instrument TGA 2950. Magnetic data were collected using a Quantum Design MPMS2 SQUID magnetometer, and were corrected for diamagnetic contributions.

1: Solid NiI_2 (54 mg, 0.17 mmol) was added to a solution of $[(Me_3tacn)Cr(CN)_3]$[7] (72 mg, 0.24 mmol) in 20 mL of water. The deep red-brown mixture was stirred and heated at reflux for 8 h, and the solution volume was reduced to 4 mL with further heating. Upon cooling to room temperature, a small amount of yellow solid was separated from the reaction mixture by filtration. The filtrate was allowed to stand for 2 d, leading to formation of large red-brown rhombic plate-shaped crystals, which were collected by filtration, washed with Et_2O (4 × 2 mL), and dried in air to yield 85 mg (64 %) of product. Absorption spectrum (H_2O): λ_{max} (ε_M): 365 (13340), 500 nm (6295, sh); IR: $\tilde{\nu}$ = 2143, 2171 (sh) cm^{-1} (ν_{CN}); ES^+ MS: *m*/*z*: 1197.331 ($[\mathbf{1}-3I-27H_2O]^{3+}$), 886.272 ($[\mathbf{1}-4I-27H_2O]^{4+}$), 667.636 ($[\mathbf{1}-5I-27H_2O]^{5+}$), 535.046 ($[\mathbf{1}-6I-27H_2O]^{6+}$); elemental analysis calcd for $C_{96}H_{222}Cr_8I_{10}N_{48}Ni_5O_{27}$: C 25.86, H 5.02, N 15.08; found: C 26.14, H 4.96, N 14.75.

2: A solution (20 mL) of compound **1** was prepared by treating $[(Me_3tacn)Cr(CN)_3]$[7] (130 mg, 0.44 mmol) with NiI_2 (100 mg, 0.32 mmol) as described above. Instead of allowing this solution to stand for 2 d, a solution of $Na_2[Ni(CN)_4]$ (410 mg, 2.0 mmol) in 12 mL of water was added, producing a fine yellow precipitate. The mixture was centrifuged, and the supernatant solution was decanted and allowed to stand for 3 d. The resulting orange hexagonal plate-shaped crystals were collected by filtration, washed with THF (2 × 1 mL), and dried in air to yield 42 mg (18 %) of product. IR: $\tilde{\nu}$ = 2123, 2145, 2160 cm^{-1} (ν_{CN}); elemental analysis calcd for $C_{144}H_{320}Cr_{10}N_{84}Ni_{12}O_{55}$: C 32.43, H 6.05, N 22.07; found: C 32.48, H 5.77, N 21.94.

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[1] a) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804 – 1816; b) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141 – 143; c) A.-L. Barra, P. Debrunner, D. Gatteschi, C. E. Schultz, R. Sessoli, *Europhys. Lett.* **1996**, *35*, 133 – 138; d) S. L. Castro, Z. Sun, C. M. Grant, J. C. Bolinger, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1998**, *120*, 2365 – 2375, and references therein.

[2] a) H. J. Buser, D. Schwarzenbach, W. Petter, A. Ludi, *Inorg. Chem.* **1977**, *16*, 2704 – 2710; b) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283 – 391, and references therein.

[3] a) T. Mallah, S. Thiébaut, M. Verdaguer, P. Veillet, *Science* **1993**, *262*, 1554 – 1557; b) W. R. Entley, G. S. Girolami, *Science* **1995**, *268*, 397 – 400; c) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet, M. Verdaguer, *Nature* **1995**, *378*, 701 – 703; d) S. M. Holmes, G. S. Girolami, *J. Am. Chem. Soc.* **1999**, *121*, 5593 – 5594.

[4] J. L. Heinrich, P. A. Berseth, J. R. Long, *Chem. Commun.* **1998**, 1231 – 1232.

[5] Analogous clusters featuring cyclopentadienyl and/or carbonyl ligands have also been reported: a) K. K. Klausmeyer, T. B. Rauchfuss, S. R. Wilson, *Angew. Chem.* **1998**, *110*, 1808 – 1810; *Angew. Chem. Int. Ed.* **1998**, *37*, 1694 – 1696; b) K. K. Klausmeyer, S. R. Wilson, T. B. Rauchfuss, *J. Am. Chem. Soc.* **1999**, *121*, 2705 – 2711.

[6] Very recently, ground states of record high spin have been observed for pentadecanuclear metal – cyanide clusters: a) Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. Ohkoshi, K. Hashimoto, *J. Am. Chem. Soc.* **2000**, *122*, 2952 – 2953; b) J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem.* **2000**, *112*, 1667 – 1672; *Angew. Chem. Int. Ed.* **2000**, *39*, 1605 – 1609.

[7] P. A. Berseth, J. J. Sokol, M. P. Shores, J. L. Heinrich, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 9655 – 9662.

[8] Crystallographic analyses: **1** ($C_{96}H_{214}Cr_8I_{10}N_{48}Ni_5O_{23}$): T = 138 K, triclinic, space group $P\bar{1}$, a = 16.3879(3), b = 17.6461(3), c = 18.1958(2) Å, α = 65.885(1), β = 64.679(1), γ = 74.817(1)°, V = 4317.0(1) Å^3, Z = 1, ρ_{calcd} = 1.688 g cm^{-3}, R_1 = 0.0729, wR_2 = 0.2154 for 21589 data (13758 independent), 914 parameters, and 40 restraints. **2** ($C_{144}H_{288}Cr_{10}N_{84}Ni_{12}O_{39}$): T = 143 K, hexagonal, space group $P6_3$, a = 22.084(2), c = 31.999(4) Å, V = 13516(2) Å^3, Z = 2, ρ_{calcd} = 1.240 g cm^{-3}, R_1 = 0.1173, wR_2 = 0.2793 for 51793 data (10313 independent), 576 parameters, and 173 restraints. Single crystals were obtained directly from the reaction products; a slightly low water content was observed in each crystal structure. Data were collected on a Siemens SMART diffractometer using graphite monochromated $Mo_{K\alpha}$ (λ = 0.71073 Å) radiation, and were corrected for Lorentz, polarization, and absorption effects. Structures were solved by direct methods and refined against all data using SHELXTL 5.0. In the structure of **1**, the cluster is disordered over a crystallographic inversion center, superimposing the open face with the opposite closed face of the cage. Also in this structure, 7 iodide anions and 13 solvate water molecules are disordered over multiple sites and were refined accordingly. The crystal of **2** was found to be a racemic twin, and eight of the solvate water molecules were modeled as disordered over multiple positions in the structure. The final agreement factors for both structures are high due to the extensive disorder present in the crystals and the accompanying poor data quality. 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-146872 (**1**) and CCDC-146873 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] R. L. McCullough, L. H. Jones, R. A. Penneman, *J. Inorg. Nucl. Chem.* **1960**, *13*, 286 – 297.

[10] K. N. Raymond, F. Basolo, *Inorg. Chem.* **1966**, *5*, 949 – 950.

[11] K. N. Raymond, P. W. R. Corfield, J. A. Ibers, *Inorg. Chem.* **1968**, *7*, 1362 – 1372.

[12] E. L. Muetterties, L. J. Guggenberger, *J. Am. Chem. Soc.* **1974**, *96*, 1748 – 1756.

[13] Significantly, the trigonal-bipyramidal complexes in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ relax to the standard square-pyramidal geometry upon dehydration of the crystals: A. Terzis, K. N. Raymond, T. G. Spiro, *Inorg. Chem.* **1970**, *9*, 2415 – 2420.

Chelate Formation around a Hexarhenium Cluster Core by the Diphosphane Ligand $Ph_2P(CH_2)_6PPh_2$**

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The octahedral hexametal cluster core $M_6(\mu_3\text{-}E)_8$ (E = chalcogenide or halide ions) is one of the most common structural units in metal cluster complexes.[1–7] Each metal ion possesses an axial (terminal) coordination site, and a pair of the axial ligands at two adjacent M sites are oriented perpendicular to each other. Thus, the unit can be regarded as a giant octahedral center. Mimicking mononuclear octahe-

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dral complexes of the substitution-inert type (such as Co^{III}) would introduce new aspects to octahedral hexametal cluster chemistry. However, this approach requires designed and controlled ligand substitution at the hexametal units.[1–6] Some features of normal octahedral complexes, including "chelate" formation and geometrical and optical isomerism, have not yet been established systematically for the hexametal clusters because of the synthetic difficulties in controlling the number and the geometry of ligands introduced into the octahedral $M_6(\mu\text{-}E)_8$ cores.

The use of hexarhenium clusters as giant octahedral centers is of special interest not only because of the substitution-inert nature of the Re^{III} center, which allows controlled substitution of a terminal ligand in a stepwise way, but also because of the redox-active and photoluminescent characters.[2, 3, 6, 8] Recently, Holm et al. reported the stepwise substitution of triethylphosphane for halide ions in $[Re_6Se_8I_6]^{3-}$ and $[Re_6S_8Br_6]^{3-}$.[1b, 3, 4] Our studies on hexarhenium clusters with pyridine derivatives yielded a new series of $[Re_6S_8]^{2+}$ clusters with well-defined structural and physicochemical properties.[2b–d, 6]

The aim of the present study was to achieve "bridge–chelate" formation on the hexarhenium cluster by using the diphosphane ligands $PPh_2(CH_2)_5PPh_2$ (dpppen) and $PPh_2(CH_2)_6PPh_2$ (dpph), as shown in Figure 1. For dpppen, the bridge-chelate coordination mode seems to be possible based on the bond lengths and angles in models, but our experiments only gave evidence of monodentate coordination for this ligand. However, the ligand dpph indeed gave the hexarhenium clusters with bridge–chelate dpph. In addition to the stepwise replacement of dpph, the influence of stepwise processes on the physical and chemical properties associated with the $Re_6Se_8^{2+}$ ion is also described herein.

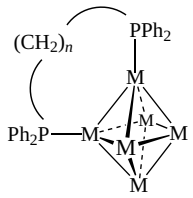
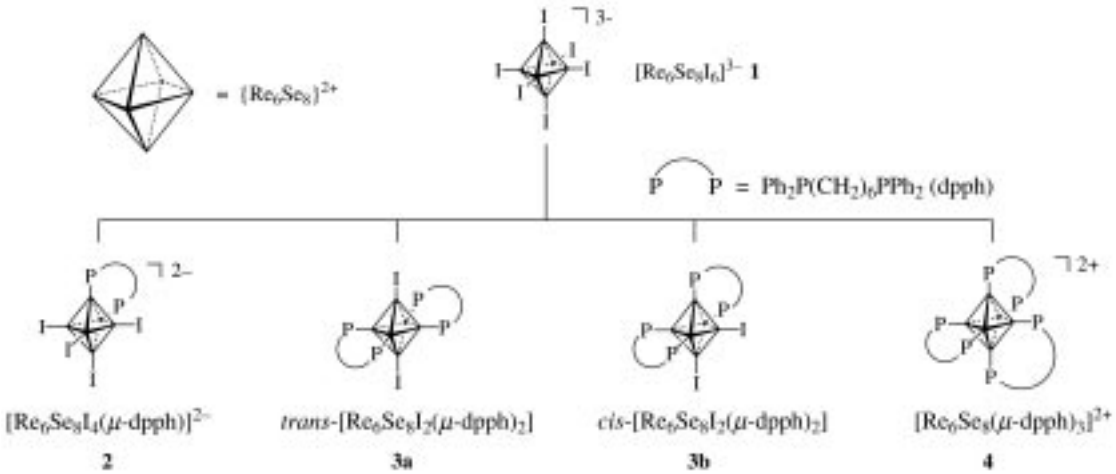


Figure 1. The bridge-chelate mode for the linear diphosphane ligands $Ph_2P(CH_2)_nPPh_2$.

Clusters with one, two, and three dpph ligands are summarized in Scheme 1: $(Bu_4N)_2[Re_6Se_8I_4(\mu\text{-dpph})]$ ($(Bu_4N)_2$-**2**), *trans*-$[Re_6Se_8I_2(\mu\text{-dpph})_2]$ (**3a**), *cis*-$[Re_6Se_8I_2(\mu\text{-dpph})_2]$ (**3b**), and $[Re_6Se_8(\mu\text{-dpph})_3](SbF_6)_2$ (**4**-$(SbF_6)_2$). Reactions between dpph and the precursor cluster anion $[Re_6Se_8I_6]^{3-}$ (**1**) were carried out in DMF with controlled temperature, reaction time, and reactant ratios (see Experimental Section). As observed for triethylphosphane and pyridine,[3, 4, 6] the ligand displacements can be controlled to afford stepwise diphosphane-substitued species, including geometric isomers. Two, four, and six iodo ligands of **1** are displaced by dpph to afford species of general formula $[Re_6Se_8I_{6-2m}(\mu\text{-dpph})_m]^{2m-4}$ ($m = 1-3$, Scheme 1). In the case of dpppen, only a monodentate diphosphane ligand was found, and the phosphorus center in the dangling arm was oxidized.[9] No sign of chelate formation was observed for dpppen. Thus, a small modification of the length of the methylene chain of the diphosphane ligands $PPh_2(CH_2)_nPPh_2$ ($n = 5, 6$) has led to a dramatic difference in the structure of the resulting hexarhenium(III) clusters. For the dpph ligand, bridge–chelate formation occurred even when the reaction was performed under aerobic conditions. Hence, it is the number n of methylene spacer groups in the diphosphane ligand $PPh_2(CH_2)_nPPh_2$ that is the main decisive factor in determining the substitution mode. Of the geometric isomers, the *cis* isomer **3b** was isolated in much higher yield (38%) than the *trans* isomer **3a** (6%).

The new dpph-substituted hexarhenium(III) clusters **2**, **3a**, **3b**, and **4** were characterized by elemental analysis, fast-atom bombardment mass spectrometry (FAB-MS), several spectroscopic methods, and, in the case of **3b**, X-ray crystallography. The expected composition for all of the complexes was unambiguously confirmed by FAB-MS. The X-ray structure of **3b** is shown in Figure 2.[10]

Two rhenium(III) centers (Re5 and Re6) are coordinated by iodo ligands and the remaining four rhenium(III) centers (Re1, Re2, Re3, and Re4) are occupied by phosphorus atoms of the dpph ligands, whereby one dpph is coordinated to Re1 and Re2, and the other to Re3 and Re4, in a bridge–chelate manner. To emphasize the view of the giant octahedron, the ring can geometrically be regarded as consisting of ten atomic members, the two Re atoms of which come from the giant



Scheme 1. Structural formulas of dpph-substituted octahedral hexarhenium(III) clusters **2**–**4** showing the substitution mode and geometry of the dpph ligands around the cluster core.

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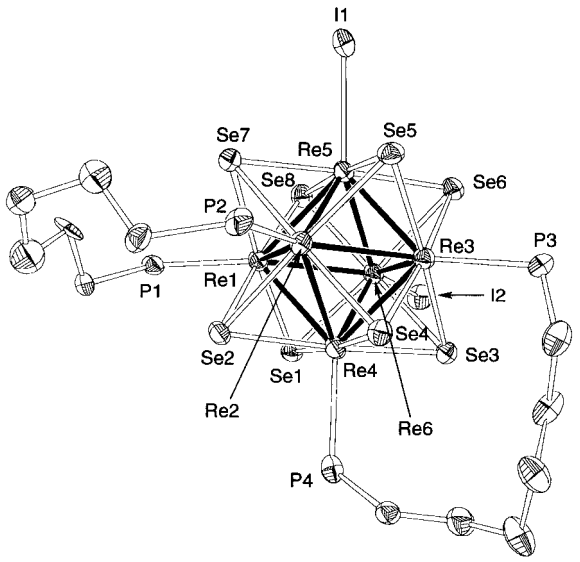

Figure 2. An ORTEP plot of **3b** at 50% probability level. Phenyl substituents on the phosphorus atoms are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Re1–Re2 2.6439(9), Re1–Re4 2.657(1), Re1–Re5 2.6388(5), Re1–Re6 2.6520(8), Re1–Se1 2.510(2), Re1–Se2 2.517(2), Re1–Se7 2.517(2), Re1–Se8 2.518(2), Re1–P1 2.488(4), Re2–Re3 2.6573(8),Re2–Re4 2.6756(9), Re2–Re5 2.6404(9), Re2–Se2 2.516(2), Re2–Se4 2.507(2), Re2–P2 2.503(4), Re2–Se5 2.520(2), Re2–Se7 2.517(2), Re3–P3 2.510(5), Re4–P4 2.490(4), Re5–I1 2.779(1), Re6–I2 2.786(1); Re2-Re1-Re4 60.63(3), Re4-Re1-Re5 89.80(3), Se1-Re1-Se2 89.56(5), Se1-Re1-Se7 176.08(6), Se1-Re1-P1 92.7(1), Se2-Re1-P1 89.0(1), Re1-Se1-Re4 63.68(4).

center. Thus, the consecutive member "P-Re-Re-P" embodies the rigid framework, while the remaining six methylene carbon atoms form the more flexible backbone of the chelate ring.[11] The bond lengths in **3b**, including Re–Re (2.6301(9) to 2.6756(9) Å), Re–Se (2.498(2) to 2.538(2) Å), Re–I (2.779(1) and 2.786(1) Å), and Re–P (2.488(4) to 2.510(5) Å), are similar to those of **1**[1b] and other octahedral hexarhenium clusters.[3, 4, 6]

In $^{31}P\{^1H\}$ NMR spectra recorded on $CDCl_3$ or CD_2Cl_2 solutions, only one signal is observed for the mono-dpph cluster **2** ($\delta = -29.9$), for the bis-dpph *trans* isomer **3a** ($\delta = -30.5$), and for the tris-dpph cluster **4** ($\delta = -29.7$), while two separate peaks are detected for bis-dpph *cis* isomer **3b** ($\delta = -31.0$ and -31.3). In all cases the results are as expected from the coordination symmetry. Similarly, in the $^{13}C\{^1H\}$ NMR spectra, six signals for the methylene groups of coordinated dpph ligands are observed for **3b**, but only three for the other clusters. Here, the observation of the structural rigidity with regard to the Re–P bonds for **2**–**4** is noteworthy; some organometallic clusters with bridged diphosphane ligands display isomerization process that change the coordination mode of the ligands on the NMR timescale.[12]

Electrochemical and photophysical properties of **2**–**4** are compared in Table 1. The corresponding data of **1** are also included for comparison. In 0.1 mol dm^{-3} $(Bu_4N)PF_6/CH_2Cl_2$, the dpph-substituted clusters **2**–**4** exhibit reversible one-electron transfer processes ascribed to $\{Re_6^{III}\}/\{Re_5^{III}Re^{IV}\}$, the redox potentials of which are significantly dependent on the number of dpph ligands on the clusters. Relative to the $E_{1/2}$ value of **1** (−0.02 V vs. Ag/AgCl), the corresponding values of the dpph-substituted clusters become more positive with increasing number of dpph ligands on the clusters (**1** → **2** → **3a**, **3b** → **4**), and this indicates that the mixed-valent form $\{Re_5^{III}Re^{IV}\}$ becomes highly destabilized upon stepwise introduction of dpph ligands.

Table 1. Electrochemical and photophysical data of clusters **1**–**4**.

Compound	$E_{1/2}$ [V][a]	λ_{em} [nm][b]	ϕ_{em}[c]	τ_{em} [μs]
$(Bu_4N)_3$-**1**	−0.02			
$(Bu_4N)_2$-**2**	+0.35	787	0.007	2.4
3a	+0.76	777	0.008	2.1
3b	+0.79	790	0.012	3.2
4-$(SbF_6)_2$	+1.06	779	0.031	6.5

[a] A reversible process. Cyclic voltammograms were recorded at 20 °C for 0.1 mol dm^{-3} $(Bu_4N)PF_6/CH_2Cl_2$ solutions at a scan rate of 100 mV s^{-1} with a glassy carbon working electrode, a platinum-coil counter electrode, and a Ag/AgCl reference electrode. The sample concentration was 1×10^{-3} mol dm^{-3}. [b] Excitation wavelength was 355 nm. The corrected emission spectra were measured in deoxygenated $CHCl_3$ at 298 K. [c] Integrated emission quantum yields ϕ_{em} were estimated relative to $(Bu_4N)_2[Mo_6Cl_{14}]$ ($\phi_{em} = 0.19$) as reference.[13]

Clusters **2**–**4** containing 24-electron Re_6 cores are highly photoluminescent with lifetimes on the microsecond scale[2, 6] (Table 1). No appreciable difference in luminescence was observed for the stepwise-substituted clusters or for the isomeric species. However, tris-dpph cluster **4** has the longest lifetime τ_{em} and the highest quantum efficiency ϕ_{em}.[2d]

In summary, we have developed a new synthetic route to hexarhenium(III) clusters with variable numbers, geometries, and coordination types of the bidentate ligands dpph and dpppen. Structurally characterized ten-membered metallacycles were obtained with the former. The synthetic methodology described here will open significant possibilities for introducing various types of ligands into the hexametal cluster frameworks $M_6(\mu\text{-}E)_8$, and this may allow the chemical and physical properties associated with the cluster chromophores to be controlled.

Experimental Section

All experiments were carried out under argon by using standard Schlenk-vessel and vacuum-line techniques. Infrared spectra were recorded on a Hitachi 270-50 infrared spectrophotometer on KBr disks. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 20 °C on a JEOL JNM-EX 270 NMR spectrometer. FAB mass spectra (3-nitrobenzyl alcohol as a matrix) were recorded on a JEOL JMS-HX110 mass spectrometer at the Center for Instrumental Analysis, Hokkaido University.

$(Bu_4N)_2$-**2**: A DMF solution (20 mL) containing $(Bu_4N)_3$-**1**[1b] (100 mg, 0.031 mmol) and dpph (57 mg, 0.124 mmol) was stirred at 100 °C for 1 h. The solution was concentrated to about 2 mL in vacuo. Addition of water (30 mL) resulted in the precipitation of the products, which were collected by filtration. The products were purified by column chromatography (silica gel, CH_2Cl_2/CH_3CN (5/1) as eluent). Yield: 78 mg (79%).

3a and **3b**: $(Bu_4N)_3$-**1** (200 mg, 0.062 mmol) and dpph (114 mg, 0.248 mmol) were dissolved in DMF (20 mL), and the solution was heated to reflux with stirring for 3 h. After the volume of solvent was reduced in vacuo to about 1 mL, water (30 mL) was added to precipitate the product. It was collected by filtration and purified by column chromatography on silica gel. The *trans* isomer **3a** was eluted with CH_2Cl_2 as the first band. Yield: 10 mg (6%). The *cis* isomer **3b** was eluted with CH_2Cl_2/CH_3CN (50/1) as the second band. Yield: 68 mg (38%).

4-$(SbF_6)_2$: A solution of chlorobenzene/DMF (2/1, 30 mL) containing $[Re_6Se_8(CH_3CN)_6](SbF_6)_2$[3b] (150 mg, 0.061 mmol) and dpph (100 mg,

0.22 mmol) was heated to reflux with stirring for 1 d. After cooling, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/ethanol (30/1) as eluent). Yield: 128 mg (59 %).

$(Bu_4N)_2$-**2**: Positive-ion FAB-MS: *m*/*z*: 3198 [M^+]; ^{13}C NMR (67.9 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 133.8$ (m, *ipso*-Ph), 131.8, 130.8 (m, *o*-Ph), 130.1 (m, *p*-Ph), 127.9 (m, *m*-Ph), 59.0 (s, Bu), 37.4 (d, ^1J(P,C) = 30.8 Hz, ($PCH_2CH_2CH_2)_2$), 17.5 (d, ^2J(P,C) = 20.0 Hz, ($PCH_2CH_2CH_2)_2$), 24.7 (s, Bu), 21.6 (d, ^3J(P,C) = 3.8 Hz, ($PCH_2CH_2CH_2)_2$), 20.4 (s, Bu), 14.1 (s, Bu); ^{31}P NMR (109.3 MHz, $CDCl_3$, 20 °C): $\delta = -29.9$ (s). **3a**: Positive-ion FAB-MS: *m*/*z*: 2914 [M^+]; ^{31}P NMR ($CDCl_3$, 20 °C): $\delta = -30.5$ (s).

3b: Elemental analysis calcd for $C_{60}H_{64}I_2P_4Se_8Re_6 \cdot CH_2Cl_2 \cdot 1.5\,H_2O$: C 24.23, H 2.30, I 8.39; found: C 24.45, H 2.35, I 8.94; positive-ion FAB-MS: *m*/*z*: 2914 [M^+]; ^{13}C NMR (CD_2Cl_2, 20 °C): $\delta = 134.8$ (m, *ipso*-Ph), 132.1 (m, *o*-Ph), 130.9 (m, *p*-Ph), 128.3 (m, *m*-Ph), 37.5 (d, ^1J(P,C) = 33.0 Hz, ($PCH_2CH_2CH_2)_2$), 37.3 (d, ^1J(P,C) = 29.6 Hz, ($PCH_2CH_2CH_2)_2$), 27.1 (d, ^2J(P,C) = 14.0 Hz, ($PCH_2CH_2CH_2)_2$), 27.0 (d, ^2J(P,C) = 14.0 Hz, ($PCH_2CH_2CH_2)_2$), 21.4 (s, ($PCH_2CH_2CH_2)_2$), 21.3 (s, ($PCH_2CH_2CH_2)_2$); ^{31}P NMR ($CDCl_3$, 20 °C): $\delta = -31.0$ (s), -31.3 (s).

4-$(SbF_6)_2$: Elemental analysis calcd for $C_{90}H_{96}F_{12}P_6Sb_2Se_8Re_6$: C 30.16, H 2.70; found C 30.18, H 2.85; positive-ion FAB-MS: *m*/*z*: 3586 [M^+]; ^{13}C NMR (CD_2Cl_2, 20 °C): $\delta = 133.6$ (m, *ipso*-Ph), 133.0 (m, *o*-Ph), 131.8, 131.4 (m, *p*-Ph), 128.7 (m, *m*-Ph), 37.9 (d, ^1J(P,C) = 33.5 Hz, ($PCH_2CH_2CH_2)_2$), 26.6 (d, ^2J(P,C) = 15.1 Hz, ($PCH_2CH_2CH_2)_2$), 21.7 (d, ^3J(P,C) = 3.9 Hz, ($PCH_2CH_2CH_2)_2$); ^{31}P NMR (CD_2Cl_2, 20 °C): $\delta = -29.7$ (s).

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[1] a) N. Prokopuk, D. F. Shriver, *Adv. Inorg. Chem.* **1999**, *46*, 1 – 49, and references therein; b) J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603 – 4616; c) T. Saito, *J. Chem. Soc. Dalton Trans.* **1999**, 97 – 105.

[2] a) C. Guilbaud, A. Deluzet, B. Domercq, P. Molinié, C. Coulon, K. Boubekeur, P. Batail, *Chem. Commun.* **1999**, 1867 – 1868; b) T. Yoshimura, S. Ishizaka, K. Umakoshi, Y. Sasaki, H.-B. Kim, N. Kitamura, *Chem. Lett.* **1999**, 679 – 680; c) T. Yoshimura, S. Ishizaka, Y. Sasaki, H.-B. Kim, N. Kitamura, N. G. Naumov, M. N. Sokolov, V. E. Fedorov, *Chem. Lett.* **1999**, 1121 – 1122; d) N. Kobayashi, S. Ishizaka, T. Yoshimura, H.-B. Kim, Y. Sasaki, N. Kitamura, *Chem. Lett.* **2000**, 234 – 235; e) T. G. Gray, C. M. Rudzinski, D. G. Nocera, R. H. Holm, *Inorg. Chem.* **1999**, *38*, 5932 – 5933.

[3] a) Z. Zheng, T. G. Gray, R. H. Holm, *Inorg. Chem.* **1999**, *38*, 4888 – 4895; b) Z. Zheng, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1997**, *119*, 2163 – 2171; c) Z. Zheng, R. H. Holm, *Inorg. Chem.* **1997**, *36*, 5173 – 5178; d) R. Wang, Z. Zheng, *J. Am. Chem. Soc.* **1999**, *121*, 3549 – 3550.

[4] M. W. Willer, J. R. Long, C. C. McLauchlan, R. H. Holm, *Inorg. Chem.* **1998**, *37*, 328 – 333.

[5] a) N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem.* **1998**, *110*, 2043 – 2045; *Angew. Chem. Int. Ed.* **1998**, *37*, 1943 – 1945; b) Y. V. Mironov, A. V. Virovets, N. G. Naumov, V. N. Ikorskii, V. E. Fedorov, *Chem. Eur. J.* **2000**, *6*, 1361 – 1365; c) Y. T. Mironov, V. E. Fedorov, C. C. McLauchran, J. A. Ibers, *Inorg. Chem.* **2000**, *39*, 1809 – 1811.

[6] a) T. Yoshimura, K. Umakoshi, Y. Sasaki, A. G. Sykes, *Inorg. Chem.* **1999**, *38*, 5557 – 5564; b) T. Yoshimura, K. Umakoshi, Y. Sasaki, S. Ishizaka, H.-B. Kim, N. Kitamura, *Inorg. Chem.* **2000**, *39*, 1765 – 1772.

[7] a) J.-C. Gabriel, K. Boubekeur, P. Batail, *Inorg. Chem.* **1993**, *32*, 2894 – 2900; b) S. Uriel, K. Boubekeur, P. Batail, J. Orduna, E. Canadell, *Inorg. Chem.* **1995**, *34*, 5307 – 5313; c) J. R. Long, A. S. Williamson, R. H. Holm, *Angew. Chem.* **1995**, *107*, 248 – 251; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 226 – 229; d) A. Decker, F. Simon, K. Boubekeur, D. Fenske, P. Batail, *Z. Anorg. Allg. Chem.* **2000**, *626*, 309 – 313.

[8] R. Arratia-Pérez, L. Hernández-Acevedo, *J. Chem. Phys.* **1999**, *110*, 2529 – 2532; R. Arratia-Pérez, L. Hernández-Acevedo, *J. Chem. Phys.* **1999**, *111*, 168 – 172.

[9] Experimental details for hexarhenium(III) clusters with the ligand dpppen will be described elsewhere.

[10] Red crystals of **3b** were obtained by slow diffusion of diethyl ether into a solution of **3b** in CH_2Cl_2. Crystal data for **3b** $\cdot CH_2Cl_2 \cdot 1.5\,H_2O$ ($C_{61}H_{69}Cl_2I_2O_{1.5}P_4Re_6Se_8$): $M_r = 3023.75$, monoclinic, space group $P2_1/c$ (no. 14), $a = 19.712(1)$, $b = 16.587(1)$, $c = 22.437(1)$ Å, $\beta = 100.321(3)°$, $V = 7217.6(7)$ Å^3, $Z = 4$; $\rho_{calcd} = 2.782$ g cm^{-3}; crystal dimensions $0.30 \times 0.20 \times 0.20$ mm^3; $\mu(Mo_{K\alpha}) = 151.20$ cm^{-1}; $T = 173$ K. Data were collected on a Rigaku R-AXIS RAPID diffractometer equipped with an image plate detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Total reflections collected 16258. Full-matrix least-squares refinement, final $R = 0.049$, $R_w = 0.064$, GOF = 1.30 for 8526 observed reflections ($I > 3\sigma(I)$) and 735 variable parameters. The maximum and minimum peaks around the rhenium atoms on the final difference Fourier map were +3.66 and −2.95 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 no. CCDC-145486. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] Selected references for structurally characterized metal clusters with bridging diphosphane ligands: a) J. Puga, A. Arce, D. Braga, N. Centritto, F. Grepioni, R. Castillo, J. Ascanio, *Inorg. Chem.* **1987**, *26*, 867 – 874; b) J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, P. T. Beurskens, M. Roseboom, J. H. Noordik, *Inorg. Chem.* **1982**, *21*, 4321 – 4324; c) C. A. Collins, I. D. Salter, V. Sik, S. A. Williams, T. Adatia, *J. Chem. Soc. Dalton Trans.* **1998**, 1107 – 1114; d) S. S. D. Brown, I. D. Salter, L. Toupet, *J. Chem. Soc. Dalton Trans.* **1988**, 757 – 767.

[12] M. R. Churchill, R. A. Lashewycz, *Inorg. Chem.* **1980**, *19*, 1277 – 1285.

[13] A. W. Maverick, J. S. Najdzionek, D. MacKenzie, D. G. Nocera, H. B. Gray, *J. Am. Chem. Soc.* **1983**, *105*, 1878 – 1882.

Coordinatively Unsaturated Metal Centers as Building Blocks for High Coordination Number Metallomesogens**

Koen Binnemans* and Katleen Lodewyckx

Most literature on metal-containing liquid crystals (metallomesogens) is devoted to compounds with Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, Cu^{II}, and Ag^I as the central metal ion, because these complexes have a linear or planar geometry and mimic therefore conventional organic calamitic (rodlike) liquid crystals.[1] Obtaining high coordination number calamitic metallomesogens is a challenge.[2] One approach is to make the ligand as anisometric as possible by increasing the number of aromatic rings.[3, 4]

The design of lanthanide-containing liquid crystals is difficult[5] because the trivalent lanthanide ions have even

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