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Syntheses and Spectroscopic, Structural, Electrochemical, Spectroelectrochemical, and Theoretical Studies of Osmium(II) Mono- and Bis-Alkynyl Complexes

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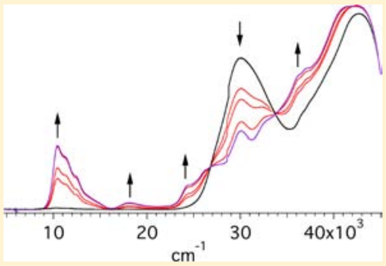
Supporting Information

ABSTRACT: The syntheses of *trans*-$[Os(C\equiv C\text{-}4\text{-}C_6H_4X)Cl(dppe)_2]$ [X = Br (**3**), I (**4**)], *trans*-$[Os(C\equiv C\text{-}4\text{-}C_6H_4X)(NH_3)(dppe)_2](PF_6)$ [X = H (**5**(PF_6)), I (**6**(PF_6))], and *trans*-$[Os(C\equiv C\text{-}4\text{-}C_6H_4X)(C\equiv C\text{-}4\text{-}C_6H_4Y)(dppe)_2]$ [X = Y = H (**7**), X = I, Y = $C\equiv CSiPr^i_3$ (**8**)] are reported, together with improved syntheses of *cis*-$[OsCl_2(dppe)_2]$ (*cis*-**1**), *trans*-$[Os(C\equiv CPh)Cl(dppe)_2]$ (**2**), and *trans*-$[Ru(C\equiv C\text{-}4\text{-}C_6H_4I)(NH_3)(dppe)_2](PF_6)$ (**9**(PF_6)) (the last-mentioned direct from *trans*-$[Ru(C\equiv C\text{-}4\text{-}C_6H_4I)Cl(dppe)_2]$), and single-crystal X-ray structural studies of **2**–**4**, **5**(PF_6), **6**(PF_6), and **7**. Ammine complexes **5**(PF_6)/**6**(PF_6) are shown to afford a facile route to both symmetrical (**7**) and unsymmetrical (**8**) osmium bis(alkynyl) complexes. A combination of cyclic voltammetry, UV–vis–NIR spectroelectrochemistry, and time-dependent density functional theory (TD-DFT) has permitted identification and assignment of the intense transitions in both the resting state and the oxidized forms of these complexes. Cyclic voltammetric data show fully reversible oxidation processes at 0.32–0.42 V (**3**, **4**, **7**, **8**) (with respect to ferrocene/ferrocenium 0.56 V), assigned to the (formal) $Os^{II/III}$ couple. The osmium(III) complex (di)cations $\mathbf{5}^{2+}$ and $\mathbf{7}^{+}$ were obtained by in situ oxidation of $\mathbf{5}^{+}$ and **7** using an optically transparent thin-layer electrochemical (OTTLE) cell. The UV–vis–NIR optical spectra of $\mathbf{5}^{2+}$ and $\mathbf{7}^{+}$ reveal low-energy bands in the near IR region, in contrast to $\mathbf{5}^{+}$ and **7** which are optically transparent at frequencies below 22 000 cm^{-1}. TD-DFT calculations on *trans*-**1**, **2**, $\mathbf{5}^{+}$, and **7** and their oxidized forms suggest that the lowest-energy transitions are chloro-to-metal charge transfer (*trans*-**1**), chloro-to-phenylethynyl charge transfer (**2**), and metal-to-phenylethynyl charge transfer ($\mathbf{5}^{+}$, **7**) in the resting state and chloro-to-metal charge transfer (*trans*-$\mathbf{1}^{+}$), phosphorus-to-metal charge transfer ($\mathbf{5}^{2+}$), alkynyl-to-metal charge transfer ($\mathbf{7}^{+}$), or phenylalkynyl-centered $\pi \rightarrow \pi^*$ ($\mathbf{2}^{+}$) following oxidation. The presence of intense CT bands in the resting states and oxidized states and their significantly different nature across the two states, coupled to their strong charge displacement suggest that these species have considerable potential as electrochemically switchable nonlinear optical materials, while the facile unsymmetrical bis(alkynyl)osmium(II) construction suggests potential in construction of multistate heterometallic modular assemblies.



INTRODUCTION

Metal alkynyl complexes have attracted significant recent interest, the π system of the $C\equiv C$ group facilitating efficient delocalization between the metal and the alkynyl ligand. Such complexes may have applications in nonlinear optics or as conducting materials or artificial light-harvesting chromophores, among a range of possibilities.[1−3] While there are examples of alkynyl complexes of essentially all of the metals of the transition series, ruthenium(II) alkynyl complexes have been of special interest because they have been shown to be highly efficient as nonlinear optical (NLO) materials[4−6] and because bis(alkynyl)ruthenium(II) complexes (both symmetrical and unsymmetrical) are readily accessible using straightforward protocols under mild conditions,[7−13] the latter rapidly affording a diversity of oligoruthenium structures.[7−16] Osmium(II) alkynyl complexes are potentially of similar interest, particularly because optical nonlinearities have been shown to increase in group 8 metal alkynyl complexes in proceeding from the 4d to the 5d metal,[17] but while many mono(alkynyl) complexes of osmium(II) have appeared,[18−23] there are far fewer reports of bis(alkynyl) complexes[24−33] and only one of unsymmetrical bis(alkynyl) complexes, synthesized in ca. 30% yields from a reaction involving alkynyltin reagents.[34] We report herein a facile route into unsymmetrical osmium(II) bis(alkynyl) complexes via a procedure that should permit the use of this potentially difunctional osmium unit in a diversity of applications. We also report studies of the spectroscopic and electrochemical properties of the new complexes and theoretical studies rationalizing the spectroscopic observations, highlighting their potential as molecular optical and nonlinear optical switches, together with comparisons, where appropriate, to data from related ruthenium alkynyl complexes.

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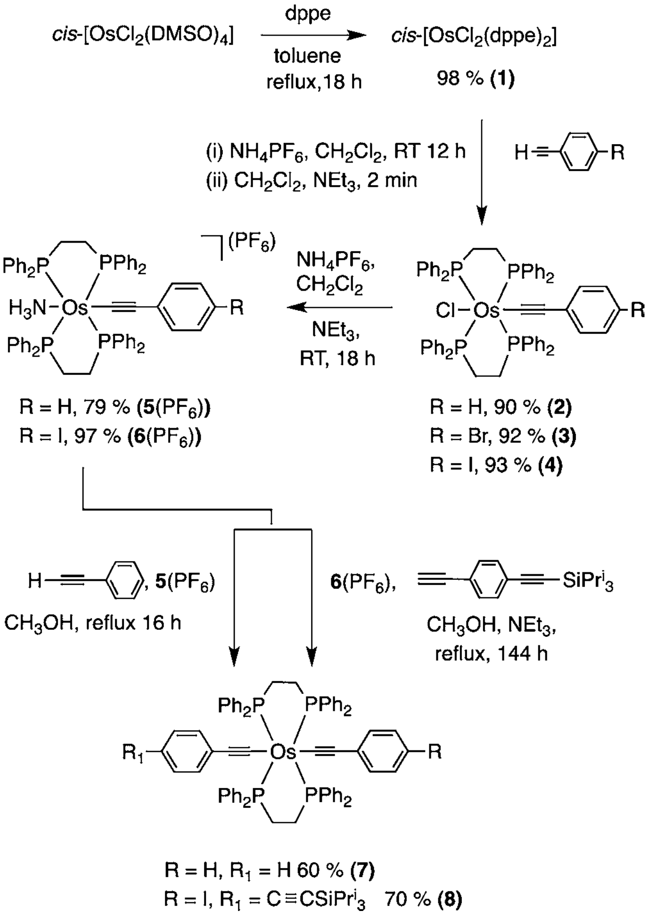
■ RESULTS

The mono(alkynyl) complex *trans*-[Os(C≡CPh)Cl(dppe)$_2$] (**2**) has been prepared previously from *cis*-[OsCl$_2$(dppe)$_2$] (*cis*-**1**) and phenylacetylene in refluxing toluene in the presence of ammonium hexafluorophosphate for 18 h.[20] The starting material, *cis*-[OsCl$_2$(dppe)$_2$] (*cis*-**1**), is itself available in 40% yield from reaction between [Os$_2$(μ-Cl)$_3$(PEt$_2$Ph)$_6$]Cl and dppe at 200 °C in the absence of solvent, although no spectroscopic data were reported.[35] In seeking a more straightforward procedure to access *cis*-**1** and thereafter analogues of **2**, we found that heating *cis*-[OsCl$_2$(DMSO)$_4$] with dppe in refluxing toluene overnight affords *cis*-**1** in 98% yield (Scheme 1). We also noted that **2** can be formed under significantly milder conditions and in greater yield than previously reported (refluxing toluene, 44% (ref 20), c.f. room temperature, dichloromethane, 90% (present work)).

Scheme 1. Syntheses of Complexes 1–4, 5(PF$_6$), 6(PF$_6$), 7, and 8



We were unable to prepare bis(alkynyl) complexes of osmium(II) by extending the existing and successful ruthenium(II) bis(alkynyl) complex synthetic methodology (reaction of a ruthenium(II) alkynyl chloro complex with an alkyne in the presence of base and a large noncoordinating anion)[36,37] but found that stirring *trans*-[Os(C≡CPh)Cl(dppe)$_2$] (**2**) with ammonium hexafluorophosphate and triethylamine in dichloromethane at room temperature for 18 h afforded the ammine complex *trans*-[Os(C≡CPh)(NH$_3$)(dppe)$_2$](PF$_6$) (**5**(PF$_6$)), which on reaction with phenylacetylene in refluxing methanol gave the desired symmetrical bis(alkynyl) complex, *trans*-[Os(C≡CPh)$_2$(dppe)$_2$] (**7**), in excellent yield (Scheme 1). Complexes **3** and **4**, containing potentially functionalizable bromo/iodophenylalkynyl ligands, were synthesized in an analogous fashion to **2**. When treated with NH$_4$PF$_6$/triethylamine in refluxing dichloromethane, complex **4** afforded the (ammine)(iodophenylalkynyl) complex **6**(PF$_6$), which was reacted with 4-ethynyl-1-triisopropylsilylethynylbenzene in a refluxing methanol/triethylamine mixture to afford the unsymmetrical bis(alkynyl) complex **8**. Both **7** and **8** were obtained in good yields; phenylacetylene formed the corresponding bis(alkynyl) complex **7** much faster than [4-(ethynylphenyl)ethynyl]tri(isopropyl)silane formed **8**, but as a comparatively cheap and liquid phase reagent, phenylacetylene was employed in greater than 30-fold excess. Synthesis of **8** was a slower reaction and aided by addition of triethylamine to convert the intermediate vinylidene complex into the product and thereby minimize decomposition. Complexes **2**–**4**, **5**(PF$_6$), **6**(PF$_6$), **7**, and **8** were characterized by the usual spectroscopic techniques (Experimental Section), and the identities of **2**–**4**, **5**(PF$_6$), **6**(PF$_6$) and **7** were confirmed crystallographically (Figures 1 and S1–S5, Supporting Information), with all bond lengths and angles found to be within previously established ranges for related complexes.[18−23]

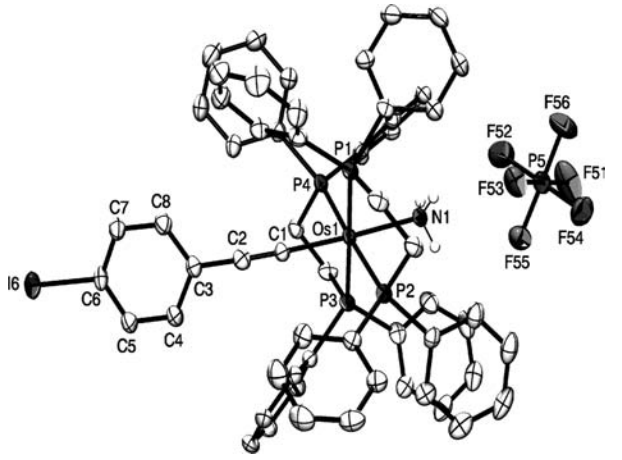
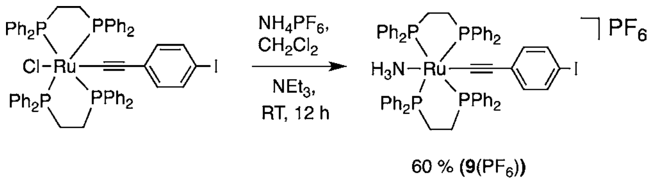


Figure 1. Molecular structure and atomic numbering scheme for *trans*-[Os(C≡C-4-C$_6$H$_4$I)(NH$_3$)(dppe)$_2$](PF$_6$) (**6**(PF$_6$)). Thermal ellipsoids are displayed at the 40% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Angstroms): Os–P(1) 2.3741(9), Os–P(2) 2.3735(9), Os–P(3) 2.3961(9), Os–P(4) 2.3859(9), Os–N 2.244(3), Os–C(1) 2.042(4), C(1)–C(2) 1.199(5).

While undertaking the present studies, we noted formation of the (ammine)(alkynyl) complex *trans*-[Ru(C≡C-4-C$_6$H$_4$I)(NH$_3$)(dppe)$_2$](PF$_6$) (**9**(PF$_6$)) from the chloro precursor *trans*-[Ru(C≡C-4-C$_6$H$_4$I)Cl(dppe)$_2$] under mild conditions (Scheme 2). Related complex cations *trans*-[Ru(C≡CR)-

Scheme 2. Synthesis of *trans*-[Ru(C≡C-4-C$_6$H$_4$I)(NH$_3$)(dppe)$_2$](PF$_6$) (9(PF$_6$))



$(NH_3)(dppe)_2]^+$ (R = Ph, Bu^n, $SiMe_3$) have been reported as forming in excellent yields (73−81%) from reactions of the bis(alkynyl) complexes *trans*-[Ru(C≡CR)$_2$(dppe)$_2$] with 5 equiv of NH_4PF_6 in CH_2Cl_2 for 12 h.[36] The same products were obtained from reaction of *trans*-[Ru(C≡CR)Cl(dppe)$_2$] and 2 equiv of NH_4PF_6 after 72 h, but no yields were given.[37] Addition of triethylamine in the present reaction affords good yields of **9** in a reasonable reaction time. Complex **9**(PF_6) was characterized by a combination of IR, UV−vis, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, ESI MS, and satisfactory microanalyses (Experimental Section).

Cyclic voltammetric data for complexes **2**−**4**, **5**(PF_6), **6**(PF_6), **7**, **8**, and **9**(PF_6) are collected in Table 1. CVs of the (4-halophenylalkynyl) complexes *trans*-[Os(C≡C-4-C_6H_4X)-Cl(dppe)$_2$] (X = Br (**3**), Cl (**4**)) each contain a single reversible oxidation process (0.37 V) that can be assigned to a formal one-electron oxidation at the Os^{II} center by comparison to the reported data for the related *trans*-[Os(C≡CPh)Cl(dppe)$_2$] (**2**);[20] not surprisingly, proceeding to the cationic (ammine)-(phenylalkynyl) derivative *trans*-[Os(C≡CPh)(NH_3)-(dppe)$_2$](PF_6) (**5**(PF_6)) results in a significant anodic shift to 0.84 V. The Os$^{II/III}$ oxidation is somewhat easier (0.32 V) for the bis(alkynyl) complex *trans*-[Os(C≡CPh)$_2$(dppe)$_2$] (**7**) compared to the mono(alkynyl) example **2**, whereas the same process for the analogous (4-iodophenylalkynyl)-containing complex *trans*-[Os(C≡C-4-C_6H_4I)(C≡CC_6H_4-4-C≡CSiPr$^i_3$)(dppe)$_2$] (**8**) is shifted to slightly more positive potentials (0.42 V). Proceeding from the osmium-containing ammine complex **6**(PF_6) to its ruthenium analogue **9**(PF_6) results in the anticipated increase in difficulty of oxidation usually observed on replacing a 5d metal with its 4d group member. Complexes **7** and **8** exhibit a second and significantly less reversible oxidation process at 1.22 and 1.25 V, respectively.

Table 1. Cyclic Voltammetric Data for Complexes 2−4, 5(PF$_6$), 6(PF$_6$), 7, 8, and 9(PF$_6$)

complex	$E_{1/2}$ [i_{pc}/i_{pa}]^a (V)
trans-[Os(C≡CPh)Cl(dppe)$_2$] (**2**)	0.36 [1]^b
trans-[Os(C≡C-4-C_6H_4Br)Cl(dppe)$_2$] (**3**)	0.37 [1]
trans-[Os(C≡C-4-C_6H_4I)Cl(dppe)$_2$] (**4**)	0.37 [1]
trans-[Os(C≡CPh)(NH_3)(dppe)$_2$](PF_6) (**5**(PF_6))	0.84 [1]
trans-[Os(C≡C-4-C_6H_4I)(NH_3)(dppe)$_2$](PF_6) (**6**(PF_6))	0.87 [1]
trans-[Os(C≡CPh)$_2$(dppe)$_2$] (**7**)	0.32 [1], 1.22 [0.8]
trans-[Os(C≡C-4-C_6H_4I)(C≡CC_6H_4-4-C≡CSiPr$^i_3$)(dppe)$_2$] (**8**)	0.42 [1], 1.25 [0.9]
trans-[Ru(C≡C-4-C_6H_4I)(NH_3)(dppe)$_2$](PF_6) (**9**(PF_6))	1.05 [1]

^{a}CH_2Cl_2, Ag/AgCl reference electrode, platinum working and auxiliary electrodes; ferrocene/ferrocenium couple at 0.56 V, ΔE_p = 0.09 V. ^{b}Reference 20.

In situ oxidation of complex cation **5**$^+$ and complex **7** in an optically transparent thin-layer electrochemical (OTTLE) cell affords a convenient method for obtaining electronic spectra of the corresponding (di)cationic species **5**$^{2+}$ and **7**$^+$, the results being summarized in Table 2 together with those for **2**/**2**$^+$ [20] and representative spectra being shown in Figures S6, Supporting Information (**5**(PF_6)), and 2 (**7**). In each case, oxidation results in the appearance of a low-energy band in the region 10 000−15 000 cm^{-1}, with that for the bis(alkynyl) complex cation **7**$^+$ being particularly intense.

Table 2. UV−vis−NIR Spectral Data Obtained on Electrolysis of 2, 5$^+$, and 7 in an OTTLE Cell

complex	ν_{max} (cm^{-1}) [ε] (10^4 M^{-1} cm^{-1})^a
2	30 865 [2.5]^b
2$^+$	14 000 [0.9]^b
5$^+$	32 930 [2.4]
5^{2+}	14 775 [0.4], 16 490 br, sh [0.4], 25 222 [0.5], 26 680 sh [0.6], 29 545 [1.2]
7	29 910 [2.8], 42 590 [3.8]
7$^+$	10 435 [1.2], 11 330 sh [1.0], 12 385 sh [0.7], 18 070 [0.2], 24 420 [0.5], 26 370 [0.8], 30 100 [1.5], 41 220 [3.8]

^{a}Electronic spectra were obtained at 298 K in CH_2Cl_2 using potentials ca. 200 mV beyond $E_{1/2}$ for each couple. ^{b}Reference 20.

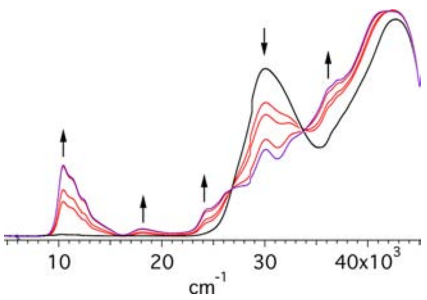


Figure 2. UV−vis−NIR spectral changes during the first electrochemical oxidation step of *trans*-[Os(C≡CPh)$_2$(dppe)$_2$] (**7**).

Bands in the linear absorption spectra of the complexes and their oxidized forms can be assigned from DFT calculations (Tables S1 (*trans*-**1**, **2**) and S2 (**5**$^+$, **7**), Supporting Information). Computed electronic spectra for the formally Os^{II} species, determined at the SAOP/TZP//PBE/TZP level of theory, are characterized by negligible spectral intensity below 25 000−30 000 cm^{-1}, in broad agreement with laboratory spectra. Oxidation of these complexes results in the emergence of reasonably prominent peaks below 20 000 cm^{-1}. Using the example of **7**$^+$ (Figure 2; results for **5**$^{2+}$ are broadly similar), the experimental spectroelectrochemical outcomes show peaks due to the Os^{III} species at 10 435, 18 070, and 24 420 cm^{-1}, which compare well with computed peaks at 9500 (^{6}A, 1.224 eV, f = 0.081), 17 500 (^{13}A, 2.154 eV, f = 0.082), and 26 000 cm^{-1} (^{23}A, 3.311 eV, f = 0.058). These transitions are characterized by β-spin electron promotion to the virtual 145*b* orbital (an orbital dominated by C_2 π and Os d character) from, respectively, the 139*b*, 133*b*, and 123*b* orbitals of **7**$^+$, with these occupied orbitals dominated by C_2 π, axial phenyl, and phosphine phenyl character to varying degrees (Figure 3). Thus, the most prominent spectral features of **7**$^+$ are categorizable, to some degree, as ligand-to-metal charge-transfer processes. In contrast, the lowest-frequency major peak in the laboratory spectrum of the analogous Os^{II} species, **7**, is matched in the computed UV−vis spectrum with transition ^{23}A (3.840 eV, f = 0.085), for which the dominant contributions are from the 144*b* (occupied) and 152*b* (virtual) orbitals, with 144*b* dominated by Os d and C_2 π character and 152*b* possessing C_2 π* character. This transition is thus a π-to-π* excitation with a contribution from metal-to-ligand charge transfer.

■ DISCUSSION

As discussed above, unsymmetrical bis(alkynyl) complexes have attracted significant interest as crucial building blocks in the

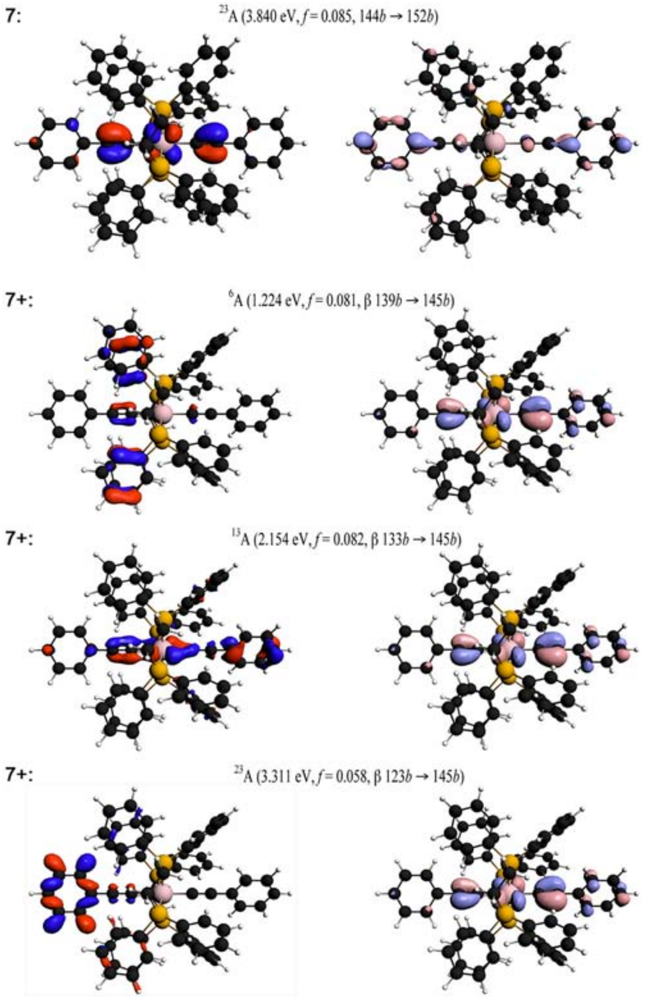


Figure 3. Orbital diagrams for **7** and **7**$^+$.

flexible construction of π-delocalizable organic frameworks with embedded ligated metal centers. To achieve this composition, stepwise replacement of chloro by alkynyl ligands at bis(bidentate diphosphine)ruthenium centers has been exploited by several groups.[7,8,14,33,34,37,38] The most broadly successful procedure to unsymmetrical bis(alkynyl) complexes involves synthesis of a chloro alkynyl complex, either in "one pot" from a dichloro precursor in the presence of $NaPF_6$ or via the intermediacy of an isolable five-coordinate chlorobis(diphosphine)ruthenium cation followed by reaction of the alkynyl chloro complex with a second 1-alkyne in the presence of $NaPF_6$ and NEt_3. Despite the considerable interest in such unsymmetrical bis(alkynyl) complexes, there had been only one report of an unsymmetrical bis(alkynyl)osmium complex before the present work (in moderate (30%) yields and involving potentially toxic alkynyltin reagents). The significant and increasing interest that has been shown in their ruthenium analogues over the past 15 years suggests that the high-yielding procedure into unsymmetrical bis(alkynyl) osmium complexes presented herein, which should in principle afford similar diversity in composition to that available in the ruthenium system, is timely and ripe for exploitation. Indeed, we recently (a) employed this methodology to synthesize *trans*-[Os(C≡C-4-C_6H_4I)(C≡CC_6H_4-4-C≡CC_6H_4-4-C≡$CSiPr^i_3$)(dppe)$_2$], a phenylethynyl-containing higher homologue of **8**, and (b) successfully carried out Sonogashira coupling of trimethylsilyacetylene at the iodo functionality of both **8** and its higher homologue as the next step toward osmium-embedded π-delocalizable frameworks.[39]

Although no (ammine)(alkynyl)osmium complexes have been prepared before the present studies, a series of ruthenium complex cations, *trans*-[Ru(C≡CR)(NH_3)(dppe)$_2$]$^+$ (R = Ph, Bu^n, $SiMe_3$), has been reported in pioneering studies by Dixneuf, Touchard, and co-workers from reactions of either the mono(alkynyl) *trans*-[Ru(C≡CR)Cl(dppe)$_2$][37] or the bis(alkynyl) *trans*-[Ru(C≡CR)$_2$(dppe)$_2$][36] with NH_4PF_6 in CH_2Cl_2. The latter reaction was carried out under mild conditions and resulted in high yields, in contrast to the former reaction (the analogue of the present osmium procedure), which proceeded very slowly (72 h, with no yields reported). The procedure to synthesize a ruthenium example (**9**(PF_6)) described in the present work improves upon this earlier report. Although formation of unsymmetrical bis(alkynyl)ruthenium complexes generally proceeds in a straightforward fashion (vide supra), it is possible that the high-yielding formation of an (ammine)(alkynyl)ruthenium complex direct from an (alkynyl)(chloro) precursor demonstrated in the present work may prove useful in the synthesis of "difficult" unsymmetrical bis(alkynyl)ruthenium complex examples (e.g., complexes with one 4-nitrophenylethynyl ligand for which formation of the bis(4-nitrophenylethynyl) complex can be observed when employing the established procedure to synthesize an unsymmetrical bis(alkynyl) complex).[40]

Structural studies of **2**−**4** provide key reference data for mono(alkynyl)osmium complexes within this coligand environment. The subtle variation across the three complexes (replacing phenylethynyl 4-H (**2**) with 4-Br (**3**) or 4-I (**4**)) results in no significant effect on Os−P, Os−Cl, or Os−C(1) distances, while metal variation (replacing Os by Ru in proceeding from **2** to its Ru-containing analogue) results in a contraction in the M−Cl vector [from 2.5017(7) to 2.4786(13) Å] but leaves the other metal-containing bonds essentially invariant; a less significant shortening of the M−Cl vector was observed in $MCl(PPh_3)_2(\eta^5\text{-}C_5H_5)$ [M = Os 2.460(2) Å, Ru 2.453(2) Å].[41] Structural studies of **5**(PF_6) and **6**(PF_6) provide the first such data for (ammine)bis(diphosphine)osmium(II) complexes. As with **2** and **4**, the phenylethynyl 4-H (**5**(PF_6)) for 4-I (**6**(PF_6)) replacement results in no significant changes to the metal-containing bond distances, while metal replacement in *trans*-[M(C≡CPh)(NH_3)(dppe)$_2$]PF_6 results in a small variation (within 3 esd) in the M−C(1) vector [M = Os 2.043(7) Å, Ru 2.014(5) Å[36]] but no difference in the M−NH_3 distance. Structural study of **7** affords the opportunity for bond length comparison at bis(alkynyl)bis(diphosphine)metal centers, for which the M−P vectors and M−C(1) distances are equivalent within the 3σ confidence level. Finally, the series **2**, **5**, and **7** permits assessment of the effect of trans ligand variation at Os(C≡CPh)dppe)$_2$ centers on structural parameters. There is a significant lengthening of the Os−C(1) distance in proceeding from **2** and **5** to **7**, consistent with the trans influence series of $C_2Ph > NH_3$, Cl in these formally Os^{II} complexes.

The oxidation potentials for complexes **2**−**4** (*trans*-[Os(C≡C-4-C_6H_4X)Cl(dppe)$_2$], X = H, Br, I) are essentially invariant, as expected for relatively subtle modifications at the phenylalkynyl ligand. Proceeding from these monoalkynyl complexes to the bis-alkynyl complex **7** results in a 0.04−0.05 V increase in ease of oxidation, in contrast to the analogous ruthenium complexes for which no variation in oxidation potential for this structural modification was noted;[12] we previously commented on the lack of ligand additivity effects in both electrochemical and nonlinear optical parameters in related complexes.[7] The ammine-containing complexes **5**(PF_6) and **6**(PF_6) are oxidized at significantly more positive potentials, with little variation seen for the 4-H for 4-I variation in arylalkynyl ligand in proceeding from the former to the latter. The CVs of the bis(alkynyl)osmium complexes **7** and **8** differ from those of the alkynyl chloro complexes and ammine alkynyl complex cations in that they display a second quasi-reversible oxidation process. Unlike related iron alkynyl complexes, theoretical studies have suggested that oxidation processes at ruthenium alkynyl complexes should not be regarded as metal centered but rather involve orbitals with significant alkynyl ligand character. This is also likely to be the case for the present osmium complexes, but the definitive assignment of the differing behavior of the bis(alkynyl)osmium complexes **7** and **8** to the existence of two alkynyl ligands and to significant alkynyl ligand involvement in the second oxidation processes necessitates further theoretical studies.

The osmium alkynyl complexes have been shown to undergo reversible oxidation processes at potentials ca. 0.2 V removed from those of ruthenium complexes with analogous ligand environments. Indeed, the range of oxidation potentials exhibited by the osmium complexes in the present study (0.3−0.4 V for the neutral species and 0.8−0.9 V for the ammine-containing cations) together with those exhibited by related ruthenium complexes (0.5−0.6 V for the neutral species and 1.05 V for **9**(PF_6)) and coupled with the facile unsymmetrical bis(alkynyl) complex formation demonstrated in the present work suggests the possibility of constructing modular heterometallic assemblies with multiple accessible and fully reversible oxidation processes. Note that the typical ruthenium alkynyl complex redox potentials (0.5−0.6 V) can be extended by introduction of strongly polarizing substituents on the phenylethynyl ring (both electron donating and withdrawing in nature; for example, the oxidation potentials for *trans*-[Ru(C≡C-4-C_6H_4X)Cl(dppe)$_2$] span the range from 0.24 (X = NMe_2) to 0.73 V (X = NO_2).[42] We have taken steps to couple redox-active metal alkynyl modules using iron and ruthenium centers, the resultant species (η^5-C_5Me_5)(dppe)Fe-(C≡C-1,4-C_6H_4C≡C)-*trans*-[RuX(dppe)$_2$] (X = Cl, C≡C-1,4-C_6H_4C≡CH) being used to demonstrate cubic NLO switching in solution[43,44] and stepwise oxidation supported on hydrogenated silicon,[45] both outcomes exploiting the reversible oxidation at the iron center which occurs at −0.3 V. Modular construction of a linear heterotrimetallic complex that would possess well-separated and fully reversible oxidation processes accompanied by strong linear and nonlinear optical changes should now be achievable.

As with the ruthenium system, oxidation in the present osmium complexes is accompanied by strong changes in their linear optical spectra and, in particular, the appearance of low-energy optical bands in a spectral range that is transparent in the resting state (i.e., these osmium complexes behave as molecular optical switches). The pronounced structure in the NIR bands of the oxidized bis(alkynyl species (Figure 2) is distinctive and similar to that seen with related ruthenium complexes (see, for example, ref 46). In the ruthenium complexes *trans*-[Ru(C≡CPh)$_2$(dppe)$_2$], *trans*-[Ru(C≡C-4-C_6H_4C≡CPh)(C≡CPh)(dppe)$_2$], and *trans*-[Ru(C≡C-4-C_6H_4OMe)$_2$(16-TMC)] (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane), reversible oxidation afforded cationic species exhibiting similar NIR bands with structure assigned to vibronic progressions that are ν(C≡C) in character and with $\Delta\nu$ values of 2050,[46] 2040,[46] and 1790 cm^{-1},[47] respectively. In the osmium system, a similar ν(C≡C) vibronic progression may be present if there are two distinct transitions contributing to the absorption band at 10 435 cm^{-1} (with $\Delta\nu$ 1950 cm^{-1}), but we have not attempted deconvolution of this band.

TD-DFT calculations have been employed to suggest the origin of the optical absorption bands in both the resting and the oxidized states of the osmium complexes and confirm their charge-transfer character. The results obtained can be compared with those gleaned for the analogous Ru-containing compounds[46] (while being mindful of the additional approximation employed with the latter, namely, replacement of the diphosphines with PH_3 ligands). The most intense transitions found for *trans*-**1** are characterizable as ligand (primarily chloride)-to-metal charge transfer, in reasonable agreement with the earlier study on the Ru^{II} analogue where the most intense transitions were also chloride-to-metal charge transfer in character. For *trans*-$\mathbf{1}^+$, the low-energy transition at 8300 cm^{-1} is also ligand-to-metal charge transfer, involving electron promotion from the dppe Ph π systems to Os, while the transitions clustered around 28 000−32 000 cm^{-1} are more or less evenly distributed between ligand-to-metal charge transfer and charge migration from Cl to P; no calculations were undertaken on the analogous Ru-containing cation. For **2**, the predominance of ligand-to-metal CT in our results is at some variance with characterization of MLCT features for the Ru^{II} analogue, although the peak positions for the Ru^{II} and Os^{II} structures do show close correspondence. The spectrum for $\mathbf{2}^+$ is found to contain both LMCT and MLCT features, with the lowest-energy transition (at 17 921 cm^{-1}) attributable to a π-to-π^* feature centered on the phenylethynyl moiety. In contrast, the spectrum of the ruthenium(III) analogue contains a low-energy band at 12 040 cm^{-1} assigned to chloro-to-metal charge transfer as well as a higher-energy band at 16 980 cm^{-1} assigned to π-to-π^* on the phenylethynyl ligand and thereby assigned analogously to that seen with the osmium complex. The present studies have assigned the low-energy bands for **7** as OsC_2 π to Ph π^*, broadly similar to the analogous assignment in the spectrum of the bis(phenylethynyl)ruthenium analogue, while the low-energy transition for $\mathbf{7}^+$ has been assigned as alkynyl-to-metal charge transfer, again in agreement with the earlier calculations on the ruthenium system. Overall, there is a close correspondence in the low-energy band assignments of the Ru/Os complex and complex cation pairs.

As has been seen with ruthenium analogues[12,15,41] and suggested above, the substantial changes in linear optical properties accompanied by significant charge displacement suggest that these osmium alkynyl complexes have considerable potential as redox-switchable nonlinear optical materials and in modular assemblies as multistate NLO switches. Studies directed at exploring these possibilities are currently underway.

■ EXPERIMENTAL SECTION

General. Reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques with no precautions to exclude air during workup. Dichloromethane was dried by distilling over calcium hydride, methanol was dried according to the literature,[48] and all other solvents were used as received. "Petrol" refers to a fraction of petroleum ether of boiling range 60−80 °C. Solvents and reagents were obtained from commercial sources and used as received unless otherwise indicated. [(4-Ethynylphenyl)ethynyl](triisopropyl)silane,[49] 1-bromo-4-ethynylbenzene,[50] 1-iodo-4-ethynylbenzene,[51] and *cis*-[OsCl$_2$(DMSO)$_4$][52] were prepared according to the literature. Electrospray ionization mass spectra (ESIMS) were obtained using a VG Quattro II triple quadrupole MS instrument; peaks are reported as *m/z* (assignment, relative intensity). Microanalyses were carried out by the Microanalysis Service Unit, Australian National University. Infrared spectra were recorded as dichloromethane solutions using a Perkin-Elmer System 2000 FT-IR. ^{1}H (300 MHz), ^{13}C{^{1}H} (75 MHz), and ^{31}P (121 MHz) NMR spectra were recorded using a Varian Mercury-300 FT-NMR spectrometer and referenced to residual chloroform (7.26 (^{1}H) and 77.0 ppm (^{13}C)) or external 85% H$_3$PO$_4$ (0.0 ppm); vtt refers to a virtual triplet of triplets. UV−vis spectra were recorded as dichloromethane solutions in 1 cm quartz cells using a Cary 5 spectrophotometer. Cyclic voltammetry measurements were recorded using an e-corder and EA161 potentiostat from eDaq Pty Ltd. Measurements were carried out at room temperature using Pt disk working, Pt wire auxiliary, and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (i_{pc}/i_{pa} = 1, ΔE_p 0.09 V). Scan rates were typically 100 mV s^{-1}. Electrochemical solutions contained 0.1 M (NBu$^n{}_4$)(PF$_6$) and ca. 10^{-3} M complex in dried and distilled dichloromethane. Solutions were purged and maintained under a nitrogen atmosphere. Electronic spectra were recorded using a Cary 5 spectrophotometer. Solution spectra of the oxidized species were obtained at 298 K by electrogeneration in an optically transparent thin-layer electrochemical cell with potentials ca. 200 mV beyond $E_{1/2}$ for each couple to ensure complete electrolysis; solutions were made up in 0.3 M (NBu$^n{}_4$)(PF$_6$) in dichloromethane. All processes displayed isosbestic points and were reversible on application of the appropriate voltage.

Synthesis of cis-[OsCl$_2$(dppe)$_2$] (cis-1). This complex has been reported previously,[35] the following being a higher-yielding procedure. A mixture of 1,2-bis(diphenylphosphino)ethane (527 mg, 1.325 mmol) and *cis*-[OsCl$_2$(DMSO)$_4$] (380 mg, 0.662 mmol) was heated in refluxing toluene (40 mL) for 18 h. The solution was allowed to cool to room temperature. The toluene-insoluble component was collected by filtration and washed with diethyl ether. The cream powder was identified as *cis*-**1** (690 mg, 98%).^{1}H NMR: δ 6.65−8.14 (m, 40H, Ar), 2.50−2.92 (m, 8H, CH$_2$). ^{31}P NMR: δ 7.6 (t, $^2J_{PP}$ = 6 Hz), 5.3 (t, $^2J_{PP}$ = 6 Hz).

*Synthesis of trans-[Os(C≡CPh)Cl(dppe)$_2$] (**2**).* This complex has been reported previously,[20] the following being a higher-yielding procedure. A mixture of *cis*-[OsCl$_2$(dppe)$_2$] (*cis*-**1**, 600 mg, 0.567 mmol), NH$_4$PF$_6$ (115 mg, 0.709 mmol), and phenylacetylene (579 mg, 5.67 mmol) was stirred at room temperature in dichloromethane (100 mL) for 18 h. Triethylamine (5 mL) was added, and the solution was reduced in volume to 50 mL. Methanol was added, and the resulting precipitate was collected and washed with *n*-hexane (50 mL), affording **2** as a yellow powder (573 mg, 90%), identified by comparison to the literature[20] (^{31}P NMR δ 16.4).

*Synthesis of trans-[Os(C≡C-4-C$_6$H$_4$Br)Cl(dppe)$_2$] (**3**).* A mixture of *cis*-[OsCl$_2$(dppe)$_2$] (*cis*-**1**, 800 mg, 0.756 mmol), NH$_4$PF$_6$ (154 mg, 0.945 mmol), and 1-bromo-4-ethynylbenzene (206 mg, 1.13 mmol) was stirred in dichloromethane (100 mL) for 12 h. Triethylamine (5 mL) was added, and the solution was reduced to 50 mL. The solution was added to methanol (150 mL), precipitating a solid that was collected and washed with *n*-hexane (50 mL), affording **3** as a yellow powder (836 mg, 92%). ESI MS: 1199 ([M − Cl + CH$_3$OH]$^+$, 100). Anal. Calcd for C$_{60}$H$_{52}$BrClOsP$_4$: C, 59.93; H, 4.36. Found: C, 60.22; H, 4.28. UV−vis: λ 340 nm, ε 21 000 M^{-1} cm^{-1}. IR: 2067 cm^{-1} ν(OsC≡C). ^{1}H NMR: δ 6.45−7.51 (m, 44H, Ar), 2.62 (m, 8H, CH$_2$). ^{31}P NMR: δ 16.2. ^{13}C NMR: δ 135.7, 134.8 (C$_{47}$, C$_{43}$, vtt,$|^1J_{PC} + {}^3J_{PC}|$ = 22 Hz), 134.3, 134.2 (C$_{48}$, C$_{44}$), 132.0 (C$_{37}$), 130.3 (C$_{36}$), 129.9 (C$_{38}$), 129.0, 128.8 (C$_{50}$, C$_{46}$), 127.2 and 126.9 (C$_{49}$, C$_{45}$), 115.5 (C$_{35}$), 108.3 (C$_{39}$), 105.5 (C$_{40}$, quint, $^2J_{PC}$ = 12 Hz), 31.4 (C$_{42}$, vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 26 Hz).

*Synthesis of trans-[Os(C≡C-4-C$_6$H$_4$I)Cl(dppe)$_2$] (**4**).* A mixture of *cis*-[OsCl$_2$(dppe)$_2$] (*cis*-**1**, 3.65 g, 3.45 mmol), NH$_4$PF$_6$ (703 mg, 4.31 mmol), and 1-iodo-4-ethynylbenzene (1.18 g, 5.17 mmol) was stirred in dichloromethane (150 mL) for 12 h. Triethylamine (10 mL) was added, and the solution was reduced in volume to 80 mL and added to methanol, precipitating a product that was collected and washed with *n*-hexane (50 mL) to give **4** as a yellow powder (4.02 g, 93%). ESI MS: 1247 ([M − Cl + CH$_3$OH]$^+$, 100). Anal. Calcd for C$_{60}$H$_{52}$ClIOsP$_4$: C, 57.67; H, 4.19. Found: C, 57.59; H, 4.04. UV−vis: λ 364 nm, ε 22 000 M^{-1} cm^{-1}. IR: 2064 cm^{-1} ν(OsC≡C). ^{1}H NMR: δ 6.34−7.51 (m, 44H, Ar), 2.61 (m, 8H, CH$_2$). ^{31}P NMR: δ 16.2. ^{13}C NMR: δ 136.2 (C$_{36}$) 135.7, 134.8 (C$_{47}$, C$_{43}$, vtt, $|^1J_{PC} + {}^3J_{PC}|$= 22 Hz), 134.3, 134.2 (C$_{48}$, C$_{44}$), 132.5 (C$_{37}$), 130.4 (C$_{38}$), 129.0, 128.8 (C$_{50}$, C$_{46}$), 127.1, 126.9 (C$_{49}$, C$_{45}$), 108.5 (C$_{35}$), 106.3 (C$_{40}$, coupling not visible), 86.1 (C$_{39}$), 31.4 (C$_{42}$, vtt, $|^1J_{PC} + {}^3J_{PC}|$= 24 Hz).

*Synthesis of trans-[Os(C≡CPh)(NH$_3$)(dppe)$_2$](PF$_6$) (**5**(PF$_6$)).* A mixture of *trans*-[Os(C≡CPh)Cl(dppe)$_2$] (**2**, 270 mg, 0.240 mmol), NH$_4$PF$_6$ (58 mg, 0.360 mmol), and triethylamine (6 mL) was stirred in dichloromethane (100 mL) for 18 h. The solution was reduced to 50 mL, and the product was precipitated from petrol (200 mL), collected, and washed with methanol, affording **5**(PF$_6$) as a pale yellow powder (238 mg, 79%). The sample can be further purified through crystallization from toluene. ESI MS: 1089 ([Os(C≡CPh)(dppe)$_2$]$^+$, 100), 988 ([Os(dppe)$_2$]$^+$, 30). Anal. Calcd for C$_{60}$H$_{56}$F$_6$NOsP$_5$: C, 57.65; H, 4.51; N, 1.12. Found: C, 57.54; H, 4.74; N, 1.12. IR: ν(OsC≡C) 2076 cm^{-1}. UV−vis: λ 275 nm, ε 17 700 M^{-1} cm^{-1}; 301 nm, ε 18 600 M^{-1} cm^{-1}. ^{1}H NMR: δ 6.42−8.20 (m, 45H, Ph), 2.61 (m, 8H, CH$_2$), 1.00 (s, 3H, NH$_3$). ^{31}P NMR: δ 19.9. ^{13}C NMR: δ 135.4 (C$_{47,}$ vtt, $|^1J_{PC} + {}^3J_{PC}|$= 24 Hz), 134.4 (C$_{48}$), 131.7 (C$_{49}$), 130.4, 130.2 (C$_{50}$, C$_{46}$), 129.9 (C$_{37}$), 129.7 (C$_{43}$, coupling not observed), 129.3 (C$_{45}$), 128.1 (C$_{35}$), 127.8 (C$_{44}$), 124.0 (C$_{36}$), 31.2 (C$_{42,}$ vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz); C$_{40}$, C$_{39}$, C$_{38}$ not detected.

*Synthesis of trans-[Os(C≡C-4-C$_6$H$_4$I)(NH$_3$)(dppe)$_2$](PF$_6$) (**6**(PF$_6$)).* A mixture of *trans*-[Os(C≡C-4-C$_6$H$_4$I)Cl(dppe)$_2$] (**4**, 4.00 g, 3.20 mmol), NH$_4$PF$_6$ (1.04 g, 6.4 mmol), and triethylamine (4 mL) was stirred in dichloromethane (200 mL) for 18 h. The solution was reduced to 100 mL, and the product was precipitated by addition of the solution to petrol. The product was collected and washed with methanol, affording **6**(PF$_6$) as a pale yellow powder (4.269 g, 97%). ESI MS: 1232 ([M − PF$_6$]$^+$, 100). Anal. Calcd for C$_{60}$H$_{55}$F$_6$INOsP$_5$: C, 52.37; H, 4.03; N, 1.02. Found: C, 52.36; H, 3.92; N, 1.04. UV−vis: λ 319 nm, ε 29 000 M^{-1} cm^{-1}. IR: 2076 cm^{-1} ν(OsC≡C). ^{1}H NMR: δ 6.42−8.13 (m, 44H, Ar), 2.61 (m, 8H, CH$_2$), 1.02 (s, 3H, NH$_3$). ^{31}P NMR: δ 19.9. ^{13}C NMR: δ 137.2 (C$_{36}$), 135.8 (C$_{47}$, vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 22 Hz), 134.4 (C$_{48}$), 131.6 (C$_{43}$, vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 20 Hz), 131.5 (C$_{37}$), 131.3 (C$_{49}$), 130.2, 130.5 (C$_{50}$, C$_{46}$), 129.4 (C$_{45}$), 128.4 (C$_{38}$), 128.0 (C$_{44}$), 119.9 (C$_{40}$, quint, $^2J_{PC}$ = 16 Hz), 116.4 (C$_{39}$), 88.7 (C$_{35}$), 30.3 (C$_{42,}$ vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz).

*Synthesis of trans-[Os(C≡CPh)$_2$(dppe)$_2$] (**7**).* A mixture of *trans*-[Os(C≡CPh)(NH$_3$)(dppe)$_2$](PF$_6$) (**5**(PF$_6$), 200 mg, 0.160 mmol) and phenylacetylene (0.5 mL, 5 mmol) was heated in refluxing methanol (100 mL) for 16 h. The solution was allowed to cool to room temperature, and the pale yellow powder was collected by filtration and identified as **7** (114 mg, 60%). The sample can be further purified through crystallization from toluene. ESI MS: 1190 ([Os(C≡CPh)$_2$(dppe)$_2$]$^+$, 100), 1089 ([Os(C≡CPh)(dppe)$_2$]$^+$, 60), 988 ([Os(dppe)$_2$]$^+$, 20). Anal. Calcd for C$_{68}$H$_{58}$OsP$_4$: C, 68.67; H, 4.92. Found: C, 68.57; H, 5.08. IR: 2060 cm^{-1} ν(OsC≡C). UV−vis: λ 336 nm, ε 28 600 M^{-1} cm^{-1}. ^{1}H NMR: δ 6.50−7.50 (m, 50H, Ph), 2.58 (m, 8H, CH$_2$). ^{31}P NMR: δ 16.7. ^{13}C NMR: δ 136.2 (C$_{47}$, C$_{43}$), 134.3 (C$_{48}$, C$_{44}$, coupling not observed), 130.5, 127.4 (C$_{37}$, C$_{36}$), 128.7 (C$_{50}$, C$_{46}$), 127.0 (C$_{49}$, C$_{45}$), 122.7 (C$_{35}$), 32.6 (C$_{42}$, coupling not observed); C$_{38}$, C$_{39}$, C$_{40}$ not detected.

*Synthesis of trans-[Os(C≡C-4-C$_6$H$_4$I)(C≡CC$_6$H$_4$-4-C≡CSiPr$^i{}_3$)(dppe)$_2$] (**8**).* A mixture of *trans*-[Os(C≡C-4-C$_6$H$_4$I)(NH$_3$)(dppe)$_2$](PF$_6$) (**6**(PF$_6$), 2.30 g, 1.67 mmol), [(4-ethynylphenyl)ethynyl]tri(isopropyl)silane (1.88 g, 6.68 mmol), and triethylamine (1 mL) was heated in refluxing methanol (200 mL) for 144 h. The resulting solid was collected and washed with methanol (50 mL) and *n*-hexane (50 mL), affording **8** as a yellow powder (1.76 g, 70%). HRMS (ESI): Calcd 1497.348 [M + H]$^+$. Found: 1497.352. Anal. Calcd for C$_{79}$H$_{77}$IOsP$_4$Si: C, 63.45; H, 5.19. Found: C, 63.44; H, 5.35. IR: 2055 cm^{-1} ν(OsC≡C), 2150 cm^{-1} ν(C≡CSi). UV−vis: λ 378 nm, ε 46 000 M^{-1} cm^{-1}. ^{1}H NMR: δ 6.40−7.43 (m, 52H, Ph), 2.57 (m, 8H,

CH_2), 1.14 (s, 21H, Pr^i). ^{31}P NMR: δ 16.7. ^{13}C NMR: δ 136.3 (C_{57}), 135.6 (C_{47}, C_{43}, vtt, $|^1J_{PC} + {}^3J_{PC}|$= 24 Hz), 134.1 (C_{48}, C_{44}), 132.2 (C_{56}), 131.3 (C_{37}), 131.1 (C_{38}), 130.3 (C_{55}), 130.0 (C_{36}), 128.8 (C_{50}, C_{46}), 127.0 (C_{49}, C_{45}), 119.7, 117.7 (C_{40}, C_{53}, quint, $^2J_{PC}$ = 12 Hz), 116.9, 115.0, 113.7 (C_{35}, C_{39}, C_{54}), 108.5 (C_{34}), 89.7 (C_{33}), 86.7 (C_{58}), 31.4 ($C_{42,}$ vtt, $|^1J_{PC} + {}^3J_{PC}|$= 26 Hz), 18.7 (C_{52}), 11.4 (C_{51}).

*Synthesis of trans-[Ru(C≡C-4-C_6H_4I)(NH_3)(dppe)$_2$](PF_6) (**9**(PF_6)).* A mixture of *trans*-[Ru(C≡C-4-C_6H_4I)Cl(dppe)$_2$] (250 mg, 0.215 mmol), NH_4PF_6 (105 mg, 0.646 mmol), and triethylamine (1 mL) was stirred in CH_2Cl_2 (60 mL) for 12 h. The solution was reduced to 10 mL and added to petrol (100 mL), precipitating a solid that was collected on a sintered glass filter and washed with methanol to give **9**(PF_6) as a pale yellow powder (167 mg, 60%). ESI MS: 1126 ([Ru(C≡C-4-C_6H_4I)(dppe)$_2$]$^+$, 100), 898 ([Ru(dppe)$_2$]$^+$, 50). Anal. Calcd for $C_{60}H_{55}F_6INP_5Ru$: C, 56.00; H, 4.31; N, 1.09. Found: C, 55.69; H, 4.54; N, 1.03. IR: 2076 cm^{-1} ν(RuC≡C). UV−vis (CH_2Cl_2): λ 318 nm, ε 18 000 M^{-1} cm^{-1}. ^1H NMR: δ 6.42−8.13 (m, 44H, Ph), 2.63 (m, 8H, CH_2), 0.28 (s, 3H, NH_3). ^{31}P NMR: δ 54.0 (s, PPh_2), −143.7 (sept, J_{PF} = 714 Hz, PF_6). ^{13}C NMR: δ 137.2 (C_{36}), 135.8 (C_{47}, vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 22 Hz), 134.4 (C_{48}), 131.6 (C_{43}, vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 20 Hz), 131.5 (C_{37}), 131.3 (C_{49}), 130.2, 130.5 (C_{50}, C_{46}), 129.4 (C_{45}), 128.4 (C_{38}), 128.0 (C_{44}), 119.9 (C_{40}, quint, $^2J_{PC}$ = 16 Hz), 116.4 (C_{39}), 88.7 (C_{35}), 30.3 (C_{42}, vtt, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz).

Crystallographic Section. Crystals suitable for X-ray crystallographic structure determination were obtained by slow diffusion of *n*-hexane into toluene (**2**, **5**(PF_6)) or CH_2Cl_2 (**3**, **4**, **6**(PF_6)) solutions or from toluene (**7**). They were coated with a thin layer of the viscous cryoprotectant Paratone-N (Hampton Research) and attached to a glass fiber.

Crystallographically unique data sets were collected on a Nonius Kappa CCD diffractometer.[53] φ-Scans and ω-scans of 1.1° (**2**), 1.2° (**3**), 0.4° (**4**), 1.0° (**5**(PF_6)), 1.2° (**6**(PF_6)), or 2.0 (**7**) width were carried out using graphite-monochromated Mo Kα radiation with a wavelength of λ = 0.71073 Å to determine the unit cell parameters. The latter were obtained by least-squares refinement of 15 388 (**2**), 12 843 (**3**), 12 387 (**4**), 15 029 (**5**(PF_6)), 12 764 (**6**(PF_6)), or 7880 (**7**) unique reflections (N and N_0 of these with $I \geq 2.0\ \sigma(I)$) using the DENZO software package.[54] The theta range for each data set was 2.6° ≤ θ ≤ 30.0° (**2**), 2.6° ≤ θ ≤ 27.5° (**3**, **4**), 1.9° ≤ θ ≤ 27.5° (**5**(PF_6)), 2.7° ≤ θ ≤ 27.9° (**6**(PF_6)), and 2.9° ≤ θ ≤ 27.9° (**7**). The temperature during data collection was maintained at 200 K in a nitrogen cryostream, with a nominal stability of ±0.02 K. After complete data collection, crystal faces were measured to permit numerical absorption corrections via the Gaussian method[55] implemented from within MAXUS.[56] Equivalent reflections were merged, the structures solved by direct methods using the SIR92 software,[57,58] and peaks of electron density located by difference Fourier techniques.[59] The full-matrix least-squares structure refinements were carried out using the CRYSTAL software package.[58,60−64] Apart from the molecular unit, solvent molecules were located in the asymmetric unit (**2**, **3**, **5**(PF_6), **7**). During refinement of structure **4**, Fourier peaks of significant height were found but could not be assigned, so the Platon SQUEEZE function[65−67] was used to account for the residual electron density. In all structures, anisotropic thermal parameters were refined for all non-hydrogen atoms. Slight disorder was found in the solvent molecules of **2**, **5**(PF_6), and **6**(PF_6), which could be resolved by implementing soft restraints and constraints on the corresponding moieties. H atoms were located in difference Fourier maps. Restraints on their bond lengths and angles were applied to regularize their geometry. C−H bond lengths were set to be 0.950 Å, and U_{iso}(H) were kept at values corresponding to 1.2 × U_{eq} of the parent atoms. In the course of structure refinements, the positions of the hydrogen atoms were refined with riding constraints and recalculated frequently. Residuals R on $|F|$ considering only reflections with $I \geq 2.0\ \sigma(I)$ are given. All-data residuals R_w are reported. Graphical representations of structures **2**−**4**, **5**$^+$, **6**$^+$, and **7** (Figures 1 and S1−S5, Supporting Information) were generated in ORTEP[68] and graphically refined using the POV-Ray software.[69] A comparison of selected bond lengths and angles and a summary of the crystallographic data are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structures and atomic numbering schemes for **2**−**4**, **5**(PF_6), and **7**, calculated optical transitions for *trans*-**1**, *trans*-**1**$^+$, **2**, **2**$^+$, **5**$^+$, **5**$^{2+}$, **7**, and **7**$^+$, selected bond lengths and angles for **2**−**4**, **5**(PF_6), **6**(PF_6), and **7**, crystallographic data for **2**−**4**, **5**(PF_6), **6**(PF_6), and **7**, ^{13}C NMR spectroscopy numbering scheme, ^1H, ^{31}P, and ^{13}C NMR spectra for **3**, **4**, **5**(PF_6), **6**(PF_6), and **7**−**9**, CVs for **5**(PF_6) and **7**, UV−vis−NIR spectral changes during electrochemical oxidation of *trans*-[Os(C≡CPh)(NH_3)(dppe)$_2$](PF_6) (**5**(PF_6)), details of theoretical methods employed, and X-ray crystallographic files in CIF format for structure determinations of **2**−**4**, **5**(PF_6), **6**(PF_6), and **7** (CCDC 844466−844471). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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