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Luminescent Nitridoosmium(VI) Complexes with Aryl- and Alkylacetylide Ligands: Spectroscopic Properties and Crystal Structures

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A series of air- and moisture-stable nitridoosmium(VI) complexes with arylacetylide ligands, $[^n\mathrm{Bu_4N}][\mathrm{OsN(C{\equiv}CC_6H_4R\text{-}}p)_4]$ (R = H (**1**), Et (**2**), OEt (**3**), Ph (**4**)), and the alkyl analogue $[^n\mathrm{Bu_4N}][\mathrm{OsN(C{\equiv}C^tBu)_4}]$ (**5**) were synthesized. The structures of **1**, **2**, and **4** were determined by X-ray crystal analyses. The Os≡N (1.65(1) Å in **1**, 1.620(8) Å in **2**, and 1.619(6) Å in **4**) and Os−C (mean 2.03 Å) distances are similar to that observed for $[\mathrm{OsN(CH_2SiMe_3)_4}]^-$, whereas the C≡C distances (mean 1.20 Å) correspond to terminal arylacetylide groups. The UV−vis absorption spectra of **1**−**4** display intense absorptions at 248−324 nm ($\epsilon \approx 5 \times 10^4$ dm^3 mol^{-1} cm^{-1}) that are attributed to overlapping of the $[\mathrm{p}_{\pi^*}(\mathrm{N}^{3-}) \rightarrow \mathrm{d}_{\pi^*}(\mathrm{d}_{xz}, \mathrm{d}_{yz})]$ and [$\pi \rightarrow \pi^*$(arylacetylides)] transitions. The moderately intense absorptions at $\lambda_{\max}$ 403−418 nm ($\epsilon \approx 10^3$ dm^3 mol^{-1} cm^{-1}) are assigned to admixture of $[(\mathrm{d}_{xy})^2 \rightarrow (\mathrm{d}_{xy})^1(\mathrm{d}_{\pi^*})^1]$ with intraligand charge-transfer transition of the arylacetylides. The broad structureless solid-state luminescence of **1**−**5** at 298 ($\lambda_{\max}$ 600−632 nm) and 77 K ($\lambda_{\max}$ 599−635 nm) are assigned to the triplet $^3[(\mathrm{d}_{xy})^1(\mathrm{d}_{\pi^*})^1]$ excited state. The 77 K glassy solutions of **1**−**5** also exhibit $^3[(\mathrm{d}_{xy})^1(\mathrm{d}_{\pi^*})^1]$ emissions at $\lambda_{\max}$ 597−628 nm. Like $[\mathrm{OsNX_4}]^-$ (X = Cl, Br), complexes **1**−**5** are nonemissive in dichloromethane at room temperature. Notably, **1** emits weakly at $\lambda_{\max}$ 643 nm in benzene at room temperature, whereas **5** exhibits a more intense and long-lived luminescence at $\lambda_{\max}$ 640 nm in diethyl ether. Correspondingly, a well-defined absorption at $\lambda_{\max}$ 428 nm in the excitation spectrum of **5** (λ_{em} 640 nm, concentration 8×10^{-4} mol dm^{-3}) is assigned to the $^1[(\mathrm{d}_{xy})^2] \rightarrow {}^1[(\mathrm{d}_{xy})^1(\mathrm{d}_{\pi^*})^1]$ transition.

Introduction

There is growing interest in transition-metal−alkynyl complexes for their spectroscopic and photoluminescent properties, as well as their potential applications in materials science.[1−3] Hopkins and co-workers recently presented a review on M−CCR π-interactions. Notwithstanding X-ray crystallographic and vibrational spectroscopic techniques, these researchers reported the employment of electronic spectroscopy for studying the bonding in metal−alkynyl moieties, including those in alkynyl-substituted, metal−metal quadruply bonded compounds of the type $\mathrm{M_2(C{\equiv}CR)_4(PMe_3)_4}$ (M = Mo, W; R = H, alkyl, Ph, SiMe$_3$).[4]

In comparison to alkyl and aryl ligands, terminal alkyl- and arylacetylides are less sensitive to moisture, as a consequence of the higher acidity of the RC≡CH protons. Moreover, arylacetylide moieties are suitable ancillary ligands for the preparation of organometallic derivatives in high oxidation states. Indeed, electrochemical studies on the *trans*-$[\mathrm{Ru^{II}(16\text{-}TMC)(C{\equiv}CAr)_2}]$ (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) complexes revealed that the electrochemically generated *trans*-$[\mathrm{Ru^{IV}(16\text{-}TMC)(C{\equiv}CAr)_2}]^{2+}$ species with $E_{1/2}$ values of 0.54−0.80 V vs $\mathrm{Cp_2Fe^{0/+}}$ are stable on the cyclic voltammetric time scale.[5] We[6,7] and others[8] have extensively studied the spectroscopy and

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photochemical reactivities of high-valent osmium−ligand multiply bonded species, and emissive long-lived $^3[(d_{xy})^1(d_{xz}, d_{yz})^1]$ excited states from dioxo- and nitridoosmium(VI) complexes supported by amine, cyanide, polypyridine, halide, and thiolate ligands are well documented. However, comparable photophysical studies on organometallic oxo- and nitridoosmium(VI) derivatives are sparse in the literature. Oxotetrakis((trimethylsilyl)methyl)osmium(VI)[9] was first reported by Wilkinson and co-workers, but the low product yield has hindered extensive photophysical and photochemical studies. Nitridoalkylosmium(VI) complexes that have appeared in the literature are supported by cyclopentadienyl (e.g. $(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{OsN(CH_2SiMe_3)_2}$ (R = H, Me)),[10] thiolate,[11] and phosphine[12] auxiliaries. The dearth of stable organoosmium(VI) derivatives prompted us to utilize arylacetylide ligands to stabilize osmium−oxo and −nitrido moieties and facilitate their isolation.

This paper describes the preparation and spectroscopic properties of the luminescent nitridoosmium(VI) arylacetylide complexes $[^n\mathrm{Bu_4N}][\mathrm{OsN(C{\equiv}CC_6H_4R}\text{-}p)_4]$ (R = H (**1**), Et (**2**), OEt (**3**), Ph (**4**)), and comparisons with the aliphatic analogue $[^n\mathrm{Bu_4N}][\mathrm{OsN(C{\equiv}C^tBu)_4}]$ (**5**) are described.

Experimental Section

General Procedures. All starting materials were purchased from commercial sources and used as received. $[^n\mathrm{Bu_4N}][\mathrm{OsNCl_4}]$ was prepared by the literature method.[13] Dichloromethane for photophysical studies was washed with concentrated sulfuric acid, 10% sodium hydrogen carbonate, and water, dried by calcium chloride, and distilled over calcium hydride. All other solvents were of analytical grade and purified according to conventional methods.[14] All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques.

Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded on a DPX 500 Bruker FT-NMR spectrometer with chemical shifts (in ppm) relative to tetramethylsilane. Elemental analyses were performed by an Elementar Vario EL instrument. Infrared spectra were recorded on a Bio-Rad FT-IR spectrophotometer. Raman spectra were recorded on a Bio-Rad FT-Raman spectrophotometer. UV−vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer.

Emission and Lifetime Measurements. Steady-state emission spectra were recorded on a SPEX Fluorolog-2 Model 1680 spectrophotometer. Low-temperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5 mm diameter quartz tubes which were placed in a liquid-nitrogen Dewar equipped with quartz windows. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability.

Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix Model 2430 digital oscilloscope. Errors for λ values (±1 nm), τ values (±10%), and ϕ values (±10%) are estimated. Details of emission quantum yield determinations using the method of Demas and Crosby[15] have been provided previously.[16]

Synthesis. $[^n\mathrm{Bu_4N}][\mathrm{OsN(C{\equiv}CC_6H_4R}\text{-}p)_4]$ ($[^n\mathrm{Bu_4N}]$1−4; R = H (1), Et (2), OEt (3), Ph (4)). To a solution of $\mathrm{HC{\equiv}CC_6H_4R}\text{-}p$ (1.36 mmol) in THF (40 mL) at room temperature was added ^{n}BuLi (1.6 M in hexane, 0.85 mL, 1.36 mmol). The resultant yellow mixture was stirred for 30 min, and $[^n\mathrm{Bu_4N}][\mathrm{OsNCl_4}]$ (0.20 g, 0.34 mmol) was added in small portions. The mixture was stirred at room temperature for 6 h to afford a brown solution, which was evaporated to dryness. Water was added to the residue, the product was extracted with dichloromethane and dried over anhydrous $\mathrm{MgSO_4}$, and the volume of extract was reduced. Addition of *n*-hexane afforded a yellow precipitate, which was recrystallized by slow diffusion of diethyl ether into a dichloromethane solution to yield yellow-orange crystals.

$[^n\mathrm{Bu_4N}]$**1**: yield 0.21 g, 73%. Anal. Calcd for $\mathrm{C_{48}H_{56}N_2Os\cdot 3H_2O}$: C, 63.69; H, 6.90; N, 3.09. Found: C, 63.30; H, 6.36; N, 3.04. Negative FAB-MS: *m/z* 610 [M$^-$]. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 0.88 (t, 12H, J = 7.2 Hz, $\mathrm{C}H_3(\mathrm{CH_2})_3$), 1.26−1.33 (m, 8H, $\mathrm{CH_3(C}H_2)_3$), 1.35−1.41 (m, 8H, $\mathrm{CH_3(C}H_2)_3$), 2.95 (m, 8H, $\mathrm{CH_3(C}H_2)_3$), 7.19 (t, 4H, J = 7.5 Hz, Ph), 7.31 (t, 8H, J = 7.7 Hz, Ph), 7.47 (d, 8H, J = 7.5 Hz, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 13.1 ($C\mathrm{H_3(CH_2)_3}$), 19.4; 23.5; 58.4 ($\mathrm{CH_3(}C\mathrm{H_2)_3}$), 102.7 ($\mathrm{Os{-}C{\equiv}}C$), 126.3, 126.4, 127.2 ($\mathrm{Os{-}}C\mathrm{{\equiv}C}$), 127.8, 131.5. IR (Nujol): ν 2122, 2109 (m, C≡C), 1109 (s, Os≡N) cm^{-1}. Raman: ν 2123 (s, C≡C), 1112 (m, Os≡N) cm^{-1}.

$[^n\mathrm{Bu_4N}]$**2**: yield 0.19 g, 58%. Anal. Calcd for $\mathrm{C_{56}H_{72}N_2Os}$: C, 69.82; H, 7.53; N, 2.91. Found: C, 69.74; H, 7.40; N, 2.73. Negative FAB-MS: *m/z* 723 [M$^-$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.72 (t, 12H, J = 6.6 Hz, $\mathrm{C}H_3(\mathrm{CH_2})_3$), 1.18 (m, 16H, $\mathrm{CH_3(C}H_2)_3$), 1.21 (t, 12H, J = 7.6 Hz, $\mathrm{C_6H_4CH_2C}H_3$), 2.63 (q, 8H, J = 7.6 Hz, $\mathrm{C_6H_4C}H_2$), 2.90 (m, 8H, $\mathrm{CH_3(C}H_2)_3$), 7.08 (d, 8H, J = 8.1 Hz, $\mathrm{C_6H_4}$), 7.38 (d, 8H, J = 8.1 Hz, $\mathrm{C_6H_4}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 13.6 ($C\mathrm{H_3(CH_2)_3}$), 15.5 ($\mathrm{C_6H_4CH_2}C\mathrm{H_3}$), 19.6; 23.8 ($\mathrm{CH_3(}C\mathrm{H_2)_3}$), 28.7 ($\mathrm{C_6H_4}C\mathrm{H_2}$), 58.2 ($\mathrm{CH_3(}C\mathrm{H_2)_3}$), 102.4 ($\mathrm{Os{-}C{\equiv}}C$), 124.2, 127.4, 127.8 ($\mathrm{Os{-}}C\mathrm{{\equiv}C}$), 132.5, 142.8. IR (Nujol): ν 2120, 2111 (m, C≡C), 1109 (s, Os≡N) cm^{-1}. Raman: ν 2120, 2112 (s, C≡C), 1110 (m, Os≡N) cm^{-1}.

$[^n\mathrm{Bu_4N}]$**3**: yield 0.23 g, 66%. Anal. Calcd for $\mathrm{C_{56}H_{72}N_2O_4Os}$: C, 65.47; H, 7.06; N, 2.73. Found: C, 64.71; H, 6.94; N, 2.59. Negative FAB-MS: *m/z* 787 [M$^-$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.70 (t, 12H, J = 6.9 Hz, $\mathrm{C}H_3(\mathrm{CH_2})_3$), 1.16 (m, 16H, $\mathrm{CH_3(C}H_2)_3$), 1.40 (t, 12H, J = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 2.84 (m, 8H, $\mathrm{CH_3(C}H_2)_3$), 4.02 (q, 8H, J = 7.0 Hz, $\mathrm{OCH_2}$), 6.79 (d, 8H, J = 8.7 Hz, $\mathrm{C_6H_4}$), 7.40 (d, 8H, J = 8.7 Hz, $\mathrm{C_6H_4}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 13.7 ($C\mathrm{H_3(CH_2)_3}$), 14.9 ($\mathrm{OCH_2}C\mathrm{H_3}$), 19.6; 23.8; 58.1 ($\mathrm{CH_3(}C\mathrm{H_2)_3}$), 63.4 ($\mathrm{OCH_2}$), 101.6 ($\mathrm{Os{-}C{\equiv}}C$), 114.0, 119.3, 127.5 ($\mathrm{Os{-}}C\mathrm{{\equiv}C}$), 134.1, 158.0. IR (Nujol): ν 2116 (sh), 2107 (m, C≡C), 1104 (s, Os≡N) cm^{-1}. Raman: ν 2118, 2110 (s, C≡C), 1106 (m, Os≡N) cm^{-1}.

$[^n\mathrm{Bu_4N}]$**4**: yield 0.20 g, 51%. Anal. Calcd for $\mathrm{C_{72}H_{72}N_2Os\cdot H_2O}$: C, 73.69; H, 6.36; N, 2.39. Found: C, 73.69; H, 6.21; N, 2.39. Negative FAB-MS: *m/z* 915 [M$^-$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.80 (t, 12H, J = 7.0 Hz, $\mathrm{C}H_3(\mathrm{CH_2})_3$), 1.24−1.33 (m, 16H, $\mathrm{CH_3(C}H_2)_3$), 2.98 (m, 8H, $\mathrm{CH_3(C}H_2)_3$), 7.32 (t, 4H, J = 7.4 Hz, Ph), 7.42 (t, 8H, J = 7.7 Hz, Ph), 7.53 (d, 8H, J = 8.4 Hz, Ph),

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Table 1. Crystal Data

	[^{n}Bu$_4$N]**1**	[^{n}Bu$_4$N]**2**	[^{n}Bu$_4$N]**4**
formula	$C_{48}H_{56}N_2Os$	$C_{56}H_{72}N_2Os$	$C_{72}H_{72}N_2Os$
fw	851.15	963.36	1155.52
cryst size, mm	0.20 × 0.10 × 0.05	0.25 × 0.25 × 0.15	0.40 × 0.30 × 0.15
cryst system	trigonal	orthorhombic	monoclinic
space group	*R*3*c*	*Pnma*	*P*2$_1$/*n*
a, Å	36.550(5)	15.860(3)	11.134(2)
b, Å		26.132(5)	16.242(3)
c, Å	17.147(3)	12.774(3)	33.898(7)
α, deg	90	90	90
β, deg	90	90	92.78(3)
γ, deg	120	90	90
V, Å^3	19 838(5)	5294(2)	6123(2)
Z	18	4	4
D_c, g cm^{-3}	1.282	1.209	1.254
μ, cm^{-1}	29.24	24.43	21.24
$2\theta_{max}$, deg	49.24	50.62	50.68
no. of unique data	5591	3761	6673
no. of obsd data ($I \geq 2\sigma(I)$)	4082	2624	4021
no. of variables	227	193	532
R,[a] R_w[b]	0.043, 0.11	0.052, 0.15	0.045, 0.12
residual *ρ*, e Å^{-3}	+0.40, −0.42	+0.78, −0.83	+0.51, −0.53

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

7.58 (d, 16H, *J* = 8.4 Hz, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 13.7 ($CH_3(CH_2)_3$), 19.7; 23.9; 58.5 ($CH_3(CH_2)_3$), 104.2 (Os−C≡*C*), 125.9, 126.5, 126.9, 127.2, 127.7 (Os−*C*≡C), 128.8, 132.7, 139.2, 140.6. IR (Nujol): *ν* 2120 (sh), 2109 (m, C≡C), 1115 (s, Os≡N) cm^{-1}. Raman: *ν* 2122, 2113 (sh) (s, C≡C), 1116 (m, Os≡N) cm^{-1}.

[^{n}Bu$_4$N][OsN(C≡C^{t}Bu)$_4$] ([^{n}Bu$_4$N]5). The procedure for [^{n}Bu$_4$N]**1** was adopted using *tert*-butylacetylene (0.12 g, 1.46 mmol) to afford an orange-brown solid: yield 0.17 g, 65%. Anal. Calcd for $C_{40}H_{72}N_2Os \cdot H_2O$: C, 60.87; H, 9.45; N, 3.55. Found: C, 60.39; H, 9.73; N, 3.29. Negative FAB-MS: *m*/*z* 530 [M$^-$]. ^{1}H NMR ($CDCl_3$): *δ* 1.03 (t, 12H, *J* = 7.3 Hz, $CH_3(CH_2)_3$), 1.28 (s, 36H, ^{t}Bu), 1.45−1.51 (m, 8H, $CH_3(CH_2)_3$), 1.56−1.61 (m, 8H, $CH_3(CH_2)_3$), 3.15 (m, 8H, $CH_3(CH_2)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 13.8 ($CH_3(CH_2)_3$), 19.8; 24.1 ($CH_3(CH_2)_3$), 29.3 ($C(CH_3)_3$), 32.6 ($C(CH_3)_3$), 59.0 ($CH_3(CH_2)_3$), 89.4 (Os−C≡*C*), 136.0 (Os−*C*≡C). IR (Nujol): *ν* 2118, 2111 (sh) (m, C≡C), 1113 (s, Os≡N) cm^{-1}.

X-ray Crystallography. Crystals of [^{n}Bu$_4$N]**1**, [^{n}Bu$_4$N]**2**, and [^{n}Bu$_4$N]**4** were grown by slow diffusion of diethyl ether into dichloromethane solutions. Their crystal data and details of data collection and refinement are summarized in Table 1.

Diffraction data for [^{n}Bu$_4$N]**1**, [^{n}Bu$_4$N]**2**, and [^{n}Bu$_4$N]**4** were collected on a MAR diffractometer with graphite-monochromated Mo Kα radiation (*λ* = 0.710 73 Å). The structure was solved by direct methods (SIR97).[17] Refinement of structures was performed by full-matrix least squares using the program SHELXL-97[18] on a PC. Os and many non-H atoms were located according to direct methods and successive least-squares Fourier cycles. Positions of other non-hydrogen atoms were found after successful refinement by full-matrix least squares. For **1** and **4**, one crystallographic asymmetric unit consists of one formula unit, including one cation, whereas for **2** a crystallographic asymmetric unit consists of half of a formula unit with the atoms of the cation and Et groups refined isotropically.

Results and Discussion

Synthesis and Characterization. [^{n}Bu$_4$N][$OsNCl_4$] is a convenient precursor for the preparation of nitridoosmium(VI) compounds.[7,8,19] As reported by Shapley and co-workers,[20] direct alkylation of $OsNCl_4^-$ with alkylating agents gave nitridoosmium(VI) alkyl complexes in poor yields, and high yields of these complexes were obtained by reacting [^{n}Bu$_4$N][$OsN(OSiMe_3)_4$] with alkylating agents such as MgR_2 (R = CH_2CMe_3, CH_2Ph, CH_2SiMe_3) and $AlMe_3$. However, these alkylosmium(VI) complexes are air- and moisture-sensitive. In this work, treatment of [^{n}Bu$_4$N][$OsNCl_4$] with 4 equiv of Li(C≡CC_6H_4R-*p*) (R = H, Et, OEt, and Ph) in THF afforded yellow or orange crystalline solids of [^{n}Bu$_4$N][OsN(C≡CC_6H_4R-*p*)$_4$] (**1**−**4**, respectively) in moderate to high yields (51−73%). A similar reaction between [^{n}Bu$_4$N][$OsNCl_4$] and Li(C≡C^{t}Bu) yielded [^{n}Bu$_4$N][OsN(C≡C^{t}Bu)$_4$] (**5**). Complexes **1**−**5** are stable toward air and moisture in solid state and are soluble in a wide variety of solvents, including dichloromethane, acetonitrile, benzene, and even diethyl ether (for **5**).

The parent molecular ion [M$^-$] is evident in the FAB mass spectra of **1**−**5**. The ^{1}H NMR spectra of **1**−**5** show four equivalent acetylide ligands, which are consistent with the square-based-pyramidal geometry. The $^{13}C\{^1H\}$ NMR spectra of **1**−**4** display α- and *β*-acetylide carbon atoms at *δ* 127.2−127.8 and 101.6−104.2, whereas those observed for **5** appear at 136.0 and 89.4 ppm, respectively. The IR spectra of **1**−**5** reveal two *ν*(C≡C) stretching frequencies (symmetric and asymmetric) in the 2107−2122 cm^{-1} range, which are comparable to that of 2113 cm^{-1} observed in [(Cy_3P)Au(C≡CPh)].[21] In addition, the *ν*(Os≡N) absorptions (1104−1115 cm^{-1}) in the IR spectra of **1**−**5** are diagnostic for nitridoosmium(VI) complexes. The FT Raman spectra of **1**−**4** show strong acetylenic stretching modes at ~2120 cm^{-1} and one moderate Os≡N stretch at ~1110 cm^{-1}. Addition of piperidine or morpholine to an acetonitrile solution of [^{n}Bu$_4$N]**1** gave no observable reaction upon stirring at room temperature for 3 h, revealing the stability of these nitridoosmium(VI) arylacetylide complexes toward nucleophilic attack. This can be explained by the strong *σ*-donating effect of the four arylacetylide groups, which increases electron density around the osmium atom and lessens the extent of *π* electron donation from the nitrido group to osmium. This is consistent with the lower osmium−nitrogen stretching frequencies (~1110 cm^{-1}) in the IR spectra of these acetylide complexes compared to $OsNCl_4^-$ (1125 cm^{-1}).

Crystal Structures. X-ray structural determinations of [^{n}Bu$_4$N]**1**, [^{n}Bu$_4$N]**2**, and [^{n}Bu$_4$N]**4** have been performed (Figure 1 for **2**). In their molecular structures, the osmium atom adopts a distorted-square-pyramidal geometry with the nitrido group occupying an apical position and four equatorial arylacetylide ligands protruding below the plane of the metal, as observed in the crystal structures of [Ph_4As][$OsNCl_4$][22] and [^{n}Bu$_4$N][OsN(CH_2SiMe_3)$_4$].[23] Hence, the average N−Os−C(α) angles are 106° for **1**, 107° for **2**, and 107° for **4**, while the average trans C(α)−Os−C(α) bond angle is ca. 147°. The Os≡N bond distances (1.65(1) Å in **1**, 1.620(8) Å in **2**, and 1.619(6) Å in **4**) are comparable to that of 1.631-

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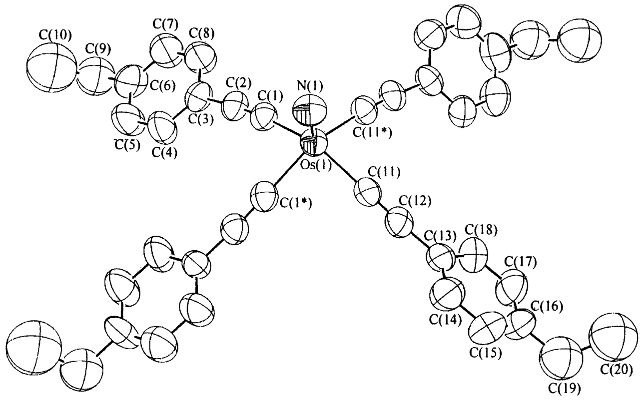

Figure 1. Perspective view of **2** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Os(1)−N(1) = 1.620(8), Os(1)−C(1) = 2.016(9), C(1)−C(2) = 1.21(1), C(2)−C(3) = 1.44(1); N(1)−Os(1)−C(1) = 107.3(3), C(1)−Os(1)−C(11) = 146.3(3), C(1)−Os(1)−C(11*) = 87.4(3), Os(1)−C(1)−C(2) = 173.8(7), C(1)−C(2)−C(3) = 174.6(8).

Table 2. UV−Visible Absorption Data in Dichloromethane at 298 K

$[^nBu_4N]^+$	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})
1	268 (55 700), 283 (sh, 46 200), 310 (sh, 25 200), 403 (1160)
2	248 (sh, 48 000), 270 (61 200), 286 (sh, 50 700), 314 (sh, 33 800), 406 (1540)
3	251 (sh, 51 300), 268 (58 700), 302 (43 800), 324 (42 000), 410 (2400)
4	274 (sh, 56 900), 312 (89 700), 418 (2400)
5	253 (15 600), 381 (sh, 420)
$OsNCl_4^-$	354 (40), 390 (60), 438 (90), 490 (100), 534 (sh, 80)
$OsNBr_4^-$	251 (3310), 271 (3320), 423 (sh, 80), 463 (140), 501 (150), 555 (sh, 100)

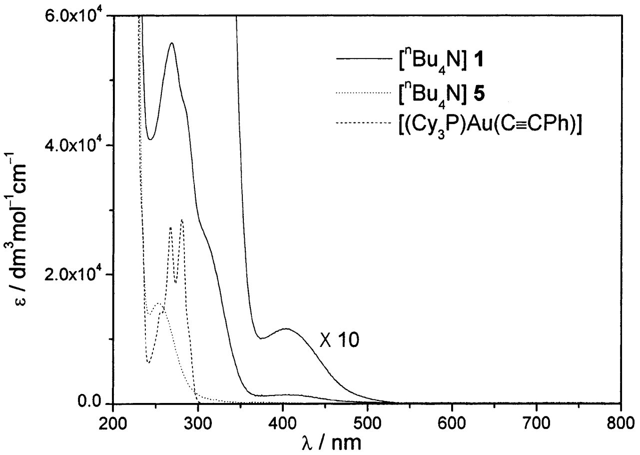

Figure 2. UV−vis absorption spectra of $[^nBu_4N]$**1**, $[^nBu_4N]$-**5**, and $[(Cy_3P)Au(C{\equiv}CPh)]$ in dichloromethane at 298 K.

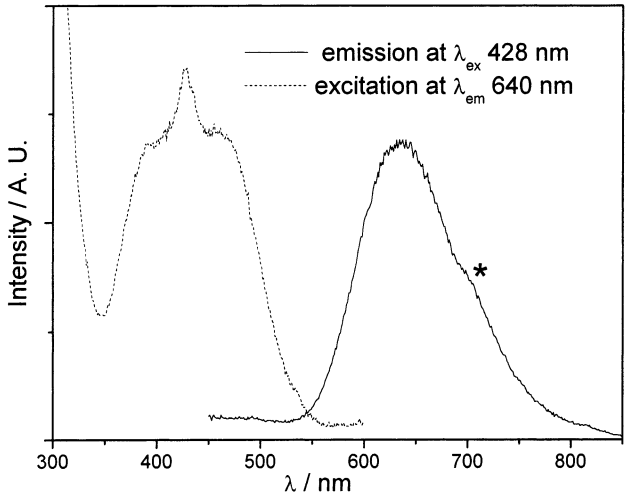

Figure 3. Excitation and emission spectra of $[^nBu_4N]$**5** in diethyl ether at 298 K (concentration 8 × 10^{-4} M; the asterisk denotes an instrumental artifact).

(8) Å in $[^nBu_4N][OsN(CH_2SiMe_3)_4]$.[23] The mean C≡C bond distance of 1.20 Å is typical for terminal acetylide groups. These structural data suggest insignificant π-conjugation among the metal−nitride and alkynyl moieties. The average osmium−carbon bond distance (2.03 Å), which is 0.1 Å shorter than that in $[OsN(CH_2SiMe_3)_4]^-$ (2.13 Å),[23] is consistent with the predicted 0.08 Å contraction for the difference between the covalent radii of sp- and sp^3-hybridized carbons.[24] The average Os−C≡C and C≡C−C(C_6H_4-*p*) bond angles are 174 and 176°, respectively, for **1** (174 and 175° for **2**; 173 and 176° for **4**), which indicate that the arylacetylide ligands remain close to linearity.

Absorption Spectroscopy. The UV−visible spectral data of **1**−**5** in dichloromethane are listed in Table 2 (see Figure 2 for **1** and **5**). The UV−visible absorption spectra of **1**−**4** are dominated by intense high-energy absorptions at 248−324 nm ($\epsilon \approx 5 \times 10^4$ dm^3 mol^{-1} cm^{-1}). Comparisons can be made with the gold(I) complex $[(Cy_3P)Au(C{\equiv}CPh)]$ (Figure 2), in which the $[Au(PCy_3)]^+$ unit is isolobal with H^+ and does not display strong absorptions at $\lambda > 250$ nm.[1c,21] The intraligand transitions of the coordinated phenylacetylides in **1** show no clear difference in energy compared to $[(Cy_3P)Au(C{\equiv}CPh)]$, which suggests insignificant perturbation by the nitridoosmium(VI) moiety on the intraligand transition. We tentatively assign the 248−324 nm bands of **1**−**4** to the ligand-localized transition(s) of the arylacetylide groups which overlap with the $p_{\pi^*}(N^{3-}) \rightarrow d_{\pi^*}(d_{xz}, d_{yz})$ charge-transfer transition.[25] The moderately intense broad absorptions at λ_{max} 403−418 nm exhibit ϵ_{max} values (1160−2400 dm^3 mol^{-1} cm^{-1}) that are noticeably higher than would be expected for spin-allowed d−d transitions. We note that **5** does not show such an absorption in the same spectral region. Previous studies demonstrated that the $d_{xy} \rightarrow d_{\pi^*}$ transitions of $[OsNX_4]^-$ (X = Cl, Br) in dichloromethane occur at λ_{max} 354−555 nm ($\epsilon \approx 40$−150 dm^3 mol^{-1} cm^{-1}).[8a] Thus, the high ϵ_{max} values for **1**−**4** cannot be ascribed to the $d_{xy} \rightarrow d_{\pi^*}$ transition only. We suggest that there may be mixing of the $d_{xy} \rightarrow d_{\pi^*}$ transition at λ_{max} 403−418 nm with the neighboring high-energy charge-transfer transition, presumably the intraligand transition of arylacetylides. As for $[ReO_2(py)_4]^+$ (py = pyridine),[26] the more intense absorption band at ~400 nm ($\epsilon \approx 1200$ dm^3 mol^{-1} cm^{-1}) is assigned to a d−d transition with intensity stealing from a higher energy charge-transfer

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Table 3. Solid-State and Solution Emission Data (400 nm Excitation)

	solid state		fluid (concn 5×10^{-4} M)	
$[^nBu_4N]^+$	298 K λ_{max}/nm; τ_0/μs	77 K λ_{max}/nm; τ_0/μs	298 K[a] λ_{max}/nm; τ_0/μs; ϕ_0	77 K[b] λ_{max}/nm; τ_0/μs
1	632; 2.9	635; 10.6	643;[c] ≤0.1; 2.4×10^{-4}	621; 14
2	608; 4.0	606; 9.7	nonemissive	613; 18
3	600; 6.6	599; 11.0	nonemissive	597; 24
4	627; 1.7	633; 7.7	nonemissive	628; 13
5	628; 7.3	631; 22.0	640;[d] 1.9; 2.4×10^{-3}	599; 28
$OsNCl_4^-$	nonemissive	nonemissive	nonemissive	nonemissive
$OsNBr_4^-$	662, 695; 0.17	655, 702; 8.9	nonemissive	662, 708; 7.7

[a] Measured in dichloromethane. [b] Measured in EtOH/MeOH (4:1). [c] Measured in benzene. [d] Measured in diethyl ether.

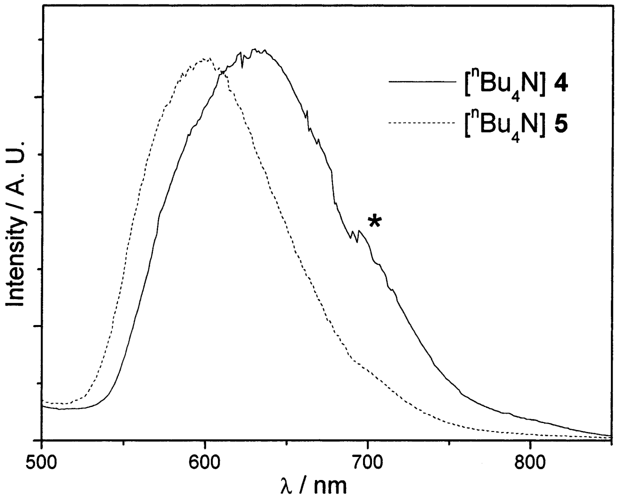

Figure 4. Emission spectra of $[^nBu_4N]$**4** and $[^nBu_4N]$**5** in glassy EtOH/MeOH (4:1) solution at 77 K (λ_{ex} 400 nm, concentration 5×10^{-4} M, normalized intensities; the asterisk denotes an instrumental artifact).

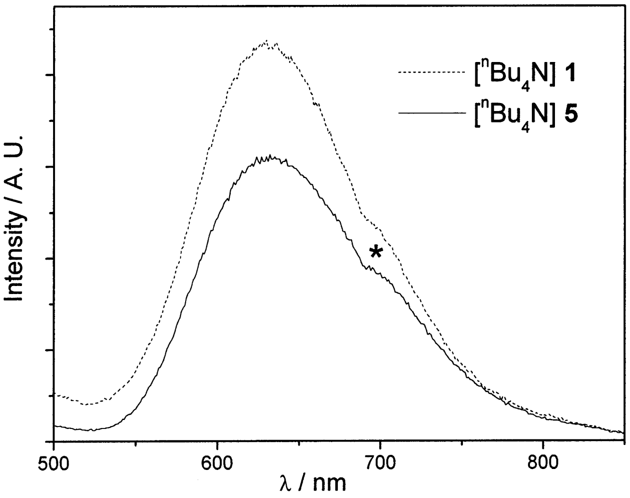

Figure 5. Solid-state emission spectra of $[^nBu_4N]$**1** and $[^nBu_4N]$**5** at 298 K (λ_{ex} 400 nm; the asterisk denotes an instrumental artifact).

transition. This is in contrast to the normal ϵ value observed for the d−d transitions in $[ReO_2(en)_2]^+$ (en = ethylenediamine) and $[ReO_2(CN)_4]^{3-}$ ($\epsilon < 50$ dm^3 mol^{-1} cm^{-1}). For **5**, the intense high-energy absorption at 253 nm ($\epsilon = 1.56 \times 10^4$ dm^3 mol^{-1} cm^{-1}) is attributed to the $p_{\pi^*}(N^{3-}) \rightarrow d_{\pi^*}(d_{xz}, d_{yz})$ charge-transfer transition, because the *tert*-butylacetylide moiety exhibits no low-lying ligand-localized excited states. The weak absorption tail from 381 to 450 nm is tentatively assigned to a $^1[(d_{xy})^2] \rightarrow {}^1[(d_{xy})^1(d_{\pi^*})^1]$ ligand-field transition, although it is difficult to accurately determine the λ_{max} value due to the low ϵ values ($\epsilon \leq 420$ dm^3 mol^{-1} cm^{-1} at $\lambda \geq 381$ nm).

Luminescence Spectroscopy. Like the previously reported $[OsNX_4]^-$ (X = Cl, Br), **1**−**4** are nonemissive in dichloromethane at room temperature. However, **1** emits very weakly at λ_{max} 643 nm with a quantum yield of 2.4×10^{-4} in a degassed benzene solution at room temperature. Complex **5** exhibits a more intense and long-lived orange luminescence at λ_{max} 640 nm ($\phi_0 = 2.4 \times 10^{-3}$; $\tau_0 = 1.9$ μs) in diethyl ether at room temperature (Figure 3). When the emission is monitored at 640 nm, the excitation spectrum exhibits a pronounced maximum at 428 nm (Figure 3), which is assigned to the $^1[(d_{xy})^2] \rightarrow {}^1[(d_{xy})^1(d_{\pi^*})^1]$ transition. Self-quenching of the emission of **5** in the 10^{-3}−10^{-2} mol dm^{-3} concentration range is evident at 298 K in Et_2O solution ($k_q = 3.6 \times 10^7$ dm^3 mol^{-1} s^{-1}). The luminescent behavior of **1**−**5** in glassy MeOH/EtOH (1:4) solutions at 77 K has also been examined (Table 3; see Figure 4 for **4** and **5**); intense orange emissions at λ_{max} 597−628 nm upon excitation at 400 nm are observed. Replacing the aryl rings by *tert*-butyl groups results in a similar emission maximum for **5** at 599 nm, suggesting that the former exerts little influence on the excited states. Lifetimes ranging from 13 (for **4**) to 28 μs (for **5**) are detected. The large Stokes shifts of the emissions from the respective lowest absorption energy and the long emission lifetimes suggest that the emission is phosphorescence. With reference to earlier reports on nitridoosmium(VI) complexes,[7,8] the excited state is $^3[(d_{xy})^1(d_{\pi^*})^1]$ in nature.

The solid-state luminescence data for **1**−**5** are listed in Table 3 (Figure 5 for **1** and **5**). At 298 K, microcrystalline samples of **1**−**5** display a structureless emission with λ_{max} in the 600−632 nm range. When the temperature is lowered to 77 K, complexes **1**−**3** and **5** show no significant changes in the emission maximum but **4** exhibits a slight red shift from 627 to 633 nm. The observed lifetimes increase from 1.7−7.3 to 7.7−22 μs upon decrease in temperature. With reference to previous reports,[7,8] the emissions are also assigned to originate from $^3[(d_{xy})^1(d_{\pi^*})^1]$ excited states.

Conclusion

Direct replacement of chloride ligands in $[OsNCl_4]^-$ by p-$RC_6H_4C{\equiv}C^-$ or $^tBuC{\equiv}C^-$ provides a straightforward pathway for generating nitridoosmium(VI) alkyl- and arylacetylide complexes. In contrast to the synthesis of nitridoosmium(VI) alkyl complexes which involves the preparation of an alkoxide precursor, the reactions described in this work afforded a series of air- and moisture-stable organoosmium(VI) nitrido complexes in reasonably high yields. The structural data reveal no significant deviations of the bond distances in the osmium nitride and acetylenic moieties. The intraligand $\pi \rightarrow \pi^*$(arylacetylide) absorptions in the electronic spectra of **1**−**4** do not undergo a notable red shift from that of [(Cy$_3$P)Au(C≡CPh)]. This further illustrates the minute interaction between the osmium nitrido and acetylenic groups. The solid-state and glassy emissions of **1**−**5** display triplet $^3[(d_{xy})^1(d_{\pi^*})^1]$ emission at λ_{max} 597−635 nm regardless of the nature of the acetylide substituents, confirming that the aryl/alkyl group has little effect upon the excited states. The excitation spectrum of **5** in diethyl ether at 298 K (concentration $\geq 8 \times 10^{-4}$ mol dm^{-3}), when the emission wavelength is monitored at 640 nm, exhibits a well-defined absorption at 428 nm, which is assigned to the $^1[(d_{xy})^2] \rightarrow {}^1[(d_{xy})^1(d_{\pi^*})^1]$ transition.

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Supporting Information Available: Listings of crystal data, atomic coordinates, calculated coordinates, anisotropic displacement parameters, and bond lengths and angles for [^{n}Bu$_4$N]**1**, [^{n}Bu$_4$N]**2**, and [^{n}Bu$_4$N]**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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