Bridging N,P Ligands

Stable, Water-Soluble Pta-Based Ru–Ag Organometallic Polymers**

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One of the latest trends in supramolecular chemistry is the quest for reproducible methods to achieve controlled self-organization of discrete units to form homo- and heterometallic coordination networks, aggregates, and polymers.[1] This development is based on the use of appropriate organic, inorganic, and organometallic building blocks that allow the synthesis of 1D linear or twisted chains, 2D squares and polygons, and 3D cubes and polyhedra.[2] Among the organic spacers, nitrogen-based aromatic heterocycles are the most widely used due to their good donor properties and rigidity. These ligands can act as corner units (bipy, phen)[3] and spacers (pyrazines,[4] terpy,[5] porphyrinates,[6] tetraazamacrocycles[7]). P-donor ligands as spacers have received less attention:[8] P_2 and P_5 ligands have been studied by Scheer and co-workers,[9] whereas the use of multidentate phosphanes has been reviewed recently.[10] To the best of our knowledge, the use of mixed N,P ligands as metal-coordinating spacers has not been reported to date.

Very few coordination polymers are water soluble, an example being the poly(ferrocenylsilane)-β-poly(aminomethacrylate) copolymer recently described by Manners and co-workers[11] as part of their ongoing study on metallocene-based polymers,[12] which can be prepared by ring-opening polymerization to afford either macromolecules with pendant ferrocenyl substituents in the polymer side chains[13] or poly(ferrocenylsilane)s.[14] Other examples of ligands that afford coordination polymers with various topologies and applications are ferrocenyl ligands bearing bipyridines[15] or carboxylates.[16]

Herein we describe the first known case of a water-soluble, air-stable, heterobimetallic polymeric structure based on two metal-containing moieties ($[CpRu]^+$ and $[AgCl_2]^-$) bridged by a cagelike, water-soluble monodentate phosphane, 1,3,5-triaza-7-phosphaadamantane (pta), in an unprecedented N,P coordinating mode.

We recently reported the synthesis and characterization of the water-soluble cyclopentadienylruthenium complex $[CpRuCl(pta)_2]$ (**1**), which is stabilized by the phosphaadamantane-like pta ligand, and described its catalytic and biological properties.[17] As part of our studies on new water-soluble organometallic derivatives based on the $[CpRu(pta)_2]^+$ moiety,[18] we treated **1** with one equivalent of AgOTf (OTf = OSO_2CF_3) in DMSO to remove the chloro ligand. Unexpectedly, no AgCl precipitated from the resulting orange solution, and neither did it contain the expected product $[CpRu(OTf)(pta)_2]$ (**2**), which was obtained by treatment of **1** with TlOTf.[19]

Intrigued by this apparently odd result, we repeated the experiment in an NMR tube. $^{31}P\{^1H\}$ NMR analysis in $[D_6]$DMSO indicated the formation of a 1:1 mixture of the new complex $[CpRu(pta)_2(dmso\text{-}\kappa S)]OTf$ (**3**; singlet at $\delta = -28.13$ ppm) and the bimetallic neutral coordination polymer $[\{CpRu(pta)_2(dmso\text{-}\kappa S)\}\{AgCl_2\}]_\infty$ (**4**; singlet at $\delta = -23.19$ ppm), as shown in Scheme 1.

Quantitative formation of **4** could be attained by adding one equivalent of NH_4Cl to a reaction mixture containing **1** and AgOTf. The elemental analysis and spectroscopic data are consistent with one molecule of DMSO being incorporated in the compound (see Experimental Section).

Upon repetition of the latter experiment in noncoordinating $CDCl_3$ instead of $[D_6]$DMSO, a similar Ru–Ag polymeric structure was obtained with the coordination sphere of Ru completed by an η^1-*O*-coordinated triflate anion, as suggested by the corresponding IR stretching frequency ν_{OSO} at $\tilde{\nu} = 1261\ cm^{-1}$ [20] and $^{19}F\{^1H\}$ NMR chemical shift at $\delta = -78.77$ ppm.[21] The negative charge of the repeating unit in this coordination polymer is likely to be balanced by the ammonium cation (Scheme 2). The complex $\{NH_4[\{CpRu(OTf)(pta)_2\}\{AgCl_2\}]\}_\infty$ (**5**) is characterized by a singlet at $\delta = -20.85$ ppm ($CDCl_3$) in the $^{31}P\{^1H\}$ NMR spectrum. When dissolved in DMSO, **5** is quantitatively converted into **4** with elimination of NH_4OTf.

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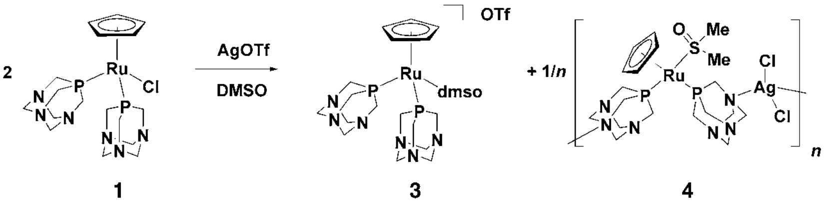
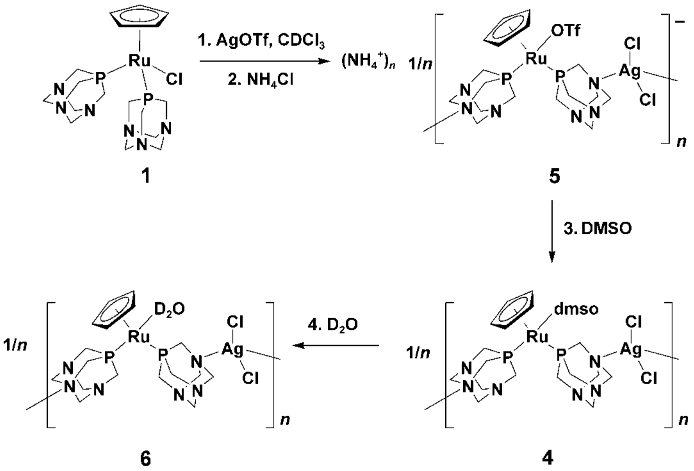


Scheme 1. Chloride abstraction from **1** with AgOTf leads to the soluble organometallic polymer **4**.



Scheme 2. Synthesis of the organometallic polymers **4**, **5**, and **6**.

Complex **4** is air stable both in the solid state and in solution, and dissolves in D_2O ($S_{25^\circ C} = 12\ \text{mg mL}^{-1}$) with reversible exchange of the coordinated dmso ligand to yield the aquo complex $[\{CpRu(pta)_2(D_2O)\}\{AgCl_2\}]_\infty$ (**6**) (singlet at $\delta = -24.83$ ppm in D_2O in the ^{31}P NMR spectrum) as shown in Scheme 2. Slow crystallization of a dilute DMSO solution in air gave pale yellow crystals that were suitable for an X-ray diffraction study.[22] In the solid state **4** is a linear-chain polymer formed by alternating $[CpRu(dmso\text{-}\kappa S)]^+$ cations and $[AgCl_2]^-$ anions, with bridging pta ligands as tethering units between the two metal aggregates ($d_{Ru\cdots Ag} = 6.52(1)$ Å). Selected bond lengths and angles are provided in the caption of Figure 1.

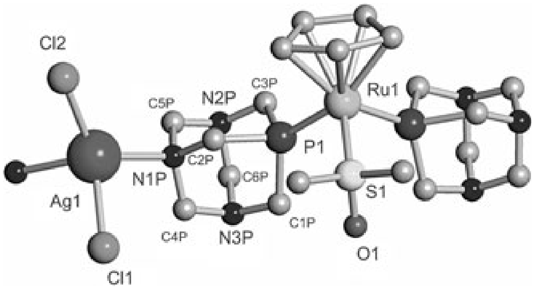


Figure 1. X-ray crystal structure of **4** (repeating unit). Selected bond lengths [Å] and angles [°]: Ru1–P1 2.285(2), Ru1–S1 2.248(3), Ru1–$Cp_{centroid}$ 1.925(1), S1–O1 1.482(7), Ag1–N1P 2.423(6), Ag1–Cl1 2.573(3), Ag1–Cl2 2.507(4); P1-Ru1-P1A 93.8(1), S1-Ru-P1 92.48(7), Cl1-Ag1-Cl2 124.07(12), Cl1-Ag1-N1P 98.15(14), Cl2-Ag1-N1P 98.50(17).

The crystal structure includes a molecule of water, which is kept in place by hydrogen bonding to an uncoordinated pta nitrogen atom belonging to a different polymer chain ($d_{O\cdots N} = 2.919(2)$ Å). The most striking feature of this solid-state structure is that pta is behaving for the first time as a bidentate ligand, bonded to the ruthenium center in the conventional way through the lone pair of the P atom and to the dichloroargentate(I) moiety through one of the three nitrogen atoms contained in the adamantane cage. The $[AgCl_2]^-$ moiety bridges two $[CpRu(pta)_2(dmso)]^+$ units to give a strongly distorted tetrahedron with the Cl1-Ag1-Cl2 angle opened up to 124.07° and the two N-Ag-Cl angles closed to about 98°. Crystallographically authenticated compounds containing $[AgCl_2]^-$ units are very rare; the average Ag–Cl distance for these complexes is 2.523 Å in a range between 2.097 and 2.915 Å.[23] The Ag–Cl distance in **4** is 2.540 Å (average value), which is near to the average Ag–Cl distance reported in the literature. The Ag–N distance (2.423(6) Å) is longer than that found for other diaminoargentato complexes (2.38 Å).[24]

The coordination geometry around ruthenium is more regular, with the Ru–$Cp_{centroid}$ distance (1.925 Å) slightly longer than in **1** (1.846 Å),[25] while the Ru–P separation (2.2856(19) Å) matches that found for the few other X-ray authenticated Ru–pta derivatives.[18,25,26] A symmetry plane in the molecule contains the atoms Ru1, S1, and O1, as well as one carbon atom of the Cp ring. The effects of the bridging pta phosphane, for which N-coordination to a transition metal is unprecedented,[27] are much more intriguing regarding the structural parameters of the ligand. The coordination of the dichloroargentate unit to the nitrogen atom of pta does not affect significantly the structural features of the cage with respect to other Ru–pta complexes.[17,18,25]

The Ru–Ag chains are kept together in a 2D array by electrostatic interactions between the $[CpRu(dmso)]^+$ and $[AgCl_2]^-$ units, with an interchain separation between the metal ions of 6.5673(9) Å (Figure 2). The 2D arrays are stacked in the lattice through a network of hydrogen bonds to water molecules that bridge a chlorine atom of one layer and a pta nitrogen atom of the adjacent one (Figure 3). The shortest hydrogen contacts between atoms in contiguous layers are 2.699(1) Å (Cl2–H17C) and 2.7382(11) Å (Cl1–H17B), which are longer than a normal hydrogen bond but shorter than the sum of the van der Waals radii. The Cp groups within adjacent layers alternate to minimize their steric interactions.[28]

Dynamic light-scattering (DLS) experiments[29] were carried out on **6** to determine the size of the particles in water and to verify whether the polymeric structure is retained in solution or shorter oligomeric substructures are formed.[30] The mean averaged diffusion coefficient was determined and the mean particle size calculated from the Einstein–Stokes equation.[31] The resulting hydrodynamic diameter indicates a monodisperse sample of about 500 nm, which suggests that the coordination polymer does not

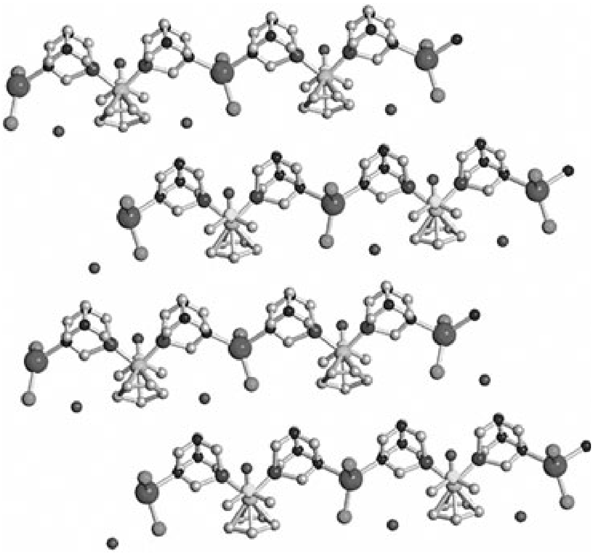


Figure 2. Spatial distribution of **4** showing the 2D arrangement formed by different polymeric chains intercalated by water molecules.

dissociate in water. DLS experiments were also performed with complexes **4** and **5**, both of which were obtained in situ as shown in Scheme 2. These measurements showed that the polymeric structure is also retained in $CHCl_3$ (**5**, 312 nm) and DMSO (**4**, 247 nm).

Macromolecular chains of organometallic species assembled into supramolecular structures by an extensive network of hydrogen-bonding interactions are rare,[8,32] and systems such as **4**–**6** that incorporate both half-sandwich cyclopentadienyl units and phosphanes have not been reported until now. Additionally, these coordination polymers are the first example of such organometallic macromolecules that are also water soluble.

Experiments are in progress to verify the N,P-coordination ability of pta with other transition-metal moieties and to establish the conductivity and electrochemical behavior of these organometallic polymers, as well as their chemical behavior in water.

Experimental Section

Complex **4** was obtained as pale yellow microcrystals from a DMSO solution (0.5 mL) of **5** (100 mg, 0.12 mmol) after standing at room temperature in the air for a week. Yield: 86 mg, 95%.

Alternatively, **4** was prepared by adding 0.5 mL of a DMSO solution of AgOTf (100 mg, 0.39 mmol) to a solution of **1** (201 mg, 0.39 mmol) and NH_4Cl (20.8 mg, 0.39 mmol) in the same solvent (0.5 mL). The reaction mixture was heated at 40 °C for 1 h. Addition of *n*-hexane (3 mL) gave **4** as a white powder, which was collected by filtration, washed with *n*-hexane (2 × 1.5 mL), and dried under vacuum. Yield: 283 mg, 96%. Elemental analysis (%) calcd for **4**·H_2O, $C_{19}H_{37}AgCl_2N_6O_2P_2RuS$ (753.96): C 30.24, H 4.95, N 11.14, S 4.24; found C 30.00, H 4.99, N 10.95, S 4.00. IR (KBr): $\tilde{\nu} = 1012\ \mathrm{cm}^{-1}$ (S=O). ^{1}H NMR (300.13 MHz, 20 °C, $SiMe_4$, [D_6]DMSO): $\delta = 4.12$–4.19 (m, pta protons: PCH_2N + PCH_2NAg, 12 H), 4.59, 4.82 (br, AB part of an ABCD spin system, $^2J_{H_AH_B} = 12.4$ Hz, $^4J_{H_AH_D} = 3.0$ Hz, pta protons: NCH_2NAg, 8 H), 4.50, 4.71 (br, CD part of an ABCD system, $^2J_{H_CH_D} = 14.1$ Hz, $^4J_{H_AH_D} = 3.0$ Hz, pta protons: NCH_2N, 4 H), 5.23 ppm (s, Cp, 5 H); $^{13}C\{^1H\}$ NMR (75.47 MHz, 20 °C, $SiMe_4$, [D_6]DMSO): $\delta = 48.0$ (sept, $^1J_{C,D} = 21.4$ Hz, CD_3 of κS-coordinated [D_6]DMSO, exchange of coordinated DMSO with [D_6]DMSO takes place), 55.1 (br s, 2 × PCH_2N + PCH_2NAg), 71.1, 71.7 (partially overlapping br s, 2 × NCH_2N + NCH_2NAg), 83.6 ppm (s, Cp); $^{31}P\{^1H\}$ NMR (121.49 MHz, 20 °C, 85% H_3PO_4, [D_6]DMSO): $\delta = -23.19$ ppm (br s).

5: A solution of AgOTf (300 mg, 1.17 mmol) in 2 mL of $CHCl_3$ was added to a stirred solution of **1** (500 mg, 0.97 mmol) and NH_4Cl (54 mg, 1.0 mmol) in 5 mL of $CHCl_3$. The orange solution obtained after 1 h stirring at room temperature was filtered, and the solvent was removed from the solute under vacuum to afford **5** as an orange powder. Yield: 665 mg, 83%. Elemental analysis (%) calcd for $C_{18}H_{33}AgCl_2F_3N_7O_3P_2RuS$ (826.35): C 26.18, H 4.03, N 11.88, S 3.88; found C 25.90, H 4.19, N 11.46, S 3.40. IR (KBr): $\tilde{\nu} = 1260\ \mathrm{cm}^{-1}$ $(OSO)_{OTf}$. ^{1}H NMR (300.13 MHz, 20 °C, TMS, $CDCl_3$): $\delta = 3.90$–4.22 (m, pta protons: PCH_2N + PCH_2NAg, 12 H), 4.42–4.62 (m, pta protons: NCH_2N + NCH_2NAg, 12 H), 4.86 ppm (s, Cp, 5 H); $^{13}C\{^1H\}$ NMR (75.47 MHz, 20 °C, TMS, $CDCl_3$): $\delta = 55.9$ (br s, 2 × PCH_2N + PCH_2NAg), 70.5 (br s, 2 × NCH_2N + NCH_2NAg), 80.3 ppm (s, Cp), CF_3SO_3 not observed; $^{19}F\{^1H\}$ NMR (282.40 MHz, 20 °C, $CFCl_3$, $CDCl_3$): $\delta = -78.77$ ppm (s, CF_3SO_3); $^{31}P\{^1H\}$ NMR (121.49 MHz, 20 °C, 85% H_3PO_4, $CDCl_3$): $\delta = -20.85$ ppm (s).

Complex **6** was obtained quantitatively by dissolving **4** in D_2O. A pale cream powder was obtained after evaporating the solvent under vacuum. Yield: 92%. Elemental analysis (%) calcd for **6**·4 D_2O, $C_{17}H_{29}AgCl_2D_8N_6O_4P_2Ru$ (739.35): C 27.61, H+D 6.13, N 11.37; found C 27.40, H+D 6.20, N 11.68. ^{1}H NMR (300.13 MHz, 20 °C, TMS, D_2O): $\delta = 4.15$–4.18 (m, pta protons: PCH_2N + PCH_2NAg, 12 H), 4.59, 4.81 (br, AB part of an ABCD spin system, $^2J_{H_AH_B} = 12.4$ Hz, $^4J_{H_BH_D} = 1.1$ Hz, pta protons: NCH_2NAg, 8 H), 4.51, 4.79 (br, CD part of an ABCD system, $^2J_{H_CH_D} = 13.1$ Hz, $^4J_{H_BH_D} = 1.1$ Hz, pta protons: NCH_2N, 4 H), 5.37 ppm (s, Cp, 5 H); $^{13}C\{^1H\}$ NMR (75.47 MHz, 20 °C, TMS, D_2O): $\delta = 54.4$–54.7 (br m, 2 × PCH_2N + PCH_2NAg), 70.6 (br s, 2 × NCH_2N + NCH_2NAg), 83.5 ppm (s, Cp);

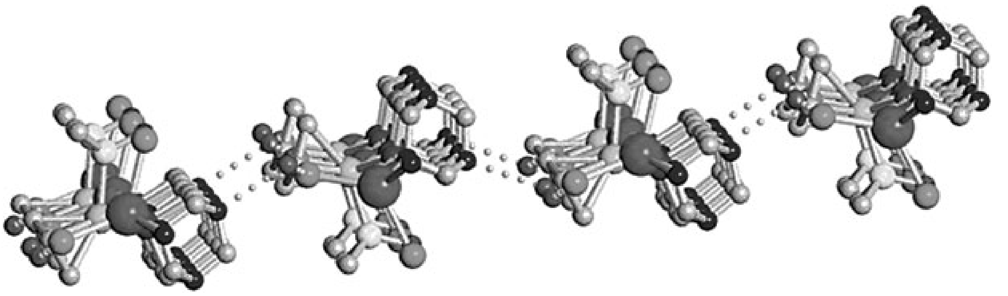


Figure 3. Spatial distribution of **4** showing the hydrogen-bonding network connecting the polymeric chains between a chlorine atom of one layer and a pta nitrogen atom of the adjacent one.

$^{31}P\{^1H\}$ NMR (121.49 MHz, 20 °C, 85 % H_3PO_4, D_2O): $\delta = -24.83$ ppm (s).

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[1] a) J.-M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, **1995**; b) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, J. Liu, *Supramolecular Architecture*, American Chemical Society, New York, **1992**, Ch. 19; c) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *111*, 2798; d) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502; e) D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375; f) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975; g) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; h) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[2] a) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645; b) G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91; c) Z. He, C. He, Z.-M. Wang, E.-Q. Gao, Y. Liu, C.-H. Yan, *Dalton Trans.* **2004**, 502; d) C. Janiak, *Dalton Trans.* **2003**, 2781.

[3] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638.

[4] D. L. Reger, K. J. Brown, J. R. Gardinier, M. D. Smith, *Organometallics* **2003**, *22*, 4973.

[5] a) M. Barboiu, G. Vaughan, R. Graff, J.-M. Lehn, *J. Am. Chem. Soc.* **2003**, *125*, 10257; b) A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 1803.

[6] D. W. Smithenry, S. R. Wilson, K. S. Suslick, *Inorg. Chem.* **2003**, *42*, 7719.

[7] J. D. Chartres, L. F. Lindoy, G. V. Meehan, *Coord. Chem. Rev.* **2001**, *216–217*, 249, and references cited therein.

[8] X. L. Lu, W. K. Leong, T. S. A. Hor, L. Y. Goh, *J. Organomet. Chem.* **2004**, *689*, 1746, and references cited therein.

[9] a) J. Bai, E. Leiner, M. Scheer, *Angew. Chem.* **2002**, *114*, 820; *Angew. Chem. Int. Ed.* **2002**, *41*, 783; b) J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem.* **2002**, *114*, 1808; *Angew. Chem. Int. Ed.* **2002**, *41*, 1737.

[10] S. L. James, X. Xu, R. V. Law, *Macromol. Symp.* **2003**, *196*, 187, and references cited therein.

[11] a) X.-S. Wang, M. Winnik, I. Manners, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *86*, 93; b) X.-S. Wang, M. Winnik, I. Manners, *Macromol. Rapid Commun.* **2002**, *23*, 210.

[12] a) I. Manners, *Synthetic Metal-Containing Polymers*, Wiley-VCH, Weinheim, **2003**; b) I. Manners, *Science* **2001**, *294*, 1164.

[13] P. Nguyen, P. Gómez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515.

[14] a) D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* **1992**, *114*, 6246; b) Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **1996**, *118*, 4102.

[15] See for example: a) C. Bucher, C. H. Devillers, J. C. Moutet, G. Royal, E. Saint-Aman, *Chem. Commun.* **2003**, 888; b) E. Lindner, R. F. Zong, K. Eichele, U. Weisser, M. Ströbele, *Eur. J. Inorg. Chem.* **2003**, 705; c) D. M. Shin, I. S. Lee, Y. K. Chung, *Eur. J. Inorg. Chem.* **2003**, 2311; d) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, L. Sturba, F. Grepioni, *Organometallics* **2003**, *22*, 2142.

[16] a) I. S. Lee, D. M. Shin, Y. K. Chung, *Cryst. Growth Des.* **2003**, *3*, 521; b) G. Li, H. W. Hou, L. K. Li, X. R. Meng, Y. T. Fan, Y. Zhu, *Inorg. Chem.* **2003**, *42*, 4995; c) C. M. Zakaria, G. Ferguson, A. J. Lough, C. Glidewell, *Acta Crystallogr. Sect. B* **2002**, *58*, 786.

[17] D. N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava, A. Bergamo, *Chem. Commun.* **2003**, 264.

[18] a) S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa, M. Peruzzini, *J. Mol. Catal. A* **2004**, *224*, 61; b) A. Romerosa, L. Gonsalvi, M. Peruzzini, unpublished results.

[19] Complex **2** was obtained as an orange microcrystalline compound by treating **1** with TlOTf in $CHCl_3$ (Yield: 85 %). Elemental analysis (%) calcd for $C_{18}H_{29}F_3N_6O_3P_2RuS$ (629.54): C 34.34, H 4.64, N 13.35, S 5.09; found C 34.10, H 4.30, N 12.94, S 4.69; IR (KBr): $\tilde{\nu} = 1261$, 1170, 1031 cm^{-1} (OTf); ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, Me_4Si): $\delta = 3.85–4.58$ (m, CH_2(pta), 24 H), 4.67 ppm (s, Cp, 5 H); $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 20 °C, 85 % H_3PO_4): $\delta = -15.47$ ppm.

[20] G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17.

[21] See for example: B. K. Bennett, S. Lovell, J. M. Mayer, *J. Am. Chem. Soc.* **2001**, *123*, 4336.

[22] Crystals of **4** were obtained by slow evaporation at room temperature of a DMSO solution of **5** in the air over one month. Crystal data for **4**: $C_{19}H_{37}AgCl_2N_6O_2P_2RuS$, orthorhombic, space group *Pnma* (no. 62), $a = 11.8733(9)$, $b = 12.9333(10)$, $c = 17.4306(13)$ Å, $V = 2676.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.864$ Mg m^{-3}, final R_1 value 0.0495 for 1583 independent reflections ($I > 2\sigma(I)$). The data collection was performed at room temperature on a Bruker APEX CCD area-detector diffractometer, using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) by the ω scan method, within the limits $1.96 < \theta < 23.29°$. No empirical absorption correction was applied. The structure was solved by direct methods (SIR97) and refined by full-matrix least-squares on F^2 (SHELX 97). Anisotropic thermal factors were assigned to all the non-hydrogen atoms. The disordered O30 and Cl2 atoms were found and an average model was refined. The cyclopentadienyl C-atoms were statistically distributed around the Ru atom. All the H atoms except those bonded to O30 and the Cp carbon atoms were placed in calculated positions and not refined. All the diagrams were generated by using the SHELXL program. CCDC-241789 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.

[23] a) G. Helgesson, S. Jagner, *Inorg. Chem.* **1991**, *30*, 2574; b) K. M. Lee, H. M. Wang, I. J. B. Lin, *J. Chem. Soc. Dalton Trans.* **2002**, 2852; c) G. Helgesson, S. Jagner, *J. Chem. Soc. Dalton Trans.* **1993**, 1069; d) Z. Xie, B.-M. Wu, T. C. W. Mak, J. Manning, C. A. Reed, *J. Chem. Soc. Dalton Trans.* **1997**, 1213; e) R. W. Turner, E. L. Amma, *J. Am. Chem. Soc.* **1966**, *88*, 3243; f) G. Exarchos, S. C. Nyburg, S. D. Robindon, *Polyhedron* **1998**, *17*, 1257; g) C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Cham, Z. Xie, *Inorg. Chem.* **2000**, *39*, 5851.

[24] Cambridge Structural Database (CSD): http://www.ccdc.cam.ac.uk/products/csd/ (October **2004**).

[25] B. J. Frost, C. A. Mebi, *Organometallics* **2004**, *23*, 5317.

[26] a) D. J. Darensbourg, F. Joó, M. Kannisto, A. Katho, J. H. Reibenspies, *Organometallics* **1992**, *11*, 1990; b) D. J. Darensbourg, F. Joó, M. Kannisto, A. Katho, J. H. Reibenspies, D. J. Daigle, *Inorg. Chem.* **1994**, *33*, 200; c) C. S. Allardyce, P. J. Dyson, D. J. Ellis, S. L. Heath, *Chem. Commun.* **2001**, 1396; d) D. J. Darensbourg, F. A. Beckford, J. H. Reibenspies, *J. Cluster Sci.* **2000**, *11*, 95.

[27] A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **2004**, *248*, 955.

[28] The orientation of the Cp rings is predetermined by the symmetry operations in the space group of **4**.

[29] *Dynamic Light Scattering* (Eds. B. Bruce, R. Pecora), Wiley, New York, **1976**; B. J. Berne, R. Pecora, *Dynamic Light Scattering*

with Applications to Chemistry, Biology, and Physics, Dover Publications, Dover, **2000**.

[30] Examples of solid poly(stannasiloxane)s that reversibly form smaller macrocycles in solution have been reported, see: J. Beckmann, K. Jurkschat, D. Schollmeyer, M. Schürmann, *J. Organomet. Chem.* **1997**, *543*, 229.

[31] A Malvern 4700 system operating with a 6328 Å-wavelength He–Ne laser was employed for recording the DLS measurement. The temperature was controlled with a precision of 0.1 K using both a Peltier thermocouple and an external bath. Light intensity was recorded at a fixed scattering angle, $\theta = 40°$. The time correlation function of the scattered intensity, $\langle I(0)I(\tau)\rangle$, was then calculated and the mean hydrodynamic diameter obtained by standard cumulated analysis. The sample temperature was equilibrated for 20 min before every measurement. Low particle concentrations were used for DLS measurements to diminish the effect of colloidal interactions as well as multiple scattering.

[32] a) L. Brammer, J. C. M. Rivas, R. Atencio, S. Fang, F. C. Pigge, *J. Chem. Soc. Dalton Trans.* **2000**, 3855; b) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441; c) D. L. Reger, R. F. Semeniuc, M. D. Smith, *J. Chem. Soc. Dalton Trans.* **2002**, 476; d) M. P. Thornberry, C. Slebodnick, P. A. Deck, F. R. Fronczek, *Organometallics* **2000**, *19*, 5352.