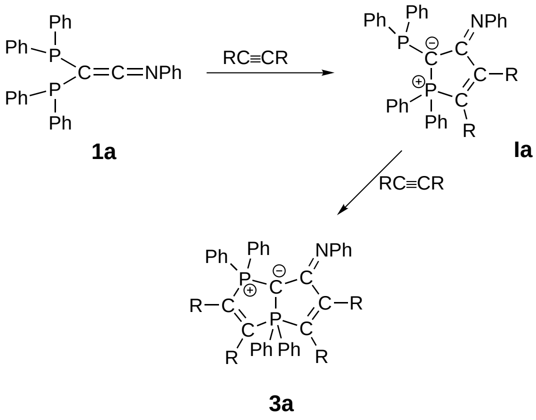

Scheme 2. Two [2+3] cycloaddition reactions of **1a** with dimethyl acetylenedicarboxylate provide **3a**. R = CO_2Me.

Experimental Section

2a: A solution of **1a** (0.1 g, 0.2 mmol) in hexane (10 mL) was very slowly evaporated to dryness under vacuum. Hexane (10 mL) was added to the residue, giving an orange precipitate corresponding to the dimer **2a**; the monomer **1a** remained in solution. The solution was filtered off and then retreated with hexane to afford a new fraction of **2a**. The process was repeated three times; yield 70% (0.07 g). The yield can be improved by repeating the process as many times as possible. Crystals suitable for X-ray diffraction were grown from a solution in CH_2Cl_2/hexane. Elemental analysis calcd for $C_{64}H_{50}N_2P_4$: C 79.16, H 5.19, N 2.88; found: C 78.84, H 5.27, N 2.78; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.90$ (4H, dd, $^3J_{P,H} = 13$, $^3J_{H,H} = 7$ Hz), 6.4–7.4 (44H, m), 5.85 (2H, d, $^3J_{H,H} = 7$ Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 28.5$ (ddd, $^2J_{P,P} = 52$, $^3J_{P,P} = 24$, $^3J_{P,P} = 6$ Hz), 14.3 (dd, $^3J_{P,P} = 24$, $^3J_{P,P} = 4$ Hz), 6.8 (dd, $^3J_{P,P} = 4$, $^3J_{P,P} = 6$ Hz), −22.8 (d, $^2J_{P,P} = 52$ Hz).

2b: Compound **2b** was prepared analogous to **2a**. Elemental analysis calcd for $C_{66}H_{54}N_2P_4$: C 79.35, H 5.45, N 2.80; found: C 79.26, H 5.32, N 2.75; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.85$ (4H, dd, $^3J_{P,H} = 13$, $^3J_{H,H} = 7$ Hz), 6.4–7.4 (42H, m), 5.84 (2H, d, $^3J_{H,H} = 7$ Hz), 2.35 (3H, s), 2.12 (3H, s); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 28.6$ (m), 13.7 (m), 6.5 (s, br), −23.8 (m).

3a: To a solution of **1a** (0.05 g, 0.1 mmol) in CH_2Cl_2 (10 mL) was added dimethyl acetylenedicarboxylate (0.025 mL, 0.2 mmol). The color changed to red instantly. After 5 min of stirring at room temperature the solvent was evaporated to dryness, and the brown residue recrystallized from CH_2Cl_2/hexane to afford red crystals; yield 85% (0.065 g). Elemental analysis calcd for $C_{44}H_{37}NO_8P_2$: C 68.65, H 4.84, N 1.81; found: C 68.43, H 4.80, N 1.83; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.99$ (4H, dd, $^3J_{P,H} = 14$, $^3J_{H,H} = 7$ Hz), 6.8–7.8 (19H, m), 6.52 (2H, d, $^3J_{H,H} = 7$ Hz), 3.50 (3H, s), 3.35 (3H, s), 3.27 (3H, s), 2.89 (3H, s); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 8.97$ (d, $^2J_{P,P} = 71$ Hz), −81.40 (d, $^2J_{P,P} = 71$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 199.43$ (dd, $J_{P,C} = 32$, 22 Hz), 170.30 (dd, $J_{P,C} = 25$, 4 Hz), 170.05 (dd, $J_{P,C} = 14$, 10 Hz), 169.15 (dd, $J_{P,C} = 3$, 1 Hz), 166.51 (dd, $J_{P,C} = 6$, 2 Hz), 162.41 (dd, $J_{P,C} = 16$, 2 Hz), 159.52 (dd, $J_{P,C} = 23$, 13 Hz), 151.86 (d, $J_{P,C} = 5$ Hz), 131.28 (dd, $J_{P,C} = 12$, 7 Hz), 117.2 (dd, $J_{P,C} = 93$, 6 Hz), 52.60 (s, 1 × CH_3), 51.57 (s, 3 × CH_3); signals for phenyl groups not given.

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[6] Crystal data for **2a** ($C_{64}H_{50}N_2P_4$): $M_r = 970.94$, orthorhombic, space group $P2_12_12_1$, $a = 10.609(7)$, $b = 13.36(1)$, $c = 36.06(2)$ Å, $V = 5111(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.262$ g cm^{-3}, $F(000) = 2032$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.191$ mm^{-1}; crystal dimensions 0.20 × 0.20 × 0.13. Diffraction data were collected on a Enraf-Nonius at 293 K. The structure was solved with direct methods and refined using full-matrix least squares on F^2 with all non-hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions, isotropically refined with common thermal parameters, and allowed to ride on their parent carbon atoms. For 5590 unique reflections and 632 parameters, $R = 0.063$ and $wR2 = 0.109$. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136772. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] The H(1) atom, together with C(1), C(2), and C(11), completes a virtual distorted tetrahedron around N(1): C(1)-N(1)-H(1) 132°, C(2)-N(1)-H(1) 107°, C(11)-N(1)-H(1) 77°, C(1)-N(1)-C(2) 111°, C(1)-N(1)-C(11) 111°, C(2)-N(1)-C(11) 115°.

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Dianionic Homoleptic Biphosphinine Complexes of Group 4 Metals**

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The stabilization of anionic transition metal centers is generally associated with the use of ancillary ligands possessing strong π-acceptor properties. For the most part, it was achieved with molecules such as CO,[1] isocyanides,[2] ethylene,[3] and arenes[4] which display a suitable synergistic effect between σ-donor and π-acceptor capabilities, and in rare cases, by using tailored tertiary phosphanes.[5] However, only little is known about the stabilizing effects provided by

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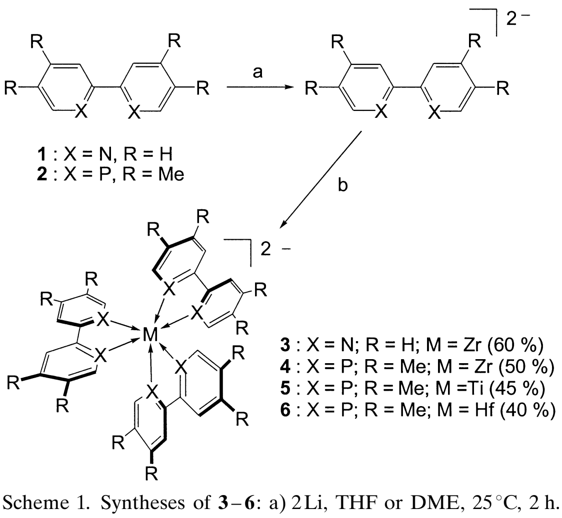
heterocycle-based ligands. Herzog et al. reported on the synthesis of some homoleptic neutral and anionic complexes of 2,2′-bipyridine (bpy),[6] and more recently it was shown that bipyridine radical anions efficiently stabilize lanthanide complexes.[7]

Several years ago, we proposed that 2,2′-biphosphinines could efficiently stabilize reduced metal centers.[8] This proposal was based on preliminary studies which showed that these ligands display a lower σ-donor but a better π-acceptor capability than their nitrogen counterparts. Although electrochemical reduction led to the formation of stable reduced species, anionic complexes remained to be isolated and structurally characterized. Here we report on the synthesis of complexes of the Group 4 metal dianions, carbonyl derivatives of which have attracted much attention.[9] To facilitate structural comparisons between biphosphinine and bipyridine complexes, we synthesized $[Zr(bpy)_3]^{2-}$, which was discovered by Herzog et al. but whose X-ray structure remained unknown.[10] Both complexes were synthesized by the same experimental procedure (Scheme 1), which involves the reaction of the dianion of bipyridine **1**[11] or biphosphinine **2** (tmbp)[12] with MCl_4 (M = Ti, Zr, Hf) in THF or dimethoxyethane (DME) at low temperature (see Experimental Section).



1 : X = N, R = H
2 : X = P, R = Me

3 : X = N; R = H; M = Zr (60 %)
4 : X = P; R = Me; M = Zr (50 %)
5 : X = P; R = Me; M =Ti (45 %)
6 : X = P; R = Me; M = Hf (40 %)

Scheme 1. Syntheses of **3**–**6**: a) 2Li, THF or DME, 25 °C, 2 h. b) $MCl_4 \cdot n$THF, −78 to 25 °C, 15 min.

Complexes **3**–**6** were isolated as dark colored, extremely air-sensitive solids and were characterized by NMR spectroscopy (^{31}P, ^{1}H, ^{13}C). The crystal structure analysis of the $[Li_2(thf)_{8.5}]^{2+}$ salt of **3** showed that the coordination geometry around zirconium is between octahedral and trigonal prismatic ($\Theta = 33.4°$, where Θ is the angle between the medians of the triangles formed by three nitrogen atoms; $\Theta = 60°$ for a regular octahedron). Most interestingly, while the N–Zr bond length lies in the usual range, the C–C and C–N bond lengths differ strongly from those of the free ligand. The alternation of short and long C–C distances clearly shows that the aromaticity of each pyridine unit is totally disrupted. This phenomenon is also evidenced by the shortening of the C–C bridge, which now has double-bond character (1.36(1) Å).[13] Conversely, the internal C=N bonds are lengthened (from 1.346(2) Å in free bipyridine to 1.435(7) Å in **3**) and approach the usual values recorded for C–N single bonds. These data, which indicate electron transfer into the symmetrical LUMO of the ligand, are very similar to those of a bipyridine dianion whose structure was reported recently.[11]

Structure determinations for **4**–**6** were also carried out. The structure of **4** is shown in Figure 1.[14] In the three complexes, $[Li_3(dme)_6Cl]$-**4**, $[Li_3(thf)_9Cl]$-**5**, and $[Li_3(thf)_9Cl]$-**6** the overall geometry around the metal center is trigonal prismatic ($\Theta = 3°$ for **4**, 0° for **5** and **6**). A comparison between their Zr–P bond lengths and those of other complexes is difficult because of the lack of data. In **4** these distances (2.5248(8)–2.563(1) Å) are shorter than in the only other known phosphinine zirconium complex, the η^2-phosphabenzyne zirconocene complex (av P–Zr 2.69 Å).[15] As in **3**, disruption of the aromaticity is observed in each phosphinine subunit. However, the C–C bridge and the internal C=P bond lengths exhibit smaller variations than in **3**. With lengths of 1.428(4)–1.438(4) and 1.774(3)–1.785(3) Å, respectively, these two bonds are intermediate between single and double bonds. The same phenomenon is observed in **5** and **6**.

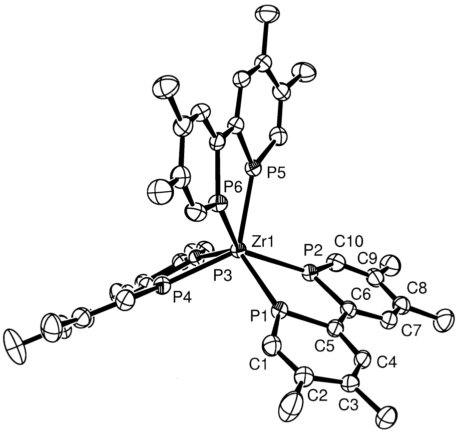


Figure 1. Structure of **4** in the crystal (50 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°] of one biphosphinine unit: P1-Zr1 2.5441(8), P2-Zr1 2.563(1), P3-Zr1 2.551(1), P4-Zr1 2.5248(8), P5-Zr1 2.5486(8), P6-Zr1 2.532(1), P1-C1 1.753(3), C1-C2 1.362(4), C2-C3 1.428(5), C3-C4 1.368(4), C4-C5 1.414(4), C5-P1 1.779(3), C5-C6 1.434(4), C6-P2 1.779(3), P2-C10 1.752(3), C10-C9 1.380(5), C9-C8 1.429(5), C8-C7 1.370(5), C7-C6 1.422(4); P1-Zr-P2 69.91(3), C5-P1-C1 100.4(2).

From these data, it is clear that the −2 oxidation state of Zr is only formal. Interestingly, the two ligands seem to accommodate the release of electron density from the metal center in different ways. Whereas **3** can be described as the coordination of three bipyridine dianions to a Zr^{IV} center, **4** has a delocalized character that makes the assignment of a precise oxidation state difficult (Scheme 2).[16] This assumption is reinforced by the striking analogy between the bond lengths in **4** and those of the complex $[Mn_2(tmbp)(CO)_6]$, in which a $[Mn(CO)_3]^+$ fragment is η^5-coordinated to a delocalized $[P_2C_2Mn(CO)_3]^-$ unit.[17]

A second important point is the overall geometry of **3** and **4**. If the two ligands display the same geometrical constraints

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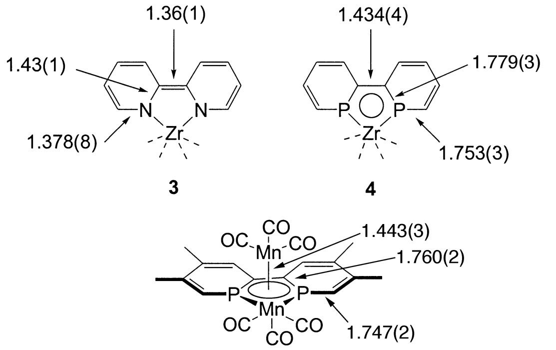

Scheme 2. Bonding modes in complexes **3** and **4** in comparison with those of a Mn complex of tmbp. Bond lengths in Ångström.

(bulk and bite angles are nearly identical), only electronic factors can explain the observed differences. According to Hoffmann's prediction,[18] ML_6 complexes of chelating ligands can adopt a trigonal-prismatic geometry if the ligands possess a low-lying symmetrical LUMO (the shape of this orbital is similar in biphosphinine and bipyridine). This was verified previously for $[W(tmbp)_3]$, which, like **4**–**6**, displays a strong preference for this geometry ($\Theta = 15°$).[19] At this stage and without any further theoretical data it is difficult to fully rationalize why complex **3** adopts an intermediate geometry.

In conclusion, we have shown that biphosphinine dianions, like their nitrogen counterparts, can be used as efficient precursors of previously unknown homoleptic dianionic Group 4 metal complexes. Additionally, the first examples of Ti and Hf η^1-phosphinine complexes were also synthesized. Extension of this work to other metals is currently underway.

Experimental Section

All manipulations were conducted by using Schlenk and glove-box techniques under an argon atmosphere. Complexes **3**–**6** were prepared by the same methodology. To a solution of the ligand (123 mg, 0.50 mmol) in dry THF or DME (10 mL) was added an excess (about 10 equiv) of lithium in pieces. The excess lithium was removed after 2 h, and the resulting solution of **1** or **2** was cooled to −78 °C. Solid $ZrCl_4 \cdot 2THF$, $TiCl_4 \cdot 2THF$, or $HfCl_4$ (0.16 mmol) was then added, and the resulting solution was stirred at −78 °C for 5 min then slowly warmed to room temperature. The compounds separated from the solution over ca. 12 h as small deep purple to black crystals, which were collected by filtration in the glove box. Complexes **3**–**6** are very sensitive towards air and moisture.

4: (114 mg, 50%) ; m.p. > 220 °C (decomp); ^{31}P NMR (C_4D_8O/DME 1/9, 81 MHz, 25 °C): $\delta = 226.30$; ^1H NMR (C_4D_8O/DME 1/9, 400 MHz, 25 °C): $\delta = 2.32, 2.48$ (s, 18H, Me), 8.02 (brs, 6H, H^3, $H^{3'}$), 8.84 (brs, 6H, H^6, $H^{6'}$); ^{13}C NMR (C_4D_8O/DME 1/9, 100 MHz, 25 °C): $\delta = 23.35$ and 24.80 (s, Me), 121.15 (s, C^4, $C^{4'}$ or C^5, $C^{5'}$), 125.30 (brs, C^3, $C^{3'}$), 131.85 (s, C^5, $C^{5'}$ or C^4, $C^{4'}$), 139.30 (brs, C^2, $C^{2'}$), 146.10 (brs, C^6, $C^{6'}$); C,H analysis calcd for $C_{66}H_{108}ClLi_3O_{12}P_6Zr$ (1426.9): C 55.56, H 7.63; found : C 55.80, H 7.70.

5: (107 mg, 45%); m.p. > 220 °C (decomp); ^{31}P NMR (C_4D_8O/DME 1/9, 81 MHz, 25 °C): $\delta = 252.95$; ^1H NMR (C_4D_8O/DME 1/9, 400 MHz, 25 °C): 2.33 and 2.56 (s, 18H, Me), 7.98 (brs, 6H, H^3, $H^{3'}$), 9.28 (brs, 6H, H^6, $H^{6'}$); ^{13}C NMR (C_4D_8O/DME 1/9, 100 MHz, 25 °C): $\delta = 23.05$ and 23.45 (s, Me), 120.15 (s, C^4, $C^{4'}$ or C^5, $C^{5'}$), 124.95 (brs, C^3, $3C'$), 132.35 (s, C^5, $C^{5'}$ or C^4, $C^{4'}$), 141.60 (brs, C^2, $C^{2'}$), 146.05 (brs, C^6, $C^{6'}$); C,H analysis calcd for $C_{78}H_{120}ClLi_3O_9P_6Ti$ (1491.8): C 62.80, H 8.11; found : C 62.40, H 8.17.

6: (104 mg, 40%); m.p. > 220 °C (decomp); ^{31}P NMR (C_4D_8O/DME 1/9, 81 MHz, 25 °C): $\delta = 214.90$; ^1H NMR (C_4D_8O/DME 1/9, 400 MHz, 25 °C): $\delta = 2.34$ and 2.50 (s, 18H, Me), 8.06 (brs, 6H, H^3, $H^{3'}$), 8.81 (brs, 6H, H^6, $H^{6'}$). The poor solubility of **6** precluded recording a ^{13}C NMR spectrum; C,H analysis calcd for $C_{78}H_{120}ClHfLi_3O_9P_6$ (1622.4): C 57.74, H 7.46; found: C 57.85, H 7.42.

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[14] X-ray structure data: Nonius Kappa CCD diffractometer, ϕ and ω scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with maXus,[20] refinement against F^2 (SHELXL97[21]) with anisotropic thermal parameters for all non-hydrogen atoms; calculated hydrogen positions with riding isotropic thermal parameters. Data collection for **4**: crystal dimensions $0.16 \times 0.16 \times 0.14$ mm, triclinic, space group $P\bar{1}$, $a = 15.0930(4)$, $b = 22.6420(7)$, $c = 23.7110(7)$ Å, $\alpha = 76.592(2)$, $\beta = 74.626(2)$, $\gamma = 89.957(2)°$, $V = 7584.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.250$ g cm^{-3}, $\mu = 0.360$ cm^{-1}, $F(000) = 3024$, $\theta_{max} = 26.40°$, h,k,l ranges: 0 to 18, −28 to 28, −28 to 29; 30043 reflections collected, of which 30043 were unique ($R_{int} = 0.05$); 21458 reflections with $I > 2\sigma(I)$ and 1694 parameters refined; GOF(F^2) 1.032, final R indices: $R_1 = 0.0480$, $wR_2 = 0.1350$, max./min. residual electron density 0.849(0.091)/ −0.582(0.091) e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136105 (**3**), -136106 (**4**), -136107 (**5**), and -136108 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Investigation of Electronic Communication and Guest Inclusion Using Photoluminescent Macrocyclic Receptors with Ru^{II} Centers and $Ph_2P{-}C{\equiv}C{-}C{\equiv}C{-}PPh_2$ Spacers[**]

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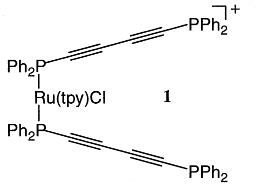
The study of photoluminescent and redox-active supramolecular systems has attracted recent attention as a consequence of a rapid growing interest in designing artificial arrays for applications in photonic and electronic devices.[1, 2] Systems with various designs have been studied using the assembly of active (for example, metal-based chromophores and redox-active moieties) and passive components (for example, rigid or flexible spacers) as a basis.[1–7] Such systems are constructed to gain a practical insight into parameters and factors that govern processes, such as signal transportation, by electron/energy transfer, electronic and excitonic interaction, as well as guest inclusion and selective molecular sensing.

We have become interested in investigating the photoluminescent and redox-active macrocyclic inorganic cyclophanes for their dual capability in molecular recognition through host–guest interaction and electronic communication between multiple redox centers within a macrocyclic platform. Monomeric model complex $[RuCl(tpy)(`C_4P_2')_2](PF_6)$ (**1**), rectangular dimer $[\{RuCl(tpy)(`C_4P_2')\}_2](PF_6)_2$ (**2**), and triangular macrocycle $[\{RuCl(tpy)(`C_4P_2')\}_3](PF_6)_3$ (**3**) have been prepared from [RuCl(tpy)]-based moieties (tpy = 2,2′:6′,2″-terpyridine) and rigid ditopic phosphane spacer $Ph_2P{-}C{\equiv}C{-}C{\equiv}C{-}PPh_2$ ('C_4P_2'), in order to study the redox interaction and guest inclusion by electrochemical and optical methods. The short alkyne bridge affords the desired structural rigidity to provide controllable cavity sizes in the systems. The Ru^{II}-based moieties with polypyridine and polyphosphane ligands also have well-behaved reversible redox properties and photoluminescence characteristics. Such properties are extremely important for the design and applications of new spectral and electrochemical sensory agents for organic guests based on organometallic and coordination receptor systems.[4]



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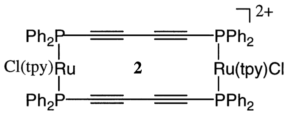

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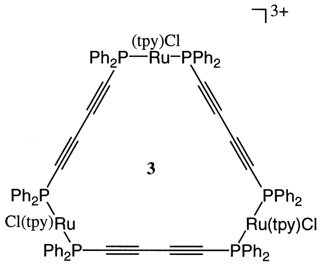

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Herein, the synthesis, chromatographic separation, and characterization of **1**–**3** are reported. Other properties have also been studied, including the ground-state absorption, excited-state emission, redox characteristics, and guest inclusion using anisole and 1,4-dimethoxybenzene as guest molecules. Specifically, the emission intensities of hosts **2** and **3** increase steadily upon addition of guest molecules, and the binding constants of both guest molecules increase significantly when the trimeric system **3** with the larger cavity is used. In addition, the redox interaction between the metal-based corner units is also investigated using cyclic and square-wave voltammetry. The best electronic communication is observed between the two terminal Ru^{II} centers in the doubly bridged complex **2**.

The spacer 'C_4P_2' is prepared from $Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3$ by treatment with 2.5 equivalents of $MeLi \cdot LiBr$ and then 2.5 equivalents of $ClPPh_2$. Complexes **1**–**3** are obtained upon reaction of 'C_4P_2' and $[RuCl_3(tpy)]$ (3/1 ratio, with an excess NH_4PF_6) in refluxing THF/ethylene glycol mixture (4/1), in yields of 15, 30, and 12 %, respectively, after purification. When a 1/1 ratio of 'C_4P_2' and $[RuCl_3(tpy)]$ is used only **2** and **3** (35 and 15 % yield, respectively, after chromatographic separation) are obtained.

The identification of all new complexes was accomplished using $^{31}P\{^1H\}$ NMR spectroscopy and electrospray mass spectrometry (ESI-MS). The $^{31}P\{^1H\}$ NMR measurements show two peaks at $\delta = +13.6$ (corresponding to the coordinated PPh_2 group in 'C_4P_2') and $\delta = -29.7$ (free PPh_2 group in 'C_4P_2') for **1**. Only one peak at $\delta = +23.1$ for **2** and $\delta = +19.3$ for **3** are observed, both corresponding to the coordinated PPh_2 units in the 'C_4P_2' spacer. ESI-MS measurements offered a straightforward identification of **1**–**3**, giving fragments with single or double positive charges. A representative ESI mass spectrum of **3** is shown in Figure 1, as well as the comparison of the observed and simulated isotope distributions for the doubly charged fragment at m/z 1255.5 $[\mathbf{3} - 2PF_6]^{2+}$.

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) can be used to probe the redox characteristics and electronic communication between the Ru^{II} termini in the macrocyclic molecular systems and the corresponding model complex. Only a single redox peak at +1.06 V (1e$^-$, $\Delta E_p = 81$ mV) for **1** or +1.30 V (3e$^-$, $\Delta E_p = 96$ mV) for **3** is observed for the Ru^{II}/Ru^{III} redox couples, while two consecutive one-electron redox waves (1:1 ratio, peak separation $\Delta E^0 = E_2^0 - E_1^0 = 100$ mV) are found at +1.03 V (1e$^-$, $\Delta E_p = 84$ mV) and +1.13 V (1e$^-$, $\Delta E_p = 85$ mV) for **2** (Figure 2). All redox

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