,2-$Os_3(CO)_{10}$(bpcd) (**2b**), as the *m*-xylene solvate, were grown by slow diffusion of *m*-xylene into a CH_2Cl_2 solution containing **2b** at 5 °C. The X-ray-quality crystals of 1,1-$Os_3(CO)_{10}$(bpcd) (**2c**) were obtained from a CH_2Cl_2 solution containing the cluster that had been layered with hexane, while single crystals of $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$ (**4**), as the toluene solvate, were grown from toluene and hexane. The tiny satellite crystals attached to **4** were too small to remove and consequently contributed to some of the observed reflections, lowering slightly the final agreement factor. All X-ray data were collected on a Bruker SMART 1000 CCD-based diffractometer at 300(2) K for cluster **2c** and 213(2) K for clusters **2b** and **4**. The frames were integrated with the available SAINT software package using a narrow-frame algorithm,[24] and the structure was solved and refined using the SHELXTL program package.[25] The molecular structure was checked by using PLATON,[26] and all non-hydrogen atoms were refined anisotropically, with the hydrogen atoms assigned calculated positions and allowed to ride on the attached heavy atom. The refinement for **2b** converged at $R = 0.0477$ and $R_w = 0.0782$ for 10 128 independent reflections with $I > 2\sigma(I)$ and for **2c** at $R = 0.0249$ and $R_w = 0.0582$ for 5120 independent reflections with $I > 2\sigma(I)$. The benzyne-substituted cluster **4** afforded convergence values of $R = 0.0780$ and $R_w = 0.1643$ for 9724 independent reflections with $I > 2\sigma(I)$.

Kinetic Studies. All UV−vis studies were carried out in the specified solvent at a cluster concentration of ca. 10^{-4} M using 1.0 cm quartz UV−visible cells that were equipped with a high-vacuum Teflon stopcock to facilitate handling on the vacuum line and glovebox transfers. Stock solutions of all clusters, when not in use, were stored in the dark under argon or CO. 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, which regulated the reaction temperature to within ±0.5 K. The ^{1}H NMR kinetic studies were conducted in 5 mm NMR tubes that possessed a J. Young valve for easy evacuation or the admission of atmospheric pressure of argon or CO gas or in NMR tubes configured for attachment to the vacuum line, which after three freeze−pump−thaw degassing cycles were flame-sealed. All NMR studies employed either benzene-d_6 or toluene-d_8 as a solvent with a cluster concentration of ca. 10^{-2} M. The NMR samples were heated in the same VWR temperature bath and quenched in an external ice bath immediately before NMR analysis.

The UV−vis kinetics for the isomerization **2b** → **2c** were monitored by following the increase of the 364 nm absorbance band as a function of time typically for 3−4 half-lives, while the extent of the reaction involving cluster **3** in the presence of phosphine traps and the reaction leading to the benzyne-substituted cluster **4** were determined by following the absorbance decrease in the 396 nm band of **3** for at least 3 half-lives. The rate constants quoted for these reactions were determined by nonlinear regression analysis using the single-exponential function[27]

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

The quoted activation parameters were calculated from plots of $\ln(k/T)$ versus T^{-1},[28] with the error limits representing deviation of the data points about the least-squares line of the Eyring plot.

Results and Discussion

Syntheses, X-ray Diffraction Structures of 1,2-$Os_3(CO)_{10}$(bpcd) and 1,1-$Os_3(CO)_{10}$(bpcd), and Isomerization Kinetics. Exploratory reactions between $Os_3(CO)_{12}$ and bpcd were carried out in refluxing toluene. A complicated mixture composed of at least four distinct bpcd-derived products was confirmed when the reaction was monitored by ^{1}H NMR spectroscopy. The low selectivity and complicated nature of the reactions are not surprising and can be attributed to the severe conditions necessary to effect the activation of the parent cluster.[29] A cleaner reaction was achieved when the labile cluster $Os_3(CO)_{10}$-

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[23] A ^{1}H spin−lattice (T_1) relaxation study on cluster **3** in benzene-d_6 was conducted, and the T_1 values for the hydride (1.9 s) and the methylene (0.3 s) groups were determined by using the standard inversion−recovery pulse sequence. Accurate integration intensities, free from saturation effects, were thus obtained for our KIE and EIE experiments with $Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) by employing an acquisition delay of 10 s (>5T_1).

[24] SAINT, Version 6.02; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997−1999.

[25] SHELXTL, Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1998.

[26] Spek, A. L. PLATON-A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2001.

[27] All rate calculations were performed with the aid of the commercially available programs Origin6.0 and KaleidaGraph. Here the initial (A_0) and final (A_∞) absorbances and the rate constant were floated to give the quoted least-squares value for the first-order rate constant *k*.

[28] Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley-Interscience: New York, 1984.

[29] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

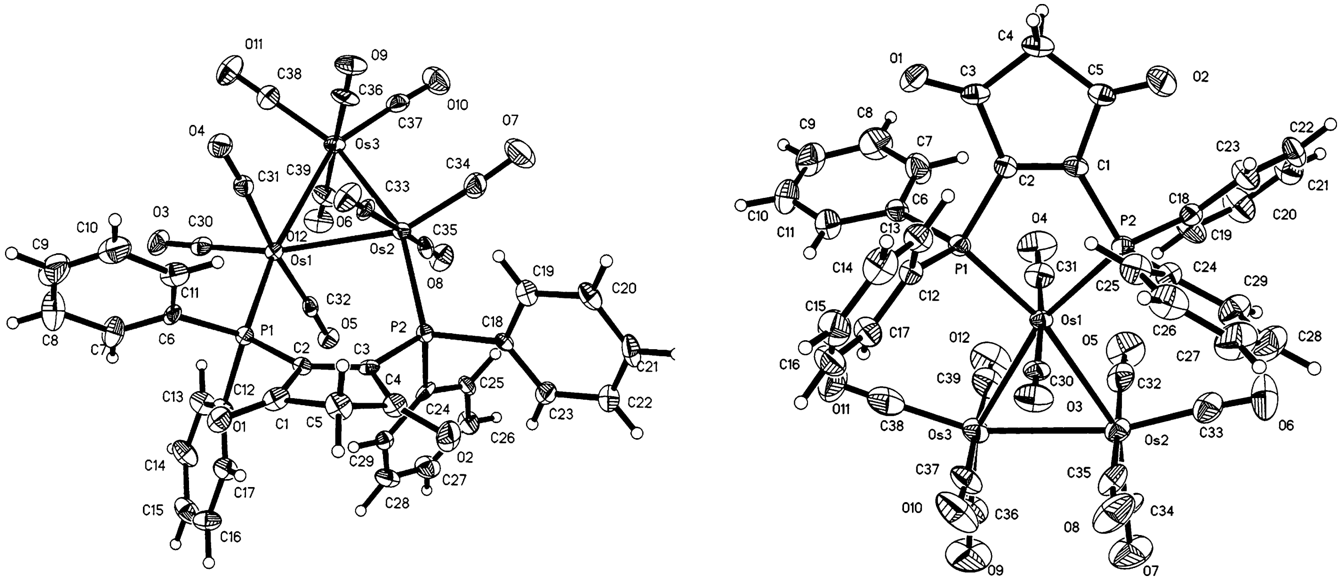

Figure 1. Thermal ellipsoid plots of 1,2-$Os_3(CO)_{10}$(bpcd) (**2b**, left) and 1,1-$Os_3(CO)_{10}$(bpcd) (**2c**, right) showing thermal ellipsoids at the 50% probability level.

Table 1. X-ray Crystallographic Data and Processing Parameters for the Triosmium Clusters 2b,c and 4

	2b	2c	4
CCDC entry no.	277346	277347	277348
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
a, Å	14.031(4)	11.028(1)	22.350(6)
b, Å	30.89(1)	19.913(3)	11.511(3)
c, Å	11.881(4)	18.382(3)	17.383(5)
β, deg	115.05(2)	100.107(2)	111.281(5)
V, Å^3	4665(3)	3915(2)	4167(2)
mol formula	$C_{39}H_{22}Os_3O_{12}P_2$[a]	$C_{39}H_{22}Os_3O_{12}P_2$	$C_{44}H_{29}Os_3O_{10}P_2$
fw	1411.19	1315.11	1350.21
formula units per cell (Z)	4	4	4
D_{calcd} (Mg/m^3)	2.009	2.231	2.152
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
abs coeff (mm^{-1})	8.279	9.857	9.260
R_{merge}	0.0998	0.0596	0.2122
abs cor factor	0.9751−0.4934	0.7019−0.1409	1.000−0.515
total no. of rflns	37 461	22 472	34 779
no. of indep rflns	10 128	5120	9724
no. of data/restraints/params	10 128/0/537	5120/0/506	9724/0/534
R	0.0477	0.0249	0.0780
R_w	0.0782	0.0582	0.1643
GOF on F^2	0.923	0.966	0.993
weights	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$
largest diff in peak and hole (e/Å^3)	1.779, −0.891	1.298, −1.127	7.498, −2.449

[a] Disordered *m*-xylene is also present.

$(MeCN)_2$ (**1**) was employed as the starting osmium cluster, allowing us to establish a definitive course of reaction in a methodical fashion.

Treatment of an equimolar mixture of **1** and bpcd in benzene gives rise to a rapid reaction and formation of the bpcd-substituted cluster $Os_3(CO)_{10}$(bpcd), as assessed by TLC and IR analyses that confirmed the consumption of cluster **1** but not the coordination mode adopted by the bpcd ligand. The bridging of adjacent osmium centers by the bpcd ligand was established by ^{31}P NMR and X-ray diffraction analysis. The ^{31}P NMR spectrum of 1,2-$Os_3(CO)_{10}$(bpcd) (**2b**) exhibits a high-field singlet at δ −17.55, in agreement with signals for the related derivative 1,2-$Os_3(CO)_{10}[(Z)\text{-}Ph_2PCH{=}CHPPh_2]$[30] and other triosmium clusters containing saturated diphosphine ligands.[31] The bridging nature of the bpcd ligand and the overall molecular structure of **2b** were established by X-ray crystallography, as seen in the thermal ellipsoid plot displayed in Figure 1. Tables 1 and 2 summarize the pertinent X-ray data. The Os−Os bond distances range from 2.8535(8) Å (Os(2)−Os(3)) to 2.8633(8) Å (Os(1)−Os(3)) and exhibit an average distance of 2.857 Å, consistent with those distances in other structurally characterized phosphine-substituted Os_3 derivatives.[32] The mean length of 2.320 Å for the Os−P bonds and the D_3 twisting of the axial carbonyl groups in **2b** are typical for this genre of cluster.[33,34] The bridging of the Os(1) and Os(2) centers by the bpcd ligand leads to ground-state destabilization in **2b** that

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Table 2. Selected Bond Distances (Å) and Angles (deg) in the Triosmium Clusters 2b,c and 4[a]

Cluster **2b**

Bond Distances

Os(1)−Os(2)	2.855(2)	Os(1)−Os(3)	2.8633(8)
Os(2)−Os(3)	2.8535(8)	Os(1)−P(1)	2.318(2)
Os(2)−P(2)	2.322(2)	P(1)···P(2)	3.797(7)
C(1)−C(2)	1.52(1)	C(1)−C(5)	1.54(1)
C(3)−C(4)	1.51(1)	C(4)−C(5)	1.49(1)
C(2)−C(3)	1.36(1)		

Bond Angles

P(1)−Os(1)−Os(2)	103.09(6)	P(1)−Os(1)−Os(3)	159.62(6)
P(2)−Os(2)−Os(1)	97.13(6)	P(2)−Os(2)−Os(3)	154.38(6)
C(2)−P(1)−Os(1)	118.6(3)	C(3)−P(2)−Os(2)	114.4(3)
C(3)−C(2)−P(1)	131.3(7)	C(2)−C(3)−P(2)	130.8(7)
C(31)−Os(1)−Os(2)	93.5(3)	C(32)−Os(1)−Os(2)	81.3(3)
C(31)−Os(1)−Os(3)	77.5(3)	C(32)−Os(1)−Os(3)	96.1(3)
C(35)−Os(2)−Os(3)	76.7(3)	C(33)−Os(2)−Os(3)	97.7(3)
C(35)−Os(2)−Os(1)	94.9(3)	C(33)−Os(2)−Os(1)	79.3(3)
C(39)−Os(3)−Os(2)	98.0(3)	C(36)−Os(3)−Os(2)	76.2(3)
C(39)−Os(3)−Os(1)	77.0(3)	C(36)−Os(3)−Os(1)	97.2(3)

Cluster **2c**

Bond Distances

Os(1)−Os(2)	2.9143(5)	Os(1)−Os(3)	2.9092(5)
Os(2)−Os(3)	2.8988(6)	Os(1)−P(1)	2.295(2)
Os(1)−P(2)	2.303(2)	P(1)···P(2)	3.169(4)
C(1)−C(2)	1.340(8)	C(1)−C(5)	1.519(9)
C(2)−C(3)	1.516(9)	C(3)−C(4)	1.509(9)
C(4)−C(5)	1.503(9)		

Bond Angles

P(1)−Os(1)−Os(3)	108.68(4)	P(1)−Os(1)−Os(2)	167.82(4)
P(2)−Os(1)−Os(2)	104.32(4)	P(2)−Os(1)−Os(3)	163.97(4)
C(2)−P(1)−Os(1)	105.8(2)	C(1)−P(2)−Os(1)	106.0(2)
C(2)−C(1)−P(2)	118.7(5)	C(1)−C(2)−P(1)	120.9(5)
P(1)−Os(1)−P(2)	87.15(6)	C(30)−Os(1)−Os(3)	88.1(2)
C(31)−Os(1)−Os(3)	88.9(2)	C(30)−Os(1)−Os(2)	87.6(2)
C(31)−Os(1)−Os(2)	93.3(2)	C(32)−Os(2)−Os(3)	90.6(2)
C(35)−Os(2)−Os(3)	88.5(2)	C(32)−Os(2)−Os(1)	86.5(2)
C(35)−Os(2)−Os(1)	88.5(2)	C(39)−Os(3)−Os(2)	87.0(2)
C(37)−Os(3)−Os(2)	90.5(2)	C(39)−Os(3)−Os(1)	87.8(2)
C(37)−Os(3)−Os(1)	89.2(2)		

Cluster **4**

Bond Distances

Os(1)−Os(2)	2.918(1)	Os(2)−Os(3)	2.818(1)
Os(1)···Os(3)	3.809(1)	Os(1)−P(1)	2.350(3)
Os(1)−P(2)	2.373(4)	Os(3)−P(2)	2.374(3)
P(1)···P(2)	3.238(4)	Os(1)−C(24)	2.17(1)
Os(2)−C(24)	2.31(1)	Os(2)−C(25)	2.33(2)
Os(3)−C(25)	2.16(1)	C(1)−C(5)	1.38(2)
C(1)−C(2)	1.50(2)	C(2)−C(3)	1.52(2)
C(3)−C(4)	1.49(2)	C(4)−C(5)	1.52(2)
C(24)−C(25)	1.39(2)	C(24)−C(29)	1.44(2)
C(25)−C(26)	1.47(2)	C(26)−C(27)	1.32(2)
C(27)−C(29)	1.40(2)	C(28)−C(29)	1.40(2)

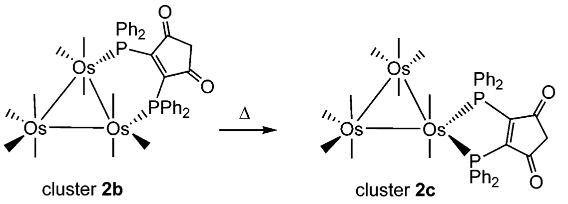
Bond Angles

Os(3)−Os(2)−Os(1)	83.18(2)	P(1)−Os(1)−P(2)	86.6(2)
Os(1)−P(2)−Os(3)	106.7(1)	C(5)−P(1)−Os(1)	106.5(4)
C(1)−P(2)−Os(3)	114.7(4)	C(5)−C(1)−P(2)	121(1)
C(1)−C(5)−P(1)	120(1)	C(24)−Os(2)−C(25)	34.9(5)
Os(1)−C(24)−Os(2)	81.2(4)	Os(3)−C(25)−Os(2)	77.6(4)
C(25)−C(24)−Os(1)	123(1)	C(24)−C(25)−Os(3)	125(1)

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

manifests itself in an internuclear P(1)···P(2) distance of 3.797(7) Å, which is ca. 0.60 Å longer than the corresponding distance reported for the free ligand (*Z*)-Ph$_2$PCH=CHPPh$_2$ and the chelating isomer **2c** (vide infra). The P(1)−C(2)−C(3) and P(2)−C(3)−C(2) bond angles of 131.3(7) and 130.8(7)° associated with the C=C π bond of the bpcd moiety are ca. 10° larger than the analogous linkages in (*Z*)-Ph$_2$PCH=CHPPh$_2$.[35]

Heating cluster **2b** at ambient temperature (<70 °C) leads to bpcd isomerization and formation of the chelated cluster 1,1-Os$_3$(CO)$_{10}$(bpcd) (**2c**), as shown in eq 1. The extent of the reaction was easily assessed by ^{1}H and ^{31}P NMR spectroscopy due to the downfield shift of the methylene singlet belonging to the dione ring and the phosphorus groups of the product. Here the initial methylene resonance (in CDCl$_3$) at δ 3.06 in cluster **2b** is replaced by a new signal in the ^{1}H NMR spectrum at δ 3.74 for **2c**, with the associated phenyl resonances remaining invariant in terms of their general chemical shift information. The ^{31}P NMR spectrum is accompanied by a similar transformation insomuch as a new ^{31}P resonance at δ 17.97 is observed, whose large nuclear deshielding is consistent with a chelating bpcd ligand.[36] The isomeric clusters display the same R_f value on silica gel, and the IR data are virtually indistinguishable given their idealized C_{2v} symmetry, negating the use of TLC analysis and IR spectroscopy as probes for the study of this reaction.



(1)

The molecular structure of cluster **2c** was ascertained by X-ray crystallography. Figure 1 confirms the chelation of the bpcd ligand to the Os(1) atom in **2c**. The mean Os−Os and Os−P bond lengths of 2.9074 and 2.299 Å, respectively, are unremarkable with respect to those in **2b** and other phosphine-substituted osmium clusters, while the 10 ancillary carbonyls are all linear in nature. The axial CO groups exhibit only a slight twist or canting relative to the corresponding axial CO groups in cluster **2b**. The nonbonding P(1)···P(2) bond distance of 3.169(4) Å in **2c** is ca. 0.63 Å shorter than the internuclear P(1)···P(2) separation in **2b** and is consistent with the internuclear P···P distance displayed by mono- and polynuclear compounds containing a chelating bpcd ligand.[37] The experimentally determined angles of 105.8(2), 106.0(2), 120.9(5), and 118.7(5)° found for the Os(1)−P(1)−C(1), Os(1)−P(2)−C(2), P(1)−C(1)−C(2), and P(2)−C(2)−C(1) linkages, respectively, show minimal deviation from the idealized bond angles of 109° for phosphorus and 120° for carbon atoms and reinforce the fact that cluster **2c** is thermodynamically more stable than **2b**.

The kinetics for the conversion of cluster **2b** to cluster **2c** were next studied because of the small but growing number of reports on nondissociative phosphine isomerization reactions at

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(33) Orpen, A. G.; Brammer, L.; Allen, F. K.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(34) (a) Alex, R. F.; Einstein, F. W. B.; Jones, R. H.; Pomeroy, R. K. *Inorg. Chem.* **1987**, *26*, 3175. (b) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Skelton, B. H.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 157. (c) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Patrick, J. M.; Skelton, B. H.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 181. (d) Bruce, M. I.; Liddell, M. J.; Skawkataly, O. B.; Hughes, C. A.; Skelton, B. H.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 207.

(35) Berners, S. J.; Colquhoun, L. A.; Healy, P. C.; Byriel, K. A.; Hanna, J. V. *J. Chem. Soc., Dalton Trans.* **1992**, 3357.

(36) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Richmond, M. G.; Kochi, J. K. *Inorg. Chem.* **1987**, *6*, 254.

(37) (a) Shen, H.; Williams, T. J.; Bott, S. G.; Richmond, M. G. *J. Organomet. Chem.* **1995**, *505*, 1. (b) Bott, S. G.; Shen, H.; Richmond, M. G. *Struct. Chem.* **2001**, *12*, 225. (c) Shen, H.; Bott, S. G.; Richmond, M. G. *Inorg. Chim. Acta* **1996**, *241*, 71.

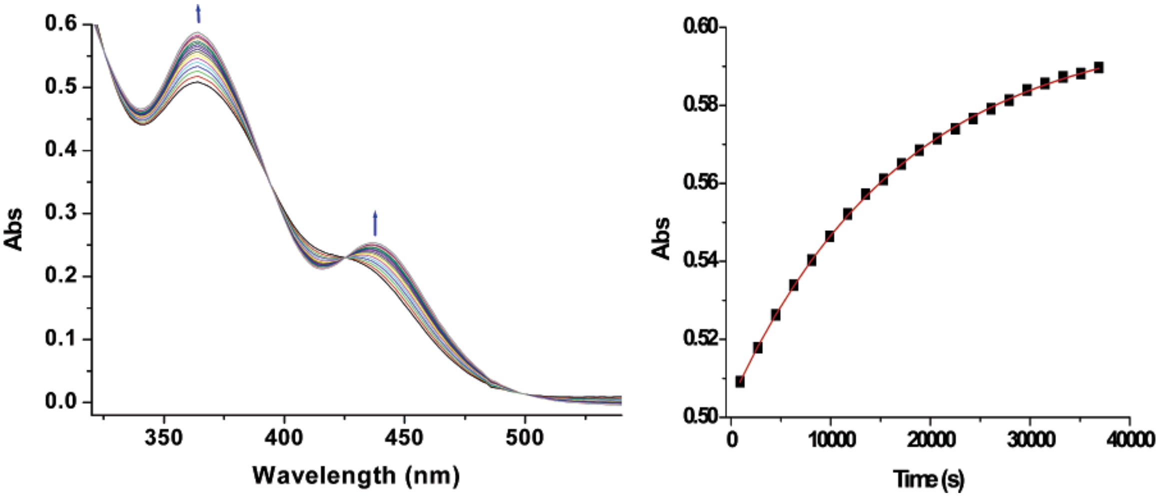

Figure 2. UV−vis spectral changes for **2b** → **2c** recorded at 323 K in benzene (left) and the absorbance versus time curve for the experimental data (■) and the least-squares fit (—) of the first-order rate constant *k* (right).

Table 3. Experimental Rate Constants for the Isomerization of 1,2-$Os_3(CO)_{10}$(bpcd) (2b) to 1,1-$Os_3(CO)_{10}$(bpcd) (2c)[a]

temp (K)	10^4k (s^{-1})	trapping ligand	method
323.0	0.58 ± 0.01		UV−vis
323.0	0.51 ± 0.01		NMR
328.0	0.78 ± 0.03		UV−vis
328.0	1.02 ± 0.07	6.8 atm of CO	UV−vis[b]
328.0	0.87 ± 0.01		NMR
333.0	1.91 ± 0.06		UV−vis
333.0	1.74 ± 0.01	25 equiv of PPh_3	UV−vis
333.0	1.60 ± 0.02		NMR
338.0	3.04 ± 0.23		UV−vis
338.0	2.81 ± 0.05		NMR
338.0	2.82 ± 0.05	25 equiv of PPh_3	UV−vis
338.0	3.18 ± 0.08	1.0 atm of CO	UV−vis
338.0	2.67 ± 0.01	10 equiv of PPh_3	NMR
338.0	2.87 ± 0.06	10 equiv of $P(OEt)_3$	NMR
343.0	5.82 ± 0.09		UV−vis
343.0	4.62 ± 0.06		NMR

[a] The UV−vis kinetic data were collected in benzene using ca. 10^{-4} M 1,2-$Os_3(CO)_{10}$(bpcd) by following the increase in the absorbance of the 368 nm band, and the NMR kinetics were conducted in benzene-d_6 with 1,2-$Os_3(CO)_{10}$(bpcd) at an initial concentration of ca. 10^{-2} M in the presence of an internal standard (either *p*-dimethoxybenzene or *tert*-butylbenzene). The extent of the isomerization was followed by monitoring the decrease in intensity of the methylene singlet of the bridging isomer at δ 1.78. [b] Experiment conducted in a Fischer−Porter tube under constant CO pressure, where aliquots were removed and analyzed by UV−vis spectroscopy.

di- and polynuclear compounds.[8a,c,30,38] The isomerization rates for **2b** → **2c** were conveniently measured by both UV−vis and ^{1}H NMR spectroscopy over the temperature range of 323−343 K, with the reaction rates being reported in Table 3. The UV−vis-derived rates were obtained by following the increase in the absorbance of the 364 nm band belonging to cluster **2c**. Figure 2 shows the UV−vis spectral changes for the thermolysis of **2b** in benzene solution at 323 K, where multiple, well-defined isosbestic points accompany the reaction. The fit of the least-squares regression curve and the absorbance data displayed in Figure 2 underscore the fact that the isomerization is well-behaved and is free from kinetic complications. Complimentary ^{1}H NMR kinetic studies were also conducted in benzene-d_6 by monitoring the decrease in the methylene moiety of **2b** at δ 1.78. The complete consumption of this resonance was accompanied by the growth of a methylene singlet at δ 2.45 belonging to cluster **2c**. The NMR data conclusively showed that the isomerization furnished **2c** in quantitative yield, unlike the isomerization found for the related cluster $Os_3(CO)_{10}$[(*Z*)-$Ph_2PCH{=}CHPPh_2$], where a reversible equilibrium that favored the chelating isomer was found (K_{eq} = 6.9 for chelate/bridge clusters over the temperature range of 358−382 K).[30] Treatment of the NMR data by traditional ln[**2b**] versus time plots or by nonlinear regression analysis afforded first-order rate constants that were in excellent agreement with each other and with those data obtained from the UV−vis studies. Moreover, plots of the total cluster concentration (**2b** and **2c**) versus time displayed smooth exponential decay and growth curves for the consumption and formation of **2b** and **2c**, respectively. Inspection of the data in Table 3 reveals that the isomerization is unaffected by added phosphine, phosphite, and CO trapping ligands. The invariant rates in the presence of added ligands and the Eyring activation parameters (UV−vis, $\Delta H^\ddagger = 25.0(0.7)$ kcal/mol and $\Delta S^\ddagger = -2(2)$ eu; NMR, $\Delta H^\ddagger = 23.9(0.4)$ kcal/mol and $\Delta S^\ddagger = -4(1)$ eu) strongly support a nondissociative, rate-limiting unimolecular rearrangement of the bpcd ligand.

These kinetic data undeniably support an intramolecular migration or transit of one of the phosphorus atoms across an Os−Os bond to afford a diphosphine-chelated osmium center, as opposed to a process involving the dissociative release of one of the PPh_2 moieties of the bpcd ligand. This latter scenario would lead to the formation of an unsaturated cluster with an η^1-bpcd ligand that could be scavenged by any trapping ligand present; however, the expected substituted clusters $Os_3(CO)_{10}L$-(η^1-bpcd) (L = CO, PR_3, $P(OEt)_3$) have not been observed.[39,40] Given the clean conversion of **2b** to **2c**, the two most likely isomerization processes that are consistent with the kinetic data and activation parameters are shown in Scheme 2. A pairwise exchange of a CO ligand with an adjacent phosphorus atom, through the intermediacy of the doubly bridged cluster Os_3-$(CO)_9$(μ-CO)(μ-bpcd), gives rise to cluster **2c**. Alternatively,

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[38] (a) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2994. (b) Adams, R. D.; Captain, B.; Fu, W.; Pellechia, P. J. *Inorg. Chem.* **2003**, 3111. (c) See also: Persson, R.; Monari, M.; Gobetto, R.; Russo, A.; Aime, S.; Calhorda, M. J.; Nordlander, E. *Organometallics* **2001**, *20*, 4150.

[39] This assertion concerning the formation of an unsaturated intermediate as a steady-state species is valid, provided that the rate of ring closure (to either the bridged or chelated cluster) is slow relative to the rate of the ligand trapping reaction. For some related examples, see: (a) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479. (b) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130. (c) Jones, W. D.; Libertini, E. *Inorg. Chem.* **1986**, *25*, 1794.

[40] We note that an independently prepared sample of $Os_3(CO)_{11}(\eta^1$-bpcd) was found to be stable toward ring closure to $Os_3(CO)_{10}$(bpcd) under conditions identical with those employed in our isomerization reaction.

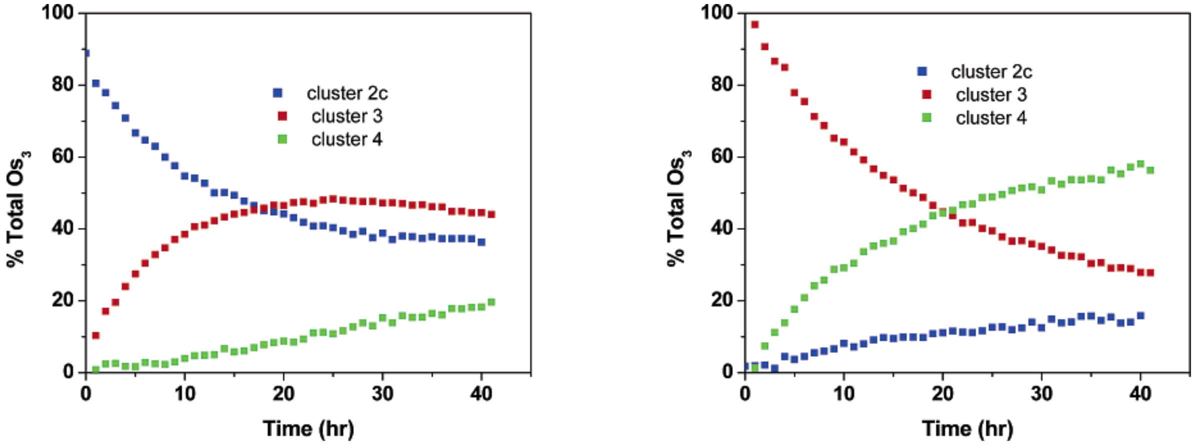
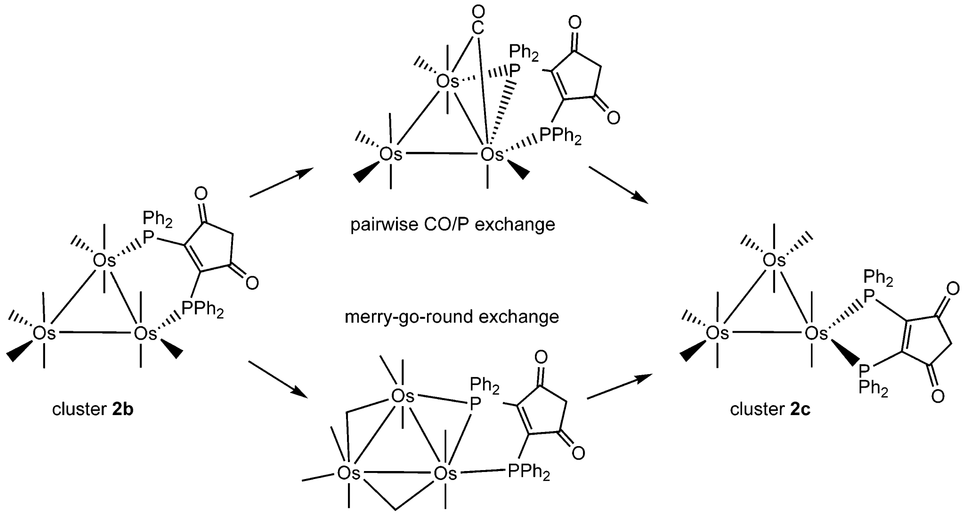


Figure 3. Plots of the cluster distribution of **2c**, **3**, and **4** versus time from the thermolysis starting from cluster **2c** (left) and cluster **3** (right) in benzene-d_6 at 90 °C. The extent of the reaction was determined by ^{1}H NMR analysis using the methylene group from each cluster species.

Scheme 2



the merry-go-round migration involving two equatorially disposed CO ligands and a phosphorus atom can also furnish the cluster **2b** upon bridge−terminal opening of the three bridging participants.

Distinction between these two exchange processes was sought through examination of the VT ^{13}C NMR spectra of cluster **2b**. The slow-exchange ^{13}C NMR spectral data for ^{13}CO-enriched **2b** (ca. 20%) in toluene-d_8 recorded at 233 K confirm the presence of four terminal carbonyl resonances at δ 193.07, 184.78, 178.17, and 173.12 in a 2:1:1:1 integral ratio, in excellent agreement with the structure of **2b**. Heating **2b** from 233 to 273 K leads to the disappearance of the CO groups at the bpcd-bridged osmium atoms (δ 193.07 and 178.17), due to an in-plane merry-go-round scrambling of these groups.[30,31b,41] Continued heating to 358 K promotes the turnstile scrambling of the remaining axial and equatorial CO groups at the Os-$(CO)_4$ center. The rate of CO scrambling at coalescence in **2b** can be conservatively estimated as ca. 1500 and 600 s^{-1} for the in-plane merry-go-round and turnstile processes, respectively.[42] Consequently, any attempt to use the ^{13}C NMR data from **2b** to elucidate the isomerization mechanism for the slower bpcd migration to cluster **2c** will meet with failure.[43,44] Of importance to this body of work is the fact that the bpcd ligand isomerization is facile and gives cluster **2c** as the platform for the ortho metalation described below.

Thermal and Photochemical Activation of 1,1-$Os_3(CO)_{10}$-(bpcd) and Characterization of $HOs_3(CO)_9[\mu$-$(PPh_2)C{=}C$-$\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ and $HOs_3(CO)_8(\mu_3$-$C_6H_4)[\mu_2,\eta^1$-$PPhC{=}C(PPh_2)C(O)CH_2C(O)]$. Thermolysis of cluster **2c** at elevated temperatures provided evidence for the activation of the bpcd ligand, as shown in Figure 3 (left) for the ^{1}H NMR distribution data from a sealed-tube thermolysis conducted at 90 °C in toluene-d_8.[45] Here a rapid production of the hydrido cluster $HOs_3(CO)_9[\mu$-$(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (**3**, red boxes) is observed, followed by the slower formation of the benzyne-substituted cluster $HOs_3(CO)_8(\mu_3$-$C_6H_4)[\mu_2,\eta^1$-

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[41] For analogous CO scrambling pathways in other phosphine-substituted Os_3 clusters, see: (a) Deeming, A. J.; Donovan-Mtunzi, S,; Kabir, S. E. *J. Organomet. Chem.* **1985**, *281*, C43. (b) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437. (c) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

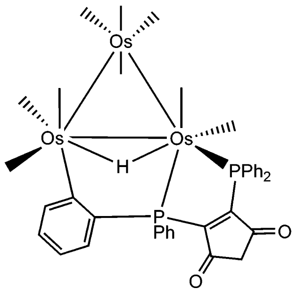
[42] The quoted rate constants for CO scrambling at the coalescence temperature were estimated by use of the equation $k_{\text{coalescence}} = (\pi(\delta\nu))/(2^{1/2})$: Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1993.

[43] This situation is akin to assigning the locus of CO dissociation in a metal carbonyl cluster when the rate of carbonyl scrambling about the cluster polyhedron exceeds the rate of dissociative CO loss by several orders of magnitude. See: Richmond, M. G.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 1334.

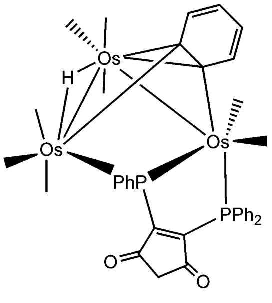
[44] The VT ^{13}C NMR behavior of cluster **2c** has also been studied in toluene-d_8 solution, with comparable CO fluxionality, vis-à-vis **2b**, observed.

[45] The small amount of cluster **3** in the thermolysis starting with cluster **2c** does not adversely affect the outcome of the reaction.

$PPhC{=}C(PPh_2)C(O)CH_2C(O)]$ (**4**, green boxes). Heating a sealed NMR tube containing cluster **3** under analogous conditions furnished **4** as the major product along with **2c**, as shown in Figure 3 (right). Two important points emerging from these thermolysis experiments are that cluster **2c** serves as the direct precursor for the formation of the hydride cluster **3** and that this latter cluster can be converted back to **2c** through a reversible ortho-metalation sequence. Carrying out the thermolyses at 110 °C with purging of the liberated CO furnishes cluster **4** as the dominant product in solution. The two new clusters, whose structures are depicted below, were subsequently isolated by column chromatography and fully characterized in solution; in addition, X-ray diffraction analysis was used in the case of **4**.



cluster **3**



cluster **4**

Definitive support for the ortho metalation of an aryl group in **3** comes from the ^1H NMR spectrum, where a high-field triplet at δ −15.91 is observed in benzene-d_6 solvent. The small J_{P-H} coupling of 13 Hz indicates that the bridging hydride group is situated mutually cis to the two inequivalent phosphorus centers. The diastereotopic methylene hydrogens belonging to the bpcd residue are solvent sensitive and appear as an AB quartet centered at δ 2.07 in benzene-d_6 and as a singlet at δ 3.54 in $CDCl_3$. The ^{31}P NMR spectrum of **3** shows a pair of inequivalent phosphorus resonances at δ 26.70 and 19.18, and the nine terminal carbonyl groups found in a ^{13}CO-enriched sample of the cluster at 223 K are fully consistent with the proposed structure.[46] The ortho metalation of the ancillary bpcd ligand in **3** is a phenomenon that has been seen in related triosmium clusters containing the diphosphine ligands dppm, dppe, and dppp.[11a,47]

The ^1H NMR data for the benzyne-substituted cluster **4** include resonances at δ −16.88 and 3.66 for the bridging hydride and the methylene group associated with the dione ring, respectively. A ^1H COSY spectrum of **4** revealed that the four hydrogens belonging to the benzyne moiety exist as an ABXY spin system that is buried within the aromatic hydrogens of the other three phenyl groups. The ^{31}P NMR spectrum shows two resonances at δ 10.96 and −72.18, with the latter readily assignable to a phosphido moiety that spans two nonbonded osmium centers.[48] The eight distinct carbonyl resonances found in the ^{13}C NMR spectrum of a ^{13}CO-enriched sample of **4** (Experimental Section) are in full agreement with the proposed structure. Unequivocal support for the presence of a benzyne moiety and an opened cluster core in **4** is derived from the X-ray diffraction structure (Figure 4). Cluster **4** contains 50 valence electrons, which is two electrons in excess of the electron-precise count of 48 valence electrons found for numerous triangular Os_3 clusters, accounting for the observed polyhedral opening of the metallic frame.[49] Despite our inability to locate the lone bridging hydride group during data refinement, the significantly different Os(1)−Os(2) (2.919(1) Å) and Os(2)−Os(3) (2.818(1) Å) bond distances allow us to confidently assign the bridging hydride group to the longer Os(1)−Os(2) vector. The Os(1)···Os(3) internuclear distance of 3.809(1) Å clearly precludes any direct bonding interaction between these osmium atoms. The benzyne ligand is composed of the atoms C(24)−C(29) and functions as a typical four-electron, face-capping ligand, where the two Os−C σ bonds (Os(1)−C(24) = 2.17(1) Å and Os(3)−C(25) = 2.16(1) Å) and the Os−C π bonds (Os(2)−C(24) = 2.31(1) Å and Os(2)−C(25) = 2.33(2) Å) are similar in distance to those in other benzyne-substituted osmium clusters.[12f,50] The phosphido ligand, which is defined by the P(2) atom, is equatorially situated and serves to tether the nonbonded Os(1) and Os(3) atoms. The distorted four-membered ring defined by the Os(1)−Os(2)−Os(3)−P(2) atoms is nearly planar on the basis of $\sigma_p = 0.08$ Å. The phosphorus atom P(1) behaves as a normal phosphine ligand and is bound in an η^1 fashion to the Os(1) center. The Os−P distances range from 2.350(3) Å (Os(1)−P(1)) to 2.374(3) Å (Os(3)−P(2)), with a mean distance of 2.366 Å.

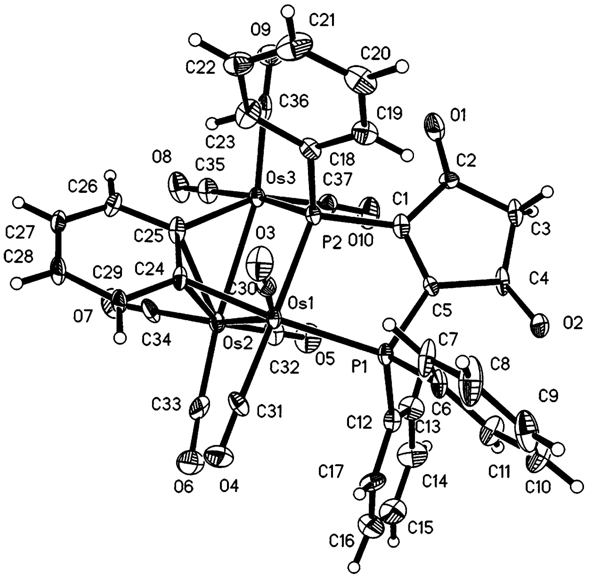


Figure 4. Thermal ellipsoid plot of $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$ (**4**) showing thermal ellipsoids at the 50% probability level.

With the identities of the two product clusters established from the thermolysis of **2c**, we next explored the photochemical activation of **2c**. Irradiation of **2c** in either benzene or CH_2Cl_2 solvent with 366 nm light leads to CO loss and clean conversion to **3**, as verified by NMR and UV−vis analyses. A quantum efficiency (Φ) of 0.02 was found for this ortho metalation at

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[46] The chelation of the ortho-metalated bpcd ligand in **3** via axial and equatorial sites at the osmium center is strengthened by a recent X-ray structure of the related hydride-bridged cluster $HOs_3(CO)_9[\mu\text{-}PhP(C_6H_4)C{=}CC(O)C({=}CHFc)C(O)PPh_2]$. Unpublished results.

[47] Deeming, A. J.; Hardcastle, K. I.; Kabir, S. E. *J. Chem. Soc., Dalton Trans.* **1988**, 827.

[48] Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987.

[49] Cluster **4**, with its seven skeletal electron pairs (SEP), may also be viewed as possessing a three-vertex hypho architecture when treated within the framework of polyhedral skeletal electron pair (PSEP) theory. See: Mingos, D. M. P.; Wales, D. J. Introduction to Cluster Chemistry; Prentice Hall: Englewood Cliffs, NJ, 1990.

[50] (a) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2257. (b) Chen, G.; Deng, M.; Lee, C. K.; Leong, W. K. *Organometallics* **2002**, *21*, 1227. (c) Leong, W. K.; Chen, G. *Organometallics* **2001**, *20*, 2280. (d) Tay, C. T.; Leong, W. K. *J. Organomet. Chem.* **2001**, *625*, 231.

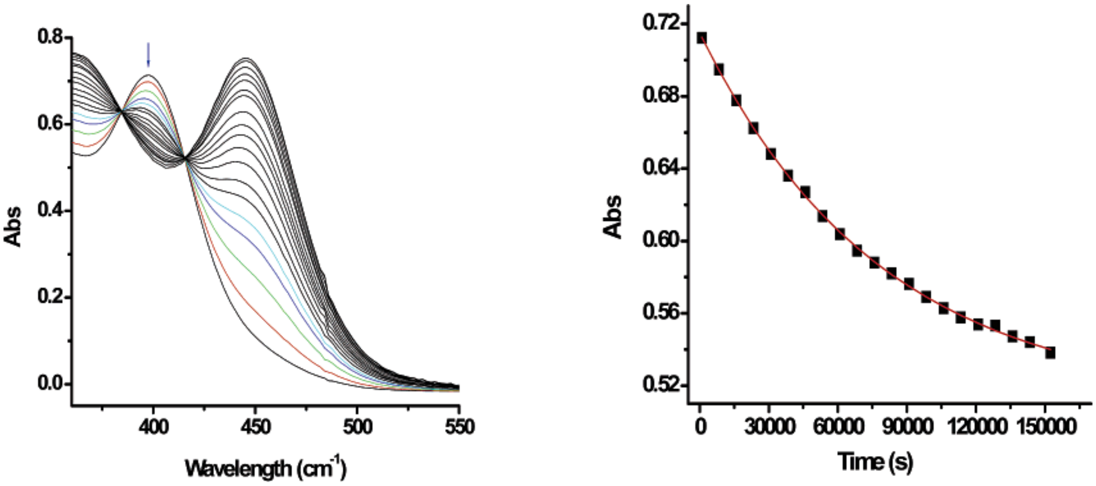

Figure 5. UV−vis spectral changes for the reaction of **3** in the presence of PPh_3 (25 equiv) recorded at 331 K in toluene (left) and the absorbance versus time curve for the experimental data (■) for the decay of **3** and the least-squares fit (—) of the first-order rate constant k_H (right).

18 °C in benzene, with the formation of cluster **3** being retarded when the irradiation was conducted under 1 atm of CO. The observed CO inhibition supports the generation of the coordinatively unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd) upon optical excitation. That CO is lost from **2c** is of interest, as the related clusters $Os_3(CO)_{10}$(α-diimine) are resistant to dissociative CO loss on excitation, producing spectroscopically observable biradical and zwitterionic species from Os−Os bond cleavage reactions, depending on the polarity of the solvent employed.[51,52] No evidence for the activation of the benzene or CH_2Cl_2 solvents was observed in our photolysis experiments when the reaction solutions were monitored by ^1H and ^{31}P NMR spectroscopy.

Table 4. Experimental Rate Constants for the Conversion of $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (3) to 1,1-$Os_3(CO)_9$(P)(bpcd) and of $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$ to 1,1-$Os_3(CO)_9$(P)(bpcd-d_{20})[a]

temp (K)	10^4k_H (s^{-1})[b]	10^4k_D (s^{-1})[b,c]	trapping ligand	k_H/k_D[d]
331.0	0.13 ± 0.03	0.15 ± 0.01	25 equiv of PPh_3	0.87
338.0	0.30 ± 0.02	0.33 ± 0.04	25 equiv of PPh_3	0.91
346.0	0.74 ± 0.06	0.90 ± 0.08	25 equiv of PPh_3	0.82
353.0	1.66 ± 0.01		10 equiv of PPh_3	
353.0	1.62 ± 0.01		10 equiv of $P(OEt)_3$	
353.0	1.62 ± 0.02	1.78 ± 0.01	25 equiv of PPh_3	0.91
353.0	1.64 ± 0.04		25 equiv of PCy_3	
359.0	3.47 ± 0.08	3.99 ± 0.07	25 equiv of PPh_3	0.87

[a] The UV−vis kinetic data were collected in toluene using ca. 10^{-4} M $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (**3**) and $DOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{10})C{=}C\{P(Ph\text{-}d_5)(C_6D_4)\}C(O)CH_2C(O)]$ by following the decrease in the absorbance of the 396 nm band. [b] The quoted rate constants k_H and k_D represent the rates of reaction for the reductive coupling of the hydride cluster **3** and its deutride isotopomer, respectively. [c] The Eyring activation parameters were determined as $\Delta H^\ddagger = 26.8(0.8)$ kcal/mol and $\Delta S^\ddagger = 0(2)$ eu. [d] The average of the five k_H/k_D values is 0.88 ± 0.05.

Proof of Reversible Ortho Metalation Through Ligand Trapping of the Unsaturated Intermediate 1,1-$Os_3(CO)_9$-(bpcd). The observation of minor amounts of **2c** from the thermolysis of **3** (Figure 3) signaled that the ortho metalation of the aryl ligand is reversible, and as such, we wished to study this reaction in more detail, given its relevance to hydrocarbon activation. Cluster **3** was found to react readily with added CO (1 atm) at 75 °C in a variety of solvents to furnish **2c** in quantitative yield when monitored by ^1H NMR and UV−vis spectroscopy. The carbonylation proceeded cleanly, without the presence of spectroscopically observable intermediates. Having established the reversible C−H bond formation in the reaction of **3** with added CO, we next turned our attention to the kinetic trapping of the postulated unsaturated intermediate 1,1-$Os_3(CO)_9$(bpcd) with donor ligands other than CO.[53] The reaction of the hydride cluster **3** with excess trapping ligand (>10 equiv) was investigated in toluene solution over the temperature range of 331−359 K. The progress of each reaction was followed by monitoring the decrease in the absorbance of the 396 nm band for **3**, as illustrated in Figure 5 for the absorbance versus time plot (left) for the reaction with PPh_3. The UV−vis changes for this reaction are clean, and the isosbestic points observed at 383 and 452 nm support the formation of 1,1-$Os_3(CO)_9(PPh_3)$(bpcd) as the major product.[54] The first-order rate constants quoted in Table 4 were obtained from nonlinear regression analysis. Examination of entries 4−7 in Table 4 confirms that the rate of the reaction is independent of added ligand, allowing us to eliminate from consideration a rate-limiting bimolecular process involving the cluster and ligand. The activation parameters for these data are $\Delta H^\ddagger = 26.8(0.5)$ kcal/mol and $\Delta S^\ddagger = 0(2)$ eu.

In keeping with the current body of knowledge on alkane and arene activation by mononuclear complexes, the demonstrated reductive C−H bond coupling in **3** is expected to proceed by way of an intermediate π-complex, prior to the rate-limiting

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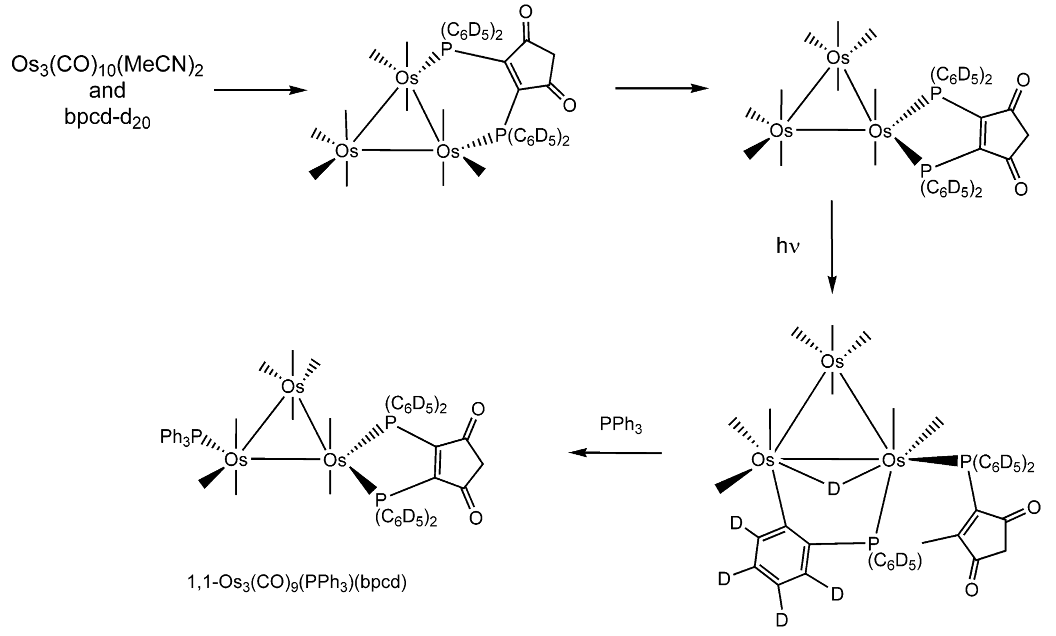
(51) (a) van Outersterp, J. W. M.; Oostenbrink, M. T. G.; Nieuwenhuis, H. A.; Stufkens, D. J.; Hartl, F. *Inorg. Chem.* **1995**, *34*, 6312. (b) Bakker, M. J.; Hartl, F.; Stufkens, D. J.; Jina, O. S.; Sun, X.-Z.; George, M. W. *Organometallics* **2000**, *19*, 4310. (c) Vergeer, F. W.; Kleverlann, C. J.; Stufkens, D. J. *Inorg. Chim. Acta* **2002**, *327*, 126. (d) Vergeer, F. W.; Kleverlaan, C. J.; Matousek, P.; Towrie, M.; Stufkens, D. J.; Hartl, F. *Inorg. Chem.* **2005**, *44*, 1319.

(52) For $Os_3(CO)_{12}$ photochemistry involving CO loss, see: Bentsen, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4518 and references therein.

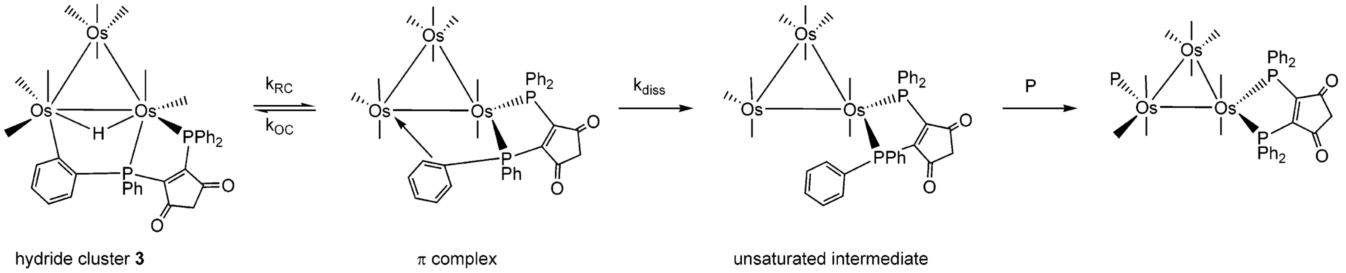
(53) Preliminary studies on the kinetic trapping of the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd), as generated from cluster **3**, in the presence of CO (low pressure) show saturation kinetics arising from the competitive capture of 1,1-$Os_3(CO)_9$(bpcd) by the arene π bond and CO. Unpublished results.

(54) A preparative-scale reaction between cluster **3** and excess PPh_3 (1:10 mole ratio) has been carried out and 1,1-$Os_3(CO)_9(PPh_3)$(bpcd) isolated by column chromatography. On the basis of ^1H and ^{31}P NMR data, the major stereoisomer present (>90%) found in solution contains a chelating bpcd ligand and one equatorially bound PPh_3 ligand that is attached to an adjacent osmium atom. ^{31}P NMR (C_6D_6, 298 K): δ 16.62 (1P, d, bpcd, $J_{P-P} = 12$ Hz), 15.47 (1P, d, bpcd, $J_{P-P} = 12$ Hz), −6.64 (s, 1P, PPh_3). ^1H NMR (C_6D_6, 298 K): δ 6.85−8.00 (35 H, multiplet), 2.43 (2H, s, methylene).

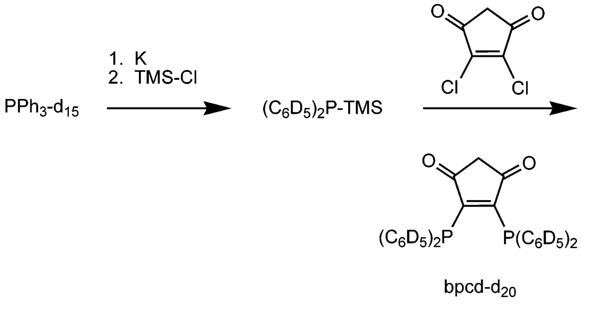
Scheme 3



Scheme 4



formation of the unsaturated cluster 1,1-$Os_3(CO)_9(bpcd)$.[55] Such aspects of our reaction could readily be probed through parallel kinetic studies employing an isotopically substituted bpcd ligand where all the aryl hydrogens have been replaced by deuterium atoms. To this end, we have synthesized the diphosphine ligand bpcd-d_{20} (eq 2) and have used this ligand in the preparation of



(2)

the deuteride cluster $DOs_3(CO)_9[\mu$-$(PPh_2$-$d_{10})C{=}C\{P(Ph$-$d_5)$-$(C_6D_4)\}C(O)CH_2C(O)]$ (**3**-d_{20}) and kinetic trapping studies of the latter by PPh_3, as shown in Scheme 3.

The reaction of the cluster **3**-d_{20} and excess PPh_3 (25 equiv) was investigated in toluene solution by UV−vis spectroscopy, as described for **3**-d_0 (vide supra), with the first-order rate constants (k_D) for the consumption of **3**-d_{20} reported in Table 4. The observed inverse isotope effect of 0.88 ± 0.05 (average value for all five runs) for the reductive C−H bond coupling is best interpreted as arising from an equilibrium isotope effect (EIE) that is coupled with a slower, isotope-insensitive step (i.e., $K{\cdot}k$). In the present study, such a scenario is easily rationalized within a multistep manifold that involves a rapid and reversible preequilibrium step between the hydride (deuteride) cluster and an arene π complex (k_{rc}/k_{oc}) that precedes the rate-limiting dissociation of the arene π bond from the osmium center (k_{diss}).[56] Scheme 4 illustrates this stepwise progression from the hydride cluster **3** to the phosphine-substituted cluster 1,1-$Os_3(CO)_9P$-(bpcd). While many paradigms provide unequivocal evidence for the involvement of σ-alkane and π-arene intermediates through equilibrium isotope effects in reductive coupling reactions at mononuclear complexes,[55,57,58] to our knowledge, the data reported here represent the first such isotope work concerning the ortho metalation of an aryl moiety at a polynuclear system.[59]

Thermodynamic and Kinetic Ortho Metalation in 1,1-Os_3-$(CO)_9$(bpcd) and H/D Scrambling in the π-Arene Intermediate. Apart from the inverse isotope effect experimentally determined from the ligand trapping studies employing **3**-d_0 and **3**-d_{20}, intramolecular H/D scrambling between the bridging hydride or deuteride of cluster **3** and an appropriately labeled ortho-metalated aryl moiety (C_6D_4 for the hydride and C_6H_4 for the deuteride) would also furnish corroborating evidence for our intermediate π complex. Replacement of the bridging hydride in **3**-d_0 by deuterium or the bridging deuteride in **3**-d_{20}

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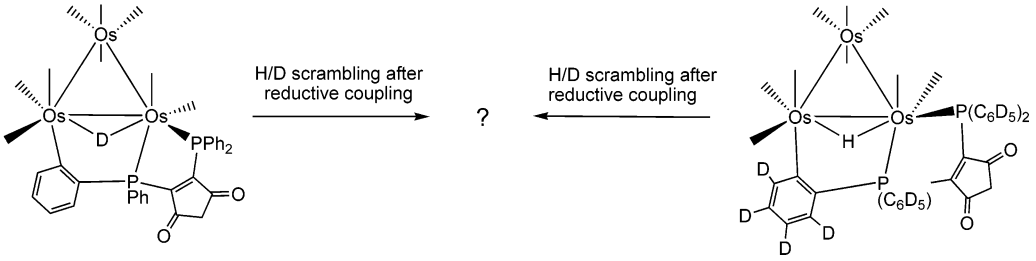
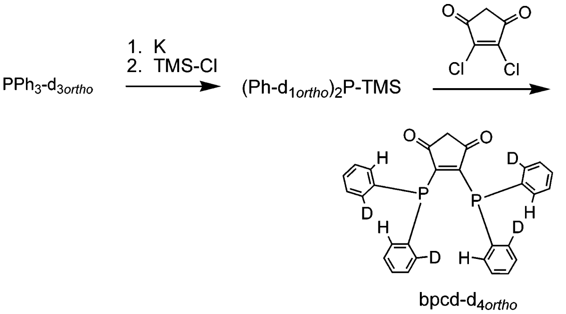
(55) (a) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (c) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140. (d) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403. (e) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475. (f) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471.

Scheme 5



by hydrogen would give isotopically substituted clusters (shown above) that could be used to probe H/D scrambling in **3**. Unfortunately, attempts to deprotonate the hydride ligand in **3**-d_0 using BuLi or Et_3N, followed by acidification with acetic acid-*d* or D_2O, did not furnish the desired deuteride cluster $DOs_3(CO)_9$-[μ-(PPh_2)C=C{PPh(C_6H_4)}C(O)CH_2C(O)] (left-hand cluster depicted in Scheme 5) but led to deuterium incorporation into the methylene group of the dione ring, along with substantial decomposition of the starting cluster. Analogous methodologies have been utilized by many researchers to demonstrate isotopic exchange via a transient π-arene complex and σ-alkane complex. Two classic examples that demonstrate the involvement of a π-arene and σ-alkane intermediate in H/D scrambling sequences are the mononuclear complexes Cp*Rh(PMe_3)H(C_6D_5)[57d] and Cp*Rh(PMe_3)D($^{13}CH_2CH_3$),[60] respectively.

Since the hydride deprotonation/acidification route employing cluster **3** could not be used to synthesize a suitable probe cluster for the H/D scrambling study, an isotopically substituted alternative was sought, one where the ancillary bpcd ligand contains one ortho hydrogen and deuterium relative to the phosphorus atom. This was achieved by starting with the isotopically substituted phosphine PPh_3-$d_{3,ortho}$ and preparing the diphosphine ligand bpcd-$d_{4,ortho}$ through the standard protocols outlined in eq 3. The bpcd-$d_{4,ortho}$ ligand was then used in the synthesis of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$), which in turn can be used to generate the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd-$d_{4,ortho}$) through photochemical activation.



(3)

Near-UV irradiation of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) is expected to lead to CO loss and formation of 1,1-$Os_3(CO)_9$(bpcd-$d_{4,ortho}$), as illustrated in the lower portion of Scheme 6. Coordination of one of the aryl groups to an osmium center adjacent to the bpcd-chelated osmium center furnishes a labile π complex that is in equilibrium with the ortho-metalated hydride and deuteride clusters depicted in the upper portion of Scheme 6. On the basis of our earlier trapping studies with cluster **3**, the partitioning of the π complex between the hydride and deuteride clusters is predicted to be rapid at ambient temperatures relative to the rate-limiting dissociation of the coordinated aryl ligand from the cluster, since this would regenerate the high-energy unsaturated cluster. The important ortho-metalation equilibria may be treated in terms of the relative concentrations of the product hydride/deuteride clusters, where K_{eq} = [deuteride]/[hydride]. Alternatively, K_{eq} may be expressed as a function of the individual rate constants for the forward and reverse reactions so that $K_{eq} = [k(H)_{RC}k(D)_{OC}]/[k(D)_{RC}k(H)_{OC}]$, which may also be rearranged in terms of the reductive coupling and oxidative coupling kinetic isotope effects: $K_{eq} = [k(H)_{RC}/k(D)_{RC}]/[k(H)_{OC}/k(D)_{OC}]$. As pointed out by Jones, extraction of two of the three related isotope effects allows for a complete understanding of the preequilibrium isotope contributions to our ortho-metalation reaction.[55c]

Irradiation of a sealed NMR tube containing 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) in toluene-d_8 at 0 °C allowed the kinetic selectivity for the ortho metalation to be established. Here we found a 55:45 mixture of the corresponding hydride and deuteride clusters.[61] This product ratio affords $k(H)_{OC}/k(D)_{OC} = 1.22 \pm 0.03$ for the C−H(D) bond activation for the ortho-metalation step. Our observation of a small normal KIE is on par with the value of 1.4 found for the oxidative cleavage of 1,3,5-$C_6H_3D_3$ by Cp*Rh(PMe_3).[57d] Heating kinetically generated samples of our cluster over the temperature range of 40−60 °C led to the equilibration of the hydride and deuteride clusters and a final isomer composition of 67:33 in favor of the hydride cluster with $K_{eq} = 0.49 \pm 0.04$.[62] Irradiation of 1,1-$Os_3(CO)_{10}$(bpcd-$d_{4,ortho}$) at

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(56) No kinetic distinction between a π-arene or an agostic interaction involving the ortho C−H(D) bond can be made on the basis of the data at hand. However, given the preponderance of structural and solution examples of η^2-bound arene complexes, we will treat the intermediate in our ortho-metalation reaction similarly. See: (a) Cheng, T.-Y.; Szalda, D. J.; Bullock, R. M. *Chem. Commun.* **1999**, 1629. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724.

(57) For some representative examples, see: (a) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. B. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (c) Janowicz, A. H.; Bergman, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (e) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614. (f) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974. (g) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897.

(58) On the basis of the totality of the available data for reductive coupling processes not proceeding via free-radical paths, we neglect a single-step reaction having a product-like or late transition state and invoke a multistep sequence for the formation of the aryl C−H bond in cluster **3**.

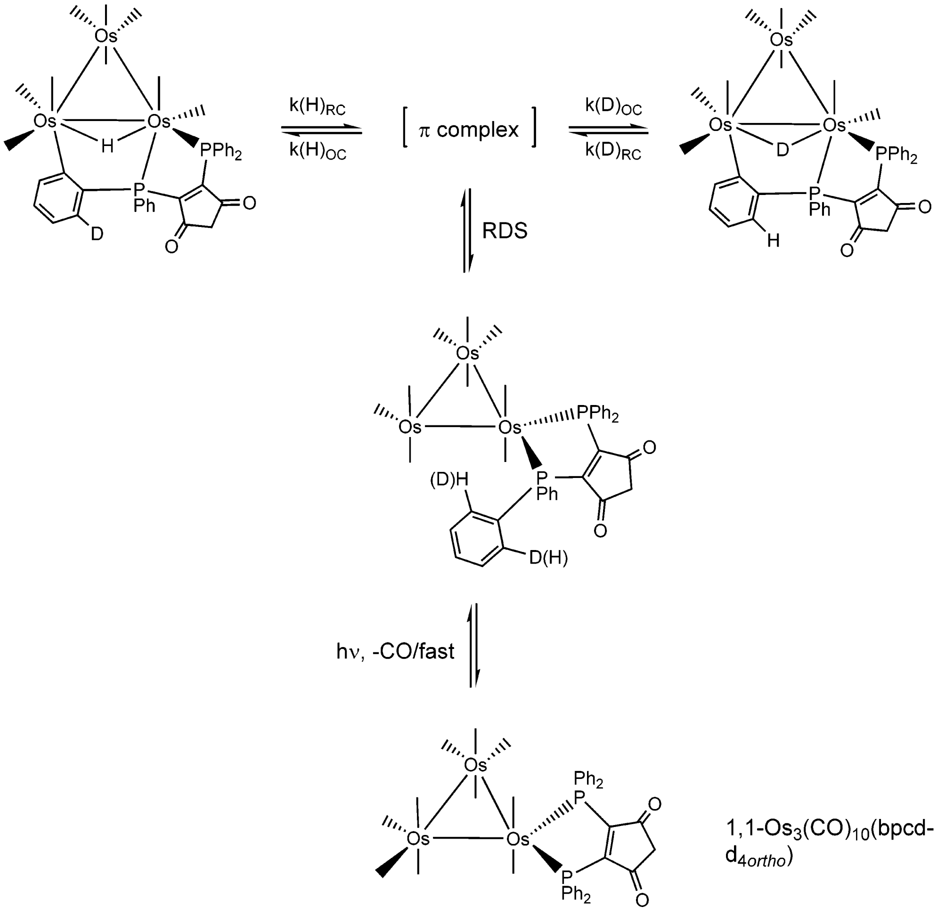
(59) For isotope studies involving hydride/deuteride fluxionality and related C−H bond activation reactions at Ru_3 and Os_3 clusters, see: (a) Rosenberg, E. *Polyhedron* **1989**, *8*, 383. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225. (c) Duggan, T. P.; Golden, M. J.; Keister, J. B. *Organometallics* **1990**, *9*, 1656.

(60) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

(61) The presence of the bridging deuteride ligand in $DOs_3(CO)_9$[μ-(PPh_2-$d_{2,ortho}$)C=C{P(Ph-d_{ortho})(C_6H_4)}C(O)CH_2C(O)] was also verified by ^2H NMR analysis, which revealed a broadened, high-field resonance at ca. −16 ppm.

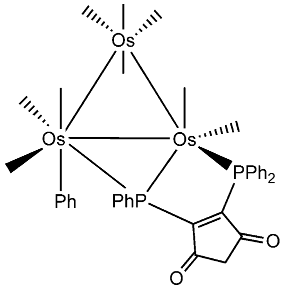
(62) The difference in the EIE values (0.88 vs 0.49) obtained from the two different ligands (bpcd-d_{20} vs bpcd-$d_{4,ortho}$) presumably reflects the effect of isotopic substitution at the α, β, and γ aryl C−H(D) bonds (relative to the ortho-metalated carbon) between the two ligands.

Scheme 6



40 °C in benzene-d_6 gave a K_{eq} value identical with that obtained from the thermally equilibrated cluster samples. That the hydride cluster is thermodynamically favored over the corresponding deuteride cluster is understood within the tenets of the Born–Oppenheimer approximation, where changes in the vibrational energies of the participant bonds control the direction of the hydride/deuteride equilibrium in this ortho-metalation reaction.[63] The smaller zero-point energy difference between the bridging osmium–hydride (–deuteride) bonds vis-á-vis the fully formed arene ortho C–H(D) bonds in the ortho-metalated aryl ring guarantees that the hydride-bridged cluster with its stronger arene C–D bond will dominate the equilibrium and favor the hydride-bridged cluster $HOs_3(CO)_9[\mu\text{-}(PPh_2\text{-}d_{2,ortho})C{=}C\{P(Ph\text{-}d_{ortho})(C_6H_3D)\}C(O)CH_2C(O)]$. From these data we find that the reductive coupling step exhibits an inverse KIE with $k(H)_{RC}/k(D)_{RC} = 0.60$. The gross characteristics for the reversible ortho metalation in 1,1-$Os_3(CO)_{10}(bpcd)$ are remarkably similar to the activation of benzene by $Cp^*Rh(PMe_3)H_2$.[57d] Taken collectively, our data on the multistep conversion of the hydride clusters **3**-d_0 and **3**-d_{20} to 1,1-$Os_3(CO)_9L(bpcd)$ in the presence of trapping ligands are best described by the reaction coordinate depicted in Figure 6.[64]

Kinetics for the Conversion of $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (3) to $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$ (4). The relationship of cluster **3** to cluster **4** was examined next. Conceptually, an attractive route for conversion of **3** to **4** would involve a P–C bond cleavage of the activated aryl group in **3**, as this would serve to liberate the benzyne ligand. However, such a path would violate the principle of microscopic reversibility that requires the regeneration of the coordinatively unsaturated cluster 1,1-$Os_3(CO)_9(bpcd)$, which in turn must function as a precursor for the production of cluster **4**. The kinetics for the conversion of **3** to **4** were studied over the temperature range 363–383 K in toluene solvent by following the decrease in the 396 nm absorbance band belonging to **3**. Regression analysis provided the first-order rate constants that are quoted in Table 5, from which the values of $\Delta H^\ddagger = 29.2(1.1)$ kcal/mol and $\Delta S^\ddagger = 4(3)$ eu were determined by Eyring analysis. The activation data are in excellent agreement with those data obtained from the ligand trapping studies employing **3**, as expected. Under these higher temperature conditions 1,1-$Os_3(CO)_9(bpcd)$, once formed, can undergo an irreversible P–C bond activation and ultimately furnish the benzyne cluster **4**. The exact nature of the aryl group formed upon P–C bond cleavage cannot be determined on the basis of the present data, but the generation of a cluster-bound η^1-Ph moiety would not be unreasonable, as depicted below for $Os_3(CO)_9(\eta^1\text{-}Ph)[\mu\text{-}(PPh_2)C{=}C(PPh)C(O)CH_2C(O)]$.[65] Sub-



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[63] (a) Bullock, R. M.; Bender, B. R. Isotope Methods in Homogeneous Catalysis. In *Encyclopedia of Catalysis*; Horváth, I. T., Ed.; Wiley: New York, 2003. (b) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *7*, 225.

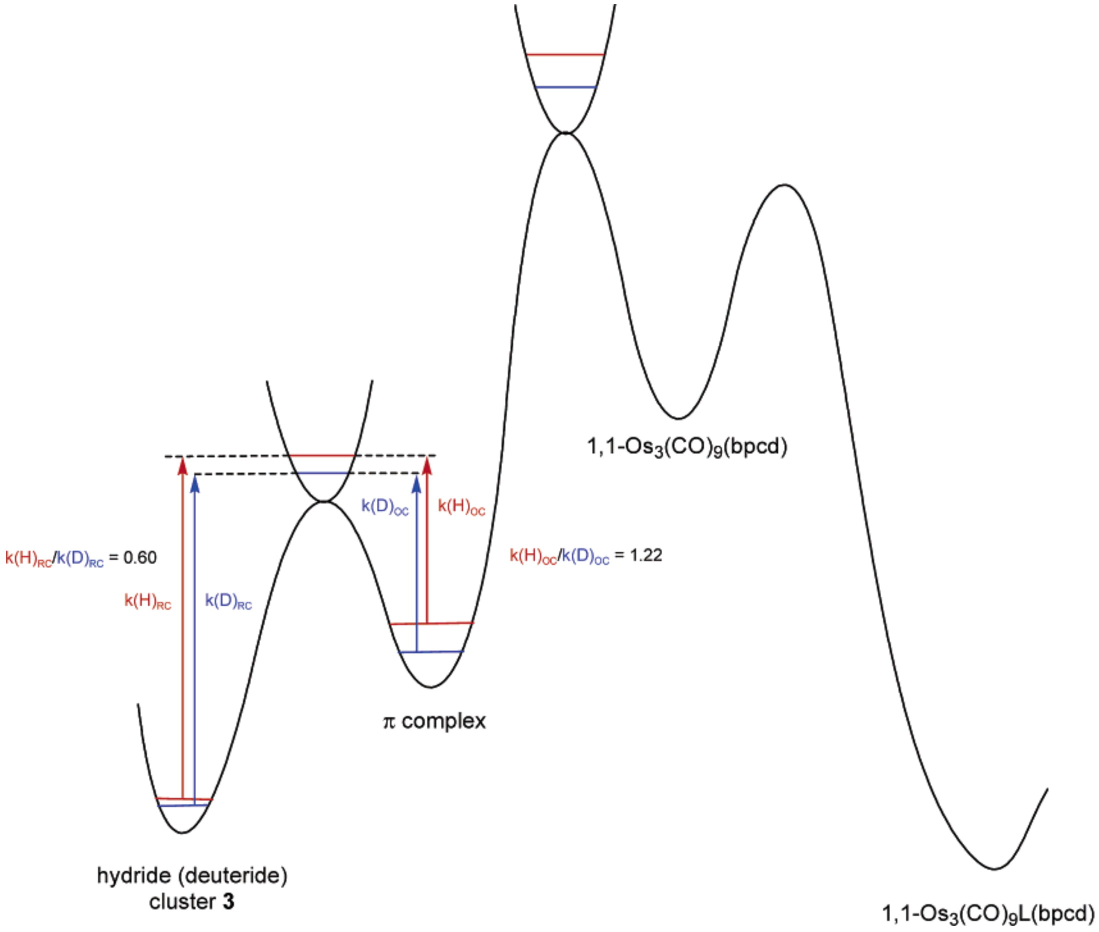

Figure 6. Reaction coordinate for the multistep conversion of cluster **3** to 1,1-$Os_3(CO)_9$L(bpcd) in the presence of trapping ligands.

sequent ortho metalation of the η^1-Ph moiety could then give the coordinated benzyne ligand found in **4**.

Conclusions

The reaction between the diphosphine ligand bpcd and $Os_3(CO)_{10}(MeCN)_2$ has been investigated and found to give 1,2-$Os_3(CO)_{10}$(bpcd) as the kinetic product of ligand substitution. Nondissociative ligand isomerization to the chelated cluster 1,1-$Os_3(CO)_{10}$(bpcd) occurs upon heating, followed by the loss of CO and formation of the hydride cluster $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ through an ortho-metalation sequence. The ortho-metalation reaction is reversible and proceeds by way of a transient π complex. The individual kinetic isotope effects associated with the preequilibrium step have been determined, and the role of the unsaturated cluster 1,1-$Os_3(CO)_9$(bpcd) as a common precursor for the formation of both the hydride cluster **3** and the benzyne-substituted cluster **4** is confirmed. In the present study, the benzyne ligand is derived from an irreversible P−C bond cleavage reaction, followed by an ortho metalation of the cluster-bound phenyl moiety. Future work will concentrate on the mechanistic examination of other cluster-mediated ligand degradation reactions, and the influence that the metal cluster has on the magnitude of the isotope contributions for the ortho-metalation step will be probed.

Table 5. Experimental Rate Constants for the Conversion of $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (3) to $HOs_3(CO)_8(\mu_3\text{-}C_6H_4)[\mu_2,\eta^1\text{-}PPhC{=}C(PPh_2)C(O)CH_2C(O)]$ (4)[a]

temp (K)	10^4k (s^{-1})	temp (K)	10^4k (s^{-1})
363.0	1.31 ± 0.04	378.0	7.10 ± 0.10
368.0	2.21 ± 0.03	383.0	11.0 ± 0.3
373.0	3.58 ± 0.04		

[a] The UV−vis kinetic data were collected in toluene using ca. 10^{-4} M $HOs_3(CO)_9[\mu\text{-}(PPh_2)C{=}C\{PPh(C_6H_4)\}C(O)CH_2C(O)]$ (**3**) by following the decrease in the absorbance of the 396 nm band.

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Supporting Information Available: Tables and CIF files giving crystallographic data for **2b**,**c** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic

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(64) Technically, the observed reductive coupling step requires a short-lived terminal Os−H(D) ligand prior to the formation of the coordinated π complex on the basis of microscopic reversibility. VT ^{1}H NMR analysis of **3**-d_0 showed no evidence for hydride fluxionality over the temperature range 298−340 K, as only a sharp high-field triplet at δ −15.91 (in benzene-d_6) was observed. In terms of the reaction coordinate depicted in Figure 6, we show the reductive coupling arising directly from the bridging clusters to the corresponding π complex directly for simplicity. It is acknowledged that the situation is more complex with the small equilibrium isotope effect expected between the bridging hydride (deuteride) clusters and the terminal hydride (deuteride) isomers that furnish the π complex.

(65) For structurally characterized clusters possessing an η^1-phenyl moiety, see: (a) Bruce, M. I.; Humphrey, P. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *526*, 85. (b) Deeming, A. J.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1993**, 3383. (c) de Araujo, M. H.; Vargas, M. D.; Braga, D.; Grepioni, F. *Polyhedron* **1998**, *17*, 2865. (d) Briard, P.; Cabeza, J. A.; Llamazares, L.; Riera, V. *Organometallics* **1993**, *12*, 1006. (e) Chen, G.; Deng, M.; Lee, C. K.; Leong, W. K. *Organometallics* **2002**, *21*, 1227. (f) See also ref 50c.

data for the structural analyses have also been deposited with the Cambridge Crystallographic Data Center: CCDC No. 277346 for **2b**, 277347 for **2c**, and 277348 for **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ U.K. (fax, +44(1223)336-033; e-mail, deposit@ccdc.ac.uk; web, http://www:ccdc.cam.ac.uk).

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