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Dicarbonyl{[2-(diphenylphosphino)ethyl]cyclopentadienyl} Group VI Metal Hydrides, Halides, and Anions: Precursors for Olefin Epoxidation Catalysts

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Supporting Information

ABSTRACT: Oxidative decarbonylation of (η^5-C_5R_5)Mo(CO)$_3$X and isoelectronic four-legged piano-stool Mo(II) precursors to homogeneous olefin epoxidation catalysts has garnered significant attention as an alternative to organorhenium oxides $RReO_3$. An emerging theme has been the introduction of donor-functionalized cyclopentadienyl ligands to tune catalyst performance. However, the utility of the [2-(diphenylphosphino)ethyl]cyclopentadienyl (Cp^{PPh}) ligand under oxidative decarbonylation conditions has not been explored. The application of Mo(VI) and W(VI) compounds containing mono- and bidentate phosphine oxide ligands as epoxidation catalysts suggests that screening MoX(CO)$_2$(η^5:η^1-Cp^{PPh}) as catalyst precursors is a worthy objective. To this end, HM(CO)$_2$(η^5:η^1-Cp^{PPh}) (M = Cr (**1**), Mo (**2**), W (**3**)) were synthesized; the hydrides **1** and **3** are of interest, since **2** is an established precursor for ionic hydrogenation catalysts. Hydrogen−halogen exchange using **1**−**3** afforded MX(CO)$_2$(η^5:η^1-Cp^{PPh}) (M = Cr, X = I (**4**); M = Mo, X = Cl (**5**), Br (**6**), I (**7**); M = W, X = Br (**8**)), while deprotonation of **1**−**3** provided [K(18C6)][M(CO)$_2$(η^5:η^1-Cp^{PPh})] (M = Cr (**9**), Mo (**10**), W (**11**)). Complexes **1** and **3**−**11** have been characterized in solution and by X-ray crystallography. Treatment of **5**−**7** with *t*-BuOOH resulted in active cyclooctene and 1-dodecene epoxidation catalysts, with conversion curves and activities similar to those afforded by MoCl(CO)$_3$(η^5-C_5R_5) and MoR(CO)$_3$(η^5-C_5R_5) precursors.

INTRODUCTION

The application of cyclopentadienyl molybdenum(II) carbonyl complexes as precursors to Mo(VI) oxidation catalysts has been intensively investigated since 2003, when Kühn and Romão reported the facile preparation of (η^5-C_5R_5)MoO$_2$Cl for olefin epoxidation by reaction of (η^5-C_5R_5)Mo(CO)$_3$Cl and *t*-BuOOH (TBHP).[1] While oxidative decarbonylation of (η^5-C_5R_5)Mo(CO)$_3$X and isoelectronic four-legged piano-stool Mo(II) precursors to homogeneous olefin epoxidation catalysts[2] has garnered significant attention as a less toxic and more economical alternative to organorhenium oxides $RReO_3$,[3] this strategy has been extended to sulfoxidation,[4] olefin cis-dihydroxylation,[5] amine oxidation,[6] and alcohol oxidation.[7] Olefin epoxidation with cyclopentadienyl molybdenum(II) carbonyl precatalysts upon their grafting to molecular sieves and zeolites,[8] introduction into two-phase mixtures with ionic liquids,[9] immobilization in ß-cyclodextrins,[10] and promotion by microwave-assisted heating[11] reflect the tolerance and robustness of these systems.

With (η^5-C_5R_5)Mo(CO)$_3$R and (η^5-C_5R_5)Mo(CO)$_3$X, retention of ancillary R/X and cyclopentadienyl to afford unique catalysts with (η^5-C_5R_5)MoO$_2$ fragments upon oxidative decarbonylation is well established; different tricarbonyl precursor ancillary ligands significantly impact catalyst performance.[1,2] Ligands that render the Mo(II) center less electron rich are advantageous; decreasing Cp donor ability generally increases catalyst activity, as demonstrated by the exceptionally high olefin epoxidation activity of (η^5-($C_5(CH_2Ph)_5$)MoO$_2$Cl.[1]

An emerging theme has been introduction of donor-functionalized cyclopentadienyl ligands to tune catalyst performance (Figure 1).[12] Molybdenum carbonyl complexes

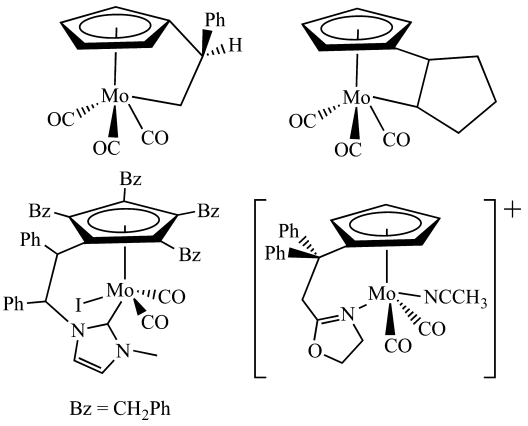

Figure 1. Divalent molybdenum complexes with donor-functionalized cyclopentadienyl ligands that are olefin epoxidation catalyst precursors.

with functionalized η^5-cyclopentadienyl ligands and stereogenic centers located in the tethered side chain are precursors for asymmetric olefin epoxidation catalysts,[13] and related Mo

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complexes with cycloalkyl moieties as pendant units display a high selectivity in the epoxidation of *cis*- and *trans*-stilbene.[14] Molybdenum(II) complexes containing cyclopentadienyl functionalized N-heterocyclic carbenes[15] and Cp ligands bearing a chiral oxazoline pendant group[16] exhibit catalytic olefin epoxidation activity with enhanced stability under oxidative conditions, permitting longer reaction times. The utility of the [2-(diphenylphosphino)ethyl]cyclopentadienyl (Cp^{PPh}) ligand under oxidative decarbonylation conditions has not been explored, undoubtedly due to the expectation of phosphine oxide pendant group formation. However, the application of Mo(VI) and W(VI) compounds containing mono- and bidentate phosphine oxide ligands as epoxidation catalysts with TBHP and H_2O_2 as oxidants suggests that screening $MoX(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ as catalyst precursors is a worthy objective.[17]

Hydrogen−halogen exchange using $HM(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (M = Cr (**1**), Mo (**2**), W (**3**)) was hypothesized as a convenient route to $MX(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$. Bullock reported **2**, $HMo(CO)_2(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR'_2)$ (R′ = Cy, ^{t}Bu), and $HW(CO)_2(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PtBu_2)$ as precursors for solvent-free ketone ionic hydrogenation catalysts.[18] While **2** was fully characterized in solution and the solid state, pure **3** could not be isolated, due to the high kinetic stability of the $HW(CO)_3(\eta^5\text{-}Cp^{PPh})$ intermediate.[18a]

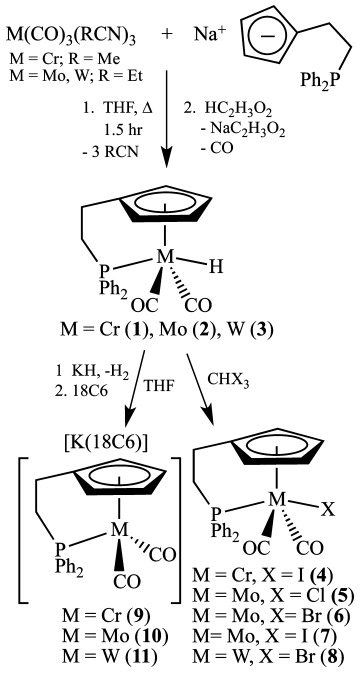
As part of our ongoing exploration of Cp^{PPh} group VI metal carbonyl complexes,[19] we have fully characterized hydrides **1** and **3** and have explored the reactivity of **1**−**3** toward hydrogen−halogen exchange and deprotonation. The resulting metal halides $MX(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (M = Cr, X = I (**4**); M = Mo, X = Cl (**5**), Br (**6**), I (**7**); M = W, X = Br (**8**) and $[K(18C6)][M(CO)_2((\eta^5{:}\eta^1\text{-}Cp^{PPh})]$ (M = Cr (**9**), Mo (**10**), W (**11**)),[20] salts of the hydride conjugate bases, have been characterized in solution and by X-ray crystallography. The utility of **5**−**7** as catalyst precursors for cyclooctene and 1-dodecene epoxidation with TBHP as an oxidant was investigated for comparison to the $MoCl(CO)_3(\eta^5\text{-}Cp)$ benchmark.

RESULTS AND DISCUSSION

Synthesis and Characterization. Moderately air-sensitive, pale yellow (**1**) and colorless (**3**) microcrystalline hydrides were synthesized (Scheme 1) via a modification of the procedure reported for **2**.[18a] Reactions of $NaCp^{PPh}$ [21] and $M(CO)_3(RCN)_3$ provided $Na[M(CO)_3(\eta^5\text{-}Cp^{PPh})]$ on the basis of IR spectroscopy.[19b] Addition of acetic acid resulted in formation of $HM(CO)_3(\eta^5\text{-}Cp^{PPh})$; the chromium hydride converted to dicarbonyl **1** within 1 h at ambient temperature. The kinetic stability of intermediate $HW(CO)_3(\eta^5\text{-}Cp^{PPh})$ (**12**)[18a] toward CO dissociation and intramolecular pendant phosphine coordination was surmounted by an extended toluene reflux of mixtures of **3** and **12**. Pure **3** was ultimately separated from residual **12** by fractional crystallization. Decomposition of **12** and **3** under reflux is likely responsible for the reduced isolated yield of analytically pure **3** (36%) relative to **1** (70%).[22]

Hydrides of general formula $HCr(CO)_2(PR_3)(\eta^5\text{-}Cp)$ have been of interest as trapping products of 17-electron $Cr(CO)_2(PR_3)(\eta^5\text{-}Cp)$,[23] but solution NMR and IR spectroscopic data have only been reported for $HCr(CO)_2(PPh_3)(\eta^5\text{-}Cp)$ and $HCr(CO)_2(PPh_2(C_6H_{11}))(\eta^5\text{-}Cp)$ (**13**).[23b,e] The IR ν(CO) spectral data of **1** and **13** in toluene (**1**, 1930, 1857 cm^{-1}; **13**, 1925, 1858 cm^{-1}) and their ^{1}H NMR Cr−H doublets

Scheme 1



(**1**, δ −5.66 ($^2J_{PH}$ = 66), **13**, δ −5.56 ($^2J_{PH}$ = 80) are very similar. Isoelectronic $HW(CO)_3(PPh_3)(\eta^5\text{-}Cp)$ (**14**)[24] and **3** exhibit nearly indistinguishable IR ν(CO) spectra (**3**, 1936, 1856 cm^{-1}; **14**, 1944, 1865 cm^{-1}) and broad ^{1}H NMR W−H singlets at ambient temperature (**3**, δ −6.80; **14**, δ −6.97). These data confirm weaker donation of PPh_3 and pendant 2-(diphenylphosphino)ethyl tethered ligand, respectively, relative to that in $HW(CO)_2(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2)$ (IR ν(CO), 1917, 1836 cm^{-1}; ^{1}H NMR, W−H δ −7.29 (d, $^2J_{PH}$ = 27.1)).[18a] Broad resonances in the ^{1}H and ^{31}P NMR spectra of **3** (e.g., ^{31}P NMR δ 40.8 (s, $w_{1/2}$ = 38 Hz)) are reminiscent of those exhibited by **14**[24] and **2**,[18a] indicative of cis−trans isomerization in solution. Isomerization between the cis and trans isomers of $HMo(CO)_2(PR_3)(\eta^5\text{-}Cp)$ has long been known[25] and was recently examined in the related $HMo(CO)_2(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR_2)$ (R = Ph (**2**), Cy, ^{t}Bu).[18a]

Deprotonation of **1**−**3** with KH, followed by complexation with 18C6, afforded salts **9**−**11** as analytically pure bright yellow to orange microcrystals in 50−80% yields (Scheme 1). The zerovalent chromium anion of **9** is related to $[Cr(CO)_2(PR_3)(\eta^5\text{-}Cp)]^-$ (R = Ph, Et, OCH_3); the PEt_3 dicarbonyl anion is sufficiently electron rich to engage unique charge transfer with bis(triphenylphosphine)iminium (PPN^+).[26] The IR ν(CO) spectra of **9** and $[Et_4N][Cr(CO)_2(PPh_3)(\eta^5\text{-}Cp)]$ (**15**) in THF (**1**, 1785, 1700 cm^{-1}; **15**, 1780, 1704 cm^{-1}) are unsurprisingly very similar. Charge transfer between the cation and anion in **15** was deemed essentially absent in THF. The nearly identical IR ν(CO) spectra of **9** in both THF and Nujol (1781, 1698 cm^{-1}) suggest the extent of interaction between $[K(18C6)]^+$ and $[Cr(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})]^-$ is not significantly different in these media. The anions of **10** and **11** are isoelectronic with $[Mo(CO)_2(PPh_3)(\eta^5\text{-}Cp)]^-$ [27a] and $[M(CO)_2(P(OMe)_3)(\eta^5\text{-}Cp)]^-$ (M = Mo, W).[27b] These readily accessible yet highly nucleophilic species continue to find application. It was recently reported that N−O ligand bond cleavage occurs, resulting in CO_2 release, when $[M(CO)_2L(\eta^5\text{-}Cp)]^-$ (M = Mo, W; L =

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PPh_3, $P(OMe)_3$) react with $[M'(CO)_2(NO)(\eta^5\text{-Cp}')]BF_4$ (M′ = Mn, Re) to give the heterobimetallic derivatives $[MM'(\eta^5\text{-Cp})(\eta^5\text{-Cp}')(\mu\text{-N})(CO)_3L]$ with linearly bridging nitride ligands.[28] The anions of **10** and **11** are worthy alternatives for these studies, due to their slightly more electron rich metal centers, coupled with the kinetic stability for phosphine binding leveraged by $\eta^5{:}\eta^1\text{-Cp}^{PPh}$ ligand chelation. The ^{13}CO NMR resonances for **9**−**11** ((C_4D_8O) **9**, δ 252; **10**, δ 242; **11**, δ 232) are 5−6 ppm downfield from those of $[K(18C6)][M(CO)_3(\eta^5\text{-Cp}^{PPh})]$ (M = Cr (**16**), Mo (**17**), W (**18**))[19b] with unbound tethered phosphines ((CD_3CN) **16**, δ 247; **17**, δ 237; **18**, δ 227). The substitution of a carbonyl ligand in **16**−**18** by the phosphine of the Cp^{PPh} ligand has a rather modest effect on the chemical shift of the ^{13}CO NMR resonances.

Hydrides **1**−**3** react with haloforms, resulting in divalent group VI metal halides **4**−**8** (Scheme 1) in 50−75% yields. Immediately upon CHX_3 addition, solutions contain kinetic mixtures of cis and trans isomers on the basis of IR spectroscopy.[29] These metal dicarbonyl halides react slowly with haloforms, or presumed methylene halide products, to afford uncharacterized species; prompt workup is necessary to obtain pure **4**−**8**. Isomerization leading to enrichment in the trans isomers occurs during the workup. The consistently obtained ratios of trans to cis isomers in analytically pure isolated samples on the basis of ^{31}P NMR spectroscopy range from 74:26 (**4**), to 80:20 (**5**), 93:7 (**6**), 94:6 (**8**), and 100:0 (**7**, cis undetectable). Thermodynamic and kinetic investigations of these isomerizations have not been carried out to date. Four-legged piano-stool complexes **4**−**8** are analogous to classical $MX(CO)_2(PPh_3)(\eta^5\text{-Cp})$;[30] the latter parent Cp complex with X = Br has been utilized recently as a precursor to cyclopentadienyl molybdenum(II) N-heterocyclic carbene complexes.[15]

Structural Characterization. Hydride **1** (Figure 2) joins **13**[23c] as the only structurally characterized $HCr(CO)_2(PR_3)(\eta^5\text{-Cp})$ complexes. Although the hydride position could not be determined in **13**, its position was inferred as cis relative to the phosphine on the basis of a large P−Cr−C(O) angle (106.2(2)°). The hydride ligand of **1** was located trans to the pendant phosphine, with large P−Cr−H (134.8(9)°) and C(1)−Cr−C(2) (102.04(7)°) angles supportive of this isomer. The apparent Cr−H distance (1.52(2) Å) in **1** is significantly longer than that recently determined for $HCr(CO)_3(\eta^5\text{-Cp})$ (1.30(6) Å) but very similar to the DFT calculated distance in $HCr(CO)_3(\eta^5\text{-Cp})$ (1.58 Å).[31] This DFT study suggested that in X-ray crystallography a Cr−H distance between 1.45 and 1.50 Å is reasonable for this class of complexes.[31] Tungsten hydride **3** (Figure 3) is isostructural with Mo−H **2**, with the hydride trans to the phosphine. The W−H distances in **3** (1.65(3) Å), **2** (1.680(23) Å),[18a] and $HW(CO)_3(\eta^5\text{-Cp})$ (1.61(8) Å)[31] are statistically indistinguishable and longer than the apparent W−H distance in *cis*-$WH(CO)_2(PMe_3)(\eta^5\text{-Cp})$ (1.30(8) Å).[32] The DFT calculated W−H distance in $HW(CO)_3(\eta^5\text{-Cp})$ is 1.72 Å, and W−H distances are typically underestimated by X-ray crystallography.[31]

Salts **9**−**11**, containing three-legged piano stool anions, were characterized by X-ray crystallography. The molecular structure of **10** is shown in Figure 4; those of **9** and **11** are given in the Supporting Information. Caulton's $[Cat][Cr(CO)_2(PEt_3)(\eta^5\text{-Cp})]$ (Cat = Et_4N, PPN) and Bullock's $[C_5H_9N_2][W(CO)_2(PMe_3)(\eta^5\text{-Cp})]$ are the only previous structurally characterized salts containing an anion of general formula $[M(CO)_2(PR_3)(\eta^5\text{-Cp})]^-$.[26] In both triethylphosphine-substituted chromium salts, no structural perturbations due to cation/anion interactions were observed in the solid state, despite ion pairing in THF solutions of $[PPN][Cr(CO)_2(PEt_3)(\eta^5\text{-Cp})]$ resulting in charge transfer from the anion to the cation.[26a] While solvent molecules do not occupy the axial positions of $[K(18C6)]^+$ in the related **9**, and the

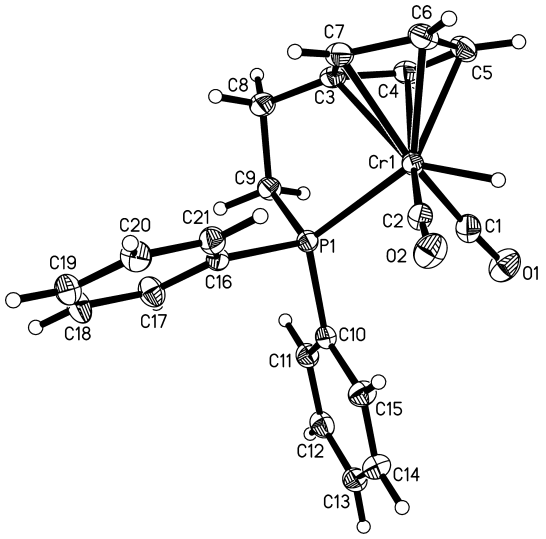

Figure 2. Molecular structure of **1** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.8241(16), Cr−C(2) = 1.8202(16), Cr−P = 2.3072(4), Cr−H = 1.52(2), Cr−C(3) = 2.2248(15), Cr−C(4) = 2.2180(15), Cr−C(5) = 2.1775(15), Cr−C(6) = 2.1715(16), Cr−C(7) = 2.2029(15), Cr−C(dienyl) (av) = 2.20(2), C(1)−O(1) = 1.1627(19), C(2)−O(2) = 1.1689(19); C(1)−Cr−C(2) = 102.04(7), C(2)−Cr−P = 90.87(5), C(1)−Cr−P = 84.70(5), P−Cr−H = 134.8(9), C(1)−Cr−H = 67.6(9), C(2)−Cr−H = 62.9(9), Cr−P−C(9) = 104.25(5).

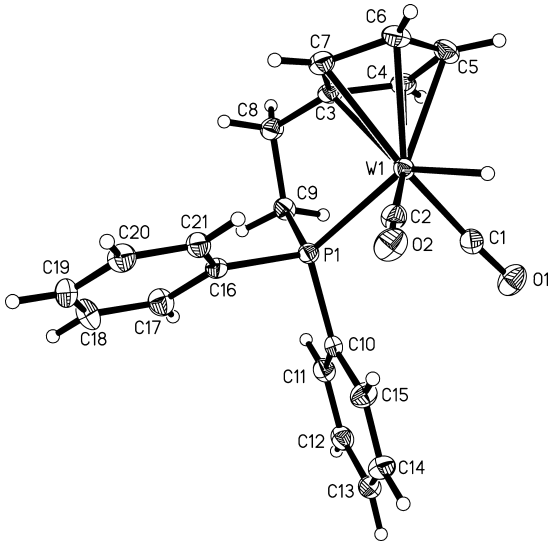

Figure 3. Molecular structure of **3** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): W−C(1) = 1.961(3), W−C(2) = 1.954(3), W−P = 2.4309(6), W−H = 1.65(3), W−C(3) = 2.360(2), W−C(4) = 2.374(2), W−C(5) = 2.318(2), W−C(6) = 2.305(2), W−C(7) = 2.342(2), W−C(dienyl) (av) = 2.34(3), C(1)−O(1) = 1.160(3), C(2)−O(2) = 1.166(3); C(1)−W−C(2) = 99.47(10), C(2)−W−P = 89.35(7), C(1)−W−P = 83.32(7), P−W−H = 138.2(12), C(1)−W−H = 69.8(12), C(2)−W−H = 65.3(12), W−P−C(9) = 103.36(8).

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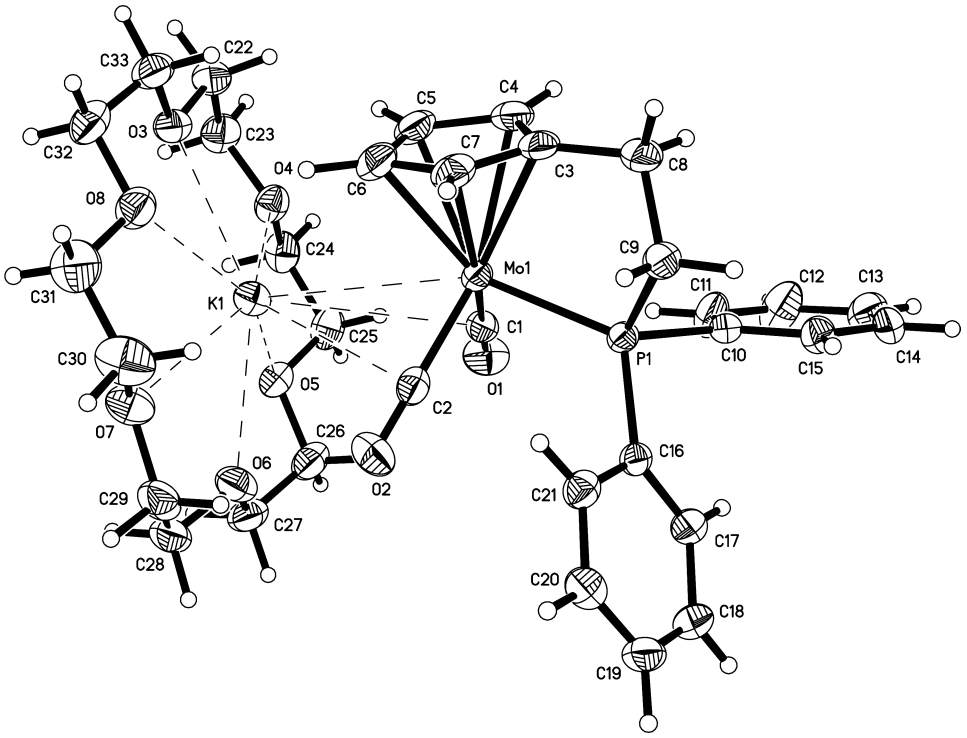

Figure 4. Molecular structure of **10** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo−C(1) = 1.928(2), Mo−C(2) = 1.916(2), Mo−P = 2.3566(5), C(1)−O(1) = 1.191(2), C(2)−O(2) = 1.182(2), Mo−C(3) = 2.3504(18), Mo−C(4) = 2.3735(19), Mo−C(5) = 2.3534(18), Mo−C(6) = 2.3458(19), Mo−C(7) = 2.3595(19), Mo−C(dienyl) (av) 2.36(1), K−Mo = 3.7562(5); C(1)−Mo−C(2) = 89.52(8), P−Mo−C(1) = 95.58(5), P−Mo−C(2) = 90.96(6), Mo−P−C(9) = 103.59(6).

potassium ion is directed toward the Cr center (K−Cr = 3.7128(9) Å), the C(1)−Cr−C(2) angle in **9** (90.26(7)°), one that might be expected to widen due to approach of the cation, is very similar to that in $[Et_4N][Cr(CO)_2(PEt_3)(\eta^5\text{-Cp})]$ (90.00(13)°). No perturbation of the anion of **9** due to its electrostatic interaction with $[K(18C6)]^+$ is detectable. Neither is distortion of the three-legged piano-stool geometries evident in the more electron-rich and isostructural anions of **10** and **11**, which feature slightly longer K−M separations (**10**, 3.7562(5) Å; **11**, 3.7611(10) Å) and unremarkable C(1)−M−C(2) angles (**10**, 89.52(8)°; **11**, 89.98(16)°) despite the cation approach. The steric impact of the coordinated phosphine in **9**−**11** is mostly manifested by expansion of the P−M−C(1) angle (**9**, 97.09(5)°; **10**, 95.58(5)°; **11**, 95.79(11)°). These angles are roughly 10° larger than the average O(C)−M−C(O) angles that define the three-legged piano-stool geometries of $[K(18C6)][M(CO)_3(\eta^5\text{-Cp}^{PPh})]$ (**16**, 87(1)°; **17**, 85.0(6)°; **18**, 85.5(5)°).[19b] The P−W−C(O) angles in **11** (91.17(12), 95.79(11)°; the O(C)−W−C(O) angle is 89.98(16)°) are also substantially larger relative to the corresponding angles in $[C_5H_9N_2][W(CO)_2(PMe_3)(\eta^5\text{-Cp})]$ (86.68(10), 86.45(8)°; the (O)C−W−C(O) angle is 90.32(12)°). This is interesting since the W−P distances in **11** (2.3539(10) Å) and $[C_5H_9N_2][W(CO)_2(PMe_3)(\eta^5\text{-Cp})]$ (2.3646(10) Å) are nearly identical.[26b] On the basis of these structural parameters, the impact of trimethylphosphine is less relative to the tethered diphenylphosphinoethyl ligand in this system. It is noteworthy that the average Cr−C(O), C−O, and Cr−C(dienyl) distances in **9** (1.793(7), 1.187(4), 2.20(1) Å), as well as the average W−C(O), C−O, and W−C(dienyl) lengths in **11** (1.921(8), 1.191(5), 2.35(1) Å), are statistically indistinguishable from the corresponding averages in **16** (1.80(1), 1.179(4), 2.23(2) Å) and **18** (1.913(6), 1.198(6), 2.38(3) Å), respectively. The different donor/acceptor ability of the pendant phosphine relative CO does not significantly impact these structural parameters.

The four-legged piano-stool structures of metal halides **4**−**8** were determined by X-ray crystallography and are displayed in Figure 5 (**5**) and the Supporting Information (**4**, **6**−**8**). In each case, crystals of trans isomers (the more prevalent isomer in isolated bulk samples on the basis of NMR spectroscopy) were selected for analysis, but visual differences among crystals of **4**−**8**, respectively, could not be perceived. Few chromium iodides of general formula $CrI(CO)_{3-x}(PR_3)_x(\eta^5\text{-Cp})$ (x = 0, 1) have been structurally characterized, with $[CrI(CO)_3(\eta^5\text{-}C_5H_4(CH_2)_2NMe_3]I$[33] (**19**) and **4** the only examples. The Cr−I and average Cr−(dienyl) distances in **4** (2.8094(4), 2.21(2) Å) and **19** (2.7817(8), 2.19(3) Å) are nearly identical. Substitution of a more bulky pendant phosphine for CO trans to the iodide ligand modestly impacts angles between the trans ligands of the $CrI(CO)_2(PR_3)$ fragment; these angles in **4** (C(1)−Cr−C(2), 106.69(10)°; P−Cr−I, 140.34(2)°) are roughly 10° more acute and obtuse, respectively, than the related angles in **19** (116.5(2)°, 131.71(17)°). Complexes **5**−**8** join $MoX(CO)_2(PPh_3)(\eta^5\text{-Cp})$ (X = Br,[34a] I[34b]), $MoI(CO)_2(P^nBu_3)(\eta^5\text{-Cp})$,[34c] $MoI(CO)_2(PEt_2Ph)(\eta^5\text{-Cp})$,[34d] and $WCl(CO)_2(PH(^tBu)_2)(\eta^5\text{-Cp})$[34e] as structurally characterized $M'X(CO)_2(PR_3)(\eta^5\text{-Cp})$ (M′ = Mo, W) complexes. The geometric parameters that define the unremarkable four-legged piano-stool structures of **5**−**8**, except for the increasing M−X lengths with greater halide radius (**5**, 2.5338(6) Å; **6**, 2.6647(4) Å; **7**, 2.8619(6) Å; **8**, 2.6654(10) Å), are nearly indistinguishable.

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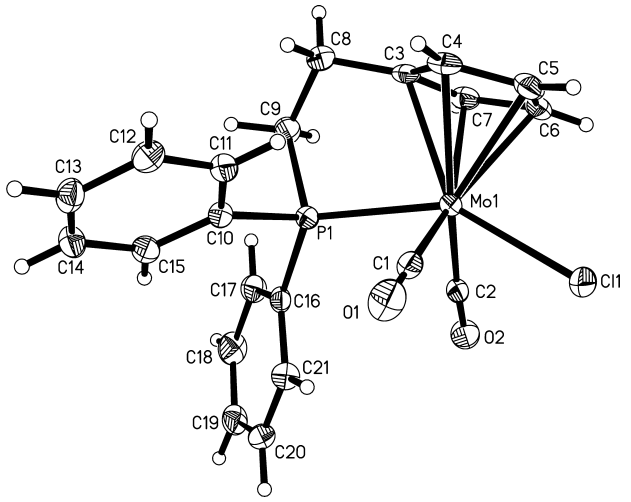

Figure 5. Molecular structure of **5** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo−C(1) = 2.000(2), Mo−C(2) = 1.992(2), Mo−P = 2.4695(6), Mo−Cl = 2.5338(6), Mo−C(3) = 2.349(2), Mo−C(4) = 2.370(2), Mo−C(5) = 2.329(2), Mo−C(6) = 2.317(2), Mo−C(7) = 2.347(2), Mo−C(dienyl) (av) = 2.34(2), C(1)−O(1) = 1.129(3), C(2)−O(2) = 1.138(2); C(1)−Mo−C(2) = 103.53(8), C(2)−Mo−P = 80.87(6), C(1)−Mo−P = 80.95(6), P−Mo−Cl = 145.625(19), C(1)−Mo−Cl = 78.23(6), C(2)−Mo−Cl = 77.83(6), Mo−P−C(9) = 105.77(7).

Olefin Epoxidation Catalysis. Complexes **5**−**7** were examined as precatalysts for the epoxidation of cyclooctene and 1-dodecene with *tert*-butyl hydroperoxide (TBHP) by employing the in situ catalyst generation protocol pioneered by Kühn and Romão[1] to examine the impact of the pendant phosphine and halide variation on catalytic activities. Standard conditions ($CHCl_3$, 55 °C, precatalyst:alkene substrate:TBHP = 0.01:1:2 (1 mol % catalyst loading), alkene concentration 0.84 M) were employed to permit direct comparison to related four-legged piano-stool molybdenum(II) precatalysts. Control experiments showed that no significant amount of epoxide formed in the absence of precatalyst. Treatment of **5**−**7** with TBHP resulted in active cyclooctene epoxidation catalysts, with conversion curves (Figure 6) similar to those afforded by $MoCl(CO)_3(\eta^5\text{-}C_5R_5)$ and $MoR(CO)_3(\eta^5\text{-}C_5R_5)$ precursors.[1,2]

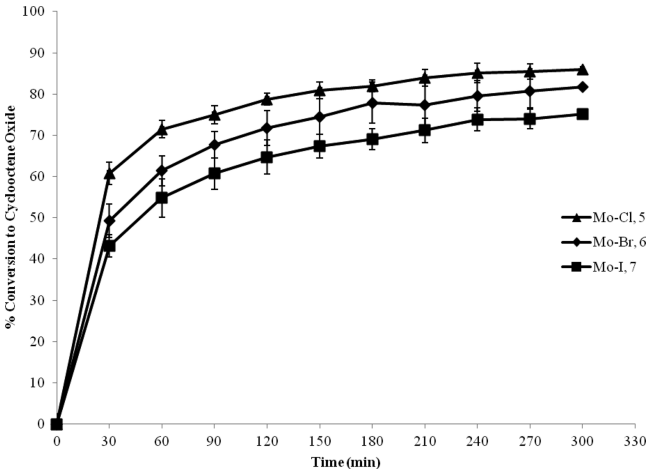

Figure 6. Time-dependent conversion of cyclooctene (0.84 M) to cyclooctene oxide using **5**−**7** as catalyst precursors at 55 °C in $CHCl_3$ ((**5**−**7**):cyclooctene:TBHP = 0.01:1:2 (1 mol % catalyst loading)).

No appreciable oxidation products other than cyclooctene oxide (e.g., diols or other byproducts) were observed by GC/MS during these reactions. With **5**−**7**, essentially quantitative conversion to cyclooctene oxide occurred within 24 h, with catalytic epoxidation activity still evident at this point upon injection of additional cyclooctene. After 5 h of reaction time (Figure 6), conversions to cyclooctene oxide did not vary dramatically with precatalyst (**5**, 86(2)%; **6**, 82(4)%; **7**, 75(2)%). However, initial catalyst TOF (measured at 2 min into each catalytic run for comparison to TOF values measured by Kühn and Romão[1]) afforded by oxidation of **5** (1400 h^{-1}) was significantly higher than those of **6** (370 h^{-1}) and **7** (230 h^{-1}). The highly electronegative chloride ligand renders its catalyst most active toward cyclooctene, as expected. It is noteworthy that precatalyst **5**, despite the coordinated phosphine, affords a catalyst with a TOF very similar to that produced by $MoCl(CO)_3(\eta^5\text{-Cp})$ (**20**); an initial TOF of 1300 h^{-1} was determined for the latter via the same precatalyst to cyclooctene to TBHP ratio (0.01:1:2 (1 mol % catalyst loading)) at 55 °C in $CHCl_3$.[1] However, the catalyst afforded by oxidative decarbonylation of **20** effected 100% conversion of cyclooctene to cyclooctene oxide after 4 h under the same conditions. The reduced activities of the catalysts afforded by **5**−**7** relative to that from **20** may be due to the reduced solubilities of the former catalysts in $CHCl_3$. While **20** gives a yellow-orange solution in $CHCl_3$ upon oxidative decarbonylation,[1] **5**−**7** afford white suspensions. The unactivated alkene 1-dodecene was much less reactive than cyclooctene toward the catalysts generated by **5**−**7**, with relatively low conversions to 1,2-epoxydodecane after 24 h (**5**, 38(4)%; **6**, 33(2)%; **7**, 19(3)%). No diols or other byproducts were detected by GC/MS during these catalyst trials, run under the same conditions as those described for cyclooctene epoxidation. It is noteworthy that this conversion from catalyst precursor **5** is higher than that reported for **20** and 1-octene under the same conditions (<20% conversion to 1,2-epoxyoctane after 24 h).

Attempts to isolate these presumed $MoXO_2(\eta^5\text{-Cp})$ catalysts via oxidative decarbonylation of **5**−**7** were unsuccessful due to their apparent temperature instability as solids. However, conversion of precatalysts **5**−**7**, respectively, to catalysts was examined by ^{31}P NMR spectroscopy in $CDCl_3$. In each case, the ^{31}P resonances due to the cis and trans isomers of **5**− **7** disappeared upon addition of TBHP with the appearance of a single resonance (**5**, δ 36.28; **6**, δ 36.18; **7**, δ 35.03) indicative of phosphine oxide (e.g., δ (Ph_3PO) ($CDCl_3$) 29.0). These data suggest the olefin epoxidation catalysts afforded by oxidative decarbonylation of **5**−**7** are $MO_2X(\eta^5\text{-}C_5H_4(CH_2)_2P(O)Ph_2)$ with dangling phosphine oxide pendant groups. There is no spectroscopic evidence for a phosphine oxide to metal interaction that could modulate catalyst activity. While these complexes are clearly viable olefin epoxidation catalysts, the lack of apparent advantages leveraged by a pendant phosphine oxide outweighs the disadvantages of **5**−**7** phosphine ligand oxidation consuming additional TBHP and the reduced catalyst solubility relative to $MoO_2Cl(\eta^5\text{-Cp})$ likely produced by this pendant group. The development of Cp^{PPh} metal complexes as catalysts for organic transformations continues in this research group.

EXPERIMENTAL SECTION

Similar procedures were conducted to synthesize **1** and **3**, **4**−**8**, and **9**−**11**, respectively. Representative procedures for **1**, **5**, and **9** are

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provided below. General procedures and complete experimental details are given in the Supporting Information.

$HCr(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (1). THF (50 mL) was added to $Cr(CO)_3(CH_3CN)_3$ (0.690 g, 2.66 mmol) and $NaCp^{PPh}$ (0.800 g, 2.66 mmol); the yellow solution was refluxed for 1.5 h. Addition of a 10% v/v glacial acetic acid/THF solution (1.61 mL, containing 0.168 g, 2.80 mmol of $HC_2H_3O_2$) resulted in a viscous solution, which was stirred for 1 h until all $Na[Cr(CO)_3(\eta^5\text{-}Cp^{PPh})]$ was consumed and **1** was the only carbonyl complex in solution. The solvent was removed in vacuo, and toluene (50 mL) was added to extract the hydride. The bright yellow solution was filtered through Celite. The filtrate was concentrated in vacuo until ~10 mL remained; the filtrate was cooled to −40 °C. Addition of pentane (25 mL, −30 °C) resulted in the precipitation of a yellow solid that was isolated by filtration at −30 °C, washed with pentane (−35 °C, 3 × 15 mL), and dried in vacuo. Recrystallization from toluene/pentane (−20 °C) provided yellow, air-sensitive microcrystals (0.725 g, 70%). Anal. Calcd for $C_{21}H_{19}O_2CrP$: C, 65.29; H, 4.96. Found: C, 65.16; H, 5.33. Mp: 136−137 °C dec. IR: in THF, ν(CO) 1928 (s), 1855 (m) cm^{-1}; in toluene, ν(CO) 1930 (s), 1857 (m) cm^{-1}; in Nujol, ν(CO) 1945 (s), 1938 (s, sh), 1854 (s, sh), 1836 (s), 1780 (m) cm^{-1}. ^1H NMR (C_4D_8O, 400 MHz): δ 7.60−7.55 (m, 4H, ortho, Ph), 7.39−7.31 (m, 6H, meta/para, Ph), 4.81 (app t, 2H, J = 2.0, Cp), 4.60 (app t, 2H, J = 2.0, Cp), 3.16 (dt, 2H, $^3J_{PH}$ = 8.8, J_{HH} = 7.2, CH_2CH_2P), 2.24 (dt, 2H, $^2J_{PH}$ = 23.6, J_{HH} = 7.2, CH_2CH_2P), −5.66 (d, 1H, $^2J_{PH}$ = 65.6, CrH). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 244.6 (d, $^2J_{PC}$ = 24.1, CO), 139.8 (d, J_{PC} = 19.1, ipso, Ph), 132.7 (d, $^2J_{PC}$ = 9.7, ortho, Ph), 130.8 (d. $^4J_{PC}$ = 1.8, para, Ph), 129.0 (d, $^3J_{PC}$ = 9.5, meta, Ph), 120.6 (d, $^3J_{PC}$ = 3.6, quat, Cp), 86.0 (s, Cp), 82.0 (s, Cp), 49.3 (d, J_{PC} = 27.9, CH_2CH_2P), 22.2 (d, $^2J_{PC}$ = 7.7, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 94.6 (s, $w_{1/2}$ = 8 Hz, PPh_2). While satisfactory elemental analyses were obtained for solvent-free **1**, NMR spectra of recrystallized **1** consistently indicated trace toluene even after extended drying (4 h) in vacuo.

$HW(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (3). Yield: 36%. Anal. Calcd for $C_{21}H_{19}O_2PW$: C, 48.67; H, 3.70. Found: C, 48.72; H, 4.16. Mp: 189−190 °C dec. IR: in toluene, ν(CO) 1936 (m), 1859 (s) cm^{-1}; in Nujol, ν(CO) 1922 (s), 1840 (s) cm^{-1}. ^1H NMR (C_4D_8O, 400 MHz): δ 7.59−7.53 (m, 4H, ortho, Ph), 7.42−7.34 (m, 6H, meta/para, Ph), 5.42 (s, br, 2H, Cp), 5.07 (s, br, 2H, Cp), 3.15 (s, br, 2H, CH_2CH_2P), 2.35 (dt, 2H, $^2J_{PH}$ = 26.8, J_{HH} = 7.0, CH_2CH_2P), −6.80 (s, br, 1H, WH). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 219.5 (s, br, CO), 135.8 (m, ipso, Ph), 132.2 (d, $^2J_{PC}$ = 10.6, ortho, Ph), 129.6 (d. $^4J_{PC}$ = 1.8, para, Ph), 128.0 (d, $^3J_{PC}$ = 10.0, meta, Ph), 121.8 (s, br, quat, Cp), 86.3 (s, br, Cp), 77.3 (s, br, Cp), 47.6 (s, br, CH_2CH_2P), 21.7 (d, $^2J_{PC}$ = 6.3, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 40.8 (s, br, $w_{1/2}$ = 38 Hz ($^{183}W-^{31}P$ satellites: 41.7 (s, br), 39.9 (s, br), J_{WP} = 292), PPh_2).

$CrI(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (4). Yield: 61%. Anal. Calcd for $C_{21}H_{18}O_2CrIP$: C, 49.24; H, 3.54. Found: C, 49.12; H, 3.81. Mp: 133−134 °C dec. IR: in benzene, ν(CO) 1961 (s), 1893 (m) cm^{-1}; in Nujol, ν(CO) 1955 (m, sh), 1947 (m), 1873 (s) cm^{-1}. NMR spectroscopy indicated a 74:26 trans:cis mixture. Data for *trans*-**4** are as follows. ^1H NMR (C_4D_8O, 400 MHz): δ 7.66−7.59 (m, 4H, ortho, Ph), 7.44−7.42 (m, 6H, meta/para, Ph), 5.21 (app. t, 2H, J = 2.2, Cp), 5.06 (app. quartet, 2H, J = 1.4, Cp), 3.17 (dt, 2H, $^3J_{PH}$ = 9.6, J_{HH} = 7.2, CH_2CH_2P), 2.20 (dt, 2H, $^2J_{PH}$ = 21.5, J_{HH} = 7.2, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 250.1 (d, $^2J_{PC}$ = 44.2, CO), 137.1 (d, $^2J_{PC}$ = 41.3, ipso, Ph), 133.2 (s, br, ortho, Ph), 131.3 (s, br, para, Ph), 129.5 (s, br, meta, Ph), 118.0 (d, $^3J_{PC}$ = 6.3, quat, Cp), 94.4 (s, Cp), 89.9 (s, br, Cp), 47.8 (m, CH_2CH_2P), 21.4 (m, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 95.0 (s, PPh_2).

$MoCl(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (5). Chloroform (35 mL) was added to **2** (0.400 g, 0.930 mmol), affording a deep red solution. The reaction was complete within 10 min on the basis of IR spectroscopy. The solvent was immediately removed in vacuo; the residue was dissolved in benzene (50 mL). The solution was filtered through Celite and concentrated to ~2 mL in vacuo. The addition of Et_2O (50 mL) afforded a microcrystalline red solid. Recrystallization from benzene/Et_2O (0 °C) afforded deep red microcrystals (0.233 g, 54%). Anal. Calcd for $C_{21}H_{18}O_2ClMoP$: C, 54.27; H, 3.90. Found: C, 54.37; H, 4.28. Mp: 150−153 °C dec. IR: in $CHCl_3$, ν(CO) 1987 (m), 1902 (s) cm^{-1}; in benzene, ν(CO) 1982 (m), 1901 (s) cm^{-1}; in Nujol, ν(CO) 1971 (s), 1949 (m, sh), 1886 (s) cm^{-1}. NMR spectroscopy indicated a 80:20 trans:cis mixture. Data for *trans*-**5** are as follows. ^1H NMR (C_4D_8O, 400 MHz): δ 7.68−7.63 (m, 4H, ortho, Ph), 7.51−7.48 (m, 6H, meta/para, Ph), 5.88 (m, 2H, Cp), 5.29 (app. t, 2H, J = 2.4, Cp), 2.85 (dt, 2H, $^3J_{PH}$ = 9.2, J_{HH} = 6.9, CH_2CH_2P), 2.17 (dt, 2H, $^2J_{PH}$ = 27.8, J_{HH} = 7.0, CH_2CH_2P) $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 233.1 (d, $^2J_{PC}$ = 22.1, CO), 135.2 (d, $^2J_{PC}$ = 44.8, ipso, Ph), 132.1 (d, $^2J_{PC}$ = 9.9, ortho, Ph), 130.3 (d, $^4J_{PC}$ = 2.3, para, Ph), 128.5 (d, $^3J_{PC}$ = 10.0, meta, Ph), 114.9 (d, $^3J_{PC}$ = 5.5, quat, Cp), 97.8 (s, Cp), 91.5 (s, Cp), 44.5 (d, J_{PC} = 28.8, CH_2CH_2P), 21.1 (d, $^2J_{PC}$ = 6.9, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 73.6 (s, PPh_2).

$MoBr(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (6). Yield: 68%. Anal. Calcd for $C_{21}H_{18}O_2BrMoP$: C, 49.54; H, 3.56. Found: C, 49.77; H, 3.86. Mp: 193−194 °C dec. IR: in THF, ν(CO) 1977 (m), 1897 (s) cm^{-1}; in Nujol, ν(CO) 1984 (m), 1976 (m), 1953 (w), 1887 (vs), 1862 (s, sh) cm^{-1}. NMR spectroscopy indicated a 93:7 trans:cis mixture. Data for *trans*-**6** are as follows. ^1H NMR (C_4D_8O, 400 MHz): δ 7.65−7.59 (m, 4H, ortho, Ph), 7.48−7.45 (m, 6H, meta/para, Ph), 5.79 (m, 2H, Cp), 5.30 (app t, 2H, J = 2.4, Cp), 2.88 (dt, 2H, $^3J_{PH}$ = 9.2, J_{HH} = 6.8, CH_2CH_2P), 2.13 (dt, 2H, $^2J_{PH}$ = 28.0, J_{HH} = 7.0, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 232.2 (d, $^2J_{PC}$ = 22.5, CO), 136.0 (d, $^2J_{PC}$ = 45.2, ipso, Ph), 133.3 (d, $^2J_{PC}$ = 9.7, ortho, Ph), 131.4 (d, $^4J_{PC}$ = 2.5, para, Ph), 129.5 (d, $^3J_{PC}$ = 10.0, meta, Ph), 117.3 (d, $^3J_{PC}$ = 5.9, quat, Cp), 97.2 (s, Cp), 92.3 (s, Cp), 46.3 (d, J_{PC} = 29.3, CH_2CH_2P), 21.9 (d, $^2J_{PC}$ = 6.4, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 72.0 (s, PPh_2).

$MoI(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (7). Yield: 74%. Anal. Calcd for $C_{21}H_{18}O_2IMoP$: C, 45.37; H, 3.26. Found: C, 45.47; H, 3.59. Mp: 203−205 °C dec. IR: in benzene, ν(CO) 1969 (m), 1894 (s) cm^{-1}; in THF, ν(CO) 1968 (m), 1893 (s) cm^{-1}; in Nujol, ν(CO) 2036 (w), 2018 (w), 1961 (m, sh), 1952 (M), 1873 (s) cm^{-1}. NMR spectroscopy indicated only the trans isomer. ^1H NMR (C_4D_8O, 400 MHz): δ 7.68−7.62 (m, 4H, ortho, Ph), 7.50−7.48 (m, 6H, meta/para, Ph), 5.70 (app. t, 2H, J = 2.2, Cp), 5.42 (app t, 2H, J = 2.4, Cp), 3.02 (dt, 2H, $^3J_{PH}$ = 9.2, J_{HH} = 6.8, CH_2CH_2P), 2.19 (dt, 2H, $^2J_{PH}$ = 28.1, J_{HH} = 7.0, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 232.2 (d, $^2J_{PC}$ = 22.5, CO), 136.0 (d, $^2J_{PC}$ = 45.2, ipso, Ph), 133.3 (d, $^2J_{PC}$ = 9.7, ortho, Ph), 131.4 (d, $^4J_{PC}$ = 2.5, para, Ph), 129.5 (d, $^3J_{PC}$ = 10.0, meta, Ph), 117.3 (d, $^3J_{PC}$ = 5.9, quat, Cp), 97.2 (s, Cp), 92.3 (s, Cp), 46.3 (d, J_{PC} = 29.3, CH_2CH_2P), 21.9 (d, $^2J_{PC}$ = 6.4, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 70.3 (s, PPh_2).

$WBr(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (8). Yield: 52%. Anal. Calcd for $C_{21}H_{18}O_2BrPW$: C, 42.24; H, 3.04. Found: C, 42.15; H, 3.35. Mp: 199−201 °C dec. IR: in benzene, ν(CO) 1969 (m), 1885 (s) cm^{-1}; in Nujol, ν(CO) 1973 (m), 1966 (m), 1944 (w), 1896 (m, sh), 1871 (vs), 1846 (s, sh) cm^{-1}. NMR spectroscopy indicated a 94:6 trans:cis mixture. Data for *trans*-**8** are as follows. ^1H NMR (C_4D_8O, 400 MHz): δ 7.60−7.56 (m, 4H, ortho, Ph), 7.48−7.42 (m, 6H, meta/para, Ph), 5.99 (m, 2H, Cp), 5.28 (app t, 2H, J = 2.3, Cp), 2.99 (dt, 2H, $^3J_{PH}$ = 9.2, J_{HH} = 6.8, CH_2CH_2P), 2.24 (dt, 2H, $^2J_{PH}$ = 26.4, J_{HH} = 7.0, CH_2CH_2P) $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 224.5 (d, $^2J_{PC}$ = 15.2, CO), 136.0 (d, $^2J_{PC}$ = 50.5, ipso, Ph), 133.4 (d, $^2J_{PC}$ = 10.0, ortho, Ph), 131.4 (d, $^4J_{PC}$ = 2.0, para, Ph), 129.4 (d, $^3J_{PC}$ = 11.1, meta, Ph), 114.2 (d, $^3J_{PC}$ = 6.2, quat, Cp), 94.6 (s, Cp), 91.1 (s, Cp), 47.1 (d, J_{PC} = 32.3, CH_2CH_2P), 22.0 (d, $^2J_{PC}$ = 6.0, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 37.7 (s, ($^{183}W-^{31}P$ satellites: 38.5 (m), 36.9 (m), J_{WP} = 260), PPh_2).

$[K(18C6)][Cr(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})]$ (9). THF (20 mL) was added to **1** (0.519 g, 1.34 mmol) and KH (0.065 g, 1.61 mmol). The yellow solution was stirred for 1 h until it turned red-orange. The reaction was complete on the basis of IR spectroscopy (ν(CO) 1764 (s), 1685 (s) cm^{-1}). The solution was filtered through Celite into 18-crown-6 (0.426 g, 1.61 mmol) and stirred 2 h before filtration at −10 °C. The filtrate was concentrated in vacuo to ~3 mL. Addition of Et_2O (50 mL) resulted in the precipitation of an orange solid that was isolated by filtration, washed with Et_2O (4 × 10 mL), and dried in vacuo. Recrystallization from THF/Et_2O provided red-orange, air-sensitive microcrystals (0.716 g, 77%). Anal. Calcd for $C_{33}H_{42}O_8CrKP$: C,

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57.55; H, 6.15. Found: C, 57.73; H, 6.53. Mp: 198−200 °C dec. IR: in THF, ν(CO) 1785 (s), 1700 (m) cm^{-1}; in Nujol, ν(CO) 1781 (s), 1698 (s) cm^{-1}. ^{1}H NMR (C_4D_8O, 300 MHz): δ 7.79 (app t, 4H, J = 7.5, ortho, Ph), 7.17 (app t, 4H, J = 7.2, meta, Ph), 7.06 (app t, 2H, J = 7.2, para, Ph), 4.11 (s, 2H, Cp), 3.97 (s, 2H, Cp), 3.58 (s, 24H, 18C6), 2.80 (s, br, 2H, CH_2CH_2P), 1.86 (dt, $^2J_{PH}$ = 21.9 Hz, J_{HH} = 6.0 Hz, 2H, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 252 (s, br, CO), 145.8 (s, br, ipso, Ph), 133.5 (d, $^2J_{PC}$ = 11.0 Hz, ortho, Ph), 127.5 (d, $^3J_{PC}$ = 8.0 Hz, meta, Ph), 127.2 (s, para, Ph), 77.8 (s, Cp), 77.6 (s, Cp), 71.1 (s, 18C6), 48.3 (d, J_{PC} = 15.3, CH_2CH_2P), 23.8 (d, $^2J_{PC}$ = 14.6, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 107.4 (s, br, PPh_2).

[K(18C6)][Mo(CO)$_2$(η^5:η^1-Cp^{PPh})] (10). Yield: 71%. Anal. Calcd for $C_{33}H_{42}O_8KMoP$: C, 54.10; H, 5.78. Found: C, 53.89; H, 6.09. Mp: 199−200 °C dec. IR: in THF, ν(CO) 1788 (s), 1702 (s) cm^{-1}; in Nujol, ν(CO) 1787 (s), 1701 (s) cm^{-1}. ^{1}H NMR (C_4D_8O, 300 MHz): δ 7.85−7.78 (m, 4H, ortho, Ph), 7.22−7.17 (m, 4H, meta, Ph), 7.12−7.07 (m, 2H, para, Ph), 4.82 (app t, 2H, J = 2.1, Cp), 4.50 (app t, 2H, J = 2.1, Cp), 3.58 (s, 24H, 18C6), 3.58 (app quartet, 2H, J = 6.6, CH_2CH_2P), 1.97 (dt, 2H, $^2J_{PH}$ = 24.9, J_{HH} = 7.2, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (C_4D_8O, 75 MHz): δ 241.7 (d, $^2J_{PC}$ = 9.7, CO), 145.2 (d, J_{PC} = 25.4, ipso, Ph), 133.6 (d, $^2J_{PC}$ = 12.8, ortho, Ph), 129.1 (s, para, Ph), 127.6 (d. $^3J_{PC}$ = 8.8, meta, Ph), 120.8 (d, $^3J_{PC}$ = 4.9, quat, Cp), 80.3 (s, Cp), 80.1 (s, Cp), 71.2 (s, 18C6), 49.2 (d, J_{PC} = 19.6, CH_2CH_2P), 24.3 (d, $^2J_{PC}$ = 9.7, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 121 MHz): δ 91.0 (s, PPh_2).

[K(18C6)][W(CO)$_2$(η^5:η^1-Cp^{PPh})] (11). Yield: 53%. Anal. Calcd for $C_{33}H_{42}O_8KPW$: C, 48.30; H, 5.16. Found: C, 48.58; H, 5.45. Mp: 199−201 °C dec. IR: in THF, ν(CO) 1781 (s), 1698 (s) cm^{-1}; in Nujol, ν(CO) 1783 (s), 1698 (s) cm^{-1}. ^{1}H NMR (C_4D_8O, 400 MHz): δ 7.88−7.83 (m, 4H, ortho, Ph), 7.25−7.21 (m, 4H, meta, Ph), 7.14−7.10 (m, 2H, para, Ph), 4.85 (app t, 2H, J = 1.9, Cp), 4.55 (app. t, 2H, J = 2.0, Cp), 3.62 (s, 24H, 18C6), 3.03 (app quartet, 2H, J = 6.9, CH_2CH_2P), 2.00 (dt, 2H, $^2J_{PH}$ = 24.0, J_{HH} = 7.0, CH_2CH_2P). $^{13}C\{^1H\}$ NMR (C_4D_8O, 101 MHz): δ 232.0 (d, $^2J_{PC}$ = 3.1, CO), 143.8 (d, J_{PC} = 32.9, ipso, Ph), 132.6 (d, $^2J_{PC}$ = 12.0, ortho, Ph), 126.5 (d, $^4J_{PC}$ = 1.5, para, Ph), 126.5 (d. $^3J_{PC}$ = 9.0, meta, Ph), 117.9 (d, $^3J_{PC}$ = 5.1, quat, Cp), 77.5 (s, Cp), 75.6 (app. d, J = 2.3, Cp), 70.1 (s, 18C6), 50.8 (d, J_{PC} = 25.5, CH_2CH_2P), 22.9 (d, $^2J_{PC}$ = 9.6, CH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_4D_8O, 162 MHz): δ 57.8 (m, (^{183}W−^{31}P satellites: 59.3 (m, br), 56.2 (m, br), J_{WP} = 502), PPh_2).

Recrystallization for X-ray Analysis. X-ray-quality crystals were obtained by diffusion of pentane into nearly saturated toluene solutions (**1**, **3**), of Et_2O into nearly saturated THF solutions (**6**−**11**), and of Et_2O into nearly saturated benzene solutions (**4**, **5**). Crystals were selected from the mother liquor in a N_2-filled glovebag.

Catalytic Reactions. Cyclooctene (0.397 g, 3.6 mmol), tetradecane (0.143 g, 0.72 mmol, internal standard), and catalyst precursors **5**−**7** (1 mol %, 0.036 mmol), respectively, were dissolved in $CHCl_3$ (3 mL) in air at 55 °C. The reaction was started by the addition of TBHP (5.0−6.0 M in *n*-decane; 7.2 mmol, 1.31 mL), resulting in an initial cyclooctene concentration of 0.84 M. The clear red solutions immediately turned milky white, with the exception of solutions of **7**, which took 90 min to change from milky pink to white. Reactions were monitored by quantitative GC/MS analysis. Aliquots of 250 μL were removed every 30 min for 5 h, diluted with CH_2Cl_2, and treated with a catalytic amount of MnO_2 to destroy excess peroxide and $MgSO_4$ and remove water. The resulting mixtures were filtered and run on the GC/MS column. The conversion of cyclooctene and the formation of cyclooctene oxide were calculated from prior standard curves (r^2 = 0.995). The procedure for catalytic 1-dodecene epoxidation is nearly identical and is described in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving general procedures, syntheses, and characterization details for **1** and **3**−**11**, molecular structure drawings, crystallographic data including data collection, solution, and refinement information for **1** and **3**−**11**, epoxidation catalysis procedures, standard curves, epoxide conversion graphs, and GC/MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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