# Imido/Oxo Exchange between Osmium and Tantalum as a Route to $Os(NAr)_2R_2$ and $OsO(NAr)R_2$ Complexes (NAr = N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; R = CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>CMe<sub>2</sub>Ph, CH<sub>2</sub>SiMe<sub>3</sub>) and Attempts To Induce a-Hydrogen Abstraction To Give **Alkylidene Complexes**

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Received January 11, 1995<sup>®</sup>

 $OsO_2R_2$  (R = CH<sub>2</sub>-t-Bu, CH<sub>2</sub>CMe<sub>2</sub>Ph) or  $[OsO_2(CH_2SiMe_3)_2]_n$  reacts with 1 or 2 equiv of  $Ta(NAr)(O-t-Bu)_3$  (NAr = N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) to form complexes of the type OsO(NAr)R<sub>2</sub> or Os(NAr)<sub>2</sub>R<sub>2</sub>. OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> reacts with 2 equiv of HCl or Me<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> or DME to form Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>Cl<sub>2</sub> or Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>I<sub>2</sub>, respectively, or with SiMe<sub>3</sub>X in CH<sub>2</sub>- $Cl_2$  to form green, crystalline  $Os(NAr)(CH_2-t-Bu)_2(OSiMe_3)(X)$  (X = Cl, OTf). An X-ray structure of Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)(OTf) showed it to be an approximate square pyramid with a neopentyl group in the apical position. The reaction of OsO(NAr)(CH<sub>2</sub>-t- $Bu_{2}$  with 2 equiv of trimethylaluminum in pentane yields red trans-Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>-(CH<sub>3</sub>)<sub>2</sub>. None of the Os(VI) dineopentyl complexes shows any evidence for controlled  $\alpha$ -hydrogen abstraction reactions.

## Introduction

A "Wittig-like" reaction between a metal oxo complex and an alkylidene source has been an attractive potential method of preparing alkylidene complexes for approximately two decades. For example, the reaction shown in eq 1

$$W(O)(O-t-Bu)_{4} + Ta(CH-t-Bu)Cl_{3}(PMe_{3})_{2} \xrightarrow{\text{ether/pentane}} W(O)(CH-t-Bu)Cl_{2}(PMe_{3})_{2} + Ta(O-t-Bu)_{4}Cl (1)$$

was an attempt to exchange the oxo and alkylidene ligands.<sup>1</sup> However, in this case the oxo ligand is the only one that does not exchange between tungsten and tantalum. In contrast, we recently found that tantalum alkylidene complexes are well-behaved "Wittig" reagents toward osmium oxo complexes.<sup>2,3</sup> For example, OsO<sub>2</sub>-(CH<sub>2</sub>-t-Bu)<sub>2</sub> reacts with 2 equiv of Ta(CH-t-Bu)(CH<sub>2</sub>-t- $Bu_{3}$  in pentane to yield insoluble  $[TaO(CH_{2}-t-Bu)_{3}]_{n}$  and  $syn, anti-Os(CH-t-Bu)_2(CH_2-t-Bu)_2$ . We believe this to be the first example of a Wittig-like reaction involving a metal oxo species. The other examples of reactions in which covalently doubly bound ligands exchange between metals are imido/oxo exchange between d<sup>0</sup> tungsten and molybdenum complexes<sup>4</sup> or between OsO<sub>4</sub> and phosphinimines<sup>5</sup> or molybdenum imido complexes.<sup>6</sup>

We became interested in the possibility that osmium imido complexes of the type  $Os(NAr)_2R_2$  could be prepared by exchange reactions between Os=O and Ta=NR.  $O_{S}(NAr)_{2}R_{2}$  (NAr = N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) complexes were first synthesized via a route that began with  $Os(NAr)_{3}$ ,<sup>7</sup>

0276-7333/95/2314-2699\$09.00/0

but these syntheses are relatively long and proceed in low yield. Monoimido Os(VI) complexes, particularly imido-alkylidene complexes of Os(VI), would also be of interest. In this paper we describe some imido/oxo exchange reactions that yield mono- or bis(imido) complexes of Os(VI) and attempts to form imido-alkylidene complexes by  $\alpha$ -hydrogen abstraction reactions.

### Results

 $OsO_2R_2$  complexes (R = CH<sub>2</sub>-t-Bu<sup>8</sup> or CH<sub>2</sub>CMe<sub>2</sub>Ph<sup>2</sup>) or  $[OsO_2(CH_2SiMe_3)_2]_n^2$  react readily with 2 equiv of Ta- $(NAr)(O-t-Bu)_3$  in pentane or toluene to form  $Os(NAr)_2R_2$ complexes in 50-70% yield (eq 2).  $TaO(O-t-Bu)_3$  is removed by passing the reaction mixture through silica gel. This convergent route is relatively efficient, since it requires only two steps involving osmium (starting with [PPh<sub>4</sub>]<sub>2</sub>[OsO<sub>2</sub>Cl<sub>4</sub>]) and proceeds in approximately 40% yield overall (based on osmium). Ta(NAr)(O-t-Bu)3 is readily synthesized in 10-20 g quantities from readily available Ta(NAr)Cl<sub>3</sub>(dimethoxyethane)<sup>9</sup> and 3 equiv of LiO-t-Bu in THF. If only 1 equiv of of Ta(NAr)(O-t-Bu)<sub>3</sub> is added to  $OsO_2R_2$  (R = CH<sub>2</sub>-t-Bu, CH<sub>2</sub>CMe<sub>2</sub>Ph) in THF, then purple  $OsO(NAr)R_2$  is isolated in 60-70%yield (eq 3).

$$OsO_2R_2 \xrightarrow{+2Ta(NAr)(O-t-Bu)_3} Os(NAr)_2R_2$$
(2)

$$\mathbf{R} = \mathbf{CH}_2$$
-t-Bu,  $\mathbf{CH}_2\mathbf{CMe}_2\mathbf{Ph}$ ,  $\mathbf{CH}_2\mathbf{SiMe}_3$ 

$$OsO_2R_2 \xrightarrow[-TaO(O-t-Bu)_3]{} OsO(NAr)R_2$$
(3)

$$R = CH_2$$
-t-Bu,  $CH_2CMe_2Ph$ 

If  $[OsO_2(CH_2SiMe_3)_2]_n$  is treated with 1 equiv of Ta-

- (7) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.;
  Johnson, K. H.; Davis, W. M. Inorg. Chem. 1991, 30, 3595.
  (8) Marshman, R. W.; Bigham, W. S.; Wilson, S. R.; Shapley, P. A.
- (9) Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. Inorg. Chem. 1989,
- 28, 3860.

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<sup>Abstract published in Advance ACS Abstracts, April 15, 1995.
(1) Wengrovius, J. H.; Schrock, R. R. Organometallics 1982, 1, 148.
(2) LaPointe, A. M.; Schrock, R. R.; Davis, W. M. J. Am. Chem. Soc.,</sup> 

in press. (3) LaPointe, A. M.; Schrock, R. R. Organometallics 1993, 13, 3379. (4) Jolly, M.; Mitchell, J. P.; Gibson, V. C. J. Chem. Soc., Dalton Trans. 1992, 1331.

<sup>(5)</sup> Chong, A. O.; Oshima, K.; Sharpless, K. B. J. Am. Chem. Soc. 1977, 99, 3420.

<sup>(6)</sup> Robbins Wolf, J.; Bazan, G. C.; Schrock, R. R. Inorg. Chem. 1993, 32, 4155.

Scheme 1. Reactions of OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>



 $Os(NAr)(CH_2-t-Bu)_2(OSiMe_3)X$ 

65 - 80%

 $(NAr)(O-t-Bu)_3$  in THF at -40 °C, a mixture of OsO-(NAr)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> and Os(NAr)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> is formed. (Since  $[OsO_2(CH_2SiMe_3)_2]_n$  is not a monomer in solution, the first imido/oxo exchange with the oligomeric complex is likely to be slower than the subsequent exchange reaction between monomeric OsO(NAr)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> and Ta(NAr)(O-t-Bu)<sub>3</sub>.) OsO(NAr)R<sub>2</sub> complexes probably are structurally analogous to distorted-tetrahedral OsO(Nt-Bu)(mesityl)<sub>2</sub>, which was synthesized in 5% yield from OsO<sub>3</sub>(N-t-Bu) and dimesitylmagnesium.<sup>10</sup>

Coordinating solvents such as THF significantly slow the rate of imido/oxo exchange, presumably by blocking sites for ligand transfer, most likely primarily on the more electron-poor tantalum center. For example, the reaction between  $OsO(NAr)(CH_2-t-Bu)_2$  and Ta(NAr)(O $t-Bu)_3$  in toluene- $d_8$  was essentially complete after a few minutes at -40 °C, while no reaction was observed in THF- $d_8$  until the sample was warmed to 35 °C. Unfortunately, reliable kinetic data for the exchange reaction could not be obtained by NMR methods due to overlapping resonances. The kinetics of imido/oxo exchange between  $Mo(NAr)_2(O-t-Bu)_2$  and  $MoO_2(O-t-Bu)_2$  were found to be consistent with a bimolecular mechanism.<sup>4</sup> It seems likely that the exchange reactions described here proceed in a related manner.

OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> reacts with 2 equiv of HCl in DME to yield yellow Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>Cl<sub>2</sub> in 79% yield, while red, crystalline Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>I<sub>2</sub> is formed in the reaction between Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>Cl<sub>2</sub> and 2 equiv of Me<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> or by treating OsO-(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> with 2 equiv of Me<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> or DME (Scheme 1). The neopentyl methylene protons are diastereotopic by proton NMR in Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> complexes. We think the most likely structure for Os-(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> is a square pyramid with a *cis* orientation of the neopentyl groups on the basis of the approximately square-pyramidal structure observed for  $Os(NMe)(CH_2SiMe_3)_4$ .<sup>11</sup>

The reaction of OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> and Me<sub>3</sub>SiCl or Me<sub>3</sub>SiOTf in dichloromethane yields green, crystalline Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)Cl or Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>-(OSiMe<sub>3</sub>)(OTf), respectively (Scheme 1). Proton NMR data for these complexes (in C<sub>6</sub>D<sub>6</sub>) suggest that the two *tert*-butyl groups of the neopentyl ligands are equivalent on the NMR time scale, although the methylene protons are diastereotopic. The resonances for Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)(OTf) are broadened at 25 °C in C<sub>6</sub>D<sub>6</sub>, while those for Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)Cl are relatively sharp at 25 °C in C<sub>6</sub>D<sub>6</sub>. Variable-temperature studies were not pursued.

An X-ray study of Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)(OTf) showed it to be approximately a square pyramid in the solid state (Figure 1) with one of the neopentyl groups in the apical position  $(O(1)-Os-C(11) = 92.8(3)^{\circ}, O(4) - Os-C(11) = 92.8(3)^{\circ}, O(5) = 92.8(3)^{\circ}, O($  $Os-C(11) = 109.2(3)^{\circ}, N-Os-C(11) = 95.8(3)^{\circ}, C(11) = 100.2(3)^{\circ}, C(11) = 100.2$  $Os-C(12) = 90.4(3)^{\circ}, O(1)-Os-C(12) = 172.0(3)^{\circ}, and$  $N-Os-O(4) = 153.6(3)^{\circ}$ ; Table 1). The Os-O(4) (1.832-(5) Å), Os-C(11) (2.097(8) Å), Os-C(12) (2.083(9) Å), and Os=N (1.689(6) Å) bonds are all relatively short, consistent with covalent bonds to a metal in a relatively high oxidation state and with a relatively low coordination number and possibly also indicative of significant  $\pi$  bonding between osmium and lone pairs on the alkoxide  $(Os-O(4)-Si = 147.6(4)^\circ)$  or on nitrogen (Os- $N-C(1) = 166.7(6)^{\circ}$ ). The Os-O(1) distance (2.326(6)) Å) is consistent with a considerably weaker, ionic bond, as one would expect for a triflate ligand. In solution the neopentyl groups must become equivalent on the NMR time scale in an intermediate that does not have a plane of symmetry through the methylene carbon atoms.

 $OsO(NAr)(CH_2-t-Bu)_2$  reacts cleanly with 2 equiv of AlMe<sub>3</sub> in pentane to yield red  $Os(NAr)(CH_2-t-Bu)_2(CH_3)_2$  in 80% yield (Scheme 1). The pure product is readily isolated after passing the reaction mixture through

 $X = Cl, O_3SCF_3$ 

<sup>(10)</sup> Stavropoulos, P.; Edwards, P.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. J. Chem. Soc., Dalton Trans. **1987**, 169.

<sup>(11)</sup> Marshman, R. W.; Shapley, P. A. J. Am. Chem. Soc. **1990**, 112, 8369.



Figure 1. Chem 3D drawing of the structure of  $Os(N-2,6-i-Pr_2C_6H_3)(CH_2CMe_3)_2(OSiMe_3)(O_3SCF_3).$ 

Table 1. Important Distances (Å) and Angles (deg)in Os(N-2,6-i-Pr2C6H3)(CH2CMe3)2(OSiMe3)(O3SCF3)

Distances			
Os - O(1)	2.326(6)	Os-C(12)	2.083(9)
Os - O(4)	1.832(5)	Os-N	1.689(6)
Os-C(11)	2.097(8)		
Angles			
Os-N-C(1)	166.7(6)	O(1) - Os - C(11)	92.8(3)
Os-O(1)-S	131.4(4)	O(1) - Os - C(12)	172.0(3)
Os-C(11)-C(111)	120.0(5)	O(1) - Os - O(4)	80.4(2)
Os-C(12)-C(121)	122.1(6)	O(4) - Os - C(11)	109.2(3)
Os-O(4)-Si	147.6(4)	O(4) - Os - C(12)	91.7(3)
N-Os-O(1)	90.3(3)	C(11) - Os - C(12)	90.4(3)
N-Os-O(4)	153.6(3)	N-Os-C(12)	96.7(3)
N-Os-C(11)	95.8(3)		

silica gel. Proton NMR reveals that the complex is highly symmetric in solution, with equivalent methyl and *tert*-butyl groups. All four methylene protons of the neopentyl groups are also equivalent, suggesting that on the NMR time scale the complex is a square pyramid with a *trans* orientation of the neopentyl ligands or an analogous trigonal bipyramid. The high symmetry of the molecule, the <sup>1</sup>H chemical shift of the methyl protons (3.40 ppm), the elemental analysis, and its stability to silica gel suggest that it is *not* a trimethylaluminum adduct, i.e., "Os(OAIMe<sub>3</sub>)(NAr)(CH<sub>2</sub>-*t*-Bu)<sub>2</sub>". There is also precedent in the form of structurally characterized square-pyramidal Os(NMe)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>.<sup>11</sup>

We hoped that Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> (X = Cl, I) or Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)X (X = Cl, OTf) would undergo intramolecular  $\alpha$ -hydrogen abstraction reactions to form imido-alkylidene complexes, "Os(NAr)(CHt-Bu)X<sub>2</sub>" and "Os(NAr)(CH-t-Bu)(OSiMe<sub>3</sub>)X", respectively, which would be d<sup>2</sup> analogs of d<sup>0</sup> molybdenum and tungsten imido-alkylidene complexes such as M(NAr)-(CH-t-Bu)(dimethoxyethane)Cl<sub>2</sub> or M(NAr)(CH-t-Bu)-(OR)<sub>2</sub>.<sup>12</sup> Dehydrohalogenation of Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> to form "Os(NAr)(CH-t-Bu)(CH<sub>2</sub>-t-Bu)X" is another possible route to imido-alkylidene complexes of Os(VI), although we have found in related Os(VI) systems that removing an  $\alpha$ -proton from neopentyl ligands is relatively difficult.<sup>2</sup>

Addition of excess pyridine to a toluene solution of  $Os(NAr)(CH_2-t-Bu)_2(OSiMe_3)(OTf)$  yields a precipitate

of green Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(py)(OSiMe<sub>3</sub>)(OTf) in 80% yield. In CDCl<sub>3</sub> at 25 °C, the isopropyl and pyridine peaks of Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(py)(OSiMe<sub>3</sub>)(OTf) are extremely broad, and the resonances associated with the neopentyl methylene protons could not be located. No evidence for  $\alpha$ -hydrogen abstraction reactions in Os-(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(py)(OSiMe<sub>3</sub>)(OTf) is observed, even when a CDCl<sub>3</sub> solution was heated for 1 h at 70 °C.

Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)(Cl) does not react with pyridine in C<sub>6</sub>D<sub>6</sub> at 25 °C. Likewise, no reaction was observed when pyridine was added to C<sub>6</sub>D<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub> solutions of Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> (X = Cl, I) or when Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> was dissolved in pyridine- $d_5$ , and no reaction was observed when these solutions were heated or photolyzed with a medium-pressure mercury lamp in CD<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>D<sub>6</sub> at 25 °C. Reactions between Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>X<sub>2</sub> (X = Cl, I) or Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)X (X = Cl, OTf) and trimethylphosphine in C<sub>6</sub>D<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub> gave neopentane, but no metalcontaining products could be identified.

Attempts to isolate "Os(NAr)(CH-t-Bu)(CH<sub>2</sub>-t-Bu)<sub>2</sub>" by treating OsO(NAr)R<sub>2</sub> with a variety of tantalum alky-lidene complexes were unsuccessful. These attempts included reactions between OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> and Ta(CH-t-Bu)(CH<sub>2</sub>-t-Bu)<sub>3</sub> or Ta(CH-t-Bu)(O-t-Bu)<sub>3</sub> in pentane, or in pentane to which THF or pyridine had been added. Reactions between OsO(NAr)(CH<sub>2</sub>CMe<sub>2</sub>Ph)<sub>2</sub> and Ta(CH-t-Bu)(CH<sub>2</sub>-t-Bu)<sub>3</sub> also failed to yield any tractable products.

#### Discussion

In either alkylidene/oxo or imido/oxo exchange reactions, the ancillary ligands on tantalum and osmium must be chosen with care in order to avoid a circumstance in which (i) the ancillary ligands can exchange from one one metal to another and do not have a strong preference to bind to only osmium or to only tantalum. Bulky alkyl groups (on either tantalum or osmium) are advantageous since they are unlikely to exchange readily. Alkoxides are also suitable ancillary ligands when bound to tantalum, since they are likely to remain bound to the more oxophilic metal. Some evidence in support of that conclusion is the reaction of OsO(OCH<sub>2</sub>- $CH_2O_2(py)_2$  with 1 equiv of  $Ta(NAr)(O-t-Bu)_3$  in THF to give Os(NAr)<sub>3</sub><sup>7</sup> as the only osmium-containing product. As expected, halides readily transfer from tantalum to osmium. For example,  $OsO_2(CH_2-t-Bu)_2$  reacts slowly with 1 equiv of Ta(NAr)(dimethoxyethane)Cl<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> to give Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>Cl<sub>2</sub>; OsO(NAr)(CH<sub>2</sub>-t- $Bu)_2$  is not observed by <sup>1</sup>H NMR.

It is interesting to note that  $OsO(NAr)(CH_2-t-Bu)_2$ exhibits enhanced reactivity of the oxo relative to the arylimido group, as evidenced by the selective syntheses of  $Os(NAr)(CH_2-t-Bu)_2X_2$  and  $Os(NAr)(CH_2-t-Bu)_2Me_2$ . In contrast,  $OsO_2(CH_2-t-Bu)_2$  does not react with HCl,  $Me_3SiCl$ , or triflic acid in DME.<sup>13</sup> Interestingly, Shapley observed that  $OsO(CH_2SiMe_3)_4$  does not react readily with HCl, while both  $Os(NMe)(CH_2SiMe_3)_4$  and  $[Os(N)-(CH_2SiMe_3)_4]^-$  do.<sup>11</sup> We speculate that the imido group in  $OsO(NAr)(CH_2-t-Bu)_2$  is kinetically a poorer base than the oxo group, as a consequence of its being a better  $\pi$  donor to the metal than the oxo group. The

<sup>(12)</sup> Feldman, J.; Schrock, R. R. Prog. Inorg. Chem. 1991, 39, 1.

<sup>(13)</sup> LaPointe, A. Ph.D. Thesis, Massachusetts Institute of Technology, 1994.

arylimido group is also a "protecting group" during alkylation reactions. For instance, OsO(NAr)(CH<sub>2</sub>-t- $Bu_{2}$  reacts with 2 equiv of AlMe<sub>3</sub> to form Os(NAr)(CH<sub>2</sub>t-Bu)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> with no net reduction, but OsO<sub>2</sub>(CH<sub>2</sub>-t-Bu)<sub>2</sub> is reduced under identical conditions, forming [Os(CH<sub>2</sub>t-Bu)<sub>2</sub>(CH<sub>3</sub>)]<sub>2</sub>.<sup>2</sup> The technique of using an imido ligand as a protecting group toward reduction is a key feature of the high-yield synthesis of imido-alkylidene complexes of tungsten and molybdenum.<sup>12</sup>

The fact that the  $Os(NAr)(CH_2-t-Bu)_2X_2$  (X = Cl, I) complexes show no evidence of undergoing a-hydrogen abstraction reactions in the presence of coordinating ligands is consistent with our previous observations concerning the resistance of Os(VI) neopentyl complexes toward a-abstraction reactions.<sup>2,3</sup> We found that Os-(VI) complexes require at least two metal-ligand  $\pi$ bonds in order to be stable, and that circumstance is already fulfilled in Os(NAr)(CH-t-Bu)<sub>2</sub>X<sub>2</sub> if the imido ligand is pseudo triply bound to the metal. We also found that a neopentyl group is much more reluctant to undergo an  $\alpha$ -hydrogen abstraction reaction than a neopentylidene ligand, a tendency that has been known now for some time.<sup>14</sup> Today one would say that  $\alpha$ -agostic<sup>15</sup> interactions, which are presumed to be required for  $\alpha$ -abstraction reactions, are much less favorable in alkyl ligands than in alkylidene ligands in similar circumstances.

It is interesting to note that no reaction is observed between  $OsO_2(CH_2-t-Bu)_2$  and  $Mo(NAr)_2(O-t-Bu)_2$  in  $C_6D_6$ , even at 70 °C, although  $OsO_4$  reacts readily with  $M_0(NAr)_2(O-t-Bu)_2$ .<sup>6</sup> Therefore, it appears that a more oxophilic metal (tantalum) is required for imido/oxo exchange reactions involving Os(VI), while molybdenum is sufficiently oxophilic in reactions involving OsO4. This trend parallels that observed in alkylidene/oxo exchange reactions involving  $OsO_2R_2$ .<sup>2,3</sup>

In conclusion, we have demonstrated that imido/oxo exchange between tantalum and osmium(VI) is a viable means of synthesizing a variety of Os(VI) mono- and bis(imido) complexes. Unfortunately, osmium imidoalkylidene complexes have not yet been synthesized by analogous methods or by  $\alpha$ -abstraction in imido-neopentyl complexes of Os(VI). We might speculate that other imido complexes of later transition metals perhaps can be synthesized by employing tantalum imido complexes as imido transfer agents, if the appropriate later metal oxo complexes can be prepared. Alternatively, exchange of alkoxide ligands for imido ligands may be a route to imido complexes of the later transition metals, if the appropriate later metal alkoxide complexes can be prepared.

#### **Experimental Section**

General procedures are described elsewhere.<sup>2</sup> Ta(NAr)Cl<sub>3</sub>-(dimethoxyethane) was prepared as described in the literature.<sup>9</sup>  $OsO_2R_2$  complexes were prepared from  $[PPh_4]_2[OsO_2Cl_4]$ and ZnR<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>2,3</sup> Trimethylchlorosilane, trimethylsilyl triflate, and trimethyliodosilane were purchased from Aldrich and used without further purification. Lithium tert-butoxide was purchased from Strem. Silica gel was typically 70-230 mesh (Aldrich) or 230-400 mesh (Bodman).

Ta(NAr)(O-t-Bu)<sub>3</sub>. A slurry of Ta(NAr)Cl<sub>3</sub>(DME) (5.27 g, 9.5 mmol; NAr = N-2,6-i- $Pr_2C_6H_3$ ) in 50 mL of THF was cooled to -40 °C. Solid LiO-t-Bu (2.30 g, 28.8 mmol) was added, and the mixture was warmed to room temperature and stirred for 3 h. THF was removed in vacuo from the pale yellow reaction mixture, leaving a beige solid which was extracted with pentane (40 mL). The extracts were filtered through Celite, and pentane was then removed in vacuo from the filtrate. A waxy beige solid was isolated and recrystallized from pentane at -40 °C to give two crops of colorless crystals of Ta(NAr)- $(O-t-Bu)_3$ ; yield 2.79 g (51%). The high solubility of Ta(NAr)-(O-t-Bu)<sub>3</sub> in nonpolar solvents such as pentane is believed to contribute to the relatively low isolated yield. However, the crude material obtained upon extraction with pentane is pure by <sup>1</sup>H NMR and can be used in exchange reactions without complications: <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  7.17 (br s, 2, Ar), 6.92 (t, 1, Ar), 4.22 (sept, 2, CHMe<sub>2</sub>), 1.36 (d, 12, CHMe<sub>2</sub>), 1.28 (s, 27, OCMe<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  152.1, 143.1, 122.4, 121.8, 80.0 (OCMe<sub>3</sub>), 32.3 (OCMe<sub>3</sub>), 27.6 (CHMe<sub>2</sub>), 24.4 (CHMe<sub>2</sub>). Anal. Calcd for  $TaC_{24}H_{44}NO_3$ : C, 50.08; H, 7.70; N, 2.43. Found: C; 50.13; H, 7.96; N, 2.41.

 $Os(NAr)_2(CH_2-t-Bu)_2$ .  $OsO_2(CH_2-t-Bu)_2$  (77 mg, 0.21 mmol) was dissolved in 5 mL of pentane, and the solution was cooled to -40 °C. Solid Ta(NAr)(O-t-Bu)<sub>3</sub> was added, and the mixture immediately became orange-green. The mixture was warmed to room temperature and was stirred for 1 h. It was then filtered through silica gel in order to remove TaO(O-t-Bu)<sub>3</sub>. The solvent was removed in vacuo from the filtrate to leave orange, crystalline Os(NAr)<sub>2</sub>(CH<sub>2</sub>-t-Bu)<sub>2</sub> (80 mg, 57%). NMR data match those reported.7

Os(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)<sub>2</sub>. Os(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)<sub>2</sub> was prepared from  $OsO_2(CH_2CMe_2Ph)_2$  in a manner similar to that described for Os(NAr)<sub>2</sub>(CH<sub>2</sub>-t-Bu)<sub>2</sub>, except toluene was used as the solvent: <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  7.4–6.8 (m, 16 total, Ph + NAr), 4.63 (s, 4, CH<sub>2</sub>CMe<sub>2</sub>Ph), 3.62 (sept, 4, CHMe<sub>2</sub>), 1.44 (s, 12, CMe<sub>2</sub>Ph), 1.28 (d, 24, CHMe<sub>2</sub>Ph);  ${}^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  154.3, 151.1, 145.2, 126.9, 126.0, 125.7, 123.3 (one aryl carbon resonance is apparently obscured by the solvent resonance), 44.4 (CMe<sub>2</sub>Ph), 31.7 (CMe<sub>2</sub>Ph), 29.0 (CHMe<sub>2</sub>), 24.1 (CHMe<sub>2</sub>). Anal. Calcd for  $OsC_{44}H_{60}N_2$ : C, 65.47; H, 7.49; N, 3.47. Found: C, 65.40; H, 7.66; N, 3.51.

Os(NAr)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>. Os(NAr)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> was prepared from  $[OsO_2(CH_2SiMe_3)_2]_n$  and 2 equiv of Ta(NAr)(O-t-Bu)<sub>3</sub> (per Os) in a manner identical with that used to prepare Os(NAr)<sub>2</sub>(CH<sub>2</sub>-t-Bu)<sub>2</sub>; yield 60%. NMR data match those reported.7

Os(O)(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>. OsO<sub>2</sub>(CH<sub>2</sub>-t-Bu)<sub>2</sub> (105 mg, 0.288 mmol) was dissolved in 10 mL of THF, and the solution was cooled to -40 °C. A prechilled solution of Ta(NAr)(O-t-Bu)<sub>3</sub> (170 mg, 0.300 mmol) in THF was then added dropwise. The mixture became purple-red as it was warmed to room temperature or to 22 °C. After 1 h the mixture was passed through silica gel in order to remove  $Ta(O)(O-t-Bu)_3$ , and the resulting filtrate was reduced to dryness in vacuo. The purple solid was extracted into pentane (2 mL) and recrystallized at -40 °C: yield 98 mg (65%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.20 (t, 1, Ar), 6.86 (d, 2, Ar), 4.52 (d, 2,  $J_{\rm HH} = 12$  Hz,  $CH_{\rm a}H_{\rm b}$ -t-Bu), 4.21 (d, 2,  $J_{\rm HH} = 12$ ,  $CH_{a}H_{b}$ -t-Bu), 3.66 (sept, 2,  $CHMe_{2}$ ), 1.21 (d, 12,  $J_{\rm HH}$  = 7, CHMe\_2), 1.15 (s, 18, CH\_2-t-Bu);  $^{13}{\rm C}$  NMR (C\_6D\_6)  $\delta$ 152.2 (C<sub>i</sub>), 144.9 (C<sub>o</sub>), 129.4 (C<sub>p</sub>), 123.6 (C<sub>m</sub>), 35.6 (CH<sub>2</sub>CMe<sub>3</sub>), 32.1 (CMe<sub>3</sub>), 30.5 (CH<sub>2</sub>-t-Bu), 29.1 (CHMe<sub>2</sub>), 23.3 (CHMe<sub>2</sub>); IR (Nujol) 925 cm<sup>-1</sup> (Os=O). Anal. Calcd for OsC<sub>22</sub>H<sub>39</sub>NO: C, 50.45; H, 7.51; N, 2.67. Found: C, 50.37; H, 7.40; N, 2.50.

 $OsO(NAr)(CH_2CMe_2Ph)_2$ ,  $OsO(NAr)(CH_2CMe_2Ph)_2$  was prepared from OsO<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)<sub>2</sub> and Ta(NAr)(O-t-Bu)<sub>3</sub> in a manner identical with that described for OsO(NAr)(CH2-t-Bu)<sub>2</sub>: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  6.8–7.4 (m, 13 total, *Ph* + NA*r*), 4.69 (d, 2,  $CH_aH_b$ ,  $J_{HH} = 12$  Hz), 4.50 (d, 2,  $CH_aH_b$ ,  $J_{HH} = 12$ ), 3.23 (sept, 2, CHMe<sub>2</sub>), 1.49, 1.44 (s, 6 each, CMe<sub>2</sub>Ph), 1.12 (d, 12,  $CHMe_2);\ IR\ (Nujol)\ 928\ cm^{-1}\ (Os=O).$ 

 $Os(NAr)(CH_2-t-Bu)_2Cl_2$ .  $Os(NAr)(O)(CH_2-t-Bu)_2$  (132 mg, 0.25 mmol) was dissolved in 5 mL of DME, and the solution

<sup>(14)</sup> Schrock, R. R. In Reactions of Coordinated Ligands; Braterman, P. R. Ed.; Plenum: New York, 1986.
 (15) Brookhart, M.; Green, M. L. H. J. Organomet. Chem. 1983, 250,

<sup>395.</sup> 

#### Imido/Oxo Exchange between Os and Ta

was cooled to 0 °C. A 1.0 M solution of HCl in ether (1.0 mL, 1.0 mmol) was added to the stirred solution by syringe; the reaction mixture became yellow-brown. The solution was warmed to room temperature and was stirred for 1 h. DME was removed in vacuo, and the yellow-brown solid was extracted with pentane (10 mL). The volume of the solution was reduced to 1 mL in vacuo, and the solution was cooled to -40 °C. Yellow-green prisms formed and were collected and dried in vacuo: yield 115 mg (79%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.90  $(d, 2, J_{HH} = 12 \text{ Hz}, CH_aH_b-t-Bu), 7.95 (t, 1, Ar), 7.08 (d, 2, Ar),$  $6.78 (d, 2, J_{HH} = 12, CH_aH_b-t-Bu), 2.98 (sept, 2, CHMe_2), 1.28$ (d, 12, CHMe<sub>2</sub>), 1.10 (s, 18, t-Bu); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.5, 145.4, 132.7, 126.5 (Ar), 57.0 (CH<sub>2</sub>-t-Bu), 41.4 (CMe<sub>3</sub>), 32.8 (CMe<sub>3</sub>), 32.2 (CHMe<sub>2</sub>), 23.9 (CHMe<sub>2</sub>). Anal. Calcd for OsC<sub>25</sub>-H<sub>39</sub>NCl<sub>2</sub>: C, 45.66; H, 6.79; N, 2.42. Found: C, 45.88; H, 7.07; N, 2.29.

 $Os(NAr)(CH_2-t-Bu)_2I_2$ .  $OsO(NAr)(CH_2-t-Bu)_2$  (60 mg, 0.115) mmol) was dissolved in 3 mL of dichloromethane, and the solution was cooled to -40 °C. Me<sub>3</sub>SiI (34  $\mu$ L, 0.24 mmol) was added. The solution became red immediately. After it was warmed to room temperature, the solution was stirred for 1.5 h. Dichloromethane was removed in vacuo, and the resulting red oily solid was extracted with pentane (10 mL). The extract was filtered, and the volume of the filtrate was reduced to 2 mL and cooled to -40 °C. Dark red crystals formed after several days and were collected and dried in vacuo: yield 66 mg (75%); <sup>1</sup>H NMR (toluene- $d_8$ )  $\delta$  9.29 (d, 2,  $J_{\rm CH} = 12$  Hz,  $CH_{\rm a}H_{\rm b}$ -t-Bu), 7.25 (t, 1, Ar), 7.21 (d, 2,  $J_{\rm CH} = 12$ , CH<sub>a</sub>H<sub>b</sub>-t-Bu), 6.46 (d, 2, Ar), 3.05 (sept, 2, CHMe<sub>2</sub>), 1.11 (d, 12, CHMe<sub>2</sub>), 1.09 (s, 9, t-Bu); <sup>13</sup>C NMR (toluene- $d_8$ ) 153.0, 141.6, 130.6, 126.0 (Ar), 63.3 (CH<sub>2</sub>-t-Bu), 38.8 (CMe<sub>3</sub>), 33.6 (CMe<sub>3</sub>), 31.7 (CHMe<sub>2</sub>), 23.1 (CHMe<sub>2</sub>). Anal. Calcd for OsC<sub>25</sub>-H<sub>39</sub>NI<sub>2</sub>: C, 34.70; H, 5.14; N, 1.84. Found: C, 34.69; H, 5.14; N, 2.01.

**Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)Cl.** OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> (81 mg, 0.15 mmol) was dissolved in 5 mL of dichloromethane, and the solution was chilled to -40 °C. Trimethylchlorosilane (25 μL, 0.19 mmol) was added, and the resulting green solution was warmed to 25 °C and stirred for 1 h. Dichloromethane was removed in vacuo, and the resulting green solid was recrystallized from ether/pentane at -40 °C. Dark green prisms were collected and dried in vacuo: yield 64 mg in two crops (66%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.14 (t, 1, Ar), 6.60 (d, 2, Ar), 6.31 (d, 2, CH<sub>a</sub>H<sub>b</sub>-t-Bu), 5.15 (d, 2, CH<sub>a</sub>H<sub>b</sub>-t-Bu), 3.5 (sept, 2, CHMe<sub>2</sub>), 1.30 (s, 18, t-Bu), 1.18 (d, 12, CHMe<sub>2</sub>), 0.47 (s, 9, OSiMe<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 153.1, 146.3, 130.4, 125.6 (Ar), 50.5 (CH<sub>2</sub>-t-Bu), 39.3 (CHMe<sub>2</sub>), 32.5 (CMe<sub>3</sub>), 30.8 (CMe<sub>3</sub>), 24.0 (CHMe<sub>2</sub>), 2.9 (SiMe<sub>3</sub>). Anal. Calcd for OsC<sub>25</sub>H<sub>48</sub>NClOSi: C, 47.48; H, 7.65; N, 2.21. Found: C, 47.42; H, 7.65; N, 2.17.

**Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)(OTf).** OsO(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub> (108 mg, 0.21 mmol) was dissolved in 5 mL of dichloromethane, and the solution was chilled to -40 °C. Trimethylsilyl triflate (42  $\mu$ L, 0.21 mmol) was added, and the resulting green solution was warmed to 25 °C and stirred for 1 h. Dichloromethane was removed in vacuo, and the resulting olive green solid was washed with pentane and dried in vacuo: yield 121 mg (77%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.5 (br d, 2, CH<sub>a</sub>H<sub>b</sub>-t-Bu), 7.14 (t, 1, Ar), 6.62 (d, 2, Ar), 5.8 (br d, 2, CH<sub>a</sub>H<sub>b</sub>-t-Bu), 3.25 (br m, 2, CHMe<sub>2</sub>), 1.27 (d, 12, CHMe<sub>2</sub>), 1.13 (s, 18, t-Bu), 0.33 (s, 9, OSiMe<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  153.8, 146.7, 132.0, 125.3 (Ar), 43 (br, CH<sub>2</sub>-t-Bu), 40.0 (CMe<sub>3</sub>), 31.9 (CMe<sub>3</sub>), 31.3 (CHMe<sub>2</sub>), 23.8 (CHMe<sub>2</sub>), 2.3 (OSiMe<sub>3</sub>). Anal. Calcd for OsC<sub>26</sub>H<sub>48</sub>NF<sub>3</sub>O<sub>4</sub>SiS: C, 41.86; H, 6.49; N, 1.88. Found: C, 41.59; H, 6.90; N, 1.90.

**Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(py)(OSiMe<sub>3</sub>)(OTf).** Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>(py)(OSiMe<sub>3</sub>)(OTf) was prepared in 80% yield by adding excess pyridine to a toluene solution of Os(NAr)(CH<sub>2</sub>-t-Bu)<sub>2</sub>-(OSiMe<sub>3</sub>)(OTf). The resulting green precipitate was washed with pentane and dried in vacuo: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.6 (br d, 2, py), 8.15 (t, 1, Ar), 7.75 (br t + d, 3, py), 3.0 (br, CHMe<sub>2</sub>), 1.15 (br, 12, CHMe<sub>2</sub>), 1.00 (s, 18, t-Bu), 0.38 (s, 9, SiMe<sub>3</sub>), the methylene protons could not be located; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  152.5, 147.1, 141.7, 129.3, 128.4, 126.7, 125.5 (py + Ar), 46 (br, CH<sub>2</sub>-t-Bu), 39 (br, CMe<sub>3</sub>), 32.0 (CMe<sub>3</sub>), 31.3 (CHMe<sub>2</sub>), 23.6 (CHMe<sub>2</sub>), 2.7 (SiMe<sub>3</sub>).

 $Os(NAr)(CH_3)_2(CH_2-t-Bu)_2$ .  $Os(NAr)(O)(CH_2-t-Bu)_2$  (55) mg, 0.105 mmol) was dissolved in 5 mL of pentane, and the solution was chilled to -40 °C. A solution of trimethylaluminum in hexane (0.24 mmol) was added. The reaction mixture became red and then orange as it was warmed to room temperature. After 30 min, the solution was filtered, the volatile components were removed in vacuo, and the residue was dissolved in pentane and the resulting solution was passed through silica gel. The solvent was removed in vacuo to give an orange crystalline solid: yield 47 mg (83%); <sup>1</sup>H NMR ( $C_6D_6$ ) δ 7.01 (t, 1, Ar), 6.72 (d, 2, Ar), 3.63 (s, 4, CH<sub>2</sub>-t-Bu), 3.40 (s, 6,  $CH_3$ ), 3.31 (sept, 4,  $CHMe_2$ ), 1.27 (s, 18,  $CH_2$ -*t*-Bu), 1.12 (d, 12,  $J_{\rm HH} = 7$  Hz, CHMe<sub>2</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  146.4 (C<sub>i</sub>), 142.5 (C<sub>o</sub>), 127.0 (C<sub>p</sub>), 124.5 (C<sub>m</sub>), 74.2 (CH<sub>2</sub>-t-Bu), 40.7 (CH<sub>3</sub>), 40.4 (CH<sub>2</sub>CMe<sub>3</sub>), 34.1 (CH<sub>2</sub>CMe<sub>3</sub>), 29.0 (CHMe<sub>2</sub>), 23.8 (CHMe<sub>2</sub>). Anal. Calcd for OsC<sub>24</sub>H<sub>45</sub>N: C, 53.60; H, 8.43; N, 2.60. Found: C, 53.92; H, 8.79; N, 2.56.

X-ray Study of Os(NAr)(CH<sub>2</sub>-*t*-Bu)<sub>2</sub>(OSiMe<sub>3</sub>)(OTf). The space group was found to be  $P\bar{1}$  with a = 9.785 Å, b = 10.126 Å, c = 18.712 Å,  $\alpha = 97.79^{\circ}$ ,  $\beta = 95.72^{\circ}$ ,  $\gamma = 114.61^{\circ}$ , V = 1645 Å<sup>3</sup>, Z = 2, fw = 746.01, and  $D_{calcd} = 1.506$  g/cm<sup>3</sup>. Details can be found in the supplementary material.

**Acknowledgment.** R.R.S. thanks the National Science Foundation (Grant CHE 91 22827) for research support.

**Supplementary Material Available:** Text giving experimental details for the X-ray study of  $Os(NAr)(CH_2-t-Bu)_2-(OSiMe_3)(OTf)$ , an ORTEP drawing, and tables of final coordinates and final thermal parameters (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for information.

OM950019O