ORGANOMETALLICS

Acceptor Pincer Chemistry of Osmium: Catalytic Alkane Dehydrogenation by (^{CF₃}PCP)Os(cod)(H)

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Supporting Information

ABSTRACT: Syntheses of osmium analogues of acceptor pincer (^{CF₃}PCP)Ru-(II) systems are reported. Treatment of $[Et_4N]_2OsCl_6$ with ^{CF₃}PCPH at 130 °C in ethanol in the presence of Et₃N gave the coordinatively saturated anionic carbonyl complex HNEt₃⁺[(^{CF₃}PCP)Os(CO)Cl₂]⁻, which subsequently may be converted to *cis*-(^{CF₃}PCP)Os(CO)₂Cl or *cis*-(^{CF₃}PCP)Os(CO)₂H by reaction with Me₃SiOTf or (Et₃Si)₂(μ -H)⁺B(C₆F₅)₄⁻, respectively. (^{CF₃}PCP)Os(cod)H was obtained in modest yields by thermolysis of Os(cod)(η ³-2-methylallyl)₂ with ^{CF₃}PCPH in neat cod under 3 atm of H₂ at 130 °C. The alkane dehydrogenation activity of (^{CF₃}PCP)Os(cod)H was examined: under identical conditions to previously studied (^{CF₃}PCP)Ru(cod)H (1:1 cyclooctane/*tert*-butylethylene, 200 °C), the initial turnover rate for cyclooctene production was 1520 h⁻¹, 75% the rate observed for the ruthenium analogue, but with significantly enhanced catalyst lifetime. Acceptorless cyclodecane dehydrogenation under reflux conditions gave



125 turnovers of cyclodecenes in one hour. Spectroscopic evidence on the nature of the catalyst resting state and catalyst thermal and air stability is presented.

INTRODUCTION

Alkane dehydrogenation and hydrogen transfer processes mediated by iridium pincer complexes continue to receive a good deal of attention.^{1–3} Following studies focusing on PCPand POCOP-type iridium complexes with pendant phosphine donor substituents, primarily ¹Bu and ⁱPr, we recently reported cyclooctane dehydrogenation studies using iridium(I) supported by the strongly π -accepting pincer ligand ^{CF3}PCP.⁴ Phosphine ligands with perfluoroalkyl substituents dramatically reduce electron density at metal centers relative to alkylphosphines and typically impart increased oxygen and thermal stability.⁵ The (^{CF3}PCP)Ir(I) system, while exhibiting intermediate activity between established iridium donor PCP and POCOP pincer catalysts, was notable for having significant air and moisture stability and lowered product inhibition by cyclooctene or dinitrogen.

In a related effort, we have reported the first effective alkane/ alkene hydrogen transfer catalysis by the ruthenium cyclooctadiene complex (^{CF_3}PCP)Ru(cod)H.⁶ In contrast to the markedly lower activity of rhodium relative to the iridium analogue (^{fBu}PCP)IrH₂ (1.8 vs 720 TO h⁻¹, 200 °C),⁷ this ruthenium acceptor PCP system had surprisingly high initial activity (~1000 TO h⁻¹), but underwent complete and irreversible catalyst decomposition after 30 min at 200 °C. In light of the enhanced reactivity of iridium relative to rhodium and also the generally greater stability of 5d metal systems, we report here an extension of our acceptor pincer studies to osmium. The successful syntheses of (^{CF_3}PCP)Os(cod)H and a series of Os(II) pincer complexes are presented, as well as a survey of *tert*-butylethylene-mediated and acceptorless dehydrogenation by $({}^{CF_3}PCP)Os(cod)H$. The unexpected conversion of $({}^{CF_3}PCP)Os(cod)H$ to dicarbonyl hydride *cis*- $({}^{CF_3}PCP)Os(CO)_2H$ when thermolyses were carried out in the presence of oxygen is reported.

RESULTS AND DISCUSSION

Osmium CNN pincer complexes have been shown to be efficient catalysts for transfer hydrogenation between alcohols and ketones.⁸ CNO,⁹ CNC,¹⁰ and PNP¹¹ osmium pincers have been synthesized, and recently neutral POP ether pincer ligands have been used to make osmium catalysts for the alkylation of amines with alcohols.¹² There have been several reports of osmium PCP pincer systems in the literature employing ^{Ph}PCP,^{13,14} ^{fBu}PCP,¹⁵ and ^{iPr}PCP.¹⁶ Gusev has reported that metalation of ^{tBu}PCPH with [Et₄N]₂OsCl₆ in alcohol solvents yields the osmium complexes (^{tBu}PCP)OsCl(CO) and (^{tBu}PCP)Os(H)₂Cl.^{15c} A corresponding thermolysis of [Et₄N]₂OsCl₆ with ^{CF3}PCPH at 130 °C in ethanol in the presence of Et₃N gave a single product with a phosphorus NMR resonance at 59.1 ppm and two fluorine CF₃ resonances at 51.2 and 56.1 ppm, features that are consistent with a lack of symmetry across the plane defined by meridional PCP coordination. IR spectroscopy showed a single CO stretch at 1970 cm⁻¹, and subsequent X-ray diffraction (Figure 1) confirmed that the product is not (^{CF_3}PCP)Os(CO)Cl, but rather the coordinatively saturated anionic carbonyl complex $HNEt_3^+ \textit{cis-}[({}^{CF_3}PCP)Os\dot(CO)Cl_2]^-$ (1) (Scheme 1). We have

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Figure 1. Molecular view of the associated Et_3NH^+ cation and anion $HNEt_3^+[(^{CF_3}PCP)Os(CO)Cl_2]^-$ (1). Hydrogen atoms except for the N-H-Cl hydrogen bond are not shown, and thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Os(1)-C(1): 2.111(3), Os(1)-P(1): 2.2784(8), Os(1)-P(2): 2.2663(7), Os(1)-C(13): 1.889(4), Os(1)-Cl(1): 2.4979(8), Os(1)-Cl(2): 2.4446(7), Cl(1)-H(1): 2.25(6); P(1)-Os(1)-P(2): 158.60(3), C(1)-Os(1)-Cl(1): 175.22(8), C(1)-Os(1)-P(2): 87.90(8), C(1)-Os(1)-Cl(3): 93.8(1), Cl(1)-Os(1)-Cl(2): 87.42(3), C(13)-Os(1)-Cl(1): 90.9(1), C(13)-Os(1)-Cl(2): 177.4(1).

previously reported the analogous ruthenium product derived from thermolysis of $^{\rm CF_3}PCPH/[(cod)RuCl_2]_x/Et_3N.^{17}$

As previously observed for $({}^{CF_3}PCP)Ru(CO)Cl_2^-$, chloride may be readily removed in the presence of a trapping ligand.¹⁷ Treatment of HNEt₃+*cis*-[$({}^{CF_3}PCP)Os(CO)Cl_2$]⁻ with excess trimethylsyliltriflate under 1 atm of CO afforded the neutral *cis*dicarbonyl complex *cis*-(${}^{CF_3}PCP)Os(CO)_2Cl$ (2). The *cis* carbonyl geometry is indicated by inequivalent fluorine resonances at -51.3 and -58.0 ppm and the appearance of two carbonyl stretches at 2073 and 2006 cm⁻¹. We have

Scheme 1

previously reported that the reaction of $({}^{CF_3}PCP)Ru(CO)_2Cl$ with the cationic silyl reagent $(Et_3Si)_2(\mu-H)^+B(C_6F_5)_4^-$ in the presence of 1 atm of CO resulted in the formation of the tricarbonyl cation $({}^{CF_3}PCP)Ru(CO)_3^+$.¹⁷ In contrast, $({}^{CF_3}PCP)-Os(CO)_2Cl$ under identical reaction conditions gave a dicarbonyl product $(\nu(CO) = 2064, 2020 \text{ cm}^{-1})$ with a hydride triplet at -8.10 ppm, indicating formation of the osmium hydride dicarbonyl complex $({}^{CF_3}PCP)Os(CO)_2H$ (3). The molecular structures of 2 and 3 are shown in Figure 2.

Ru(cod)(η^{3} -2-methylallyl)₂ has been shown to be a useful precursor to ruthenium polyhydride donor pincer complexes,¹⁸ as well as (^{CF₃}PCP)Ru(cod)H.⁶ Os(cod)(η^{3} -2-methylallyl)₂ similarly provides access to osmium ^{CF₃}PCP complexes. Our ruthenium study showed that monomeric (^{CF₃}PCP)Ru(cod)H was favored over dimeric products when Ru(cod)(η^{3} -2-methylallyl)₂ hydrogenation was carried out in the presence of excess cod. Accordingly, (^{CF₃}PCP)Os(cod)H (4) was similarly obtained in modest yields by thermolysis of Os(cod)(η^{3} -2-methylallyl)₂ with 1 equiv of ^{CF₃}PCPH in neat cod under ~3 atm of H₂ at 130 °C (eq 1). A key to this

synthesis is the use of a large excess of cyclooctadiene, since competitive hydrogenation of cyclooctadiene to form cyclooctane also occurs. ¹H NMR spectra for 4 closely compare to the ruthenium analogue, with distinct axial and equatorial vinylic cyclooctadiene resonances at 4.19 and 2.61 ppm as well as a hydride triplet at -12.64 ppm (² $J_{\rm HP} = 29$ Hz). The molecular structure of 4 is shown in Figure 3.

In our metalation studies with Ru(cod)(η^3 -2-methylallyl)₂ and ^{CF₃}PCPH, dimeric side products were obtained in the absence of excess cod or in the presence of excess ^{CF₃}PCPH.⁶ One of these dimers, the unusual μ,η^6,κ^3 -bridged pincer complex (μ -^{CF₃}PCPH)Ru(H)(μ -H)(μ,η^6,κ^3 -^{CF₃}PCP)Ru(H), was also obtained by the reaction of (^{CF₃}PCP)Ru(cod)H with H₂. When (^{CF₃}PCP)Os(cod)H was heated to 130 °C in benzene under 3 atm of H₂ for 48 h, a major broad ³¹P





Figure 2. Molecular views of $cis-(^{CF_3}PCP)Os(CO)_2Cl(2)$ and $cis-(^{CF_3}PCP)Os(CO)_2H(3)$. All hydrogen atoms except for the hydride ligand are not shown, and thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg) for ($^{CF_3}PCP)Os(CO)_2Cl: Os(1)-C(1)$: 2.149(3), Os(1)-P(1): 2.2971(9), Os(1)-P(2): 2.3032(9), Os(1)-C(13): 1.973(4), Os(1)-C(14): 1.894(4), Os(1)-Cl(1): 2.4422(8), P(1)-Os(1)-P(2): 157.63(3), C(1)-Os(1)-C(13): 172.10(13). Selected bond lengths (Å) and angles (deg) for ($^{CF_3}PCP)Os(CO)_2H$: Os(1)-C(1): 2.171(9), Os(1)-P(1): 2.270(3), Os(1)-P(2): 2.265(3), Os(1)-C(13): 1.853(10), Os(1)-C(14): 1.963(11), Os(1)-H(1): 1.462(1), P(1)-Os(1)-P(2): 154.1(1), C(1)-Os(1)-C(13): 169.8(4), C(1)-Os(1)-C(14): 92.3(4).



Figure 3. View of the $(^{CF_3}PCP)Os(cod)H$ molecule. All hydrogen atoms except the hydride hydrogen atom are omitted, and the thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Os(1)-C(1): 2.163(3), Os(1)-P(1): 2.2472(9), Os(1)-P(2): 2.2470(8), Os(1)-C(13): 2.245(3), Os(1)-C(14): 2.237(4), Os(1)-C(17): 2.285(3), Os(1)-C(18): 2.278(4), Os(1)-H(1): 1.59(5), P(1)-Os(1)-P(2): 129.93(3), C(1)-Os(1)-H(1): 111.4(18).

resonance at 57.1 (~55% total integrated intensity) appeared as well as smaller multiplets at 42.3 and 39.0 ppm. ¹H NMR spectra showed cyclooctane as well as diagnostic hydride resonances at δ –13.36 (pseudo quartet, ²J_{PH} = 25 Hz) and –15.84 (br doublet, ²J_{PH} = 36 Hz) in a 1:2 ratio that are very similar to resonances found for the ruthenium μ , η^6 , κ^3 -bridged pincer complex and therefore lead us to assign this product as



 $(\mu$ -^{CF₃}PCPH)Os(H) $(\mu$ -H) $(\mu,\eta^{6},\kappa^{3}$ -^{CF₃}PCP)Os(H) (5) (eq 2). ¹⁹F NMR spectra for **5** exhibit four distinctive resonances (see Experimental Section) that are also closely comparable to the ruthenium analogue. Complex **5** may be produced more cleanly by thermolysis of **4** at 200 °C for 60 min in cyclodecane (see later). Preparative-scale isolation of **5** was not attempted. One might expect that, in the presence of excess H₂, a monomeric polyhydride such as (^{CF₃}PCP)Os(H)(H₂)₂ would form; however, we have previously noted the formation of unusual bimetallic products in the hydrogenation of (^{CF₃}PCP)Ir(cod) rather than simple monomeric (^{CF₃}PCP)Ir(H)_x.⁴ This difference in reactivity may be in part due to the lower steric influence of (CF₃)₂P-substituted pincer ligands relative to ([†]Bu)₂P systems.

Crystallographic Studies. Crystallographic data obtained for (^{CF₃}PCP)Os(II) complexes 1-4 afford us a comparison with related systems. Os-P bond lengths for complexes range from 2.247(1) Å in 4 to 2.303(1) Å in 2 and roughly correlate with decreasing electron density at osmium. For comparison, the average Os-P bond length in donor (PCP)Os systems is 2.382 Å.^{13d,15b,c,16} Significantly reduced M-P bond distances to $P(CF_3)_2$ groups have been noted in platinum,¹⁹ iridium,^{4,20} and ruthenium pincer chemistry, and this is a general phenomenon observed in perfluoroalkylphosphine (PFAP) coordination chemistry.²¹ Complexes 1-3 adopt relatively undistorted octahedral coordination geometries with P-Os-P pincer angles between 154° and 158° and the remaining cis ligand angles ranging between 85° and 98°. (CF3PCP)Os(cod)H, despite being nominally six-coordinate, exhibits a nonmeridional P-Os-P angular distortion toward the hydride position, with a P-Os-P angle of 129.9°, which is more typical of trigonal bipyramidal five-coordinate d⁸ iridium systems,^{20c} and is isostructural with (^{CF3}PCP)Ru(cod)H.⁶ Despite the low steric influence of the hydride ligand, a comparison with the true five-coordinate iridium complex (^{CF3}PCP)Ir(cod) (P-Ir- $P = 119.0^{\circ}$) shows that there is a significant increase in the P-Os-P angle to accommodate the hydride ligand. Cyclooctadiene-coordinated C=C bond distances cis (1.403(6) Å)

and trans (1.384(6) Å) to the aryl ligand group in 4 are indicative of more π -back-bonding to the cis alkene group, but the difference is less pronounced than observed in (^{CF₃}PCP)-Ir(cod) (cis C=C: 1.435(6) Å; trans C=C: 1.375(6) Å). Besides the asymmetry of cod binding to (^{CF₃}PCP)M centers, an additional feature to note is that Os-C(cod) bond distances are significantly longer (2.26 Å) than other reported osmium cod structures (2.18 Å) and probably reflect steric crowding about the metal center.²²

Alkane Dehydrogenation Catalysis by (^{CF_3}PCP)Os-(cod)H. Thermolysis of 1.38 mM (^{CF_3}PCP)Os(cod)H in 1:1 mixtures of cyclooctane (coa) and *tert*-butylethylene (tbe) (3030 equiv each) at 150 and 200 °C was monitored by ¹H NMR. While (^{CF_3}PCP)Ru(cod)H shows moderate activity at 150 °C, no catalytic activity was noted for the osmium analogue at this temperature. At 200 °C, however, significant production of cyclooctene (coe) was observed (Figure 4). The initial rate



Figure 4. Comparative catalyst activity plot for $(^{CF_3}PCP)Os(cod)H$ (\blacksquare) and $(^{CF_3}PCP)Ru(cod)H$ (\bullet) in 1:1 cyclooctane/*tert*-butylethylene at 200 °C (0.033 mol % catalyst loading).

calculated at 10 min was 1520 turnovers h⁻¹, approximately 75% of that of (^{CF₃}PCP)Ru(cod)H.²³ Catalyst lifetime, however, was significantly improved: 610 turnovers of cyclo-octene were generated after 8 h, whereas the ruthenium analogue reaches a maximum TON of ~350 after only 20 min and at that point is rendered completely inactive. A control run in the presence of added elemental mercury showed no difference in activity or catalyst lifetime, consistent with a homogeneous catalytic cyclooctane dehydrogenation process. The initial rate and total turnovers for (^{CF₃}PCP)Os(cod)H are comparable to (^{rBu}PCP)IrH₂ (1170 turnovers h⁻¹, 230 TON after 40 h at 200 °C),²⁴ although significantly lower than reported for the iridium phosphinite complex (*p*-Ar^FPOCOP^{rBu})IrH₂ (8715 turnovers h⁻¹, 2200 TON at 200 °C)^{24,25} and ferrocene-bridged pincer complexes such as (^{rBu}PCP)^{Fe(C₃H₃))IrH₂ (3300 TON at 180 °C).²⁶}

Experiments to address catalyst stability and the extent of activity inhibition by cyclooctene product buildup were performed. First, catalyst activity was monitored for 3 h at 200 °C; then volatiles were removed, the residue was taken up in a fresh 1:1 coa/tbe mixture, and the thermolysis was reinitiated. As seen in Figure 5, the low TOF after 3 h (\sim 27 h⁻¹) rose to 580 h⁻¹ upon restart; this corresponds to a \sim 65% recovery of the initial catalyst activity. In a separate experiment, a series of catalyst runs with progressive amounts of added cycooctene were performed; a plot of initial activity rates versus



Figure 5. Catalyst activity plot for fresh (^{CF_3}PCP)Os(cod)H (\bullet) in 1:1 cyclooctane/*tert*-butylethylene at 200 °C (0.033 mol % catalyst loading) and a reinitiated thermolysis using catalyst residue after 180 min initial thermolysis, taken up in fresh 1:1 solution (\blacksquare).

added coe is given in Figure 6. The approximate initial TOF in the presence of 400 equiv of added coe, 468 h^{-1} , is 37% of the



Figure 6. Initial catalyst activity plot for (^{CF_3}PCP)Os(cod)H in 1:1 cyclooctane/*tert*-butylethylene at 200 °C (0.033 mol % catalyst loading), calculated at 10 min, as a function of equivalents of added cyclooctene.

initial activity.²⁷ It is significant that the TOF values at the point where 400 equiv of coe product are present in Figures 4 and 6 are ~122 and 468 h⁻¹. In light of Figure 5, part (but perhaps not all) of this ~4-fold difference in activity can be ascribed to catalyst decomposition.

The major solution osmium species under catalytic conditions evolves during the course of the reaction. After 3 h at 200 °C ¹⁹F NMR reveals a nearly complete conversion to a new pincer species having pincer CF₃ doublets at -55.5 and -59.8 ppm (Figure 7). A minor (~25%) product with an upfield resonance at -82.6 ppm is also observed. It is notable that thermolysis of (^{CF₃}PCP)Os(cod)H in cyclooctane for 24 h at 200 °C in the absence of the results in only limited decomposition (~10%).

Thermolysis of 5 mg of (^{CF₃}PCP)Os(cod)H in 1:1 coa/tbe at 200 °C for 24 h followed by removal of volatiles and addition of benzene- d_6 afforded a sample with sufficient concentration for further NMR analysis. ¹⁹F NMR confirmed the presence of CF₃ doublets at 55.5 and 59.8 ppm, and ³¹P NMR showed a single major multiplet at 61.2 ppm. ¹H NMR spectra reveal new η^4 cod vinylic singlets at δ 4.69 and 4.26, shifted downfield from those in 4, as well as inequivalent pincer benzylic resonances at δ 3.96 (dd, ²*J*_{PH} = ²*J*_{HH} = 15 Hz) and 2.95 (d, ²*J*_{HH} = 15 Hz). A



Figure 7. ¹⁹F NMR spectra monitoring the thermal conversion of $(^{CF_3}PCP)Os(cod)H(\blacktriangle)$ over time to " $(^{CF_3}PCP)Os(cod)R$ " in 1:1 cyclooctane/ tert-butylethylene at 200 °C (0.033 mol % catalyst loading).

complex series of aliphatic multiplets appear between 0.5 and 1.5 ppm. Significantly, no hydride resonance is observed. In light of these observations, we conclude that the final osmium product formed under catalytic conditions is of the general form (^{CF₃}PCP)Os(cod)X, where X is as yet undetermined, but is most likely a hydrocarbyl group such as CH₂CH₂^tBu.

Acceptorless Cycloalkane Dehydrogenation. As noted earlier, (^{CF₃}PCP)Os(cod)H is not catalytically active in coa/tbe at 150 °C, and it is therefore not surprising that acceptorless dehydrogenation of cyclooctane is not observed under neat reflux conditions (~140 °C at 590 Torr ambient pressure). Higher boiling alkanes, including cyclodecane, have been used in (PCP)Ir systems.²⁸ Refluxing 1.0 mM (^{CF₃}PCP)Os(cod)H in cyclodecane (~190 °C at 590 Torr ambient pressure) showed good catalytic activity, with 125 total equivalents of cyclodecenes (1:6.8 trans:cis) produced in the first hour (Figure 8).



Figure 8. Acceptorless catalyst activity plot for $(^{CF_3}PCP)Os(cod)H$ (\bullet) in cyclodecane under N₂ reflux conditions ($T \sim 190$ °C; 1 mmol catalyst loading).

The cis:trans cyclodecene ratio at times greater than 2 h was 1:6.0. This activity is very comparable to $\binom{^{HBu}PCP}{IrH_4}$ (101 turnovers after 1 h) and somewhat less than $\binom{^{HBu}M^ePCP}{IrH_4}$ (489 turnovers after 1 h).²⁸ Monitoring the catalyst resting state by ¹⁹F revealed that complete conversion of 4 to 5 occurred within 60 min, and after 120 min a single doublet at -69.8 ppm $\binom{^2J_{PH}}{^2} = 94$ Hz) was observed, which correlated with the loss of dehydrogenation activity. Again, despite the production of H₂ from the dehydrogenation of cyclooctane,

monomeric osmium polyhydride products are not favored relative to the formation of 5. This catalyst decomposition product was not further characterized. It is notable that thermolysis of 4 in cyclodecane at 200 °C for 24 h in a sealed NMR tube under vacuum resulted in only ~10% decomposition.

Catalyst N₂ and O₂ Stability. Previous alkane dehydrogenation studies with donor phosphine (PCP)Ir systems have been typically carried out under an argon atmosphere due to strong dinitrogen inhibition and the formation of inactive bridged $Ir_2(\mu N_2)$ products.^{25,29} In marked contrast, we have reported that the catalytic cyclooctane dehydrogenation activity of (^{CF₃}PCP)Ru(cod)H was unaffected by the presence of N₂, excess water, and even oxygen.⁶ A corresponding series of experiments have been conducted with (^{CF₃}PCP)Os(cod)H (Figure 9): catalyst runs carried out under full vacuum, under



Figure 9. Comparative catalyst activity plot for $({}^{CF_3PCP})Os(cod)H$ under vacuum (\blacksquare), 590 Torr of N₂ (red \bullet), 200 Torr of O₂ (\bullet), and with 100 equiv of added H₂O (\bullet) in 1:1 cyclooctane/*tert*-butylethylene at 200 °C (0.033 mol % catalyst loading).

590 Torr of N₂, and with 100 equiv of water added showed no significant change in initial rate, total turnovers, or decomposition products. In the presence of 200 Torr of added O₂, the initial activity of $(^{CF_3}PCP)Os(cod)H$ was unchanged. After one hour, however, catalyst activity ceased and a major (~70%) new osmium species was observed by ¹⁹F NMR (CF₃ resonances at -63.6 and -65.0 ppm), which was subsequently identified by IR as the dicarbonyl hydride *cis*- $(^{CF_3}PCP)Os(CO)_2H$ (3).

Interestingly, clean conversion of 4 to 3 after one hour at 200 $^{\circ}$ C under 200 Torr of O₂ is also observed in both cyclooctane and cyclodecane in the absence of added *tert*-butylethylene.

Oxidation Control Experiments. Preliminary experiments have been carried out in an attempt to determine how cis- $(^{CF_3}PCP)Os(CO)_2H$ (3) is produced in the thermolysis of $(^{CF_3}PCP)Os(cod)H(4)$ in the presence of oxygen. Thermolysis of 4 in cyclodecane at 200 °C under 200 Torr of O2 with 5 equiv of added mesitylene as an internal standard for one hour produced 2-3 equiv of cyclodecenes,³⁰ as well as a new resonance at δ 1.51, which was subsequently identified as the α -CH₂ resonance of cyclodecanone (2.1 equiv). ¹⁹F NMR spectra show 3 as the major (65%) osmium species present along with the hydride dimer 5 (\sim 25%). A corresponding experiment in cyclooctane gave 12 equiv of cyclooctene and 8.8 equiv of cyclooctanone. In a separate control experiment, when cyclooctane was heated in the absence of 4 to 200 °C under 200 Torr of O₂, a comparable amount of cyclooctanone was produced, showing that ketone formation from the cycloalkane solvent is an osmium-independent process. Leitner has reported the conversion of cyclooctane to cyclooctanone in the presence of oxygen; however, radical initiation was required as well as added aldehyde as an oxygen acceptor.³¹ Radicalinitiated conversion of cyclooctene to cyclooctanone has also been reported.32

Reaction of 4 with cyclooctanone was examined as a possible route to dicarbonyl hydride 3. Thermolysis of 0.3 mol % 4 in cyclooctane in the presence of 50 equiv of cyclooctanone under either N₂ or O₂ at 200 °C did not produce 3, but rather a new osmium pincer product with inequivalent ³¹P resonances at 59.6 and 52.0 ppm; this product was not characterized further.

A well-established mechanism for metal carbonyl production is by decarbonylation of aldehydes. As shown previously for $(^{CF_3}PCP)Ru(cod)H$, $(^{CF_3}PCP)Os(cod)H$ is reactive toward aldehydes: thermolysis of 4 in the presence of 4 equiv of dodecylaldehyde for 3 h at 200 °C resulted in 80% conversion to the expected dicarbonyl 3. Accordingly, our current hypothesis is that the conversion of $(^{CF_3}PCP)Os(cod)H$ to $cis-(^{CF_3}PCP)Os(CO)_2H$ in cycloalkane thermolyses under oxygen is due to the presence of small amounts of aldehydes. Cyclooctane and cyclodecane used in our dehydrogenation studies have not been analyzed in detail, but likely contain significant quantities of acyclic hydrocarbons that may convert to aldehydes under alkane dehydrogenation conditions in the presence of O₂.

SUMMARY

We have presented the synthesis of a series of osmium pincer complexes with the fluorinated acceptor pincer ligand ^{CF₃}PCP that follows our previously reported ruthenium chemistry.⁶ Compared to the dramatic increase in the reported alkane dehydrogenation activity of (^{tBu}PCP)IrH₂ relative to (^{tBu}PCP). RhH₂,⁷ the difference in activity for Os(II) and Ru(II) ^{CF₃}PCP complexes is much less pronounced: (^{CF₃}PCP)Os(cod)H has a slightly lower initial activity, but has a significantly longer catalyst lifetime. Unlike (^{CF₃}PCP)Ru(cod)H, which decomposes to a complex mixture of (^{CF₃}PCP)Ru products, (^{CF₃}PCP)Os(cod)H converts to a major (^{CF₃}PCP)Os(cod)X product; future efforts to identify this product may provide insight into catalyst decomposition pathways and lead to the development of more robust osmium (and ruthenium) systems.

An unusual feature of both the osmium and the analogous ruthenium $({}^{\rm CF_3}\rm PCP)M(\rm II)$ chemistry is the stability of dimeric

products such as **5** in the presence of excess H₂ relative to monomeric polyhydride products such as $(^{CF_3}PCP)M(H)$ - $(H_2)_2$, which are precedented in Milstein's work.¹⁸ $(\mu^{-CF_3}PCPH)M(H)(\mu,H)(\mu,\eta^6,\kappa^{3-CF_3}PCP)M(H)$ (M = Ru, Os) may be viewed formally as the condensation product of two " $(^{CF_3}PCP)_2M(H)$ " fragments with the addition of one H₂ molecule. We have previously suggested that this dimerization may be favored due to the lower steric requirements of CF₃ compared to ^tBu phosphine substituents.

The formation of catalytically inactive cis-(^{CF₃}PCP)Os-(CO)₂H from (^{CF₃}PCP)Os(cod)H thermolysis in alkane/O₂ mixtures is surprising and may serve as a cautionary note to future research involving coupled or tandem hydrocarbon activation and oxidation. Metal-mediated alkane oxidation processes that generate aldehyde intermediates or products may be susceptible to CO deactivation in cases where alkane and aldehyde C–H bond addition is competitive. Future experiments using isomerically pure cycloalkanes will test our suggestion that traces of acyclic alkane impurities are responsible for carbonyl formation.

EXPERIMENTAL SECTION

General Procedures. All manipulations were conducted under N2 or vacuum using high-vacuum line and glovebox techniques unless otherwise noted. All ambient pressure chemistry was carried out under a pressure of approximately 590 Torr (elevation ~2195 m). All solvents were dried using standard procedures and stored under vacuum. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Elemental analyses were performed by Columbia Analytical Services. NMR spectra were obtained with a Bruker DRX-400 instrument using 5 mm NMR tubes fitted with Teflon valves (Chemglass, CG-512) or in 5 mm sealed tubes containing acetone- d_6 capillaries as an internal standard. ³¹P spectra were referenced to an 85% H_3PO_4 external standard. ^{19}F spectra were referenced to an CF₃CO₂CH₂CH₃ (δ -75.32) external standard. tert-Butylethylene (Aldrich, 99.5%) was used as received. Cyclooctane and cyclodecane (95%) (Pfaltz and Bauer) were stirred over concentrated H_2SO_4 for 24 h and distilled from Na/ benzophenone; all other reagents, unless otherwise noted, were purchased from Aldrich and were used without further purification. $[Os(cod)Br_2]_{x^2}^{22d} CF_3PCPH_{,}^{19b}$ and $(Et_3Si)_2(\mu-H)^+B(C_6F_5)_4^-$ were prepared following literature procedures.³

Os(cod) $(\eta^3-2-methylallyl)_2$. A procedure adapted from Schrock's original method³⁴ was employed using $[Os(cod)Br_2]_x$ rather than $[Os(cod)Cl_2]_x$. To a stirred slurry of $[Os(cod)Br_2]_x$ (0.500 g, 1.09 mmol) in 25 mL of diethyl ether at ambient temperature was slowly added 5.5 mL of 0.5 M 2-methylallylmagnesium chloride (2.73 mmol). After stirring 15 min a white precipitate had formed in the brown solution. The suspension was stirred an additional 22 h, then pulled to dryness. Excess Grignard reagent was quenched by adding NH₄Cl (0.25 g) and 15 mL of methanol to the residue followed by stirring for 15 min. The mixture was pulled to dryness, 25 mL of petroleum ether was added, and the salts were filtered off and washed several times. Methanol (15 mL) was added to the filtrate, and petroleum ether was removed slowly under vacuum until complete precipitation was observed. The resulting white solid was filtered and dried (0.258 g, 58% yield).

HNEt₃^{-*c*}*is*-[(^{CF}₃**PCP)Os**(**CO**)**Cl**₂]⁻ (1). [Et₄N]₂OsCl₆ (0.731 g, 1.11 mmol), ^{CF₃}PCPH (300 μ L, 1.11 mmol), 3 equiv of triethylamine (463 μ L, 3.33 mmol), and ethanol (~15 mL) were combined in a heavy-walled reaction tube equipped with a Teflon valve. The mixture was stirred vigorously while heating to 130 °C for one week, and the volatiles were then removed under vacuum. The residue was taken up in benzene and filtered to remove solids. The residue was triturated with petroleum ether to give a white solid (0.440 g, 48%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexanes into a benzene solution of 1. Anal. Calcd for C₁₉H₂₃Cl₂F₁₂NOOsP₂: C,

27.41; H, 2.79. Found: C, 27.98; H, 3.04. ¹H NMR (C₆D₆, 400.13 MHz, 20 °C): δ 9.91 (br s, 1H; <u>H</u>NEt₃⁺), 6.88 (m, 3H; overlapping *m*-and *p*-C₆<u>H</u>₃(CH₂P(CF₃)₂)₂), 4.13 (dt(pseudo), ²J_{HH} = 17 Hz, J_{PH} = 5 Hz, 2H; C₆H₃(C<u>H</u>₂P(CF₃)₂)₂), 3.55 (dt(pseudo), ²J_{HH} = 17 Hz, J_{PH} = 4 Hz, 2H; C₆H₃(C<u>H</u>₂P(CF₃)₂)₂), 2.24 (m, 6H; NC<u>H</u>₂CH₃), 0.66 (t, ³J_{HH} = 7 Hz, 9H; NCH₂C<u>H</u>₃). ³¹P{H} NMR (C₆D₆, 161.97 MHz, 20 °C): δ 59.1 (m). ¹⁹F NMR (C₆D₆, 376.50 MHz, 20 °C): δ -51.2 (m, 6F; PCF₃), -56.1 (m, 6F; PCF₃). IR (CH₂CL₂, cm⁻¹): *ν*(CO) = 1970. *cis*-(^{CF₃PCP)Os(CO)₂CI (2). *cis*-[(^{CF₃PCP)Os(CO)Cl₂]⁻[HN-(CH₂CH₃)₃]⁺ (0.300 g, 0.360 mmol) and TMSOTf (327 *μ*L, 1.80 mmol) were added to toluene (~25 mL) and stirred one week at room temperature under one atmosphere of CO. The volatiles were removed, and the residue was triturated with methanol to give a white solid, which was collected by filtration and dried (0.060 g, 32% yield).}}

Crystals suitable for X-ray diffraction were grown by slow diffusion of methanol into a benzene solution of **2**. Anal. Calcd for $OsP_2F_{12}C_{10}H_7$: C, 23.26; H, 0.98. Found: C, 23.15; H, 0.86. ¹H NMR (C_6D_6 , 400.13 MHz, 20 °C): δ 6.74 (br s, 1H; p- $C_6H_3(CH_2P(CF_3)_2)_2$), 6.68 (br s, 2H; m- $C_6H_3(CH_2P(CF_3)_2)_2$), 3.79 (m, 2H; $C_6H_3(C(\underline{H})HP-(CF_3)_2)_2$)), 3.24 (m, 2H; $C_6H_3(C(\underline{H})HP(CF_3)_2)_2$)). ³¹P{H} NMR (C_6D_6 , 161.97 MHz, 20 °C): δ 59.3 (m). ¹⁹F NMR (C_6D_6 , 376.50 MHz, 20 °C): δ –51.3 (m, 6F; PCF₃), –58.0 (m, 6F; PCF₃). IR (CH₂Cl₂, cm⁻¹): ν (CO) 2073, 2006.

cis-(^{CF₃}**PCP**)**Os**(**CO**)₂**H** (3). Complex 3 was prepared on a small scale for NMR analysis: *cis*-(^{CF₃}**PCP**)**Os**(CO)₂Cl (0.012 g, 0.017 mmol) and (Et₃Si)₂(μ-H)⁺B(C₆F₅)₄⁻ (0.017 g, 0.019 mmol) were dissolved 0.5 mL of benzene-*d*₆ and placed under 1 atm of CO. NMR confirmed clean conversion of **2** to 3 after one hour. NMR data for 3: ¹H NMR (C₆D₆, 400.13 MHz, 20 °C): δ 6.84 (m, 1H; *p*-C₆<u>H₃(CH₂P(CF₃)₂)₂), 6.69 (m, 2H; *m*-C₆<u>H₃(CH₂P(CF₃)₂)₂), 3.41 (m, 2H; C₆H₃(C(<u>H</u>)HP(CF₃)₂)₂), -8.11 (t, ²J_{HP} = 24 Hz, 1H; OsH). ³¹P{H} NMR (C₆D₆, 161.97 MHz, 20 °C): δ 65.0 (m). ¹⁹F NMR (C₆D₆, 376.50 MHz, 20 °C): δ -61.0 (t, ³J_{FF} = 38 Hz, 3F; PCF₃), -62.4 (t, ³J_{FF} = 43 Hz, 3F; PCF₃). IR (CH₂Cl₂, cm⁻¹): ν(CO) = 2064, 2020. Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane to benzene.</u></u>

 $(^{CF_3}PCP)Os(cod)H$ (4). $Os(cod)(\eta^3$ -2-methylallyl)₂ (0.200 g, 0.490 mmol), $^{\rm CF_3PCPH}$ (137 $\mu L,~0.216$ g, 0.490 mmol), and 5 mL of cyclooctadiene were placed in a heavy-walled reaction tube equipped with a Teflon valve and charged with 3 atm of H₂. The mixture was stirred vigorously at 130 °C for 24 h. Upon cooling, the solution was transferred to a round-bottomed flask and pulled to dryness. The residue was taken up in 15 mL of petroleum ether and stirred at room temperature to give a yellow solution. Concentration to ~2 mL and filtration yielded 0.080 g (22% yield). Crystals suitable for X-ray diffraction were grown from a benzene solution by slow evaporation. Anal. Calcd for OsP₂F₁₂C₂₀H₂₀: C, 32.44; H, 2.72. Found: C, 32.56; H, 2.86. ¹H NMR (C₆D₆, 400.13 MHz, 20 °C): δ 6.75 (m, 3H; $C_6H_3(CH_2P(CF_3)_2)_2$, 4.19 (br s, 2H; vinylic cod C<u>H</u>), 3.76 (m, 2H; $C_6H_3(C(\underline{H})HP(CF_3)_2)_2)$, 3.25 (dm, ${}^2J_{HH} = 17$ Hz, 2H; $C_6H_3(C(H))$ <u>HP</u>(CF₃)₂)₂)), 2.61 (br s, 2H; vinylic cod C<u>H</u>), 2.25 (m, 4H; cod CH_2 , 1.82 (dd, ${}^2J_{HH} \approx {}^3J_{HH} \approx 17$ Hz, 4H; cod CH_2), -12.65 (t, ${}^2J_{HP}$ = 29 Hz, 1H; Os<u>H</u>). ³¹P{H} NMR (C₆D₆, 161.97 MHz, 20 °C): δ 67.6 (m). ¹⁹F NMR (C₆D₆, 376.50 MHz, 20 °C): δ –56.6 (m, 6F; PC<u>F</u>₃), -64.3 (m, 6F; PC<u>F</u>₃).

 $(\mu^{CF_3}PCPH)Os(H)(\mu-H)(\mu,\eta^6,\kappa^3-CF_3PCP)Os(H)$ (5). A 5 mm NMR tube fitted with a Teflon valve was charged with 5 mg of 4, 0.5 mL of benzene- d_6 and 3 atm of H₂. Warming to 130 °C for 48 h resulted in a solution with 5 as the major species (~55%) as determined by ³¹P NMR. Solutions of 5 can be alternatively prepared by thermolysis of 4 in cyclodecane at 200 °C for one hour. Partial spectroscopic data for 5: ¹H NMR (C_6D_6 , 400.13 MHz, 20 °C): δ –13.36 (ps q, ²J_{HP} = 25 Hz, 1H; OsH), –15.84 (br d, ²J_{HP} = 36 Hz, 2H; exchanging Os(μ -H) and one OsH group). ³¹P{¹H} NMR (C_6D_6 , 161.97 MHz, 20 °C): δ 57.1 (m, overlapping ^{CF₃}PCP and μ -^{CF₃}PCPH resonances). ¹⁹F NMR (C_6D_6 , 376.5 MHz, 20 °C): δ –59.4 (br s, 6F; PCF₃), –63.9 (d, ³J_{FF} = 63 Hz, 6F; PCF₃), –65.3 (d, ³J_{FF} = 66 Hz, 6F; PCF₃), –65.8 (ps t, J_{FP} = 38 Hz, 6F; PCF₃). **Transfer Dehydrogenation Studies.** A typical stock catalyst solution was prepared from 5 mg of (^{CF₃}PCP)Os(cod)H (6.8 μ mol) and 2.75 mL of cyclooctadiene (3,030 equiv). Then 250 μ L of stock solution and 240 μ L of *tert*-butylethylene (3,030 equiv) were added to a 5 mm NMR tube fitted with a Teflon valve with an acetone- d_6 capillary external lock and heated to the desired temperature in an oil bath. NMR tubes were removed from the oil bath periodically and allowed to cool to room temperature before collecting spectra. The equivalents of cyclooctene produced were calculated by integration of the vinylic cyclooctene resonance at δ 4.96 against the vinylic *tert*-butylethylene resonance at δ 5.18.

Acceptorless Dehydrogenation Studies. A typical catalyst solution was prepared from 5 mg of (^{CF₃}PCP)Ru(cod)H (7.7 mol) and 3.12 mL of cyclooctadiene (3030 equiv), and mesitylene (5.3 L, 5 equiv) was added as an internal standard. The solution was refluxed under N₂ for the desired time before cooling to room temperature and withdrawing an aliquot for NMR analysis. The equivalents of cyclooctene produced were calculated by integration of the product vinylic *cis-* and *trans*-cyclodecene resonances at 4.46 and 4.52 ppm, respectively, against the mesitylene aromatic resonance at 5.80 ppm (referenced to an acetone-*d*₆ capillary external lock).

X-ray Crystallography. The X-ray diffraction data for all complexes were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo K α fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). Crystals were attached to glass fibers using Paratone N oil. Collection and refinement details are included in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Text and tables giving X-ray diffraction data collection and refinement details and CIF files giving crystallographic data for complexes 1–4. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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