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Photoluminescent Rigid Molecular Rods with Cumulenic C_n ($n = 3, 4$) Spacers: Modulation of Electronic Interaction**

Bo Hong* and Jeffrey V. Ortega

Rigid molecular rods with linear structures, molecular wires, are currently studied as important components for the construction of functional nanoscale photonic and electronic devices.[1,2] With the incorporation of photoactive and/or redox-active metal centers, these molecular assemblies may present interesting properties based on long range electron/energy transfer and electronic communication between the two remote ends of the wires.[2–5] To ensure the directionality and also to construct multicomponent supramolecular systems with well-defined structures, rigid spacers must be used to afford restricted conformational mobility and a controllable distance between structural subunits. In addition, spacers (for example, polyphenyls,[6] alkenes,[7] or alkynes[5,8]) can also be selected to serve as electron-conducting active components to promote long-range electronic coupling between terminal subunits or (for example, saturated hydrocarbons[9]) to serve as passive connecting components.

Systems with unsaturated sp carbon chains (C_n) between two subunits constitute one of the most fundamental classes of one-dimensional molecular wires, however, intense studies in numerous laboratories have focused on the systems with alkynes or acetylenyl bridges.[2,5,8] We report here the photoluminescent and redox-active systems with Ru and Os centers spanned by allene (C_3) or cumulene (C_4) bridges, and the preliminary data on the unique molecular photophysical and redox properties of these new rigid rodlike supramolecular systems. The unique structures of the allene and cumulene bridges permit the tuning of electronic communication between the end subunits. In the C_3 chain the two terminal pπ orbitals will be rotated by 90°, while in the C_4 chain the terminal pπ orbitals remain conjugated (Figure 1).

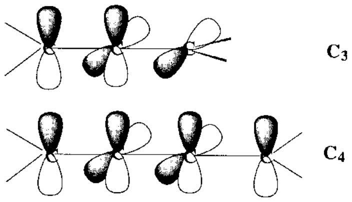

Figure 1. Comparison of the pπ orbitals in the C_3 and C_4 bridges.

As a result, the electronic coupling across the sp carbon chain can be readily controlled by changing the number of carbon atoms.

The C_n-bridged tetratopic spacers, namely, 1,1′,3,3′-tetrakis(diphenylphosphanyl)allene (C_3P_4), 1,1′,4,4′-tetrakis(diphenylphosphanyl)cumulene (C_4P_4), and the ligand 1,1′-bis(diphenylphosphanyl)ethene (C_2P_2e) are prepared according to the literature methods.[10–12] The use of the phosphane group in the spacer here has two advantages. First, it serves as a linker group between the C_n bridge and the metal-based subunits ($M(bpy)_2$ (M = Ru and Os; bpy = 2,2′-bipyridine)). Second, the incorporation of phosphane ligands in polypyridyl-osmium(II) complexes can enhance the lifetime of the ^{3}MLCT state;[13–15] the replacement of one of the σ-donating polypyridyl ligands with phosphane can result in the increase in the energy of the ^{3}MLCT excited state and the decrease of the rate of nonradiative decay.

The PF_6^- salts of the C_n-bridged ruthenium(II) and osmium(II) complexes are synthesized by treatment of C_nP_4 ($n = 3$ or 4), in a refluxing tetrahydrofuran/ethylene glycol mixture, with $[M(bpy)_2Cl_2]$ (M = Ru or Os, Table 1). Mono- or bimetallic complexes, MC_2P_2e, MC_nP_4 ($n = 3$ or 4), and MC_nP_4M ($n = 3$ or 4), are obtained by using different metal-to-ligand ratios. All new complexes have been fully characterized by $^{31}P\{^1H\}$ NMR spectroscopy, fast atom bombardment mass spectrometry (FAB-MS), and elemental analysis. Specifically, many of the fragment ions observed in FAB-MS only involve sequential loss of counteranions (PF_6) and PPh_2 units, and the inner sphere metal–ligand coordination was left intact, thus making peak identification straightforward.

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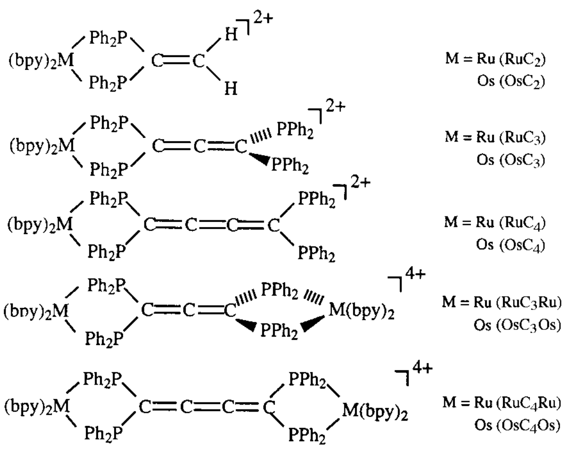

Table 1. Analytical data for the complexes.[a]

RuC$_2$P$_2$e: Yield 95%. ^{31}P{^{1}H} NMR: $\delta = 18.21$. FAB/MS: *m/z* (%): 955 (100) [$M^+ - \mathrm{PF_6}$], 809 (11) [$M^+ - 2\,\mathrm{PF_6}$]. Elemental analysis calcd for $\mathrm{C_{46}H_{38}N_4P_2Ru(PF_6)_2}$: C 50.24, N 5.10, H 3.48; found: C 50.05, N 4.50, H 5.03.

OsC$_2$P$_2$e: Yield 63%. ^{31}P{^{1}H} NMR: $\delta = -23.32$. FAB/MS: *m/z* (%): 1045 (100) [$M^+ - \mathrm{PF_6}$], 900 (50) [$M^+ - 2\,\mathrm{PF_6}$). Elemental analysis calcd for $\mathrm{C_{46}H_{38}N_4P_2Os(PF_6)_2}$: C 46.47, N 4.71, H 3.22; found: C 47.41, N 5.06, H 3.85.

RuC$_3$P$_4$: Yield 80%. ^{31}P{^{1}H} NMR: $\delta = 2.34$, -30.22. FAB/MS: *m/z* (%): 1167 (22) [$M^+ - \mathrm{PF_6} - \mathrm{PPh_2} + \mathrm{O}$], 1151 (17) [$M^+ - \mathrm{PF_6} - \mathrm{PPh_2}$), 1021 (100) [$M^+ - 2\,\mathrm{PF_6} - \mathrm{PPh_2} + \mathrm{O}$], 1005 (27) [$M^+ - 2\,\mathrm{PF_6} - \mathrm{PPh_2}$]. Elemental analysis calcd for $\mathrm{C_{51}H_{56}N_4P_2Ru(PF_6)_2 \cdot 2\,H_2O}$: C 56.25, N 3.70 , H 3.99; found: C 56.00, N 4.10, H 4.52.

OsC$_3$P$_4$: Yield 89%. ^{31}P{^{1}H} NMR: $\delta = -30.49$, -37.37. FAB/MS: *m/z* (%): 1425 (44) [$M^+ - \mathrm{PF_6}$], 1280 (26) [$M^+ - 2\,\mathrm{PF_6}$], 1241 (81) [$M^+ - \mathrm{PF_6} - \mathrm{PPh_2}$], 1095 (100) [$M^+ - 2\,\mathrm{PF_6} - \mathrm{PPh_2}$]. Elemental analysis calcd for $\mathrm{C_{51}H_{56}N_4P_2Os(PF_6)_2 \cdot 2\,H_2O}$: C 53.12, N 3.49, H 3.77; found: C 52.80, N 3.97, H 3.94.

RuC$_4$P$_4$: Yield 48%. ^{31}P{^{1}H} NMR: $\delta = 13.91$, 5.95. FAB/MS: *m/z* (%): 1512 (10) [M^+], 1381 (100) [$M^+ - \mathrm{PF_6} + 2\,\mathrm{O}$], 1365 (30) [$M^+ - \mathrm{PF_6} + \mathrm{O}$], 1349 (45) [$M^+ - \mathrm{PF_6}$]. Elemental analysis calcd for $\mathrm{C_{52}H_{56}N_4P_2Ru(PF_6)_2}$: C 57.95, N 3.75, H 3.78; found: C 57.75, N 3.78, H 3.76.

OsC$_4$P$_4$: Yield 56%. ^{31}P{^{1}H} NMR: $\delta = -26.99$, -30.74. FAB/MS: *m/z* (%): 1618 (100) [$M^+ + 2\,\mathrm{O}$], 1601 (55) [$M^+ + \mathrm{O}$], 1585 (75) [M^+], 1471 (55) [$M^+ - \mathrm{PF_6} - 2\,\mathrm{O}$], 1455 (75) [$M^+ - \mathrm{PF_6} + \mathrm{O}$], 1437 (15) [$M^+ - \mathrm{PF_6}$]. Elemental analysis calcd for $\mathrm{C_{52}H_{56}N_4P_2Os(PF_6)_2}$: C 54.69, N 3.54, H 3.57; found: C, 54.74; N, 3.85; H, 3.91.

RuC$_3$P$_4$Ru: Yield 61%. ^{31}P{^{1}H} NMR: $\delta = 140.87$. FAB/MS: *m/z* (%): 1765 (100) [$M^+ - 3\,\mathrm{PF_6} + \mathrm{O}$], 1620 (17) [$M^+ - 4\,\mathrm{PF_6} + \mathrm{O}$], 1435 (10) [$M^+ - 4\,\mathrm{PF_6} - \mathrm{PPh_2} + \mathrm{O}$], 1417 (15) [$M^+ - 4\,\mathrm{PF_6} - \mathrm{PPh_2}$). Elemental analysis calcd for $\mathrm{C_{71}H_{72}N_8P_4Ru_2(PF_6)_4}$: C 50.06, N 5.13, H 3.32; found: C 50.69, N 5.60, H 3.72.

OsC$_3$P$_4$Os: Yield 85%. ^{31}P{^{1}H} NMR: $\delta = 83.64$. FAB/MS: *m/z* (%): 2088(6) [$M^+ - 2\,\mathrm{PF_6} + \mathrm{O}$], 1943 (100) [$M^+ - 3\,\mathrm{PF_6} + \mathrm{O}$], 1797 (39) [$M^+ - 4\,\mathrm{PF_6} + \mathrm{O}$], 1280 (67) [$M^+ - 4\,\mathrm{PF_6}$]. Elemental analysis calcd for $\mathrm{C_{71}H_{72}N_8P_4Os_2(PF_6)_4}$: C 46.28, N 4.75, H 3.07; found: C 46.45, N 4.98, H 3.55.

RuC$_4$P$_4$Ru: Yield: 57%. ^{31}P{^{1}H} NMR: $\delta = -2.24$. FAB/MS: *m/z* (%): 1936 (45) [$M^+ - 2\,\mathrm{PF_6} + 2\,\mathrm{O}$], 1920 (20) [$M^+ - 2\,\mathrm{PF_6} + \mathrm{O}$], 1904 (10) [$M^+ - 2\,\mathrm{PF_6}$], 1775 (20) [$M^+ - 3\,\mathrm{PF_6} + \mathrm{O}$], 1759 (30) [$M^+ - 3\,\mathrm{PF_6}$], 1630 (35) [$M^+ - 4\,\mathrm{PF_6} + \mathrm{O}$], 1614 (25) [$M^+ - 4\,\mathrm{PF_6}$], 1427 (100) [$M^+ - 4\,\mathrm{PF_6} - \mathrm{PPh_2}$]. Elemental analysis calcd for $\mathrm{C_{72}H_{72}N_8P_4Ru_2(PF_6)_4}$: C 50.33, N 5.10, H 3.30; found: C 50.56, N 5.25, H 3.26.

OsC$_4$P$_4$Os: Yield 27%. ^{31}P{^{1}H} NMR: $\delta = -5.11$. FAB/MS: *m/z* (%): 2101 (15) [$M^+ - 2\,\mathrm{PF_6} + \mathrm{O}$], 1997 (75) [$M^+ - 3\,\mathrm{PF_6} + 3\,\mathrm{F}$], 1937 (40) [$M^+ - 3\,\mathrm{PF_6}$], 1856 (100) [$M^+ - 4\,\mathrm{PF_6} + 4\,\mathrm{O}$], 1808 (45) [$M^+ - 4\,\mathrm{PF_6} + \mathrm{O}$], 1792 (20) [$M^+ - 4\,\mathrm{PF_6}$]. Elemental analysis calcd for $\mathrm{C_{72}H_{72}N_8P_4Os_2(PF_6)_4}$: C 46.55, N 4.72, H 3.05; found: C 46.70, N 4.92, H 3.01.

[a] ^{31}P{^{1}H} NMR spectra were recorded in [D$_3$]MeCN, 202 MHz at 22 °C. The FAB-MS were recorded with *m*-nitrobenzyl alcohol as the matrix.

The redox properties of complexes with C$_2$, C$_3$, and C$_4$ carbon chains have been probed by cyclic voltammetry and the data of metal-based oxidations are included in Table 2. Several unique and interesting features exist when we compare these metal-based redox waves:

1) Each of the monomeric complexes exhibits a single reversible one-electron process for which the i_p^a/i_p^c value is approximately unity, and corresponds to the M$^{\mathrm{II}}$/M$^{\mathrm{III}}$ redox couple (M = Ru or Os).

2) The C$_n$-bridged spacers have profound influence on the metal-based oxidations in all mono- and homobimetallic complexes. As the carbon chain length increases, the M$^{\mathrm{II}}$/M$^{\mathrm{III}}$ redox potential continuously shift to significantly less positive values (Table 2). In other words, the oxidation of the M$^{\mathrm{II}}$ centers (M = Ru or Os) become more thermodynamically favored with longer chains as the rigid spacers. This may suggest that the π-acidity of the polyphosphane spacers becomes significantly weaker when the cumulenic carbon chain length is increased. As a result, the observed $E_{1/2}$(M$^{\mathrm{II}}$/M$^{\mathrm{III}}$) values of MC$_2$P$_2$e (M = Ru, +1.70 V; Os, +1.35 V) and MC$_3$P$_4$ (M = Ru, +1.55 V; Os, +1.12 V) are significantly higher than those of the metal-based redox waves in [M(bpy)$_3$](PF$_6$)$_2$ (M = Ru, +1.29 V;[4] Os, +0.81[13b, 15]), while those of MC$_4$P$_4$ (M = Ru, +1.07 V; Os, +0.80 V) have shifted to lower or approximately the same value. The electrochemical studies of Os$^{\mathrm{II}}$ complexes with mono- and bidentate phosphanes, such as dppm ($E_{1/2} = +1.27$ V versus the saturated calomel electrode (SCE) in [Os(bpy)$_2$(dppm)]$^{2+}$; dppm = Ph$_2$PCH$_2$PPh$_2$),[13b] have shown that the change from pyridyl-type ligands to the more π-accepting phosphanes cause an increase in $E_{1/2}$(Os$^{\mathrm{II}}$/M$^{\mathrm{III}}$). This shift was ascribed, in large part, to the stabilization of the dπ levels by enhanced back-bonding to the phosphane.[13b, 15]

Table 2. Electrochemical and photophysical data for the complexes.[a]

Complex	$E_{1/2}$ (M$^{\mathrm{II}}$/M$^{\mathrm{III}}$), ΔE_p[b]	λ_{EM}, nm	τ_{EM}, ns (±15%)
RuC$_2$P$_2$e	+1.70 (1e$^-$, 80)	530	25
RuC$_3$P$_4$	+1.55 (1e$^-$, 70)	535	40
RuC$_4$P$_4$	+1.07 (1e$^-$, 82)	540	15
OsC$_2$P$_2$e	+1.35 (1e$^-$, 76)	600	190
OsC$_3$P$_4$	+1.12 (1e$^-$, 74)	570	350
OsC$_4$P$_4$	+0.80 (1e$^-$, 62)	590	410
RuC$_3$P$_4$Ru	+1.07 (2e$^-$, 96)	560	45
RuC$_4$P$_4$Ru	+1.01 (1e$^-$, 69), +1.43 (1e$^-$, 63)	595	820
OsC$_3$P$_4$Os	+0.77 (2e$^-$, 100)	575	520
OsC$_4$P$_4$Os	+0.72 (1e$^-$, 78), +1.35 (1e$^-$, 76)	660	480

[a] In deoxygenated acetonitrile at 25 °C. [b] Versus SCE.

3) While the homobimetallic complexes MC$_3$P$_4$M (M = Ru or Os) feature two overlapping one-electron processes, the corresponding MC$_4$P$_4$M (M = Ru or Os) complexes have two consecutive one-electron processes (Figure 2). This is ascribed to the difference in the electronic communication between the two terminal subunits resulting from the change of spacer group.

For the binuclear complexes that can undergo multistep charge-transfer [Eq. (1)] the equilibrium constant K_c for the

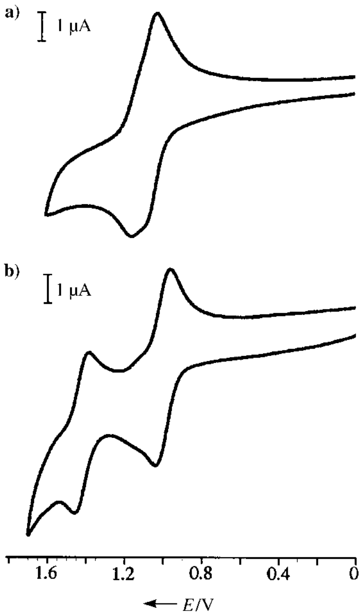

Figure 2. Cyclic voltammogram of a) RuC_3P_4Ru and b) RuC_4P_4Ru. Electrolyte: 0.1M $NtBu_4PF_6$, Pt disk (1.0 mm) working electrode, Ag/AgCl reference electrode, Pt wire counter-electrode, scan rate 100 mV s^{-1}.

comproportionation reaction is defined as shown in Equation (2), with $\Delta E^\circ = E_1^\circ - E_2^\circ$ in mV and at 298 K.[16] Here

$$M^{n+}M^{n+} \underset{e^-}{\overset{E_1^\circ}{\rightleftharpoons}} M^{(n-1)+}M^{n+} \underset{e^-}{\overset{E_2^\circ}{\rightleftharpoons}} M^{(n-1)+}M^{(n-1)+} \qquad (1)$$

$$K_c = \frac{[M^{(n-1)+}M^{n+}]^2}{[M^{n+}M^{n+}][M^{(n-1)+}M^{(n-1)+}]} = \exp[(E_1^\circ - E_2^\circ)/25.69] \qquad (2)$$

$M^{n+}M^{n+}$, for example, represent the discrete binuclear complexes. Stationary cyclic voltammetry has been applied previously to determine the ΔE° value by estimation from $\Delta E_{1/2}$.[16a] From $\Delta E_{1/2}$ a quantitative measure of the energetics for the comproportionation reactions can be achieved and K_c values range from four in the uncoupled Robin and Day Class I systems to 10^{13} in the strongly coupled Class III systems.[14b, 17] For our homobimetallic complexes MC_4P_4M (M = Ru or Os), the calculated K_c values are 1.3×10^7 for M = Ru ($\Delta E_{1/2}$ = 420 mV) and 4.5×10^{10} for M = Os ($\Delta E_{1/2}$ = 630 mV). Such K_c values are comparable or larger than those reported for species with strong electronic interaction between the two redox centers spanned by rigid spacers such as pyrazine.[14b, 16b, 17] In addition, the OsC_4P_4Os complex has a much greater K_c value than that of the corresponding RuC_4P_4Ru complex.

Previously Creutz[17] discussed the remarkable changes in the electronic coupling through a given bridge that can be accomplished by changing the nature of M^{II} and M^{III} and that the increase in the M–M interaction reflects the increasing ability of M^{II} to interact with the bridging ligand (spacer). More specifically, the increasing M–M interaction in our Ru^{II} and Os^{II} series can be ascribed to the increasing M–L interaction by virtue of dπ-Lπ* mixing (L represents the spacer). Other representative examples include the interaction between two $Ru(NH_3)_5$ units ($\Delta E_{1/2}$ = 390 mV) and $Os(NH_3)_5$ units ($\Delta E_{1/2}$ = 760 mV) bridged by pyrazine.[17]

When a molecule contains two noninteracting metal centers, it is expected that the current–potential response in stationary cyclic voltammetry will be the same as a single-step charge transfer from a monomeric center.[14b, 16, 18] The observed metal-based oxidations of MC_3P_4M (M = Ru or Os) correspond to two overlapping one-electron processes. This indicates that the electronic interaction between the two metal centers spanned by a C_3P_4 spacer is rather weak, giving apparently simultaneous one-electron oxidation of the two metal centers. Hence, by fine tuning of the number of carbon atoms in the rigid rodlike C_n chains, we can control the electronic interaction (or communication) between the two terminal redox centers.

As shown in Table 2, the monometallic complexes RuC_2P_2e (τ_{EM} = 25 ns) and RuC_nP_4 (τ_{em} = 40 and 15 ns for n = 3 and 4, respectively) have, relative to $[Ru(bpy)_3](PF_6)_2$ (λ_{em} = 582 nm, τ = 960 ns[14]), short-lived triplet excited states. This observation is presumably due to the mixing between the charge transfer band and the (higher energy) metal-centered excited states.[19] In contrast, OsC_2P_2e (τ = 190 ns) and OsC_nP_4 (τ = 350 and 410 ns for n = 3 and 4, respectively) exhibit much longer lived ^{3}MLCT excited states when compared with the corresponding osmium complex $[Os(bpy)_3](PF_6)_2$ (λ_{EM} = 746 nm, τ = 60 ns). This change in Os-based excited states is consistent with that predicted by the energy gap law:[13b] the replacement of one of the σ-donating polypyridyl ligands with phosphane can result in a decrease in the rate of nonradiative decay due to an increase of the energy gap between the emitting MLCT excited state (largely triplet in character) and the singlet ground state. Correspondingly, emissions from monomeric complexes with phosphanes shift significantly toward high energy. Typically, such a blue shift is expected when a stronger ligand (such as polyphosphane) is used to replace a relatively weak ligand (such as bpy). Homobimetallic complexes MC_nP_4M (M = Ru and Os) have red-shifted emission maxima (Table 2) relative to the corresponding monomeric species MC_nP_4, indicative of a lower triplet energy in bimetallic complexes. Lowering of the triplet energy may inhibit mixing between the MLCT triplet and the higher energy metal- or ligand-centered excited states. Such decoupling of the states will also result in the prolongation of triplet lifetimes and is largely responsible for the observed longer lifetimes in homobimetallic species. Typically, Ru^{II} complexes with polyphosphanes have electronic absorption in the visible region with λ_{max} around 380–450 nm, while Os^{II} complexes absorb with λ_{max} around 450–500 nm. These are assigned to MLCT bands from the terminal Ru^{II}/Os^{II}-polypyridyl units. A representative comparison between the absorption and emission spectra is shown in Figure 3, using data for RuC_4P_4Ru.

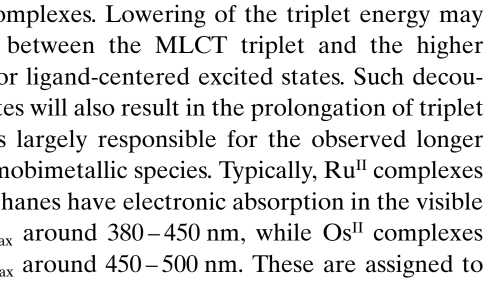

Figure 3. Comparison of the absorption and emission spectra of RuC_4P_4Ru in deoxygenated acetonitrile at 25 °C. An excitation wavelength of 480 nm was used for the measurement of the steady-state emission.

In conclusion, we have shown that rigid spacers with C_n ($n=3$, 4) sp carbon chains are suitable novel types of molecular building blocks in the construction of molecular rods. Compounds containing these types of spacers exhibit interesting photophysical properties and tunable electronic communication between the terminal sites upon change of the carbon chain length. Currently we are investigating the application of such spacers, including the ones with longer chain lengths, in the construction of functional supramolecular systems capable of performing, for example, directional intramolecular electron/energy transfer.

Experimental Section

All reactions were carried out in a nitrogen atmosphere unless otherwise noted.

General procedure for the monomeric complexes MC_2P_2e and MC_nP_4 ($n=$ 3, 4): A solution of $[M(bpy)_2Cl_2]$ ($M=Ru$ or Os) (1.0 equiv) in ethylene glycol (20 mL) was added dropwise to a refluxing solution of C_3P_4, C_4P_4, or C_2P_2e (typically, 2.2–3.0 equiv) in THF. The resulting mixture was heated under reflux for 15 h. An excess of NH_4PF_6 was then added and the mixture was heated under reflux for up to 60 h to ensure the completion of reaction. The solution was cooled to room temperature, and the THF portion of the reaction mixture was removed by rotary evaporation. The resulting ethylene glycol solution was added dropwise to a saturated solution of KPF_6 in H_2O. The precipitate was collected by vacuum filtration, washed with H_2O (3×20 mL) and diethyl ether (3×20 mL), then dried in vacuo. The product was then purified by column chromatography (basic alumina, acetonitrile/toluene (60/40) eluent).

General procedure for the synthesis of the homobimetallic complexes MC_nP_4M ($M=Ru$ or Os, $n=3$ or 4): A hot solution of C_nP_4 (1.0 equiv, $n=3$ or 4) in THF was added dropwise to a hot solution of $[M(bpy)_2Cl_2]$ ($M=Ru$ or Os) (2.2 equiv) in ethylene glycol (20 mL) at approximately 120°C. The resulting mixture was refluxed for 15 h, then allowed to cool to room temperature. An excess of NH_4PF_6 was added and the mixture was then refluxed for up to 60 h to ensure the completion of reaction. The mixture was again cooled to room temperature, and the THF portion of the solvent mixture was removed by rotary evaporation. The resulting ethylene glycol solution was added slowly to a saturated solution of KPF_6 in H_2O. The precipitate was collected by vacuum filtration, washed with H_2O (3×20 mL) and diethyl ether (3×20 mL), and dried in vacuo. The homobimetallic product was isolated by column chromatography as the second fraction, using basic alumina and acetonitrile as eluent, from the corresponding monometallic complex.

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The First Homoleptic Metallabenzene Sandwich Complex[**]

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In connection with our previous studies on the reactivity of "half-open" metallocenes, we have found examples for the insertion of organometallic fragments into the "open" side of pentadienyl ligands, leading to the formation of metallacyclic six-membered ring ligands (Scheme 1).[1, 2] Using Wade's rules, this can be regarded as the expansion of an *arachno* to a *nido* structure. The metallabenzenes thus formed (exchange of CH for an isolobal metal fragment) are one of the rarest, but nevertheless most interesting representatives of metallacycles of the transition elements.[3] They are considered to be

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