Coordination Polymers

An Oriented 1D Coordination/Organometallic Dimetallic Molecular Wire with Ag–Pd Metal–Metal Bonds**

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Dedicated to Professor Jean-Marie Lehn
on the occasion of his 65th birthday

In addition to conferring unique catalytic properties to their metal complexes when they behave as spectator ligands,

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Supporting information for this article (including crystallographic data for **4**$\cdot SO_3CF_3\cdot 0.5\,CH_2Cl_2$, **5**$\cdot SO_3CF_3\cdot 2\,CH_2Cl_2$ and **6**$\cdot SO_3CF_3$, and all the experimental and computational details) is available on the WWW under http://www.angewandte.org or from the author.

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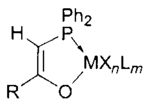
coordinated P,O-phosphanyl enolates in a moiety such as **1** also display a very rich reactivity based on their intrinsic ambident behavior.[1–3] Harder electrophiles, such as chlorophosphanes, generally react at the oxygen atom,[4] whereas softer electrophiles, for example, activated alkynes,[5] CO_2, or RNCO,[6] bind to the prochiral carbon center.



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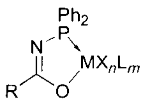


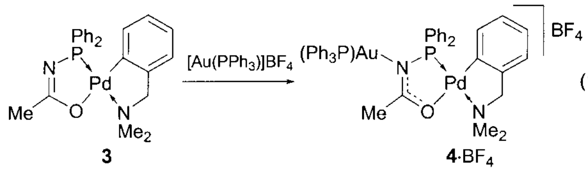
2

The latter selectivity also applies to late-transition metals and opens an interesting route to (hetero)dimetallic complexes in which the PC carbon atom has become sp^3 hybridized.[7] Although control of the stereochemistry at the PC carbon atom is possible,[8] the generation of both the *R* and *S*-configured stereogenic P-C centers is generally expected.

We thus considered that replacing the PCH functionality with the isoelectronic PN group of phosphanyl iminolates (**2**) might simplify this issue, since the nitrogen atom could retain a planar coordination geometry. Furthermore, the simple exchange of a CH group by an N atom can bring about interesting electronic and geometric differences in molecular complexes, as shown with the phosphanes $Ph_2PNHC(O)R$ and $Ph_2PCH_2C(O)R$,[9] or induce unexpectedly large effects in supramolecular chemistry.[10]

We have now found that metal coordination at the nitrogen atom of the P,O chelate in a complex of type **2**: 1) readily leads to (μ-P,N)-bridged heterodimetallic complexes, 2) occurs with retention of the planar coordination geometry at the nitrogen atom, and rather unexpectedly 3) opens an unprecedented route to ordered structures containing alternating metals in heterodimetallic units to form oriented, 1D coordination/organometallic polymers.

The new, air-stable complex **3**[11] was treated with one equivalent of $[Au(PPh_3)]BF_4$ in THF to afford **4**·BF_4 [Eq. (1)] and the structure of the analogous complex **4**·SO_3CF_3 was determined by X-ray diffraction analysis (Figure 1 and see the Supporting Information).[11]



(1)

N-metalation leads to an Au···N distance of 2.085(6) Å, similar to those found in complexes with a covalent Au–N bond in an Au-$NPPh_2$ moiety.[12] The coordination geometry around the nitrogen atom is planar, with the sum of the three bond angles around N(2) being 360.0(3)° (max deviation out of the mean plane containing the atoms Pd, P1, N2, C10, O1, and Au: 0.01 Å).[13] Accordingly, the NCH_2 protons only show a doublet in the ^1H NMR spectrum as a result of coupling to the P atom. The O1–C10 and N2–C10 bond lengths of 1.273(9) and 1.353(9) Å, respectively, are consistent with C⋯O and N⋯C bond orders intermediate between single and double bonds.[7,9,14]

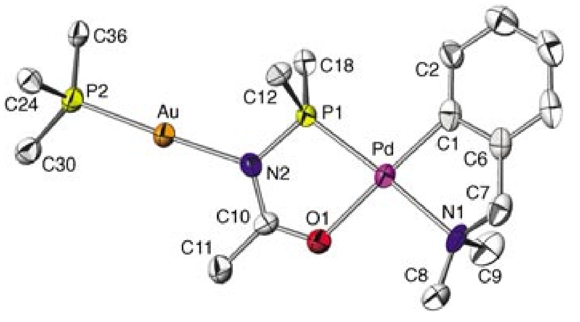
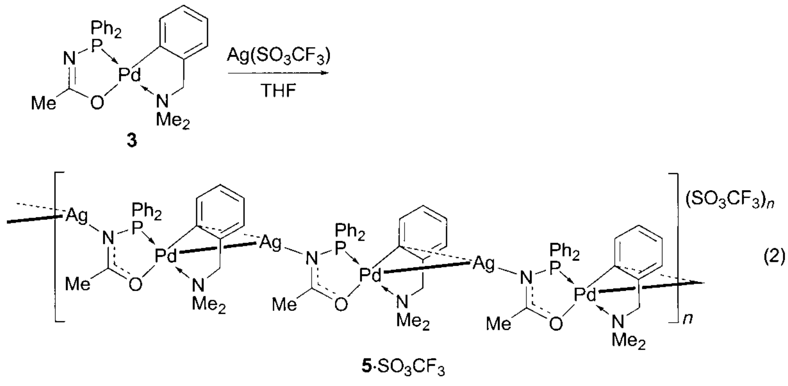


Figure 1. ORTEP view of the structure of complex **4** in **4**·SO_3CF_3·0.5 CH_2Cl_2. Only the *ipso* aryl carbon atoms on P1 and P2 are shown for clarity. Thermal ellipsoids enclose 50% of the electron density.

A solution of **3** in THF was then treated with pure, acid-free $AgSO_3CF_3$ in a 1:1 stoichiometry, and slow crystallization afforded high yields of a beige product **5**·SO_3CF_3 [Eq. (2)], which was shown by X-ray diffraction studies to be an unprecedented Ag-Pd coordination polymer (Figure 2 and see the Supporting Information).[11]



(2)

The Ag^+ ion is, as anticipated, linked to the iminolate nitrogen atom, which retains its planar coordination geometry (sum of the three bond angles around N2 = 359.5(3)°; Ag···N = 2.133(3) Å; see the Supporting Information). If only a covalent Ag–N interaction was present, the silver center would remain, with 12 electrons, coordinatively unsaturated. It was therefore expected to interact with the triflate oxygen atom(s),[15] as observed in other cases,[16] but it prefers to find the required additional electron density in the Pd–C1 σ bond involving the cyclometalated ligand of another complex molecule (Figure 2). This situation is best described as a multicentered interaction resulting in the donation of σ- and π-electron density from the Pd–C1 (p_z orbital) and Pd-bound aryl regions to the coordinatively unsaturated silver center.

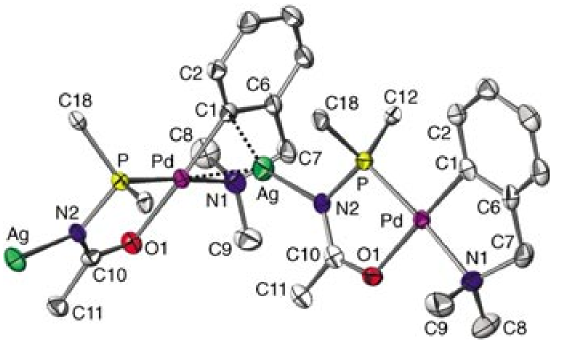


Figure 2. ORTEP view of the structure of the "repeat unit" Ag_2Pd_2 of the polymeric complex **5** in **5**$\cdot SO_3CF_3\cdot 2\,CH_2Cl_2$. Only the *ipso* aryl carbon atoms on P are shown for clarity. Thermal ellipsoids enclose 50% of the electron density.

The electronic transfer occurs from the d^8 Pd^{II} center to the d^{10} Ag^I center and results in a relatively short Ag–C1 bonding distance of 2.263(4) Å,[17] and in one of the shortest Pd–Ag bonds (2.884(1) Å) reported in the literature.[17a,18] Since two consecutive square-planar Pd^{II} units are almost orthogonal to each other (see the Supporting Information), the structural repeating unit in the extended structure is Ag_2Pd_2 (Figure 2), which results in a novel, oriented, 1D coordination/organometallic wire structure in which the metal centers are situated in the *ab* plane (Figure 3). A view along the *a* axis (see the Supporting Information) shows the adjacent rows of silver atoms flanked by two rows of palladium atoms and illustrates another remarkable feature resulting from the arrangement of these infinite zigzag chains in the solid state: the lipophilic aromatic rings are all on one side of the metal planes and this results in an unusual layered structure (see Figure 4). Attempts to obtain an analogous Ag-Pd extended structure from the isovalent phosphanyl enolate/Pd^{II} complex have remained unsuccessful, which emphasizes the differences that may result from the replacement of the CH group in **1** by an N atom in **2**.

The mass spectrum (MALDI-TOF) of **5**$\cdot SO_3CF_3$ contains two main peaks at *m*/*z* 483 for $[\mathbf{3}+H]^+$ and 1073, whose characteristic isotopic pattern indicates the composition $[Ag(\mathbf{3})_2]^+$. The structure of $[Ag(\mathbf{3})_2]^+$ cannot be predicted with certainty to reproduce the alternate bonding pattern observed for **5** and is referred as the type II structure in Scheme 1.

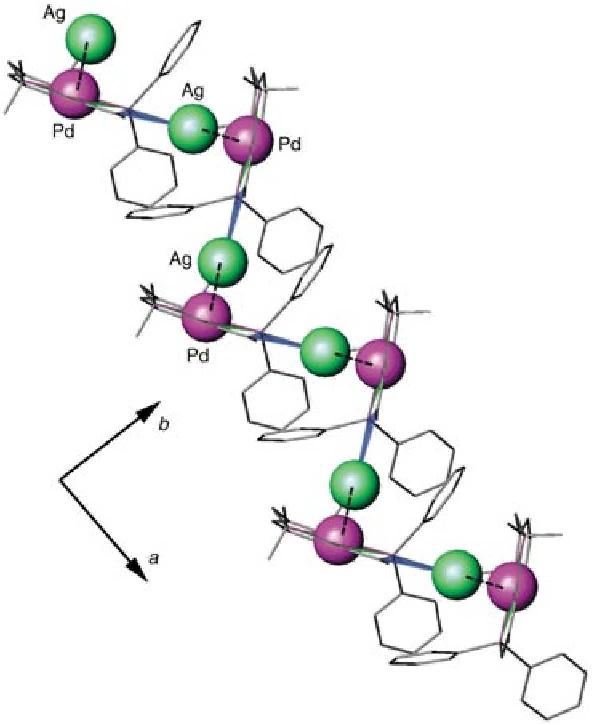
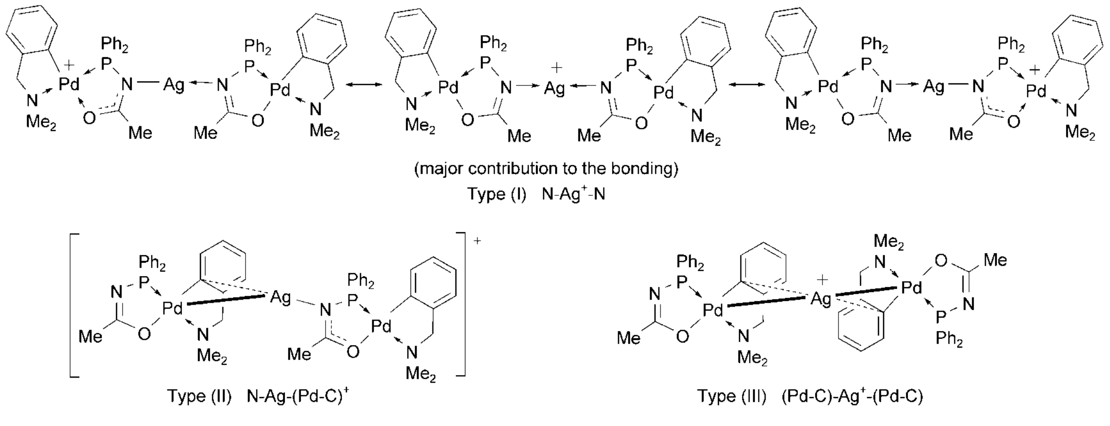


Figure 3. View in the *ab* plane of the zigzag wire structure of the polymeric complex structure of **5** in **5**$\cdot SO_3CF_3\cdot 2\,CH_2Cl_2$.

Indeed, two bonding modes in which an Ag^+ ion is coordinated to the same site of two molecules of **3** should also be considered. In a type I structure, the donation pattern can be viewed as intermediate between two limiting forms in which one nitrogen atom acts as a two-electron donor and the other as a two-electron or one-electron donor ligand, respectively. In such a model, part of the electron density from the nitrogen lone pair of electrons is transferred to the π system, thus increasing the covalent character of the Ag–N bond and affecting in return the geometry of the phosphanyl iminolate ligands. A further possibility to be considered is the



Scheme 1. Hypothetical discrete structures formed from **3** and Ag^+ ions in a 2:1 ratio. Type (I) corresponds to the actual structures of complex **6**.

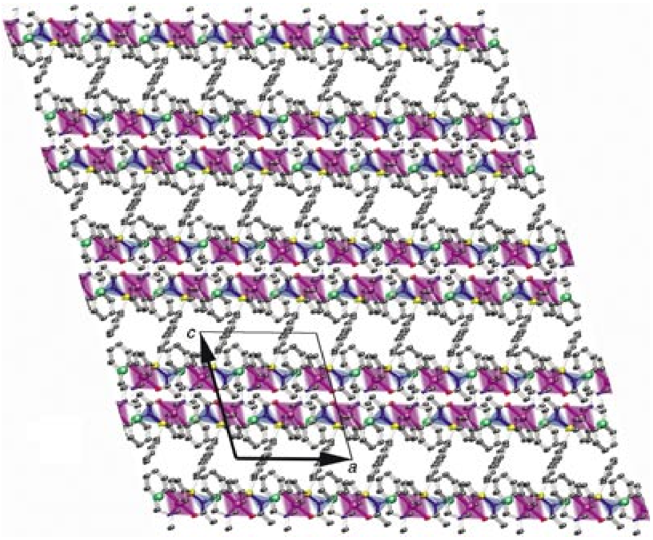


Figure 4. Projection in the *a*,*c* plane of the layered structure of **5** in **5**$\cdot SO_3CF_3\cdot 2\,CH_2Cl_2$. The space between the pairs of metal-rich layers contains the phenyl rings, the triflate anions, and solvent molecules (Ag green, Pd pink, N blue, P yellow, O orange).

formation of a complex of type (III), in which each neutral molecule of **3** behaves as an electron donor through its Pd–C σ bond and its extended Pd–aryl π system (only the transoid structure is depicted in Scheme 1).

Extended Hückel (EHT) and density functional theory (DFT) calculations have been carried out on a series of discrete structures featuring the various types of attachment that can be expected between the Ag^+ ion and one or two molecules of **3′**, a model of **3** in which the methyl and phenyl substituents have been replaced with hydrogen atoms. A model (**4′**) of the gold complex was also investigated. Technical details of the calculations, Cartesian coordinates of the optimized structures with selected interatomic distances, and an extensive discussion of the results are available in the Supporting Information. The most important conclusions of the theoretical study are as follows:

a) The amount of electron transfer to the Ag^+ ion is equivalent in the two bonding modes symbolized as Ag^+–N and Ag^+–(Pd–C). However, the nature of the two donation processes is quite different: concentrated, directional, and originating from a single source (the in-plane p orbital of N) for $N\rightarrow Ag^+$; soft, diffuse, multicentered, and long-range for $(Pd{-}C)\rightarrow Ag^+$. In the latter case, a variety of donor centers could interact with the Ag^+ ion, with the most important being the Pd–C1 σ bond (20 %); the d shell of Pd (17 %) and the π orbitals of C1 (20 %), C2 and C6 (27 %), and C4 (10 %). Both types of calculations predict that the Ag^+–N and the Ag^+–(Pd–C) bonding modes are competitive in terms of electron-transfer and bonding energy. This description confirms the dual bonding ability of **3′** and **3**, which was substantiated by the synthesis of (**5**$\cdot SO_3CF_3)_n$, and suggests that the production of monocationic, trinuclear Pd/Ag/Pd complexes could be achieved by a careful tuning of the Ag^+ supply. Such a discrete complex was indeed obtained subsequently (see below).

b) The complexation of an Ag^+ ion to one molecule of **3′** is computed to be exothermic by 2.88 eV and 2.79 eV for the Ag^+–N and Ag^+–(Pd–C) forms, respectively, compared to 1.82 eV calculated for the η^1 coordination of an Ag^+ ion to benzene. The complexation energies calculated for the three forms of $[Ag(\mathbf{3'})_2]^+$ are −5.15 eV for N-Ag^+-N (type I in Scheme 1), −4.71 eV for type II, and −4.36 eV for type III. The energy associated with the coordination of a second molecule of **3′** is just slightly reduced with respect to the first complexation for the type I system, but somewhat more for type III. At variance with the polymer, it was clear from these results that a type I structure should be predicted for $[Ag(\mathbf{3})_2]^+$.

This theoretical prediction was actually verified by the reaction between $AgSO_3CF_3$ and two equivalents of **3** affording the $AgPd_2$ complex **6**$\cdot SO_3CF_3$ in 92 % yield. The crystal-structure analysis of this complex established indeed that the coordination of both molecules of **3** to Ag^+ occurred through their nitrogen atoms (type I in Scheme 1; see Figure 5 and the Supporting Information).[11] The N2-Ag-N4 angle of 175.4(2)° allows a coordination number of two to be formally assigned to the silver ion, a situation which occurs in less than 25 % of the structures of Ag^I complexes.[19] However, a weak electrostatic interaction probably exists between the triflate anion and the Ag^+ ion, with the Ag···O3 distance of 2.82(1) Å being nevertheless in the upper range of those found on the CSD (version 5.25) which are in most cases between 2.38 and 2.55 Å (for comparison, the nearest triflate oxygen atom is at 3.86(2) Å from Ag^+ in **5**$\cdot SO_3CF_3\cdot 2\,CH_2Cl_2$). The dihedral angle between the two best Pd^{II} square planes is 75(2)°.

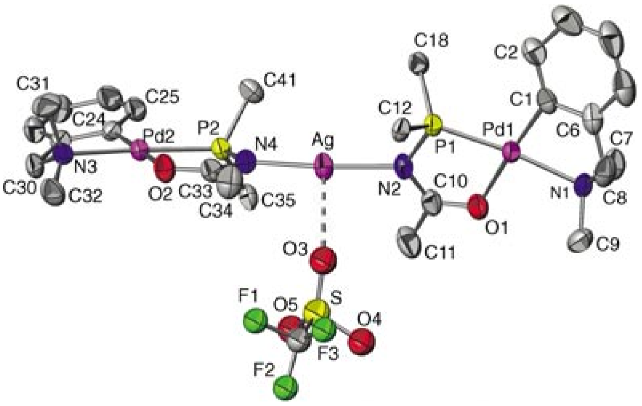


Figure 5. ORTEP view of the structure of **6**$\cdot SO_3CF_3$. Only the *ipso* aryl carbon atoms on P1 and P2 are shown for clarity. Thermal ellipsoids enclose 50 % of the electron density.

Although the term "coordination polymers" was first coined 40 years ago,[20] the corresponding research area continues to gain increasing importance.[21] Furthermore, the considerable current interest in extended metal atom chains (EMACs)[22] is partly a consequence of their expected unique and challenging physical properties.[17c,23–27] While the linking of *homo*dinuclear units through (weak) metal–metal bonding or suitable ligands allows the formation of exciting coordination polymers,[24,25,27] we believe that the structure of **5**$\cdot SO_3CF_3$ is not only an unprecedented example of perfectly alternating and ordered 1D *hetero*dimetallic polymeric structure, and the first molecular wire containing Ag–Pd bonds, but that its synthesis reaches beyond the realm of extended structures in purely inorganic chemistry[28] and opens up new perspectives in coordination/organometallic supramolecular chemistry.

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Keywords: coordination polymers · density functional calculations · heterometallic complexes · ligand reactivity · metal–metal interactions

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[1] For Ni^{II} complexes used in the catalytic oligomerization of ethylene, see, for example, P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. De Cian, J. Fischer, *J. Chem. Soc. Chem. Commun.* **1994**, 2203.

[2] For Pd^{II} complexes used in the reversible coordination of CO_2 and telomerization with butadiene, see P. Braunstein, D. Matt, D. Nobel, *J. Am. Chem. Soc.* **1988**, *110*, 3207.

[3] For Rh^{I} complexes in alkane activation, see P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio, F. Ugozzoli, *Organometallics* **1996**, *15*, 5551.

[4] a) F. Balegroune, P. Braunstein, D. Grandjean, D. Matt, D. Nobel, *Inorg. Chem.* **1988**, *27*, 3320; b) J. Andrieu, P. Braunstein, A. Tiripicchio, F. Ugozzoli, *Inorg. Chem.* **1996**, *35*, 5975.

[5] a) P. Braunstein, T. M. Gomes Carneiro, D. Matt, F. Balegroune, D. Grandjean, *Organometallics* **1989**, *8*, 1737; b) F. Balegroune, P. Braunstein, T. M. Gomes Carneiro, D. Grandjean, D. Matt, *J. Chem. Soc. Chem. Commun.* **1989**, 582.

[6] a) P. Braunstein, D. Matt, D. Nobel, *Chem. Rev.* **1988**, *88*, 747; b) P. Braunstein, D. Nobel, *Chem. Rev.* **1989**, *89*, 1927.

[7] J. Andrieu, P. Braunstein, M. Drillon, Y. Dusausoy, F. Ingold, P. Rabu, A. Tiripicchio, F. Ugozzoli, *Inorg. Chem.* **1996**, *35*, 5986.

[8] A. Apfelbacher, P. Braunstein, L. Brissieux, R. Welter, *Dalton Trans.* **2003**, 1669.

[9] P. Braunstein, C. Frison, X. Morise, R. D. Adams, *J. Chem. Soc. Dalton Trans.* **2000**, 2205.

[10] A. Affeld, G. M. Hübner, C. Steel, C. A. Schalley, *Eur. J. Org. Chem.* **2001**, 2877.

[11] For full experimental data on the synthesis, spectroscopy, and elemental analysis of the complexes see the Supporting Information. X-ray structure analysis of **4**$\cdot SO_3CF_3 \cdot 0.5\,CH_2Cl_2$, **5**$\cdot SO_3CF_3 \cdot 2\,CH_2Cl_2$, and **6**$\cdot SO_3CF_3$: Selected crystals were mounted on a Nonius Kappa-CCD area detector diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software. The absorption was corrected empirically (with Sortav). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to the stereochemistry and refined using a riding model in SHELXL97. **4**$\cdot SO_3CF_3 \cdot 0.5\,CH_2Cl_2$: $C_{42}H_{40}AuF_3N_2O_4P_2PdS \cdot 0.5\,CH_2Cl_2$; $M_r = 1133.59$, monoclinic, space group $P2_1/c$, $a = 9.379(3)$, $b = 41.299(5)$, $c = 12.061(3)$ Å, $\beta = 99.46(5)°$, $V = 4608(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.634\ g\,cm^{-3}$, $\mu = 3.796\ mm^{-1}$, $F(000) = 2228$, $T = 173$ K. Colorless crystal, dimensions $0.04 \times 0.05 \times 0.06\ mm^3$. A total of 10051 reflections were collected on a Kappa CCD diffractometer (phi scans), $1.78° < \theta < 27.50°$, 10051 independent reflections with 6631 having $I > 2\sigma(I)$; 532 parameters; $R1 = 0.0482$; $wR2 = 0.1586$, GOF = 0.982, maximum residual electronic density = 1.442 e Å^{-3}. **5**$\cdot SO_3CF_3 \cdot 2\,CH_2Cl_2$: $C_{24}H_{25}AgF_3N_2O_4P$-$PdS \cdot 2\,CH_2Cl_2$; $M_r = 909.61$, monoclinic, space group $P2_1/a$, $a = 12.437(5)$, $b = 20.109(6)$, $c = 14.107(4)$ Å, $\beta = 106.52(5)°$, $V = 3383(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.786\ g\,cm^{-3}$, $\mu = 1.586\ mm^{-1}$, $F(000) = 1800$. Colorless crystal, dimensions $0.08 \times 0.10 \times 0.13\ mm^3$. A total of 14300 reflections were collected on a Kappa CCD diffractometer (phi scans), $1.51° < \theta < 27.48°$, 7719 independent reflections with 5826 having $I > 2\sigma(I)$; 395 parameters; $R1 = 0.0397$; wR2 = 0.1388, GOF = 1.135, maximum residual electronic density = 1.253 e Å^{-3}. The figure shown in the Supporting Information was produced using the UCSF Chimera package from the Computer Graphics Laboratory, University of California, San Francisco: "Chimera: An Extensible Molecular Modeling Application Constructed Using Standard Components": C. C. Huang, G. S. Couch, E. F. Pettersen, T. E. Ferrin, *Pacific Symposium on Biocomputing* **1996**, *1*, 724. **6**$\cdot SO_3CF_3$: $C_{47}H_{50}AgF_3N_4O_5P_2Pd_2S$; $M_r = 1222.58$, triclinic, space group $P\bar{1}$, $a = 13.169(1)$, $b = 14.722(1)$, $c = 14.769(1)$ Å, $\alpha = 61.42(5)°$, $\beta = 81.93(5)°$, $\beta = 87.04(5)°$, $V = 2489.2(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.631\ g\,cm^{-3}$, $\mu = 1.269\ mm^{-1}$, $F(000) = 1224$. Colorless crystal, dimensions $0.08 \times 0.10 \times 0.12\ mm^3$. A total of 14969 reflections were collected on a Kappa CCD diffractometer (phi scans), $1.56° < \theta < 30.33°$, 14471 independent reflections with 8498 having $I > 2\sigma(I)$; 586 parameters; $R1 = 0.0545$; $wR2 = 0.1751$, GOF = 1.023, maximum residual electronic density = 1.420 e$^-$ Å^{-3}. CCDC-240188–240190 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] a) R. Uson, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1985**, 2417; b) P. A. Bella, O. Crespo, E. J. Fernandez, A. K. Fischer, P. G. Jones, A. Laguna, J. M. Lopez-de-Luzuriaga, M. Monge, *J. Chem. Soc. Dalton Trans.* **1999**, 4009.

[13] The closest interactions between the triflate anion and the metal complex in **4**$\cdot SO_3CF_3 \cdot 0.5\,CH_2Cl_2$ involve atoms F3 and O2 of the former and H27 and H28 of an aryl group bound to P2 at 2.84(1) and 2.59(1) Å, respectively.

[14] P. Braunstein, C. Frison, X. Morise, *C. R. Chim.* **2002**, *5*, 131.

[15] In the crystal structure of (**5**$\cdot SO_3CF_3 \cdot 2\,CH_2Cl_2)_n$ the triflate anion is positioned in the vicinity of the Ag^+ ion but does not act as a ligand. The shortest intermolecular contacts are found between the triflate oxygen atom O3 and H7A and H13 (2.42(1) and 2.59(1) Å, respectively), and the fluorine atoms F1 and F3 and the methyl protons H11C and H11A (2.50(1) and 2.77(1) Å, respectively).

[16] P. Braunstein, T. M. Gomes Carneiro, D. Matt, A. Tiripicchio, M. Tiripicchio Camellini, *Angew. Chem.* **1986**, *98*, 721; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 748.

[17] a) J. E. Kickham, S. J. Loeb, *Organometallics* **1995**, *14*, 3584; b) W. Xu, R. J. Puddephatt, K. W. Muir, A. A. Torabi, *Organometallics* **1994**, *13*, 3054; c) T. Yamaguchi, F. Yamazaki, T. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 743.

[18] a) For reviews, see I. D. Salter, in *Comprehensive Organometallic Chemistry II, Vol. 10* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Elsevier, Oxford, **1995**, p. 255; S.-M. Lee, W.-T. Wong, *J. Cluster Sci.* **1998**, *9*, 417; b) Y. Liu, K. H. Lee, J. J. Vittal, T. S. A. Hor, *J. Chem. Soc. Dalton Trans.* **2002**, 2747; c) E. Alonso, J. Forniés, C. Fortuño, A. Martin, A. G. Orpen, *Organometallics* **2003**, *22*, 5011.

[19] M. A. Carvajal, J. J. Novoa, S. Alvarez, *J. Am. Chem. Soc.* **2004**, *126*, 1465.

[20] J. C. Bailar in *Preparative Inorganic Reactions*, *Vol. 1* (Ed.: W. L. Jolly), Interscience, New York, **1964**, pp. 1.

[21] For recent reviews, see C. Janiak, *Dalton Trans.* **2003**, 2781; S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; and for Ag^{I}-based coordination polymers: A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk, M. Schröder, *Coord. Chem. Rev.* **2001**, *222*, 155.

[22] a) J. F. Berry, F. A. Cotton, L. M. Daniels, C. A. Murillo, X. Wang, *Inorg. Chem.* **2003**, *42*, 2418; b) J. F. Berry, F. A. Cotton, P. Lei, T. Lu, C. A. Murillo, *Inorg. Chem.* **2003**, *42*, 3534; c) J. F. Berry, F. A. Cotton, C. A. Murillo, *Organometallics* **2004**, *23*, 2503, and references therein.

[23] R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, K. Kirschbaum, C. A. Murillo, A. A. Pinkerton, A. J. Schultz, X. Wang, *J. Am. Chem. Soc.* **2000**, *122*, 6226.

[24] J. K. Bera, K. R. Dunbar, *Angew. Chem.* **2002**, *114*, 4633; *Angew. Chem. Int. Ed.* **2002**, *41*, 4453, and references therein.

[25] a) I. P. Y. Shek, W.-Y. Wong, T.-C. Lau, *New J. Chem.* **2000**, *24*, 733; b) S.-M. Peng, C.-C. Wang, Y.-L. Jang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou, M.-K. Leung, *J. Magn. Magn. Mater.* **2000**, *209*, 80; c) T. Nakajima, A. Ishiguro, Y. Wakatsuki, *Angew. Chem.* **2001**, *113*, 1096; *Angew. Chem. Int. Ed.* **2001**, *40*, 1066; d) F. Jalilehvand, L. Eriksson, J. Glaser, M. Maliarik, J. Mink, M. Sandström, I. Toth, J. Toth, *Chem. Eur. J.* **2001**, *7*, 2167; e) A. F. Heyduk, D. J. Krodel, E. E. Meyer, D. G. Nocera, *Inorg. Chem.* **2002**, *41*, 634; f) C.-Y. Yeh, C.-H. Chou, K.-C. Pan, C.-C. Wang, G.-H. Lee, Y. O. Su, S.-M. Peng, *J. Chem. Soc. Dalton Trans.* **2002**, 2670; g) C. Tejel, M. A. Ciriano, B. E. Villarroya, J. A. Lopez, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2003**, *115*, 547; *Angew. Chem. Int. Ed.* **2003**, *42*, 530; h) T. Sheng, R. Appelt, V. Comte, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **2003**, 3731; i) E. J. Fernandez, J. M. Lopez-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, A. Laguna, F. Mendizabal, A. A. Mohamed, J. P. Fackler, Jr., *Inorg. Chem.* **2004**, *43*, 3573.

[26] a) M.-M. Rohmer, M. Bénard, *Chem. Soc. Rev.* **2001**, *30*, 340; b) M.-M. Rohmer, A. Strich, M. Bénard, J.-P. Malrieu, *J. Am. Chem. Soc.* **2001**, *123*, 9126; c) N. Benbellat, M.-M. Rohmer, M. Bénard, *Chem. Commun.* **2001**, 2368; d) F.-Y. Li, L. Chen, C.-Y. Mou, S.-M. Peng, Y. Wang, *Int. J. Mol. Sci.* **2002**, *3*, 38; e) P. Kiehl, M.-M. Rohmer, M. Bénard, *Inorg. Chem.* **2004**, *43*, 3151.

[27] a) F. A. Cotton, C. A. Murillo, D. J. Timmons, *Chem. Commun.* **1999**, 1427; b) F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, *J. Chem. Soc. Dalton Trans.* **2000**, 4241; c) K.-T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee, *Chem. Commun.* **2000**, 2259; d) F. P. Pruchnik, P. Jakimowicz, Z. Ciunik, K. Stanislawek, L. A. Oro, C. Tejel, M. A. Ciriano, *Inorg. Chem. Commun.* **2001**, *4*, 19; e) F. A. Cotton, C. Lin, C. A. Murillo, *Chem. Commun.* **2001**, 11.

[28] J.-P. Lang, S.-J. Ji, Q.-F. Xu, Q. Shen, K. Tatsumi, *Coord. Chem. Rev.* **2003**, *241*, 47.