FULL PAPER

Self-Assembly by Ligand-Exchange Reactions

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Dedicated to Prof. Makoto Fujita on his 47th birthday

An interesting phenomenon of ligand exchange is observed in the DMSO solution of certain self-assembled molecules generated from *cis*-protected Pd^{II} and organic ligands. Upon heating, assemblies such as $[\{Pd(en)\}_x(ligand)_y](NO_3)_{2x}$ change to $[Pd_m(ligand)_n](NO_3)_{2m}$ and $[Pd(en)_2](NO_3)_2$. The change is also possible at room temperature when 0.5 equiv. Pd(en)(NO$_3$)$_2$ is added in excess to the system. The transformation is incomplete when the ligand moiety is monodentate in nature, for example in the case of 4-phenylpyridine. However, multinuclear assemblies containing nonchelating, polydentate ligands used in this study entirely favor the transformation. This process is not possible with some related Pt^{II} compounds.

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Introduction

Creation of discrete and definite molecular architectures using organic ligands and selected metal ions through self-assembly has received much attention in organic synthesis because of the inherent simplicity of the method.[1,2] Self-assembled structures that would result from the complexation of a metal ion with a designed ligand may be assumed to be fixed a priori.[2] However, the mode of arrangement of the participating components depends on the steric requirements, thermodynamic stability, and entropy cost of the final assembly, as well as on the guest molecule, if any, and on the solvent.[3] In the solution state, two or more isomers or structures may coexist in dynamic equilibrium depending upon the directionality/flexibility of the ligand, in particular when the metal–ligand bond of the system is labile in nature.[4] It has also been shown that it is possible in certain cases to shift such equilibria to favor one of the compounds as a single/major product by suitably controlling parameters like solvent, guest molecule, temperature, time etc.[5]

The construction of self-assembled structures under the influence of stereochemical details of the complex and the choice of pyridine-appended ligands have been studied well by Fujita[2e] and Stang[2c] in the coordination chemistry of palladium(II). Polynuclear complexes $(M_xL_y)^{n+}$ of different geometries and conformations have also been realized by the use of polydentate nonchelating ligands. Usually *cis*-protected Pd^{II}, e.g., Pd(en)$^{2+}$, has been employed,[2c,2e] and the area has been a subject of extensive study and review. Such systems require control over only two coordination sites of each metal center involved, because the other two positions are already protected. In contrast, there exist very few examples[6] of assemblies achieved from Pd^{II} where all four sites are available for coordination during the assembly process. The use of particular ligands for both *cis*-protected Pd^{II} and unprotected Pd^{II} is published as a comparative study.[6e]

Results and Discussion

We are interested in the dynamic nature of the Pd^{II}-driven self-assembly processes. The ligand **1** (Figure 1) and *cis*-protected Pd(en)(NO$_3$)$_2$ at a ratio of 1:1 form a binuclear M$_2$L$_2$ macrocycle, $[\{Pd(en)\}_2(\mathbf{1})_2](NO_3)_4$ (**5**), as a major product along with a tetranuclear macrocyclic compound, $[\{Pd(en)\}_4(\mathbf{1})_4](NO_3)_8$ (**6**) (Scheme 1), as reported earlier.[6e] The assembly process was performed in DMSO by stirring at 60 °C for 10 min. While taking another look at the dynamic equilibrium of the two self-assembled structures (**5** and **6**) resulting from ligand **1** and *cis*-protected Pd^{II}, we observed an interesting phenomenon. Our effort was to shift the equilibrium in favor of one of these two structures. When temperature was chosen as a parameter to vary, instead of the possible shift in equilibrium, we observed scrambling of the assemblies, giving rise to yet other

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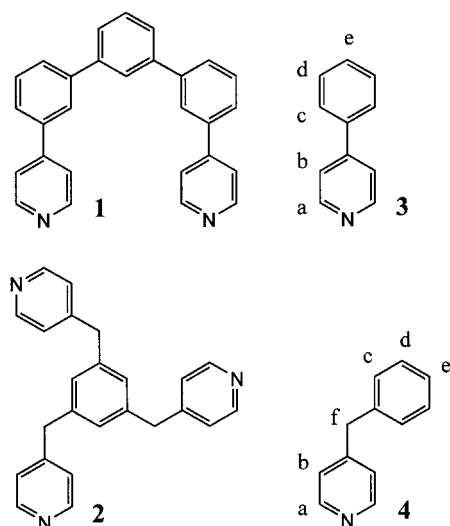
Figure 1. Structures of the ligands **1**, **2**, **3**, and **4**.

assemblies (Scheme 1). Scrambling is also observed in some other related systems and is discussed in this report.

It is observed here that for the complexation of **1** with *cis*-protected Pd(en)(NO$_3$)$_2$, heating or stirring is not required, and the system in DMSO gives rise to assemblies spontaneously at room temperature as a result of the simple combination of the components. The two compounds **5** and **6** are of course in dynamic equilibrium (Scheme 1), as is evident from the concentration-dependent nature of the equilibrium. Upon increasing the concentration, the bigger molecule **6** is favored, and with decreasing concentration, the smaller molecule **5** is favored. However, it was not possible to push the equilibrium of **5** and **6** exclusively in favor of one compound by varying the concentration.

In order to shift the equilibrium in favor of one of the assemblies we decided to vary other possible parameters. What is more interesting is the effect of heat on the dynamic equilibrium behavior. Experiments were performed at different temperatures; around 90 °C was found to be a good temperature for studying this process.[7] At a particular con-
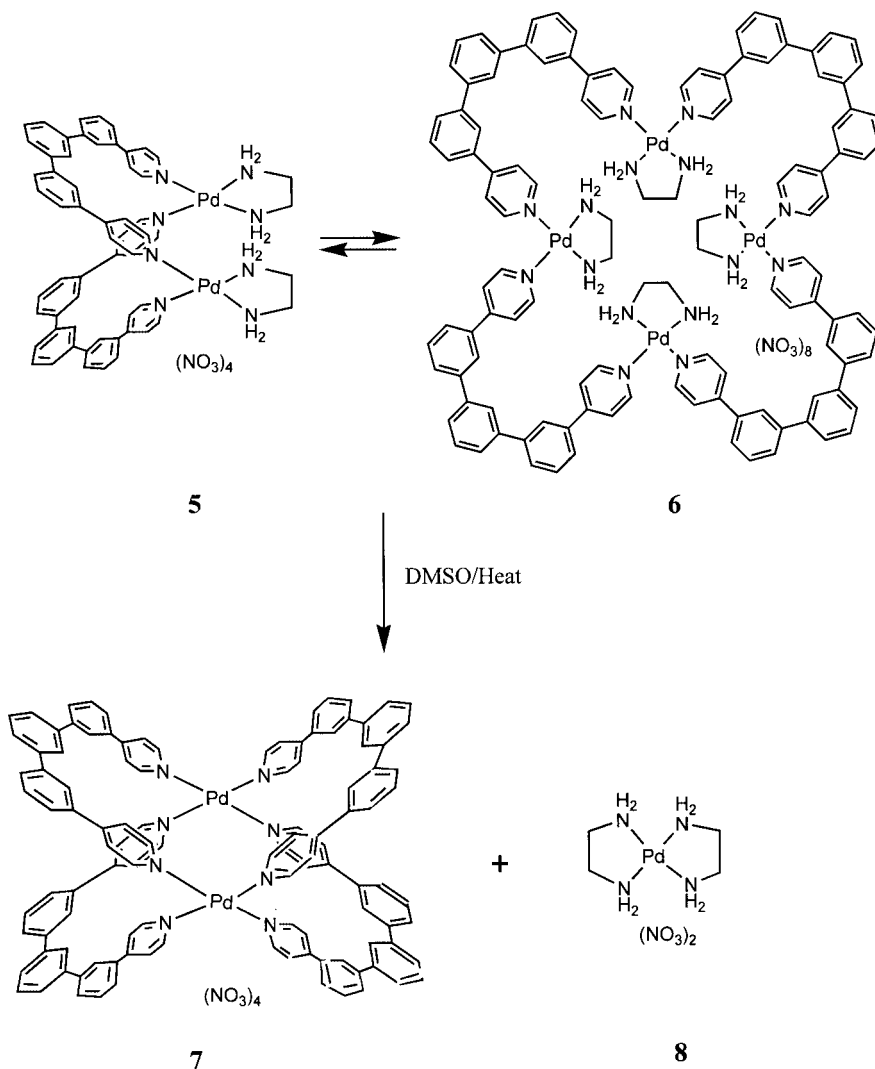
Scheme 1. Transformation of a dynamic equilibrium of **5** and **6** to a mixture of **7** and **8** occurred by ligand exchange (see ref.[6b,6e] for the synthesis of **5**, **6**, and **7**).

centration, with the increase in temperature (heating) we could not observe a shift of equilibrium in [D_6]DMSO. Rather, new peaks were observed in the proton NMR at the expense of **5** and **6**. The assemblies were identified in due course as the M_2L_4 assembly $[(Pd)_2(\mathbf{2})_4](NO_3)_4$ (**7**)[6b] and $[Pd(en)_2](NO_3)_2$ (**8**).[8] The proportion of the complexes at any given time is calculated from the integration ratio of the corresponding py_α protons as observed in their ¹H NMR spectra (e.g., Figure 2). It is worthwhile to mention here that compound **7** can be prepared by combining the ligand **1** and $Pd(NO_3)_2$ at a ratio of 2:1 in DMSO and stirring at 90 °C for 10 min. Thus, a mixture of **5** and **6** changes, upon heating, to a mixture of **7** and **8**. At an intermediate stage all four compounds **5**, **6**, **7**, and **8** coexist, and finally only **7** and **8** are detected (Figure 2). We attribute such an observation to a ligand exchange around the metal centers promoted by the increase in temperature and the solvent.
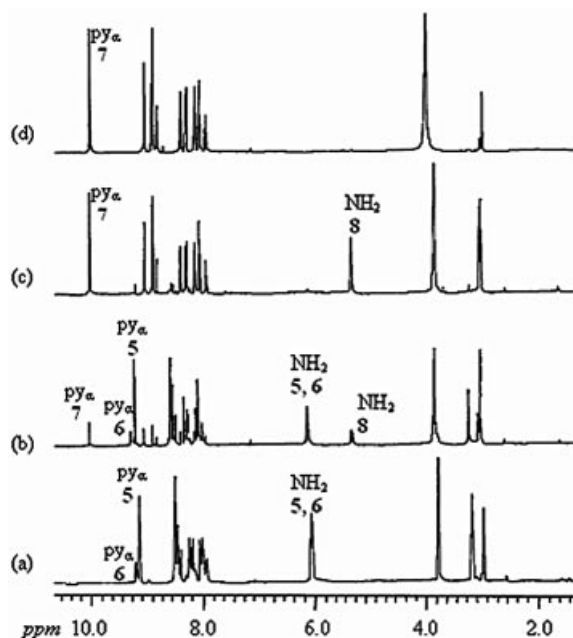

Figure 2. ¹H NMR spectra of a dynamic equilibrium mixture of $[\{Pd(en)\}_2(\mathbf{1})_2](NO_3)_4$ (**5**) and $[\{Pd(en)\}_4(\mathbf{2})_4](NO_3)_8$ (**6**), and the evolution, after this mixture was heated at 90 °C in [D_6]DMSO, of a mixture of $[(Pd)_2(\mathbf{2})_4](NO_3)_4$ (**7**) and $[Pd(en)_2](NO_3)_2$ (**8**) due to ligand exchange. NMR peaks are due to (a) **5** and **6** at $t = 0$ h (ref. [6e]); (b) **5**, **6**, **7**, and **8** at $t = 6$ h, an intermediate stage; (c) **7** and **8** at $t = 48$ h, completed scrambling; and (d) pure **7** (ref. [6e]) for comparison.

Another system considered was the assembly from ligand **2**. Ligand **2** and $Pd(en)(NO_3)_2$, at a ratio of 2:3, provide an M_3L_2 compositional assembly $[\{Pd(en)\}_3(\mathbf{2})_2](NO_3)_6$ (**9**) along with a mixture of other oligomeric compounds[9] in aqueous[5b] or DMSO solution.[6e] The assembly of ligand **2** with $Pd(NO_3)_2$ at a ratio of 8:6 gives a designed M_6L_8 molecular sphere, $[(Pd)_6(\mathbf{2})_8](NO_3)_{12}$ (**10**).[6d] As the scrambling of the ligand described (vide supra) for the ligand system **1** seemed interesting, the ligand system **2** was subjected to a similar set of experiments. A mixture of **9** and its oligo-

mers, existing in dynamic equilibrium, was heated in [D_6]-DMSO, with the expectation of forming **10** and **8**. Once again, ligand exchange was observed around the Pd^{II} centers, and the dynamic equilibrium was transformed completely to a mixture of **10** and **8** (Scheme 2).

In the ligand-exchange process observed in this work, multinuclear assemblies containing cis-protected Pd^{II} centers, i.e. $[\{Pd(en)\}_x(ligand)_y](NO_3)_{2x}$, change to multinuclear assemblies containing simple Pd^{II} centers, i.e. $[Pd_m(ligand)_n](NO_3)_{2m}$, along with $[Pd(en)_2](NO_3)_2$. When the total number of Pd^{II} ions per molecule in the resulting assembly is "m" then it is associated with "m" numbers of $[Pd(en)_2](NO_3)_2$ molecules.

So far, we have discussed the findings with the polydentate nonchelating ligands **1** and **2**. An immediate comparison is necessary with a monodentate ligand reminiscent of these ligands. Thus 4-phenylpyridine (**3**) and 4-benzylpyridine (**4**) (Figure 1) were used for a similar study. The ligands **3** and **4** being monodentate, their complexes with cis-protected Pd^{II} and unprotected Pd^{II} are only mononuclear, and the synthesis of these new complexes (**11**–**14**) is described in this work. The complex $[Pd(en)(\mathbf{3})_2](NO_3)_2$ (**11**) was expected to give $[(Pd)(\mathbf{3})_4](NO_3)_2$ (**12**) and $[Pd(en)_2](NO_3)_2$ (**8**) as before upon heating (Scheme 3). This time the expected transformation proceeded, but not to completion (Figure 3, Figure 4). Structure **11** remained in a dynamic equilibrium with a mixture of **12** and **8**. A similar result was obtained with the ligand system **4**. Here $[Pd(en)(\mathbf{4})_2](NO_3)_2$ (**13**) remained in a dynamic equilibrium with a mixture of $[(Pd)(\mathbf{4})_4](NO_3)_2$ (**14**) and **8**.

Comparison of the scrambling process observed with the different ligand systems presented in this work reveals the following points. When $[\{Pd(en)\}_x(ligand)_y](NO_3)_{2x}$, having a Pd concentration of 10 mm is heated, the speed at which the scrambling proceeds to give the resulting assemblies depends upon the ligand of choice. Probably the process is also controlled by the composition and thermodynamic stability of the concerned self-assemblies. The ligand system **2** leads to the final stage of the process very quickly in 12 h, while **1** requires more than 2 days (Figure 4). The ligands **3** and **4** also form the expected new assemblies initially; however, after a certain amount is formed (about 18–20% of the ligand in the new assembly), a dynamic equilibrium is established, and the process is incomplete.

Some experiments were performed in [D_6]DMSO to understand the stability vs. lability of the complexes through proton NMR studies. When the required amount of ethylene diamine was added to any of the Pd^{II} complexes **5**–**7** or **9**–**14**, in each case the Pd^{II} ion was sequestered as $[Pd(en)_2](NO_3)_2$ (**8**) immediately, and the corresponding ligands were released. However, addition of any of the ligands **1**–**4** to **8** caused no changes. This indicates that the above-mentioned acyclic or nonchelated cyclic complexes are kinetically labile. However, the chelated complex **8** behaved in a kinetically nonlabile manner under the conditions employed. To throw some light on stability, the following experiments were performed. Complex **8** was added to a solution of assembly **7**. Compound **7** remained un-
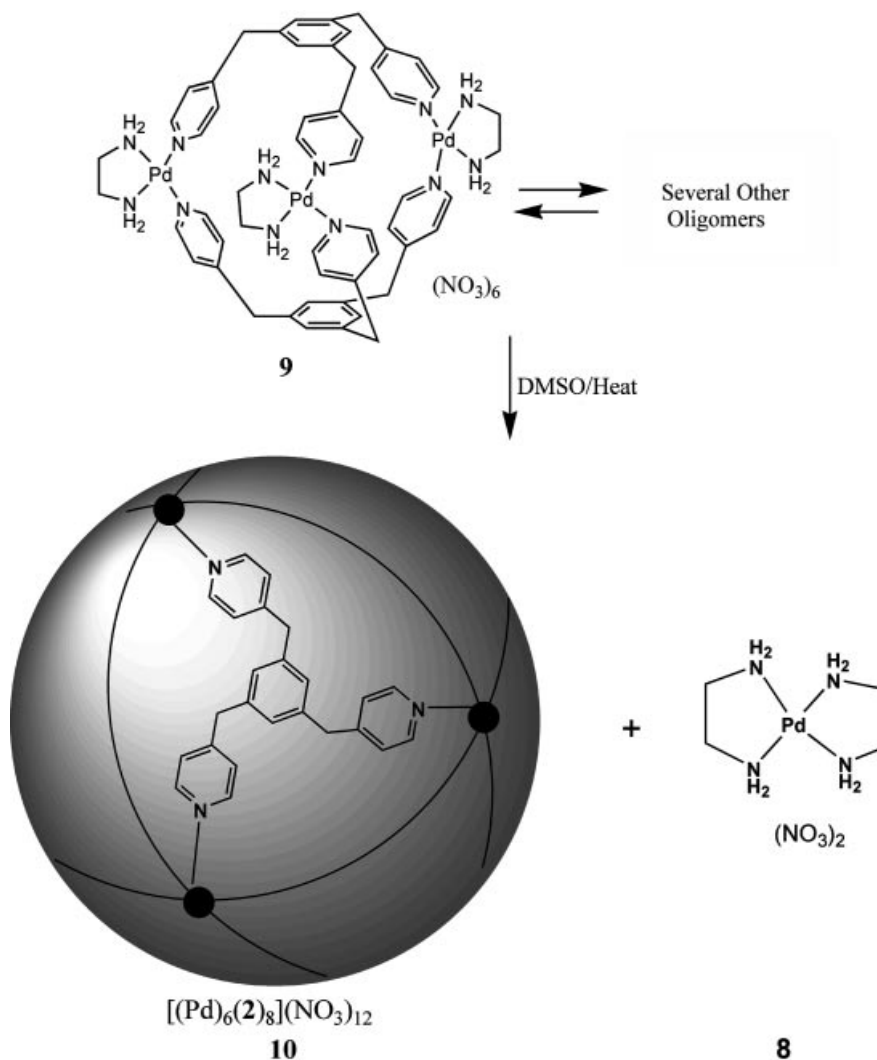
Scheme 2. Transformation of a dynamic equilibrium of **9** and its oligomers to a mixture of **10** and **8** occurred due to ligand exchange (see ref. [5b] for the synthesis of **9** and ref. [6d] and [6e] for that of **10**).

changed as observed from the proton NMR of the mixture. A similar experiment was performed by the addition of **8** to **10**; the result was that **10** also remained unchanged. However, when **8** was combined with a solution of **12**, a considerable amount of **11** was generated immediately at room temperature, and once again, an equilibrium mixture of **11**, **12**, and **8** was observed. In line with the behavior of **12**, the complex **14**, upon being combined with **8**, also generated **13**. Thus, it is possible to suggest that **7** and **10** are, although kinetically labile, still comparatively stable enough to drive the ligand-exchange reaction for the ligand systems **1** and **2** and completely in favor of **7** and **10**, respectively. As for **12** and **14**, these two complexes are labile; however thermodynamically not stable enough to drive the equilibrium completely in the forward direction. In addition, the presence of **12** or **14** with **8** allows ligand exchange around the Pd^{II} center of relatively inert **8**. Hence, there exists a final equilibrium as a result of the interplay of all participating molecules.

Another control experiment was performed to find out whether the dissociation of Pd(en)$^{2+}$ and ligands from [{Pd(en)}$_x$(ligand)$_y$](NO$_3$)$_{2x}$ occurred and whether the dissociated Pd(en)$^{2+}$ was involved in promoting the ligand-exchange process observed. Thus we added a 0.5-equiv. excess of Pd(en)(NO$_3$)$_2$ to each one of the systems and found that the speed of scrambling was increased in the case of the ligand systems **1** and **2**. Interestingly, the ligand exchange could be observed in this situation even at room temperature. However, no detectable increase in speed was observed in the cases of **3** or **4** when 0.5 equiv. excess of Pd(en)(NO$_3$)$_2$ was added.

As the *trans*-effect is important in the chemistry of Pt^{II}, we checked the possibility of similar scrambling phenomena in Pt^{II}-driven self-assemblies. When [{Pt(en)}$_x$(**2**)$_y$](NO$_3$)$_{2x}$ assemblies were heated in [D$_6$]DMSO, we could not observe the formation of any trace of [(Pt)$_6$(**2**)$_8$](NO$_3$)$_{12}$; rather the system decomposed to unidentified products upon prolonged heating.[10] The kinetic inertness of the Pt–N bond compared to the lability of the Pd–N bond[11] suggests that self-correction is inefficient in the Pt^{II} system at the given reaction conditions in this work to give discrete products through a ligand-exchange pathway.
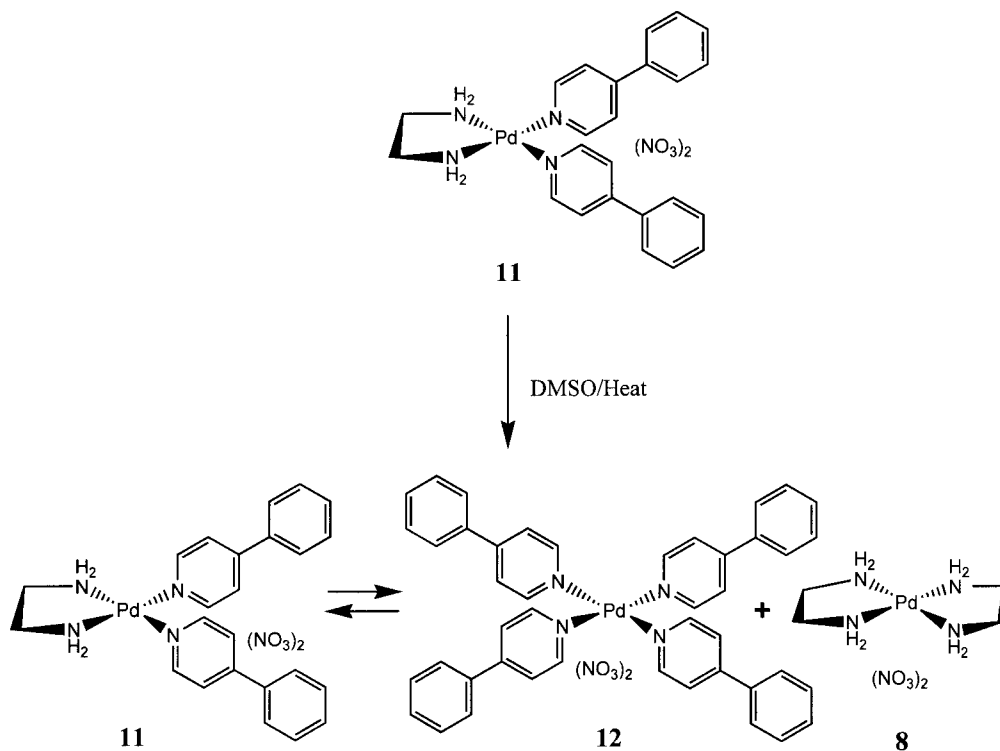
Scheme 3. Dynamic equilibrium of **11** and a mixture of **12** and **8** resulting from ligand exchange (approximately 18% of the ligand is present in **12** and 82% in **11**).
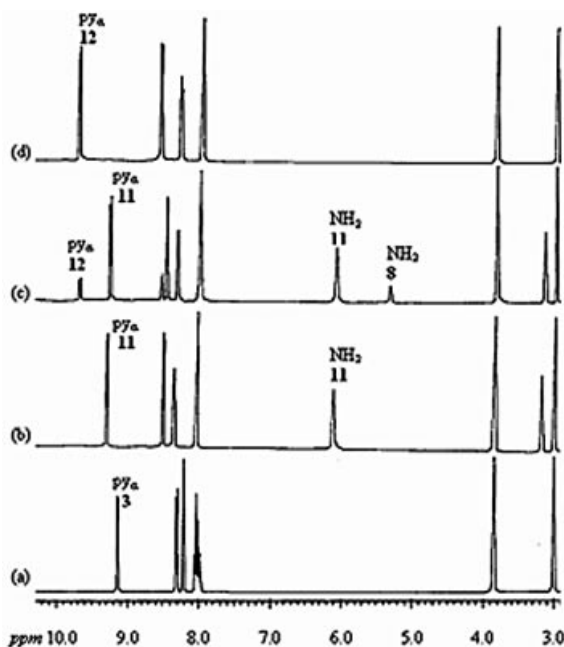

Figure 3. ^{1}H NMR spectra in [D$_6$]DMSO for (a) ligand **3**; (b) [Pd(en)(**3**)$_2$](NO$_3$)$_2$ (**11**); (c) the final equilibrium mixture of [Pd(en)(**3**)$_2$](NO$_3$)$_2$ (**11**), [Pd(**3**)$_4$](NO$_3$)$_2$ (**12**), and [Pd(en)$_2$](NO$_3$)$_2$ (**8**) obtained by heating a solution of **11** at 90 °C for 10 h; and (d) pure **12**.

Figure 4. Percentage of ligand in the Pd^{II} complex, generated as a function of time, when [{Pd(en)}$_x$(ligand)$_y$](NO$_3$)$_{2x}$ is heated at 90 °C.

In conclusion, the result opens up a concern in Pd^{II} chemistry for further study to give more generalization on the ligand-exchange process. Consideration of other parameters like the solvent, the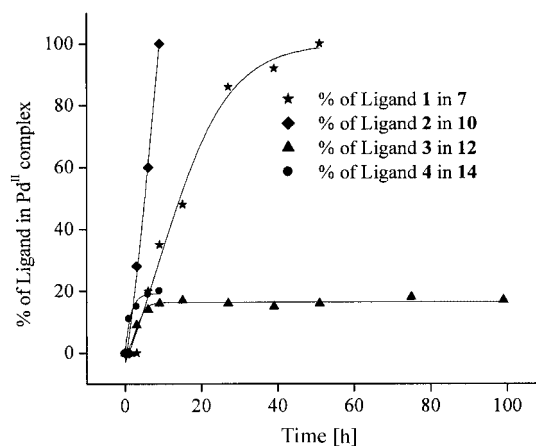 substituent on the ligand as well as that on the protecting group is certainly required to enrich the chemistry and explain the observations.

Experimental Section

The ligands **1** and **2** and complexes **5**–**10** have been synthesized by the methods reported earlier,[6e,8] while **3** and **4** are obtained from Lancaster. The complexes **11**–**14** are new and reported here. The downfield shift of the pyridine protons in **11**–**14** are attributed to complexation with Pd^{II}; the nature of the shift is in line with other related complexes. Deuterated solvent ([D$_6$]DMSO) was acquired from Aldrich and used as such for the complexation reactions for

NMR study. ^{1}H NMR spectroscopic data were obtained with a Bruker 400 MHz NMR spectrometer using external TMS in CDCl$_3$ as the reference. The assemblies of general formula [{Pd(en)}$_x$-(ligand)$_y$](NO$_3$)$_{2x}$ prepared in [D$_6$]DMSO were heated at 90 °C in NMR tubes. The desired temperature was achieved by immersing the tubes in a constant-temperature bath. The sample tubes were taken out of the bath at chosen intervals of time, and ^{1}H NMR spectra are recorded at room temperature. Formation of [Pd$_m$(ligand)$_n$](NO$_3$)$_{2m}$ and [Pd(en)$_2$](NO$_3$)$_2$ in the reaction mixture was confirmed by comparing with the data of the corresponding pure samples. The proportion of the assemblies of interest was calculated from the integration ratio of the Py$_\alpha$ protons in question. Proton NMR spectroscopic data of the ligands **3** and **4** and of the complex [Pd(en)$_2$](NO$_3$)$_2$ (**8**) in [D$_6$]DMSO was required for this work and is reported here ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): For **3**: δ = 9.136 (d, 2 H, a), 8.306 (d, 2 H, b), 8.212 (dd, 2 H, c), 8.049–7.960 (m, 3 H, d and e) ppm; for **4**: δ = 8.961 (broad, 2 H, a), 7.79–7.71(broad m, 7 H, b,c,d, and e), 4.440 (s, 2 H, f) ppm; for **8**: δ = 5.360 (s, 8 H, CH$_2$), 3.00 (s, 8 H, NH$_2$, merged with the residual solvent peaks) ppm.

Synthesis of 11–14

[Pd(en)(3)$_2$](NO$_3$)$_2$ (11): To a solution of Pd(en)(NO$_3$)$_2$, (14.5 mg, 0.05 mmol) in MeCN (5 mL) was added the ligand **3** (15.5 mg, 0.1 mmol). The mixture was stirred to get a clear solution. Subsequent addition of diethyl ether precipitated the complex **11** as a white solid (24 mg, 80%). ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 9.333 (d, 4 H, a), 8.540 (d, 4 H, b), 8.388 (m, 4 H, c), 8.062 (m, 6 H, d and e), 6.130 (s, 4 H, NH$_2$), 3.189 (s, 4 H, CH$_2$) ppm. C$_{24}$H$_{26}$N$_6$O$_6$Pd: calcd. C 47.97, H 4.36, N 13.99; found C 48.08, H 4.46, N 13.78.

[Pd(en)(4)$_2$](NO$_3$)$_2$ (12): Following the synthesis of **11**, to a solution of Pd(en)(NO$_3$)$_2$, (14.5 mg, 0.05 mmol) in MeCN (5 mL) was added the ligand **4** (16.9 mg, 0.1 mmol). Subsequent addition of diethyl ether precipitated a white solid, the complex **12** (26 mg, 83%). ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 9.097 (d, 4 H, a), 8.010 (d, 4 H, b), 7.810–7.744 (m, 10 H, c, d and e), 5.980 (s, 4 H, NH$_2$), 4.527 (s, 4 H, f), 3.103 (s, 4 H, CH$_2$) ppm. C$_{26}$H$_{30}$N$_6$O$_6$Pd: calcd. C 49.65, H 4.81, N 13.36; found C 49.74, H 4.99, N 13.58.

[Pd(3)$_4$](NO$_3$)$_2$ (13): To a solution of Pd(NO$_3$)$_2$, (11.7 mg, 0.05 mmol) in MeCN (5 mL) was added the ligand **3** (31.0 mg, 0.2 mmol), whereupon a white solid was precipitated out. The mixture was heated for a further period of 10 min at 90 °C, and the solid was separated (36 mg, 85%). ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 9.758 (d, 8 H, a), 8.608 (d, 4 H, b), 8.345–8.322 (m, 8 H, c), 8.063–8.021 (m, 12 H, d and e) ppm. C$_{44}$H$_{36}$N$_6$O$_6$Pd: calcd. C 62.08, H 4.26, N 9.87; found C 62.26, H 4.30, N 9.71.

[Pd(4)$_4$](NO$_3$)$_2$ (14): To a solution of Pd(NO$_3$)$_2$, (11.7 mg, 0.05 mmol) in MeCN (5 mL) was added the ligand **4** (33.8 mg, 0.2 mmol), whereupon a white solid precipitated out. The mixture was heated for a further period of 10 min at 90 °C, and the solid was separated (35 mg, 78%). ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 9.461 (d, 8 H, a), 7.956 (d, 8 H, b), 7.791–7.664 (m, 20 H, c, d and e), 4.462 (s, 8 H, f) ppm. C$_{48}$H$_{44}$N$_6$O$_6$Pd: calcd. C 63.54, H 4.89, N 9.26; found C 63.39, H 5.02, N 9.11.

Acknowledgments

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[7] At higher temperatures, e.g., 120 °C, the process is faster and sometimes causes decomposition on prolonged heating. At lower temperatures, e.g., 60 °C, the process is slow, and hence more time is required for the study.

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[9] However, the M$_3$L$_2$ compositional assembly [{Pd(en)}$_3$(**2**)$_2$]-(NO$_3$)$_6$ (**9**) could be obtained exclusively in aqueous solution

by using a suitable template, e.g., 4-methoxyphenyl acetate, as described in ref.[5b].

[10] When ligand **2** was treated with Pt(NO$_3$)$_2$ and heated at 90 °C for 10 min, it gave a complicated mixture, unlike the complexation of **2** with Pd(NO$_3$)$_2$. The suitable conditions for achieving [(Pt)$_6$(**2**)$_8$](NO$_3$)$_{12}$ from **2** and Pt(NO$_3$)$_2$ were found to be heating at 120 °C for 24 h.

[11] Substitution on Pd^{II} center shows 10^5-fold greater reactivity compared to Pt^{II}. See *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties and Applications of Coordination Compounds, Volume 1* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, p. 311.