Controlled Synthesis of Multinuclear Metal Complex Arrays by Cross Coupling of Coordinated Ligands

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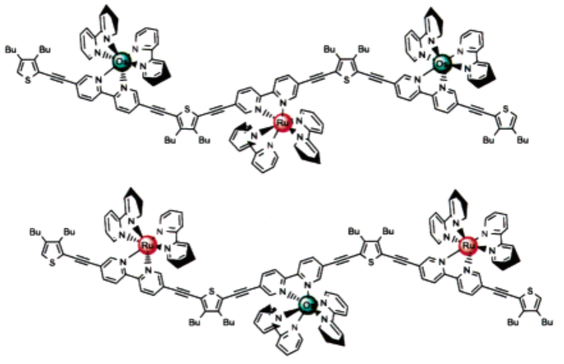

Conditions for efficient cross linking of chelating organic ligands within different metal-containing building blocks have been developed, allowing the preparation of heteronuclear Ru/Os complexes in a controlled manner. Critical to the success of this protocol is the introduction of an Os center early in the synthesis and the use of CuI under polar conditions. Noteworthy features of this method are the tolerance of the metal centers in both reaction partners and the absence of any metal scrambling during the C−C formation or ultimate complexation procedures.

Introduction

Luminescent transition-metal complexes are of continuing interest because of their wide range of possible applications, such as in luminescence sensing,[1,2] photocatalysis,[3] molecular electronics,[4,5] electron[6] or photon donation,[7] light harvesting,[8] light-emitting devices,[9,10] and energy supply systems.[11] The utility of such complexes may be improved by their incorporation into larger functional assemblies providing greater directional control of energy or electron transfer over long distances.[5] Among the most useful complexes are the tris(2,2′-bipyridine)−ruthenium(II) and −osmium(II) cations (and their derivatives), which are relatively strongly luminescent and are electrochemically well-behaved.[12] Their properties could be endowed upon many larger systems, but to ensure both kinetic and photochemical stability, we envisaged that this should be done by the formation of robust covalent bonds, rather than labile interactions, e.g., H bonding, as found in many natural[13] and some known synthetic[14] systems.

Previously, we have shown that both bi- and terpyridine chelate units may be bridged by acetylenic and olefinic chains to give a variety of multitopic ligands, some of which form complexes in which there is through-

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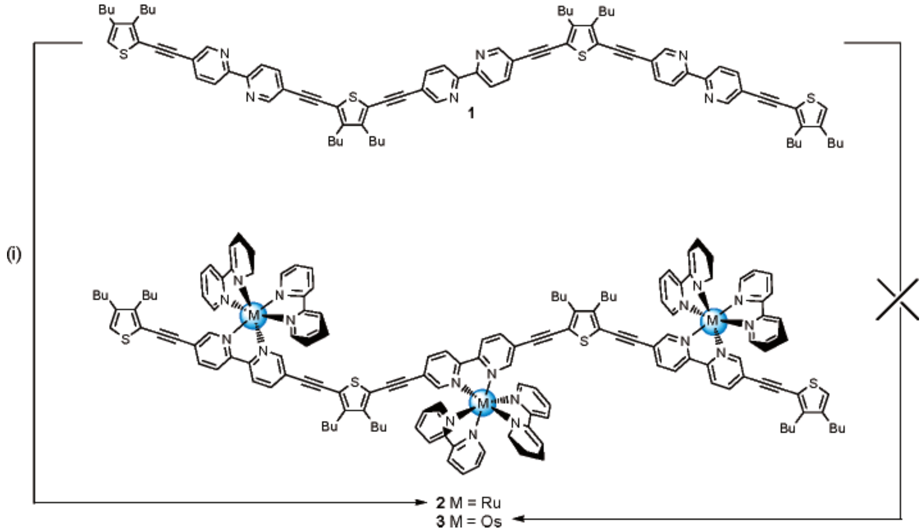
10.1021/jo050894b CCC: $30.25

SCHEME 1[a]



[a] Key: (i) $[Ru(bpy)_2Cl_2]\cdot 2H_2O$; EtOH; 90 °C; 30%.

bond electronic interaction of the terminal chelate centers.[15] Aside from photoactive Ru(II) or Os(II) polypyridine entities,[16] the termini may involve porphyrins,[17] delocalized organic fragments (carotene, thiophene, C_{60},[18] OPV,[19] etc.) and other metals, such as Re[20] and Pt.[21] Appropriate levels of unsaturation in the bridges appear to be crucial in the establishment of interactions between the chromophoric centers. On the basis of present knowledge, a bridge providing both a conduit for strong interactions and an entity conveniently adapted to end capping is an ethynylthiophene unit,[22] its use in both roles (Scheme 1) ensuring that some degree of symmetry can be retained in the ligand structure.

While a free multitopic ligand such as **1** (Scheme 1) can be prepared and then reacted with *cis*-$[Ru(bpy)_2Cl_2]$ to give the trinuclear homometallic complex **2**,[23] the yield is poor and is essentially zero when the analogous reaction with $[Os(bpy)_2Cl_2]$ is attempted, seemingly because of the instability of this reactant. Thus, without resort to complicated protection procedures and the use of less readily accessible metal reactants, prospects for a direct preparation of mixed-metal species would seem to be particularly poor.

Fortunately, we have now found that the inverse procedure of first preparing complexes of the monotopic ligands and then linking them together through coupling reactions of the coordinated ligands is an effective and subtly controllable method of obtaining the desired complexes. Thus, Pd(0)-promoted cross coupling enables a well defined series of Ru/Os complexes to be obtained using only two key starting ligands, one (**4a**) unsymmetrically and the other (**9**) symmetrically substituted (Scheme 2).

Details of the syntheses of **4a** and **9** have been described previously.[24] The dibutylalkyl chains ensure a good solubility of the ligands during the complexation procedure with the metal precursors. Both sets of complexes **7** and **8** were obtained in good or satisfactory yields in a two-step procedure using $[Ru(bpy)_2Cl_2]\cdot 2H_2O$[25] and $[Os(bpy)_2Cl_2]$ precursors.[26] The deprotection of the alkyne function in **5** and **6** is straightforward using KF in a mixture of solvents. The complexes **7** and **8** could not be prepared directly from compound **4b** (Scheme 3),[24b] an intractable mixture results from such attempts, presumably because of coordination of the alkyne unit.

The complexes **10** and **11** were produced similarly (Scheme 2). That the functions of the coordinated ligands retained the reactivity of the free forms and that the complexes would remain inert to substitution during coupling reactions was first demonstrated by the double cross-coupling reaction of 2 equiv of **7** with 1 equiv of **10** to produce the homotrinuclear Os complex **3** in 80% isolated yield.

This evidence that the coupling reactions are efficient regardless of whether the ligand is coordinated or not

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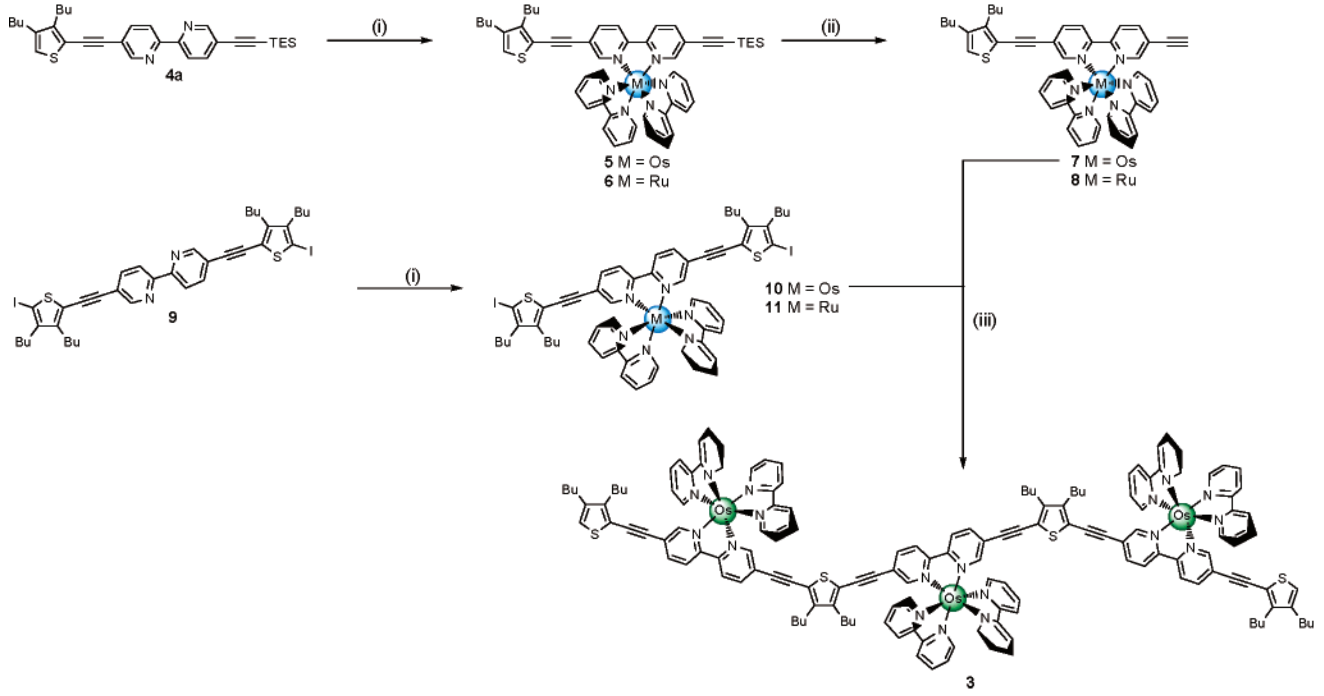
SCHEME 2[a]



[a] Key: (i) [Os(bpy)$_2$Cl$_2$] or [Ru(bpy)$_2$Cl$_2$]·2H$_2$O; EtOH; 90 °C; compound **5**, 47%; compound **6**, 82%; compound **10**, 44%; compound **11**, 94%. (ii) KF; H$_2$O; THF; EtOH; compound **7**, 96%; compound **8**, 94%. (iii) Pd(PPh$_3$)$_4$; CuI; DMF; ^{i}Pr$_2$NH; 80%.

raises the interesting prospect of coupling between coordinated and uncoordinated species. In particular, would it be possible to prepare in a controlled manner homodinuclear and mononuclear complexes bearing, respectively, one uncomplexed unit in the middle of the main axis or two uncomplexed units at the periphery of the molecule (Scheme 3). After some experimentation, we were pleased to find that complexes **12** and **13** bearing a central free bpy unit could be adequately prepared in good yields using [Pd(PPh$_3$)$_4$]/CuI/DMF/^{i}Pr$_2$NH. The diosmium complex **12** could then be directly employed in the preparation of the trinuclear Os/Ru/Os complex **14**.

Unfortunately, the same difficulties as referred to earlier in reacting [Os(bpy)$_2$Cl$_2$] with polypyridyl ligands cause the reaction of the complex **13** intended to produce an Ru/Os/Ru species to fail. An elegant circumvention of this problem, however, is provided by the use of the Os metallo-synthon **10** as the starting material. This is readily and efficiently coupled with two units **4b** to give **15** (the procedure working equally well for the Ru analogue). Reaction with two molar equivalents of [Ru(bpy)$_2$Cl$_2$]·2H$_2$O then leads to an efficient synthesis of the target complex **17**. Another option to produce complex **17** in a single step could be the cross-coupling of complex **10** (1 equiv) with complex **8** (2 equiv). Unfortunately, complex **8** is very reactive and has a high tendency to dimerize by an oxidative homo-coupling reaction catalyzed by low valent palladium(0). Such a side reaction makes the purification of complex **17** tedious and the isolated yield decrease dramatically. A similar procedure could be envisage to produce complex **14** in a single step by cross coupling 2 equiv of complex **7** with 1 equiv of complex **11** in our standard reaction conditions.

Purification of the present complexes was based on column chromatography and recrystallization from appropriate solvents. Their purity was assessed by NMR spectroscopy and elemental analysis. All exhibit well-defined proton NMR patterns in keeping with their molecular structures (typical examples are shown in Figures 1 and 2). For ligands **4b** and **9**, particularly significant resonances are the H3, H3′ doublet of doublets found near δ 8.4 (parts a and b of Figure 1). In the case of ligand **4b**, two sets of doublets are apparent due to the fact that the bipyridine is unsymmetrically substituted. Similar differences are apparent in the 4,4′ and 6,6′ proton resonances, though they are less well resolved. When complexed by Os or Ru, the H3, H3′ doublets shifted significantly and overlapped with other patterns (parts c and d of Figure 1). The complexes **7** and **10** are chiral but present only in enantiomeric forms, which are of course indistinguishable by NMR spectroscopy in an achiral solvent. Interestingly, the terminal-alkyne complexes **7** and **8**, respectively, show singlet resonances at 4.10 and 4.13 ppm for the C≡CH and at 7.25 and 7.26 ppm for the thiophene protons. The presence of the metal centers has a strong effect on the chemical shift of the C≡CH ($\Delta\delta$ 0.80 ppm) and a weaker effect on that of the thiophene protons ($\Delta\delta$ 0.35 ppm) when compared to the free ligand.

Given that the present complexation reactions were performed using racemic metal reactants, an issue arises in regard to the diastereomeric composition of the multinuclear products. While the binuclear species may adopt only two forms (meso and racemic), the trinuclear complexes may have three, with additional complications arising when heterometallic species are considered.[27] These complications are conveniently considered in terms

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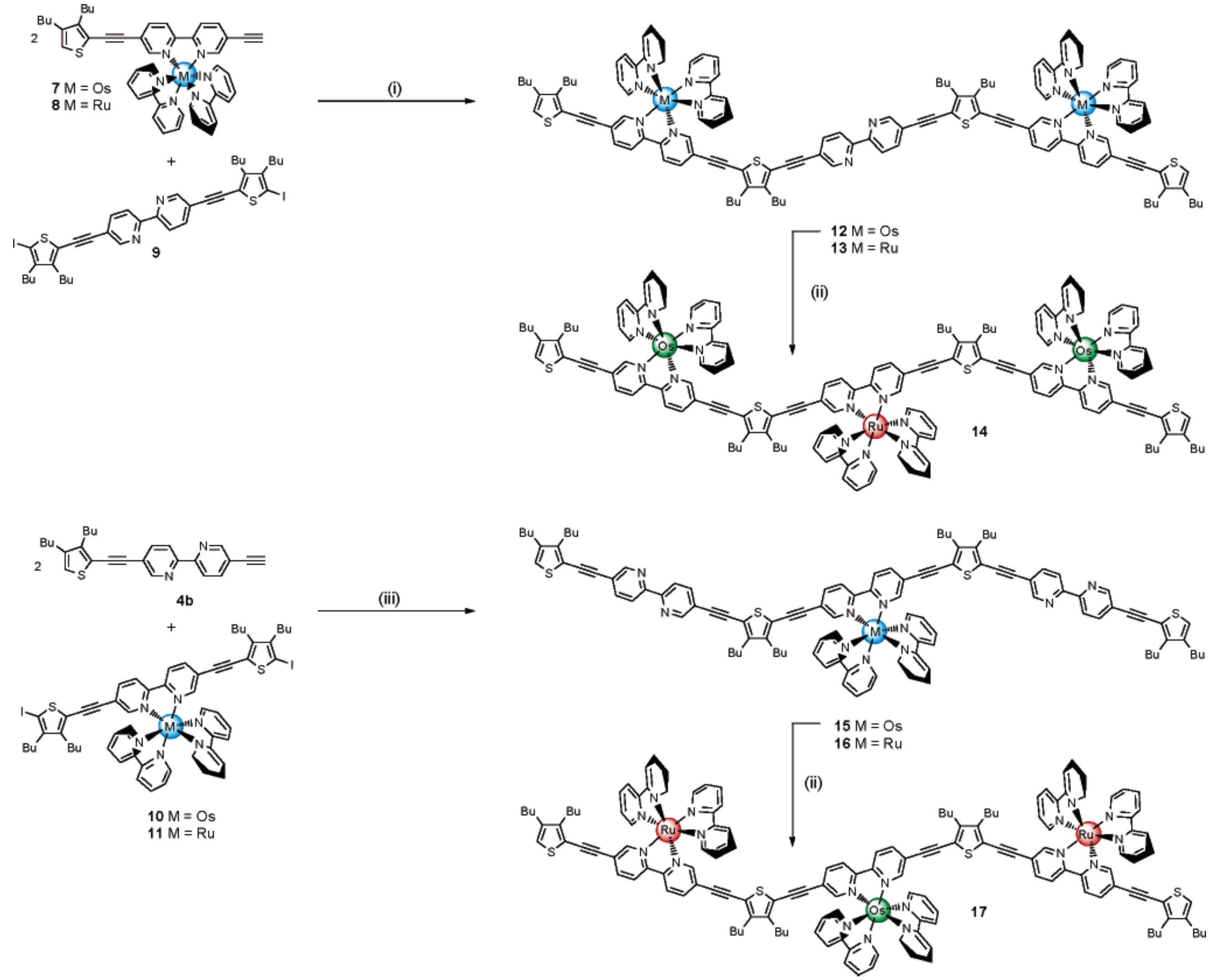
SCHEME 3[a]



[a] Key: (i) Pd(PPh$_3$)$_4$; CuI; DMF; ^{i}Pr$_2$NH; compound **12**, 83%; compound **13**, 48%. (ii) [Ru(bpy)$_2$Cl$_2$]·2H$_2$O; EtOH; 90 °C; compound **14**, 89%; compound **17**, 80%. (iii) Pd(PPh$_3$)$_4$; CH$_3$CN; ^{i}Pr$_2$NH; compound **15**, 53%; compound **16**, 84%.

of the NMR spectra of the Os species (Figure 2), which are closely similar to those of both the Ru (Figure S1) and mixed Os/Ru complexes (Figure 3).

A significant peak in the ^{1}H NMR spectrum of complex **12** is the doublet lying at 8.53 ppm ($^3J = 8.0$ Hz), assigned to the 3,3′ protons of the uncomplexed central bipyridine fragment (Figure 2b). Similarly, for **15**, clear indication of the presence of two external, noncomplexed, bpy subunits is revealed by two doublets (δ = 8.53 ppm, $^3J = 8.0$ Hz and δ = 8.52 ppm, $^3J = 8.0$ Hz), corresponding to 4 protons. As expected for the trinuclear complex **3**, all pyridine proton resonances are much more strongly overlapped (Figure 2c). While the ^{1}H NMR spectrum of complex **12** provides no evidence for the presence of both of the two possible diastereoisomers, neither in the region of the pyridine proton resonances nor that of the ring-bound thiophene methylene groups (an index found useful in triple helicates[28]), which appear as four well-defined triplets ($^3J = 7.5$ Hz in CD$_2$Cl$_2$, Figure S2), there is also no evidence of multiplicity in the ^{13}C resonances of the acetylenic carbon atoms. In light of the characteristics of related systems,[29,30] it is suggested that our complexes are present as a 1:1 mixture of diastereoisomers. No attempts have yet been made to separate these species, though of course the use of resolved reactant complexes could be used to obtain one enantiomer of the racemate.

The presence of the metal centers has a marked effect on the chemical shifts of the sp carbons on the bpy sites. Indeed, two sp carbon resonances at 87−89 ppm correspond to uncomplexed bpy units in a trans conformation, and those at 90−91 ppm correspond to complexed bpy units in a cis conformation. For complexes **15** and **16**, bearing a single metal center, there are signals at 87, 89, and 91 ppm. For **12** and **13**, clear indication of two external complexed bpy units is provided by two signals near 91 ppm and only one at 87 ppm. As expected,

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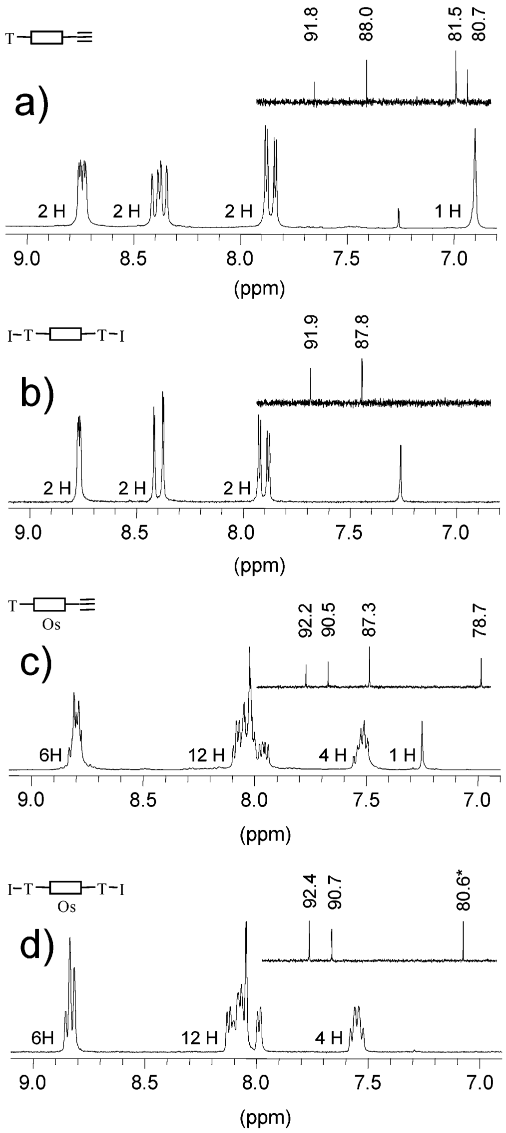

FIGURE 1. Proton spectra measured in CDCl$_3$ for (a) ligand **4b** and (b) ligand **9** and in d_6-acetone for (c) complex **7** and (d) complex **10**. For the sake of clarity, only the aromatic regions of the spectra are shown. The insets show (right) the sp carbon signals of the carbon spectra at 100.6 MHz and (left) a schematic representation of the complexes. In the ^{13}C spectrum (d), $*$ denotes the C−I resonance.

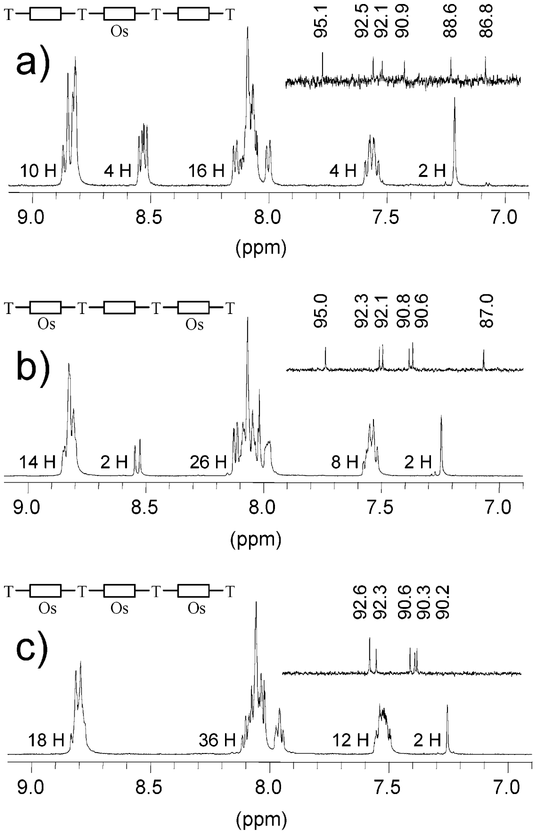

FIGURE 2. Proton spectra measured in d$_6$-acetone (at 400.1 MHz) at room temperature for (a) complex **15**, (b) complex **12**, and (c) complex **3**. For the sake of clarity, only the aromatic regions of the spectra are shown. The insets show (right) the sp-carbon signals of the carbon spectra at 100.6 MHz and (left) a schematic representation of the complexes.

the trinuclear complexes **2** and **3** only exhibit signals around 90 ppm. No splitting of the sp carbon due to the presence of diastereoisomers is observed at 100.6 MHz.

Electrospray mass spectroscopy (ESMS) is a powerful tool to confirm the structure and the overall charge of the complex, which reflects the number of metal centers. Furthermore, it is a probe for any scrambling of the metal during the additional complexation procedure. Its use is illustrated by the ESMS spectra of the hetero-trinuclear complexes, which exhibit well-defined peaks with the expected isotopic profiles: for **17** at 452.6 [Ru/Os/Ru − 4PF$_6$]$^{4+}$, 572.1 [Ru/Os/Ru − 3PF$_6$]$^{3+}$, 751.3 [Ru/Os/Ru − 2PF$_6$]$^{2+}$, 1050.1 [Ru/Os/Ru − PF$_6$]$^{+}$ (theoretical values of 452.58, 572.09, 751.35, 1050.12) and for **14** at 467.4 [Os/Ru/Os − 4PF$_6$]$^{4+}$, 589.9 [Os/Ru/Os − 3PF$_6$]$^{3+}$, 773.6 [Os/Ru/Os − 2PF$_6$]$^{2+}$, 1079.8 [Os/Ru/Os − PF$_6$]$^{+}$ (theoretical values of 467.43, 589.91, 773.63, 1079.83). In each spectrum, the absence of additional relevant peaks corresponding to the hypothetical scrambling of the metal centers confirms the stability of the resulting complexes.

This is direct proof that synthesis based on reactions of the coordinated ligands is a convenient and versatile method because of the mild conditions, the tolerance of various functions such as terminal alkyne and C−I, and the lack of any scrambling. To the best of our knowledge, this is the first time that trinuclear Ru/Os complexes have been produced in a regiochemically controlled manner.

All the ligands and complexes display well-defined electronic absorption spectra (Figure 4). The higher energy absorption lying at 290 nm is assigned to $\pi-\pi^*$ transitions of the unsubstituted bipyridine subunits.[31] With an increase in the number of M(bpy)$_2$ metal centers, this band remains unshifted and its extinction coefficient increases accordingly. The absorption band localized in the middle of the absorption spectra, around 370−410 nm, is safely assigned to the long axis polarized $\pi-\pi^*$ transitions of the trimeric organic fragment, and has a pronounced charge-transfer character.[24] As might be expected, by increasing the number of metal centers, this

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[31] De Armond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

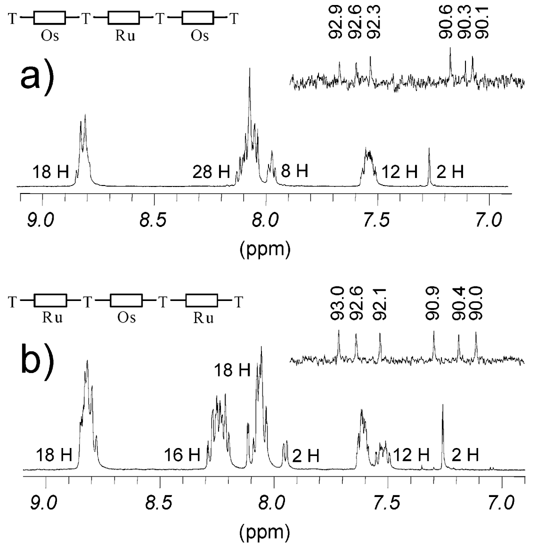

FIGURE 3. Proton spectra measured in d_6-acetone (at 400.1 MHz) at room temperature for (a) complex **14** and (b) complex **17**. For the sake of clarity, only the aromatic regions of the spectra are shown. The insets show (right) the sp-carbon signals of the carbon spectra at 100.6 MHz and (left) a schematic representation of the complexes.

transition is progressively shifted by $\Delta\lambda_{abs} \approx 30$ nm from one Os to two Os centers and overlaps with the strong absorption imported by the metal center in the trinuclear complexes. Indeed, the lower-energy absorption is due to an intense metal-to-ligand charge-transfer (MLCT) absorption band located around 470 nm. The marked low-energy tail extending over 200 nm is likely due to direct singlet−triplet absorption leading to population of the Os-centered ^{3}MLCT states, a well-known effect due to the strong spin−orbit coupling of the heavy Os center.[32] As would be expected for the related Ru complexes, this tail was not observed (Fig S3); however a similar long tail is observed in the mixed Ru/Os complexes **14** and **17** (Figure 5).

In summary, we have shown that employment of synthesis at preformed scaffolds can provide an easy entry into sophisticated complexes in which the centers are linked by alkyne spacers. The methodology encompasses a wide variety of functional groups, and it is worthwhile noting that our protocol employs both Ru and Os building blocks with reactive C−I or terminal alkyne groups. Further work is in progress to extend the present methodology to the preparation of dissymmetric complexes (e.g., Os/Os/Ru or Ru/Ru/Os) and to probe whether effective step-by-step energy-hopping processes and upper conversion of excited states is feasible.

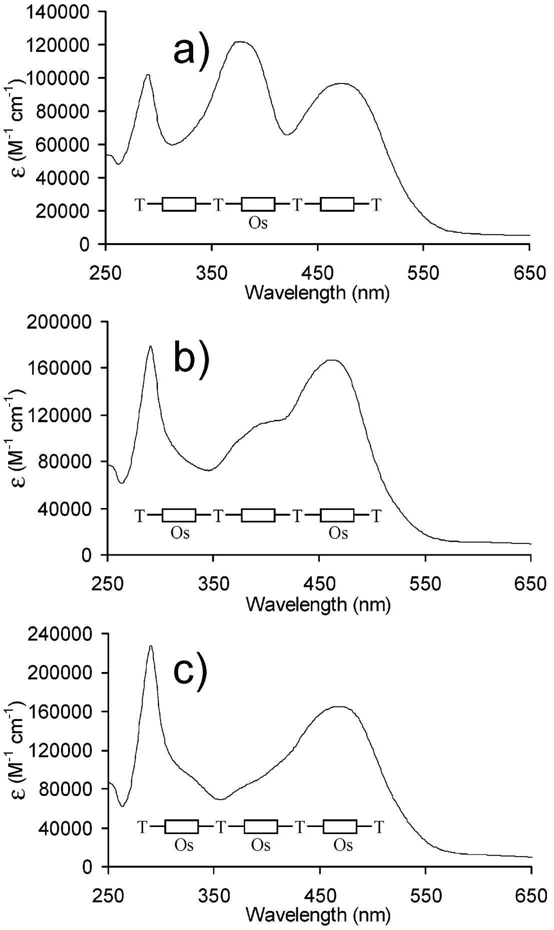

FIGURE 4. UV−Vis absorption spectra measured in dichloromethane for (a) complex **15**, (b) complex **12**, and (c) complex **3**.

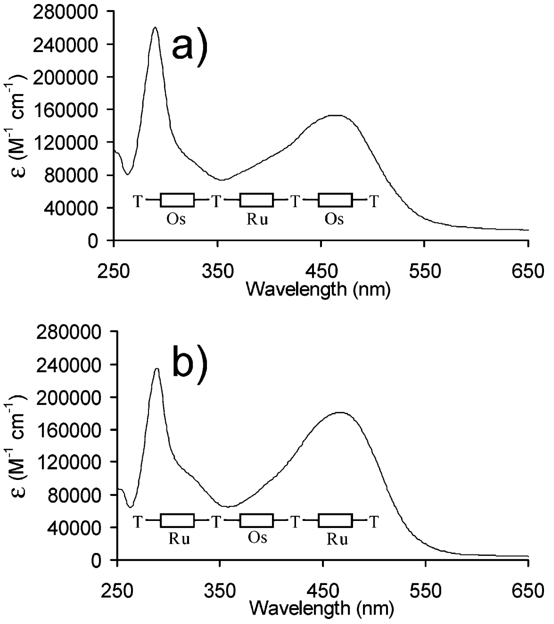

FIGURE 5. UV−Vis absorption spectra measured in dichloromethane for (a) complex **14** and (b) complex **17**.

Experimental Section

General Procedure 1 for the Complexes Carrying Alkyne Functions. A Schlenk flask was charged with the iodo and ethynyl derivatives, Pd(PPh$_3$)$_4$ (5 mol %), CuI (10 mol %), and finally with argon-degassed *N*,*N*-dimethylformamide and diisopropylamine. The solution was stirred at room temperature until complete consumption of the iodo derivative (determined by thin-layer chromatography, TLC), and then the solvent was evaporated under vacuum. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, then with a satu-

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(32) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

rated solution of KPF_6, and dried over cotton absorbent. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina and recrystallization in a mixture of acetone and cyclohexane.

General Procedure 2 for the Complexes Carrying Iodo Functions. A Schlenk flask was charged with the iodo and ethynyl derivatives, $Pd(PPh_3)_4$ (6 mol %), and finally with argon-degassed acetonitrile and diisopropylamine. The solution was heated at 60 °C until complete consumption of the iodo derivative (determined by TLC), and then the solvent was evaporated under vacuum. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, then with a saturated solution of KPF_6, and dried over cotton absorbent. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina and recrystallization in a mixture of acetone and cyclohexane.

General Procedure 3 for Ruthenium Complexation. A Schlenk flask was charged with the bipyridine derivative, $[Ru(bpy)_2Cl_2]\cdot 2H_2O$, and finally ethyl alcohol. The orange solution was heated at 90 °C until complete consumption of the starting material (determined by TLC) and then the solvent was evaporated under vacuum. The residue was treated with a saturated solution of KPF_6 and extracted with dichloromethane. The organic extracts were washed with water and dried over cotton absorbent. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina and recrystallization in a mixture of acetone and cyclohexane.

General Procedure 4 for Osmium Complexation. A Schlenk flask was charged with the bipyridine derivative, $[Os(bpy)_2Cl_2]$, and finally ethyl alcohol. The dark green solution was heated at 90 °C for 96 h, and then the solvent was evaporated under vacuum. The residue was treated with a saturated solution of KPF_6 and extracted with dichloromethane. The organic extracts were washed with water, and dried over cotton absorbent. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina and recrystallization in a mixture of acetone and cyclohexane.

General Procedure 5 for the Removal of the Triethylsilyl Group. KF (5 equiv) in H_2O was added to a solution of the triethylsilyl-protected compound in THF/ethanol. The mixture was stirred at room temperature until the complete consumption of the starting material (determined by TLC), and then the solvent was evaporated under vacuum. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, then with a saturated solution of KPF_6, and dried over cotton absorbent. The solvent was removed by rotary evaporation. The residue was purified by recrystallization in a mixture of acetone and cyclohexane.

Complex 3. Prepared using procedure 1; from **10** (17.0 mg, 0.01 mmol), **7** (27.2 mg, 0.02 mmol), $Pd(PPh_3)_4$ (1.4 mg, 1.03×10^{-3} mmol), CuI (0.4 mg, 2.06×10^{-3} mmol), DMF (3 mL), $^iPr_2NH$ (2 mL); chromatography on alumina, eluting with dichloromethane to dichloromethane−methyl alcohol (v/v 97/3) to give 38.0 mg (80%) of **3** as a brown solid after recrystallization; ^1H NMR (400.1 MHz, d_6-acetone): δ 8.83−8.79 (m, 18H), 8.11−8.02 (m, 30H), 7.97−7.94 (m, 6H), 7.56−7.49 (m, 12H), 7.25 (s, 2H), 2.80 (t, overlapping with residual water), 2.66−2.60 (m, 8H), 2.55 (t, 4H, ^3J = 7.5 Hz), 1.64−1.24 (m, 32H), 0.95−0.86 (m, 24H); ^{13}C NMR (100.6 MHz, d_6-acetone): δ 160.0, 159.99, 159.95, 159.92, 159.90, 159.3, 159.2, 158.5, 153.14, 153.10, 152.8, 152.43, 152.40, 151.9, 150.3, 150.2, 150.1, 143.5, 139.5, 139.2, 138.7, 129.3, 125.73, 125.66, 125.5, 124.9, 124.7, 120.14, 120.10, 117.1, 92.6, 92.3, 90.6, 90.3, 90.2, 33.0, 32.7, 29.1, 28.7, 28.4, 23.2, 23.1, 14.32, 14.26, 14.1; IR (KBr, cm^{-1}) 3124, 3073, 2955, 2930, 2860, 2197, 1698, 1593, 1463, 1447, 1268, 1242, 839; UV−Vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 290 (228 000), 470 (165 000); ESMS *m/z* (nature of the peak, relative intensity) 796.2 ($[M - 4PF_6]^{4+}$, 25), 608.1 ($[M - 5PF_6]^{5+}$, 100), 482.2 ($[M - 6PF_6]^{6+}$, 50). Anal. Calcd for $C_{150}H_{140}F_{36}N_{18}Os_3P_6S_4\cdot C_3H_6O$: C, 48.08; H, 3.85; N, 6.60. Found: C, 48.42; H, 4.04; N, 6.69.

Complex 12. Prepared using procedure 1; from **9** (11.3 mg, 0.01 mmol), **5** (40.0 mg, 0.03 mmol), $Pd(PPh_3)_4$ (1.5 mg, 1.29 $\times 10^{-3}$ mmol), CuI (0.5 mg, 2.51×10^{-3} mmol), DMF (2.5 mL), $^iPr_2NH$ (2 mL); chromatography on alumina, eluting with dichloromethane to dichloromethane−methyl alcohol (*v/v* 98/2) to give 33.0 mg (83%) of **12** as a brown solid after recrystallization; ^1H NMR (400.1 MHz, d_6-acetone) δ 8.85−8.80 (m, 14H), 8.53 (d, 2H, ^3J = 8.0 Hz), 8.12−7.97 (m, 26H), 7.57−7.51 (m, 8H), 7.24 (s, 2H), 2.82−2.78 (t, overlapping with residual water), 2.69 (t, 4H, ^3J = 7.5 Hz), 2.64 (t, 4H, ^3J = 7.5 Hz), 2.55 (t, 4H, ^3J = 7.5 Hz), 1.66−1.25 (m, 32H), 0.99−0.87 (m, 24H); ^{13}C NMR (100.6 MHz, d_6-acetone) δ 160.0, 159.96, 159.94, 159.1, 158.5, 155.2, 153.0, 152.8, 152.4, 152.2, 151.94, 151.91, 150.32, 150.25, 149.0, 143.5, 140.0, 139.4, 139.2, 138.7, 129.3, 125.7, 125.63, 125.58, 124.9, 121.54, 121.50, 120.8, 118.8, 117.1, 95.0, 92.3, 92.1, 90.8, 90.6, 87.0, 33.09, 33.07, 33.0, 32.7, 29.1, 28.84, 28.81, 28.5, 23.3, 23.18, 23.17, 23.1, 14.33, 14.32, 14.2, 14.1; IR (KBr, cm^{-1}: 3119, 3080, 2954, 2927, 2858, 2194, 1592, 1463, 1446, 1268, 1242, 839; UV−Vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 291 (178 000), 408 (115 000), 463 (167 000); ESMS *m/z* (nature of the peak, relative intensity) 1340.2 ($[M - 2PF_6]^{2+}$, 100), 845.2 ($[M - 3PF_6]^{3+}$, 50), 598.1 ($[M - 4PF_6]^{4+}$, 20). Anal. Calcd for $C_{130}H_{124}F_{24}N_{14}Os_2P_4S_4\cdot C_3H_6O$: C, 52.74; H, 4.33; N, 6.47. Found: C, 53.13; H, 4.67; N, 6.55.

Complex 15. Prepared using procedure 2; from **4b** (33.0 mg, 0.08 mmol), **10** (55.0 mg, 0.03 mmol), $Pd(PPh_3)_4$ (4.6 mg, 3.98×10^{-3} mmol), CH_3CN (8 mL), $^iPr_2NH$ (8 mL); chromatography on alumina, eluting with dichloromethane−hexane (*v/v* 50/50) to dichloromethane−methyl alcohol (*v/v* 99.5/0.5) to give 39.0 mg (53%) of **15** as a brown solid after recrystallization; ^1H NMR (400.1 MHz, d_6-acetone) δ 8.87−8.81 (m, 10H), 8.53 (d, 2H, ^3J = 8.0 Hz), 8.52 (d, 2H, ^3J = 8.0 Hz), 8.15−7.99 (m, 14H), 8.00 (d, 2H, ^3J = 7.0 Hz), 7.59−7.53 (m, 4H), 7.21 (s, 2H), 2.82−2.76 (m, overlapping with residual water), 2.71 (t, 4H, ^3J = 7.5 Hz), 2.60 (t, 4H, ^3J = 7.5 Hz), 1.68−1.29 (m, 32H), 1.00−0.91 (m, 24H); ^{13}C NMR (100.6 MHz, d_6-acetone) δ 160.1, 160.0, 159.0, 155.4, 154.6, 153.1, 152.5, 152.2, 152.02, 151.96, 150.3, 148.94, 148.89, 143.3, 140.0, 139.7, 139.4, 138.7, 129.34, 129.32, 125.71, 125.68, 125.6, 125.1, 124.1, 121.7, 121.45, 121.39, 120.6, 118.6, 118.3, 95.1, 92.5, 92.1, 90.9, 88.6, 86.8, 33.1, 32.8, 28.8, 28.6, 23.31, 23.27, 23.2, 14.32, 14.26, 14.20, 14.19; IR (KBr, cm^{-1}) 2951, 2927, 2858, 2194, 1590, 1463, 1447, 838; UV−Vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 290 (102 000), 377 (120 000), 475 (97 000); ESMS *m/z* (nature of the peak, relative intensity) 2033.2 ($[M - PF_6]^{+}$, 100), 944.2 ($[M - 2PF_6]^{2+}$, 35). Anal. Calcd for $C_{110}H_{108}F_{12}N_{10}OsP_2S_4$: C, 60.65; H, 5.00; N, 6.43. Found: C, 60.48; H, 4.72; N, 6.13.

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Supporting Information Available: Experimental details and complete characterization of compounds prepared. Figures including all NMR spectra and UV−Vis spectra of the ruthenium and mixed Ru/Os complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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