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Communications

Synthesis of Osmium(VI) Neopentyl, Neopentylidene, and Neopentylidyne Complexes

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Summary: $[PPh_4]_2[OsO_2Cl_4]$ *reacts with excess dineopentylzinc in dichloromethane at room temperature to yield purple-brown, water- and air-stable* $OsO_2(CH_2\text{-}t\text{-}Bu)_2$. $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ *reacts with 2 equiv of* $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ *in pentane at −40 °C to yield insoluble* $[Ta(O)(CH_2\text{-}t\text{-}Bu)_3]_x$ *and what is proposed to be pseudotetrahedral, thermally unstable* $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$. $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ *reacts with pyridinium triflate in the presence of excess pyridine to form* $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(py)_2(O_3SCF_3)$, *which when treated with* $LiN(SiMe_3)_2$, NaC_5H_5, $Na[CpCo(P(O)(OEt)_2)_3]$, *or* $NaHB(pz)_3$ *in THF yields neopentylidyne complexes of the type* $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(L)$ ($L = N(SiMe_3)_2$, $\eta^5\text{-}C_5H_5$, $CpCo[P(O)(OEt)_2]_3$, $HB(pz)_3$).

Alkylidene and alkylidyne complexes that contain a metal in its highest possible oxidation state are now relatively well-known for Mo, W, and Re.[1-3] We have been interested in determining to what extent some of the principles of their preparation, α-hydrogen abstraction[1] in particular, may be extended to osmium in its higher oxidation states. We have not yet been successful at generating neopentylidene- or neopentylidyneosmium species by alkylating known Os(VI) or Os(VIII) species, and so we have turned to alternative approaches. We report here the use of a tantalum neopentylidene complex as a means of preparing an osmium(VI) dineopentylidene complex from an osmium(VI) dioxo complex and the synthesis of Os(VI) neopentylidyne complexes by subsequent α-hydrogen abstraction reactions.[4]

The reaction between $[PPh_4]_2[OsO_2Cl_4]$[5] and excess dineopentylzinc in dichloromethane at room temperature yields purple-brown, water- and air-stable $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ (**1**) in 60–70% isolated yield.[6] We presume that **1** is structurally analogous to distorted-tetrahedral $OsO_2(mesityl)_2$.[7] Addition of 2 equiv of $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$[8] to **1** at −40 °C in pentane yielded insoluble $[Ta(O)(CH_2\text{-}t\text{-}Bu)_3]_x$[9] immediately. The reaction mixture was filtered through silica gel, and the solvent was removed from the filtrate to yield an orange-red oil (60–70% yield, >90% purity by ^1H NMR) whose ^1H and ^{13}C NMR spectra are consistent with it being $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ (**2**).[10]

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[1] Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.

[2] Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; VCH: New York, 1988.

[3] Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

[4] In this work the oxidation state of the metal will be based on the assumption that an alkylidene ligand is a dianion and an alkylidyne ligand is a trianion.

[5] Marshman, R. W.; Shapley, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 8369.

[6] $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ (**1**). Dineopentylzinc (0.853 g, 4.12 mmol) was added to a slurry of $[P(C_6H_5)_4]_2[OsO_2(Cl)_4]$ (2.00 g, 1.92 mmol) in 50 mL of CH_2Cl_2. The solution immediately became purple-brown. The solution was stirred for 30 min and then filtered through silica gel. The solvent was removed in vacuo to yield a brown-purple solid, which was then extracted with pentane; the extract was filtered, and the volume of the filtrate was reduced to 5 mL. When the resulting solution was cooled to −40 °C, purple-brown needles formed and were collected and dried; yield 460 mg (66%): ^1H NMR (C_6D_6) δ 4.21 (s, 4, CH_2-*t*-Bu), 0.97 (s, 18, *t*-Bu); ^{13}C NMR (C_6D_6) δ 34.9 (CMe_3), 34.0 (CH_2CMe_3, $J_{CH} = 133$ Hz), 31.1 (CMe_3, $J_{CH} = 126$); IR (Nujol, cm^{-1}) 937, 981 (s, OsO_2). Anal. Calcd for $OsC_{10}H_{22}O_2$: C, 32.95; H, 6.08. Found: C, 33.33; H, 6.00.

[7] Stavropoulos, P.; Edwards, P.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 169.

[8] Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

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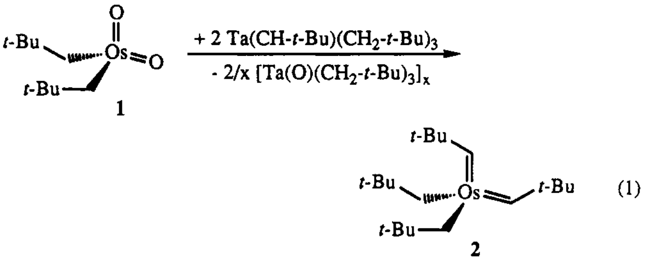
The neopentylidene ligands of **2** are inequivalent ($\delta(C_\alpha)$ 224.2 and 210.5 ppm; $\delta(H_\alpha)$ 16.33 and 11.54 ppm), the J_{CH_α} values for the neopentylidene ligands are significantly different (J_{CH} = 130 and 150 Hz), and the neopentyl ligands are related by a mirror plane. For steric reasons **2** is most likely to be a monomeric pseudotetrahedral species (eq 1).

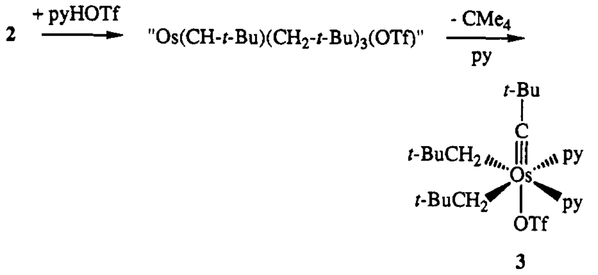


(1)

Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ is thermally and photochemically sensitive, decomposing over several hours in C$_6$D$_6$ at 25 °C in the dark to give neopentane and 2,2,5,5-tetramethylhexane; it is moderately stable at −40 °C. So far we have seen no evidence that **2** will bind a base such as pyridine, TMEDA, triphenylphosphine oxide, or dmpe.

It is interesting to note that the rare bis(alkylidene)[11] tautomeric form of **2** is preferred over Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$, which would be the d^2 analog of W(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$.[12] However, there is evidence for an equilibrium between **2** and Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$. First, the reaction between OsO$_2$(CD$_2$-*t*-Bu)$_2$ and 2 equiv of Ta(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ in toluene-*d*$_8$ at −78 °C yields Os(CH-*t*-Bu)$_2$(CD$_2$-*t*-Bu)$_2$ initially, but when the solution is warmed to 0 °C, H and D scramble among the α-carbon atoms of the neopentyl and neopentylidene ligands in Os(CH-*t*-Bu)$_2$(CD$_2$-*t*-Bu)$_2$. Second, the reaction between Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (see below) and neopentyllithium yields **2**, we presume via initial formation of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$.

Pyridinium triflate reacts with **2** in the presence of excess pyridine to yield neopentane and orange, air-stable Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (**3**; $\delta(C_\alpha)$ 275.9 ppm) in 87% yield.[13] If pyDOTf is employed, then deuterium is found in a statistical distribution on the α-carbon atoms of the neopentyl ligands in **3**, a result that is consistent with protonation of one of the neopentylidene ligands in **2** followed by α-hydrogen abstraction (perhaps induced by coordination of pyridine to osmium) in intermediate, possibly cationic "Os(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(OTf)(py)$_n$" (eq 2). In the absence of excess pyridine, analogous protonations of **2** so far have not yielded identifiable products. The proposed formation of the neopentylidyne ligand in **3** via loss of neopentane in a d^2 complex that is either cationic or contains a relatively electrophilic osmium center is consistent with generally more facile α-hydrogen abstraction reactions in d^0 complexes in which the metal is relatively electrophilic and π-donor ligands are absent.[1] NMR studies of **3** suggest that the methylene protons are diastereotopic, while the IR spectrum reveals a triflate stretch at 1303 cm^{-1}, consistent with coordinated triflate.[14] The most plausible structure of **3** is shown in eq 2. Free pyridine exchanges readily with coordinated pyridine on the NMR time scale in **3** at 25 °C in CD$_2$Cl$_2$.



(2)

We presume that loss of pyridine from **3** accounts for its ready reaction with nucleophiles. **3** reacts with LiN(SiMe$_3$)$_2$ in THF to yield brown-red Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$[N(SiMe$_3$)$_2$] (**4**; $\delta(C_\alpha)$ 268 ppm) in 75% yield; the trimethylsilyl groups in **4** are equivalent on the NMR time scale at 25 °C.[15] **3** reacts with NaC$_5$H$_5$ in THF to produce yellow, 18-electron Os(η^5-C$_5$H$_5$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (**5a**),[16] an alkylidyne relative of Os(η^5-C$_5$H$_5$)(N)(CH$_2$SiMe$_3$)$_2$.[17] Analogous reactions between **3** and Na[CpCo(P(O)-

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[9] Schrock, R. R. *J. Am. Chem. Soc.* 1976, *98*, 5399.

[10] Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ (**2**). OsO$_2$(CH$_2$-*t*-Bu)$_2$ (100 mg, 0.27 mmol) was dissolved in 10 mL of pentane, and the solution was chilled to −40 °C. Ta(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ (304 mg, 0.65 mmol) was dissolved in 3 mL of pentane. The solution was cooled to −40 °C and then added dropwise to the stirred solution of OsO$_2$(CH$_2$-*t*-Bu)$_2$. [Ta(O)(CH$_2$-*t*-Bu)$_3$]$_n$ precipitated immediately. The mixture was allowed to warm to room temperature and was stirred for 30 min. The resulting orange-brown mixture was vacuum-filtered quickly through silica gel, and solvents were removed from the filtrate in vacuo to yield an orange-red oil (83 mg, 65%) which was >90% pure by ^{1}H NMR. Occasionally, some pentane-insoluble colorless material remained after the first filtration and the crude oil was redissolved in 2–5 mL of pentane and filtered through a pipette full of silica gel: ^{1}H NMR (C$_6$D$_6$) δ 16.33 (s, 1, C*H*-*t*-Bu, J_{CH} = 150 Hz), 11.54 (s, 1, C*H*-*t*-Bu, J_{CH} = 130), 2.65 (AB quartet, 4, C*H*$_2$-*t*-Bu), 1.33 (s, 9, CH-*t*-*Bu*), 1.17 (s, 9, CH-*t*-*Bu*), 0.99 (s, 18, CH$_2$-*t*-*Bu*); ^{13}C NMR (toluene-*d*$_8$) δ 224.2 (*C*H-*t*-Bu), 210.5 (*C*H-*t*-Bu), 50.1 (*C*H$_2$-*t*-Bu), 48.2, 43.9, 32.7 (*C*Me$_3$), 33.6 (CH$_2$C*Me*$_3$), 31.0, 27.8 (CHC*Me*$_3$). **2** is too unstable to be analyzed.

[11] Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* 1978, *100*, 5964.

[12] Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* 1982, *1*, 1645.

[13] Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (**3**). **2** (83 mg, 0.176 mmol) was dissolved in 3 mL of ether, and 1 mL of pyridine was added, followed by solid pyridinium triflate (42 mg, 0.183 mmol). The resulting red-orange mixture was stirred for 3 h; the solvents were then removed in vacuo, and the solid was washed with pentane (5 mL) and ether (5 mL). The resulting orange solid (109 mg, 87%) was pure by ^{1}H and ^{19}F NMR. An analytical sample was recrystallized from a mixture of dichloromethane and ether at −40 °C: ^{1}H NMR (CD$_2$Cl$_2$) δ 8.60 (d, 4, py), 7.86 (br t, 2, py), 7.40 (br t, 4, py), 3.80 (d, 2, J_{HH} = 12 Hz, OsC*H*$_a$H$_b$-*t*-Bu), 2.94 (d, 2, J_{HH} = 12, OsCH$_a$*H*$_b$-*t*-Bu), 1.38 (s, 9, OsC-*t*-*Bu*), 1.02 (s, 18, OsCH$_2$-*t*-*Bu*); ^{13}C NMR (CD$_2$Cl$_2$) δ 275.9 (Os*C*-*t*-Bu), 152.0, 138.8, 125.4 (py), 57.5, 37.0 (*C*Me$_3$), 37.5 (Os*C*H$_2$-*t*-Bu), 33.3, 25.3 (C*Me*$_3$); ^{19}F NMR (CD$_2$Cl$_2$) δ −77.0; IR (Nujol, cm^{-1}) 1303 (coordinated OTf). Anal. Calcd for OsC$_{26}$H$_{41}$N$_2$F$_3$O$_3$S: C, 44.05; H, 5.83; N, 3.95. Found: C, 43.76; H, 5.64; N, 3.62.

[14] Lawrance, G. A. *Chem. Rev.* 1986, *86*, 17.

[15] Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(N(SiMe$_3$)$_2$) (**4**). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (70 mg, 0.099 mmol) was dissolved in 5 mL of THF, and the solution was cooled to −40 °C. A THF solution of LiN(SiMe$_3$)$_2$ (0.10 mmol) was added, and the mixture was warmed to room temperature and stirred for 45 min. Solvent was removed in vacuo, the resulting brown-red solid was extracted with pentane, and the solution was filtered through Celite. Pentane was removed in vacuo, leaving a crystalline brown solid (42 mg, 75%) that was pure by ^{1}H NMR: ^{1}H NMR (C$_6$D$_6$) δ 4.79 (d, 2, J_{HH} = 12 Hz, OsC*H*$_a$H$_b$-*t*-Bu), 2.78 (d, 2, J_{HH} = 12, OsCH$_a$*H*$_b$-*t*-Bu), 1.26 (s, 18, OsCH$_2$-*t*-*Bu*), 1.13 (s, 9, OsC-*t*-*Bu*), 0.36 (s, 18, Si*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 267.9 (Os*C*CMe$_3$), 53.7 (OsC*C*Me$_3$), 39.6 (Os*C*H$_2$-*t*-Bu), 35.0 (OsCH$_2$*C*Me$_3$), 33.4 (OsCH$_2$C*Me*$_3$), 25.6 (OsCC*Me*$_3$), 6.7 (Si*Me*$_3$).

[16] Os(η^5-C$_5$H$_5$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (**5a**). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (40 mg, 0.057 mmol) was dissolved in 3 mL of THF, and a THF solution of sodium cyclopentadienide (0.070 mmol) was added. The resulting red-brown mixture was stirred for 2 h at room temperature, and then the THF was removed in vacuo and the resulting solid was extracted with pentane to yield a yellow-brown solid (18 mg, 68%) that was pure by ^{1}H NMR. An analytical sample of **5a** was prepared by passing a pentane solution of **5a** through silica gel; pentane was then removed in vacuo to yield a yellow solid that was analytically pure: ^{1}H NMR (C$_6$D$_6$) δ 5.08 (s, 5, η^5-C$_5$*H*$_5$), 2.25 (AB quartet, 4, OsC*H*$_2$-*t*-Bu), 1.26 (s, 18, OsCH$_2$-*t*-*Bu*), 0.99 (s, 9, OsC-*t*-*Bu*); ^{13}C NMR (C$_6$D$_6$) δ 272.8 (Os*C*-*t*-Bu), 89.2 (η^5-C$_5$H$_5$), 54.1 (OsC*C*Me$_3$), 35.7 (OsCH$_2$*C*Me$_3$), 34.5 (OsCH$_2$C*Me*$_3$), 26.7 (OsCC*Me*$_3$), 19.3 (Os*C*H$_2$-*t*-Bu). Anal. Calcd for OsC$_{20}$H$_{36}$: C, 51.47; H, 7.77. Found: C, 51.28; H, 7.47.

[17] Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* 1991, *10*, 1671.

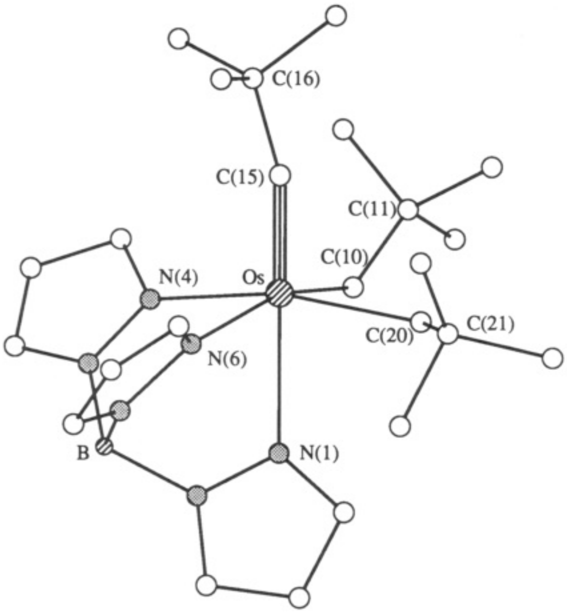

Figure 1. A drawing of Os(HB(pz)$_3$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ generated using atomic coordinates obtained by X-ray crystallography. Selected bond lengths (Å) and angles (deg): Os–C(15) = 1.73(2), Os–C(10) = 2.11(2), Os–C(20) = 2.15(3), Os–N(1) = 2.30(2), Os–N(4) = 2.20(2), Os–N(6) = 2.18(2); Os–C(15)–C(16) = 161(2), C(15–Os–N(1) = 176.8(8).

(OEt)$_2$)$_3$] (NaL$_{\mathrm{OEt}}$)[18] or NaHB(pz)$_3$ (sodium tripyrazolylborate) in THF yield Os(L$_{\mathrm{OEt}}$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (**5b**)[19] or Os(HBpz$_3$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (**5c**),[20] respectively, in 60–80% yields. Compounds **4** and **5** are all thermally stable solids. An X-ray study of **5c**[21] (Figure 1) confirms the structure. The Os≡C bond length is comparable to that found in [Os(CC$_6$H$_5$)(NH$_3$)$_5$]$^{3+}$ (1.73(1) Å[22]), while the relatively small Os–C(15)–C(16) angle (161(2)°) can be ascribed to steric interactions between *tert*-butyl groups.

Compounds **2**, **3**, **4**, and **5a–c** are rare examples of what could be called Os(VI)[4] species that contain an osmium–carbon multiple bond. To our knowledge, the only other examples are OsCl$_2$(NCS)(CC$_6$H$_4$NMe$_2$)(PPh$_3$)$_2$,[23] Os(C$_4$Me$_4$)(en)$_2$(OTf)$_2$ (an "osmacyclopentatriene" complex),[24] and [Os(CC$_6$H$_5$)(NH$_3$)$_5$]$^{3+}$.[22] We currently are exploring the reactivity of electron-deficient or coordinatively labile Os(VI) alkylidene and alkylidyne complexes in order to compare their reactivity with that of related d^0 species.

Acknowledgment. We thank the NSF for research support (Grant No. CHE 91 22827), Dr. Robert D. Simpson for a generous gift of Na{CpCo[P(O)(OEt)$_2$]$_3$}, and Dr. Rhett Kempe for the X-ray study.

Supplementary Material Available: Description of the X-ray study, an ORTEP drawing, and tables of final positional parameters, final thermal parameters, bond distances, and bond angles for **5c** (15 pages). Ordering information is given on any current masthead page.

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(18) Klaui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627.

(19) Os(L$_{\mathrm{OEt}}$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (**5b**). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (52 mg, 0.073 mmol) was dissolved in 3 mL of THF, and solid Na[CpCo(P(O)(OEt)$_2$)$_3$] (42 mg, 0.075 mmol) was added. The red-orange solution was stirred for 3 h at room temperature, and the solvent was then removed in vacuo. The orange-pink solid was extracted with 10 mL of ether. The solvent was then removed in vacuo from the extract to yield orange-pink crystals (45 mg, 66%): ^{1}H NMR (C$_6$D$_6$) δ 4.88 (s, 5, Cp), 4.38 (d, 2, J_{HH} = 12 Hz, OsC*H*$_a$H$_b$-*t*-Bu), 4.2, 4.1 (br m, 12 total, POC*H*$_2$CH$_3$), 3.32 (d, 2, J_{HH} = 12, OsCH$_a$*H*$_b$-*t*-Bu), 1.51 (s, 18, CH$_2$-*t-Bu*), 1.40 (s, 9, C-*t-Bu*), 1.2 (br m, 18, POCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 266.1 (Os*C*-*t*-Bu), 89.5 (Cp), 60.7, 60.5 (PO*C*H$_2$CH$_3$), 55.7 (Os*C*H$_2$-*t*-Bu), 37.3 (CH$_2$*C*Me$_3$), 33.4 (CH$_2$C*Me*$_3$), 28.8 (C*C*Me$_3$), 23.8 (CC*Me*$_3$), 16.9, 16.7 (POCH$_2$*C*H$_3$). Anal. Calcd for CoOsC$_{32}$H$_{66}$O$_9$P$_3$: C, 41.02; H, 7.10. Found: C, 41.39; H, 6.78. CHC*H*CH), 3.59 (d, 2, J_{HH} = 12, OsC*H*$_a$H$_b$-*t*-Bu), 2.86 (d, 2, J_{HH} = 12, OsCH$_a$*H*$_b$-*t*-Bu), 1.31 (s, 18, CH$_2$-*t*-Bu), 1.09 (s, 9, C-*t*-Bu); ^{13}C NMR (C$_6$D$_6$) δ 280.1 (Os*C*-*t*-Bu), 146.7, 141.1, 135.0, 134.6, 105.6, 105.2 (pz), 56.5 (Os*C*H$_2$-*t*-Bu), 36.4 (OsCH$_2$*C*Me$_3$), 33.9 (OsCH$_2$C*Me*$_3$), 32.6 (OsC*C*Me$_3$), 24.3 (OsCC*Me*$_3$).

(20) Os(HB(pz)$_3$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (**5c**). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (80 mg, 0.11 mmol) was dissolved in 5 mL of THF, and solid Na[HB(pz)$_3$] (26 mg, 0.11 mmol) was added. The orange solution was stirred for 2 h at room temperature, and the solvent was then removed in vacuo. The remaining orange-pink solid was extracted with 10 mL of pentane, and the solvent was then removed in vacuo to yield a crystalline orange-pink solid (58 mg, 83%). An analytical sample was recrystallized from pentane at −40 °C: ^{1}H NMR (C$_6$D$_6$) δ 8.15 (d, 2, J_{HH} = 1.8 Hz, N═C*H*), 7.87 (d, 1, J_{HH} = 2, N═C*H*), 7.35 (d, 2, J_{HH} = 2.4, NC*H*═CH), 7.21 (d, 1, J_{HH} = 2.4, NC*H*═CH), 5.91 (t, 2, CHC*H*CH), 5.78 (t, 1, CHC*H*CH), 3.59 (d, 2, J_{HH} = 12, OsC*H*$_a$H$_b$-*t*-Bu), 2.86 (d, 2, J_{HH} = 12, OsCH$_a$*H*$_b$-*t*-Bu), 1.31 (s, 18, CH$_2$-*t*-Bu), 1.09 (s, 9, C-*t*-Bu); ^{13}C NMR (C$_6$D$_6$) δ 280.1 (Os*C*-*t*-Bu), 146.7, 141.1, 135.0, 134.6, 105.6, 105.2 (pz), 56.5 (Os*C*H$_2$-*t*-Bu), 36.4 (OsCH$_2$*C*Me$_3$), 33.9 (OsCH$_2$C*Me*$_3$), 32.6 (OsC*C*Me$_3$), 24.3 (OsCC*Me*$_3$).

(21) Crystal data for **5c**: OsC$_{24}$H$_{41}$N$_6$B, fw = 614.64, monoclinic, space group $P2_1/n$, a = 10.576(1) Å, b = 13.549(2) Å, c = 19.598(3) Å, β = 104.20(1)°, V = 2722 Å^3, Z = 4, d_{calcd} = 1.500 g/cm^3, μ(Mo Kα) = 47.1 cm^{-1}; R = 0.060, R_{w} = 0.064. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 25 ± 1 °C. Of the 3983 reflections that were collected, 3807 were unique. Absorption corrections were applied to the data. The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically by full-matrix least squares. Refinement of 240 variables against 1883 reflections with $I > 4\sigma$ converged to R = 0.060 and R_{w} = 0.064.

(22) Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 371.

(23) Clark, G. R.; Edmonds, N. R.; Pauptit, R. A.; Roper, W. A.; Waters, J. M.; Wright, A. H. *J. Organomet. Chem.* **1983**, *244*, C57.

(24) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712.