Gel Catalysis

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An Air-Stable Organometallic Low-Molecular-Mass Gelator: Synthesis, Aggregation, and Catalytic Application of a Palladium Pincer Complex**

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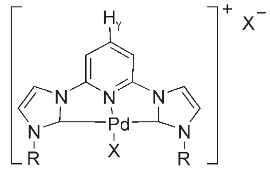
Dedicated to Professor Fritz Vögtle

Currently, gels derived from low-molecular-mass compounds are attracting increasing interest owing to the simplicity of the gelator molecules, their physical properties, and potential applications. A variety of organo- and hydrogelators based on hydrogen bonding, π stacking, and van der Waals interactions has been reported to immobilize organic fluids or water to form swellable materials, even at extremely low concentrations.[1–3] Structural requirements for low-molecular-mass gelators (LMMG) are poorly understood, and a rational correlation of molecular structure and gelation ability in a given solvent still remains a challenge. Despite the major role that organometallic compounds play in synthesis, catalysis, and materials chemistry, they have yet to be investigated as gelator-type soft materials;[4] to date, only two examples, a sugar chromium carbene amphiphile and a cholesterol titanocene derivative, were reported as organometallic low-molecular-mass organogelators.[5] With the aim to introduce the unique properties of organopalladium compounds in organic synthesis into organometallic gelators, we extended our studies towards robust functional organometallic compounds as low-molecular-mass gelators. Herein, we report the first example of a palladium-based air-stable organometallic LMMG, which is able to gelate a variety of organic solvents and to catalyze C–C bond formation even in the gel state.

Palladium CNC pincer bis(imidazolylidene) complexes **1** and **2a** were reported to catalyze cross-coupling reactions;[6] however, their poor solubility hampered a broader application in catalysis.[6a] Substitution with longer alkyl chains is a common means to enhance the solubility of compounds in organic solvents and, moreover, is expected to favor aggregation through intermolecular van der Waals interactions, which may assist gel formation.[2,7] Thus, we concentrated on CNC pincer palladium carbene complexes of type **3** bearing two C_{16} alkyl substituents as potential low-molecular-mass organometallic gelators (Scheme 1).



1: R = CH_3, X = Br
2a: R = n-C_4H_9, X = Br
2b: R = n-C_4H_9, X = I
3: R = n-$C_{16}H_{33}$, X = I

Scheme 1. Palladium CNC pincer bis(carbene) complexes.

The pincer complexes, such as **3**, are readily accessible from commercial starting materials in a modified modular high-yield synthesis.[8] Upon heating to reflux in a variety of organic solvents and subsequently cooling to room temperature, complex **3** forms thermoreversible swellable materials within a few hours. Gelation experiments with 1 wt% (wt/v; 9.81×10^{-3} M) gelator in a selection of protic and aprotic solvents are summarized in Table 1. Turbid gels were formed from methanol (MeOH), acetic acid (HOAc), and dichloroethane (DCE), whereas dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamid (DMA), and tetrahydrofuran (THF) produced translucent or transparent gels independent of the cooling rate. Because CNC complex **3** is stable towards air and moisture, long-lived gels are accessible under ambient conditions. When the concentration is increased to 2 wt%, stable gels are also formed from dichloromethane (DCM), dioxane, benzene, toluene, and acetonitrile (ACN) at room temperature. The gels darken in color with increasing coordination ability of the solvent.

The morphology of xerogels obtained from different solvents (after evaporation of the solvent) was investigated by transmission electron microscopy (TEM). Selected typical 3D networks of xerogels demonstrated that morphologies obtained from different solvents are quite different (Figure 1). Larger fibers are present in xerogels obtained

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Table 1: Gelation ability of complex **3** in various solvents.[a]

Entry	Solvent	Phase	Color	Gel type	T_g [°C][b]
1	MeOH	G	yellow	turbid	54
2	HOAc	G	red	turbid	52
3	DCM	P[c]	yellow	turbid	–[d]
4	DCE	G	light yellow	turbid	67
5	DMSO	G	orange-red	transparent	59
6	DMF	G*	orange-red	transparent	58
7	DMA	G*	orange-red	transparent	50
8	THF	G	orange	translucent	55
9	dioxane	G*[c]	yellow	turbid	53[c]
10	benzene	G*[c]	yellow	turbid	50[c]
11	toluene	G*[c]	yellow	turbid	51[c]
12	ACN	PG[c]	yellow	turbid	–[d]

[a] Gelator concentration: 1 wt%; G: gel formed at RT; G*: gel formed by cooling to 5 °C; PG: partial gel, P: precipitate. [b] Determined by DSC.[9] [c] Gel formed with 2 wt% at RT. [d] T_g could not be determined accurately by DSC.

from MeOH, HOAc, and DCE, while very dense networks result from DMF, DMSO, DMA, and THF.[10]

Gels from MeOH and DMA (Figures 1 a and d) reveal a helical (*P* and *M*) ribbon morphology at the microscopic level, which is rarely observed in gel networks formed from achiral compounds. The dimensions of the individual fibers vary with the solvent used. Their lengths amount to several micrometers with pitches of about 1280 nm from DMA and 2800 nm from MeOH. The fibers are approximately 320 nm (DMA) and 1600 nm (MeOH) wide. They are composed of tightly intertwined thinner fibers (ca. 5 nm diameter from MeOH); smaller helical ribbon morphologies, which are approximately 100 nm wide and several micrometers long with a pitch of approximately 500 nm, could be observed in the gel networks obtained from toluene and THF.[10]

Long, finer, and denser 3D networks are formed in the gels from DMF and DMSO. The fibers from DMF (several μm long and ca. 10 nm wide) are straighter and more parallel than the fibers obtained from DMSO (Figures 1 b and c). Benzene, ACN, and DCM form straight ribbon morphologies with a length of several micrometers and a width of approximately 100 nm.[10]

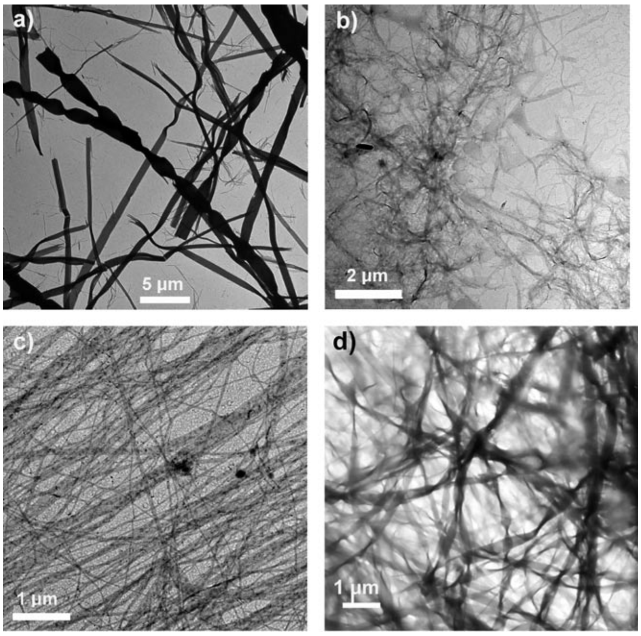


Figure 1. Selected TEM images of gels formed by pincer complex **3** (concentration 1 wt%). a) MeOH; b) DMSO; c) DMF; d) DMA.

The gel-to-solution phase-transition temperatures (T_g) of gels in selected solvents were determined by differential scanning calorimetry (DSC; Table 1).[1,9] At 1 wt% concentration, the T_g values obtained for MeOH, HOAc, and DMSO were corroborated by the "dropping ball method".[11] The DSC thermograms recorded for gel **3**/DMSO (2 wt%) revealed well-defined thermoreversible sol-gel transitions with unchanged T_g (63 °C) and enthalpy parameters ($\Delta H = 2\,\mathrm{J\,g^{-1}}$).[10] In all tested gels, the transition temperature from gel to solution ($T_{g/H}$) was found to be at least 5 °C higher than that from solution to gel ($T_{g/C}$); this hysteresis behavior is characteristic of LMMGs.[12] To examine the effect of concentration of the gelator on the solution–gel transition temperature (T_g), a series of **3**/DMSO gels with concentrations varying from 0.2 to 3.0 wt% was studied by DSC (Figure 2). $T_{g/H}$ and $T_{g/C}$ increase with increasing concentration of gelator **3** in DMSO, which demonstrates that the stability of the gel increases with gelator concentration.

The efficiency with which carbene complex **3** gelates a broad variety of solvents with different network morphologies may be based on the planarity of the metal-chelating pincer ligand, which allows for aggregation by intermolecular π stacking, possibly enhanced by van der Waals interactions between the alkyl chains and by metal–metal interactions. Temperature-dependent ^{1}H NMR spectroscopy studies of gel **3**/[D$_6$]DMSO (1 wt%) were applied to probe the role of aromatic rings in the gelation process (Figure 3). Broad proton signals for the gel state (25 °C) indicate extensive aggregation. Upon warming to 65 °C by 10 °C steps, the broad signals observed for the heteroaromatic and the NCH$_2$ hydrogen atoms steadily sharpen and are shifted downfield; for example, the signal of the γ proton of the pyridine ring is shifted from $\delta = 7.73$ to 7.93 ppm over the temperature range of 40 °C. This effect is reversible and may reflect reduced aromatic π–π interactions between gelator molecules upon warming, thus suggesting that the gelator molecules coordi-

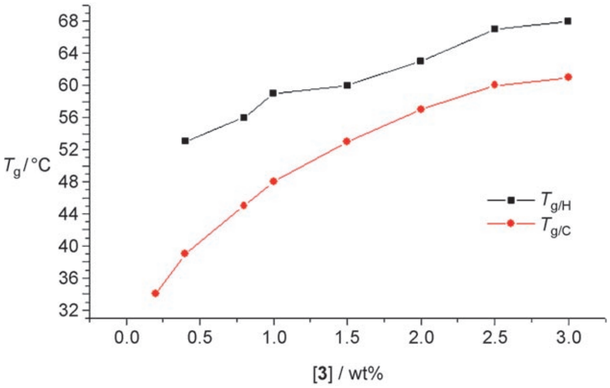


Figure 2. Sol-gel transition temperatures ($T_{g/H}$ and $T_{g/C}$) for gels **3**/DMSO as a function of gelator concentration.

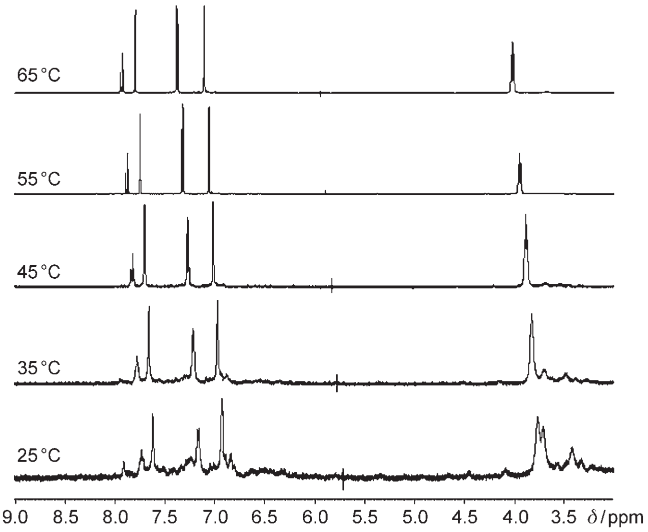


Figure 3. Temperature-dependent ^1H NMR spectra (aromatic and NCH_2 alkyl region) of gel **3**/[D_6]DMSO (1 wt %).

nate the solvent to form solvates within a modified network that is able to cage additional solvent molecules to form a gel.

The structure and dimensions of the gel network of **3**/DMSO have been studied by X-ray diffraction (Figure 4).[1,13] The most prominent features are reflections at $2\theta = 6°$ and 12° (L_{001} and L_{002}), which are assigned to a lamellar structure with a mean distance of 15.2 Å, which may reflect the distance between stacked layers of the complex. The peak at $2\theta = 23°$ (d_{001}) indicates another unit with a typical distance of 3.9 Å, which is assumed to correspond to π stacking and Pd···Pd interactions.

A possible aggregation model of gelator **3** may be based on the molecular structure of the *N*-butyl analogue **2b**·$CHCl_3$, which was established by X-ray structure analysis (Figure 5). This complex forms parallel sheets organized in bilayers that are held together by hydrogen bonds between alkyl hydrogen atoms and $CHCl_3$ guest molecules (H···Cl separation 2.81 Å) and by additional van der Waals interactions between alkyl chains with shortest distances of 2.45 Å.[10] The bilayers are assembled in aggregates resulting from π stacking of the pincer ligands (plane separation 3.4 Å) and Pd···Pd interactions (3.48 Å) and are connected by the I^- counterions; these dimensions correspond to the data obtained from the X-ray diffraction study of gel **3**/DMSO; however, the separation between the stacked layers is slightly smaller in the crystal of **2b**. This aggregation principle is reminiscent of that reported for the unsolvated bromide analogue **2a**.[6] We propose that gelation of **3** involves intercalation of additional solvent molecules supported by long alkyl chains into the bilayer, which is consistent with the ribbon morphologies observed in the gel network.

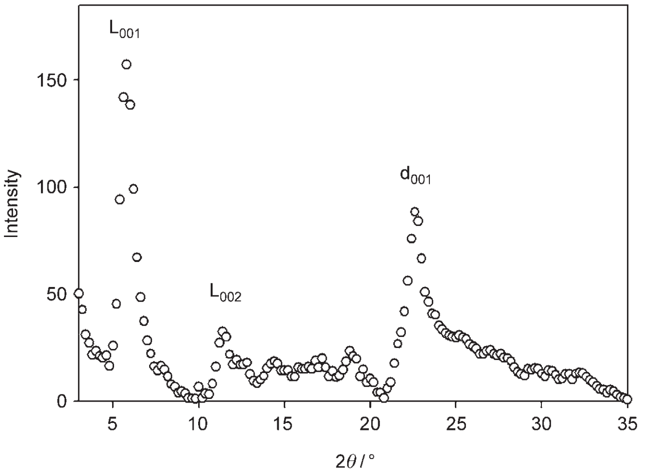


Figure 4. X-ray diffraction pattern of gel **3**/DMSO (3 wt %; after subtraction of the solvent-based background).

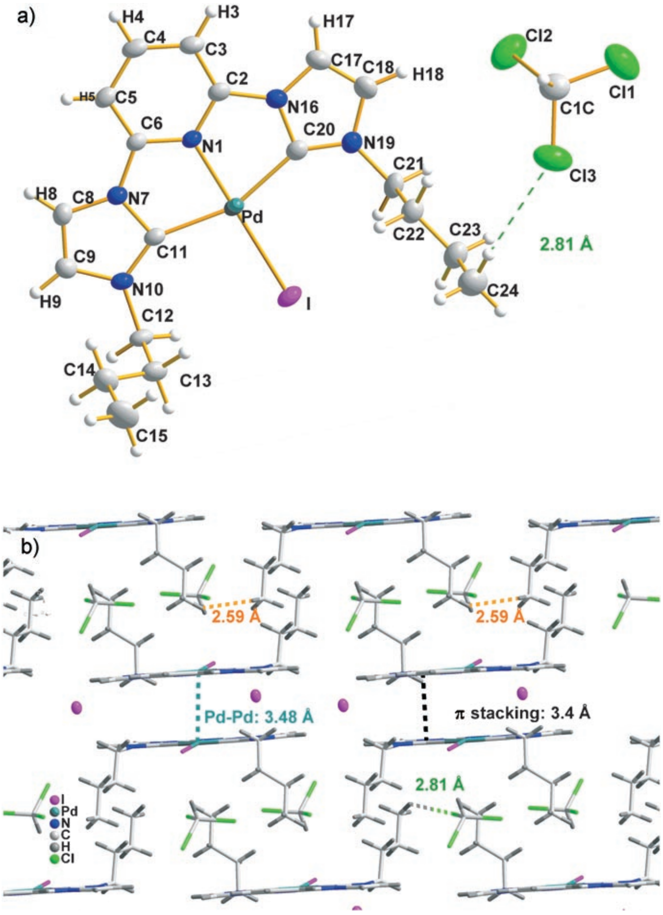
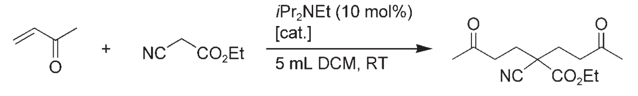


Figure 5. a) Molecular structure of **2b**·$CHCl_3$ in the crystal. b) View along the *a* axis showing part of a truncated 2×2×2 array of unit cells.

Above T_g, carbene complexes **2b** and **3** are efficient catalysts for cross-coupling reactions, for example, Suzuki, Heck, and Sonogashira reactions.[10] Complex **3** reveals similar catalytic activity to that reported for complexes **1** and **2a**;[6] complex **2b** is even more reactive. These results prompted us to test the catalytic activity of carbene complex **3** in the gel state. So far, only two examples of palladium(II) coordination compounds (one of which is a polymer gel) have been applied to catalytic reactions in the gel state; both of them showed only low turnover numbers in the oxidation of benzylic alcohol to benzaldehyde.[14]

The T_g of gels **3** allows us to test their catalytic reactions in the gel state up to approximately 50 °C. As a model reaction, we studied the double Michael addition of α-cyanoacetate to methyl vinyl ketone, which can be catalyzed by NCN and PCP pincer palladium complexes.[15,16] Strong and easy-to-handle 4 wt% gels **3**/DMF and **3**/DMSO (prepared in situ) were chosen as catalysts under very slow stirring to avoid destruction of the gel network (entries 2 and 3, Table 2). The gel **3**/DMSO revealed a catalytic activity higher than that observed for DMF, probably owing to the different structures of gel network. In order to assure that the gel state is responsible for the observed catalytic activity, a saturated solution of complex **3** in DCM was applied as catalyst (only ca. 0.08 mg Pd per mL DCM could be detected by ICP-MS); under these conditions the double Michael addition was hardly faster than in the blank test (entry 4, Table 2). DMSO and DMF as additives in the blank test did not accelerate the reaction. Similarly, the poor solubility of complex **2b** also resulted in low catalytic activity (entry 1, Table 2). Embedding the catalyst into a 3D gel network allows for its easy recovery after the reaction. Ongoing studies will focus on further improving the catalytic activity of pincer-type complexes by adjusting the gelating abilities with respect to the reaction conditions required for efficient catalysis.

Table 2: Catalytic activity of palladium pincer carbene complexes in the double Michael addition.



Entry	Catalyst	k [10^{-6} s^{-1}][a]	$t_{1/2}$ [h][b]
1	**2b**	4.3	44
2	gel **3**/DMSO (4 wt%)	24.1	7.9
3	gel **3**/DMF (4 wt%)	10.4	18.5
4	**3**	5.5	35
5	blank	3.8	51

[a] Determined by comparison of the integration of the α-CH_2 signal of ethyl α-cyanoacetate with the integration of the ethyl ester CH_2 signal by ^{1}H NMR spectroscopy; the rate constant k was determined by plotting $-\ln([CN]/[CN]_0)$ versus time (CN = ethyl α-cyanoacetate). [b] $t_{1/2} = \ln 2/(3600k)$.

In summary, palladium pincer bis(carbene) complex **3** is an efficient organometallic gelator for a variety of protic and aprotic organic solvents even in concentrations as low as 0.2 wt%. NMR spectroscopy and X-ray diffraction studies indicate that π stacking of the heteroarene moities, van der Waals interactions between the alkyl chains, and metal–metal interactions may be responsible for the aggregation. Complex **3** represents the first air-stable organometallic low-molecular-mass gelator that is readily accessible from commercial precursors and, moreover, reveals promising catalytic activity in C−C bond formation even in the gel state.

Experimental Section

Synthesis of **3**: A solution of $[CHNCHC_{16}H_{33}]I_2$[10] (915 mg, 1.0 mmol) and $Pd(OAc)_2$ (224 mg, 1.0 mmol) was stirred in DMSO (8 mL) for 3 h at room temperature and then for 12 h at 80 °C. Subsequently, the reaction mixture was heated to 165 °C for 2 h and then cooled to room temperature, which led to gelation. Cold Et_2O was added (200 mL) and the precipitate was purified three times by dissolving in $CHCl_3$ and precipitating with cold Et_2O, thus affording a yellowish solid (776 mg, 76%). ^{1}H NMR ([D$_6$]DMSO, 500 MHz, 338 K): $\delta = 7.93$ (t, 1 H, $J = 8$ Hz, pyridine γ-H), 7.79 (d, 2 H, $J = 2$ Hz, imidazole-H), 7.37 (d, 2 H, $J = 8$ Hz, pyridine β-H), 7.10 (d, 2 H, $J = 2$ Hz, imidazole-H), 4.01 (t, 4 H, $J = 7.5$ Hz, NCH_2-$C_{15}H_{31}$), 1.85 (quintet, 6 H, $J = 2$ Hz, alkyl-chain H), 1.19 (quintet, 4 H, $J = 7.5$ Hz, alkyl-chain H), 0.71 (m, 8 H, alkyl-chain H), 0.60 (br m, 38 H, alkyl-chain H), 0.21 ppm (t, 6 H, $J = 7$ Hz, $NC_{15}H_{30}CH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): $\delta =$ 166.90 (C-Pd), 149.58 (C-*ortho*), 146.52 (C-*para*), 123.82 (C-imidazole), 119.03 (C-imidazole), 110.25 (C-*meta*), 53.33 ($NCH_2C_{15}H_{31}$), 31.87 ($NC_{13}H_{26}$-$CH_2C_2H_5$), 31.68 (NCH_2-CH_2-$C_{15}H_{31}$), 29.65, 29.60, 29.53, 29.44, 29.29, 29.25, 26.19, 22.60 (alkyl-chain C), 13.98 ppm ($NC_{15}H_{30}CH_3$). MS (MALDI): m/z 892.5 $[M-I]^+$; elemental analysis (%) calcd for $C_{43}H_{73}I_2N_5Pd\cdot 2H_2O$ (1019.299): C 48.89, H 7.35, N 6.63; found: C 48.80, H 7.10, N 6.41.

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Keywords: carbene complexes · gel catalysis · gelators · palladium · self-organization

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