Exchange of Oxo Ligands in OsO_4 with Imido Ligands in $Mo(NAr)_2(O\text{-}t\text{-}Bu)_2$. A Facile Route to $Os(NAr)_2O_2$ and $Os(NAr)_3O$ and Osmium(IV) Complexes of the Type $Os(NAr)_2L_2$ (NAr = N-2,6-C_6H_3-*i*-Pr_2; L = a Phosphine)

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Introduction

The sterically demanding (2,6-diisopropylphenyl)imido ligand was first used as a means of stabilizing four-coordinate molybdenum and tungsten alkylidene complexes so that they could behave in a well-defined manner as olefin metathesis catalysts.[1-3] It has been employed in the last few years in many other circumstances to stabilize monomeric species, especially those in which the metal is in a relatively high or the highest possible oxidation state. Examples include complexes that contain niobium or tantalum,[4-6] molybdenum or tungsten,[7,8] technetium or rhenium,[9-12] or osmium.[13-15] However, in osmium chemistry there are several limitations to the preparations of some of the most unusual new types of complexes, trigonal planar $Os(NAr)_3$[13,14,16] and square planar *trans*-$Os(NAr)_2L_2$ (L = a phosphine);[13,16] the synthesis of $Os(NAr)_3$ from OsO_4 proceeds in poor yield, and osmium(VIII) complexes that are potentially useful as starting materials, such as $Os(NAr)_2O_2$, are available only in several steps from $Os(NAr)_3$ and not in high yield. (Unfortunately, methods that yield Os(VIII) complexes containing more than one *tert*-butylimido ligand, such as reactions between $Os(N\text{-}t\text{-}Bu)O_3$ and *tert*-butylphosphinimine[17] or between OsO_4 and (trimethylsilyl)-*tert*-butylamine,[14,18] so far have not produced Os(VIII) arylimido complexes in our or other laboratories.[19]) In this report we describe a simple, high-yield entry into osmium arylimido chemistry that employs an imido/oxo exchange reaction.

Results

Osmium tetraoxide reacts smoothly with 1 equiv of $Mo(NAr)_2(O\text{-}t\text{-}Bu)_2$[20,21] in THF to give $Os(NAr)_2O_2$ (**1**) and $MoO_2(O\text{-}t\text{-}Bu)_2$[21,22] in high yield (eq 1). $MoO_2(O\text{-}t\text{-}Bu)_2$, a pentane-soluble

$$OsO_4 + Mo(NAr)_2(O\text{-}t\text{-}Bu)_2 \xrightarrow{THF} \underset{\mathbf{1}}{Os(NAr)_2O_2} + MoO_2(O\text{-}t\text{-}Bu)_2 \quad (1)$$

yellow oil, can be separated from **1** by passing the reaction mixture through silica gel. If 1.5 equiv of $Mo(NAr)_2(O\text{-}t\text{-}Bu)_2$ is employed, then $Os(NAr)_3O$ (**2**) can be isolated in high yield in a similar manner. $Os(NAr)_4$ has never been observed, perhaps because the coordination sphere in **2** is too crowded for further ligand-exchange reactions involving the NAr ligand. Since $Mo(NAr)_2Cl_2(dimethoxyethane)_2$ can be obtained readily on a large scale,[23] the synthesis of **1** and **2** by this route is a significant improvement over published methods.[13] Details of the oxo/imido exchange reaction are not known. It is somewhat surprising that the reaction proceeds cleanly to only one set of products, although this type of behavior is likely to be more common if the characteristics of the two metals involved are rather different. In this case the more electronegative oxo ligands end up bound to the earlier metal. Facile scrambling of oxo and imido groups in imido alkylidene complexes of molybdenum were reported recently.[21]

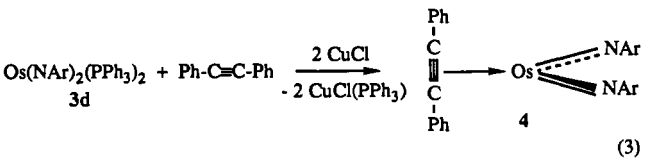
Earlier we reported that complexes of the type $Os(NAr)_2L_2$ could be prepared by adding 3 equiv of a phosphine (L = PMe_3, PMe_2Ph) to $Os(NAr)_3$.[13] We also reported that reduction of **1** by a phosphine to give $Os(NAr)_2L_2$ could be observed in an NMR-scale reaction.[13] We find that this type of reaction can be carried out on a synthetic scale. Addition of 4 equiv of L to **1** yields $Os(NAr)_2L_2$ complexes (**3**; eq 2) in high yield. Both the desired

$$\underset{\mathbf{1}}{Os(NAr)_2O_2} + 4L \rightarrow \underset{\mathbf{3}}{Os(NAr)_2L_2} + 2L{=}O \quad (2)$$

L = PMe_3 (**3a**), PMe_2Ph (**3b**), $PMePh_2$ (**3c**)

product and the phosphine oxide byproduct precipitate when pentane is employed as the reaction solvent. The phosphine oxide can be removed easily by sublimation in the case of **3a** and **3b**. **3c** is more conveniently isolated by washing away the phosphine oxide and other impurities with benzene, since **3c** is only moderately soluble in benzene. $Os(NAr)_2(PPh_3)_2$ (**3d**) also can be prepared readily, although 8 equiv of PPh_3 must be employed in order to prevent formation of a significant amount of $Os(NAr)_3$, presumably by disproportionation of intermediate $Os(NAr)_2O$.[13] **3d** can be isolated by washing away the phosphine oxide, $Os(NAr)_3$, and excess phosphine with THF, in which **3d** is only moderately soluble. Triphenylphosphine does not react readily with $Os(NAr)_3$ to give **3d**.[13]

Complex **3d** is perhaps the most interesting, since PPh_3 is likely to be the most labile of the phosphine ligands. Addition of diphenylacetylene to **3d** in the presence of copper chloride yields $Os(NAr)_2(PhC{\equiv}CPh)$ (**4**, eq 3). NMR spectra of **4** display



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only one resonance each for the isopropyl methyl and methine protons on the arylimido ligand, as well as only one resonance for the acetylenic carbon atoms (δ 201.8). **4** is analogous to recently prepared $[Re(NAr)_2(alkyne)]^-$ complexes of rhenium.[9] Since the core of $[Re(NAr)(t\text{-}BuCH_2C{\equiv}CCH_2\text{-}t\text{-}Bu)_2]^-$,[9] $[Re(NAr)_3]^-$,[9] and $Os(NAr)_3$[13] is each essentially a trigonal plane and the acetylene ligands in $[Re(NAr)(t\text{-}BuCH_2C{\equiv}CCH_2\text{-}t\text{-}Bu)_2]^-$ are oriented approximately perpendicular to the trigonal plane, we believe that **4** most likely is a monomeric pseudo trigonal planar species with a structure approximately that shown in eq 3. The reaction between **4** and 2–3 equiv of PMe_2Ph gives $Os(NAr)_2(PMe_2Ph)_2$ rapidly and quantitatively, according to ^1H NMR spectra; we had previously reported that $Os(NAr)_2(PMe_2Ph)_2$ will not react with diphenylacetylene.[13]

Experimental Section

General procedures can be found elsewhere.[13] $Mo(NAr)_2(O\text{-}t\text{-}Bu)_2$[21] was prepared by adding 2 equiv of LiO-*t*-Bu to $Mo(NAr)_2Cl_2$(dimethoxyethane).[23] Osmium tetraoxide was purchased from Platinum Chemicals, Inc. All other reagents were purchased from commercial sources and purified using standard procedures. CuCl was purchased from Aldrich and used as received. All NMR spectra were obtained in C_6D_6.

$Os(NAr)_2O_2$ (1). $Mo(NAr)_2(O\text{-}t\text{-}Bu)_2$ (4.67 g, 7.87 mmol) was added as a solid to a solution of OsO_4 (2.00 g, 7.87 mmol) in THF (250 mL), and the mixture was stirred for 2 days. The deep red THF solution was passed through a frit containing silica gel, and the red product was washed through with more THF until the washings were colorless. THF was removed from the eluent in vacuo to leave a red oil, which was extracted into hexane. The hexane was removed from the extract in vacuo to give $Os(NAr)_2O_2$ as a deep brown-red solid (3.74 g, 6.5 mmol, 83% yield). The ^1H and ^{13}C NMR and IR spectra of this compound match those reported previously.[13]

$Os(NAr)_3O$ (2). $Mo(NAr)_2(O\text{-}t\text{-}Bu)_2$ (3.50 g, 5.90 mmol) was added as a solid to a solution of OsO_4 (1.00 g, 3.94 mmol) in THF (40 mL), and the mixture was stirred for 36 h. The brown THF solution was passed through a frit containing silica gel, and the brown product was washed through with more THF until the washings were colorless. The THF was removed from the eluent in vacuo to leave behind a brown oil. The oil was extracted with hexane, and the hexane was removed from the extract to give $Os(NAr)_3O$ as a deep brown solid (2.1 g, 2.87 mmol, 73% yield). The ^1H and ^{13}C NMR and IR spectra of this compound match those reported previously.[13]

$Os(NAr)_2(PMe_3)_2$ (3a). This compound was prepared in a manner analogous to that described for $Os(NAr)_2(PMe_2Ph)_2$ using trimethylphosphine (100 μL, 0.97 mmol) and $Os(NAr)_2O_2$ (50 mg, 87 μmol). Trimethylphosphine oxide was sublimed away from the product at 0.1 Torr/50 °C in 9 h, leaving pure $Os(NAr)_2(PMe_3)_2$ as a brown solid (50 mg, 73 μmol, 83% yield) that gave purple solutions. The ^1H and ^{13}C NMR spectra of this compound match those reported previously.[13]

$Os(NAr)_2(PMe_2Ph)_2$ (3b). Dimethylphenylphosphine (800 μL, 5.59 mmol) was added all at once to a hexane solution of $Os(NAr)_2O_2$ (800 mg, 1.39 mmol). Immediately the solution turned darker and a dark precipitate started to form. The mixture was stirred for 12 h, and the solids were filtered off. Dimethylphenylphosphine oxide was sublimed away from the product at 0.1 Torr/50 °C over a period of 16 h, leaving pure $Os(NAr)_2(PMe_2Ph)_2$ as a purple solid (1.1 g, 1.22 mmol, 88% yield). The ^1H and ^{13}C NMR spectra of this compound match those reported previously.[13]

$Os(NAr)_2(PMePh_2)_2$ (3c). This compound was prepared in a manner similar to that described for **3b** from $Os(NAr)_2O_2$ (500 mg, 0.87 mmol) in pentane (12 mL) and methyldiphenylphosphine (700 mg, 3.5 mmol). Methyldiphenylphosphine oxide was removed by washing the solids with benzene (3 × 2 mL). The remaining powder was brown **3c** (650 mg 0.69 mmol, 78% yield), which formed purple solutions: ^1H NMR δ 7.91 (m, 8, Ph H_o), 7.01 (m, 12, Ph H_m and Ph H_p), 6.81 (m, 6, Ar H_m and Ar H_p), 4.22 (sept, 4, C*H*Me$_2$), 1.78 (d, 6, PMe), 1.01 (d, 24, CH*Me*$_2$); ^{13}C NMR δ 153.9 (Ar C_{ipso}), 139.7 (Ar C_o), 138.7 (Ar C_m), 134.5 (Ph C_{ipso}), 134.4 (Ph C_o), 129.7 (Ph C_m), 122.4 (Ph C_p), 121.0 (Ar C_p), 27.9 (*C*HMe$_2$), 24.0 (CH*Me*$_2$), 15.7 (PMe). Anal. Calcd for $OsC_{50}H_{60}N_2P_2$: C, 63.81; H, 6.43; N, 2.98. Found: C, 63.84; H, 6.37; N, 2.90.

$Os(NAr)_2(PPh_3)_2$ (3d). Triphenylphosphine (4.9 g, 19 mmol) was added to a solution of $Os(NAr)_2(O)_2$ (1.35 g, 2.36 mmol) in a mixture of toluene (60 mL) and THF (20 mL). The solution became darker immediately and the color slowly changed to dark purple-brown. After 16 h the solvents were removed *in vacuo*. The brown oily residue was extracted with THF (15 mL), and the insoluble material was filtered off and washed with cold THF (3 mL), leaving the brown microcrystalline product (1.0 g, 0.94 mmol, 40% yield): ^1H NMR δ 7.69 (br, 12, Ph H_o), 6.98 (br, 18, Ph H_m and Ph H_p), 6.75 (m, 6, Ar H_m and Ar H_p), 3.98 (sept, 4, C*H*Me$_2$), 0.85 (d, 24, CH*Me*$_2$); $^{13}C\{^1H\}$ NMR δ 154.8 (Ar C_{ipso}), 140.0 (Ar C_o), 135.8 (Ph C_o), 135.5 (Ph C_{ipso}), 129.8 (Ph), 122.3 (ArC_m), 121.2 (ArC_p), 28.14 (*C*HMe$_2$), 23.36 (CH*Me*$_2$). (One Ph C resonance is apparently obscured or coincident with another.) Anal. Calcd for $OsC_{60}H_{64}N_2P_2$: C, 67.65; H, 6.06; N, 2.63. Found: C, 67.51; H, 6.02; N, 2.65.

$Os(NAr)_2(PhC{\equiv}CPh)$ (4). $Os(NAr)_2(PPh_3)_2$ (190 mg, 0.166 mmol) was added to 10 mL of toluene, and diphenylacetylene (30 mg, 0.166 mmol) was added. The solution immediately became deep red-orange and homogeneous. After 0.5 h, CuCl (36 mg, 0.365 mmol) was added all at once, and the mixture was stirred vigorously. After 12 h the solution was taken to dryness and the residue was extracted with pentane. The white solid was removed by filtering the mixture through Celite. The deep red-orange filtrate was taken to dryness, leaving $Os(NAr)_2(PhC{\equiv}CPh)$ as a red-brown microcrystalline solid (80 mg, 60%): ^1H NMR δ 8.41 (d, 4, Ph H_o), 7.24 (t, 4, Ph H_m), 7.15 (overlapping multiplets, 4, Ar H_p and Ph H_p), 6.93 (d, 4, Ar H_m), 3.69 (sept, 4, C*H*Me$_2$), 1.14 (d, 24, CH*Me*$_2$); $^{13}C\{^1H\}$ NMR δ 201.8 (*C*Ph), 153.7 (Ar C_{ipso}), 142.5 (Ar C_o), 132.8 (Ph C_o), 130.4 (Ph C_{ipso}), 128.9 (Ph C_m), 126.3 (Ar C_m), 125.7 (Ar C_p), 122.9 (Ph C_p), 29.0 (*C*HMe$_2$), 22.8 (CH*Me*$_2$); HRMS (EI) *m/z* 720.3116 (M^+ calcd for $OsC_{38}H_{44}N_2$, ^{192}Os, 720.3119). Anal. Calcd for $OsC_{38}H_{44}N_2$: C, 63.48; H, 6.17; N, 3.90. Found: C, 63.96; H, 6.39; N, 3.70.

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