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Synthesis and Characterization of Osmium(II) Trispyrazolylborate Complexes

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Treatment of H_2OsBr_6 with excess 1,5-cyclooctadiene (cod) in boiling *tert*-butyl alcohol affords the polymer $[OsBr_2(cod)]_x$ (**1**), which reacts with acetonitrile to form the mononuclear adduct $OsBr_2(cod)(CH_3CN)_2$ (**2**). Polymer **1** reacts with potassium trispyrazolylborate (KTp) in ethanol to afford the hydride TpOs(cod)H (**3**) and the bromide complex TpOs(cod)Br (**4**). Bromide complex **4** reacts with sodium methoxide in methanol to afford TpOs(cod)OMe (**5**), which has been structurally characterized. Treatment of hydride **3** with methyl trifluoromethanesulfonate (MeOTf) in diethyl ether results in loss of methane and formation of the triflate complex TpOs(cod)OTf (**6**), which reacts with $MgMe_2$ to give the methyl complex TpOs(cod)Me (**7**). The addition of bis(dimethylphosphino)methane (dmpm) to the known compound $TpOs(PPh_3)_2Cl$ yields a mixture of the substitution products TpOs(η^1-dmpm)(PPh_3)Cl (**8**) and TpOs(η^2-dmpm)Cl (**9**); the latter reacts with methyllithium to generate the methyl compound TpOs(dmpm)Me (**10**). NMR and IR data for these new compounds are reported. Crystal data for **5**·MeOH at −80 °C are as follows: monoclinic, $P2_1/n$, $a = 10.728(1)$ Å, $b = 14.004(2)$ Å, $c = 13.906(2)$ Å, $\beta = 102.42(6)°$, $V = 2040.3(5)$ Å^3, $Z = 4$, $R_F = 0.0247$ for $I \geq 2\sigma(I)$, and $R_{wF2} = 0.0539$ for all data.

Introduction

Since the first preparation of polypyrazolylborates by Trofimenko in 1966,[1] a substantial body of literature (over 2000 publications) has appeared describing the syntheses and applications of polypyrazolylborate ligands in various areas of chemistry.[2] This diverse class of ligands has been used in applications ranging from modeling metalloenzymes to catalyzing a wide variety of organic reactions.[3] Complexes bearing polypyrazolylborate ligands are known for every d-block element and most of the lanthanides and actinides.[4,5]

Polypyrazolylborate osmium complexes remain less explored than those of most other d-block elements. In 1990, the first such complexes, $[TpOs(CO)_2]_2$ and $[(pzTp)Os(CO)_2]_2$, were prepared by reaction of $[Os(O_2CMe)(CO)_3]_2$ with the appropriate potassium polypyrazolylborate, where Tp = tris(pyrazolyl)borate and pzTp = tetrakis(pyrazoyl)borate.[6] Treatment of these dinuclear species with Br_2 cleaved the Os−Os bond and afforded the mononuclear complexes $TpOs(CO)_2Br$ or $(pzTp)Os(CO)_2Br$, respectively. Potassium polypyrazolylborate reagents have also been used to prepare the mixed sandwich complexes $TpOs(C_5H_5)$ and $(pzTp)Os(C_5H_5)$ from $[(C_5H_5)Os(CH_3CN)_3^+][PF_6^-]$.[7] Similarly, Schrock has used potassium trispyrazolylborate (KTp) to prepare the alkylidyne TpOs(C−^{t}Bu)(CH_2−^{t}Bu)$_2$ from Os(C−^{t}Bu)(CH_2−^{t}Bu)$_2$(py)$_2$(OTf), where OTf = trifluoromethanesulfonate,[8] and Shapley prepared the analogous nitride complex Tp′Os(N)Ph_2 from the reaction of $[Os(N)Ph_2(py)_2^+][BF_4^-]$ with KTp′, where Tp′ = tris(3,5-dimethylpyrazolyl)borate.[9]

Potassium polypyrazolylborate reagents have also been used to prepare several osmium complexes bearing phosphine ligands; occasionally, these reactions generate products with bidentate Tp ligands. For example, the complex (η^2-Tp)Os(CO)(PPh_3)$_2$Ph was prepared by treatment of Os(CO)(PPh_3)$_2$(Ph)Cl with KTp;[10] heating a solution of the isolated product

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in toluene resulted in loss of one phosphine ligand and coordination of the third pyrazolyl group to give (η^3-Tp)Os(CO)(PPh_3)Ph. Similarly, treatment of Os(CO)(P^iPr_3)$_2$HCl with NaTp afforded (η^2-Tp)Os(CO)(P^iPr_3)$_2$H, which loses a phosphine ligand when heated to reflux in toluene, generating (η^3-Tp)Os(CO)(P^iPr_3)H.[11] Protonation of TpOs(CO)(P^iPr_3)H with HBF_4 yielded the dihydrogen complex, [TpOs(CO)(P^iPr_3)(H_2)][BF_4]. Jia[12] and Hill[13] independently reported the synthesis of TpOs(PPh_3)$_2$Cl by treatment of $OsCl_2(PPh_3)_3$ with KTp, and the conversion of this compound to the monohydride TpOs(PPh_3)$_2$H by the addition of either NaOMe or KOH. Protonation of TpOs(PPh_3)$_2$H yielded the dihydrogen complex [TpOs(PPh_3)$_2$(H_2)$^+$].[12]

Apart from the compounds above, most osmium Tp complexes are made from other osmuim Tp species, as shown particularly by the work of Mayer. The osmium(VI) nitride TpOs(N)Cl_2, which can be prepared by the reaction of K[Os(N)O_3] with KTp in ethanolic HCl, is a particularly good starting material for other complexes containing the TpOs fragment.[14,15] For example, the chloride ligands can be replaced to give complexes of the type TpOs(N)X_2 (X = acetate, trihaloacetate, bromide, nitrate, and $^1/_2$ oxalate).[16]

Because the nitride ligand in TpOs(N)Cl_2 is electrophilic, Grignard reagents and phosphines add directly to the nitrogen atom. For example, treatment of TpOs(N)Cl_2 with PhMgCl yielded [TpOs(NPh)Cl_2^-], which can be protonated to afford the structurally characterized amide TpOs(NHPh)Cl_2.[15] The amido ligand in TpOs(NHPh)Cl_2 is inert to further protonation and electrophilic attack at nitrogen.[17] In contrast, the reduced form of this complex, [TpOs(NHPh)Cl_2^-], can be protonated to give the aniline complex TpOs(NH_2Ph)Cl_2.[18] The hydrogen atom self-exchange rates between TpOs(NHPh)Cl_2 and TpOs(NH_2Ph)Cl_2 have been investigated.[19] A surprising reaction is the addition of piperidine to TpOs(NHPh)Cl_2, which yields the aromatic substitution product, TpOs[NHC_6H_4-*p*-(NC_5H_{10})]Cl_2.[15] Reduction of TpOs(N)Cl_2 with PPh_3 affords the phosphiniminato complex TpOs($NPPh_3$)Cl_2, which reacts with triflic acid in acetonitrile to produce the salt [TpOs($NHPPh_3$)Cl_2]OTf.[20] The addition of excess HOTf to the same phosphiniminato complex in CH_2Cl_2 gives products of a different kind, TpOs(OTf)Cl_2 and $TpOsCl_3$, in which the nitride-derived ligands are lost.[21]

The reduced analogue [PPN^+][$TpOsCl_3^-$], where PPN^+ is the bis(triphenylphosphine)iminium cation, has been described by Meyer.[22] The triflate complex TpOs(OTf)Cl_2 is surprisingly resistant to substitution,[23] but reacts with nitriles and ammonia to afford the nitride $TpOsNCl_2$.[24] Interestingly, reduction of TpOs(OTf)Cl_2 with (C_5Me_5)$_2$Fe gives the osmium(III) salt [(C_5Me_5)$_2$$Fe^+$][TpOs(OTf)$Cl_2^-$], which reacts with a variety of Lewis bases to afford the osmium(III) complexes TpOs(L)Cl_2 (L = MeCN, PhCN, PPh_3, py, imidazole, and NH_3). Oxidation of the neutral osmium(III) complexes with [NO]BF_4 affords the corresponding osmium(IV) salts of the formula [TpOs(L)Cl_2^+][BF_4^-].[21]

An unusual reaction is the addition of BPh_2R (R = Ph, $OBPh_2$) to TpOs(N)Cl_2, which afforded the insertion product TpOs[N(Ph)(BPhR)]Cl_2. In this product, one Cl atom is coordinated to boron, forming a four-membered Os−N−B−Cl ring.[15] The nitride complex TpOs(N)Cl_2 has also served as a starting material for several polynuclear species. Reduction of TpOs(N)Cl_2 with Cp_2Co gives a salt containing a mixed-valence anion [Cp_2Co^+][$TpOs^{II}Cl_2(N{\equiv}N)Cl_2Os^{III}Tp^-$].[25] The reaction of TpOs(N)Cl_2 with CpCo[η^4-Cp(C_6F_5)] affords the complex [$TpOsCl_2(N)]_2CoCp$, in which the nitride atoms serve as donors to the cobalt center.[26] TpOs(N)Cl_2 reacts slowly with $PtCl_2(SMe_2)_2$ to give the similar donor complex $TpOsCl_2(N)-PtCl_2(Me_2S)$.[26] The surprising thermal stabilities of the latter two compounds are attributed to the π-acid character of the TpOs(N)Cl_2 fragment, which in turn arises from the electrophilic nature of the nitride ligand.

To date, the vast majority of TpOs complexes in the +2 oxidation state also bear carbonyl or triphenylphosphine ligands. As part of an effort to expand the synthetic versatility of TpOs species, we now present the synthesis and characterization of new tris(pyrazolyl)borate osmium(II) compounds of the types TpOs(cod)X (where X = H, Br, OTf, Me, OMe and cod = 1,5-cyclooctadiene) and TpOs(PR_3)$_2$Cl. Some of these reactions are summarized in Scheme 1. We also describe a useful starting material for a wide array of osmium chemistry, the dibromo(1,5-cyclooctadiene)osmium(II) polymer $[OsBr_2(cod)]_x$.

This work was undertaken in part to complement our previous studies of the chemistry of C_5Me_5 osmium complexes, particularly in relation to dihydrogen and alkane activation processes.[27−30] We became interested in expanding

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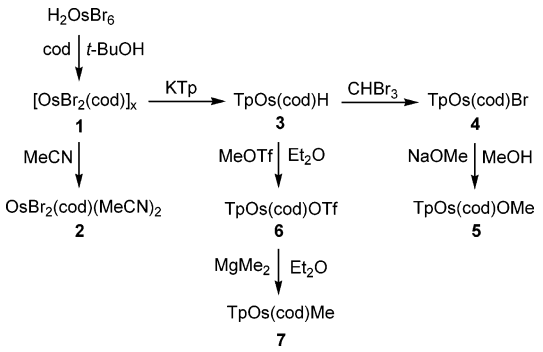
Scheme 1. Syntheses of Tp Osmium Complexes[a]



[a] cod = 1,5-cyclooctadiene, OTf = trifluoromethanesulfonate.

this investigation to related osmium complexes in which the C_5Me_5 ligand was replaced by other ancillary groups such as Tp. One especially important question is whether the strongly directional frontier orbitals of the TpM fragment (see below) would change the chemistry relative to their (C_5Me_5)Os analogues.

Results and Discussion

Synthesis of $[OsBr_2(cod)]_x$ (1) and $OsBr_2(cod)(MeCN)_2$ (2). The ruthenium polymer $[RuCl_2(cod)]_x$, cod = 1,5-cyclooctadiene, first described by Bennett and Wilkinson in 1959, has proven to be a useful precursor to a wide variety of monomeric ruthenium compounds.[13,31−37] It is readily prepared in 30−40% yield from $RuCl_3$ and cod in boiling ethanol.[38−40] The analogous osmium polymer, $[OsCl_2(cod)]_x$, is known, but its utility as a starting material has remained relatively unexplored. This compound was first prepared by Winkhaus et al. in 35% yield by the reaction of H_2OsCl_6 and cod in boiling isoamyl alcohol.[41] Lewis and Schrock claimed that a higher yield (90%) could be obtained by heating OsO_4 in a mixture of concentrated HCl and isoamyl alcohol, adding cod, and distilling off the solvent to afford the product as a yellow-brown precipitate.[42] In our hands, we obtained yields of 15−20% using this procedure. Our difficulty in obtaining high yields of $[OsCl_2(cod)]_x$ prompted us to explore the bromo analogue, $[OsBr_2(cod)]_x$.

Addition of HBr to OsO_4 generates H_2OsBr_6,[43,44] which reacts with excess cod in boiling *tert*-butyl alcohol to afford a yellow-brown precipitate of $[OsBr_2(cod)]_x$ (**1**) in 90% yield.[45] In the latter reaction, the osmium center is reduced from Os^{IV} to Os^{II}. Because the yield of **1** is so high, disproportionation processes involving soluble Os^V or Os^{VI} byproducts can be ruled out. It is also unlikely that the reductant is the *tert*-butyl alcohol solvent because this alcohol cannot be oxidized to an aldehyde. Therefore, the reductant is probably cod, which has the potential to act as a dehalogenating or dehydrohalogenating agent. Compound **1** can also be obtained by refluxing H_2OsBr_6 in neat cod but in lower yield (30−40%).

$$H_2OsBr_6 + \text{cod} \rightarrow \underset{\mathbf{1}}{[OsBr_2(cod)]_x} + Br_2 + 2HBr$$

The IR spectrum of **1** is similar to that of the known polymers $[RuCl_2(cod)]_x$[46] and $[OsCl_2(cod)]_x$.[41] Compound **1** is probably polymeric: it has a high melting point (>280 °C) and is insoluble in pentane, diethyl ether, benzene, toluene, tetrahydrofuran, and dichloromethane.

Compound **1** dissolves in refluxing acetonitrile to afford the adduct $OsBr_2(cod)(MeCN)_2$ (**2**). The chlororuthenium analogue $RuCl_2(cod)(MeCN)_2$ has been reported by Lewis.[47] The ^{1}H NMR spectrum of **2** shows a multiplet at δ 4.15 and two multiplets at δ 2.31 and 1.87, corresponding to the vinyl and two chemically inequivalent methylene protons of the cod ligand, respectively. The acetonitrile resonance occurs at δ 2.70. The NMR data indicate that **2** adopts an octahedral structure with C_{2v} symmetry.

$$[OsBr_2(cod)]_x + 2\ \text{MeCN} \rightarrow \underset{\mathbf{2}}{OsBr_2(cod)(MeCN)_2}$$

Synthesis of TpOs(cod)H (3) and TpOs(cod)Br (4). Treatment of the polymer **1** with 1.5−2 equiv of tris(pyrazolyl)borate, KTp, in boiling ethanol for 24 h affords the osmium(II) hydride TpOs(cod)H (**3**) in 96% yield. At shorter reflux times, a mixture of TpOs(cod)H (**3**) and TpOs(cod)Br (**4**) is formed (see below). The presence of the bromide complex **4** at shorter reflux times suggests that it is formed first and subsequently converts to the hydride **3** under the reaction conditions. A possible source of the hydride

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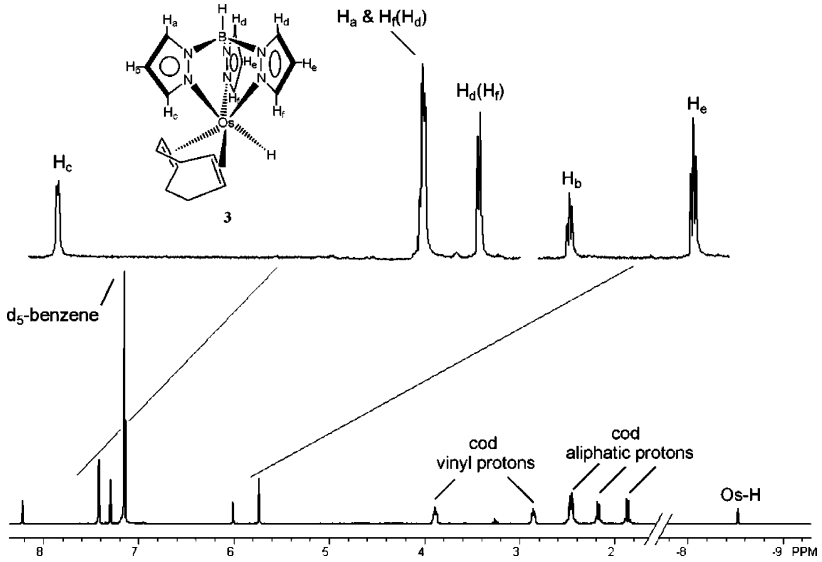

Figure 1. ^{1}H NMR spectrum (C_6D_6, 22 °C) of TpOs(cod)H (**3**).

ligand in **3** is the ethanol solvent:

$$[OsBr_2(cod)]_x + KTp + CH_3CH_2OH \rightarrow \underset{\mathbf{3}}{TpOs(cod)H} + CH_3CHO + KBr + HBr$$

Interestingly, however, if pure samples of the bromo complex **4** are heated in ethanol for 24 h, the bromo complex is recovered unchanged and no hydride **3** is formed. It is possible that cod or the KTp reagent promotes the conversion of **4** to **3** (note that the KTp is added to the polymer **1** in a slight excess).

The IR spectrum of **3** shows a B−H stretch at 2460 cm^{-1} and an Os−H stretch at 2085 cm^{-1}. The ^{1}H NMR spectrum of **3** (Figure 1) indicates that the molecule is octahedral with C_s symmetry. Two doublets at δ 8.22 (1H) and 7.42 (1H) are assigned to the protons at the 3- and 5-positions of the pyrazolyl ring that lies in the molecular mirror plane, and a triplet at δ 6.01 (1H) is assigned to the proton at the 4-position of this same ring. Two doublets at δ 7.42 (2H) and 7.30 (2H) and a triplet at δ 5.74 (2H) are due to the 3,5- and 4-protons of the two pyrazole rings that are related to one another across the molecular mirror plane. Two multiplets at δ 3.89 (2H) and 2.86 (2H) and three multiplets at δ 2.46 (2H), 2.17 (4H), and 2.87 (2H) are assigned to the cod vinyl and methylene protons, respectively. The hydride resonance appears at δ −8.52.

All compounds of the formula TpOs(cod)X described subsequently in this paper also have C_s symmetry, and the NMR signals from the Tp and cod ligands closely resemble those seen for **3** and will not be discussed further. All compounds of stoichiometry $TpOsL_2X$ in the present paper are air stable, both in solution and in the solid state.

Small amounts of pyrazole, a byproduct of the reaction, cocrystallize with **3** from pentane, diethyl ether, and toluene. For example, recrystallization from diethyl ether affords samples of **3** that contain approximately 0.5−2% of pyrazole, which is evident in the ^{1}H NMR spectrum.[48,49] The field desorption mass spectra of such samples exhibit envelopes of peaks at 514.3 and 580.4 *m*/*z*, typically in a 95:5 ratio, respectively. The former envelope corresponds to **3,** and the latter is assigned to the pyrazolyl complex TpOs(cod)(pyrazolyl)$^+$ or alternatively to the tetrakis(pyrazolyl)borate hydride (pzTp)Os(cod)H$^+$, which may be formed in the ionization process.

The initial product of the reaction of $[OsBr_2(cod)]_x$ (**1**) with KTp in boiling ethanol is the bromo complex TpOs(cod)Br (**4**), but even at short reaction times a substantial amount of the hydride TpOs(cod)H (**3**) is also present; the ratio is roughly 1:1 after 2 h. Pure samples of **4** are best prepared by heating a mixture of $[OsBr_2(cod)]_x$ (**1**) and KTp in ethanol for 2 h, followed by the addition of bromoform, $CHBr_3$. The bromoform efficiently converts the hydride to the bromo complex.

$$\underset{\mathbf{3}}{TpOs(cod)H} + CHBr_3 \rightarrow \underset{\mathbf{4}}{TpOs(cod)Br} + CH_2Br_2$$

In this way, the bromo compound **4** is isolated in 48% yield. The IR spectrum of **4** shows a B−H stretch at 2466 cm^{-1}.

Synthesis and X-ray Crystal Structure of TpOs(cod)OMe (5). Treatment of bromide **4** with NaOMe in methanol at reflux for 20 h affords the methoxide compound, TpOs(cod)OMe·MeOH (**5**), in 32% yield. At this point, the reaction mixture contains the starting material **4**, the hydride complex **3**, and the methoxy compound **5** in a 1:2:17 ratio, respectively. At longer reaction times, starting material **4** disappears, but increasing amounts of hydride **3** are formed; after 2 weeks, the ratio of **3** to **5** is 2:9.

Solutions of sodium alkoxides in alcohols are commonly used in transition metal chemistry to convert halide com-

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(49) The acidic proton of pyrazole rapidly exchanges between the two nitrogen atoms at room temperature, giving a broad resonance at δ 13.3. A doublet at δ 7.32 and a triplet at δ 6.07 correspond to the other ring protons. (We speculated whether this compound could be the protonated pyrazolium cation, PzH$^+$, which would exhibit a similar NMR spectrum. We prepared the salt [PzH$^+$][OTf$^-$] separately and found that this was not the case.)

Table 1. Crystallographic Data for TpOs(cod)OMe·MeOH (**7**)

formula	$C_{19}H_{29}BN_6O_2Os$
fw	574.49
space group	$P2_1/n$
a, Å	10.728(1)
b, Å	14.004(2)
c, Å	13.906(2)
β, deg	102.42(2)
V, Å^3	2040.3(5)
Z	4
T, °C	−80
λ, Å	0.71073
D_{calcd}, Mg m^{-3}	1.870
μ, mm^{-1}	6.279
$R_F{}^a$ ($I \geq 2\sigma(I)$)	0.0247
$R_{wF2}{}^b$ (all data)	0.0539

^{a} $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_{wF2} = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

plexes into their corresponding hydride analogues.[50] The mechanism of this conversion is thought to proceed via displacement of the halide by the alkoxide, followed by β-hydride elimination and dissociation of the aldehyde (or ketone).[51−55] The slow rate at which the methoxy complex **5** undergoes β-hydrogen elimination suggests that the pyrazole and cod ligands in TpOs(cod)X compounds are slow to dissociate from the osmium center.

The ^{1}H NMR spectrum of **5** shows a resonance at δ 2.86 for the methoxy group. For comparison, the methoxy group in $(C_6H_3Me_3)OsH(OMe)(^iPr_2PCH{=}CH_2)$ has a ^{1}H NMR chemical shift of δ 4.05.[56] The IR spectrum of **5** shows a B−H stretch at 2484 cm^{-1}.

Single crystals of the methanol solvate TpOs(cod)OMe·MeOH crystallize in the $P2_1/n$ space group. Crystal data are presented in Table 1, and selected bond distances and angles are given in Table 2. The Os−O bond length is 2.127(2) Å, and the Os−O−C angle is 125.1(2)°. There is a hydrogen bonding interaction between the oxygen atom of the Os−OMe group and the hydroxyl proton of the methanol solvate molecule (Figure 2); the O···O contact distance is 2.655(2) Å. The hydroxyl proton of the methanol could not be not located in the difference Fourier map. The average Os−N and Os−C bond distances are 2.146(3) and 2.172(3) Å, respectively.

Synthesis of TpOs(cod)OTf (6) and TpOs(cod)Me (7). Treatment of the hydride **3** with excess methyl trifluoromethanesulfonate (MeOTf) in diethyl ether at −78 °C affords the triflate complex TpOs(cod)OTf (**6**) in 54% yield. The IR spectrum of **6** shows a B−H stretch at 2506 cm^{-1}. The ^{19}F NMR spectrum consists of a singlet at δ −79.4.

$$\underset{}{\text{TpOs(cod)H}} + \text{MeOTf} \rightarrow \underset{\mathbf{6}}{\text{TpOs(cod)OTf}} + \text{MeH}$$

Treatment of **6** with 1.1 equiv of dimethylmagnesium ($MgMe_2$) in diethyl ether for 1 week, followed by an aqueous workup, affords the osmium(II) methyl compound TpOs(cod)Me (**7**) in 10% yield and other unidentified products. The ^{1}H NMR spectrum of **7** displays a singlet at δ 1.44 for the Os−Me group. The IR spectrum of **7** shows a B−H stretch at 2471 cm^{-1}.

$$\text{TpOs(cod)OTf} + \text{MgMe}_2 \rightarrow \underset{\mathbf{7}}{\text{TpOs(cod)Me}} + \text{“Mg(Me)OTf”}$$

The slow rate of methylation suggests that the triflate ligand in **6** is not particularly labile.

Synthesis of TpOs(PR$_3$)$_2$X Complexes. We investigated the reactivity of the bromo complex TpOs(cod)Br, **4**, with phosphines in an effort to replace the cod ligand. Interestingly, **4** is remarkably inert toward phosphine substitution. For example, when solutions (toluene, dmf, heptane, octane, dodecane) of TpOs(cod)Br and bis(dimethylphosphino)methane, dmpm, are heated to reflux for several days, no reaction occurs. Similar results were obtained with PMe_3. Kirchner and co-workers observed similarly slow cod substitution rates in the ruthenium analogue TpRu(cod)Cl.[57] In that system, the cod ligand could be exchanged with phosphines (and other Lewis bases) in refluxing dimethylformamide (dmf) (bp = 153 °C). Unfortunately, the osmium analogue does not undergo substitution even under these forcing conditions; the starting material **4** is recoverable in near-quantitative yield.

The sluggish nature of the cod substitution reactions in **4** is surprising in light of the relatively facile replacement of cod in similar cyclopentadienyl systems: $(C_5Me_5)Os(cod)Br$ readily reacts with dmpm in refluxing heptane to give high yields of the corresponding phosphine complex.[58] One explanation for the low lability of the cod ligand in **4** is stronger back-bonding to the cod C=C double bonds caused by the pyrazolyl groups, which are more strongly donating than cyclopentadienyl groups.

Although we were not able to prepare TpOs(dmpm)Br by treatment of TpOs(cod)Br with dmpm, we have developed an alternative route to the chloro analogue, TpOs(dmpm)Cl. Treatment of $TpOs(PPh_3)_2Cl$ with dmpm for 1 week at room temperature affords two primary products, TpOs(η^1-dmpm)(PPh_3)Cl (**8**) and TpOs(η^2-dmpm)Cl (**9**) in a 17:1 ratio, respectively. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture at this point (Figure 3) shows three resonances for **8**: a doublet at δ 2.4 corresponds to the coordinated PPh_3 ligand, and a doublet of doublets at δ −35.7 and a doublet at δ −58.0 are assigned to the bound and unbound phosphorus atoms, respectively, of the unidentate dmpm ligand. In addition, the spectrum features a singlet at

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Table 2. Selected Bond Distances and Angles for TpOs(cod)OMe·MeOH (**7**)

Distances (Å)							
Os(1)−O(1)	2.127(2)	N(1)−C(1)	1.350(4)	N(4)−C(6)	1.348(4)	C(11)−C(12)	1.523(5)
Os(1)−N(1)	2.159(3)	C(1)−C(2)	1.379(5)	B(1)−N(4)	1.535(5)	C(12)−C(13)	1.540(5)
Os(1)−N(3)	2.133(3)	C(2)−C(3)	1.365(5)	N(5)−N(6)	1.370(4)	C(13)−C(14)	1.524(5)
Os(1)−N(5)	2.147(3)	N(2)−C(3)	1.349(4)	N(5)−C(7)	1.340(4)	C(14)−C(15)	1.396(5)
Os(1)−C(10)	2.198(3)	B(1)−N(2)	1.552(5)	C(7)−C(8)	1.390(5)	C(15)−C(16)	1.517(5)
Os(1)−C(11)	2.181(3)	N(3)−N(4)	1.369(4)	C(8)−C(9)	1.367(5)	C(16)−C(17)	1.537(5)
Os(1)−C(14)	2.141(3)	N(3)−C(4)	1.347(4)	N(6)−C(9)	1.352(4)	C(10)−C(17)	1.531(5)
Os(1)−C(15)	2.166(3)	C(4)−C(5)	1.390(5)	B(1)−N(6)	1.531(5)	C(100)−O(100)	1.415(5)
O(1)−C(18)	1.312(5)	C(5)−C(6)	1.366(5)	C(10)−C(11)	1.399(5)	O(1)···H(10A)	1.816(5)
N(1)−N(2)	1.376(4)						
Angles (deg)							
O(1)−Os(1)−N(1)	157.7(1)	N(1)−Os(1)−C(11)	113.7(1)	N(3)−Os(1)−C(15)	88.6(1)	C(14)−Os(1)−N(5)	158.1(1)
O(1)−Os(1)−N(3)	87.5(1)	N(1)−Os(1)−C(15)	83.3(1)	N(5)−Os(1)−N(1)	80.7(1)	C(14)−Os(1)−C(10)	88.5(1)
O(1)−Os(1)−N(5)	78.9(1)	N(3)−Os(1)−N(1)	83.1(1)	N(5)−Os(1)−C(10)	98.6(1)	C(14)−Os(1)−C(11)	81.1(1)
O(1)−Os(1)−C(10)	113.4(1)	N(3)−Os(1)−N(5)	88.9(1)	N(5)−Os(1)−C(11)	92.0(1)	C(14)−Os(1)−C(15)	37.8(1)
O(1)−Os(1)−C(11)	76.2(1)	N(3)−Os(1)−C(10)	158.7(1)	N(5)−Os(1)−C(15)	164.0(1)	C(15)−Os(1)−C(10)	78.7(1)
O(1)−Os(1)−C(14)	79.2(1)	N(3)−Os(1)−C(11)	163.1(1)	C(10)−Os(1)−C(11)	37.3(1)	C(15)−Os(1)−C(11)	95.0(1)
O(1)−Os(1)−C(15)	116.7(1)	N(3)−Os(1)−C(14)	91.8(1)	C(14)−Os(1)−N(1)	121.1(1)	C(18)−O(1)−Os(1)	125.1(2)
N(1)−Os(1)−C(10)	78.5(1)						

δ −69.2 corresponding to the bidentate dmpm ligand in **9**.

$$TpOs(PPh_3)_2Cl + dmpm \rightarrow \underset{\mathbf{8}}{TpOs(\eta^1\text{-dmpm})(PPh_3)Cl} + PPh_3$$

$$TpOs(PPh_3)_2Cl + dmpm \rightarrow \underset{\mathbf{9}}{TpOs(\eta^2\text{-dmpm})Cl} + 2PPh_3$$

Transition metal complexes containing unidentate dmpm ligands are rare, but a few examples are known.[54,59−66] As is often the case for unidentate diphosphine complexes, the η^1-dmpm compound **8** is a kinetic product. It is best prepared by stirring $TpOs(PPh_3)_2Cl$ with dmpm for several days at room temperature. At this point, the solution still contains unreacted starting material as well as detectable amounts of the bidentate complex **9**; at room temperature, about 3 weeks are required for complete disappearance of the starting material. Loss of the remaining PPh_3 ligand in **8** is also sluggish: the conversion to **9** is not even half complete after 6 weeks of stirring at room temperature.

We obtained our highest yields of **9** by heating the mixture of $TpOs(PPh_3)_2Cl$ and dmpm in toluene for 2 days. (Heating the reaction mixture for longer than 2 days produces other unidentified products and diminishes the yield of **9**.) The reaction supernatant is filtered, concentrated, and cooled, affording **9** as a white, microcrystalline precipitate in 23% yield. Subsequent crops obtained by cooling the supernatant consist of a mixture of compounds **8** and **9**.

The ^{1}H NMR spectrum of **9** (Figure 4) indicates that, like compounds of stoichiometry TpOs(cod)X, the molecule is pseudo-octahedral with C_s symmetry. The methyl protons of the dmpm ligand appear as a pair of virtually coupled triplets at δ 1.62 and 0.91; two PMe_2 peaks are seen because the methyl groups are either promixal or distal to the Tp ligand. The backbone methylene protons of the dmpm ligand also can be either proximal or distal with respect to the Tp ligand, and they appear as two separate doublets of triplets at δ 3.72 and 3.55. The IR spectrum shows a B−H stretch at 2457 cm^{-1}.

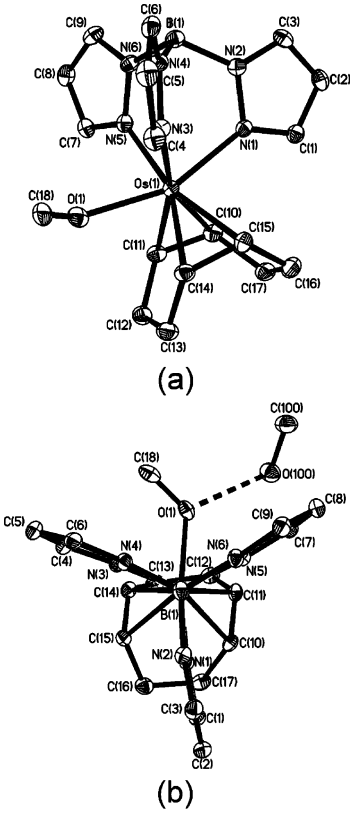

Figure 2. ORTEP diagrams of TpOs(cod)OMe·MeOH (**7**): (a) side view and (b) view down the B−Os bond axis showing the hydrogen bonding interaction with the MeOH solvent molecule. The 35% probability density surfaces are shown. The hydrogen atoms have been omitted for clarity.

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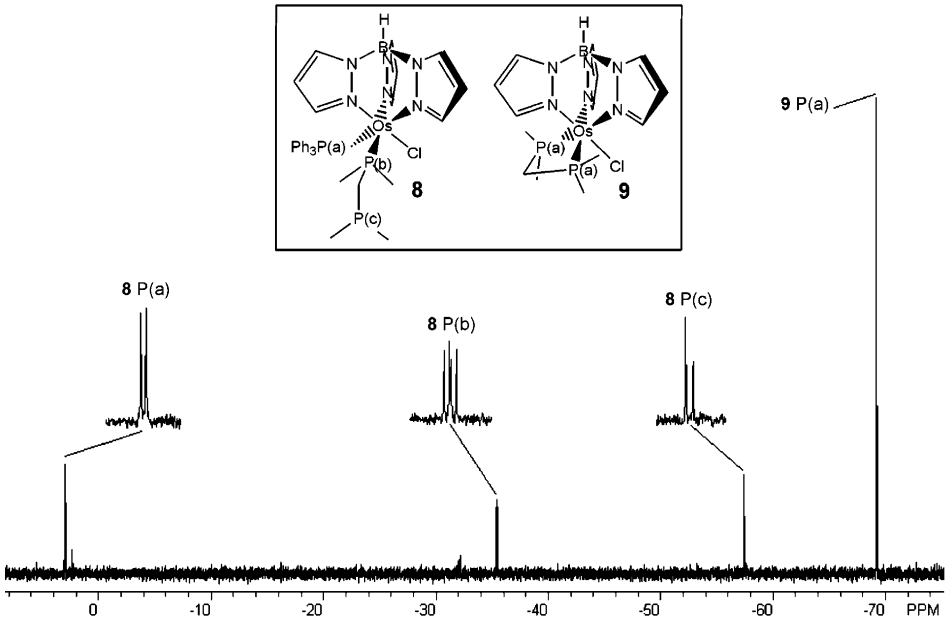

Figure 3. $^{31}P\{^1H\}$ NMR spectrum (C_7D_8, 22 °C) of TpOs(PPh_3)(η^1-dmpm)Cl (**8**) and TpOs(η^2-dmpm)Cl (**9**).

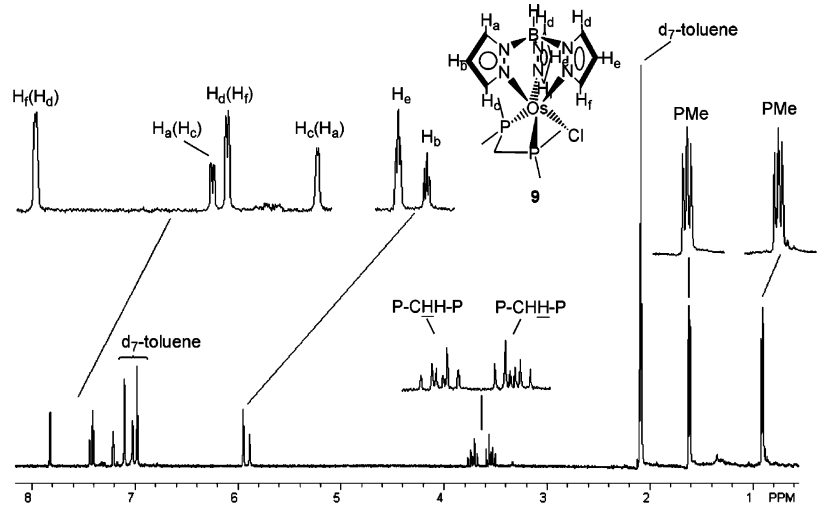

Figure 4. ^1H NMR spectrum (C_7D_8, 22 °C) of TpOs(dmpm)Cl (**9**).

Treatment of **9** with methyllithium produces the methyl compound TpOs(dmpm)Me (**10**), which was prepared in situ. The methyl resonance of TpOs(dmpm)Me appears as a triplet at δ 0.45 in the ^1H NMR spectrum.

Comparison of TpOs and (C_5Me_5)Os Chemistry. A trend resulting from this work is that ligand substitution rates appear to be significantly slower for $TpOs^{II}$ complexes than for their (C_5Me_5)Os^{II} counterparts. Whereas (C_5Me_5)Os(cod)Br reacts with phosphines in refluxing heptane (98 °C) in less than an hour to afford products in which the cod ligand has been replaced,[58] the corresponding TpOs(cod)Br is unreactive even at much higher temperatures (>150 °C). Similarly, treatment of TpOs(cod)Br with sodium methoxide affords the methoxy complex TpOs(cod)OMe, which is quite stable toward β-elimination, but the corresponding C_5Me_5 reaction affords (C_5Me_5)Os(cod)H in high yield after similar reaction times, and the methoxy complex was never observed among the reaction products.[58] Further evidence of the lower lability of the TpOs compounds is that the triflate complex TpOs(cod)(OTf) reacts sluggishly with alkylating agents, such as dimethylmagnesium (reaction times of several days), whereas the tetramethylcyclopentadienyl complex (C_5Me_4H)Os(cod)Br can be alkylated to (C_5Me_4H)Os(cod)Me in less than 8 h.[67] Thus, both neutral π-acceptors (cod) and anions (OTf) are slow to dissociate from $TpOs^{II}$ centers.

Although the strong σ-donor character of Tp versus C_5Me_5 could explain why acceptor ligands such as cod are more strongly bound, the slow dissociation kinetics cannot be so explained. Instead, as has been pointed out by other authors,[68−72] these phenomena are most likely a consequence

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of the strongly directional character of the frontier orbitals of the TpM fragment, which overlap strongly with ligands that complete a pseudo-octahedral coordination sphere about the metal center. These differences between Tp complexes and their cyclopentadienyl analogues are likely to find increasing utility in synthetic transition-metal chemistry.

Experimental Section

All operations were carried out under argon or vacuum using standard Schlenk techniques unless otherwise specified. All solvents were distilled under nitrogen from magnesium (ethanol), calcium hydride (acetonitrile, dichloromethane), or sodium benzophenone (pentane, ether, toluene). *tert*-Butyl alcohol was dried over $MgSO_4$ and distilled from magnesium under argon. Osmium tetroxide (Colonial Metals), hydrobromic acid (Aldrich), 1,5-cyclooctadiene (Aldrich), Celite (Fisher), methyl trifluoromethanesulfonate (Aldrich), NaOMe (Aldrich), triphenylphosphine (Aldrich), and pyrazole (Aldrich) were used as received. Trifluoromethanesulfonic acid and bromoform were distilled under argon before use. Potassium tris-pyrazolylborate,[73] dimethylmagnesium,[74] and ammonium hexachloroosmate[43] were prepared according to literature procedures. Bis(dimethylphosphino)methane was either used as received (Strem) or prepared by a literature route.[75]

Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Field-desorption (FD) mass spectra were performed on a 70-VSE-A mass spectrometer. The samples were loaded as CH_2Cl_2 solutions, and the spectrometer source temperature was 25 °C. All peak envelopes matched the calculated isotope distribution patterns for the respective ions. The IR spectra were obtained on a Nicolet Impact 410 spectrometer as Nujol mulls between KBr plates. The ^{1}H, ^{13}C, and ^{19}F NMR data were recorded on a Varian Unity-400 spectrometer at 9.4 T. Chemical shifts are reported in δ units (positive shifts to higher frequency) relative to TMS or $CFCl_3$. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

Dibromo(1,5-cyclooctadiene)osmium(II), $[OsBr_2(cod)]_x$ (1). A solution of OsO_4 (3.0 g, 11.8 mmol) in concentrated hydrobromic acid (80 mL) was heated to reflux for 2 h. The resulting dark red solution was taken to complete dryness on a rotary evaporator, and care was taken to ensure that the bath temperature during this step did not exceed 50 °C. The dark solid, H_2OsBr_6, was dissolved in freshly distilled *tert*-butyl alcohol (200 mL) and treated with 1,5-cyclooctadiene (6.0 mL, 63 mmol). The dark red solution was heated to reflux for 2 days, during which time a brown solid precipitated. (The supernatant should be pale yellow to colorless. If it is dark yellow-orange, the reaction mixture should be heated to reflux for 1−4 more days until the supernatant is pale yellow to colorless.) The solid was collected by filtration, washed with acetone (3 × 30 mL) and diethyl ether (3 × 30 mL), and dried under vacuum. Yield: 4.88 g (90%). Mp: >280 °C. Anal. Calcd for $C_8H_{12}Br_2Os$: C, 21.0; H, 2.6; Br, 34.9. Found: C, 20.9; H, 2.7; Br, 34.4. IR (cm^{-1}): 2721 (m), 2663 (m), 2024 (m), 1699 (m), 1327 (s), 1296 (m), 1262 (w), 1243 (w), 1207 (vw), 1181 (sh), 1165 (m), 1092 (w), 1073 (w), 1024 (w), 1009 (s), 969 (vw), 920 (w), 894 (vw), 872 (vw), 843 (vw), 816 (w), 789 (w).

Dibromo(1,5-cyclooctadiene)bis(acetonitrile)osmium(II), $OsBr_2(cod)(MeCN)_2$ (2). A brown suspension of $[OsBr_2(cod)]_x$ (0.50 g, 1.09 mmol) in acetonitrile (150 mL) was heated to reflux for 3 days. The yellow supernatant was filtered while the reaction mixture was still hot. The remaining brown solid was extracted into additional acetonitrile (3 × 20 mL), and the extracts were filtered and combined with the supernatant. The resulting solution was concentrated to ca. 6 mL and cooled to −20 °C for 8 h to afford yellow plates. Yield: 0.20 g (34%). Additional crops can be obtained by further concentrating and cooling the filtrate. Mp: 104 °C. Anal. Calcd for $C_{12}H_{18}N_2Br_2Os$: C, 26.7; H, 3.4; N, 5.2. Found: C, 27.1; H, 3.4; N, 5.4. MS (FD): 456.0 *m/z* [$OsBr_2(cod)^+$]. ^{1}H NMR (CD_3CN): δ 4.15 (m, 4H, cod), 2.70 (s, 6H, CH_3CN), 2.31 (m, 4H, cod), 1.87 (m, 4H cod). ^{13}C{^{1}H} NMR (CD_3CN): δ 124.5 (s, CH_3CN), 77.0 (s, cod), 32.1 (s, cod), 4.8 (s, CH_3CN). IR (cm^{-1}): 2723 (m), 2670 (m), 2363 (w), 2285 (w), 2246 (m), 2037 (w), 1410 (m), 1333 (m), 1305 (m), 1215 (m), 1192 (m), 1179 (m), 1168 (m), 1088 (m), 1013 (m), 1002 (m), 969 (m), 951 (m), 918 (m), 870 (m), 846 (m), 835 (m), 818 (m), 785 (m), 668 (w), 606 (w), 537 (w), 503 (w), 491 (w), 447 (w), 433 (w).

[Tris(pyrazolyl)borato]hydrido(1,5-cyclooctadiene)osmium(II), TpOs(cod)H (3). A mixture of $[OsBr_2(cod)]_x$ (0.50 g, 1.09 mmol) and KTp (0.41 g, 1.64 mmol) in ethanol (150 mL) was heated to reflux for 24 h. Over this time, the initially brown slurry produced a yellow supernatant and white solid. The solvent was removed on a rotary evaporator, and the resulting yellow residue was extracted with Et_2O (2 × 20 mL). The extracts were filtered through Celite on a sintered glass frit, combined, concentrated to ca. 3 mL, and cooled to −20 °C for 24 h to afford yellow plates. Yield 0.54 g (96%). Anal. Calcd for $C_{17}H_{23}N_6BOs$: C, 39.9; H, 4.5; N, 16.4. Found: C, 40.1; H, 4.8; N, 15.9. MS (FD): 514.3 *m/z* [TpOs(cod)H$^+$], 580.4 *m/z* [TpOs(cod)(pyrazolyl)$^+$]. ^{1}H NMR (C_6D_6): δ 8.22 (d, 1H, J_{HH} = 1.5 Hz, Tp), 7.42 (d, 3H, J_{HH} = 2.0 Hz, Tp), 7.30 (d, 2H, J_{HH} = 2.0 Hz, Tp), 6.01 (t, 1H, J_{HH} = 2.3 Hz, Tp), 5.74 (t, 2H, J_{HH} = 2.3 Hz, Tp), 3.89 (m, 2H, cod), 2.86 (m, 2H, cod), 2.46 (m, 4H, cod), 2.17 (m, 2H, cod), 2.87 (m, 2H, cod), −8.52 (s, 1H, Os−H). ^{13}C{^{1}H} NMR (C_6D_6): δ 142.9 (s, Tp), 140.9 (s, Tp), 134.9 (s, Tp), 106.1 (s, Tp), 105.5 (s, Tp), 58.0 (s, cod), 54.5 (s, cod), 35.7 (s, cod), 31.3 (s, cod). IR (cm^{-1}): 2460 (m), 2085 (m), 1506 (sh), 1496 (w), 1428 (w), 1412 (m), 1397 (m), 1377 (m), 1366 (sh), 1352 (w), 1321 (w), 1306 (m), 1288 (m), 1262 (w), 1236 (w), 1213 (m), 1182 (w), 1156 (w), 1117 (m), 1076 (w), 1070 (w), 1047 (m), 1040 (m), 1003 (w), 981 (w), 977 (w), 929 (w), 920 (w), 897 (w), 878 (w), 850 (vw), 836 (vw), 826 (vw), 816 (w), 791 (w), 749 (m), 731 (m), 663 (vw), 619 (w), 531 (vw), 508 (vw), 499 (w).

[Tris(pyrazolyl)borato]bromo(1,5-cyclooctadiene)osmium(II), TpOs(cod)Br (4). A mixture of $[OsBr_2(cod)]_x$ (2.80 g, 6.11 mmol) and KTp (3.08 g, 12.22 mmol) in ethanol (70 mL) was heated to reflux for 2 h. Over this time, the initially brown slurry produced a light yellow supernatant and white solid. (In different reaction runs, the supernatant sometimes turned dark orange. A darker color had no effect on the final yield.) The reaction mixture was treated with freshly distilled $CHBr_3$ (ca. 1 mL). After the mixture had stirred for 5 min, the solvent was evaporated on a rotary evaporator. The product was extracted into Et_2O (3 × 30 mL), and the extracts were filtered through Celite on a sintered glass frit and combined. The resulting solution was concentrated to 7 mL and cooled to −20 °C for 8 h to afford a yellow microcrystalline solid. Yield 1.72 g (48%). A small amount of pyrazole may cocrystallize with **6**. The pyrazole can be removed by stirring the solid product in pentane (200 mL) for 12 h, followed by filtration. Mp: 215−218 °C. Anal. Calcd for $C_{17}H_{22}N_6BrBOs$: C, 34.5; H, 3.8; N, 13.8.

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Found: C, 35.1; H, 3.7; N, 13.8. MS (FD): 592.1 *m/z* [TpOs(cod)Br$^+$]. ^{1}H NMR (C_6D_6): δ 7.74 (d, 1H, J_{HH} = 2.4 Hz, Tp), 7.62 (d, 2H, J_{HH} = 2.4 Hz, Tp), 7.26 (d, 2H, J_{HH} = 2.4 Hz, Tp), 7.19 (d, 1H, J_{HH} = 2.8 Hz, Tp), 5.83 (t, 2H, J_{HH} = 2.2 Hz, Tp), 5.75 (t, 1H, J_{HH} = 2.4 Hz, Tp), 5.09 (m, 2H, cod), 3.75 (m, 2H, cod), 3.14 (m, 2H, cod), 2.40 (m, 2H, cod), 2.21 (m, 2H, cod), 2.03 (m, 2H, cod). ^{13}C{^{1}H} NMR (C_6D_6): δ 144.1 (s, Tp), 142.1 (s, Tp), 136.3 (s, Tp), 134.7 (s, Tp), 106.2 (s, Tp), 106.2 (s, Tp), 76.9 (s, cod), 71.1 (s, cod), 33.5 (s, cod), 32.3 (s, cod). IR (cm^{-1}): 3187 (w), 3123 (w), 3111 (w), 2722 (w), 2671 (w), 2617 (w), 2515 (vw), 2464 (m), 2433 (w), 2389 (w), 2354 (w), 2006 (w), 1915 (w), 1506 (w), 1495 (w), 1415 (sh), 1406 (m), 1397 (s), 1327 (m), 1311 (s), 1300 (s), 1229 (s), 1219 (s), 1211 (s), 1195 (m), 1183 (m), 1175 (m), 1164 (m), 1122 (s), 1075 (m), 1054 (s), 1046 (s), 1011 (m), 1005 (m), 989 (m), 980 (m), 925 (w), 917 (w), 900 (w), 889 (m), 880 (m), 868 (w), 841 (w), 818 (w), 793 (m), 767 (s), 754 (s), 731 (m), 663 (w), 654 (w), 619 (m), 534 (w), 505 (w), 484 (w), 465 (vw), 457 (vw), 447 (vw), 430 (vw), 418 (w), 415 (w), 407 (vw).

[Tris(pyrazolyl)borato]methoxy(1,5-cyclooctadiene)osmium(II), TpOs(cod)(OMe)·MeOH (5). To a mixture of TpOs(cod)Br (0.26 g, 0.44 mmol) and NaOMe (0.10 g, 1.8 mmol) was added methanol (50 mL), and the yellow suspension was refluxed for 20 h. The solvent was evaporated, and the yellow residue was extracted into Et_2O (2 × 20 mL). The Et_2O extracts were filtered through a sintered glass frit, combined, concentrated to ca. 2 mL, and cooled to −20 °C for 8 h to afford yellow plates. Yield: 0.08 g (32%). Mp: 198 °C. Anal. Calcd for $C_{19}H_{29}N_6BO_2Os$ [TpOs(cod)OMe·MeOH]: C, 39.7; H, 5.1; N, 14.6. Found: C, 39.6; H, 4.9; N, 14.4. ^{1}H NMR (C_6D_6): δ 7.67 (d, 1H, J_{HH} = 2.0 Hz, Tp), 7.64 (d, 2H, J_{HH} = 1.6 Hz, Tp), 7.33 (d, 2H, J_{HH} = 2.0 Hz, Tp), 7.25 (d, 1H, J_{HH} = 2.4 Hz, Tp), 5.85 (t, 2H, J_{HH} = 2.4 Hz, Tp), 5.77 (t, 1H, J_{HH} = 2.4 Hz, Tp), 4.54 (m, 2H, cod), 3.85 (m, 2H, cod), 3.48 (s, *Me*OH), 2.86 (s, 3H, Os−OMe), 2.83 (m, 2H, cod), 2.29 (m, 2H, cod), 2.16 (m, 4H, cod). ^{13}C{^{1}H} NMR (C_6D_6): δ 144.2 (s, Tp), 140.3 (s, Tp), 136.1 (s, Tp), 134.5 (s, Tp), 106.0 (s, Tp), 105.8 (s, Tp), 79.1 (s, cod), 73.6 (s, cod), 56.2 (s, OMe), 50.3 (s, CH_3OH), 33.3 (s, cod), 30.9 (s, cod). IR (cm^{-1}): 2484 (m), 1410 (m), 1396 (m), 1309 (m), 1228 (m), 1214 (m), 1208 (m), 1196 (w), 1159 (vw), 1124 (m), 1119 (m), 1076 (m), 1047 (s), 1020 (sh), 922 (m), 977 (m), 917 (w), 890 (w), 874 (w), 849 (w), 814 (m), 801 (m), 792 (m), 781 (m), 767 (m), 753 (m), 681 (w), 668 (w), 652 (w), 625 (w), 617 (w), 605 (vw), 534 (vw), 527 (vw), 487 (w), 462 (m), 450 (m), 438 (m), 427 (m), 419 (m), 411 (m).

[Tris(pyrazolyl)borato]trifluoromethanesulfonato(1,5-cyclooctadiene)osmium(II), TpOs(cod)OTf (6). To a solution of TpOs(cod)H (0.30 g, 0.59 mmol) in diethyl ether (60 mL) at 0 °C was added methyl trifluoromethanesulfonate (0.13 mL, 1.2 mmol). The solution was stirred for 5 h at 0 °C, after which time a small amount of yellow precipitate had formed. The yellow supernatant was filtered, concentrated to 8 mL, and cooled to −20 °C for 24 h to afford orange crystals. Yield: 0.21 g (52%). Anal. Calcd for $C_{20}H_{27}N_6O_{3.5}BF_3SOs$ [TpOs(cod)OTf·0.5Et_2O]: C, 34.4; H, 3.9; N, 12.0. Found: C, 34.0; H, 3.9; N, 11.7. ^{1}H NMR (C_6D_6): δ 7.68 (d, 2H, J_{HH} = 2.0 Hz, Tp), 7.29 (d, 2H, J_{HH} = 2.0 Hz), 7.22 (d, 1H, J_{HH} = 2.0 Hz,Tp), 7.07 (d, 1H, J_{HH} = 2.0 Hz, Tp), 5.91 (t, 2H, J_{HH} = 2.0, Tp), 5.60 (t, 1H, J_{HH} = 2.0 Hz, Tp), 5.22 (m, 2H, cod), 4.12 (m, 2H, cod), 3.25 (q, J_{HH} = 7.0 Hz, Et_2O), 2.76 (m, 2H, cod), 2.16 (m, 2H, cod), 2.05 (m, 2H, cod), 1.99 (m, H cod), 1.11 (t, J_{HH} = 7.0 Hz, Et_2O). ^{13}C{^{1}H} NMR (C_6D_6): δ 145.0 (s, Tp), 142.6 (s, Tp), 137.2 (s, Tp), 135.6 (s, Tp), 106.8 (s, Tp), 106.6 (s, Tp), 84.0 (s, cod), 79.7 (s, cod), 66.1 (s, Et_2O), 33.1 (s, cod), 30.6 (s, cod), 15.8 (s, Et_2O). ^{19}F NMR (C_6D_6): δ −79.4 (s, SO_2CF_3). IR (cm-^{1}): 3180 (w), 3146 (w), 3134 (w), 3113 (w), 3037 (m), 3024 (m), 2723 (w), 2623 (w), 2506 (m), 2386 (w), 2353 (w), 1504 (m), 1416 (s), 1401 (s), 1319 (s), 1280 (sh), 1260 (s), 1229 (s), 1216 (s), 1203 (s), 1180 (s), 1125 (s), 1082 (s), 1075 (s), 1048 (s), 1014 (s), 1001 (s), 984 (s), 938 (m), 926 (m), 918 (m), 891 (m), 882 (m), 867 (m), 834 (m), 819 (m), 795 (m), 770 (sh), 760 (s), 731 (m), 676 (w), 662 (w), 652 (w), 631 (s), 618 (s), 583 (m), 567 (w), 518 (w), 507 (w), 478 (w), 413 (sh), 403 (vw).

[Tris(pyrazolyl)borato]methyl(1,5-cyclooctadiene)osmium(II), TpOs(cod)Me (7). To a solution of TpOs(cod)OTf·0.5Et_2O (0.15 g, 0.22 mmol) in diethyl ether (30 mL) was added dimethylmagnesium (0.31 mL of a 0.80 M solution in Et_2O, 0.25 mmol). The solution was stirred at room temperature for 24 h, during which time the solution color changed from yellow to colorless. Distilled water (30 mL) was added to the reaction solution. The Et_2O layer was separated in air in a separatory funnel. The organic layer was washed with distilled water (3 × 30 mL) and brine solution (30 mL) and then dried over $MgSO_4$. The colorless Et_2O solution was filtered, concentrated to 8 mL, and cooled to −20 °C for 48 h to afford white plates. Yield: 0.011 g (10%). Anal. Calcd for $C_{18}H_{25}N_6BOs$: C, 41.1; H 4.8. Found: C, 40.5; H, 5.1. MS (FD): 528.3 *m/z* [TpOs(cod)Me$^+$]. ^{1}H NMR (C_6D_6): δ 8.13 (d, 1H, J_{HH} = 2.0 Hz, Tp), 7.36 (d, 1H, J_{HH} = 2.0 Hz, Tp), 7.30 (d, 2H, J_{HH} = 2.4 Hz, Tp), 7.20 (d, 2H, J_{HH} = 2.0 Hz, Tp), 5.93 (t, 1H, J_{HH} = 2.2 Hz, Tp), 5.78 (t, 2H, J_{HH} = 2.2 Hz, Tp), 3.55 (m, 2H, cod), 3.11 (m, 2H, cod), 2.58 (m, 2H, cod), 2.45 (m, 2H, cod), 1.97 (m, 2H, cod), 1.84 (m, 2H, cod), 1.44 (s, 3H, Os−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 143.3 (s, Tp), 138.4 (s, Tp), 135.4 (s, Tp), 134.5 (s, Tp), 106.1 (s, Tp), 106.0 (s, Tp), 68.8 (s, cod), 61.1 (s, cod), 32.3 (s, cod), 32.1 (s, cod), −3.1 (s, Os−Me). IR (cm^{-1}): 2471 (w), 1498 (w), 1408 (m), 1398 (m), 1304 (m), 1262 (m), 1217 (m), 1212 (m), 1155 (w), 1122 (m), 1114 (m), 1083 (m), 1075 (m), 1051 (sh), 1044 (s), 985 (w), 976 (w), 903 (vw), 877 (w), 819 (m), 803 (m), 794 (m), 753 (s), 737 (w), 667 (vw), 660 (vw), 621 (w), 497 (w).

Dichlorotris(triphenylphosphine)osmium(II), $OsCl_2(PPh_3)_3$. This procedure is a modification of that in ref 76. A solution of *tert*-butyl alcohol (300 mL) and deionized water (120 mL) was frozen at −78 °C and evacuated in three successive freeze−pump−thaw cycles. The solution was then sparged with argon for 20 min (complete exclusion of air throughout the procedure is crucial to obtain a high yield of product). Ammonium hexachloroosmate(IV) (3.80 g, 8.65 mmol) and triphenylphosphine (15.96 g, 60.84 mmol) were added to the solution, and the mixture was heated to reflux for 3 h, during which time the red-white suspension turned deep green. The mixture was filtered hot on a sintered glass frit, and the filtrate was washed with ethanol (6 × 30 mL) and ether (6 × 30 mL) and dried in a vacuum. (If the reaction mixture is not filtered hot, a substantial amount of PPh_3 will cocrystallize with the product.) The green solid was extracted into dichloromethane (30 mL); the extract was filtered, and the filtrate was diluted with heptane (10 mL). The green solution was concentrated to 15 mL and cooled to −20 °C for 8 h to afford green plates. The product was isolated by filtration and dried in a vacuum. Yield: 4.10 g (45%). Additional crops could be obtained by further concentrating the filtrate.

[Tris(pyrazolyl)borato]chloro[bis(triphenylphosphine)]osmium(II), $TpOs(PPh_3)_2Cl$. This procedure is a modification of that in ref 13. To a mixture of $OsCl_2(PPh_3)_2$ (3.80 g, 6.49 mmol) and KTp (3.27 g, 12.98 mmol) was added dichloromethane (70 mL). The mixture was stirred for 4 h, during which time the reaction

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mixture turned dark green/yellow. The solvent was evaporated, the residue was extracted with toluene (2 × 10 mL), and the extracts were filtered and combined. The green solution was diluted with heptane (20 mL), concentrated to ca. 25 mL, and cooled to −20 °C for 48 h to afford a yellow microcrystalline solid. Yield: 1.40 g (23%). Additional crops can be obtained by further concentration. Anal. Calcd for $C_{45}H_{40}N_6BP_2ClOs$: C, 56.1; H, 4.2; N, 8.7. Found: C, 56.4; H, 4.5; N, 8.3.

[Tris(pyrazolyl)borato]chloro[η^1−bis(dimethylphosphino)-methane]triphenylphosphineosmium(II), TpOs(PPh$_3$)(η^1-dmpm)-Cl (8). To a solution of TpOs(PPh$_3$)$_2$Cl (15 mg, 0.016 mmol) in C_7D_8 (1 mL) was added $Me_2PCH_2PMe_2$ (0.012 mL, 0.078 mmol). The green solution was stirred for 4 days to yield TpOs(PPh$_3$)(η^1-dmpm)Cl, TpOs(dmpm)Cl (characterization given below), free PPh$_3$, and starting materials, as observed by NMR spectroscopy and mass spectrometry. MS(FD): 838.2 *m*/*z* [TpOs(PPh$_3$)(η^1-dmpm)Cl$^+$]. $^{31}P\{^1H\}$ NMR (C_7D_8): δ 2.4 (d, 1P, J_{PP} = 33 Hz, Os−PPh$_3$), −35.7 (dd, 1P, J_{PP} = 33, 45 Hz, Os−*P*Me$_2$CH$_2$PMe$_2$), −58.0 (d, 1P, J_{PP} = 45 Hz, Os−PMe$_2$CH$_2$*P*Me$_2$).

[Tris(pyrazolyl)borato]chloro[bis(dimethylphosphino)methane]-osmium(II), TpOs(dmpm)Cl (9). A solution of TpOs(PPh$_3$)$_2$Cl (0.60 g, 0.62 mmol) and $Me_2PCH_2PMe_2$ (0.19 mL, 1.24 mmol) in toluene (150 mL) was heated to reflux for 2 days. During this time, the solution turned from yellow to green, and a small amount of white precipitate formed. The supernatant was filtered, concentrated, and cooled to −20 °C for 8 h to afford a green microcrystalline solid. Yield: 0.12 g (23%). Anal. Calcd for $C_{15.75}H_{26}N_6ClBP_2Os$ [TpOs(dmpm)Cl·0.25C_7H_8]: C, 31.7; H, 4.4; N 14.1; Cl, 5.9. Found: C, 31.0; H, 4.5; N, 13.6; Cl, 6.1. ^1H NMR (C_7D_8): δ 7.83 (d, 2H, J_{HH} = 1.6 Hz, Tp), 7.44 (d, 1H, J_{HH} = 2.4 Hz, Tp), 7.41 (d, 2H, J_{HH} = 2.4 Hz, Tp), 7.21 (d, 1H, J_{HH} = 1.6 Hz, Tp), 5.95 (t, 2H, J_{HH} = 2.0 Hz, Tp), 5.89 (t, 1H, J_{HH} = 2.2 Hz, Tp), 3.72 (dt, 1H, J_{HH} = 14.4 Hz, J_{PH} = 10.4, PCH$_2$P), 3.55 (dt, 1H, J_{HH} = 14.4 Hz, J_{HP} = 9.6 Hz, PCH$_2$P), 1.62 (t, 6H, J_{HP} = 5.0 Hz, PMe), 0.91 (t, 6H, J_{HP} = 4.6 Hz, PMe). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 145.9 (s, Tp), 143.5 (s, Tp), 135.3 (s, Tp), 133.6 (s, Tp), 105.7 (s, Tp), 105.3 (s, Tp), 57.1 (s, PCH$_2$P), 14.4 (t, J_{PC} = 12.9 Hz, PMe), 13.5 (t, J_{PC} = 15.0 Hz, PMe). $^{31}P\{^1H\}$ NMR (C_7D_8): δ −69.2 (s). IR (cm^{-1}): 2457 (m), 1417 (m), 1399 (m), 1335 (vw), 1308 (m), 1298 (m), 1278 (m), 1240 (vw), 1212 (m), 1197 (m), 1157 (w), 1136 (w), 1111 (m), 1043 (w), 1037 (w), 1027 (w), 980 (vw), 942 (w), 929 (w), 891 (w), 864 (vw), 842 (vw), 816 (vw), 792 (w), 763 (w), 757 (w), 742 (w), 715 (w), 695 (m), 665 (w), 644 (vw), 621 (m).

[Tris(pyrazolyl)borato]methyl[bis(dimethylphosphino)methane]-osmium(II), TpOs(dmpm)Me (10). A solution of TpOs(dmpm)-Cl·0.25C_7H_8 (0.40 g, 0.67 mmol) in tetrahydrofuran (60 mL) was treated with methyllithium (1.49 mL of a 1.80 M solution in diethyl ether, 2.68 mmol). The resulting yellow solution was stirred for 24 h, and then the solvent was evaporated. ^1H NMR (C_4D_8O): δ 7.84 (s, 1H, Tp), 7.62 (d, 1H, J_{HH} = 2.4 Hz, Tp), 7.56 (d, 2H, J_{HH} = 2.4 Hz, Tp), 7.45 (d, 2H, J_{HH} = 2.4 Hz, Tp), 6.09 (t, 1H, J_{HH} = 2.4 Hz, Tp), 6.04 (t, 2H, J_{HH} = 2.4 Hz, Tp), 4.17 (dt, 1H, J_{HH} = 14.0 Hz, J_{PH} = 12.0, PCH$_2$P), 3.66 (dt, 1H, J_{HH} = 14.0 Hz, J_{HP} = 12.0 Hz, PCH$_2$P), 1.50 (t, 6H, J_{HP} = 4.7 Hz, PMe), 1.43 (t, 6H, J_{HP} = 4.7 Hz, PMe), 0.45 (t, 3H, J_{HP} = 5.9 Hz, Os−Me). $^{31}P\{^1H\}$ NMR (C_4D_8O): −69.6 (s).

Pyrazolium Trifluoromethansulfonate, [$C_3H_5N_2$][OTf]. To a solution of pyrazole (0.30 g, 4.4 mmol) in Et$_2$O (60 mL) at 0 °C, was added trifluoromethanesulfonic acid (0.39 mL, 4.4 mmol). A white, flocculent precipitate formed immediately. The reaction mixture was warmed to room temperature and stirred for 30 min. The solid was isolated by filtration and dried in a vacuum. Yield: 0.35 g (36%). Mp: 139−140 °C. Anal. Calcd for $C_4H_5N_2O_3F_3S$: C, 22.0; H, 2.3; N, 12.8. Found: C, 22.0; H, 2.3; N, 12.4. ^1H NMR (C_4D_8O): δ 14.82 (s, 2H, NH), 8.36 (d, 2H, J_{HH} = 2.8 Hz, 3,5-CH), 6.83 (t, 1H, J_{HH} = 2.8 Hz, 4-CH). $^{13}C\{^1H\}$ NMR ($C_4D_{10}O$): δ 135.5 (s, 3,5-C), 108.6 (s, 4-C). ^{19}F NMR (C_4D_8O): δ −79.9 (s, SO_3CF_3). IR (cm^{-1}): 3193 (br), 2725 (s), 2677 (sh), 2520 (m), 2475 (m), 2382 (m), 2366 (sh), 2311 (w), 2251 (w), 2212 (w), 2176 (w), 2113 (w), 1986 (w), 1933 (w), 1839 (m), 1563 (s), 1522 (s), 1422 (s), 1162 (s), 1111 (s), 1046 (s), 927 (sh), 915 (s), 907 (s), 793 (s), 765 (s), 650 (s), 613 (s), 578 (s), 520 (s).

Crystallographic Studies.[77] Single crystals of TpOs(cod)OMe·MeOH, **7**·MeOH, grown by layering a methanol solution with diethyl ether, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and least-squares refinement using 19 322 reflections yielded the cell dimensions given in Table 1.

Data were collected with an area detector. Systematic absences for 0*k*0 ($k \neq 2n$) and *h*0*l* ($h + l \neq 2n$) were only consistent with space group $P2_1/n$. The measured intensities were reduced to structure factor amplitudes, and their estimated standard deviations (esd's) were reduced by correction for background, scan speed, Lorentz, and polarization effects. Although corrections for crystal decay were unnecessary, a face-indexed absorption correction was applied, the maximum and minimum transmission factors being 0.855 and 0.109, respectively. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. All 5004 data were used in the least-squares refinement.

The structure was solved by direct methods using SHELXTL, and the correct positions for the Os and non-hydrogen atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0272P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. All hydrogen atoms except the methanol hydroxyl hydrogen were located in the difference Fourier map, and their locations were independently refined with each being given an individual isotropic displacement factor. The hydroxyl hydrogen on the methanol was fixed in an "idealized" position with the O−H bond equal to 0.84 Å and its displacement parameter set equal to 1.5 times that of O(100). Successful convergence was indicated by the maximum shift/error of 0.000 for the last cycle. The largest peak in the final Fourier difference map (0.89 e Å^{-3}) was located 0.06 Å from Os1. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

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Supporting Information Available: X-ray crystallographic file in CIF format for TpOs(cod)OMe·MeOH (**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(77) For details of the crystallographic methods used, see Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 3139−2144.