[27] This value is taken from a DFT(VWN-PW91)/TZDP optimization: A. Ghosh, T. Vangberg, *Theor. Chem. Acc.* **1997**, *97*, 143.
[28] A. Ghosh, K. Jynge, *Chem. Eur. J.* **1997**, *3*, 823.
[29] A. Ghosh, T. Vangberg, M. Bröring, E. Vogel, unpublished results.
[30] H. Benedict, H.-H. Limbach, M. Wehlan, W.-P. Fehlhammer, N. S. Golubev, R. Janoschek, *J. Am. Chem. Soc.* **1998**, *120*, 2939.

Cyano-Bridged 4f–3d Coordination Polymers with a Unique Two-Dimensional Topological Architecture and Unusual Magnetic Behavior[**]

Bao-Qing Ma, Song Gao,* Gang Su, and Guang-Xian Xu

Cyano-bridged dimetallic hybrid Prussian Blue one- to three-dimensional (1D–3D) coordination polymers based on $[M(CN)_6]^{3-}$ (M = Fe, Cr, Mn) have attracted great attention because of their rich and interesting structures and magnetic behavior.[1] These studies were mainly focused on transition metals. In principle, it would be possible to enhance the coercive field by the introduction of paramagnetic lanthanide ions because these possess rather large and anisotropic magnetic moments. However, the magnetism, rarely investigated, for known cyano-bridged lanthanide / transition metal complexes such as ion pairs, dinuclear, trinuclear, tetranuclear, and one-dimensional chains,[2], does not seem exciting, since the couplings between the lanthanide and transition metals are very weak, because of the effective shielding of the 4f electrons by the outer-shell electrons. However, the 3D polymer $[SmFe(CN)_6]\cdot 4H_2O$, with strong anisotropic coercive field, exhibits a long-range ferrimagnetic ordering below 3.5 K, and that $[TbCr(CN)_6]\cdot 4H_2O$ has the highest known Curie temperature ($T_C = 11.7$ K) for 4f–3d molecule-based magnets.[3] This implies that increasing the number of dimensions may enhance and improve bulk magnetic properties. Our strategy for the rational synthesis of a high-dimensional network is to use a suitable combination of cyanide groups and other bridging ligands. Here, 2,2′-bipyrimidine (bpym) was selected, in preference to 4,4′-bipyridine and pyrazine, because it is more capable of transmitting magnetic interactions[4] and its bis(chelating) coordination modes facilitate connection between lanthanide ions. Unexpectedly, two novel coordination polymers $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ (M = Fe (**1**), Co (**2**)) were obtained, which have a unique 2D topological architecture, and exhibit unusual magnetic behavior.

Compounds **1** or **2** were obtained by the slow diffusion of $K_3[Fe(CN)_6]$ or $K_3[Co(CN)_6]$ and bpym with $Nd(NO_3)_3$ in a 1:1:1 molar ratio in aqueous solution (30 mL); X-ray diffraction analysis reveals that the compounds are isomorphous.[5] The structure of **1** (Figure 1) consists of a 2D net with alternating fused rows of rhombuslike $Fe_2Nd_2(CN)_4$ rings and six-sided $Fe_4Nd_4(CN)_8$ rings. Each Nd^{3+} ion is nine coordinate being bound by two N atoms from one chelating bpym molecule (the mean length of Nd–N = 2.7084 Å), four O atoms from water molecules (the mean length of Nd–O = 2.4706 Å) and three N atoms from three bridging CN^- groups (the mean length of Nd–N = 2.5825 Å), yielding a monocapped square anti-prism. The top and bottom planes are defined by O1, O2, N2, N10A and O3, O4, N1, N5, respectively, and N8 occupies the cap position. The bpym ligand coordinates to the Nd ions in a chelating fashion, and the remaining two N atoms form the hydrogen bonds with the coordinated water molecules of neighboring Nd^{3+} ion (not shown: O3⋯N3A 2.929 Å, O3–H5⋯N3A 155.80°; O2⋯N4A 2.850 Å, O2–H3⋯N4A 160.08°; symmetry: A: x, $y+1$, z). Although on chelation bpym and 2,2′-bipyridine (bipy) ligands have similar steric effects, they give different structures with $K_3[Fe(CN)_6]$ and $Nd(NO_3)_3$. For the latter, an ion pair compound $[FeNd_2(CN)_6(bipy)_4(H_2O)_8][Fe(CN)_6]\cdot 8H_2O$ is formed.[2f] The difference is tentatively attributed to the different affinity of both ligands.

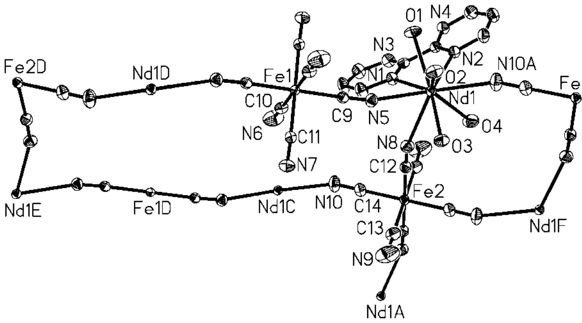

Figure 1. ORTEP plot of **1**. Selected bond lengths [Å]: Nd1-O1 2.423510), Nd1-O2 2.4524(11), Nd1-O3 2.4739(11), Nd1-N5 2.5105(10), Nd1-O4 2.5326(10), Nd1-N10A 2.5972(15), Nd1-N8 2.6399(13), Nd1-N1 2.6875(13), Nd1-N2 2.7293(10) (Symmetry codes: A: $x+1$, y, z).

In the structure of **1** there are two crystallographically unequal Fe atoms per asymmetric unit; they are located at inversion centers. The Fe2 center employs four CN^- groups in the same plane to connect the Nd^{3+} ions, giving rise to a double strand chain as found in $[\{Cu(dien)_2Cr(CN)_6\}_n][\{Cu(dien)(H_2O)Cr(CN)_6\}_n]\cdot 4nH_2O$ (dien = diethylenetri-

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amine).[6] Thus, a 12-membered rhombus subunit $Fe_2Nd_2(CN)_4$ is generated with the distances between the cyanide-bridged metal centers Nd1 ··· Fe2 and Nd1 ··· Fe2a being 5.616 and 5.606 Å, respectively, similar to those observed in $[Fe_2(CN)_4(phen)_4Yb_2Cl_6(H_2O)_2] \cdot 2H_2O \cdot 2CH_3OH$.[21] Fe1 uses two *trans* CN^- groups to link neighboring chains (Nd1 ··· Fe1 5.381 Å), leading to an unusual 2D sheet structure (Figure 2a and schematically represented in Figure 2b; a discussion of spin frustration in compound **2** is given below). The shortest interlayer Nd ··· Fe, Nd ··· Nd, and Fe ··· Fe distances are 9.390, 8.897, and 9.197 Å, respectively. The Fe−C distances are in the range of 1.9171 – 1.9450 Å and Fe-C≡N bond angles are nearly linear. The bridging cyanide ligands link the Nd^{3+} ions in a bent fashion with the Nd−N≡C bond angles ranging from 158.52(9)° to 166.11(11)°. The lattice water molecules reside between layers and link the 2D sheets into a 3D network through extensive hydrogen bonding.

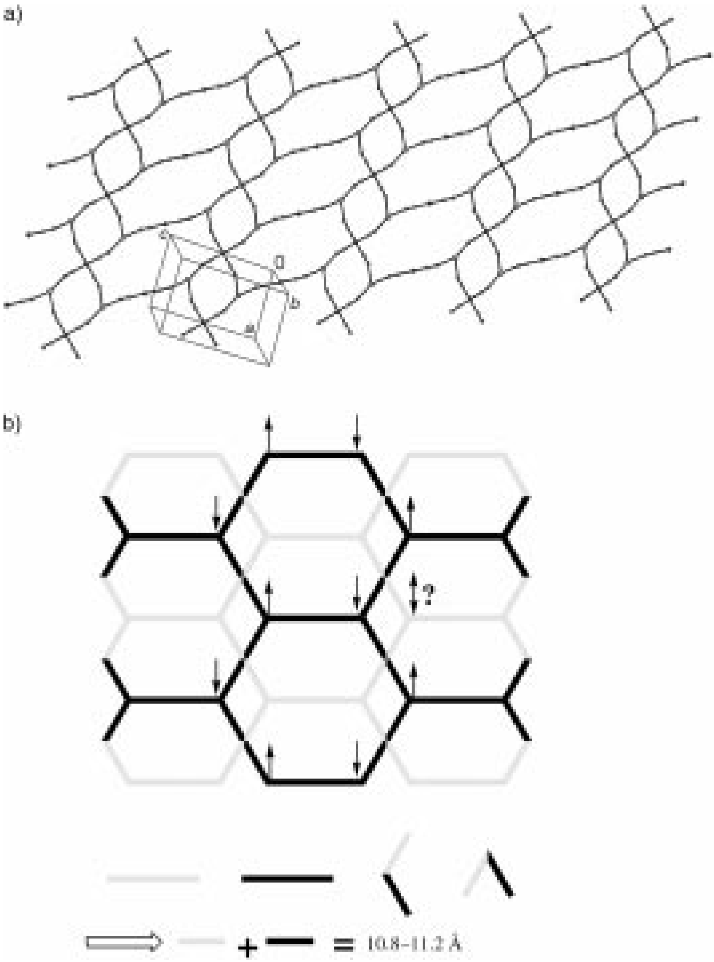

Figure 2. a) Layer structure of **1**, exhibiting a unique topological architecture. For clarity, only the cyanide groups and metal centers are shown. b) The 2D connection of the Nd^{3+} ions can be viewed as two sets of equivalent honeycombs (black and gray). The rods (either black or gray) and the two different modes of joining black and gray rods represent the three different kind of link between the Nd^{3+} ions in the 2D structure. This arrangement leads to spin frustration in compound **2** (see text for details).

The previously reported cyanide-bridged 4f – 3d complexes with mixed ligands have an isolated 0D or 1D structure. The compounds **1** and **2** reported herein are the first two-dimensional cyanide-bridged compounds containing both lanthanide and transition metal ions. More interestingly, they have a 2D topological architecture type that is very different from the known 2D cyanide-bridged structures: square,[7] honeycomb,[8] brick wall,[9] partial cubane structures,[10] and also of other 2D coordination polymers (grid, kagome, herring bone, triangular).[11]

The temperature dependences of the $\chi_M T$ for crystalline samples **1** and **2** confined in parafilm, measured at 10 kOe and 500 Oe fields, are shown in Figure 3 and in the inset respectively. The observed $\chi_M T$ values for **1** and **2** at 300 K are 1.87 and 1.49 $cm^3 mol^{-1} K$, respectively, slightly smaller than the calculated values of 2.00 and 1.64 $cm^3 mol^{-1} K$ for non-interacting free ions per NdFe and NdCo unit, respectively (the Co^{3+} ion is diamagnetic in the present strong-field case). Upon cooling, the $\chi_M T$ of **2** decreases continuously from 300 to 2 K, while the $\chi_M T$ of **1** is roughly parallel with that of **2** above 80 K. The difference varies little, it is approximately 0.38 $cm^3 mol^{-1} K$ which is the value for an isolated iron(III) ion. These observations suggest that the decrease of $\chi_M T$ with decreasing temperature must be considered as an intrinsic characteristic of the Nd ion, which may be attributed to the depopulation of its Stark levels.[12a] With further cooling, the $\chi_M T$ of **1** reaches a minimum at approximately 10 K, then increases rapidly. To exclude the contribution of spin-orbital coupling of the Nd^{3+} ion, the $\chi_M T$ of **2** was subtracted from that of **1**. It is found that the difference (solid line in the inset of Figure 3) increases steadily with cooling, indicative of ferromagnetic interactions between the Nd^{3+} and Fe^{3+} ions. No long-range ordering was observed down to 2 K based on

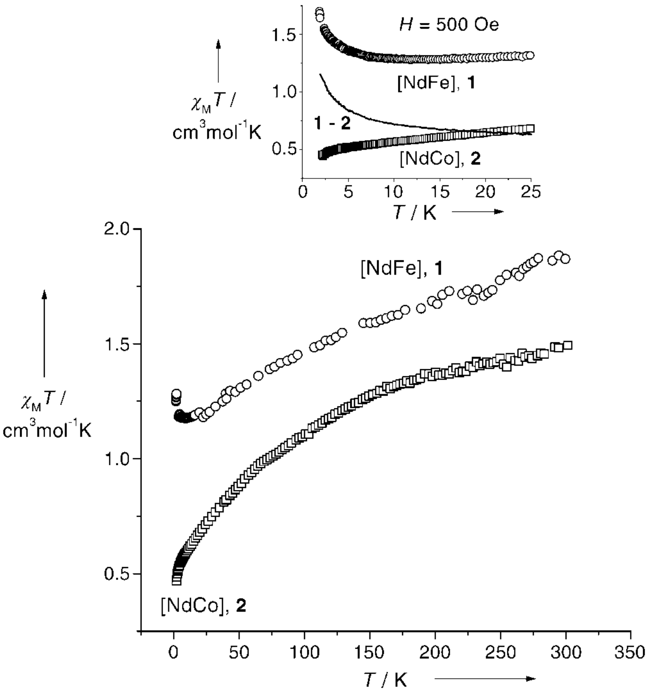

Figure 3. Temperature dependence of $\chi_M T$ for [NdFe] **1** (○) and [NdCo] **2** (□) at 10 kOe. Inset is the curves of $\chi_M T$ versus T at 500 Oe. More magnetic measurements can be found in the Supporting Information.

measurements of the field-dependent magnetization and the zero-field alternating current (AC) susceptibility, however. The field dependence of magnetization (*M*) for **1** and **2** was measured at 1.8 K. The magnetization values at 50 kOe are 2.06 and 1.05 Nβ, respectively, close to saturation. For the Nd^{3+} ions in **2**, the crystalline field resolves the 10-fold degenerate $^4I_{9/2}$ ground states into five doublets, only one of which is populated at 20 K or below.[12b] If the saturation magnetization value of **2** is taken as 1.09 Nβ (60 kOe), the effective spin in the ground state for one Nd^{3+} ion is ½, and *g′* is 2.18, consistent with the above argument. The difference *M* for **1** and **2** yields 1.01 Nβ for the Fe^{3+} ions, in reasonable accord with the theoretical value 1 Nβ.

Compound **2** containing only one type of paramagnetic Nd^{3+} ion was magnetically investigated in some detail. The zero field AC susceptibility was measured in the 3–8 K range at different frequencies (111–1111 Hz), and shown in the upper panel of Figure 4. Normal paramagnetic behavior of the in-phase component χ'_M and negligible small signal of the out-of-phase component χ''_M, indicate the absence of long-range ordering and any spin-glasslike behavior. However, under an intermediate direct current DC bias field (2 kOe), two peaks (T_P) appear for both χ'_M and χ''_M, respectively, as shown in the lower panel of Figure 4. Moreover, χ'_M and χ''_M are strongly frequency dependent with a considerably larger ϕ value 0.37 ($\phi = \Delta T_P/(T_P\Delta(\log f))$) than that for normal spin glass (<0.1),[13] suggesting the unusual glasslike behavior, which may be attributed to the geometrically frustration of Nd^{3+} ions as shown in Figure 2b. The 2D connection of the Nd^{3+} ions can be viewed as two sets of honeycombs (gray and black) with very similar linear five-atom N-C-Co-C-N bridges close to 11 Å in length. If just one set of honeycombs, for example, the black one, is considered, the antiferromagnetic (AF) coupling between neighboring Nd^{3+} ions should not give rise to frustration. However, since the pathways between the two sets of honeycombs are also through N-C-Co-C-N five-atom bridges, the magnetic interaction between the neighboring spins on different honeycombs might be comparable with that in each honeycomb, so that the magnetic moments located in Nd^{3+} will be frustrated.

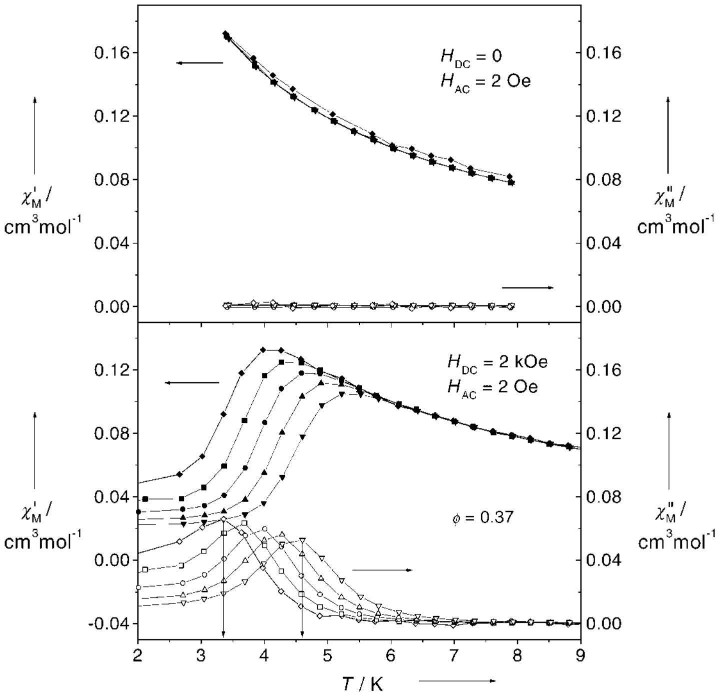

Figure 4. Frequency dependence of AC susceptibility at zero and 2 kOe DC bias field for compound **2**. ◇ = 111 Hz, □ = 199 Hz, ○ = 355 Hz, △ = 633 Hz, ▽ = 1111 Hz. The filled symbols are for the in-phase component χ'_M, the open symbols are for the out-of-phase component χ''_M.

Experimentally, at zero field no frustration was observed for **2** because of very weak AF interactions between the Nd^{3+} ions, whereas the introduction of a DC field might enhance the AF correlation, which gives rise to the unusual field-dependent magnetic relaxation.

Experimental Section

bpym was purchased from Aldrich and used without further purification. $K_3[Co(CN)_6]$ was prepared by the literature method.[14] Compound **1** was prepared by mixing $K_3[Fe(CN)_6]$ (1 mmol) and bpym (1 mmol) in aqueous solution (20 mL), followed by the slow addition of an aqueous solution of $Nd(NO_3)_3$ (1 mmol; 10 mL) without stirring. The resulting solution was allowed to slowly diffuse and evaporate at room temperature in the dark. After two weeks, bright yellow single crystals were obtained, which were collected by filtration, washed with small amounts of water and ethanol, and dried in air (41% yield). Elemental analysis calcd for $C_{14}H_{20}FeNdN_{10}O_7$ (%): C 26.23, H 3.12, N 21.86; found: C 26.86, H 2.78, N 22.26. Compound **2** was synthesized following the same procedure as **1**, but $K_3[Fe(CN)_6]$ was replaced by $K_3[Co(CN)_6]$ (43% yield). Elemental analysis calcd for $C_{14}H_{20}CoNdN_{10}O_7$ (%): C 26.09, H 3.11, N 21.77; found: C 26.43, H 2.83, N 22.16.

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[1] See, for example: a) M. Ohba, N. Usuki, N. Fukita, H. Okawa, *Angew. Chem.* **1999**, *111*, 1909; *Angew. Chem. Int. Ed.* **1999**, *38*, 1795; b) H. Z. Kou, S. Gao, B. Q. Ma, D. Z. Liao, *Chem. Commun.* **2000**, 713; c) A. Marvillers, S. Parsons, E. Riviere, J. P. Audiere, T. Mallah, *Chem. Commun.* **1999**, 2217; d) S. M. Holmes, G. S. Girolami, *J. Am. Chem. Soc.* **1999**, *121*, 5593; e) K. V. Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Inorg. Chem.* **1997**, *36*, 5006; f) M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli, D. Gatteschi, *Angew. Chem* **1996**, *108*, 2081; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1947; g) M. Ohba, N. Maruono, H. Okawa, T. Enoki, J. M. Latour, *J. Am. Chem. Soc.* **1994**, *116*, 11566.

[2] a) G. Adachi, T. Yamase, J. Inanaga, M. Komiyama, K. Machida, *New Development of Studies on Rare Earth Complexes*, Rare Earth Society of Japan, **1997**; b) H. Z. Kou, G. M. Yang, D. Z. Liao, P. Cheng, Z. H. Jiang, S. P. Yan, X. Y. Huang, G. L. Wang, *J. Chem. Crystallogr.* **1998**, *28*, 303; c) S. Gao, B. Q. Ma, Z. M. Wang, T. Yi, C. S. Liao, C. H. Yan, G. X. Xu, *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 201. d) J. A. Kautz, D. F. Mullica, B. P. Cunningham, R. A. Combs, J. M. Farmer, *J. Mol. Struct.* **2000**, *523*, 175; e) D. F. Mullica, J. M. Farmer, B. P. Cunningham, J. A. Kautz, *J. Coord. Chem.* **2000**, *49*, 239; f) T. Yi, S. Gao, X. W. Chen, C. H. Yan, B. G. Li, *Acta Crystallogr. Sect. C* **1998**, *54*, 41; g) S. Garcia-Granda, A. D. Morales, E. R. Ruiz, J. F. Bertran, *Acta Crystallogr. Sect. C* **1996**, *52*, 1679; h) D. W. Knoeppel, J. P. Liu, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **1998**, *37*, 4828; i) D. W. Knoeppel, S. G. Shore, *Inorg. Chem.* **1996**, *35*, 5328. j) D. W. Knoeppel, S. G. Shore, *Inorg. Chem.* **1996**, *35*, 1747. k) J. P. Liu, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **1998**, *37*, 5410; l) K. Harada, J. Yuzurihara, Y. Ishii, N. Sato, H. Kambayashi, Y. Fukuda, *Chem. Lett.* **1995**, 887.

[3] F. Hulliger, M. Landolt, H. Vetsch, *J. Solid State Chem.* **1976**, *18*, 283.

[4] a) G. D. Munno, M. Julve, G. Viau, F. Lloret, J. Faus, D. Viterbo, *Angew. Chem.* **1996**, *108*, 1931; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*,

1807; b) R. Cortes, L. Lezama, J. L. Pizarro, M. I. Arriortua, T. Rojo, *Angew. Chem.* **1996**, *108*, 1934; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1810; c) G. de Munno, M. Julve, F. Nicolo, F. Lloret, J. Faus, R. Ruiz, E. Sinn, *Angew. Chem.* **1993**, *105*, 588; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 613; d) G. de Munno, R. Ruiz, F. Lloret, J. Faus, R. Sessoli, M. Julve, *Inorg. Chem.* **1995**, *34*, 2356.

[5] Crystal data. Compound **1**: $C_{14}H_{20}FeNdN_{10}O_7$, $M_r = 640.49$, triclinic, $P\bar{1}$, $a = 8.9399(5)$, $b = 9.1967(3)$, $c = 15.4335(7)$ Å, $\alpha = 76.054(3)$, $\beta = 89.359(3)$, $\gamma = 67.756(3)^\circ$, $V = 1135.31(9)$ Å^3, $Z = 2$, $\rho = 1.874$ Mg m^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 2.957$ mm^{-1}, $F(000) = 632$, GoF = 1.055. A total of 18535 reflections were collected and 5364 are unique ($R_{int} = 0.0507$). The final $R1$ and $wR2$ are 0.0310 and 0.0758, respectively, for 345 parameters and 4889 reflections ($I > 2\sigma(I)$). Compound **2**: $C_{14}H_{20}CoNdN_{10}O_7$, $M_r = 643.57$, triclinic, $P\bar{1}$, $a = 8.7801(5)$, $b = 9.2011(5)$, $c = 15.4319(10)$ Å, $\alpha = 76.337(4)$, $\beta = 88.982(4)$, $\gamma = 67.542(4)^\circ$, $V = 1115.89(11)$ Å^3, $Z = 2$, $\rho = 1.915$ Mg m^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 3.102$ mm^{-1}, $F(000) = 634$, GoF = 1.029. A total of 14884 reflections were collected and 5118 are unique ($R_{int} = 0.1088$). The final $R1$ and $wR2$ are 0.0638 and 0.1483, respectively, for 345 parameters and 3829 reflections ($I > 2\sigma(I)$). The data of both compounds were collected on a Nonius Kappa CCD with $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direction method and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. 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-147180 (**1**) and CCDC-147181 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[6] D. G. Fu, J. Chen, X. S. Tan, L. J. Jiang, S. W. Zhang, P. J. Zheng, W. X. Tang, *Inorg. Chem.* **1997**, *36*, 220.

[7] a) M. Ohba, N. Usuli, N. Fukita, M. Okawa, *Inorg. Chem.* **1998**, *37*, 3349; b) M. Ohba, N. Fukita, H. Okawa, Y. Hashimoto, *J. Am. Chem. Soc.* **1997**, *119*, 1011.

[8] a) H. Z. Kou, S. Gao, W. M. Bu, D. Z. Liao, B. Q. Ma, Z. H. Jiang, S. P. Yan, Y. G. Fan, G. L. Wang, *J. Chem. Soc. Dalton Trans.* **1999**, 2477; b) S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolome, P. Veillet, M. Verdaguer, *J. Chem. Soc. Chem. Commun.* **1996**, 2481; c) E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, F. Lloret, J. M. Moreno, H. Stoeckli-Evans, *Chem. Commun.* **1999**, 987.

[9] H. Z. Kou, S. Gao, B. Q. Ma, D. Z. Liao, *Chem. Commun.* **2000**, 1309.

[10] J. A. Smith, J. R. Galan-Mascaros, R. Clerac, K. R. Dunbar, *Chem. Commun.* **2000**, 1077.

[11] a) S. Maruti, L. W. ter Haar, *J. Appl. Phys.* **1994**, *75*, 5949; b) M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, M. Schröder, *New J. Chem.* **1999**, *23*, 573; c) W. Fujita, K. Awaga, *Inorg. Chem.* **1996**, *35*, 1915; d) D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta, R. C. Haushalter, *Angew. Chem.* **1997**, *109*, 904; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 873; e) A. J. Blake, S. J. Hill, P. Hubberstey, W. S. Li, *J. Chem. Soc. Dalton Trans.* **1997**, 913.

[12] a) J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Chem. Eur. J.* **1998**, *4*, 1616; b) R. L. Carlin, *Magnetochemistry*, Springer, **1986**, p. 245.

[13] J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor and Francis, London, **1993**.

[14] J. H. Bigelow, J. C. Bailar, *Inorg. Synth.* **1946**, *7*, 205.

Immobilization of Homogeneous Palladium(II) Complex Catalysts on Novel Polysiloxanes with Controllable Solubility: Important Implications for the Study of Heterogeneous Catalysis on Silica Surfaces[**]

Yaw-Shyan Fu and Shuchun J. Yu[*]

Immobilization of homogeneous transition metal complex catalysts by tethering them to silica supports has been intensively studied during the past few decades.[1] These supported homogeneous transition metal complex catalysts should in principle combine the advantages of both heterogeneous and homogeneous systems. However, the problems of significant metal leaching[2] and low catalyst selectivity[1h, 3] are major drawbacks that prevent their potential use. Due to the insoluble nature of these supported catalysts, it has been difficult to obtain detailed information about the exact chemical structures of the catalyst systems and to estimate any loss of activity resulting from heterogenization. Therefore, a major development in this field would be the development of a method that would allow silica-supported homogeneous transition metal complexes and their reactions to be investigated by NMR spectroscopy with the resolution typically attained for soluble systems.[4] Here we describe the preparation and characterization of homogeneous Pd^{II} complex catalysts tethered to a range of polysiloxanes. These materials were designed to mimic the surface of silica gel but with properties that are more readily controlled than those of silica gel. The molecular weight and degree of cross-linking can be systematically varied to provide catalyst systems ranging from soluble, homogeneous model compounds to heterogeneous three-dimensional networks. The structures and reaction chemistry of the soluble system were studied by NMR spectroscopy in solution, while the reactivity and regioselectivity were investigated in the catalytic [2+2+2] cyclotrimerization of alkynes.

The incomplete acid-catalyzed hydrolysis[5] of $(MeO)_3Si(CH_2)_{11}N_3$ (**1**) in THF generated silica fragments small enough to be soluble in conventional organic solvents. Subsequent silylation with trimethylsilyl chloride (TMSCl) was performed to end-cap the remaining Si-bound hydroxy groups to prevent further self-condensation of polysiloxanes (Scheme 1). The resulting polysiloxane **2** can then be readily derivatized with $P(2\text{-py})_3$ (2-py = 2-pyridyl) in situ or after isolation to afford polysiloxane **3** with $NHP(O)(2\text{-py})_2$ functionality.[6] Polysiloxanes **2** and **3** with molecular weights around 5500 and polydispersity indexes of about 1.5 were thus obtained.[7] As expected, these polymers exhibited excellent

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