The PXRD analysis of δ-GeS$_2$ was carried out on a Siemens D5000 diffractometer with Bragg–Brentano $\theta/2\theta$ geometry. The source radiation (Cu$_{K\alpha}$, $\lambda = 1.54059$ Å) was obtained from a high-power line-focus Cu target, and the secondary beam was monochromatized by a Kevex solid-state detector. The diffraction pattern was initially indexed with the program ITO,[18] which provided a tetragonal, I-type unit cell. Further lattice refinement was performed with the Appleman and Evans program[19] by using the first 51 measured reflections (34 unique) within the range $14 \leq 2\theta \leq 70°$. The refinement [$M_{20} = 23.3$, $F_{30} = 27.5$ (0.012, 89)] gave the space group $I4_1/acd$ (no. 142) based on both general and special conditions for systematic absences/extinctions, as discussed in the text. Several other related space groups were also tested as possible sub- or superlattices, but were not fitted successfully. The final structure was obtained by refinement of atomic parameters with the program GSAS 6.0 (PC version).[20] Crystallographic data for δ-GeS$_2$: $I4_1/acd$, $a = 11.0650(1)$, $c = 18.7178(2)$ Å, $V = 2291.71$ Å^3, $\rho_{\text{calcd}} = 3.17$ g cm^{-3}, $Z = 32$, $R_{wp} = 0.1159$, $R_p = 0.0842$, $R_{\text{Bragg}} = 0.0927$, $\chi^2 = 4.351$, measurement range $12 \leq 2\theta \leq 80°$, 3400 data points, 372 observed reflections, 34 parameters refined. The peak profiles were fitted by a pseudo-Voigt function,[21] and a Finger–Cox–Jephcoat asymmetry correction was applied.[22]

Raman spectra were recorded on a Bomems MB-157 FT spectrometer with an InGaAs NIR laser (100 mW). The instrument was configured in the 180° backscattering mode, and samples were sealed in glass capillary tubes. Spectra were recorded with a resolution of 4 cm^{-1}, and about 100 scans were made to achieve an excellent signal-to-noise ratio.

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[1] a) M. Saji, H. Kubo, *Nagoya Kogyo Daigaku Gakuho* **1981**, *32*, 213; b) Z. G. Ivanova, *Thin Solid Films* **1995**, *256*, 257; c) A. A. Lavrentyev, A. N. Gusatinskii, I. Y. Nikiforov, N. Y. Safontseva, *Physica B* **1995**, *209*, 344; d) D. R. Simons, A. J. Faber, H. Dewaal, *J. Non-Cryst. Solids* **1995**, *185*, 283; e) D. Marchese, G. Kakarantzas, A. Jha, B. N. Samson, J. Wang, *J. Mod. Optics* **1996**, *43*, 963.

[2] P. P. Pogoretskii, E. N. Sal'kova, M. S. Soskin, D. I. Bletskan, I. F. Kopinets (Institute of Physics, Academy of Sciences, Ukranian S.S.R.), SU-B 453976, **1976** [*Chem. Abstr.* **1976**, *85*, 134491z].

[3] M. Haase, H. Bechtel, W. Czarnojan, D. Waedow (Philips Electronics N.V.), EP-B 714966, **1996** [*Chem. Abstr.* **1996**, *125*, 99556v].

[4] S. Kondo, K. Takada (Matsushita Electric Ind. Co. Ltd.), JP-B 05205741, **1993** [*Chem. Abstr.* **1994**, *120*, 34524k].

[5] a) G. Dittmar, H. Schäfer, *Acta Crystallogr. B* **1976**, *32*, 1188; b) G. Dittmar, H. Schäfer, *Acta Crystallogr. B* **1975**, *31*, 2060; c) D. I. Bletskan, I. M. Mitrovtsii, V. A. Stefanovich, M. V. Potorii, Yu. V. Voroshilov, V. Yu. Slivka, *Sov. Phys. Crystallogr. (Engl. Transl.)* **1987**, *32*, 224.

[6] C. T. Prewitt, H. S. Young, *Science* **1965**, *149*, 535.

[7] W. Viaene, G. H. Moh, *Neues Jahrb. Mineral. Abh.* **1973**, *119*, 113.

[8] N. Wang, E. Horn, *Neues Jahrb. Mineral. Monatsh.* **1973**, 413.

[9] P. P. H. Fourcroy, D. Carré, J. Rivet, *Acta Crystallogr. B* **1978**, *34*, 3160.

[10] Other structures with similar frameworks are known. For example, an Na$_2$SnAs$_2$ Zintl phase which is isostructural and isoelectronic to δ-GeS$_2$ has been prepared from the elements: M. A. Asbrand, B. Eisenmann, *Z. Naturforsch. B* **1993**, *48*, 452.

[11] O. M. Yaghi, Z. Sun, D. A. Richardson, T. L. Groy, *J. Am. Chem. Soc.* **1994**, *116*, 807.

[12] C. L. Bowes, A. J. Lough, A. Malek, G. A. Ozin, S. Petrov, D. Young, *Chem. Ber.* **1995**, *129*, 283.

[13] C. L. Cahill, J. B. Parise, *Chem. Mater.* **1997**, *9*, 807.

[14] T. Kemin, A. Darovsky, J. B. Parise, *J. Am. Chem. Soc.* **1995**, *117*, 7039.

[15] K. Tan, Y. Ko, J. B. Parise, A. Darovsky, *Chem. Mater.* **1996**, *8*, 448.

[16] W. M. Meier, D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd ed., Butterworth-Heinemann, Toronto, **1992**.

[17] D. Taylor, *Br. Ceram. Trans. J.* **1992**, *9*, 217.

[18] J. W. Visser, *J. Appl. Crystallogr.* **1969**, *2*, 89.

[19] D. E. Appleman, H. T. Evans, Jr., Job 9214, *U.S. Geol. Survey* **1973** NTIS, Doc. PB2–16188; revised PC version by P. H. Benoit, **1987**.

[20] R. B. von Dreele, A. C. Larson, *General Structure Analysis System*, Los Alamos National Laboratory Report LAUR 86–748, **1990**.

[21] P. Thompson, D. E. Cox, J. B. Hastings, *J. Appl. Crystallogr.* **1987**, *20*, 79.

[22] L. W. Finger, D. E. Cox, A. P. Jephcoat, *J. Appl. Crystallogr.* **1994**, *27*, 892.

Metal–Metal "Communication" of Rh or Pd with Nd in Novel Heterobinuclear Complexes**

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Dedicated to Professor Carl Krüger
on the occasion of his 65th birthday

For heterobinuclear complexes which contain an early and a late transition metal and in which the metal centers can "communicate" with one another, interesting properties have been predicted, such as multifunctionality and cooperative effects.[1] However, the problems encountered in the realization of the differing coordination chemical requirements of both metals in close proximity to one another are just as great as the expectations.[2] We report here on the synthesis and structure of heterobinuclear complexes in which interactions of Group 9 (Rh) or Group 10 (Pd) metals with a lanthanide (Nd) are possible.[3] A decisive factor for this enlargement of the class of "early–late heterobimetallics" (ELHB) is a novel ligand system incorporating bisaminopyridinato ligands.[4]

If two equivalents of dilithiated O(SiMe$_2$ApH)$_2$ are treated in situ with NdCl$_3$ in THF, the neodymium "ate" complex **1** is obtained in good yields as a violet, crystalline compound (Scheme 1; O(SiMe$_2$ApH)$_2$ = O[Si(CH$_3$)$_2$NH-(4-CH$_3$C$_5$H$_3$N)]$_2$). The IR spectrum of **1** displays the signals typical for O(SiMe$_2$Ap)$_2$, and the elemental analysis is in agreement with the formula given in Scheme 1. The reaction of **1** with [{(cod)RhCl}$_2$] (cod = 1,5-cyclooctadiene) in *n*-hexane gives yellow crystals of the heterobinuclear compound **2** (Scheme 1). The X-ray crystal structure analysis[5] of this compound (Figure 1) shows there is an almost square-planar coordination geometry at the rhodium center,[6] and that two amido N atoms coordinate the {Rh(cod)} fragment (N(1)-Rh(1)-N(3) 84.1(5)°). For the aminopyridinato fragments,

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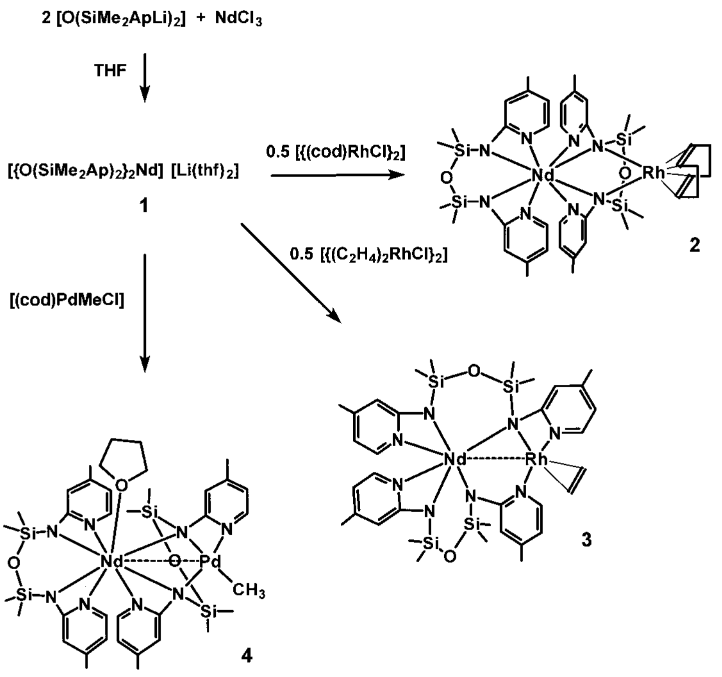

Scheme 1. Synthesis of **1**–**4**.

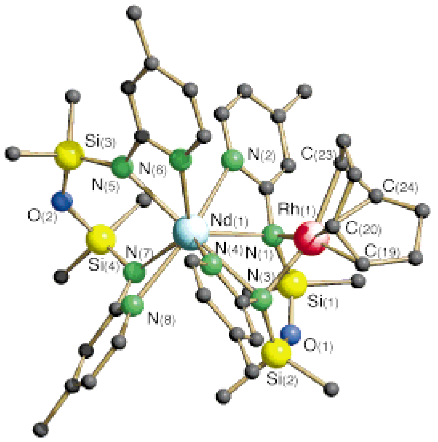

Figure 1. Crystal structure of **2**. Selected bond lengths [Å] and angles [°]: N(1)–Rh(1) 2.142(12), N(1)–Nd(1) 2.646(12), N(2)–Nd(1) 2.585(12), N(3)–Rh(1) 2.138(11), N(3)–Nd(1) 2.699(10), N(4)–Nd(1) 2.603(12), N(5)–Nd(1) 2.514(11), N(6)–Nd(1) 2.478(13), N(7)–Nd(1) 2.463(10), N(8)–Nd(1) 2.527(13), Rh(1)–Nd(1) 3.228(2); N(1)-Rh(1)-N(3) 84.1(5), N(1)-Rh(1)-D[C(23)/C(24)] 96.2(6), D[C(23)/C(24)]-Rh(1)-D[C(19)/C(20)] 86.1(6), N(3)-Rh(1)-D[C(19)/C(20)] 93.5(6), N(7)-Nd(1)-N(6) 133.1(5), N(6)-Nd(1)-N(5) 53.0(4), N(7)-Nd(1)-N(8) 54.3(4), N(2)-Nd(1)-N(1) 51.4(4), N(4)-Nd(1)-N(3) 50.9(4).

which act as bridges between the two metal centers, the elongation of the Nd–N distances is about 0.1 Å. The differences in the lengths of the $Nd-N_{amido}$ and the $Nd-N_{pyridine}$ bonds are slight, which indicates a delocalized bonding mode.[7]

The magnetic moment[8] of **2** $\mu_{eff} = 4.38\,\mu_B$ corresponds to the value expected for a $4f^3$ electron configuration. A metal–metal bond (the Nd–Rh distance is 3.2283(15) Å) can be excluded, since the only orbitals on the rhodium atom which are eligible for an interaction (orthogonal to the coordination plane)[9] are not directed towards the neodymium atom.[10] On the other hand, such an orientation of the orbitals is present in the Nd–Rh–ethylene complex **3**,[10] which is formed by the treatment of **1** with $[\{(C_2H_4)_2RhCl\}_2]$ in *n*-hexane (Scheme 1). Its molecular structure, determined by X-ray crystallography,[5] is depicted in Figure 2. The Nd–Rh distance in **3** is 2.9744(15) Å,[11] which is in good agreement with the value for a M–M single bond.[12] There is an almost planar coordination geometry[6] at the rhodium atom. Three of the coordination sites are used by the two bis(Ap) ligands (bis(Ap) = bisaminopyridinato); one ligand contributes a pyridine and the other an aminopyridinato functionality. It is remarkable how strained amido ligands can still coordinate to late transition metal centers (N(8)-Rh(1)-N(7) 64.9(2)°) as the combination of a soft metal center with the hard amido ligand is unfavorable.[13]

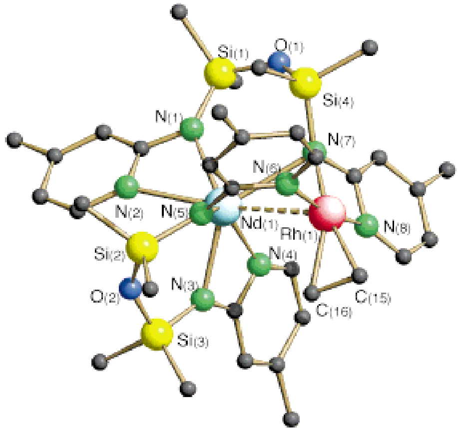

Figure 2. Crystal structure of **3**. Selected bond lengths [Å] and angles [°]: N(1)–Nd(1) 2.465(4), N(2)–Nd(1) 2.509(4), N(3)–Nd(1) 2.382(5), N(4)–Nd(1) 2.566(5), N(5)–Nd(1) 2.449(5), N(6)–Rh(1) 2.050(5), N(7)–Rh(1) 2.128(4), N(7)–Nd(1) 2.626(4), N(8)–Rh(1) 2.035(5), Rh(1)–Nd(1) 2.974(2); N(8)-Rh(1)-N(7) 64.9(2), N(6)-Rh(1)-N(7) 103.2(2), N(6)-Rh(1)-D[C(15)/C(16)] 90.9(3), N(8)-Rh(1)-D[C(15)/C(16)] 101.6(3), N(3)-Nd(1)-N(5) 92.2(2), N(1)-Nd(1)-N(2) 54.0(2), N(3)-Nd(1)-N(4) 54.1(2).

The general applicability of this stabilization concept for heterobinuclear compounds by the use of bisaminopyridinato ligands is evident from the reaction of **1** with [(cod)PdMeCl],[14] which produces the Nd–Pd–alkyl complex **4** (Scheme 1) as a light yellow powder. Crystals suitable for a X-ray structural analysis[5] were obtained from a mixture of *n*-hexane and THF. The molecular structure of **4** (Figure 3) shows a planar coordination geometry, characteristic of Pd^{II} compounds,[6] and a Nd–Pd distance of 3.0345(12) Å. In contrast to the situation in **3**, the two metal centers in **4** are bridged by only one bis(Ap) ligand.

Decisive for the preparation as well as the stabilization of the heterobimetallic compounds **2**–**4** is that lanthanide "ate" complexes react with chlorides of electron-rich transition metals by salt elimination and that bisaminopyridinato ligands can prevent the ligand transfer from early to late transition metals and thus the decomposition of the bimetallic complex.[15] The flexible coordination mode of the bis(Ap) ligands allows a coordinative saturation of the lanthanide metal center, leaving two or three nitrogen donor groups for a square-planar coordination geometry at the late transition metal as well as an interaction between the two metals. Currently, we are investigating the consequences of this

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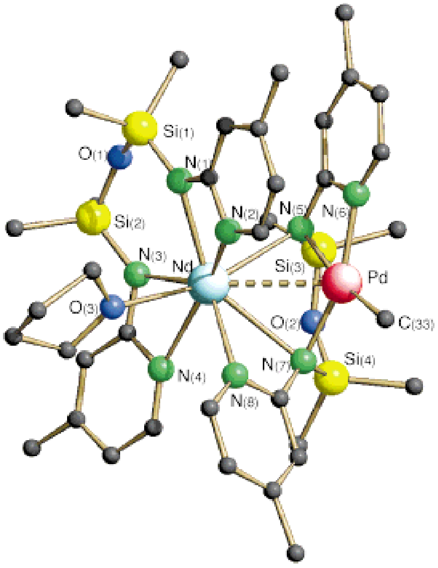

Figure 3. Crystal structure of **4**. Selected bond lengths [Å] and angles [°]: Nd–N(3) 2.475(8), Nd–N(1) 2.480(8), Nd–N(2) 2.542(9), Nd–N(4) 2.547(9), Nd–N(8) 2.612(9), Nd–N(5) 2.659(8), Nd–N(7) 2.761(8), Nd–Pd 3.0345(12), Pd–N(6) 2.048(9), Pd–N(7) 2.062(8), Pd–N(5) 2.187(8); N(3)-Nd-N(1) 84.8(3), N(1)-Nd-N(2) 54.4(3), N(3)-Nd-N(4) 54.0(3), C(33)-Pd-N(6) 104.7(4), C(33)-Pd-N(7) 95.3(4), N(6)-Pd-N(5) 64.9(3), N(7)-Pd-N(5) 95.1(3).

"communication" in stoichiometric and catalytic reactions, and whether such reactions are also transferable to other "ate" complexes, for example to the complexes containing bisalkoxy ligands reported by Shibasaki et al.[16]

Experimental Section

All work was performed with the exclusion of oxygen and moisture under an atmosphere of argon. NMR spectra were recorded in [D$_8$]THF at 25 °C.

1: $O(SiMe_2ApH)_2$ (5.45 g, 15.7 mmol) in THF (20 mL) was treated at −78 °C with *n*BuLi in *n*-hexane (2.5 M, 12.6 mL, 31.5 mmol), stirred for a further 2 h at room temperature, and subsequently added to a hot suspension of $NdCl_3$ (1.97 g, 7.86 mmol) in THF (50 mL). The mixture was stirred for 16 h at room temperature, filtered, concentrated to about 30 mL, and then treated with diethyl ether. After removal of LiCl by filtration, violet crystals of **1** (5.22 g, 67 %) were obtained at −30 °C. M.p. 212 °C; elemental analysis calcd for $C_{40}H_{64}LiN_8NdO_4Si_4$ (984.52): C 48.80, H 6.55, N 11.38; found: C 48.88, H 6.57, N 10.31; ^{1}H NMR (400 MHz): $\delta = -0.02$ (s, 3 H), 0.13 (s, 2 H), 1.78 (m, 4 H), 3.63 (m, 4 H), 4.75 (s, 6 H), 4.83 (s, 1 H), 5.61 (s, 1 H), 10.90 (s, 1 H); ^{13}C NMR (100.6 MHz): $\delta = 12.8$, 20.7, 26.3, 68.1, 115.6, 122.7, 125.4, 147.1, 148.6; ^{29}Si NMR (79.5 MHz): $\delta = -10.6$, −18.1; IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1595 vs and 1530 s (arom. C=C), 1332 s, 1294 vs, 1243 vs (MeSi), 1178 vs, 1026 vs, 990 vs (SiOSi), 883 vs, 838 s, 792 vs ($SiMe_2$), 728 s, 674 m, 575 s, 428 m.

2–**4**: Compound **1** (985 mg, 1 mmol) and either [{(cod)RhCl}$_2$] (247 mg, 0.5 mmol), [{$(C_2H_4)_2$RhCl}$_2$] (194 mg, 0.5 mmol), or [(cod)PdMeCl][14] (265 mg, 1 mmol) were suspended in *n*-hexane (60 mL) and stirred at room temperature for 16 h. The mixture was filtered, the residue was washed several times with *n*-hexane/diethyl ether, and the combined filtrates were concentrated to about 15 mL. Crystals were obtained at −30 °C: **2** (595 mg, 57 %, yellow crystals), **3** (424 mg, 44 %, yellow crystals), and **4** (431 mg, 42 %, light yellow powder), respectively.

2: M.p. 150 °C; elemental analysis calcd for $C_{40}H_{60}N_8NdO_2RhSi_4$ (1044.46) · 0.5 $C_2H_5OC_2H_5$: C 46.64, H 6.06, N 10.36; found: C 46.87, H 5.97, N 10.32; IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1604 vs, 1545 m and 1533 m (arom. C=C), 1410 s, 1395 s, 1331 m, 1315 m, 1295 s, 1286 s, 1249 s (MeSi), 1171 s, 1054 s, 1016 m, 995 s, br (SiOSi), 966 m, 887 s, 877 s, 847 m, 839 m, 807 s ($SiMe_2$), 784 s, 774 s, 726 m, 675 w, 630 w, 624 w, 588 m, 581 m, 565 w, 529 w; $\mu_{eff} = 4.38\,\mu_B$.

3: M.p. 171 °C; elemental analysis calcd for $C_{34}H_{52}N_8NdO_2RhSi_4$ (964.33) · 0.5 C_6H_{14}: C 44.11, H 5.90, N 11.12; found: C 43.95, H 5.82, N 11.00; IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1607 vs and 1530 m (arom. C=C), 1418 s, 1324 s, 1289 s, 1251 s (MeSi), 1216 m, 1180 s, 1160 m, 1123 w, 1023 vs, 1006 vs (SiOSi), 965 s, 879 s, 858 m, 845 m, 794 vs ($SiMe_2$), 726 s, 678 w, 651 w, 617 w, 599 m, 587 s, 555 w, 528 w, 434 m; $\mu_{eff} = 4.33\,\mu_B$.

4: M.p. > 280 °C; elemental analysis calcd for $C_{37}H_{59}N_8NdO_3PdSi_4$ (1026.93): C 43.28, H 5.79, N 10.91; found: C 43.05, H 5.88, N 10.72; IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1604 vs, 1546 w and 1531 w (arom. C=C), 1328 m, 1291 m, 1250 s (MeSi), 1177 m, 1026 s, br (SiOSi), 970 m, 880 s, 847 m, 786 s ($SiMe_2$), 725 m, 581 w, 443 w; $\mu_{eff} = 4.46\,\mu_B$.

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[1] D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41–107.

[2] W. A. Herrmann, B. Cornils, *Angew. Chem.* **1997**, *109*, 1074–1095; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1049–1067.

[3] The combination of a lanthanide with metals of Groups 9 and 10 are rare. For examples of nondistal heterobinuclear complexes, see a) L. F. Lindoy, H. C. Lip, H. W. Louie, M. G. B. Drew, M. J. Hudson, *J. Chem. Soc. Chem. Commun.* **1977**, 778–780; b) C. J. Burns, R. A. Andersen, *J. Am. Chem. Soc.* **1987**, *109*, 915–917; c) D. J. Schwartz, G. E. Ball, R. A. Andersen, *J. Am. Chem. Soc.* **1995**, *117*, 6027–6040.

[4] a) M. Oberthür, P. Arndt, R. Kempe, *Chem. Ber.* **1996**, *129*, 1087–1091; b) M. Oberthür, G. Hillebrand, P. Arndt, R. Kempe, *Chem. Ber.* **1997**, *130*, 789–794.

[5] Crystal structure analyses of **2**–**4**: General: STOE-IPDS-diffractometer, $Mo_{K\alpha}$ radiation (graphite monochromator, $\lambda = 0.71069$ Å), the structure was solved by direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467), and refined by full-matrix least squares against F^2 (SHELXL-93); graphical representation: Schakal-92. The 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-100884. 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). Compound **2**: crystal dimensions: 0.4 × 0.2 × 0.2 mm, yellow prisms, space group $P2_1/c$, monoclinic, $a = 13.146(3)$, $b = 11.787(2)$, $c = 32.939(7)$ Å, $\beta = 90.80(3)°$, $V = 5103.5(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.378$ g cm^{-3}; of 6056 reflections measured, 3601 were independent of symmetry and 2726 were observed ($I \geq 2\sigma I$); $R = 0.052$, wR^2 (all data) = 0.149, 511 parameters. Compound **3**: crystal dimensions: 0.5 × 0.4 × 0.4 mm, yellow prisms, space group $P\bar{1}$, triclinic, $a = 11.664(2)$, $b = 11.712(2)$, $c = 23.150(5)$ Å, $\alpha = 97.44(3)$, $\beta = 95.09(3)$, $\gamma = 115.65(3)°$, $V = 2789.5(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.353$ g cm^{-3}; of 8185 reflections measured, 8185 were independent of symmetry and 6799 were observed ($I \geq 2\sigma I$); $R = 0.048$, wR^2 (all data) = 0.141, 539 parameters. Compound **4**: crystal dimensions: 0.3 × 0.3 × 0.1 mm, light yellow platelets, space group $P2_1/c$, monoclinic, $a = 13.744(3)$, $b = 12.948(3)$, $c = 30.208(6)$ Å, $\beta = 91.96(3)°$, $V = 5373(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.323$ g cm^{-3}; of 10379 reflections measured, 5528 were independent of symmetry and 4229 were observed ($I \geq 2\sigma I$); $R = 0.049$, wR^2 (all data) = 0.154, 509 parameters.

[6] The maximum deviations were 0.07 (**2**), 0.15 (**3**), and 0.06 Å (**4**).

[7] The negative charge on the aminopyridinato ligand is not localized on the amido nitrogen atom.

[8] The magnetic moments were determined by the method according to Evans: a) D. F. Evans, *J. Chem. Soc.* **1959**, 2003–2005; b) J. L. Deutsch, S. M. Poling, *J. Chem. Educ.* **1969**, *46*, 167–168; c) J. Löliger, R. Scheffold, *J. Chem. Educ.* **1972**, *49*, 646–647.

[9] T. A. Albright, J. K. Burdett, M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, **1985**.

[10] The angle between the vectors parallel to the shortest metal–metal distance and orthogonal to the coordination plane of the rhodium center were 50.6° (**2**) and 26.9° (**3**).

[11] A Nd–Rh single bond, in the sense of a σ bond, cannot be assumed here. It is conceivable that there is an interaction of the d_{z^2} orbital, which are directed orthogonal to the coordination plane, with the neodymium atom.

[12] Metal–metal distances for unbridged single bonds have not, as far as we know, been reported for the combinations Ln–M (M = Co, Rh, Ir, Ni, Pd, Pt). The Lu–Ru distance in $[Cp_2(thf)LuRuCp(CO)_2]$ is 2.955(2) Å: I. P. Beletskaya, A. Z. Voskoboynikov, E. B. Chuklanova, N. I. Kirillova, A. K. Shestakova, I. N. Parshina, A. I. Gusev, G. K.-I. Magomedov, *J. Am. Chem. Soc.* **1993**, *115*, 3156–3166. The shortest metal–metal distance in bridged systems was found for $[Cp^*_2Yb(\mu\text{-}H)(\mu\text{-}CH_3)Pt(dippe)]$[3c] and is 3.388(9) Å. $Cp^* = C_5Me_5$, dippe = $i Pr_2P(CH_2)_2P i Pr_2$.

[13] a) R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539; b) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 581–587; c) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 643–654.

[14] R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, *Inorg. Chem.* **1993**, *32*, 5769–5778.

[15] A. Spannenberg, P. Arndt, R. Kempe, *Angew. Chem.* **1998**, *110*, 824–827; *Angew. Chem. Int. Ed.* **1998**, *37*, 832–835.

[16] a) H. Sasai, T. Arai, Y. Satow, K. N. Houk, M. Shibasaki, *J. Am. Chem. Soc.* **1995**, *117*, 6194–6198; b) T. Arai, Y. M. A. Yamada, N. Yamamoto, H. Sasai, M. Shibasaki, *Chem. Eur. J.* **1996**, *2*, 1369–1372.

Self-Assembly of Nanometer-Sized Macrotricyclic Complexes from Ten Small Component Molecules**

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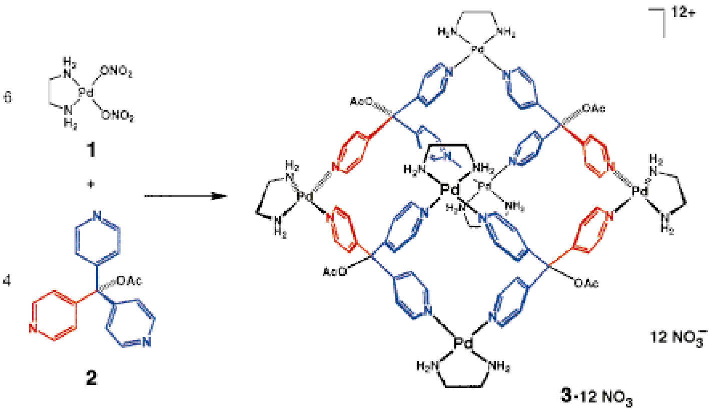
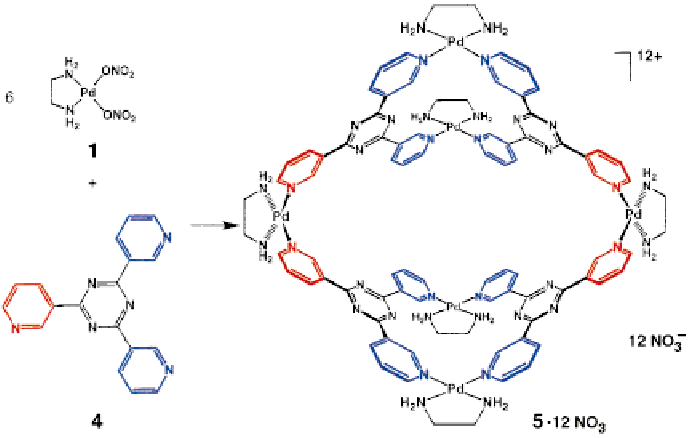
Transition metals with specific coordination geometries have been employed for the rational design and construction of highly ordered supramolecular structures.[1] We have shown that the simple combination of the square-planar coordination geometry of palladium (90° bond angle) with pyridine-based bridging ligands leads to the quantitative self-assembly of nanometer-sized, discrete organic frameworks[2] such as “molecular squares”[3, 4] and an adamantanoid cages.[5] Here we report the efficient self-assembly of nanometer-sized macrotricycles from ten small components. Treatment of $[Pd(NO_3)_2(en)]$ (**1**) with the tripyridylmethane **2**[6] results in self-assembly to the nanometer-sized macrotricyclic framework **3**, in which four ligand molecules are held together by six metal ions (Scheme 1). A similar ten-component self-assembly process leads to formation of the nanoscale macrotricycle **5** from **1** and the triazine-based ligand **4** (Scheme 2). Recently, there were a few reports of the metal-directed self-assembly of nanometer-sized macrocycles.[7, 8] However, their structures have often been deduced from spectroscopic data.[8] In contrast, the structures of nanometer-sized macrotricycles **3** and **5** were unambiguously determined by X-ray crystallographic analyses.



Scheme 1. Synthesis of **3**.



Scheme 2. Synthesis of **5**.

Ligand **2** was suspended in an aqueous solution of **1** (1.5 equiv), and the mixture was heated at 70 °C.[9] After 40 min a colorless clear solution was obtained. Analysis by NMR spectroscopy of the solution obtained by carrying out the reaction in D_2O showed the quantitative self-assembly of **1** and **2** to form a single product. The addition of aqueous $NaClO_4$ (1 M) resulted in precipitation of $\mathbf{3}\cdot 12\,ClO_4$ in 85 % yield. When ethanol/water was employed as the solvent, the product was obtained from the solution directly as a NO_3^- salt by cooling to about 5 °C for several days. The elemental analyses agreed with the empirical formulas of $\mathbf{3}\cdot 12\,ClO_4\cdot 8\,H_2O$ and $\mathbf{3}\cdot 12\,NO_3\cdot 12\,H_2O$. The NMR spectra of **3** contain only one acetoxyl signal (^{1}H NMR: $\delta = 2.24$ (Figure 1); ^{13}C

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[++] Crystal structure analysis.

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