

Synthesis and Characterization of Osmium(II) Trispyrazolylborate Complexes

Paul W. Dickinson and Gregory S. Girolami*

School of Chemical Sciences, The University of Illinois at Urbana–Champaign,
600 South Mathews Avenue, Urbana, Illinois 61801

Received February 9, 2006

Treatment of H_2OsBr_6 with excess 1,5-cyclooctadiene (cod) in boiling *tert*-butyl alcohol affords the polymer $[\text{OsBr}_2(\text{cod})]_x$ (**1**), which reacts with acetonitrile to form the mononuclear adduct $\text{OsBr}_2(\text{cod})(\text{CH}_3\text{CN})_2$ (**2**). Polymer **1** reacts with potassium trispyrazolylborate (KTp) in ethanol to afford the hydride $\text{TpOs}(\text{cod})\text{H}$ (**3**) and the bromide complex $\text{TpOs}(\text{cod})\text{Br}$ (**4**). Bromide complex **4** reacts with sodium methoxide in methanol to afford $\text{TpOs}(\text{cod})\text{OMe}$ (**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 $\text{TpOs}(\text{cod})\text{OTf}$ (**6**), which reacts with MgMe_2 to give the methyl complex $\text{TpOs}(\text{cod})\text{Me}$ (**7**). The addition of bis(dimethylphosphino)methane (dmpm) to the known compound $\text{TpOs}(\text{PPh}_3)_2\text{Cl}$ yields a mixture of the substitution products $\text{TpOs}(\eta^1\text{-dmpm})(\text{PPh}_3)\text{Cl}$ (**8**) and $\text{TpOs}(\eta^2\text{-dmpm})\text{Cl}$ (**9**); the latter reacts with methyl lithium to generate the methyl compound $\text{TpOs}(\text{dmpm})\text{Me}$ (**10**). NMR and IR data for these new compounds are reported. Crystal data for **5**·MeOH at -80°C are as follows: monoclinic, $P2_1/n$, $a = 10.728(1)\text{ \AA}$, $b = 14.004(2)\text{ \AA}$, $c = 13.906(2)\text{ \AA}$, $\beta = 102.42(6)^\circ$, $V = 2040.3(5)\text{ \AA}^3$, $Z = 4$, $R_F = 0.0247$ for $l \geq 2\sigma(l)$, and $R_{wF_2} = 0.0539$ 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, $[\text{TpOs}(\text{CO})_2]_2$ and $[(\text{pzTp})\text{Os}(\text{CO})_2]_2$, were prepared by reaction of $[\text{Os}(\text{O}_2\text{CMe})(\text{CO})_3]_2$ with the appropriate potassium polypyrazolylborate, where $\text{Tp} = \text{tris}(\text{pyrazolyl})\text{borate}$ and $\text{pzTp} = \text{tetrakis}(\text{pyrazolyl})\text{borate}$.⁶ Treatment of these dinuclear species with Br_2 cleaved

the Os–Os bond and afforded the mononuclear complexes $\text{TpOs}(\text{CO})_2\text{Br}$ or $(\text{pzTp})\text{Os}(\text{CO})_2\text{Br}$, respectively. Potassium polypyrazolylborate reagents have also been used to prepare the mixed sandwich complexes $\text{TpOs}(\text{C}_5\text{H}_5)$ and $(\text{pzTp})\text{Os}(\text{C}_5\text{H}_5)$ from $[(\text{C}_5\text{H}_5)\text{Os}(\text{CH}_3\text{CN})_3]^+[\text{PF}_6]^-$.⁷ Similarly, Schrock has used potassium trispyrazolylborate (KTp) to prepare the alkylidyne $\text{TpOs}(\text{C}=\text{Bu})(\text{CH}_2=\text{Bu})_2$ from $\text{Os}(\text{C}=\text{Bu})(\text{CH}_2=\text{Bu})_2(\text{py})_2(\text{OTf})$, where $\text{OTf} = \text{trifluoromethanesulfonate}$,⁸ and Shapley prepared the analogous nitride complex $\text{Tp}'\text{Os}(\text{N})\text{Ph}_2$ from the reaction of $[\text{Os}(\text{N})\text{Ph}_2(\text{py})_2]^+[\text{BF}_4]^-$ with KTp' , where $\text{Tp}' = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$.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 $(\eta^2\text{-Tp})\text{Os}(\text{CO})(\text{PPh}_3)_2\text{Ph}$ was prepared by treatment of $\text{Os}(\text{CO})(\text{PPh}_3)_2(\text{Ph})\text{Cl}$ with KTp;¹⁰ heating a solution of the isolated product

* To whom correspondence should be addressed. E-mail: girolami@scs.uiuc.edu.

(1) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842–1844.

(2) Trofimenko, S. *Polyhedron* **2004**, *23*, 197–203.

(3) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(4) Paulo, A.; Correia, J.; Campello, M.; Santos, S. *Polyhedron* **2004**, *23*, 331–360.

(5) Santos, S.; Marques, N. *New J. Chem.* **1995**, *19*, 551–571.

(6) Steyn, M. M. d. V.; Singleton, E.; Hietkamp, S.; Liles, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 2991–2997.

(7) Freedman, D. A.; Gill, T. P.; Blough, A. M.; Koefod, R. S.; Mann, K. R. *Inorg. Chem.* **1997**, *36*, 95–102.

(8) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1993**, *12*, 3379–3381.

(9) Hunt, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071–4076.

(10) Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552–1557.

in toluene resulted in loss of one phosphine ligand and coordination of the third pyrazolyl group to give (η^3 -Tp)-Os(CO)(PPh₃)Ph. Similarly, treatment of Os(CO)(PⁱPr₃)₂HCl with NaTp afforded (η^2 -Tp)Os(CO)(PⁱPr₃)₂H, which loses a phosphine ligand when heated to reflux in toluene, generating (η^3 -Tp)Os(CO)(PⁱPr₃)H.¹¹ Protonation of TpOs(CO)(PⁱPr₃)H with HBF₄ yielded the dihydrogen complex, [TpOs(CO)-(PⁱPr₃)(H₂)] [BF₄]⁻. Jia¹² and Hill¹³ independently reported the synthesis of TpOs(PPh₃)₂Cl by treatment of OsCl₂(PPh₃)₃ with KTp, and the conversion of this compound to the monohydride TpOs(PPh₃)₂H by the addition of either NaOMe or KOH. Protonation of TpOs(PPh₃)₂H yielded the dihydrogen complex [TpOs(PPh₃)₂(H₂)]⁺.¹²

Apart from the compounds above, most osmium Tp complexes are made from other osmium Tp species, as shown particularly by the work of Mayer. The osmium(VI) nitride TpOs(N)Cl₂, which can be prepared by the reaction of K[Os(N)O₃] 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)X₂ (X = acetate, trihaloacetate, bromide, nitrate, and 1/2 oxalate).¹⁶

Because the nitride ligand in TpOs(N)Cl₂ is electrophilic, Grignard reagents and phosphines add directly to the nitrogen atom. For example, treatment of TpOs(N)Cl₂ with PhMgCl yielded [TpOs(NPh)Cl₂]⁻, which can be protonated to afford the structurally characterized amide TpOs(NHPh)Cl₂.¹⁵ The amido ligand in TpOs(NHPh)Cl₂ is inert to further protonation and electrophilic attack at nitrogen.¹⁷ In contrast, the reduced form of this complex, [TpOs(NHPh)Cl₂]⁻, can be protonated to give the aniline complex TpOs(NH₂Ph)Cl₂.¹⁸ The hydrogen atom self-exchange rates between TpOs(NHPh)Cl₂ and TpOs(NH₂Ph)Cl₂ have been investigated.¹⁹ A surprising reaction is the addition of piperidine to TpOs(NHPh)Cl₂, which yields the aromatic substitution product, TpOs[NHC₆H₄-*p*-(NC₅H₁₀)]Cl₂.¹⁵ Reduction of TpOs(N)Cl₂ with PPh₃ affords the phosphiniminato complex TpOs(NPPH₃)Cl₂, which reacts with triflic acid in acetonitrile to produce the salt [TpOs(NHPPH₃)Cl₂]OTf.²⁰ The addition of excess HOTf to the same phosphiniminato complex in CH₂Cl₂ gives products of a different kind, TpOs(OTf)Cl₂ and TpOsCl₃, in which the nitride-derived ligands are lost.²¹

The reduced analogue [PPN⁺][TpOsCl₃⁻], where PPN⁺ is the bis(triphenylphosphine)iminium cation, has been described by Meyer.²² The triflate complex TpOs(OTf)Cl₂ is surprisingly resistant to substitution,²³ but reacts with nitriles and ammonia to afford the nitride TpOsNCl₂.²⁴ Interestingly, reduction of TpOs(OTf)Cl₂ with (C₅Me₅)₂Fe gives the osmium(III) salt [(C₅Me₅)₂Fe⁺][TpOs(OTf)Cl₂⁻], which reacts with a variety of Lewis bases to afford the osmium(III) complexes TpOs(L)Cl₂ (L = MeCN, PhCN, PPh₃, py, imidazole, and NH₃). Oxidation of the neutral osmium(III) complexes with [NO]BF₄ affords the corresponding osmium(IV) salts of the formula [TpOs(L)Cl₂]⁺[BF₄⁻].²¹

An unusual reaction is the addition of BPh₂R (R = Ph, OBPh₂) to TpOs(N)Cl₂, which afforded the insertion product TpOs[N(Ph)(BPhR)]Cl₂. 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)Cl₂ has also served as a starting material for several polynuclear species. Reduction of TpOs(N)Cl₂ with Cp₂Co gives a salt containing a mixed-valence anion [Cp₂Co⁺][TpOs^{IV}Cl₂(N≡N)Cl₂Os^{III}Tp⁻].²⁵ The reaction of TpOs(N)Cl₂ with CpCo[η^4 -Cp(C₆F₅)] affords the complex [TpOsCl₂(N)]₂CoCp, in which the nitride atoms serve as donors to the cobalt center.²⁶ TpOs(N)Cl₂ reacts slowly with PtCl₂(SMe₂)₂ to give the similar donor complex TpOsCl₂(N)–PtCl₂(Me₂S).²⁶ The surprising thermal stabilities of the latter two compounds are attributed to the π -acid character of the TpOs(N)Cl₂ 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(PR₃)₂Cl. 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 [OsBr₂(cod)]_x.

This work was undertaken in part to complement our previous studies of the chemistry of C₅Me₅ osmium complexes, particularly in relation to dihydrogen and alkane activation processes.^{27–30} We became interested in expanding

(11) Bohanna, C.; Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Martinez, M.-P. *Organometallics* **1997**, *16*, 4464–4468.

(12) Ng, W. S.; Jia, G.; Hung, M. Y.; Lau, C. P.; Wong, K. Y.; Wen, L. *Organometallics* **1998**, *17*, 4556–4561.

(13) Buriez, B.; Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. *Organometallics* **1999**, *18*, 1504–1516.

(14) Crevier, T. J.; Lovell, S.; Mayer, J. M. *J. Chem. Soc., Chem. Commun.* **1998**, 2371–2372.

(15) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059–1071.

(16) Dehestani, A.; Kaminsky, W.; Mayer, J. M. *Inorg. Chem.* **2003**, *42*, 605–611.

(17) Soper, J. D.; Bennett, B. K.; Lovell, S.; Mayer, J. M. *Inorg. Chem.* **2001**, *40*, 1888–1893.

(18) Soper, J. D.; Rhile, I. J.; DiPasquale, A. G.; Mayer, J. M. *Polyhedron* **2004**, *23*, 323–329.

(19) Soper, J. D.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 12217–12229.

(20) Bennett, B. K.; Saganic, E.; Lovell, S.; Kaminsky, W.; Samuel, A.; Mayer, J. M. *Inorg. Chem.* **2003**, *42*, 4127–4134.

(21) Bennett, B. K.; Pitteri, S. J.; Pilobello, L.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Chem. Soc., Dalton Trans.* **2001**, 3489–3497.

(22) Demadis, K. D.; El-Samanody, E.-S.; Meyer, T. J.; White, P. S. *Polyhedron* **1999**, *18*, 1587–1594.

(23) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2004**, *125*, 15734–15735.

(24) Bennett, B. K.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 4336–4337.

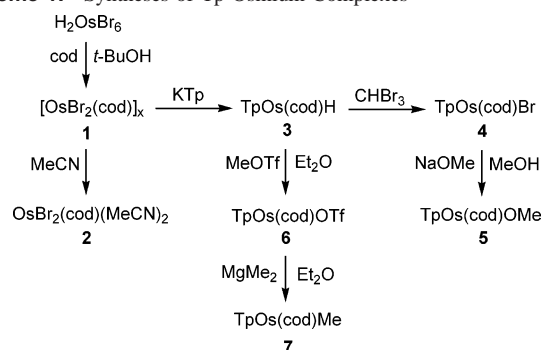
(25) Demadis, K. D.; El-Samanody, E.-S.; Coia, G. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 535–544.

(26) Crevier, T. J.; Lovell, S.; Mayer, J. M.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 6607–6608.

(27) Brumaghim, J. L.; Pripot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139–2144.

(28) Gross, C.; Girolami, G. S. *J. Am. Chem. Soc.* **1998**, *120*, 6605–6606.

(29) Webster, C. E.; Gross, C. L.; Young, D. M.; Girolami, G. S.; Schultz, A. J.; Hall, M. B.; Eckert, J. *J. Am. Chem. Soc.* **2005**, *127*, 15091–15101.

Scheme 1. Syntheses of Tp Osmium Complexes^a

^a cod = 1,5-cyclooctadiene, OTf = trifluoromethanesulfonate.

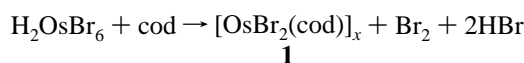
this investigation to related osmium complexes in which the C₅Me₅ ligand was replaced by other ancillary groups such as Tp. One especially important question is whether the strongly directional frontier orbitals of the TpM fragment (see below) would change the chemistry relative to their (C₅Me₅)Os analogues.

Results and Discussion

Synthesis of [OsBr₂(cod)]_x (1) and OsBr₂(cod)(MeCN)₂ (2). The ruthenium polymer [RuCl₂(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 RuCl₃ and cod in boiling ethanol.^{38–40} The analogous osmium polymer, [OsCl₂(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 H₂OsCl₆ and cod in boiling isoamyl alcohol.⁴¹ Lewis and Schrock claimed that a higher yield (90%) could be obtained by heating OsO₄ 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,

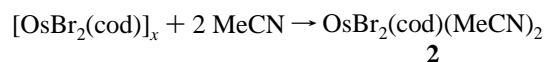
we obtained yields of 15–20% using this procedure. Our difficulty in obtaining high yields of [OsCl₂(cod)]_x prompted us to explore the bromo analogue, [OsBr₂(cod)]_x.

Addition of HBr to OsO₄ generates H₂OsBr₆,^{43,44} which reacts with excess cod in boiling *tert*-butyl alcohol to afford a yellow-brown precipitate of [OsBr₂(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 H₂OsBr₆ in neat cod but in lower yield (30–40%).



The IR spectrum of **1** is similar to that of the known polymers [RuCl₂(cod)]_x⁴⁶ and [OsCl₂(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 OsBr₂(cod)(MeCN)₂ (**2**). The chlororuthenium analogue RuCl₂(cod)(MeCN)₂ has been reported by Lewis.⁴⁷ The ¹H 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.



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

- (30) Mui, H. D.; Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 3264–3272.
- (31) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001–4003.
- (32) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867–3869.
- (33) Cucullu, M. E.; Nolan, S. P.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1999**, *18*, 1299–1304.
- (34) Coalter, J. N. I.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 679–684.
- (35) Schroder, M.; Stephenson, T. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 5, pp 363–364.
- (36) Bennett, M. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 7, p 748.
- (37) Alvarez, P.; Gimeno, J.; Lastra, E.; Garcia-Granda, S.; van der Maelen, J. F.; Bassetti, M. *Organometallics* **2001**, *20*, 3762–3771.
- (38) Bennett, M. A.; Wilkinson, G. *Chem. Ind. (London, U.K.)* **1959**, 1516.
- (39) Albers, M. O.; Singleton, E.; Yates, J. E. *Inorg. Synth.* **1989**, *26*, 249–258.
- (40) Albers, M. O.; Ashworth, T. V.; Oosthuizen, H. E.; Singleton, E. *Inorg. Synth.* **1989**, *26*, 68–77.
- (41) Winkhaus, G.; Singer, H.; Kricke, M. Z. *Naturforsch., B: Chem. Sci.* **1966**, *21*, 1109–1110.
- (42) Schrock, R. R.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.* **1974**, 951–959.

- (43) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 204–207.
- (44) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601–1604.
- (45) To obtain the best yields of **1**, the hexabromoosmic acid must be dried thoroughly at temperatures not exceeding 50 °C. Failure to do so results in a greenish reaction mixture and little precipitate (<20% yield). The *tert*-butyl alcohol solvent must also be very dry; if it is not, the reaction could take up to 6 days to reach completion.
- (46) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178–3182.
- (47) Johnson, B. F. G.; Lewis, J.; Ryder, I. E. *J. Chem. Soc., Dalton Trans.* **1977**, 719–724.

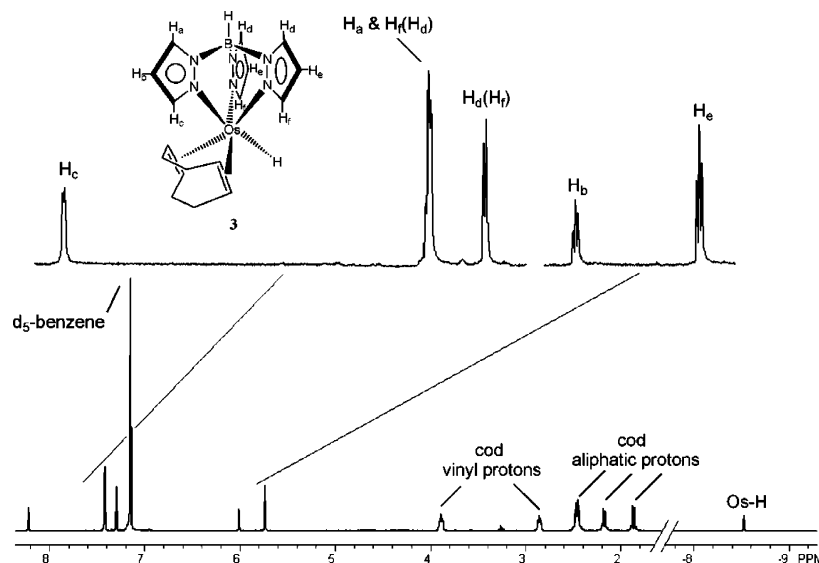
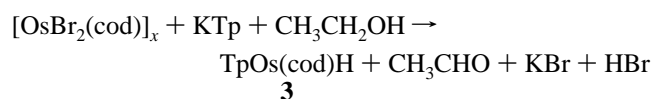


Figure 1. ^1H NMR spectrum (C_6D_6 , 22°C) of $\text{TpOs}(\text{cod})\text{H}$ (**3**).

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



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).

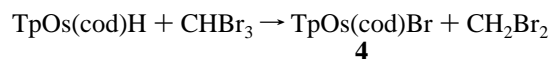
The IR spectrum of **3** shows a B–H stretch at 2460 cm^{-1} and an Os–H stretch at 2085 cm^{-1} . The ^1H NMR spectrum of **3** (Figure 1) indicates that the molecule is octahedral with C_s symmetry. Two doublets at δ 8.22 (1H) and 7.42 (1H) are assigned to the protons at the 3- and 5-positions of the 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 $\text{TpOs}(\text{cod})\text{X}$ 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 ^1H 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 $\text{TpOs}(\text{cod})$ -(pyrazolyl)⁺ or alternatively to the tetrakis(pyrazolyl)borate hydride $(\text{pzTp})\text{Os}(\text{cod})\text{H}^+$, which may be formed in the ionization process.

The initial product of the reaction of $[\text{OsBr}_2(\text{cod})]_x$ (**1**) with KTp in boiling ethanol is the bromo complex $\text{TpOs}(\text{cod})\text{Br}$ (**4**), but even at short reaction times a substantial amount of the hydride $\text{TpOs}(\text{cod})\text{H}$ (**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 $[\text{OsBr}_2(\text{cod})]_x$ (**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.



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 $\text{TpOs}(\text{cod})\text{OMe}$ (5**).** Treatment of bromide **4** with NaOMe in methanol at reflux for 20 h affords the methoxide compound, $\text{TpOs}(\text{cod})\text{OMe}\cdot\text{MeOH}$ (**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-

(48) Williams, J. K. *J. Org. Chem.* **1964**, *29*, 1377–1379.

(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 $[\text{PzH}^+][\text{OTf}^-]$ 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 ₆ O ₂ Os
fw	574.49
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.728(1)
<i>b</i> , Å	14.004(2)
<i>c</i> , Å	13.906(2)
β , deg	102.42(2)
<i>V</i> , Å ³	2040.3(5)
<i>Z</i>	4
<i>T</i> , °C	−80
λ , Å	0.71073
<i>D</i> _{calcd} , Mg m ^{−3}	1.870
μ , mm ^{−1}	6.279
<i>R</i> _F ^a (<i>I</i> ≥ 2 σ (<i>I</i>))	0.0247
<i>R</i> _{wF₂} ^b (all data)	0.0539

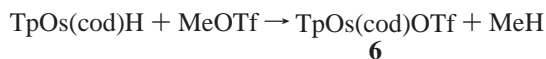
$$^a R_F = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}. \quad ^b R_{wF_2} = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

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 ¹H NMR spectrum of **5** shows a resonance at δ 2.86 for the methoxy group. For comparison, the methoxy group in (C₆H₃Me₃)OsH(OMe)(^tPr₂PCH=CH₂) has a ¹H NMR chemical shift of δ 4.05.⁵⁶ The IR spectrum of **5** shows a B–H stretch at 2484 cm^{−1}.

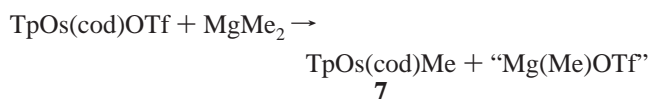
Single crystals of the methanol solvate TpOs(cod)OMe·MeOH crystallize in the *P*2₁/*n* space group. Crystal data are presented in Table 1, and selected bond distances and angles are given in Table 2. The Os–O bond length is 2.127(2) Å, and the Os–O–C angle is 125.1(2)°. There is a hydrogen bonding interaction 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 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 ¹⁹F NMR spectrum consists of a singlet at δ −79.4.



Treatment of **6** with 1.1 equiv of dimethylmagnesium (MgMe₂) 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 ¹H 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}.



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

Synthesis of TpOs(PR₃)₂X 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 PMe₃. 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: (C₅Me₅)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(PPh₃)₂Cl with dmpm for 1 week at room temperature affords two primary products, TpOs(η^1 -dmpm)(PPh₃)Cl (**8**) and TpOs(η^2 -dmpm)Cl (**9**) in a 17:1 ratio, respectively. The ³¹P{¹H} 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 PPh₃ 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

(50) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 90.

(51) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582–4592.

(52) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805–4813.

(53) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390–391.

(54) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1710–1719.

(55) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531–1533.

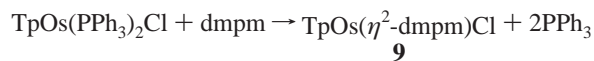
(56) Werner, H.; Henig, G.; Windmuller, B.; Gevert, O.; Lehmann, C.; Herbst-Irmer, R. *Organometallics* **1999**, *18*, 1185–1195.

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**.



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 $\text{TpOs}(\text{PPh}_3)_2\text{Cl}$ 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 $\text{TpOs}(\text{PPh}_3)_2\text{Cl}$ 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**.

- (57) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998–4004.
- (58) Gross, C. L.; Girolami, G. S. *Organometallics* **1996**, *15*, 5359–5367.
- (59) Chisholm, M. H.; Foltling, K.; Huffman, J. C.; Kramer, K. S.; Tatz, R. J. *Organometallics* **1992**, *11*, 4029–4036.
- (60) Cotton, F. A.; Dikarev, E. V.; Herrero, S. *Inorg. Chem.* **1999**, *38*, 490–495.
- (61) Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1997**, *16*, 2987–2994.
- (62) Mague, J. T. *Inorg. Chem.* **1994**, *33*, 4261–4270.
- (63) Mague, J. T.; Balakrishna, M. S. *Polyhedron* **1996**, *15*, 4259–4268.
- (64) Palma-Ramirez, P.; Cole-Hamilton, D. J.; Pogorzelec, P.; Campora, J. *Polyhedron* **1990**, *9*, 1107–1112.
- (65) Wong, W. K.; Chiu, K. W.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1985**, *4*, 1231–1237.
- (66) Wong, W. K.; Chiu, K. W.; Wilkinson, G.; Howes, A. J.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1985**, *4*, 603–614.

The ^1H NMR spectrum of **9** (Figure 4) indicates that, like compounds of stoichiometry $\text{TpOs}(\text{cod})\text{X}$, 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 proximal 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} .

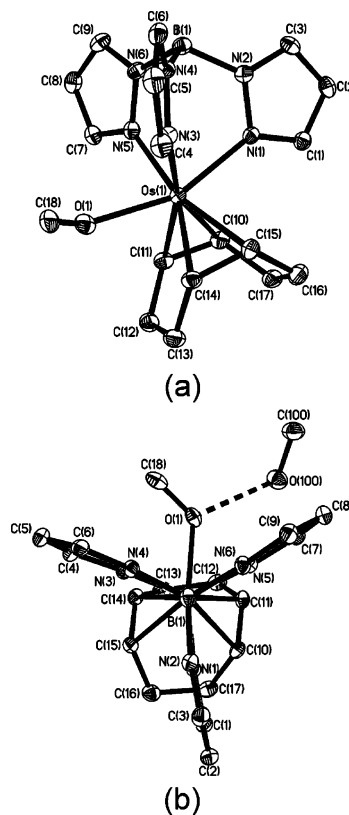


Figure 2. ORTEP diagrams of $\text{TpOs}(\text{cod})\text{OMe}\cdot\text{MeOH}$ (**7**): (a) side view and (b) view down the B–Os bond axis showing the hydrogen bonding interaction with the MeOH solvent molecule. The 35% probability density surfaces are shown. The hydrogen atoms have been omitted for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

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 cyclooctadienyl 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 MgSO₄ 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 tri-pyrazolylborate,⁷³ dimethylmagnesium,⁷⁴ and ammonium hexachloroosmate⁴³ 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 CH₂Cl₂ 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 ¹H, ¹³C, and ¹⁹F 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 CFCl₃. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

Dibromo(1,5-cyclooctadiene)osmium(II), [OsBr₂(cod)]_x (1). A solution of OsO₄ (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, H₂OsBr₆, 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 C₈H₁₂Br₂Os: 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).

(71) Bergman, R. G.; Cundar, T. R.; Gillespie, A. M.; Gunnoe, T. B.; Harman, W. D.; Klinckman, T. R.; Temple, M. D.; White, D. P. *Organometallics* **2003**, *22*, 2331–2337.

(72) Beach, N. J.; Williamson, A. E.; Spirak, G. T. *J. Organomet. Chem.* **2005**, *690*, 4640–4647.

(73) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170–3177.

(74) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262–264.

(75) Mainz, V. V. Compounds Containing Multiple Metal–Metal Bonds: Synthesis and Reactions. Ph.D. Dissertation, University of California, Berkeley, CA, 1981.

Dibromo(1,5-cyclooctadiene)bis(acetonitrile)osmium(II), OsBr₂(cod)(MeCN)₂ (2). A brown suspension of [OsBr₂(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 C₁₂H₁₈N₂Br₂Os: 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* [OsBr₂(cod)⁺]. ¹H NMR (CD₃CN): δ 4.15 (m, 4H, cod), 2.70 (s, 6H, CH₃CN), 2.31 (m, 4H, cod), 1.87 (m, 4H, cod). ¹³C{¹H} NMR (CD₃CN): δ 124.5 (s, CH₃CN), 77.0 (s, cod), 32.1 (s, cod), 4.8 (s, CH₃CN). 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 [OsBr₂(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 Et₂O (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 C₁₇H₂₃N₆BO: 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)⁺]. ¹H NMR (C₆D₆): 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). ¹³C{¹H} NMR (C₆D₆): 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 [OsBr₂(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 CHBr₃ (ca. 1 mL). After the mixture had stirred for 5 min, the solvent was evaporated on a rotary evaporator. The product was extracted into Et₂O (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 C₁₇H₂₂N₆BrBO: C, 34.5; H, 3.8; N, 13.8.

Found: C, 35.1; H, 3.7; N, 13.8. MS (FD): 592.1 m/z [TpOs(cod)-Br⁺]. ¹H NMR (C₆D₆): δ 7.74 (d, 1H, $J_{\text{HH}} = 2.4$ Hz, Tp), 7.62 (d, 2H, $J_{\text{HH}} = 2.4$ Hz, Tp), 7.26 (d, 2H, $J_{\text{HH}} = 2.4$ Hz, Tp), 7.19 (d, 1H, $J_{\text{HH}} = 2.8$ Hz, Tp), 5.83 (t, 2H, $J_{\text{HH}} = 2.2$ Hz, Tp), 5.75 (t, 1H, $J_{\text{HH}} = 2.4$ 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). ¹³C{¹H} NMR (C₆D₆): 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 Et₂O (2 × 20 mL). The Et₂O 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 C₁₉H₂₉N₆BO₂Os [TpOs(cod)OMe·MeOH]: C, 39.7; H, 5.1; N, 14.6. Found: C, 39.6; H, 4.9; N, 14.4. ¹H NMR (C₆D₆): δ 7.67 (d, 1H, $J_{\text{HH}} = 2.0$ Hz, Tp), 7.64 (d, 2H, $J_{\text{HH}} = 1.6$ Hz, Tp), 7.33 (d, 2H, $J_{\text{HH}} = 2.0$ Hz, Tp), 7.25 (d, 1H, $J_{\text{HH}} = 2.4$ Hz, Tp), 5.85 (t, 2H, $J_{\text{HH}} = 2.4$ Hz, Tp), 5.77 (t, 1H, $J_{\text{HH}} = 2.4$ Hz, Tp), 4.54 (m, 2H, cod), 3.85 (m, 2H, cod), 3.48 (s, MeOH), 2.86 (s, 3H, Os-OMe), 2.83 (m, 2H, cod), 2.29 (m, 2H, cod), 2.16 (m, 4H, cod). ¹³C{¹H} NMR (C₆D₆): 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, CH₃OH), 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 C₂₀H₂₇N₆O_{3.5}BF₃SO₃ [TpOs(cod)OTf·0.5Et₂O]: C, 34.4; H, 3.9; N, 12.0. Found: C, 34.0; H, 3.9; N, 11.7. ¹H NMR (C₆D₆): δ 7.68 (d, 2H, $J_{\text{HH}} = 2.0$ Hz, Tp), 7.29 (d, 2H, $J_{\text{HH}} = 2.0$ Hz), 7.22 (d, 1H, $J_{\text{HH}} = 2.0$ Hz, Tp), 7.07 (d, 1H, $J_{\text{HH}} = 2.0$ Hz, Tp), 5.91 (t, 2H, $J_{\text{HH}} = 2.0$ Hz, Tp), 5.60 (t, 1H, $J_{\text{HH}} = 2.0$ Hz, Tp), 5.22 (m, 2H, cod), 4.12 (m, 2H, cod), 3.25 (q, $J_{\text{HH}} = 7.0$ Hz, Et₂O), 2.76 (m, 2H, cod), 2.16 (m, 2H, cod), 2.05 (m, 2H, cod), 1.99 (m, H cod), 1.11 (t, $J_{\text{HH}} = 7.0$ Hz, Et₂O). ¹³C{¹H} NMR (C₆D₆): 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, Et₂O), 33.1 (s, cod), 30.6 (s, cod), 15.8 (s, Et₂O). ¹⁹F NMR (C₆D₆): δ -79.4 (s, SO₂CF₃). 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·0.5Et₂O (0.15 g, 0.22 mmol) in diethyl ether (30 mL) was added dimethylmagnesium (0.31 mL of a 0.80 M solution in Et₂O, 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 Et₂O 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 MgSO₄. The colorless Et₂O 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 C₁₈H₂₅N₆BOs: C, 41.1; H 4.8. Found: C, 40.5; H, 5.1. MS (FD): 528.3 m/z [TpOs(cod)Me⁺]. ¹H NMR (C₆D₆): δ 8.13 (d, 1H, $J_{\text{HH}} = 2.0$ Hz, Tp), 7.36 (d, 1H, $J_{\text{HH}} = 2.0$ Hz, Tp), 7.30 (d, 2H, $J_{\text{HH}} = 2.4$ Hz, Tp), 7.20 (d, 2H, $J_{\text{HH}} = 2.0$ Hz, Tp), 5.93 (t, 1H, $J_{\text{HH}} = 2.2$ Hz, Tp), 5.78 (t, 2H, $J_{\text{HH}} = 2.2$ 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). ¹³C{¹H} NMR (C₆D₆): 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), OsCl₂(PPh₃)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 PPh₃ 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(PPh₃)₂Cl. This procedure is a modification of that in ref 13. To a mixture of OsCl₂(PPh₃)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

(76) Elliott, G. P.; Mcauley, N. M.; Roper, W. R. *Inorg. Synth.* **1989**, *26*, 184-189.

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 C₄₅H₄₀N₆Bp₂ClOs: C, 56.1; H, 4.2; N, 8.7. Found: C, 56.4; H, 4.5; N, 8.3.

[Tris(pyrazolyl)borato]chloro[η¹-bis(dimethylphosphino)methane]triphenylphosphineosmium(II), TpOs(PPh₃)(η¹-dmpm)-Cl (8). To a solution of TpOs(PPh₃)₂Cl (15 mg, 0.016 mmol) in C₇D₈ (1 mL) was added Me₂PCH₂PMe₂ (0.012 mL, 0.078 mmol). The green solution was stirred for 4 days to yield TpOs(PPh₃)(η¹-dmpm)Cl, TpOs(dmpm)Cl (characterization given below), free PPh₃, and starting materials, as observed by NMR spectroscopy and mass spectrometry. MS(FD): 838.2 *m/z* [TpOs(PPh₃)(η¹-dmpm)Cl⁺]. ³¹P{¹H} NMR (C₇D₈): δ 2.4 (d, 1P, *J*_{PP} = 33 Hz, Os-PPh₃), -35.7 (dd, 1P, *J*_{PP} = 33, 45 Hz, Os-PMe₂CH₂PMe₂), -58.0 (d, 1P, *J*_{PP} = 45 Hz, Os-PMe₂CH₂PMe₂).

[Tris(pyrazolyl)borato]chloro[bis(dimethylphosphino)methane]osmium(II), TpOs(dmpm)Cl (9). A solution of TpOs(PPh₃)₂Cl (0.60 g, 0.62 mmol) and Me₂PCH₂PMe₂ (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}H₂₆N₆ClBp₂Os [TpOs(dmpm)Cl·0.25C₇H₈]: 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 (C₇D₈): 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, PCH₂P), 3.55 (dt, 1H, *J*_{HH} = 14.4 Hz, *J*_{HP} = 9.6 Hz, PCH₂P), 1.62 (t, 6H, *J*_{HP} = 5.0 Hz, PMe), 0.91 (t, 6H, *J*_{HP} = 4.6 Hz, PMe). ¹³C{¹H} NMR (C₇D₈): 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, PCH₂P), 14.4 (t, *J*_{PC} = 12.9 Hz, PMe), 13.5 (t, *J*_{PC} = 15.0 Hz, PMe). ³¹P{¹H} NMR (C₇D₈): 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·0.25C₇H₈ (0.40 g, 0.67 mmol) in tetrahydrofuran (60 mL) was treated with methylolithium (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 (C₄D₈O): 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, PCH₂P), 3.66 (dt, 1H, *J*_{HH} = 14.0 Hz, *J*_{HP} = 12.0 Hz, PCH₂P), 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). ³¹P{¹H} NMR (C₄D₈O): -69.6 (s).

Pyrazolium Trifluoromethanesulfonate, [C₃H₅N₂][OTf]. To a solution of pyrazole (0.30 g, 4.4 mmol) in Et₂O (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 C₄H₅N₂O₂F₃S:

C, 22.0; H, 2.3; N, 12.8. Found: C, 22.0; H, 2.3; N, 12.4. ¹H NMR (C₄D₈O): 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). ¹³C{¹H} NMR (C₄D₁₀O): δ 135.5 (s, 3,5-C), 108.6 (s, 4-C). ¹⁹F NMR (C₄D₈O): δ -79.9 (s, SO₃CF₃). 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*kl* (*k* ≠ 2*n*) and *h0l* (*h* + *l* ≠ 2*n*) were only consistent with space group *P*2₁/*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.

Acknowledgment. We thank the American Chemical Society Petroleum Research Fund for support.

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>.

IC0602291

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