Formation of Super Wires of Clusters by Self-Assembly of Transition Metal Cluster Anions with Metal Cations

Takayuki Nakajima, Atsushi Ishiguro, and
Yasuo Wakatsuki*

The self-assembly approach to the construction of supramolecules or extended frameworks based on coordination complexes is one of the major current research areas in inorganic and organometallic chemistry.[1] In the vast majority of such compounds, the molecular building blocks are held together by strong metal–(linking ligand)–metal bonding interactions or weaker forces such as hydrogen bonding between ligands coordinating to the different metal units. In some cases, however, the metal dσ stacking force of square-planar complexes can lead to stacklike, one-dimensional (1D) metal–metal bonds in the solid state. Thus, there has been a series of reports on $(Pt-Pt)_\infty$ chains in which metal–metal separations indicative of weak interactions or of discrete bonds have been found.[2] A similar 1D stacking polymer $[\{Ru(CO)_4\}_\infty]$ has been structurally characterized by powder diffraction,[3] and a 1D Rh–Rh polymeric complex has been prepared by the electrochemical reduction of an $Rh^{II}-Rh^{II}$ dimer that only has acetonitrile ligands.[4] This reaction has been explained as a radical polymerization of an unstable $[Rh_2^{I,II}]$ species generated at the electrode. Crystals of a nonstacked zigzag chain of Co–Cu atoms have been prepared by a simpler route, that is, the reaction of $Na[Co(CO)_4]$ with CuCl.[5] Herein we report a new class of 1D complexes that consist of high-nuclearity cluster species and have infinite, heteroleptic metal–metal bonded chains. This unprecedented “super wire” has been prepared by alternative self ordering of anionic cluster complexes with a cationic metal species.

In 1983, Heaton and co-workers reported an interesting observation from NMR spectrocopy which was that on addition of Ag^+ ions to a solution of $[Rh_6C(CO)_{15}]^{2-}$, the oligomeric species $[Ag_n\{Rh_6C(CO)_{15}\}_n]^{n-}$ ($n > 3$) is formed, although the crystals that they isolated were from a structurally simpler sandwich-type complex $[Ag\{Rh_6C(CO)_{15}\}_2]^{3-}$.[6] Therefore, it appeared interesting to us to examine a similar reaction of the analogous ruthenium clusters because the Ru_6 core is hexagonal whereas the Rh_6 core has a trigonal prismatic structure. It was known that the reactions of high-nuclearity ruthenium cluster anions with Ag^+[7] and Cu^+ ions[7a, 8] gave sandwich-type complexes such as the rhodium complex isolated by Heaton. However, almost all of these isolated ruthenium products are stabilized by the inclusion of a chloride ligand from the [PPN]Cl ($PPN = N(PPh_3)_2^+$) used in the reactions.

We wondered what the product would be if chloride is excluded from the reaction system, thus, we attempted the reaction of the hexanuclear dianionic ruthenium cluster $[PPN]_2[Ru_6C(CO)_{16}]$ ($[PPN]_2$**1**) in THF, with an equivalent of $AgNO_3$ at room temperature. Over 12 h a characteristic $\tilde{\nu}$(CO) band at 1998 cm^{-1} in the IR spectrum gradually increased while that of **1** at 1973 cm^{-1} disappeared completely, during this time the solution remained homogeneous. On evaporation of the solvent the crude micro-crystals obtained in 97% yield had the composition $[PPN][AgRu_6C(CO)_{16}]$ ([PPN]**2**). This complex is soluble in acetone and probably has an oligomeric structure in solution as observed by Heaton for the rhodium complex.[4] The solid-state IR spectrum of [PPN]**2** is very similar to that in solution: it shows the $\tilde{\nu}$(CO) band, though broader than the corresponding peak in solution, at 1999 cm^{-1} (KBr). Dark red crystals grown from acetone/methanol have the X-ray structure shown in Figure 1.

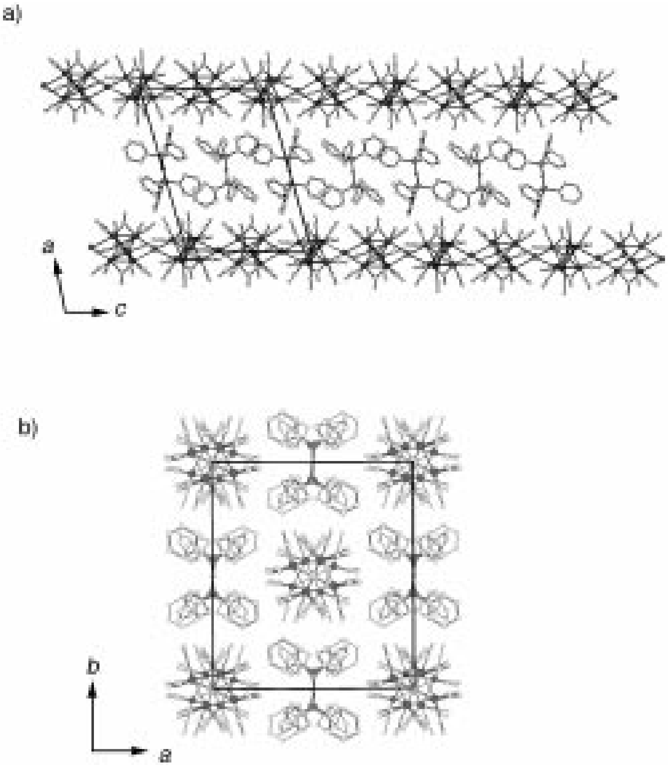

Figure 1. Crystal packing of $\{[PPN]\mathbf{2}\}_\infty$ viewed along a) the *b* axis and b) the *c* axis.

The infinite chains of alternating ruthenium clusters and silver ions are separated from each other by layers of PPN cations (Figure 1 a). The view along the polymer-chain axis (Figure 1 b) indicates that the Ru cluster and PPN are comparable in size which probably aids the crystal packing of $\{[PPN]\mathbf{2}\}_\infty$. Looking closer at this rigid metal chain (Figure 2), one notices that the bridging silver atom has a distorted tetrahedral orientation, the dihedral angle Ag-Ru12-Ru13/Ag-Ru12*-Ru13* being 49.9°. There is a point of inversion at the carbido center of the Ru_6 core, as well as at the silver atom, so that only three Ru atoms and one Ag atom are crystallographically independent. The Ag–Ru12 and Ag–Ru13 bond lengths are 2.9185(4) and 2.9425(4) Å, respectively. The edge bridged by the silver atom, Ru12–Ru13, is 3.046(1) Å, which is distinctly longer than the five independent Ru–Ru bonds (av. 2.907 Å). The polymeric complex with the PPh_4 cation $\{[PPh_4]\mathbf{2}\}_\infty$ was

---

[*] Dr. Y. Wakatsuki, Dr. T. Nakajima, Dipl.-Chem. A. Ishiguro
RIKEN (The Institute of Physical and Chemical Research)
Wako-shi, Saitama 351-0198 (Japan)
Fax: (+81) 484-62-4665
E-mail: waky@postman.riken.go.jp

1433-7851/01/4006-1066 $ 17.50+.50/0

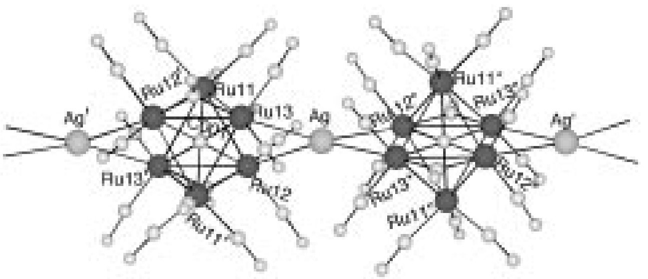

Figure 2. A section of the structure of anion **2** in {[PPN]**2**}$_\infty$. Selected interatomic distances [Å] and angles [°]: Ag-Ru12 2.9185(4), Ag-Ru13 2.9425(4), Ru11-Ru12 2.8903(5), Ru11-Ru13 2.9348(6), Ru12-Ru13 3.046(1), Ru11′-Ru12 2.9405(6), Ru11′-Ru13 2.9006(5), Ru12-Ru13′ 2.8545(4), C001-Ru11 2.0372(4), C001-Ru12 2.0856(4), C001-Ru13 2.0888(4); Ru12-Ag-Ru13 62.62(1).

synthesized in the same way from $[PPh_4]_2$**1** and $AgNO_3$ in 93 % yield and structurally characterized. The anion in the solid state has a structure quite similar to that of {[PPN]**2**}$_\infty$.

No change was observed spectroscopically on heating an acetone solution of {[PPN]**2**}$_\infty$ at 60 °C for 12 h and {[PPN]**2**}$_\infty$ was recovered quantitatively. In contrast, more soluble {$[PPh_4]$**2**}$_\infty$ did show some reactivity; when {$[PPh_4]$**2**}$_\infty$ (50 mg) was suspended in MeOH (20 mL) at 60 °C, the solution soon became homogeneous and the IR spectra began to show a slow change. After 12 h a dark red crystalline complex was isolated from this solution in around 42 % yield. This was not the recovered polymeric or oligomeric complex but had the composition $[PPh_4]_2[\{AgRu_6C(CO)_{15}\}_2]$ ($[PPh_4]_2$**3**) resulting from the loss of one CO ligand per Ru_6 unit. The overall structure of anion **3** (Figure 3), as determined by single-crystal X-ray analysis, turned out to be very similar to that of the mixed-metal palladium–ruthenium cluster $[PPN]_2[Pd_2Ru_{12}C_2(CO)_{30}]$ recently prepared from $[PPN]_2$**1** and $[Pd(CH_3CN)_4]^{2+}$.[9] There is a crystallographic center of symmetry at the center of the molecule **3** (mid point between Ag–Ag*). Two Ag atoms bridge two Ru_6 moieties by capping the trigonal faces. Each Ag atom has, therefore, six Ag–Ru bonds ranging from 2.816(2) to 2.883(2) Å. As in the case of the Pd analogue, the atoms Ru14 and Ru15 (and Ru14* and Ru15*) are interacting with the two bridging metals (Ag) and are thus no longer bonded to each other, the Ru···Ru distance being 3.222(2) Å.

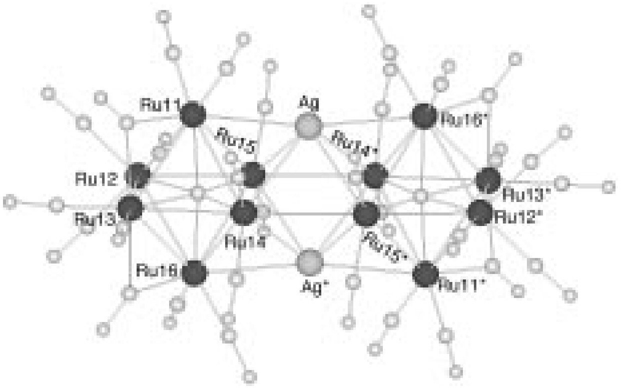

Figure 3. Structure of anion **3** in the crystal. Selected interatomic distances [Å] and angles [°]: Ag-Ru11 2.883(2), Ag-Ru14 2.848(1), Ag-Ru15 2.826(2), Ag*-Ru16 2.881(2), Ag*-Ru14 2.874(2), Ag*-Ru15 2.816(2), Ru14-Ru15* 3.033(2), Ru14-Ru15 3.222(2); Ru14-Ag-Ru15 69.20(4), Ru14*-Ag-Ru15 64.29(4), Ru14-Ag-Ru15* 64.77(4), Ru14*-Ag-Ru15* 68.97(4), Ag-Ru14-Ag* 77.06(4), Ag-Ru15-Ag* 78.36(4).

In conclusion, we have shown that high nuclearity anionic clusters can undergo self-assembly with cationic metal species into a novel 1D polymeric form in the solid state. This cluster wire is remarkably stable: dissolution into oligomer and reformation of the infinite chain can be repeated at room temperature without any decomposition. Only after prolonged heating in solution does the polymeric complex with a PPh_4 cation rearrange to a dimeric form by loss of one CO ligand per cluster unit and concomitant shift of the Ag units from edge to face coordination of the Ru cluster core.

Experimental Section

All reactions were carried out in dry solvents under argon. All data collections for X-ray analysis were made on a Rigaku RAXIS-IV imaging plate diffractometer with graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. Structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix against $|F^2|$. All calculations were performed using the teXsan crystallographic software package (Molecular Structure Corporation (1992)). 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-152134 ({[PPN]**2**}$_\infty$), CCDC-152136 ({$[PPh_4]$**2**}$_\infty$), CCDC-152135 ($[PPh_4]_2$**3**). 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).

$\{[PPN][AgRu_6C(CO)_{16}]\}_\infty$: A mixture of $[PPN]_2[Ru_6C(CO)_{16}]$ (200 mg, 0.09 mmol) and $AgNO_3$ (16 mg, 0.09 mmol) in THF (30 mL) was stirred at room temperature for 12 h in a 100 mL Schlenk flask wrapped with aluminum foil. The reaction mixture was filtered through Celite before drying under vacuum, the residual red solid was washed with methanol to remove $[PPN]NO_3$ and yield red micro-crystals of {[PPN]**2**}$_\infty$. (155 mg, 97 %). Analytically pure material was obtained as dark-red plates by recrystallization from acetone/methanol at room temperature. IR(THF) $\tilde{\nu}$(CO) 1998(s) cm^{-1}; elemental analysis (%) calcd for $C_{53}H_{30}AgNO_{16}P_2Ru_6$ (1713.05): C 37.16, H 1.77, N 0.82; found: C 37.15, H 1.74, N 0.79. Crystal data for {[PPN]**2**}$_\infty$: M_w(unit) = 1713.06, monoclinic, space group $C2/c$ (no. 15), $a = 20.490(4)$, $b = 17.702(7)$, $c = 15.722(2)$ Å, $\beta = 104.09(1)°$, $V = 5530(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.060$ g cm^{-3}, $\mu = 20.4$ cm^{-1}, data collection at 20 °C, $R1 = 0.031$, $R2 = 0.038$ for 4730 data with $I > 4\sigma(I)$.

{$[PPh_4]$**2**}$_\infty$: Dark red plates; IR(THF) $\tilde{\nu}$(CO) 1998(s) cm^{-1}; elemental analysis (%)calcd for $C_{41}H_{20}AgO_{16}PRu_6$ (1513.86): C 32.52, H 1.33; found: C 32.20, H 1.30. Crystal data for {$[PPh_4]$**2**}$_\infty$: unit M_w(unit) = 1514.46, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.938(6)$, $b = 22.029(9)$, $c = 15.775(9)$ Å, $\alpha = 99.23(3)$, $\beta = 107.65(2)$, $\gamma = 104.95(5)°$, $V = 4925(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.055$ g cm^{-3}, $\mu = 22.8$ cm^{-1}, data collection at 20 °C, $R1 = 0.052$, $R2 = 0.086$ for 9518 data with $I > 4\sigma(I)$.

$[PPh_4]_2[Ru_{12}C_2(CO)_{30}Ag_2]$: A suspension of {$[PPh_4]$**2**}$_\infty$ (50 mg, 0.033 mmol) in methanol (20 mL) was stirred at 60 °C for 12 h in a 100 mL Schlenk flask. The solvent was evaporated under reduced pressure and the residual dark red solid was purified by chromatography on SiO_2 (deactivated with 10 wt % H_2O). The dark red solution eluted with CH_2Cl_2 was collected and evaporated to dryness to yield dark red solid $[PPh_4]_2$**3** (21 mg, 0.007 mmol). Analytically pure material was obtained as dark red needles by recrystallization from CH_2Cl_2/methanol. IR(THF) $\tilde{\nu}$(CO) 2033(s), 2017(s), 2002(s) cm^{-1}, elemental analysis (%) calcd for $C_{80}H_{40}Ag_2O_{30}P_2Ru_{12}$ (2971.70): C 32.32, H 1.36; found: C 32.12, H 1.38. Crystal data for $[PPh_4]_2$**3**: $M_w = 2972.90$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.417(2)$, $b = 13.967(2)$, $c = 14.728(2)$ Å, $\alpha = 63.25(1)$, $\beta = 65.26(1)$, $\gamma = 87.17(1)°$, $V = 2205.3(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.237$ g cm^{-3}, $\mu = 25.4$ cm^{-1}, data collection at 20 °C, $R1 = 0.055$, $R2 = 0.058$ for 4537 data with $I > 2\sigma(I)$.

Received: November 16, 2000 [Z 16121]

[1] Recent reviews: a) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502; b) D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375; c) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474; d) P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863; e) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853.

[2] a) G. Gliemann, H. Yersin, *Struct. Bonding (Berlin)* **1985**, *62*, 87; b) K. Sakai, M. Takeshita, Y. Tanaka, T. Ue, M. Yanagisawa, M. Kosaka, T. Tsubomura, M. Ato, T. Nakano, *J. Am. Chem. Soc.* **1998**, *120*, 11353; c) K. Sakai, Y. Tanaka, Y. Tsuchiya, K. Hirata, T. Tsubomura, S. Iijima, A. Bhattacharjee, *J. Am. Chem. Soc.* **1998**, *120*, 8366.

[3] N. Masciocchi, M. Morest, P. Cairati, F. Ragani, A. Sinori, *J. Chem. Soc. Chem. Commun.* **1993**, 471.

[4] M. E. Prater, L. E. Pence, R. Clérac, G. M. Finniss, C. Campana, P. Auban-Senzier, D. Jérome, E. Canadell, K. R. Dunbar, *J. Am. Chem. Soc.* **1999**, *121*, 8005.

[5] P. Klüfers, *Angew. Chem.* **1985**, *97*, 59; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 70.

[6] B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, V. G. Albano, D. Braga, *J. Chem. Soc. Dalton Trans.* **1983**, 2175.

[7] a) S. M. Draper, A. D. Hattersley, C. E. Housecroft, A. L. Rheingold, *J. Chem. Soc. Chem. Commun.* **1992**, 1365; b) D. S. Shephard, T. Maschmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R. D. Oldroyd, R. G. Bell, *Angew. Chem.* **1997**, *109*, 2337; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2242.

[8] a) M. A. Beswick, J. Lewis, P. R. Raithby, M. C. Ramirez de Arellano, *J. Chem. Soc. Dalton Trans.* **1996**, 4033; b) M. A. Beswick, J. Lewis, P. R. Raithby, M. C. Ramirez de Arellano, *Angew. Chem.* **1997**, *109*, 303; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 291; c) M. A. Beswick, J. Lewis, P. R. Raithby, M. C. R. Ramirez de Arellano, *Angew. Chem.* **1997**, *109*, 2311; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2227.

[9] T. Nakajima, A. Ishiguro, Y. Wakatsuki, *Angew. Chem.* **2000**, *112*, 1175; *Angew. Chem. Int. Ed.* **2000**, *39*, 1131.