Metallacycles
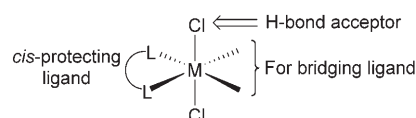
A Self-Complementary Assembly of Metallamacrocycles Directed by Ru−Cl···H−N Hydrogen Bonds and Its Reversible Dichotomy by Halide Anions in Solution**

Young Jun Park, Jik-Soo Kim, Kyoung-Tae Youm, Nam-Kyu Lee, Jaejung Ko,* Hye-seo Park,* and Moo-Jin Jun*

The coordination-directed self-assembly approach is an extremely powerful strategy for the synthesis of various 2- and 3D metallasupramolecules and can provide a structural and functional basis for its potential application toward

[*] Prof. Dr. J. Ko
Department of Chemistry
Korea University
Chochiwon, Chugnam 339-700 (Korea)
Fax: (+ 82) 41-867-5396
E-mail: jko@korea.ac.kr

Dr. Y. J. Park, J.-S. Kim, Dr. K.-T. Youm, N.-K. Lee, Prof. H.-s. Park, Prof. Dr. M.-J. Jun
Department of Chemistry and Center for Bioactive Molecular Hybrids
Yonsei University
Seoul 120-749 (Korea)
Fax: (+ 82) 2-364-7050
E-mail: hsp@yonsei.ac.kr
         mjjun@yonsei.ac.kr

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

molecular sensing and catalysis by using supramolecular chemistry.[1] In particular, discrete 3D self-assemblies derived from the multiple noncovalent interactions between monomeric metallo-subunits, such as chains, squares, and/or cages, are very intriguing because they are structurally complex but symmetrically simple and synthetically convenient to make.[2] Whereas various functional groups have been utilized for such purposes, little attention has been paid to metal–halide bonds, although they are well known as hydrogen-bond acceptors in molecular recognition and crystal engineering.[3] The halides are usually destined to be eliminated, presumably as a result of limited coordination sites on the metal center for incoming ligands.[1] These facts prompted us to explore the way to get the metal–halide groups to participate in both the coordination-directed and noncovalent self-assembly processes without their abstraction. Considering the molecular library model,[1g] we envisioned that the octahedral geometry of a transition metal might provide a novel approach for the use of metal–halide bonds as a self-assembly motif. For example, octahedral transition-metal centers with axial halide and *cis*-protecting ligands could serve as a 90° building block. The axial halide, then, may participate in hydrogen bonding with suitably functionalized bridging ligands.

Herein, we demonstrate the unprecedented self-complementary dimer of Ru^{II} metallamacrocycles which uses the intact metal–halide bonds in the coordination-directed self-assembly process and its reversible dissociation/association behavior, which is controlled by halide anions in solution.

The ligand *N,N′*-bis(pyridin-4-yl)pyridine-2,6-dicarboxamide (**1**) was quite suitable for our purpose because it has central amide protons as hydrogen-bonding donors and is well known for bridging two metal centers, thus giving metallamacrocycles.[4] In addition, its bisamide configuration has proven to be very useful in hydrogen-bonding-mediated rotaxane formation[5] and anion recognition[6] with metallasupramolecules. As a precursor for the metal center, [RuCl$_2$(PPh$_3$)$_3$] (**2**) was chosen for its ability to give a *trans*-Cl$_2$-*cis*-N$_2$-*cis*-P$_2$ coordination environment around the Ru^{II} center by reaction with a chelating phosphine and N-donor ligands.[7]

Stirring equimolar amounts of **1**, **2**, and 1,3-bis(diphenylphosphino)propane (DPPP) in acetone at room temperature yielded the orange solid of **3**$_2$ in good yield (87 %; Scheme 1).

A single-crystal X-ray structure determination of **3**$_2$ unambiguously revealed an interesting supramolecular association between two severely folded molecules of Ru^{II} metallamacrocycle **3** (Figure 1).[8]
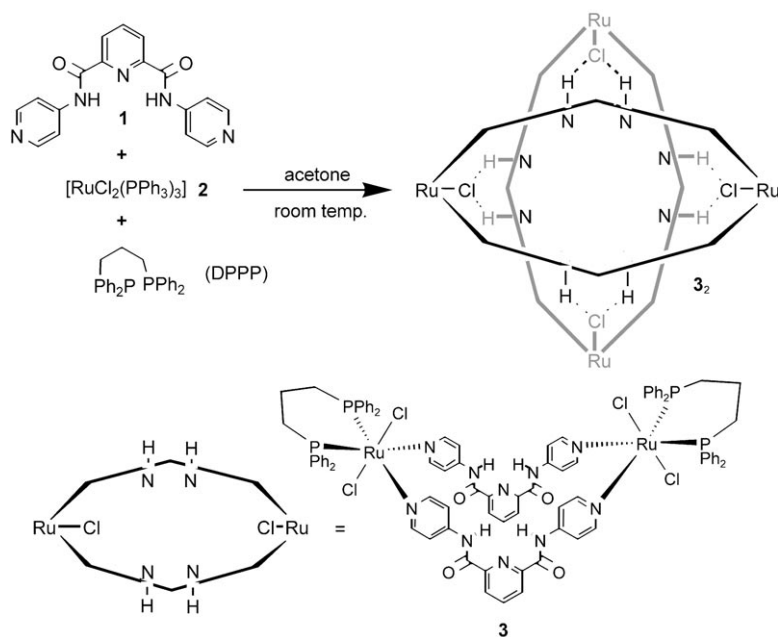
The folded metallacycles **3**, self-complementary monomers of **3**$_2$, are oriented orthogonally to each other. This orthogonal assembly seems to be directed by N-H···Cl-Ru hydrogen bonds. Though the eight hydrogen-bonding distances (H···Cl: 2.68–2.72 Å) indicated a rather weak inter-

Scheme 1. Synthesis of **3**₂.

the observed structure of **3**₂ is not clear at the present time. However, the role of the chelating phosphine moieties seems to be important in forming the discrete structure of **3**₂, because only DPPP gave an informative ^{1}H NMR spectrum out of the chelating phosphines investigated (see the Supporting Information).

Another interesting feature of the solid-state structure of **3**₂ is the infinite 1D tubular array found in the packing diagram (Figure 2).

Each dimeric **3**₂ unit is stacked along the crystallographic *b* axis with the next forming four hydrogen-bonding pairs between the carbonyl oxygen atom and the 3,5-protons of the central pyridine groups. It is noteworthy that the hydrogen-bonding interactions are also networked in a self-complementary fashion in this case.

The complex **3**₂ gave well-resolved but rather unusual ^{1}H NMR spectra in solution (CD₂Cl₂),
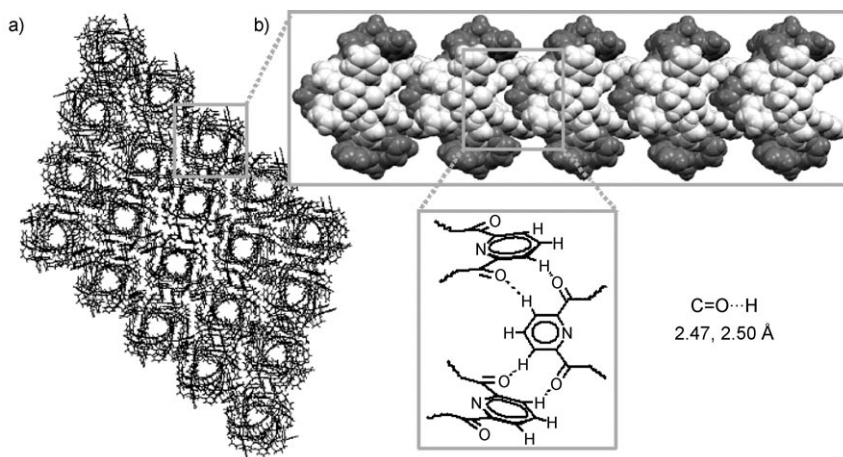
action[3a], the difference in Ru–Cl bond lengths found in two crystallographically independent NH···Cl$_A$-Ru-Cl$_B$ moieties (Ru−Cl$_A$: 2.4531(11) and 2.4537(12) Å; Ru−Cl$_B$: 2.4196(12) and 2.4292(13) Å) may be found from these hydrogen-bonding interactions. The resulting hourglass-shaped internal cavity has the volume of 355 Å^3 (calculated by PLATON[9]), but no other molecules were found in the cavity of the assembly. On the other hand, the additional stabilizing interactions might be intermolecular π···π and C-H···π contacts between the phenyl groups of DPPP and pyridine rings of **1**. There are approximately 16 short contacts within the sum of their van der Waals radii. The exact extent of the contribution of each noncovalent interaction to
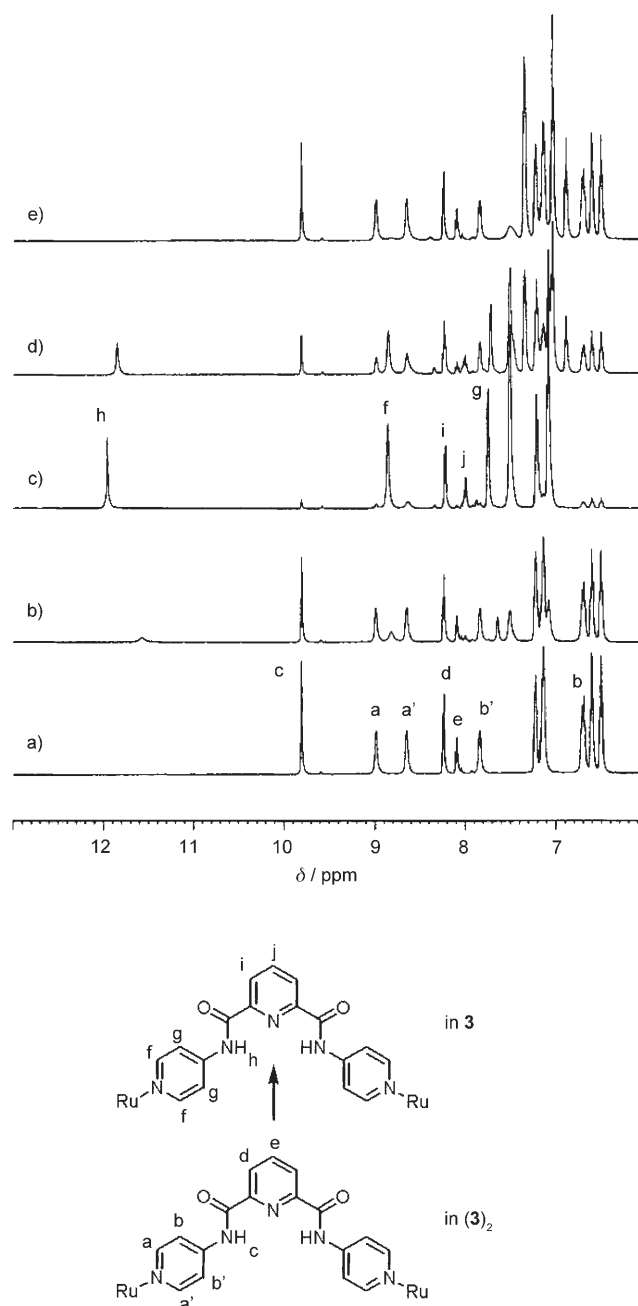

Figure 2. Packing diagram of **3**₂. a) Perspective view along the *b* axis showing an infinite 1D tubular array. b) Side view of one of the infinite 1D tubes showing intermolecular hydrogen bonding.
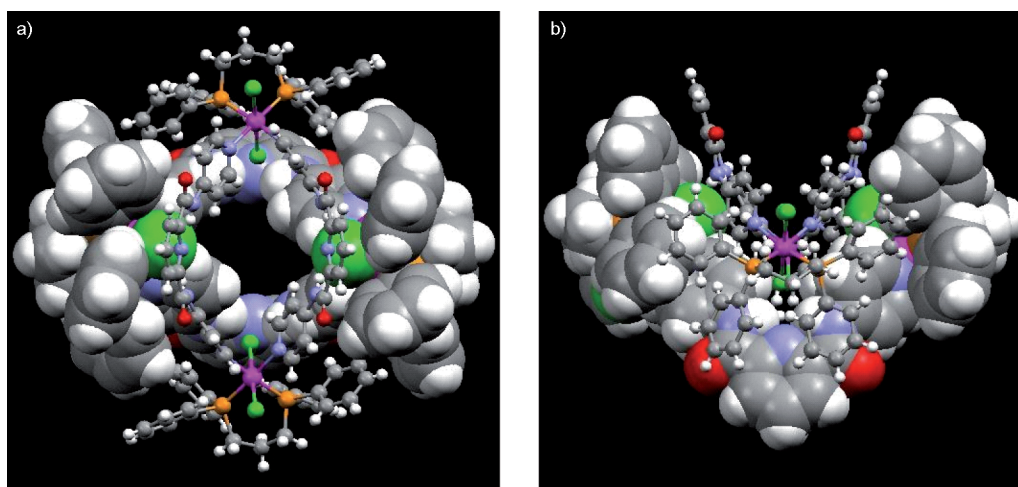
Figure 1. X-ray structure of **3**₂. a) Top and b) side views. Purple = Ru, green = Cl, orange = P, red = O, blue = N, gray = C, and white = H. One of two metallamacrocycles is presented as a CPK model.

along with a single, sharp ^{31}P NMR resonance, thus indicating a single symmetric species. For example, NMR signals for the α and β protons of the coordinated pyridine group of **1** were observed in four different fields. The corresponding chemical-shift assignments are depicted in Figure 3a (determined by DQF-COSY, NOESY, and variable-temperature NMR spectroscopic analysis; see the Supporting Information).

The broken local C_2 symmetry of the terminal pyridine groups of **1** suggests that those protons in solution are surrounded by the rigid unsymmetrical environments, as in the solid-state structure of **3**$_2$. In addition, NOE interaction studies show that cross-peaks between H_d and the phenyl protons of DPPP might be an intermolecular spatial correlation based on the solid-state structure of **3**$_2$ because the intramolecular spatial correlation is too distal to be observed (Figure 4).

Figure 3. Partial ^1H NMR spectra (CD$_2$Cl$_2$) showing reversible dissociation and association of **3**$_2$ upon addition of TEACl followed by NaBPh$_4$. a) **3**$_2$ alone, b) 1 equiv of TEACl, c) 6 equiv of TEACl, d) 1 equiv of NaBPh$_4$, and e) excess NaBPh$_4$.
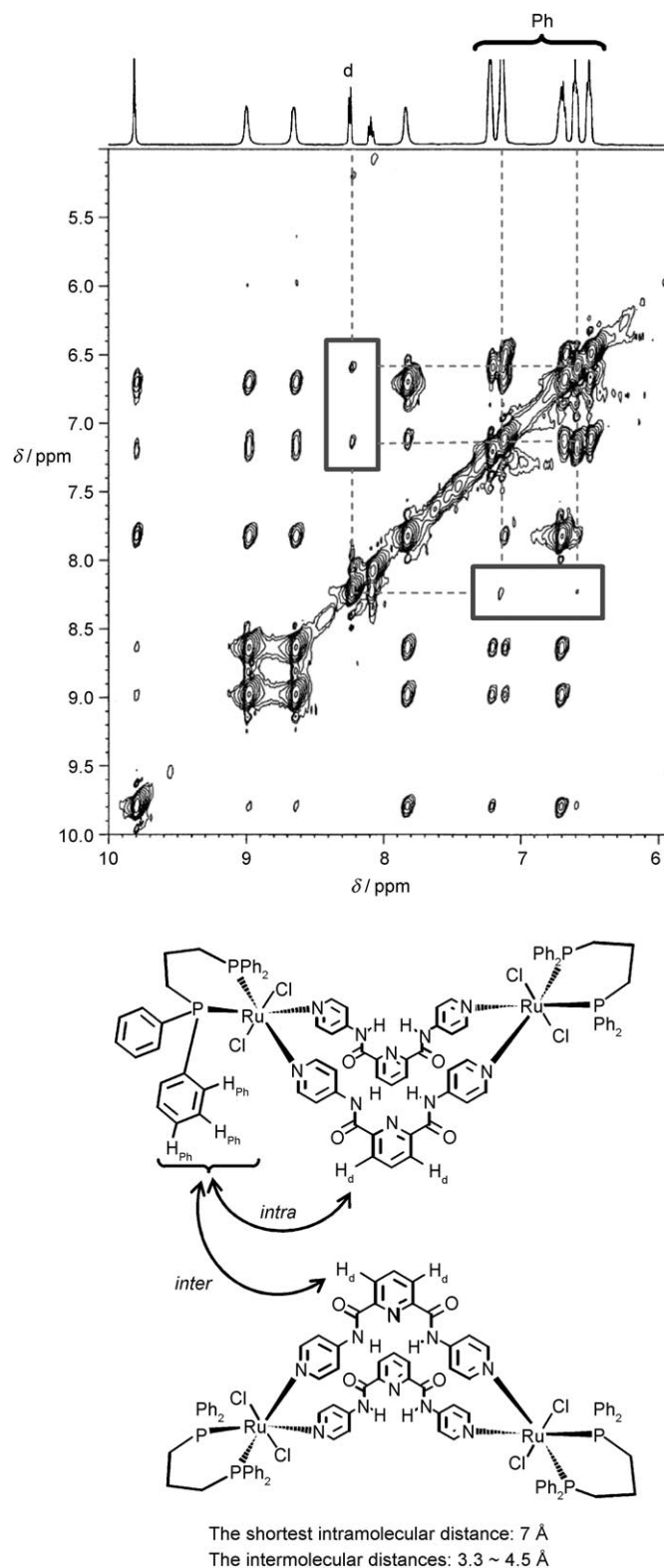
Figure 4. Partial NOESY spectrum of **3**$_2$, and the intermolecular spatial correlation between H_d and phenyl protons (gray box).

The shortest intramolecular distance: 7 Å
The intermolecular distances: 3.3 ~ 4.5 Å

More definite evidence of the self-complementary assembly of 3_2 in solution was obtained by the following ^{1}H NMR experiments: Upon addition of chloride anions, as the tetraethylammonium (TEA) salt, new peaks started to grow accompanied by a diminishment of the original peaks of 3_2, and the local C_2 symmetry of the terminal pyridine groups of **1** was re-established when six equivalents of TEACl were added (Figure 3b,c). In addition, these ^{1}H NMR spectral changes are quite different from those observed by the variable-temperature ^{1}H NMR experiments (see the Supporting Information), especially in the aromatic region.

When the homogeneous mixture of 3_2 and eight equivalents of TEACl in CH_2Cl_2 stood for several days in a closed vial, the orange crystals could be obtained in good yield. Fortunately, this new species could be characterized by single-crystal X-ray structure determination and was the dissociation product of 3_2, the flattened monomer **3** with bound two chloride ions (Figure 5).[10] It is noteworthy that all Ru−Cl bond lengths are now almost identical (2.4054(17)–2.4070(15) Å) to those of 3_2.
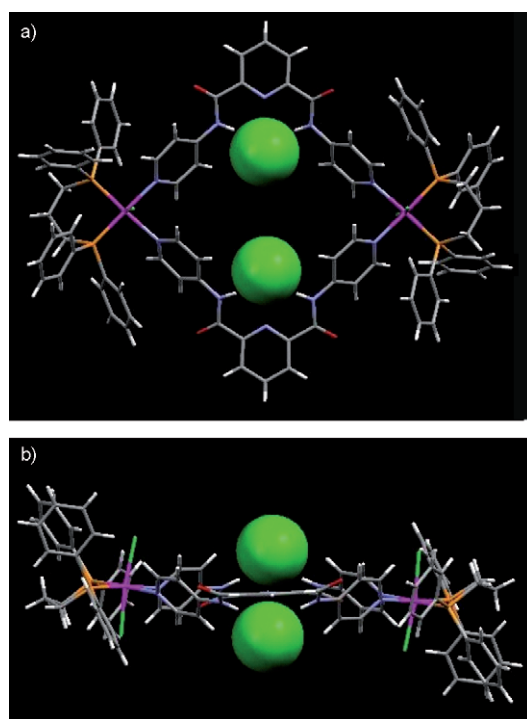
Figure 5. X-ray structure of **3**·2 TEACl·H_2O·2 CH_2Cl_2. a) Top and b) side views. Purple = Ru, green = Cl, orange = P, red = O, blue = N, gray = C, and white = H. Two chloride anions are presented as a CPK model. Solvents, water molecules, and TEA cations are omitted for clarity.

Although a direct correlation between the solid structure of **3**·2 TEACl·H_2O·2 CH_2Cl_2 and the major species observed in the mixture of 3_2 and eight equivalents of TEACl by ^{1}H and ^{31}P NMR spectroscopy (see the Supporting Information) should be done carefully,[11] their relationship could be considered from two points of view: First, both species observed by X-ray crystallography and NMR spectroscopy

are each major products in the solid and solution states. Second, the ^{1}H NMR spectra of 3_2 obtained by gradually addition of increased amounts of TEACl could be restored to the original spectra of 3_2 by addition of NaBPh$_4$ (thereby causing elimination of NaCl) and successive simple shakings of the NMR tube at room temperature (Figure 3). In other words, it seems to be that the self-assembled structure of 3_2 can be halved by the chloride anions in solution into the disassembled state, such as the structure of **3**·2 TEACl·H_2O·2 CH_2Cl_2, and reassembled into the original structure of 3_2 by eliminating the chloride anions. Such a reversible dissociation/association of self-assembled molecules by chemical stimuli is a potentially useful property in supramolecular chemistry.[12]

To assess the relative response of 3_2 toward other anions, preliminary ^{1}H NMR experiments were carried out by adding five equivalents of other kinds of TEA salts, and the intensity ratio of amide protons (H_h and H_c in Figure 3) was compared with that of the chloride. Complex 3_2 showed a rather weak response to bromide and a very weak one to iodide, and there was no interaction at all with NO_3^-, ClO_4^-, BF_4^-, and PF_6^-. The relative strengths to dissociate 3_2 into **3** were approximately 2 (Br$^-$) and 200 (I$^-$) times weaker than that of Cl$^-$.[13]

In summary, we have shown a novel self-assembled dimer of Ru[II] metallamacrocycles with noncovalent interactions, including hydrogen bonding between the Ru−Cl and N−H bonds, and its reversible dissociation/association process, which can be selectively controlled by anions in solution. More detailed studies on the solution behavior of 3_2 and its application in supramolecular chemistry are underway.

Experimental Section

Compound 3_2: Equimolar amount of ligand **1** (0.16 g, 0.5 mmol), [RuCl$_2$(PPh$_3$)$_3$] (**2**; 0.48 g), and DPPP (0.21 g) were suspended in acetone (200 mL) and stirred at room temperature. The initial brown turbid solution gradually turned to a clear orange. After 6 h, the solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (20 mL) and filtered to remove any insoluble materials. *n*-Hexane (100 mL) was added to the filtrate. The resulting yellow precipitate was collected on the sintered glass, washed with methanol and *n*-hexane, and dried in vacuo to yield 3_2 as a yellow–orange solid (0.39 g, yield = 87%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ = 9.8 (s, 2 H, NH), 9.0 (s, 2 H, PyH$_\alpha$), 8.6 (s, 2 H, PyH$_{\alpha'}$), 8.2 (d, 2 H, PyH$_{3,5}$, J = 7.8 Hz), 8.0 (t, 1 H, PyH$_4$, J = 7.8 Hz), 7.8 (s, 2 H, PyH$_{\beta'}$), 7.2–7.1 (m, 12 H, PPh), 6.7–6.4 (m, 8 H + 2 H, PPh + PyH$_\beta$), 3.1 (br t, 2 H, PCH), 2.2 (m, 1 H, PCH$_2$CH), 2.0 (br s, 2 H, PCH), 1.5 ppm (br s, 1 H, PCH$_2$CH); ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz): δ = 163.0, 154.1, 151.9, 148.8, 144.7, 138.9, 137.6, 136.0, 134.5, 132.5, 128.9, 128.7, 127.2, 127.0, 126.6, 114.0, 27.8, 20.1 ppm; ^{31}P NMR (CD$_2$Cl$_2$, 202 MHz): δ = 38.2(s) ppm; IR (KBr): $\tilde{\nu}$ = 3055, 1700, 1580, 1511, 1421, 1336, 1210, 1125, 1092, 973, 836, 743, 696, 650, 514 cm^{-1}; elemental analysis (%) calcd for C$_{176}$H$_{156}$Cl$_8$N$_{20}$O$_8$P$_8$Ru$_4$: C 58.48, H 4.35, N 7.75; found: C 58.43, H 4.57, N 7.55. Single crystals of X-ray quality were grown by slow diffusion of *n*-hexane into the solution of 3_2 in CH_2Cl_2.

Compound **3**·2 TEACl·H_2O·2 CH_2Cl_2: IR (KBr): $\tilde{\nu}$ = 3462, 2956, 2919, 2356, 1695, 1593, 1516, 1419, 1342, 1219, 1135, 1004, 840, 748, 697, 533 cm^{-1}; elemental analysis (%) calcd for

[1] For recent reviews: a) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem.* **2004**, *116*, 3728; *Angew. Chem. Int. Ed.* **2004**, *43*, 3644; b) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972; c) G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91; d) B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2076; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022; e) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759; f) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509; g) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; h) D. L. Caulder, K. N. Raymond, *J. Chem. Soc. Dalton Trans.* **1999**, 1185; i) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975; j) P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 102; k) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417.

[2] For some recent examples: a) H.-J. van Manen, V. Paraschiv, J. J. García-López, H. Schönherr, S. Zapotoczny, G. J. Vancso, M. Crego-Calama, D. N. Reinhoudt, *Nano Lett.* **2004**, *4*, 441; b) R. García-Zarracino, H. Höpfl, *Angew. Chem.* **2004**, *116*, 1533; *Angew. Chem. Int. Ed.* **2004**, *43*, 1507; c) A. Md. Alam, M. Nethaji, M. Ray, *Angew. Chem.* **2003**, *115*, 1984; *Angew. Chem. Int. Ed.* **2003**, *42*, 1940; d) A. J. Goshe, I. M. Steele, B. Bosnich, *J. Am. Chem. Soc.* **2003**, *125*, 444; e) L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem.* **2002**, *114*, 4418; *Angew. Chem. Int. Ed.* **2002**, *41*, 4244; f) K. M. Kim, J. S. Park, Y.-S. Kim, Y. J. Jun, T. Y. Kang, Y. S. Sohn, M.-J. Jun, *Angew. Chem.* **2001**, *113*, 2524; *Angew. Chem. Int. Ed.* **2001**, *40*, 2458; g) S.-Y. Yu, T. Kusukawa, K. Biradha, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 2665; h) L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem.* **2001**, *113*, 1113; *Angew. Chem. Int. Ed.* **2001**, *40*, 1079.

[3] a) T. Steiner, *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48; b) G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton, A. G. Orpen, *Chem. Commun.* **1998**, 653; c) G. P. A. Yap, A. L. Rheingold, P. Das, R. H. Crabtree, *Inorg. Chem.* **1995**, *34*, 3474; d) A. Angeloni, P. C. Crawford, A. G. Orpen, T. J. Podesta, B. J. Shore, *Chem. Eur. J.* **2004**, *10*, 3783; e) L. Brammer, *Chem. Soc. Rev.* **2004**, *33*, 476.

[4] a) Z. Qin, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.* **2003**, *42*, 1956; b) Z. Qin, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.* **2002**, *41*, 3967; c) Z. Qin, M. C. Jennings, R. J. Puddephatt, *Chem. Commun.* **2001**, 2676.

[5] a) K.-S. Jeong, Y. L. Cho, S.-U. Chang, T.-Y. Park, J. U. Song, *J. Org. Chem.* **1999**, *64*, 9459; b) K.-S. Jeong, Y. L. Cho, J. U. Song, H.-Y. Chang, M.-G. Choi, *J. Am. Chem. Soc.* **1998**, *120*, 10982; c) K.-S. Jeong, Y. L. Choi, S.-U. Chang, H.-Y. Chang, *Angew. Chem.* **2000**, *112*, 1758; *Angew. Chem. Int. Ed.* **2000**, *39*, 1692; d) S.-Y. Chang, H.-Y. Jang, K.-S. Jeong, *Chem. Eur. J.* **2003**, *9*, 1535.

[6] a) S.-S. Sun, A. J. Lees, *Chem. Commun.* **2000**, 1687; b) P. D. Beer, F. Szemes, V. Balzani, C. M. Sala, M. G. B. Drew, S. W. Dent, M. Maestri, *J. Am. Chem. Soc.* **1997**, *119*, 11864.

[7] F. H. Jardine, *Prog. Inorg. Chem.* **1984**, *31*, 265.

[8] Crystal data for 3_2: $C_{88}H_{78}Cl_4N_{10}O_4P_4Ru_2$, $M_r = 1807.42$, monoclinic, space group $C2/c$, $a = 39.6773(5)$, $b = 15.1882(3)$, $c = 37.4826(6)$ Å, $\beta = 115.3320(15)°$, $V = 20416.0(6)$ Å^3, $Z = 8$, $T = 150(1)$ K. Refinement of 1009 parameters on 23033 independent reflections out of 61496 measured reflections ($R_{int} = 0.0731$) led to $R_1 = 0.0683$ ($I > 2\sigma(I)$), $wR_2 = 0.1793$, and GOF $= 1.006$. CCDC-277154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht (Netherlands), **2003**.

[10] Crystal data for **3**: $C_{107}H_{126}Cl_{12}N_{12}O_6P_4Ru_2$, $M_r = 2427.62$, triclinic, space group $P\bar{1}$, $a = 10.8060(3)$, $b = 14.8440(5)$, $c = 19.6340(5)$ Å, $\alpha = 75.8720(13)$, $\beta = 74.5810(16)$, $\gamma = 88.5470(14)°$, $V = 2941.56(15)$ Å^3, $Z = 1$, $T = 150(2)$ K. Refinement of 686 parameters with 73 restrains on 13462 independent reflections out of 35562 measured reflections ($R_{int} = 0.0945$) led to $R_1 = 0.0904$ ($I > 2\sigma(I)$), $wR_2 = 0.2535$, and GOF $= 1.060$. CCDC-277155 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] The single crystals were obtained from the homogeneous solution of 3_2 and 8 equivalents of TEACl in CH_2Cl_2 after 4–5 days in 80–90% yields without any cosolvent. However, after spontaneous crystallization in CH_2Cl_2, the crystals of $3 \cdot 2$ TEACl$\cdot H_2O \cdot 2$ CH_2Cl_2 were almost insoluble in common organic solvents, including MeOH. The solubility problem made it impossible to obtain clear NMR spectra of $3 \cdot 2$ TEACl$\cdot H_2O \cdot 2$ CH_2Cl_2 as a pure form. Similar difficulties were encountered during the ^{13}C NMR measurement of 3_2 in the presence of 8 equivalents of TEACl because the long data-acquisition period and the limited volume of NMR solvent caused crystal formation of the $3 \cdot 2$ TEACl species.

[12] J.-M. Lehn, *Supramolecular Chemistry, Concepts, and Perspectives*, VCH, Weinheim, **1995**.

[13] An organic dianion with an appropriate geometry, such as the terephthalate, can also change the ^{1}H NMR spectral features of 3_2. A full study on the relation between the shape of the dianions and the mode of interactions will be reported elsewhere. We greatly appreciate one of the referees for his/her kind suggestions about these experimental ideas. In the case of fluoride anions, irreversible decomposition of 3_2 into an intractable product was observed.