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Alkyl, Alkylidene, and Alkylidyne Complexes of Osmium(VI)

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Abstract: Addition of dialkylzinc reagents to $[PPh_4]_2[OsO_2Cl_4]$ gives OsO_2R_2 complexes (R = neopentyl, neophyl, or (trimethylsilyl)methyl). The reaction between $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ and 2 equiv of $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ gave *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$, while $[OsO_2(CH_2SiMe_3)_2]_n$ reacted to give a 1:1 mixture of *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ and *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$. Isolated *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ was shown in an X-ray study to be a distorted tetrahedron in which the two neopentylidene ligands lie in the same plane. Extended Hückel calculations performed on $Os(CH_2)_2(CH_3)_2$ suggest that the HOMO is an orbital of primarily d_{z^2} character that lies between and in the plane of the OsC_2 fragment, the LUMO is the π^* system of the bis(methylidene), and the HOMO-1 and HOMO-2 are bonding combinations of the π system. $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ reacts with neat trimethylphosphine to give $Os(PMe_3)_3(\eta^2\text{-}t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)$ which was shown in an X-ray study to be a pseudotetrahedral species in which $C{\equiv}C$ = 1.30 (1) Å. *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ reacts with pyridinium triflate in the presence of pyridine to yield $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(py)_2(OTf)$, while $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ reacts with 1 equiv of $Ta(CH\text{-}t\text{-}Bu)(py)_2X_3$ (X = Cl, Br) to form $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(py)_2X_2$. $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2L$ (L = O-*t*-Bu or $N(SiMe_3)_2$), $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2\{CpCo[P(O)(OEt)_2]_3\}$, and $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2[HB(pyrazolyl)_3]$ could all be prepared from $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(py)_2(OTf)$. An X-ray study of $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(HBpz_3)$ showed it to be a pseudooctahedral molecule in which $Os{\equiv}C$ = 1.73(2) Å.

Introduction

Alkylidene[1,2] and alkylidyne[3] complexes that contain a metal in its highest possible formal oxidation state are well-known for Mo, W, and Re. These are d^0 species if the alkylidene ligand is viewed as a dianion and the alkylidyne ligand as a trianion. We became interested in the extent to which the principles of synthesizing alkylidene and alkylidyne complexes, namely α-hydrogen abstraction reactions, carry over to osmium. d^0 osmium analogs of the known Mo, W, and Re complexes would be unrealistic goals, in part because known Os(VIII) oxo and imido complexes are readily reduced and since, to our knowledge, no organometallic complex of Os(VIII) has been reported. On the other hand, a variety of Os(VI) alkyl complexes have been reported[4−8] in which at least two metal−oxygen or metal−nitrogen π bonds are present; examples are $[Os(N)(CH_2SiMe_3)_4]^-$ [4] and $Os(O)Me_4$.[8] (It is generally assumed that an oxo ligand is pseudo triply bound to the metal, if the metal is in a relatively high oxidation state.) Therefore we felt that Os(VI) compounds that contain metal−carbon double or triple bonds might be stable under the right circumstances. If Os(VI) alkylidene or alkylidyne complexes could be prepared, we would be interested in the extent to which these complexes would behave as metathesis catalysts for olefins or acetylenes, respectively. With these goals in mind, we began to investigate the organometallic chemistry of Os(VI). The results of this research are presented here. Part of this work has been reported previously.[9]

Results

Synthesis of Alkyl Complexes. Addition of dineopentylzinc to $[PPh_4]_2[OsO_2Cl_4]$[10] in dichloromethane gave $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ in 66% yield (recrystallized). $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ is not alkylated further at room temperature. Although the recrystallized yield is moderate, the reaction is very clean, and the crude product, which can be used without further purification, can be obtained in 80−85% yield by extraction with pentane. The analogous neophyl complex can be obtained similarly (eq 1). $OsO_2(mesityl)_2$, which was prepared in 29% yield from OsO_4 by Wilkinson and co-workers,[11] was shown in an X-ray study to have a distorted tetrahedral structure.[12] We assume that $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ and $OsO_2(CH_2CMe_2Ph)_2$ also have essentially tetrahedral structures. The only other Os(VI) neopentyl (or neophyl) complexes that have been reported to our knowledge are $[Os(N)(CH_2\text{-}t\text{-}Bu)_4]^-$ [4] and $Os(NAr)_2(CH_2\text{-}t\text{-}Bu)_2$.[5]

$$\underset{R\,=\,CH_2\text{-}t\text{-}Bu,\ CH_2CMe_2Ph}{[PPh_4]_2[OsO_2Cl_4] + ZnR_2} \xrightarrow[25°C]{CH_2Cl_2} \underset{55\text{ - }85\%}{OsO_2R_2} \qquad (1)$$

An analogous reaction between $Zn(CH_2SiMe_3)_2$ and $[PPh_4]_2[OsO_2Cl_4]$ in dichloromethane gave "$OsO_2(CH_2SiMe_3)_2$". By proton and carbon NMR the two trimethylsilyl groups are inequivalent, and the four methylene protons are inequivalent. Therefore we propose that "$OsO_2(CH_2SiMe_3)_2$" is not a monomer. Addition of pyridine to $[OsO_2(CH_2SiMe_3)_2]_n$ converts it to known monomeric *trans*-$OsO_2(CH_2SiMe_3)_2(py)_2$.[13] It is generally accepted that although a (trimethylsilyl)methyl group is larger than a neopentyl group, the steric bulk is further

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away from the metal center, and bimetallic species therefore are more easily formed.

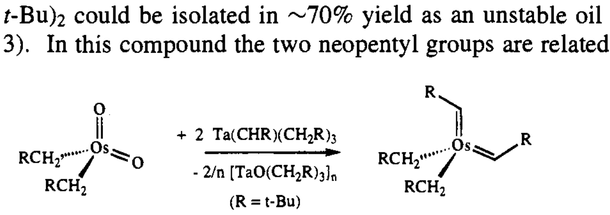
Reactions between $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ and a variety of alkylating agents were investigated as possible routes to alkylidene and alkylidyne complexes. $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ reacts with 1 equiv of trimethylaluminum in pentane to yield diamagnetic orange crystals of a compound that appears to have the formula $[Os(CH_3)(CH_2\text{-}t\text{-}Bu)_2]_n$, according to NMR data and elemental analysis. The product is readily purified by passing a pentane solution through silica gel and is isolated in 43% yield. The neopentyl groups are equivalent on the NMR time scale, and the α protons are also equivalent. We propose that $[Os(CH_3)(CH_2\text{-}t\text{-}Bu)_2]_n$ is a dimeric species similar to the triply bonded dimers, $[Ru(CH_3)(CH_2\text{-}t\text{-}Bu)_2]_2$, $[Ru(CH_2\text{-}t\text{-}Bu)_3]_2$, and $[Os(\eta^3\text{-}C_3H_5)(CH_2\text{-}t\text{-}Bu)_2]_2$.[14] Addition of $Al(CH_2\text{-}t\text{-}Bu)_3(THF)$ to $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ in THF yields a red compound whose proton and carbon NMR spectra, IR spectrum (980 cm^{-1}, Os=O), and elemental analysis are consistent with the formulation $[OsO(CH_2\text{-}t\text{-}Bu)_2]_n$. (The two neopentyl groups are inequivalent and the four α protons are inequivalent.) Reactions between $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ and more powerful alkylating reagents ($LiCH_2\text{-}t\text{-}Bu$, $Mg(CH_2\text{-}t\text{-}Bu)_2(dioxane)$, and $ClMgCH_2\text{-}t\text{-}Bu$) gave only mixtures of $[OsO(CH_2\text{-}t\text{-}Bu)_2]_n$, $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ (see below), and unidentified products. The reaction of $[PPh_4]_2[OsO_2Cl_4]$ with 6 equiv of NpMgCl in dichloromethane yielded a similar mixture of products. These experiments suggest that reduction of osmium(VI) by alkylating agents is facile. Therefore, we needed a synthetic route to neopentylidene complexes that avoided alkylation.

Bis(neopentylidene) Complexes. A "Wittig-like" reaction between a metal oxo complex and an alkylidene source has been an attractive and often proposed method of preparing alkylidene complexes for approximately two decades, but to our knowledge there is still no unambiguous example of this reaction. For example, in the reaction shown in eq 2, it was hoped that the

$$W(O)(O\text{-}t\text{-}Bu)_4 + Ta(CH\text{-}t\text{-}Bu)Cl_3(PR_3)_2 \xrightarrow{\text{ether/pentane}} W(O)(CH\text{-}t\text{-}Bu)Cl_2(PR_3)_2 + Ta(O\text{-}t\text{-}Bu)_4Cl \quad (2)$$

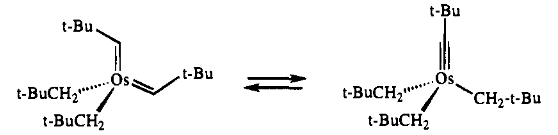
oxo would exchange with the alkylidene.[15] However, the oxo ligand is the only one that does *not* exchange between tungsten and tantalum. This reaction emphasizes an important point in terms of seeking successful exchange reactions; the "supporting" ligands may themselves exchange more readily that the multiply bonded ligands.

The reaction between $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ and 2 equiv of $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$[16] in pentane yields $[TaO(CH_2\text{-}t\text{-}Bu)_3]_n$ as a precipitate. The reaction mixture was passed through silica gel and from the filtrate orange-red *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ could be isolated in ~70% yield as an unstable oil (eq 3). In this compound the two neopentyl groups are related by a mirror plane (the methylene protons are diastereotopic) and the two neopentylidene ligands are inequivalent ($\delta(H_\alpha)$ = 16.33, 11.55 ppm; $\delta(C_\alpha)$ = 224.2, 210.5 ppm; J_{CH_α} = 150, 130 Hz). These data are consistent with one of the neopentylidene ligands having its *tert*-butyl group oriented toward the second neopentylidene ligand (*syn* orientation) and the second neopentylidene having its *tert*-butyl group pointed away from the first neopentylidene (*anti* orientation). *Syn* and *anti* alkylidenes have been observed in a wide variety of four-, five-, and six-coordinate d^0 Mo, W, and Re alkylidene complexes and typically have characteristically different J_{CH_α}, $\delta(H_\alpha)$, and $\delta(C_\alpha)$ values.[2,17] In four-coordinate d^0 species, *syn* alkylidenes exhibit a lower C−H coupling constant and an upfield chemical shift (relative to the *anti* rotamer) of both the H_α and C_α resonances. The only other product typically observed in this synthesis is a small amount (<10%) of the rotational isomer, *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ (see below). It should be noted that d^0 bis(neopentylidene) complexes are extremely rare, examples being known only for tantalum and niobium.[1]



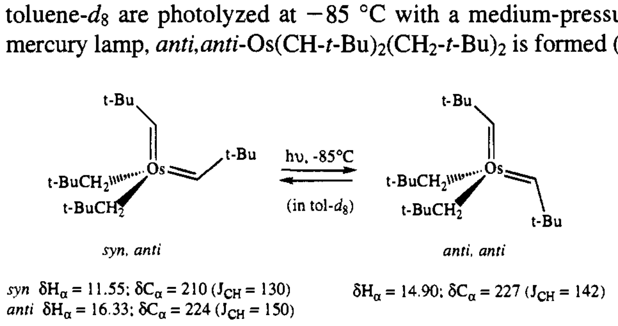
(3)

The reaction between $OsO_2(CD_2\text{-}t\text{-}Bu)_2$ and 2 equiv of $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ in toluene-d_8 at −78 °C yields *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CD_2\text{-}t\text{-}Bu)_2$ initially, but when the solution is allowed to warm to 0 °C H and D scramble among the α-carbon atoms of the neopentyl and neopentylidene ligands, according to NMR studies. Since steric hindrance will prevent rapid intermolecular reactions, H_α/D_α scrambling is more likely to be intramolecular. Two possibilities are a degenerate H (or D) transfer from C_α of a neopentyl group to C_α of a neopentylidene group or H (or D) transfer from one neopentylidene ligand to the other to give $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$, the d^2 analog of $W(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$,[18] as an intermediate (eq 4). We prefer the latter possibility for two reasons. First, α-hydrogen abstraction is known to occur more readily from an alkylidene ligand than an alkyl ligand.[1] Second, the reaction between $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(py)_2(O_3SCF_3)$ or $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(py)_2Cl_2$ (see later) and 1 or 2 equiv of neopentyl lithium, respectively, yields $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$, presumably via intermediate $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$. It is interesting to note that in the d^0 manifold, $W(CSiMe_3)(CH_2CMe_3)_3$ is converted into $W(CCMe_3)(CH_2CMe_3)_2(CH_2SiMe_3)$ only relatively slowly, and kinetic data support the intermediacy of a bis(alkylidene) species in this transformation.[19]



(4)

When solutions of *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ in toluene-d_8 are photolyzed at −85 °C with a medium-pressure mercury lamp, *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ is formed (eq 5). A photostationary state is reached which typically consists of a 1:1 mixture of the two forms. NMR data for *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ are similar to those for *anti,anti*-



(5)

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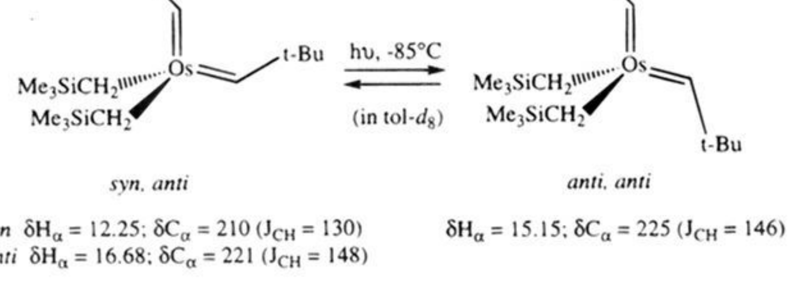
Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters

	$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$	$Os(PMe_3)_3(\eta^2\text{-}t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)$	$Os(HBpz_3)(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$
empirical formula	$C_{18}H_{40}Si_2Os$	$C_{19}H_{45}P_3Os$	$C_{24}H_{41}N_6BOs$
formula weight	502.89	556.69	614.64
crystal color, habit	orange, prismatic	orange, parallelepiped	red, prismatic
crystal dimensions (mm)	0.180 × 0.210 × 0.280	0.120 × 0.120 × 0.280	0.16 × 0.36 × 0.36
crystal system	monoclinic	monoclinic	monoclinic
no.of reflcns used for unit cell determination (2θ range)	25 (14.0−27.0)	25 (15.0−28.0)	25 (18.0−26.0)
a, Å	24.007(3)	9.4148(8)	10.5759(9)
b, Å	6.146(1)	17.317(1)	13.549(2)
c, Å	20.110(3)	15.467(1)	19.598(3)
β, deg	126.02(2)	90.98(2)	104.20(1)
V, Å^3	2399(2)	2521(5)	2722(1)
space group	$C2/c$	$P2_1/n$	$P2_1/n$
Z	4	4	4
D_{calc}, g/cm^3	1.392	1.466	1.500
temperature, °C	−72	−78	25
F_{000}	1008	1120	1232
μ(Mo Kα), cm^{-1}	54.14	52.50	47.08
scan mode	ω-2θ	ω-2θ	ω-2θ
total no. of unique reflcns	5044	10484	3807
no. of parameters with $I > x\sigma(I)$	2297 ($x = 3$)	1738 ($x = 3$)	1883 ($x = 4$)
R	0.045	0.032	0.060
R_w	0.041	0.037	0.064
GOF	1.34	1.62	1.92
no. of variables	97	208	240

$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$, which has been structurally characterized (see below). Absolute chemical shifts of H_α and C_α are not precise indicators of whether an alkylidene is *syn* or *anti*, so the fact that $\delta(H_\alpha)$ value of 14.90 ppm in the *anti,anti* form is between the $\delta(H_\alpha)$ values in the *syn,anti* rotamer should be regarded as circumstantial.

$[OsO_2(CH_2SiMe_3)_2]_n$ reacts with 2 equiv of $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ in pentane to yield a 1:1 mixture of *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ and *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$. Pure *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ can be isolated by passing the reaction mixture through silica gel, since the *syn,anti* rotamer decomposes on silica gel. *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ is a thermally stable orange solid which can be crystallized from a mixture of acetonitrile and ether or (with difficulty) from pentane at −40 °C. In *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$, there is no evidence for α-hydrogen transfer from a CH_2SiMe_3 group to a neopentylidene C_α to give $Os(CHSiMe_3)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(CH_2SiMe_3)$ or from one neopentylidene C_α to the other to give $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(CH_2SiMe_3)_2$. (The latter could be reversible and therefore undetectable if the equilibrium lies toward the bis(alkylidene).) No H/D scrambling is observed when pure *anti,anti*-$Os(CD\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ is stored for 24 h at 25 °C in C_6D_6 in the dark. Upon photolysis, *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ is converted into a mixture of the *anti,anti* and *syn,anti* rotamers (eq 6). NMR data for *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ and *syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ are very similar to the NMR data for the analogous dineopentyl complexes (eq 5).



(6)

Crystals of *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ suitable for X-ray diffraction were taken from a batch grown from pentane at −40 °C over a period of 1 month. A drawing of the molecular structure of *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ is shown in Figure 1 and selected bond distances and angles are shown in Table 2. The core of the molecule is a distorted tetrahedron; the angle between the two neopentylidene groups (C(2)−Os−C(2′)) is only 94.9(4)°, while the angle between the two trimethylsilyl groups (C(1)−Os−C(1′)) is 122.7(4)°. The Os=C bond distance (1.836(7) Å) is comparable to the Os=C distances observed in (for example) $Os(CH_2)(Cl)(\eta^2\text{-}C(O)C_6H_4\text{-}$

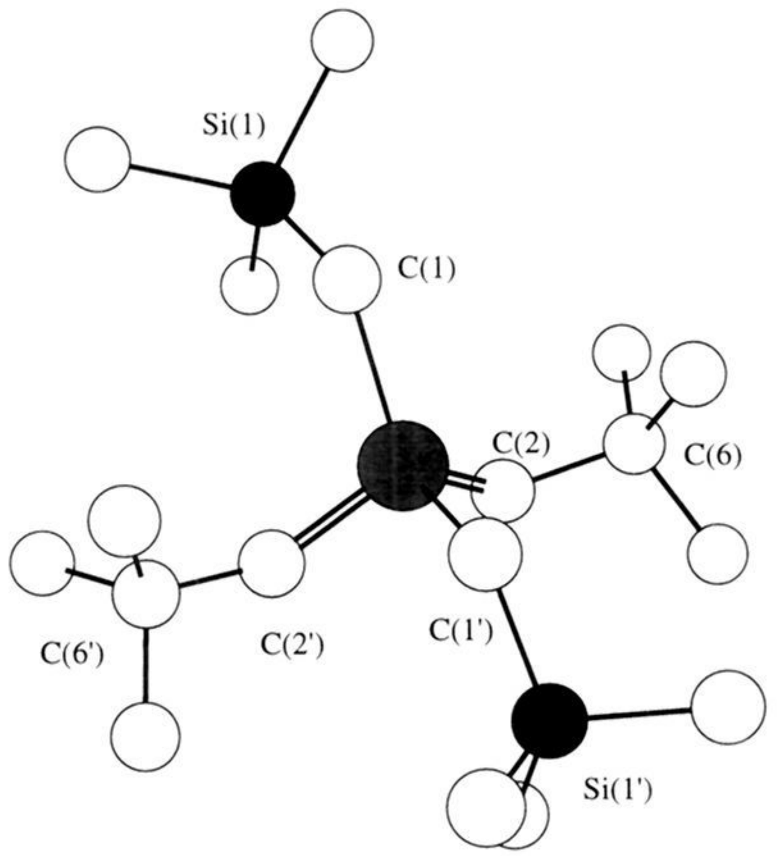


Figure 1. A Chem 3D drawing of *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$.

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$

Distances			
Os−C(1)	2.070(6)	Os−C(2)	1.836(7)
Angles			
C(1)−Os−C(1′)	122.7(4)	C(1)−Os−C(2)	109.2(3)
C(1)−Os−C(2′)	108.6(3)	Os−C(1)−Si(1)	125.6(4)
C(2)−Os−C(2′)	94.9(4)	Os−C(2)−C(6)	130.9(6)

$CH_3)(PPh_3)_2$[20] (1.86(1) Å) or *trans*-Os(TTP)($CHSiMe_3$)(THF) (1.79(2) Å; TPP = tetraphenylporphyrin).[21] The distance between the two alkylidene α carbons is 2.71 Å, which is much too long for any bonding interaction between these carbon atoms. The two *tert*-butyl groups also lie in the C=Os=C plane, an orientation that is perpendicular to that expected in an olefin adduct and therefore only consistent with the *anti,anti*-bis(alkylidene) proposal.

The M=C−C bond angles in d^0 alkylidene complexes range from ~115° to ~170°.[1,2] The larger angles might arise in part as a consequence of an α agostic interaction in such species.[22] In the only structurally characterized d^0 four-coordinate *anti* alkylidene complex, Re(C-*t*-Bu)(CHFc)[OC(CF_3)$_2$$CH_3$]$_2$ (Fc = Fe(Cp)(C_5H_4)),[23] the Re=C−C bond angle is only 114.8(7) Å. In five-coordinate *anti*-W(N-2,6-C_6H_3-*i*-Pr_2)(CHCH=CHCH_3)[OC(CF_3)$_2$Me]$_2$(quinuclidine) the W=C−C bond angle is 126.3(5)°.[24] An alkylidene in a d^2 complex of a transition metal in the earlier part of the transition metal series (Ta, V, W) usually has a relatively large M=C−C angle as a consequence of the strong α agostic interaction, especially in the absence of other π bound ligands.[1] In *anti,anti*-Os(CH-*t*-Bu)$_2$(CH_2SiMe_3)$_2$, the Os=C−C bond angle is 130.9(6)°, a value that is more or less in the middle of the range of alkylidene M=C−C bond angles. There does not appear to be any α agostic interaction. In any case, osmium is considerably less electrophilic than the earlier metals and would be much less susceptible to "oxidation" to an Os(VIII) alkylidyne hydride complex (i.e., to hypothetical Os(C-*t*-Bu)(H)(CH-*t*-Bu)(CH_2SiMe_3)$_2$), which would be the extreme end result of an α agostic interaction in a d^2 species.[25]

Extended Hückel calculations performed on $Os(CH_2)_2(CH_3)_2$ using the CaCHe system provide a point of reference. Atomic coordinates for osmium and the methyl and methylidene carbons were taken from the structure of *anti,anti*-Os(CH-*t*-Bu)$_2$(CH_2SiMe_3)$_2$. The hydrogen atoms on the methylene ligands were placed in the plane formed by the metal center and the two methylidene carbons, and the Os−C−H angle was set at 120°. For the purposes of the calculations, the atomic coordinates were chosen so that the metal center and the two methylidene ligands were located on the *xz* plane, bisected by the *z* axis. The results of the calculations are shown in Figure 2. Several features are noteworthy. The HOMO is an orbital of primarily d_{z^2} symmetry, while the LUMO is the π* system of the bis(methylidene) unit. The HOMO-1 and HOMO-2 are bonding combinations of the π system. The sizable contributions from both the metal d orbitals and the carbon p orbitals suggest that the metal carbon double bonds are largely covalent.

Reactions between OsO_2R_2 and a variety of metal alkylidene complexes were also investigated. No reaction was observed between OsO_2(CH_2-*t*-Bu)$_2$ and Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$.[26] The reaction of OsO_2(CH_2-*t*-Bu)$_2$ and Cp_2Ti(μ-CH_2)(μ-Cl)Al(CH_3)$_2$[27] in the presence of DMAP (*p*-(dimethylamino)pyridine) resulted in formation of an insoluble precipitate, but no tractable Os-containing products were obtained. The titanacyclobutane complex, Cp_2Ti[CH(*t*-Bu)CH_2CH_2],[28] does not react with OsO_2(CH_2-*t*-Bu)$_2$ at room temperature in C_6D_6. Cp_2Ti[CH(*t*-Bu)CH_2CH_2] reacts with OsO_2(CH_2-*t*-Bu)$_2$ in neat neohexene to give an immediate precipitate of $[Cp_2TiO]_n$, but [OsO(CH_2-*t*-Bu)$_2$]$_n$ is the only product that could be isolated from the reaction mixture.

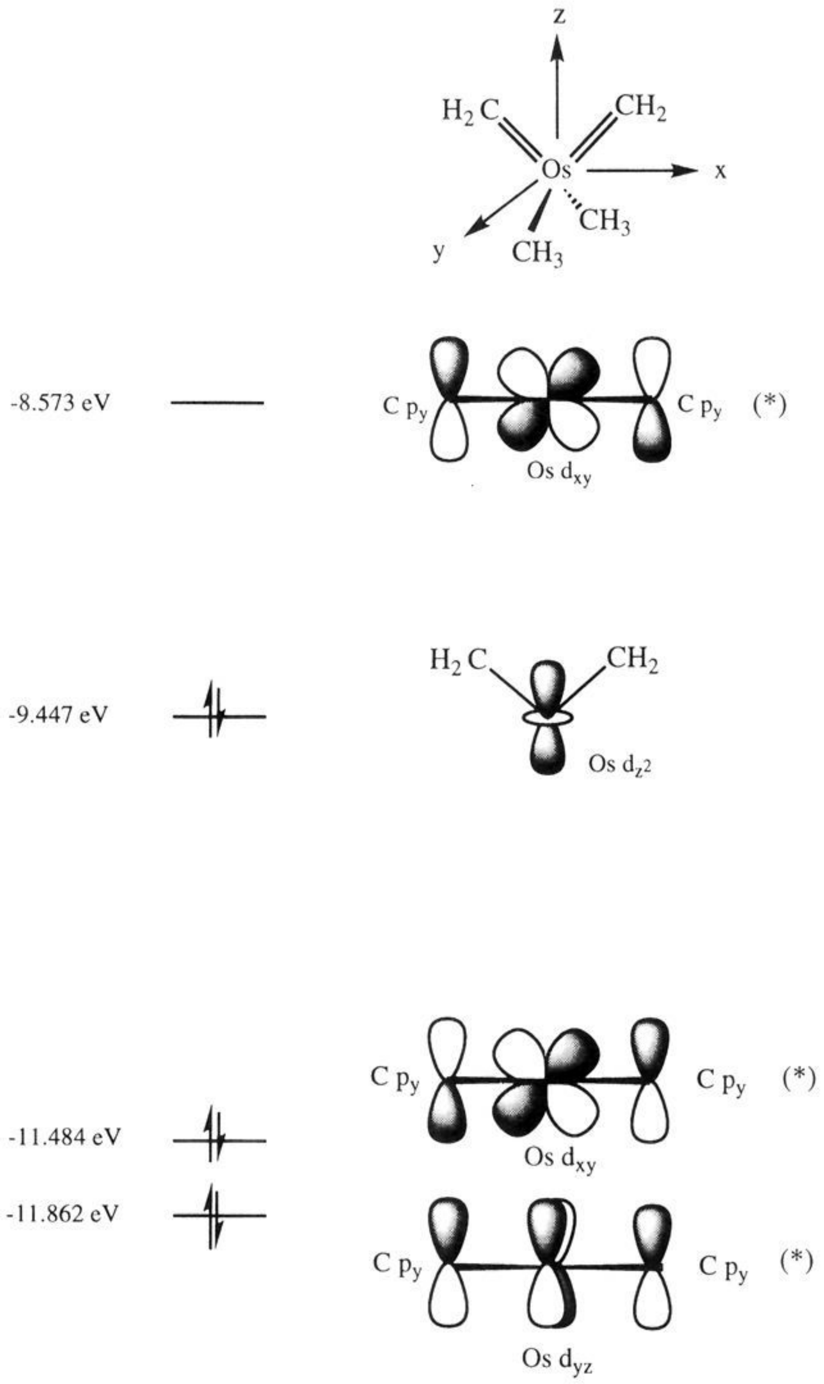


Figure 2. Bonding in $Os(CH_2)_2(CH_3)_2$ (according to extended Huckel calculations; MO's with an asterisk are viewed looking down the *z* axis.).

Reaction of *syn,anti*-Os(CH-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ with Donor Ligands. *syn,anti*-Os(CH-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ does not bind ligands such as pyridine, acetonitrile, or triphenylphosphine oxide. Sterics are most likely responsible, since Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$,[16] W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$,[29] and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$[30] also do not form simple adducts with donor ligands. However, Os(CH-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ does react with phosphines such as trimethylphosphine, dimethylphenylphosphine, dmpe, or methyldiphenylphosphine (as do Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$ and W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$). Neopentane is observed when the reaction of Os(CH-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ with phosphines is monitored by ^{1}H NMR, but hypothetical products such as Os(C-*t*-Bu)(CH-*t*-Bu)(CH_2-t-Bu)(PR_3)$_2$ could not be identified. On the other hand, when Os(CH-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$

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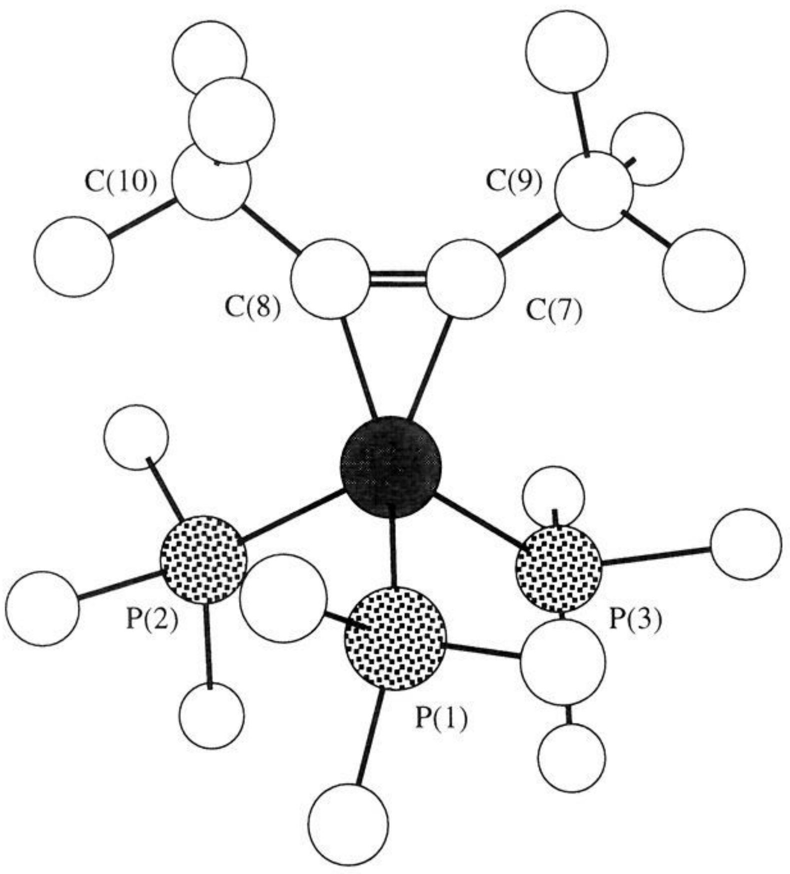
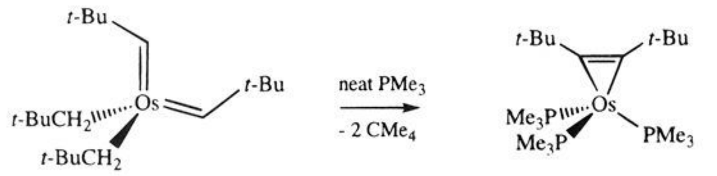


Figure 3. A Chem 3D drawing of Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu).

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu)

	Distances		
Os−P(1)	2.219(3)	Os−C(7)	2.02(1)
Os−P(2)	2.291(3)	Os−C(8)	2.01(1)
Os−P(3)	2.295(3)	C(7)−C(8)	1.30(1)
	Angles		
P(1)−Os−P(2)	93.5(1)	P(3)−Os−C(7)	107.2(3)
P(1)−Os−P(3)	94.0(1)	C(7)−Os−C(8)	37.6(4)
P(2)−Os−P(3)	96.5(1)	Os−C(7)−C(8)	70.5(7)
P(1)−Os−C(8)	115.3(3)	Os−C(7)−C(9)	145.4(9)
P(1)−Os−C(7)	116.0(3)	Os−C(8)−C(7)	71.9(7)
P(2)−Os−C(8)	106.4(4)	Os−C(8)−C(10)	148.2(9)
P(2)−Os−C(7)	139.8(3)	C(7)−C(8)−C(10)	140(1)
P(3)−Os−C(8)	140.8(3)	C(8)−C(7)−C(9)	144(1)

is dissolved in *neat* trimethylphosphine, orange-red, pentane-soluble Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) could be isolated in 30−40% yield (recrystallized) after 1 h (eq 7). Evidently neat



(7)

trimethylphosphine is required in order for the rate of formation of Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) to be competitive with (probably intermolecular) reaction pathways that lead to less stable products. The proton NMR spectrum of Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) contains only two sharp resonances for trimethylphosphine and a *tert*-butyl group. A resonance at 192 ppm was found in the ^{13}C NMR spectrum, which is significantly upfield from a typical terminal mono(alkylidyne) C$_\alpha$ resonance (250−300 ppm[31]). The bis(carbyne) complexes, *trans*-[M(dmpe)$_2$(CNHMe)$_2$]$^{2+}$ (M = Mo, W), have C$_\alpha$ resonances at 190−205 ppm.[32] The C$_\alpha$ resonance at 192 ppm is almost 100 ppm downfield from the alkyne carbon resonance observed in Os(CO)$_4$(RCCR).[33,34] Since the IR spectrum of Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) failed to confirm that an η^2-acetylene was present, there seemed to be some possibility that this molecule was a bis(neopentylidyne) complex instead of a di-*tert*-butylacetylene complex.

Crystals of Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) suitable for X-ray diffraction were grown by slow evaporation of ether from ether/acetonitrile mixtures at 25 °C over a period of several days. The structure of Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) is shown in Figure 3 and bond distances and angles are listed in Table 3. The C−C bond length of the coordinated alkyne, 1.30(1) Å, is slightly longer than that observed in Os(CO)$_4$(Me$_3$SiC≡CSiMe$_3$) (1.273(8) Å)[34] and is well within the range of normal C−C bond lengths in electron-rich alkyne complexes.[35] The strength of the metal−alkyne interaction can more readily be assessed by the metal−C(alkyne) bond distance and the degree to which the substituents on the alkyne ligand are "bent back" from the C−C axis. The Os−C(7) and Os−C(8) bond lengths are 2.02(1) and 2.01(1) Å, respectively. This is significantly shorter than the bond lengths observed in Os(CO)$_4$(Me$_3$SiC≡CSiMe$_3$) (2.267(6) and 2.244(6) Å). The "bend-back" angles at C(7) (34.6(9)°) and C(8) (31.8(9)°) also are larger than those observed in Os(CO)$_4$(Me$_3$SiC≡CSiMe$_3$) (20.9(6)° and 26.3(6)°). These structural data suggest that the metal−alkyne interaction is significantly stronger in Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu) than it is in Os(CO)$_4$(Me$_3$SiC≡CSiMe$_3$). This conclusion is consistent with ^{13}C data, electron-counting and coordination arguments, and the fact that the carbonyl ligands should compete more effectively with the alkyne in π backbonding than will PMe$_3$.

Two plausible mechanisms for forming Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) are shown in Figure 4. (In neat trimethylphosphine intramolecular C−C coupling mechanisms seem much more likely than intermolecular mechanisms.) In both proposed mechanisms phosphine-induced α-hydrogen abstraction first yields Os(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(PMe$_3$)$_2$. In the "bis(alkylidyne)" mechanism, an additional α-hydrogen abstraction occurs to form transient Os(C-*t*-Bu)$_2$(PMe$_3$)$_2$. Coordination of a third phosphine then induces coupling of the two neopentylidyne ligands to form Os(PMe$_3$)$_3$(*t*-BuC≡C*t*-Bu). Alternatively, the alkylidene and alkylidyne fragments could couple to yield a "η^2-vinyl" intermediate, which then eliminates neopentane to form Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu). A third mechanism, which consists of phosphine-induced formation of Os(η^2-*t*-BuCHCH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(PMe$_3$)$_n$ (n = 2, 3) from Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$, followed by dehydrogenation of bound di-*tert*-butylethylene to form Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu) and 2 equiv of neopentane, cannot be excluded. Of the three possible mechanisms, we prefer the second, the "carbene−carbyne" mechanism, on the basis of the fact that it is similar to the mechanism proposed for reductive coupling of carbon monoxide and isocyanides by anionic group 5 and 6 metal complexes,[36,37] as well as coupling of a methylidyne ligand with carbon monoxide in the presence of Lewis acids.[38] In these systems, mechanistic studies support the intermediacy of a carbene−carbyne complex, but no studies have yet been able to reveal the intimate details of the C−C coupling process.[36] A possibly related reaction in a d^0 system is that between W(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)-

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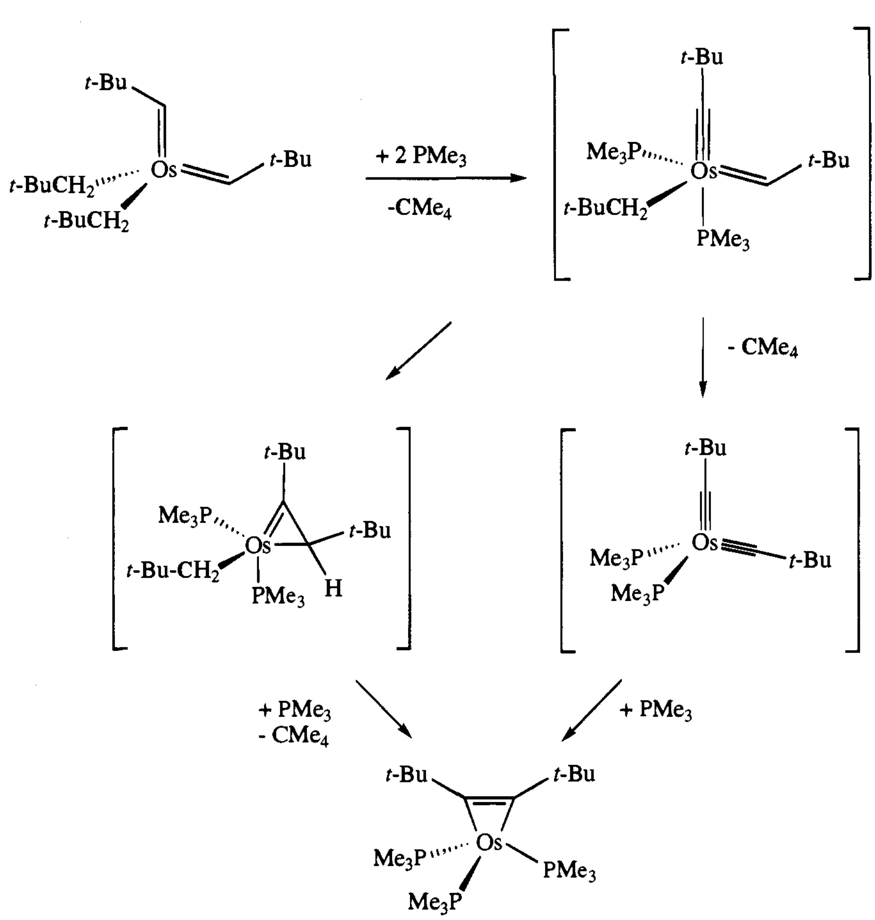


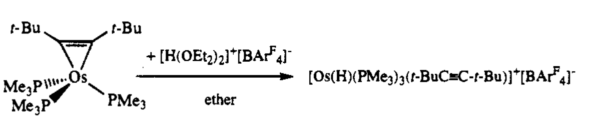
Figure 4. Possible mechanisms of forming Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu).

(dmpe) and dmpe to form W(C-*t*-Bu)(H)(dmpe)$_2$ and di-*tert*-butylethylene.[39]

Mononuclear complexes of Os(0) are extremely rare, and the majority of those that have been characterized contain several π-acid ligands, usually carbonyls, olefins, or acetylenes. For example, air- and water-stable Os(CO)$_4$(RC≡CR) (R = H, SiMe$_3$, CF$_3$) complexes have been prepared by Takats and coworkers via the photochemical reaction of Os$_3$(CO)$_{12}$ with alkynes.[33,34] Os(PMe$_3$)$_5$ is the only Os(0) phosphine complex that has been reported to our knowledge.[40] We prepared Os(PMe$_3$)$_5$ and found that it does not react with bis(trimethylsilyl)acetylene or 2-butyne to form Os(PMe$_3$)$_3$(RC≡CR) complexes. Os(PMe$_3$)$_5$ can undergo reversible phosphine dissociation to form intermediate Os(PMe$_3$)$_4$,[40] but intermediates such as Os(PMe$_3$)$_4$(alkyne) or Os(PMe$_3$)$_3$ may be sterically crowded or relatively high-energy species. Even if Os(PMe$_3$)$_4$(alkyne) does form, it might simply lose alkyne rather than PMe$_3$.

Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) does not react with neat 2-butyne or bis(trimethylsilyl)acetylene at room temperature, with excess acetonitrile, ethylene, tricyclohexylphosphine (3 equiv), or 2 equiv of bipyridyl or TMEDA. Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) reacts with carbon monoxide in benzene or pentane to form colorless Os(PMe$_3$)$_2$(CO)$_2$(η^2-*t*-BuC≡C-*t*-Bu). In the presence of a large excess of CO neither phosphine nor di-*tert*-butylacetylene is displaced. In Os(PMe$_3$)$_2$(CO)$_2$(η^2-*t*-BuC≡C-*t*-Bu), the acetylene does not have a significant degree of "metallacyclopropene" character, as suggested by the chemical shift of the acetylenic carbon (106.8 ppm), which is almost 100 ppm upfield from the acetylenic carbon chemical shifts in the complexes where di-*tert*-butylacetylene is a "four-electron donor." The structure of Os(PMe$_3$)$_2$(CO)$_2$(η^2-*t*-BuC≡C-*t*-Bu) cannot be unambiguously assigned on the basis of NMR and IR data.

Os(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu) is extremely air- and water-sensitive. It reacts rapidly with acids and pyridinium salts, but a clean product could be isolated only when [H(ether)$_2$]$^+$[BAr$^F_4$]$^-$ (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$)[41] was employed as the proton source. In that case, yellow, crystalline [Os(H)(PMe$_3$)$_3$(η^2-*t*-BuC≡C-*t*-Bu)]$^+$[BAr$^F_4$]$^-$ was isolated in 70% yield (eq 8). The hydride resonance is found at −6.16 ppm. Its quartet structure (J_{HP} = 12 Hz) suggests that it is equally coupled to the three phosphine ligands on the NMR time scale.

 (8)

In the presence of 5−10 equiv of PMe$_3$ in dichloromethane [Os(H)(*t*-BuC≡C-*t*-Bu)(PMe$_3$)$_3$]$^+$[BAr$^F_4$]$^-$ loses di-*tert*-butylacetylene to form colorless cubes of [Os(H)(PMe$_3$)$_5$]$^+$[BAr$^F_4$]$^-$ in 90% yield, a compound that has been reported previously as the triflate salt.[40] It is interesting to note that in the presence of trimethylphosphine, di-*tert*-butylacetylene is readily lost from the more electrophilic Os(II) species but not from the neutral Os(0) species, even though di-*tert*-butylacetylene may be regarded as a four-electron donor in both cases. This is an example of the greater affinity of Os(II) for σ-donor ligands such as PMe$_3$ compared to a π-acceptor ligand; the opposite is observed in the Os(0) complex, Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu).

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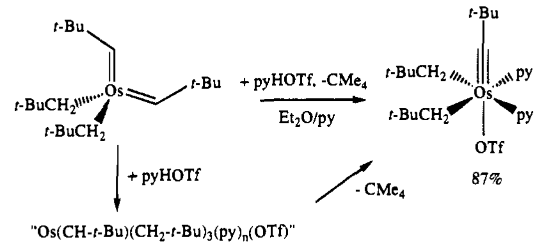
$Os(PMe_3)_3(\eta^2$-*t*-BuC≡C-*t*-Bu) reacts with dihydrogen in the presence of excess trimethylphosphine to give *cis*-$OsH_2(PMe_3)_4$[42] and di-*tert*-butylethylene. In the absence of excess phosphine, $Os(PMe_3)_3(\eta^2$-*t*-BuC≡C-*t*-Bu) in C_6D_6 reacts with dihydrogen (1 atm) to form di-*tert*-butylethylene, but the fate of the metal could not be determined. No further hydrogenation of di-*tert*-butylethylene was observed in the presence or absence of PMe_3, and no hydrogenation of added 4-octyne was observed.

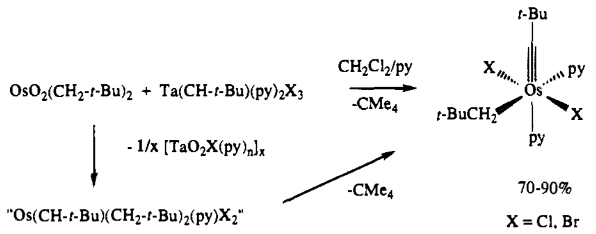
Os(VI) Alkylidyne Complexes. *syn,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ reacts with pyridinium triflate in the presence of excess pyridine to yield neopentane and orange, air- and water-stable Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) (eq 9). If pyDOTf is used, deuterium is found statistically distributed among the α-carbon atoms of the neopentyl ligands in Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf), consistent with protonation of one of the neopentylidene ligands in Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ followed by α-hydrogen abstraction in intermediate "[Os(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(py)$_n$]$^+$" and coordination of the triflate (eq 9). α-Hydrogen abstraction in a cationic intermediate is proposed since α-hydrogen abstraction is believed to be more facile in d^0 complexes that are strongly polarized or actually cationic.[1] (For instance, in a closely related d^0 system, Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ reacts with triflic acid in non-coordinating solvents to yield the stable complex, Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(OTf), which then reacts readily with added pyridine to form neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(OTf). The analogous reaction between Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$Cl and pyridine is significantly slower.[43a]) In the proton NMR spectrum of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) the two neopentyl groups are related by a mirror plane and the two bound pyridines are equivalent. Added pyridine exchanges with coordinated pyridine on the NMR time scale at 25 °C in CD_2Cl_2. The IR spectrum reveals an absorption at 1303 cm^{-1}, which suggests that the triflate ion is bound to the metal.[44] All data are consistent with the structure shown in eq 9. Attempts to grow crystals of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) that are suitable for X-ray diffraction have not yet been successful.



(9)

In the absence of pyridine, the reaction between Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ and triflic acid failed to yield any isolable products, although neopentane was observed to form when the reaction was monitored by ^{1}H NMR. Although the proposed product, "Os(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(OTf)", would appear to be quite similar to the stable d^0 rhenium complex, Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(OTf), in the rhenium complex only a neopentyl α proton is available for abstraction and two metal−ligand π bonds are able to stabilize the metal in the high oxidation state. Os(VI) complexes such as Os(O)R$_4$,[10] [Os(N)R$_4$]$^-$,[6] and Os(NAr)(CH$_2$-*t*-Bu)$_2$X$_2$ (X = Cl, I, CH$_3$),[43] where the oxo, nitrido, and imido ligands can be viewed as triply-bonded ligands, have not been reported to undergo any controlled α-hydrogen abstraction reactions.

OsO$_2$(CH$_2$-*t*-Bu)$_2$ reacts with 1 equiv of Ta(CH-*t*-Bu)(py)$_2$X$_3$ (X = Cl, Br)[45] in dichloromethane/pyridine mixtures to form neopentane and orange Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$X$_2$. Yields are lower in the absence of excess pyridine. When OsO$_2$(CD$_2$-*t*-Bu)$_2$ and Ta(CH-*t*-Bu)(py)$_2$Cl$_3$ are employed, Os(C-*t*-Bu)(CD$_2$-*t*-Bu)(py)$_2$Cl$_2$ is formed exclusively. This finding suggests that the neopentylidene ligand that is transferred from tantalum to osmium is the one that eventually is converted into the neopentylidyne ligand. We propose that this remarkable reaction involves removal of two oxo ligands from osmium in exchange for a neopentylidene and two halide ligands to give intermediate "Os(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$X$_2$(py)$_n$" (eq 10), which may be cationic, e.g., [Os(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$X(py)$_2$]$^+$X$^-$. Since "Os(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$X$_2$(py)$_n$" contains only one metal−ligand π-bond it loses neopentane in the presence of pyridine to yield an alkylidyne complex. Migration of D$_\alpha$ from a neopentyl ligand in intermediate "Os(CH-*t*-Bu)(CD$_2$-*t*-Bu)$_2$X$_2$(py)$_n$" to the neopentylidene ligand would be expected to be inherently slower than α-hydrogen abstraction to give the neopentylidyne ligand. This "one-pot" synthesis is a mechanistically more complex version of the two-step synthesis of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf). Os(C-*t*-Bu)(CH-*t*-Bu)(py)$_2$X$_2$ is relatively stable to air and water in the solid state.



(10)

The reaction between OsO$_2$(CH$_2$-*t*-Bu)$_2$ and Ta(CH-*t*-Bu)L$_2$Cl$_3$ (L = THF, $^1/_2$bpy, PMe$_3$) in CD$_2$Cl$_2$ yields products whose NMR spectra suggest that they are analogous to Os(C-*t*-Bu)(CH-*t*-Bu)(py)$_2$X$_2$, but so far we have not been able to isolate them. We believe such species to be present, since (for example) addition of pyridine to solutions of "Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(THF)$_2$Cl$_2$" results in formation of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$Cl$_2$. The reaction between OsO$_2$(CH$_2$-*t*-Bu)$_2$ and Ta(CHPh)(PMe$_3$)$_2$Cl$_3$ in CD$_2$Cl$_2$ did not yield any identifiable products, nor did the reaction between [OsO$_2$(CH$_2$SiMe$_3$)$_2$]$_n$ and Ta(CH-*t*-Bu)(py)$_2$Cl$_3$. Perhaps in the reactions that do not involve both neopentyl and neopentylidene ligands other modes of decomposition of intermediate "Os(CHR)(CH$_2$R$'$)$_2$Cl$_2$" can compete with α-hydrogen abstraction. Once again, these results suggest that in the absence of another multiply-bonded ligand, mono(alkylidene) complexes of osmium(VI) are unstable with respect to formation of a metal−carbon triple bond. It should be noted that *cis*-Os(NAr)(CH$_2$-*t*-Bu)$_2$X$_2$ (X= Cl, I)[43b] does not react with pyridine; *cis*-Os(NAr)(CH$_2$-*t*-Bu)$_2$X$_2$ already has two metal−ligand π-bonds (in the imido ligand) and it lacks a neopentylidene ligand, from which α-hydrogen abstraction reactions are most facile.

In view of the existence of rhenium(VII) neopentylidyne/neopentylidene complexes of the type Re(C-*t*-Bu)(CH-*t*-Bu)X$_2$ (X = Cl, OR, etc.),[47] we thought that it might be possible to deprotonate Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) to form Os(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$. However, we found that the metal was attacked more rapidly, perhaps in part because the

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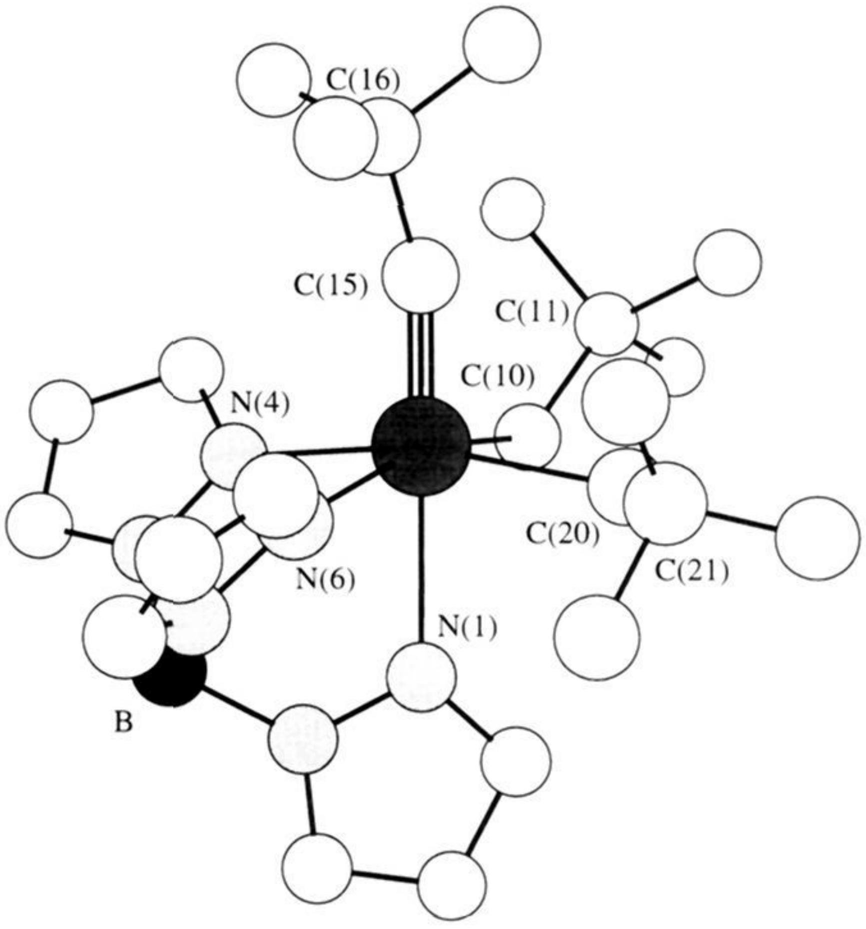
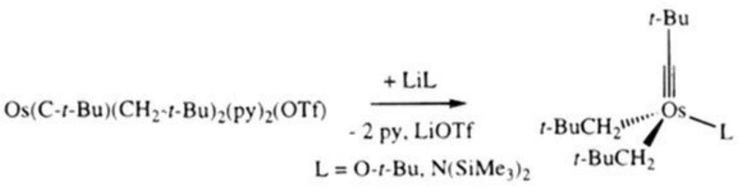


Figure 5. A Chem 3D drawing of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(HBpz)$_3$.

pyridine and triflate ligands are labile, and in part because deprotonation of a neopentyl is rarely a facile reaction, even in d^0 alkyl chemistry. For example, Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) reacts with LiO-*t*-Bu or LiN(SiMe$_3$)$_2$ in THF to yield the four-coordinate alkylidyne complexes shown in eq 11 in



(11)

60–80% yield. Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$[N(SiMe$_3$)$_2$] is a crystalline brown-red solid which is exceedingly soluble in pentane. It can be recrystallized from ether/acetonitrile mixtures at −40 °C. The two trimethylsilyl groups are equivalent on the NMR time scale at 25 °C. Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(O-*t*-Bu) could be obtained only as a brown oil. Attempts to sublime it without decomposition were not successful.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) reacts with NaC$_5$H$_5$ in THF to yield yellow, 18-electron Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(η^5-C$_5$H$_5$), an alkylidyne analog of Os(N)(η^5-C$_5$H$_5$)(CH$_2$SiMe$_3$)$_2$.[48] Analogous reactions between Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) and Na{CpCo[P(O)(OEt)$_2$]$_3$} (NaL$_{\mathrm{OEt}}$)[49] or sodium trispyrazolylborate (NaHBpz$_3$) in THF yield Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(L$_{\mathrm{OEt}}$) or Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(HBpz$_3$), respectively, in 60–80% yields. These compounds are thermally stable pink solids that are also stable to air and water in the solid state.

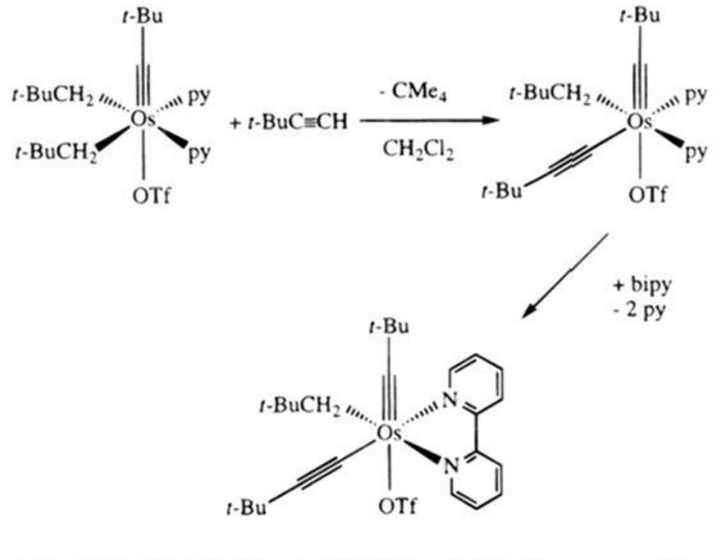
Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$X$_2$ (X = Cl, Br) does not react with NaC$_5$H$_5$, KO-*t*-Bu, or NaHBpz$_3$ in THF or dichloromethane, probably because the pyridine and chloride ligands are too tightly bound. The reaction of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$X$_2$ with 2 equiv of LiR (R = CH$_2$-*t*-Bu, CH$_2$SiM$_3$) in THF yields mixtures that contain *syn,anti*- and *anti,anti*-Os(CH-*t*-Bu)$_2$R$_2$.

Crystals of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(HBpz$_3$) suitable for X-ray diffraction were obtained from pentane at −40 °C. A drawing of the structure of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(HBpz$_3$) is shown in Figure 5, and selected bond lengths and angles are listed in Table 4. The Os≡C bond length (1.73(2) Å) is comparable to that found in [Os(CC$_6$H$_5$)(NH$_3$)$_5$]$^{3+}$ (1.73(1) Å).[50] The relatively small Os−C(15)−C(16) angle (161(2)°) can be ascribed to steric interactions between *tert*-butyl groups. The Os−N distances (2.18(2), 2.20(2) Å) for the pyrazolyl nitrogens *trans* to the two neopentyl groups are significantly shorter than that for the pyrazolyl nitrogen *trans* to the neopentylidyne (2.30(2) Å), as one would expect on the basis of the *trans* influence of the alkylidyne ligand.

Table 4. Selected Intramolecular Distances (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(HBpz$_3$)

	Distances		
Os−N(4)	2.20(2)	Os−C(15)	1.73(2)
Os−N(1)	2.30(2)	Os−C(10)	2.11(2)
Os−N(6)	2.18(2)	Os−C(20)	2.15(3)
	Angles		
Os−C(10)−C(11)	130(2)	N(1)−Os−C(10)	82.1(8)
Os−C(15)−C(16)	161(2)	N(1)−Os−C(15)	176.8(8)
Os−C(20)−C(21)	127(2)	N(1)−Os−C(20)	86(1)
C(10)−Os−C(15)	97(1)	N(4)−Os−C(10)	87.8(9)
C(10)−Os−C(20)	83(1)	N(4)−Os−C(15)	96.1(9)
C(15)−Os−C(20)	97(1)	N(4)−Os−C(20)	164.5(9)
N(1)−Os−N(4)	80.9(8)	N(6)−Os−C(10)	161.4(9)
N(1)−Os−N(6)	80.4(7)	N(6)−Os−C(15)	100.5(9)
N(4)−Os−N(6)	83.3(8)	N(6)−Os−C(20)	102(1)

None of the osmium neopentylidyne complexes reacts with an internal alkyne such as 2-butyne. The six-coordinate complexes Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(L) (L = Cp, L$_{\mathrm{OEt}}$, HBpz$_3$) and Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$X$_2$ (X = Cl, Br) do not react with terminal alkynes such as phenylacetylene or *tert*-butylacetylene, even at elevated temperatures. However, Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) reacts with *tert*-butylacetylene in CD$_2$Cl$_2$ to yield neopentane and the η^1-acetylide complex, Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(C≡C-*t*-Bu)(py)$_2$(OTf) (eq 12). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(C≡C-*t*-Bu)(py)$_2$(OTf) is stable for several hours in CD$_2$Cl$_2$ at 25 °C, but it is somewhat unstable in the solid state. Addition of 1 equiv of 2,2′-bipyridyl yields isolable crystalline Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(C≡C-*t*-Bu)(bpy)(OTf). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(C≡C-*t*-Bu)(bpy)(OTf) also can be prepared in CD$_2$Cl$_2$ in a slow reaction (several days) from excess *tert*-butyl acetylene and Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(bpy)(OTf). The analogous reaction is complete in minutes when Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) is used, presumably since pyridine can dissociate and *tert*-butylacetylene can attack the metal and undergo σ-bond metathesis to form neopentane and Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(C≡C-*t*-Bu)(py)$_2$(OTf). Direct protonation of a neopentyl group by the free acetylene seems unlikely in view of the fact that Os-



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$(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(py)_2(OTf)$ is stable to proton sources such as water or pyHOTf. $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(C{\equiv}C\text{-}t\text{-}Bu)(py)_2(OTf)$ appears to react with a second equivalent of *tert*-butylacetylene, but no stable product could be identified.

The four-coordinate alkylidyne complexes, $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)$ and $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2[N(SiMe_3)_2]$, do not react with excess phenylacetylene at room temperature in C_6D_6. At elevated temperatures they decompose; *tert*-butyl alcohol and $HN(SiMe_3)_2$, respectively, were the only products that could be identified.

Discussion

Group 4 or 5 transition metal alkylidene complexes,[1] like phosphoranes, often react with ketones or aldehydes in a "Wittig-like" manner to give olefins. If one draws an analogy between a metal oxo complex and a carbonyl group, then one might propose that an alkylidene complex could be prepared by treating that metal oxo complex with a phosphorane or an early transition metal alkylidene complex. However, although alkylidene/oxo exchange reactions have been attractive proposed methods of preparing alkylidene complexes for many years, we know of no examples other than those reported here.

Several other types of exchange reactions have been reported. Oxo/imido exchange has been reported for several d^0 tungsten and molybdenum complexes.[51] Imido/oxo exchange reactions between OsO_4 and phosphinimines[52] or molybdenum imido complexes[46] have been reported to give $Os(NR)_n(O)_{4-n}$ (n = 2–3) complexes. Alkoxide/alkylidene exchange reactions between tantalum and tungsten have been reported (eq 2), but in this case the only ligand that is *not* exchanged between tungsten and tantalum is the oxo group.[15]

$Os(CH\text{-}t\text{-}Bu)_2(CH_2R)_2$ complexes are related structurally to members of the d^0 series of complexes, $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$,[53] $W(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$,[29] and $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$.[30] The only other reported bis(neopentylidene) complexes, which incidentally also have the *syn,anti* configuration, are niobium and tantalum complexes of the type $M(CH\text{-}t\text{-}Bu)_2(X)L_2$, e.g., $Ta(CH\text{-}t\text{-}Bu)_2Cl(PMe_3)_2$.[1] The only other "Os(VI)" alkylidene complex that has been reported is $Os(C_4Me_4)(en)_2(OTf)_2$, an "osmacyclopentatriene" complex.[54] d^2 alkylidene complexes of earlier transition metals tend to contain a highly distorted alkylidene ligand that is interacting in an α agostic fashion with the metal. In some cases d^0 alkylidyne hydride complexes actually are preferred. In contrast, the neopentylidene ligands in *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_2$ are not distorted to a significant degree, perhaps in part because there must be little tendency for Os(VI) to be "oxidized" to Os(VIII) through α elimination to give "$Os(C\text{-}t\text{-}Bu)(H)(CH\text{-}t\text{-}Bu)(CH_2SiMe_3)_2$".

There are several features of the $Os(CH\text{-}t\text{-}Bu)_2(R)_2$ complexes that are puzzling. One is that the two rotameric forms of $Os(CH\text{-}t\text{-}Bu)_2(R)_2$ exhibit markedly different reactivity. For example, for a given alkyl group, the *syn,anti* isomer is much less thermally stable than the *anti,anti* rotamer and decomposes with loss of neopentane or tetramethylsilane over several hours at 25 °C in C_6D_6 or toluene-d_8. Also, the *syn,anti* isomers react with acids, while the *anti,anti* isomers are stable under identical conditions. Lastly, it is puzzling why $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ is not a lower energy species than $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$, while $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)$ (for example) is preferred over hypothetical $Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)$. It is interesting to note that in C_{3v} symmetric $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ the d_{xy} and $d_{x^2-y^2}$ orbitals (if the z axis passes through the $Os{\equiv}C$ bond) would be degenerate and d^2 $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ therefore could be paramagnetic. That degeneracy could be broken in the Os(VI) neopentylidyne complexes reported here as a consequence of π bonding (e.g., between Os and O in $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)$).

The syntheses of the Os(VI) neopentylidyne complexes $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2(py)_2(OTf)$ and $Os(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(py)_2X_2$ provide the first examples of α-hydrogen abstraction reactions at osmium. The majority of carbyne complexes of ruthenium and osmium that have been reported can be described as M(IV) if, for consistency, the carbyne ligand is viewed as being a trianionic ligand. To our knowledge, the only other "Os(VI)" carbynes known are $OsCl_2(NCS)(CC_6H_4NMe_2)(PPh_3)_2$,[55] $[Os(CR)(NH^3)_5]^{3+}$ (R = C_6H_5,[50] $(CH_2)_2CHO$[56]), and $OsCl_2(CCH_2R)(H)[P(i\text{-}Pr)_3]_2$.[57] These six-coordinate complexes are all prepared from lower oxidation state osmium precursors. The driving force for the α-hydrogen elimination appears to spring from the requirement that Os(VI) complexes contain more than one metal–ligand π-bond. Therefore proposed intermediates such as "$Os(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3(OTf)$" and "$Os(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2X_2$" cannot be observed. α-Hydrogen abstraction can occur in the absence of strongly coordinating ligands, most likely in a complex intermolecular fashion. Only when intermediates react with coordinating ligands can intramolecular α-abstraction be promoted and products observed.

We were somewhat surprised by the extraordinarily low reactivities of the metal–carbon multiple bonds in the complexes described here, especially since some of the protonation and α-hydrogen abstraction reactions that were observed are analogous to those in d^0 systems. However, it should be noted that d^0 Re alkylidene complexes in general are much less reactive than tungsten or molybdenum alkylidene complexes.[23] The low reactivity of Os(VI) alkylidene and alkylidyne complexes is a continuation of this general trend. It also should be noted that the LUMO in $Os(CH_2)_2(CH_3)_2$ is not metal-based, according to the extended Hückel calculations reported here. On the other hand, the LUMO in complexes of the type $Mo(CHR)(NR')(OR'')_2$ is metal-based,[22] and it is believed that an olefin must add to the metal before a metallacyclobutane intermediate can form.[1,2] Consequently, the complexes reported here do not fall neatly into a category of metal–carbon multiple bond reactivity on the basis of formal oxidation state, type of substituent at C_α, or coordination number. Actually, there is considerable precedent for the "amphoteric" nature of Os carbene and carbyne complexes. For example, the "Os(VI)" benzylidyne complex, $[Os(CPh)(NH_3)_5]^{3+}$, is electrophilic at C_α, reacting with propylamine in acetonitrile to form $\{Os[C(Ph)(NHPr)](NH_3)_4(MeCN)\}^{2+}$ and NH_4^+,[50] while the "Os(IV)" benzylidyne complex, $Os(CC_6H_4CH_3)Cl(CO)(PPh_3)_2$, is nucleophilic at C_α, reacting with HCl to form $OsCl_2(CHC_6H_5CH_3)(CO)(PPh_3)_2$.[58]

The oxo/alkylidene exchange reactions reported here represent a new synthetic route to alkylidene complexes. Almost certainly a significant factor leading to the success of the oxo/alkylidene exchange reaction is the weakness of a later transition metal

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oxo bond relative to the tantalum oxo bond. On this basis one might predict that future successful alkylidene exchange reactions also will involve oxo complexes of later transition metals. At this stage we can only speculate about the possibility of exchanging an alkylidene ligand on tantalum or another early transition metal with other ligands that are not commonly found in later transition metal chemistry (e.g., imido, amido, or alkoxide ligands) and the degree to which the oxo/alkylidene exchange reaction might prove useful for replacing oxo ligands on metal oxide surfaces with alkylidene ligands.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE-43 drybox or using standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95/5 v/v), aqueous sodium bicarbonate solution, and then water, stored over $CaCl_2$, and then distilled from sodium benzophenone ketyl. Ether, tetrahydofuran, benzene, and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen or argon. Toluene was distilled from molten sodium under nitrogen or argon, and dichloromethane, acetonitrile, and pyridine were distilled from calcium hydride under nitrogen or argon. All deuterated NMR solvents were purchased from Cambridge Isotopes. Tetrahydrofuran-d_8 was vacuum transferred from sodium benzophenone ketyl. C_6D_6, CD_2Cl_2, $CDCl_3$, CD_3CN, and pyridine-d_5 were stored over activated molecular sieves in the drybox. Methanol-d_4 was used as received.

OsO_4 was purchased from Strem Chemicals and converted into $K_2[OsO_2(OH)_4]$ by the literature procedure,[59] or reclaimed from osmium-containing wastes by hypochlorite oxidation and distillation into KOH solution. Ethanol was added to the resulting solution in order to precipitate $K_2[OsO_2(OH)_4]$. $[PPh_4]_2[OsO_2Cl_4]$,[10] $Zn(CH\text{-}t\text{-}Bu)_2$,[16] $Zn(CD_2\text{-}t\text{-}Bu)_2$,[16] $Mg(CH_2\text{-}t\text{-}Bu)_2(dioxane)$, $LiCH_2\text{-}t\text{-}Bu$,[16] $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$,[27] $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$,[16] $Ta(CD\text{-}t\text{-}Bu)(CD_2\text{-}t\text{-}Bu)_3$,[16] $Ta(CH\text{-}t\text{-}Bu)(py)_2Cl_3$,[45] $Os(PMe_3)_5$,[40] and $[H(OEt_2)_2]^+[BAr^F{}_4]^-$ [41] were prepared by literature methods. $Ta(CH\text{-}t\text{-}Bu)(py)_2Br_3$ was prepared from $Ta(CH_2\text{-}t\text{-}Bu)_2Br_3$ and pyridine in a manner analogous to that used to prepare $Ta(CH\text{-}t\text{-}Bu)(py)_2Cl_3$.[45] $t\text{-}BuCD_2Cl$ was prepared in a modification of the literature procedure;[60] under argon, a solution of $t\text{-}BuCD_2OH$ in DMF was added to a slurry of $[Me_2N{=}CHCl]^+Cl^-$ in DMF at 0 °C. The solution was then heated to 80−100 °C and $t\text{-}BuCD_2Cl$ was distilled from the reaction mixture, dried over $CaCl_2$, and redistilled. $Al(CH_2\text{-}t\text{-}Bu)_3(THF)$ was prepared from $AlCl_3$ and $t\text{-}BuCH_2MgCl$ in THF and then sublimed. NaL_{OEt}[49] was provided by Dr. R. D. Simpson. Trimethylphosphine was purchased from Strem or Aldrich. Silica gel was typically 70−230 mesh (Aldrich) or 230−400 mesh (Bodman).

NMR spectra were recorded on Bruker WM-250, Varian XL-300, Varian UNITY-300, or Varian VXR-500 spectrometers. ^1H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced by the residual solvent proton peak. ^{19}F data are listed in parts per million downfield from CF_2Cl_2 and were externally referenced. ^{31}P data are listed in parts per million downfield from 85% H_3PO_4 and are externally referenced. Coupling constants are listed in hertz. Obvious multiplicities and routine coupling constants are usually not listed. IR spectra were recorded on a Mattson spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer in our laboratories. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer; a complete description of data collection, structure solution, and structure refinement can be found in the supplementary material.

$OsO_2(CH_2\text{-}t\text{-}Bu)_2$. Dineopentylzinc (0.853 g, 4.12 mmol) was added to a slurry of $[P(C_6H_5)_4]_2[OsO_2Cl_4]$ (2.00 g, 1.92 mmol) in 50 mL of dichloromethane. 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 purple-brown solid, which was then extracted with pentane. The mixture was filtered, and the volume of the filtrate was reduced to 5 mL. Upon cooling the solution to −40 °C, purple-brown needles formed and were collected and dried; yield 460 mg (66%). Higher yields (80−85%) can be obtained by evaporating the pentane solution to dryness. The microcrystalline solid thus obtained is pure by ^1H NMR and can be used without further purification: ^1H NMR (C_6D_6) δ 4.21 (s, 4, $CH_2\text{-}t\text{-}Bu$), 0.97 (s, 18, *t*-Bu); ^{13}C NMR (C_6D_6) δ 34.9 (CMe_3), 34.0 (CH_2CMe_3, $J_{CH} = 133$), 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.

$OsO_2(CH_2CMe_2Ph)_2$. $[P(C_6H_5)_4]_2[OsO_2Cl_4]$ (0.99 g, 0.95 mmol) was slurried in 10 mL of dichloromethane and the mixture was cooled to −40 °C. $Zn(CH_2CMe_2Ph)_2$ (0.330 mg, 1.00 mmol) was added and the mixture immediately darkened. The solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed in vacuo to yield a brown-purple solid, which was then extracted with toluene. The toluene was then removed in vacuo to yield a brown oil which was pure $OsO_2(CH_2CMe_2Ph)_2$ by ^1H NMR (260 mg, 56%): ^1H NMR (C_6D_6) δ 7.0−7.2 (m, 5, Ph), 4.44 (s, 4, CH_2CMe_2Ph), 1.29 (s, 12, CH_2CMe_2Ph); ^{13}C NMR (C_6D_6) δ 148.4, 127.3, 126.2, 125.8 (Ph), 41.6 (CH_2CMe_2Ph), 34.1 (CH_2CMe_2Ph), 29.5 (CH_2CMe_2Ph); IR (Nujol) cm^{-1} 979, 936 (Os=O).

$[OsO_2(CH_2SiMe_3)_2]_n$. $[P(C_6H_5)_4]_2[OsO_2Cl_4]$ (0.998 g, 0.96 mmol) was slurried in 10 mL of dichloromethane and the mixture was cooled to −40 °C. $Zn(CH_2SiMe_3)_2$ (0.45 g, 1.88 mmol) was added and the mixture immediately darkened. The solution was allowed to warm to room temperature and stirred for 30 min and then passed through silica gel. The solvent was removed in vacuo to yield a purple-brown solid, which was then extracted with pentane. After removal of the pentane in vacuo, a purple-brown microcrystalline solid was obtained (204 mg, 52%): ^1H NMR (C_6D_6) δ 5.07, 4.20, 4.16, 3.51 (d, 1 each, CH_2SiMe_3, $J_{HH} = 9$), 0.36, 0.17 (s, 9 each, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 41.4, 30.6 (CH_2SiMe_3), 1.4, 0.8 ($SiMe_3$); IR (Nujol) cm^{-1} 860 (Os=O).

$[OsO(CH_2\text{-}t\text{-}Bu)_2]_n$. $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ (179 mg, 0.41 mmol) was dissolved in 5 mL of THF and solid $Al(CH_2\text{-}t\text{-}Bu)_3(THF)$ (125 mg, 0.40 mmol) was added. The resulting red solution was stirred for 1.5 h at room temperature and the volatile components were removed *in vacuo* to yield a red solid which was dissolved in pentane and passed through silica gel to remove the aluminum-containing byproducts. The solvents were removed from the resulting red solution to give a red film of pure $[OsO(CH_2\text{-}t\text{-}Bu)_2]_n$ according to NMR spectra; yield 108 mg (75%). A crystalline sample for elemental analysis was obtained from ether/acetonitrile solutions at −40 °C: ^1H NMR (C_6D_6) δ 5.83 (d, 1, $CH_aH_b\text{-}t\text{-}Bu$, $J_{HH} = 10$), 4.99 (d, 1, $CH_aH_b\text{-}t\text{-}Bu$, $J_{HH} = 10$), 5.20 (d, 1, $CH_aH_b\text{-}t\text{-}Bu$, $J_{HH} = 12$), 4.40 (d, 1, $CH_aH_b\text{-}t\text{-}Bu$, $J_{HH} = 12$), 1.40, 1.33 (s, 9 each, *t*-Bu); ^{13}C NMR (C_6D_6) δ 53.5, 42.5 ($CH_2\text{-}t\text{-}Bu$), 37.5, 36.5 (CH_2CMe_3), 32.6 (CH_2CMe_3, the two *tert*-butyl peaks are coincident); IR (Nujol) cm^{-1} 980 (vs, Os=O). Anal. Calcd for $OsC_{10}H_{22}O$: C, 34.47; H, 6.36. Found: C, 34.38; H, 6.14.

$[Os(CH_3)(CH_2\text{-}t\text{-}Bu)_2]_2$. $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ (225 mg, 0.60 mmol) was dissolved in 10 mL of pentane and the solution was cooled to −40 °C. Trimethylaluminum (0.96 mmol, as a 2.0 M solution in hexane) was added and the mixture was allowed to warm to room temperature. The mixture became dark and a precipitate formed. After 20 min, the solution was filtered through Celite to yield a bright orange solution, and the volatiles were removed *in vacuo*, leaving an orange crystalline solid (93 mg, 43%) that was >95% pure by ^1H NMR. An analytical sample was recrystallized from ether/acetonitrile at −40 °C: ^1H NMR (C_6D_6) δ 3.46 (s, 3, CH_3), 3.03 (s, 4, CH_2CMe_3), 1.23 (s, 18, CMe_3); ^{13}C NMR (C_6D_6) δ 66.7 ($CH_2\text{-}t\text{-}Bu$), 37.9 (CMe_3), 32.7 (CMe_3), 31.4 (CH_3). Anal. Calcd for $Os_2C_{22}H_{50}$: C, 38.02; H, 7.25. Found: C, 38.15; H, 7.79.

***syn,anti*-$Os(CH\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$.** $OsO_2(CH_2\text{-}t\text{-}Bu)_2$ (100 mg, 0.27 mmol) was dissolved in 10 mL of pentane and the solution was chilled to −40 °C. $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ (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 stirring solution of $OsO_2(CH_2\text{-}t\text{-}Bu)_2$. $[Ta(O)(CH_2\text{-}t\text{-}Bu)_3]_n$ 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 ^1H NMR. (The main impurity is the rotational isomer, *anti,anti*-$Os(CH\text{-}t\text{-}Bu)_2$-

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[59] Malin, J. M. *Inorg. Synth.* **1980**, *20*, 61.

[60] Hepburn, D. R.; Hudson, H. R. *J. Chem. Soc., Perkin Trans.* **1976**, *1*, 754.

(CH$_2$-*t*-Bu)$_2$.) 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 pipet full of silica gel: ^{1}H NMR (C$_6$D$_6$) δ 16.33 (s, 1, C*H*-*t*-Bu, J_{CH} = 150), 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*$_3$). *syn,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ is too unstable to be analyzed.

***anti,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$.** A 1:1 mixture of *syn,anti*- and *anti,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ was prepared by photolysis of a toluene-*d*$_8$ solution of *syn,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ with a low-pressure mercury lamp at −85 °C. ^{1}H NMR (tol-*d*$_8$) δ 14.90 (s, 2, C*H*-*t*-Bu), 2.28 (s, 4, C*H*$_2$-*t*-Bu), 1.26, 0.88 (s, 18 each, *t*-Bu); ^{13}C (toluene-*d*$_8$) δ 226.9 (*C*H-*t*-Bu, J_{C-H} = 142), 61.0 (*C*H$_2$-*t*-Bu), 45.6, 35.1 (*C*Me$_3$), 34.9, 31.9 (C*Me*$_3$).

***anti,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$SiMe$_3$)$_2$.** In the dark, [OsO$_2$(CH$_2$SiMe$_3$)$_2$]$_n$ (244 mg, 0.62 mmol per *n*) was dissolved in 10 mL of pentane and the solution was chilled to −40 °C. Ta(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ (603 mg, 1.29 mmol) was dissolved in 3 mL of pentane and the solution was chilled to −40 °C and then added to the stirred cold solution of [OsO$_2$(CH$_2$SiMe$_3$)$_2$]$_n$. TaO(CH$_2$-*t*-Bu)$_3$ precipitated as the mixture warmed to room temperature. The brown reaction mixture was stirred for 45 min and then vacuum-filtered quickly through silica gel. Pentane was removed from the filtrate in vacuo to yield an orange-brown solid; yield 120 mg (38%). *anti,anti*-**1b** can be easily recrystallized from ether/acetonitrile mixtures at −40 °C or with difficulty from pentane or hexamethyldisiloxane at −40 °C: ^{1}H NMR (C$_6$D$_6$) δ 15.15 (s, 2, C*H*-*t*-Bu), 1.18 (s, 18, CH-*t-Bu*), 0.83 (s, 4, C*H*$_2$SiMe$_3$), 0.00 (s, 18, Si*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 225.1 (*C*H-*t*-Bu, J_{CH} = 146), 47.4 (*C*Me$_3$), 28.6 (C*Me*$_3$), 22.6 (*C*H$_2$SiMe$_3$), 3.04 (SiMe$_3$).

***syn,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$SiMe$_3$)$_2$.** A 1:1 mixture of *syn,anti*- and *anti,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$SiMe$_3$)$_2$ was prepared by photolysis of a toluene-*d*$_8$ solution of *syn,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$SiMe$_3$)$_2$ with a low-pressure mercury lamp at −85 °C. ^{1}H NMR (C$_6$D$_6$) δ 16.70 (s, 1, *anti*-OsC*H*-*t*-Bu), 12.27 (s, 1, *syn*-OsC*H*-*t*-Bu), 1.32, 1.17 (s, 9 each, *t*-Bu), 0.11 (s, 18, Si*Me*$_3$); the diastereotopic CH$_2$'s could not be located; ^{13}C NMR (toluene-*d*$_8$; partial data) δ 221 (*anti*-Os*C*H-*t*-Bu, J_{CH} = 148), 210 (*syn*-Os*C*H-*t*-Bu, J_{CH} = 130).

Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu). Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ (175 mg, 0.37 mmol) was dissolved in 2 mL of trimethylphosphine. The red solution was stirred for 1 h at room temperature, and then PMe$_3$ was removed in vacuo. The resulting dark red solid was extracted with 5 mL of pentane and the solution was filtered. Pentane was removed in vacuo to give an orange solid which was recrystallized from ether/acetonitrile to yield 65 mg (32%) of orange flakes. Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu) can also be purified by sublimation (0.01 Torr, 60 °C): ^{1}H NMR (C$_6$D$_6$) δ 1.55 (s, 18, *t*-Bu), 1.48 (d, 27, P*Me*$_3$, $^2J_{PH}$ = 6); ^{13}C NMR (C$_6$D$_6$) δ 192.3 (br d, *t*-BuC≡C-*t*-Bu, $^2J_{CP}$ = 10), 37.9 (*C*Me$_3$), 33.6 (C*Me*$_3$), 29.4 (d, P*Me*$_3$, $^1J_{CP}$ = 30); ^{31}P NMR (C$_6$D$_6$) δ −39.5. Anal. Calcd for OsC$_{19}$H$_{45}$P$_3$: C, 40.99; H, 8.15. Found: C, 41.32; H, 8.36.

Os(PMe$_3$)$_2$(CO)$_2$(*t*-BuC≡C-*t*-Bu). Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu) (30 mg, 0.057 mmol) was dissolved in 5 mL of pentane and the solution was placed under 0.8 atm of CO. The mixture immediately became pale. After 1 h pentane and PMe$_3$ were removed in vacuo to yield a colorless crystalline solid which was pure Os(PMe$_3$)$_2$(CO)$_2$(*t*-BuC≡C-*t*-Bu) by NMR; yield 25 mg (83%). Os(PMe$_3$)$_2$(CO)$_2$(*t*-BuC≡C-*t*-Bu) is quite volatile and can be further purified by sublimation at 50 °C under a *static* vacuum of 0.01 Torr: ^{1}H NMR (C$_6$D$_6$) δ 1.35 (s, 18, *t*-Bu), 1.15 (t, 18, P*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 195.6 (*C*O), 106.8 (*C*≡C), 34.0 (*C*Me$_3$), 31.2 (C*Me*$_3$), 19.4 (P*Me*$_3$); ^{31}P NMR (C$_6$D$_6$) δ −53.3; IR (Nujol, cm^{-1}) 1948, 1885 (vs, CO), 1772 (w, C≡C). Anal. Calcd for OsC$_{18}$H$_{36}$O$_2$P$_2$: C, 40.29; H, 6.76. Found: C, 40.37; H, 6.68.

[Os(H)(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu)]$^+$[BAr^F$_4$]$^-$. Os(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu) (40 mg, 0.072 mmol) was dissolved in 5 mL of ether and the solution was cooled to −40 °C. Solid HBAr^F$_4$(Et$_2$O)$_2$ was added and the orange-yellow solution was warmed to room temperature and stirred for 1.5 h. Ether was removed in vacuo and the resulting yellow solid was washed with 5 mL of pentane and recrystallized at room temperature by slow diffusion of pentane into an ether solution of the crude product. Yellow plates were collected, washed with pentane, and dried; yield 71 mg (70%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.73 (br s, 8, Ar$_{ortho}$), 7.57 (br s, 4, Ar$_{para}$), 1.77 (br s, 27, PMe$_3$), 1.45 (s, 18, *t*-Bu), −6.16 (q, Os*H*, $^1J_{PH}$ = 12); ^{13}C NMR (CD$_2$Cl$_2$) δ 172.1 (m, *t*-Bu*C*≡*C*-*t*-Bu), 160.6 (q, C$_{ipso}$, J_{CB} = 20), 133.6 (C$_{ortho}$), 127.7 (q, C$_{meta}$, $^2J_{CF}$ = 31), 123.5 (q, *C*F$_3$, J_{CF} = 271), 37.4 (*C*Me$_3$), 31.6 (C*Me*$_3$), 24.1 (br d, P*Me*$_3$, J_{CP} = 40); ^{31}P NMR (CD$_2$Cl$_2$) δ −41.5. Anal. Calcd for OsC$_{51}$H$_{58}$F$_{24}$BP$_3$: C, 43.11; H, 4.11. Found: C, 43.13; H, 3.95.

[Os(H)(PMe$_3$)$_5$]$^+$[BAr^F$_4$]$^-$. [Os(H)(PMe$_3$)$_3$(*t*-BuC≡C-*t*-Bu)]$^+$[BAr^F$_4$]$^-$ (20 mg, 0.014 mmol) was dissolved in 3 mL of dichloromethane. Excess PMe$_3$ (15 μL, 0.14 mmol) was added. The solution immediately became colorless. After 1 h, dichloromethane and excess PMe$_3$ were removed in vacuo, leaving a colorless solid that was crystallized from an ether/pentane mixture at −40 °C. Colorless cubes were collected; yield 18 mg (90%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.73 (s, 8, Ar$_{ortho}$), 7.56 (s, 4, Ar$_{para}$), 1.68 (s, 36, PMe$_3$), 1.49 (d, 9, PMe$_3$, J_{PH} = 7), −12.25 (dp, 1, Os*H*); ^{31}P NMR (CD$_2$Cl$_2$) δ −53.4, −58.4 (*P*Me$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 162.1 (q, C$_{ipso}$, J_{CB} = 50), 135.2 (C$_{ortho}$), 129.2 (q, C$_{meta}$, $^2J_{CF}$ = 30), 125.0 (q, *C*F$_3$, J_{CF} = 271), 27.2 (overlapping m, P*Me*$_3$). Anal. Calcd for OsC$_{47}$H$_{58}$BF$_{24}$P$_5$: C, 43.43; H, 4.07. Found: C, 43.70; H, 4.17.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$). Os(CH-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ (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 allowed to stir 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, C*H*$_a$H$_b$-*t*-Bu), 2.94 (d, 2, J_{HH} = 12, CH$_a$*H*$_b$-*t*-Bu), 1.38 (s, 9, C-*t-Bu*), 1.02 (s, 18, CH$_2$-*t-Bu*); ^{13}C NMR (CD$_2$Cl$_2$) δ 275.9 (*C*-*t*-Bu), 152.0, 138.8, 125.4 (py), 57.5, 37.0 (*C*Me$_3$), 37.5 (*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.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$Cl$_2$. OsO$_2$(CH$_2$-*t*-Bu)$_2$ (100 mg, 0.27 mmol) was dissolved in 3 mL of dichloromethane. Pyridine (50 μL, 0.63 mmol) was added and the resulting solution was cooled to −40 °C. A −40 °C solution of Ta(CH-*t*-Bu)Cl$_3$(py)$_2$ in 2 mL of dichloromethane was added dropwise to the stirred cold solution of OsO$_2$(CH$_2$-*t*-Bu)$_2$. The mixture became red-orange immediately. After the solution was stirred at room temperature for 2 h, dichloromethane was removed in vacuo and the resulting orange solid was washed with pentane and extracted with benzene. The mixture was filtered through Celite and benzene was removed in vacuo from the filtrate to give an orange solid (128 mg, 82%): ^{1}H NMR (C$_6$D$_6$) δ 9.6, 9.2 (br d, 2 each, py), 7.4, 7.2 (br t, 1 each, py), 6.8, 6.6 (br t, 2 each, py), 4.37 (C*H*$_2$-*t*-Bu), 1.64, 1.13 (*t-Bu*); ^{13}C NMR (CD$_2$Cl$_2$) δ 285.7 (*C*-*t*-Bu), 152.9, 150.1, 138.4, 137.1, 124.6, 123.9 (py), 57.8 (*C*H$_2$-*t*-Bu), 36.8, 32.1 (*C*Me$_3$), 32.6, 22.4 (C*Me*$_3$).

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$Br$_2$. OsO$_2$(CH$_2$-*t*-Bu)$_2$ (110 mg, 0.30 mmol) was dissolved in 5 mL of dichloromethane and 100 μL of pyridine was added. The solution was chilled to −40 °C and solid Ta(CH-*t*-Bu)(py)$_2$Br$_3$ was added. The red-brown mixture was allowed to warm to room temperature and was stirred for 1 h. Dichloromethane was removed in vacuo and the solid was washed with pentane (5 mL) and extracted with ether (10 mL). The mixture was filtered and ether was removed in vacuo from the filtrate to yield an orange solid (135 mg, 71%): ^{1}H NMR (C$_6$D$_6$) δ 9.6, 9.1 (br d, 2 each, py), 6.9, 6.6 (br t, 1 each, py), 6.4, 6.25 (br t, 2 each, py), 4.56 (s, 2, C*H*$_2$-*t*-Bu), 1.65, 1.17 (s, 9 each, *t-Bu*). Anal. Calcd for OsC$_{20}$H$_{30}$N$_2$Br$_2$: C, 37.04; H, 4.66; N, 4.32. Found: C, 36.99; H, 4.51; N, 4.02.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$[N(SiMe$_3$)$_2$]. A solution of Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (70 mg, 0.099 mmol) in 5 mL of THF 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 resulting solution was filtered through Celite. Pentane was removed in vacuo to give 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, C*H*$_a$H$_b$-*t*-Bu), 2.78 (d, 2, J_{HH} = 12, CH$_a$*H*$_b$-*t*-Bu), 1.26 (s, 18, CH$_2$-*t-Bu*), 1.13 (s, 9, C-*t-Bu*), 0.36 (s, 18, Si*Me*$_3$);

^{13}C NMR (C_6D_6) δ 267.9 (*C*CMe$_3$), 53.7 (C*C*Me$_3$), 39.6 (*C*H$_2$-*t*-Bu), 35.0 (CH$_2$*C*Me$_3$), 33.4 (CH$_2$C*Me$_3$*), 25.6 (CC*Me$_3$*), 6.7 (Si*Me$_3$*).

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(O-*t*-Bu). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) (95 mg, 0.135 mmol) was dissolved in 5 mL of THF, solid LiO-*t*-Bu (11 mg, 0.14 mmol) was added, and the brown mixture was stirred for 45 min. THF was removed in vacuo, the resulting brown-red solid was extracted with pentane, and the solution was filtered. Pentane was removed in vacuo, leaving a brown oil (40 mg, 62%) that was pure by ^{1}H NMR: ^{1}H NMR (C_6D_6) 4.70 (d, 2, J_{HH} = 12, C*H*$_a$H$_b$-*t*-Bu), 3.14 (d, 2, J_{HH} = 12, CH$_a$*H*$_b$-*t*-Bu), 1.42 (s, 9, O-*t-Bu*), 1.27 (s, 18, CH$_2$-*t-Bu*), 1.14 (s, 9, C-*t-Bu*); ^{13}C NMR (C_6D_6) δ 261.4 (*C*-*t*-Bu), 79.5 (O*C*Me$_3$), 54.6 (*C*H$_2$-*t*-Bu), 36.0, 35.1 (*C*Me$_3$), 33.1, 29.4, 26.6 (C*Me$_3$*).

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(η^5-C$_5$H$_5$). 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. 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. A sample of Os(η^5-C$_5$H$_5$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ that was pure enough for elemental analysis was prepared by passing a solution of Os(η^5-C$_5$H$_5$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ in pentane through silica gel; pentane was then removed in vacuo to yield a yellow solid that was analytically pure: ^{1}H NMR (C_6D_6) δ 5.08 (s, 5, η^5-C$_5$*H$_5$*), 2.25 (AB quartet, 4, C*H$_2$*-*t*-Bu), 1.26 (s, 18, CH$_2$-*t-Bu)*, 0.99 (s, 9, C-*t-Bu*); ^{13}C NMR (C_6D_6) δ 272.8 (*C*-*t*-Bu), 89.2 (η^5-C$_5$H$_5$), 54.1 (C*C*Me$_3$), 35.7 (CH$_2$*C*Me$_3$), 34.5 (CH$_2$C*Me$_3$*), 26.7 (CC*Me$_3$*), 19.3 (*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.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(L$_{OEt}$). 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 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_6D_6) δ 4.88 (s, 5, Cp), 4.38 (d, 2, J_{HH} = 12, C*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, CH$_a$*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_6D_6) δ 266.1 (*C*-*t*-Bu), 89.5 (Cp), 60.7, 60.5 (PO*C*H$_2$CH$_3$), 55.7 (*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.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(HBpz$_3$). 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[HBpz$_3$] (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 orange-pink solid was extracted with 10 mL of pentane and the solvent was removed in vacuo to yield a crystalline orange-pink solid; yield 58 mg (83%): ^{1}H NMR (C_6D_6) δ 8.15 (d, 2, J_{HH} = 1.8, 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, C*H*$_a$H$_b$-*t*-Bu), 2.86 (d, 2, J_{HH} = 12, CH$_a$*H*$_b$-*t*-Bu), 1.31 (s, 18, CH$_2$-*t*-Bu), 1.09 (s, 9, C-*t*-Bu); ^{13}C NMR (C_6D_6) δ 280.1 (*C*-*t*-Bu), 146.7, 141.1, 135.0, 134.6, 105.6, 105.2 (pz), 56.5 (*C*H$_2$-*t*-Bu), 36.4 (CH$_2$*C*Me$_3$), 33.9 (CH$_2$C*Me$_3$*), 32.6 (C*C*Me$_3$), 24.3 (CC*Me$_3$*). Anal. Calcd for OsC$_{24}$H$_{41}$N$_6$B: C, 46.90; H, 6.72; N, 13.67. Found: C, 47.49; H, 6.78; N, 13.67. Two other attempts to obtain consistent and satisfactory elemental analyses failed for unknown reasons. However, this compound has been structurally characterized.

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)(C$\equiv$C-*t*-Bu)(bpy)(OTf). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) (42 mg, 0.60 mmol) was dissolved in 5 mL of dichloromethane and pyridine (20 μL) was added. The solution was chilled to −40 °C and *tert*-butylacetylene (20 μL, 0.17 mmol) was added. The resulting mixture was stirred for 2 h at room temperature, and solid 2,2′-bipyridyl (9 mg, 0.57 mmol) was added. The mixture became red immediately. After allowing the mixture to stir for 20 min, dichloromethane and pyridine were removed in vacuo, and the resulting red solid was washed with pentane and recrystallized from a dichloromethane/pentane mixture at −40 °C: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.5–9.7 (m, 8 total, bpy), 2.53, 1.96 (d, 2 each, J_{HH} = 12, C*H$_2$*-*t*-Bu), 1.42, 1.18, 0.99 (s, 9 each, *t-Bu*); ^{13}C NMR (CD$_2$Cl$_2$) δ 294.3 (*C*-*t*-Bu), (bpy) 84.0, 82.0 (C$\equiv$C), 57.0 (*C*H$_2$-*t*-Bu), 33.0, 32.9, 23.1 (C*Me$_3$*), 35.9, 29.8, 25.0 (*C*Me$_3$). IR (Nujol, cm^{-1}) 2359 (C$\equiv$C stretch), 1285 (coordinated OTf).

Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(bpy)(OTf). Os(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$(py)$_2$(OTf) (47 mg, 0.067 mmol) was dissolved in 5 mL of dichloromethane and solid 2,2′-bipyridyl (10 mg, 0.07 mmol) was added. The mixture immediately became red and was stirred for 1 h at 25 °C. Dichloromethane and pyridine were removed in vacuo to give a crystalline red solid. Recrystallization from a dichloromethane/pentane mixture at −40 °C yielded red needles which were collected, washed with pentane, and dried; yield 45 mg (96%): ^{1}H NMR (CD$_2$Cl$_2$) δ 9.7–7.2 (m, 8 total, bpy), 3.5 (overlapping d, 3 total, C*H$_a$*H$_b$-*t*-Bu), 2.2 (d, 2, J_{CH} = 12, CH$_a$*H$_b$*-*t*-Bu), 1.61, 0.88, 0.55 (*t*-Bu). Note that the two neopentyl groups are inequivalent.

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Supplementary Material Available: A detailed description of X-ray data collection, structure solution and refinement, labeled ORTEP diagrams, tables of fractional coordinates, isotropic and anisotropic thermal parameters, intramolecular distances, intramolecular angles, and torsional angles for *anti,anti*-Os(CH-*t*-Bu)$_2$(CH$_2$SiMe$_3$)$_2$ and Os(PMe$_3$)$_3$(*t*-BuC$\equiv$C-*t*-Bu) (18 pages) (X-ray data for Os(HBpz$_3$)(C-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ have been deposited previously.[9]) This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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