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Article

Dinuclear and Tetranuclear Palladium(II) Complexes of a Thiolato-Functionalized, Benzannulated N-Heterocyclic Carbene Ligand and Their Activities toward Suzuki−Miyaura Coupling

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The thiolato-bridged dimeric Pd(II) benzimidazolin-2-ylidene complex **1**, with a $[Pd_2S_2]$ core, was conveniently prepared by the reaction of the thiol-functionalized benzimidazolium salt **C** and $Pd(OAc)_2$. More straightforwardly, **1** can also be synthesized by direct treatment of the thioester-functionalized benzimidazolium salt **B** with $Pd(OAc)_2$ in wet DMSO under in situ hydrolysis of the thioester function. A subsequent salt metathesis reaction of **1** with AgO_2CCF_3 afforded the mixed dicarboxylato/NHC analogue **2** in quantitative yield, leaving the sulfur bridges of the $[Pd_2S_2]$ core unaffected despite the use of the soft Ag(I) ions. Treatment of **1** with Me_3OBF_4 resulted in an unexpected bromido abstraction of **1** leading to an unusual rearrangement/dimerization reaction to give the tetranuclear NHC complex **3**, which features a $[Pd_4S_4]$ macrocylic square with sulfur corners. These reactions demonstrate the structural diversity of the thiolato-functionalized N-heterocyclic carbene complexes and may offer access to metallo-NHC-based supramolecular architectures. A comparative catalytic study revealed the superiority of NHC/thiolato complex **2** over complexes **1** and **3** in aqueous Suzuki−Miyaura couplings at very low catalyst loading.

Introduction

N-heterocyclic carbenes (NHCs) have become common ligands in organometallic chemistry and catalysis due to their unique properties.[1] A particularly interesting feature is that NHCs can be modified in many ways by introducing functionalities at the nitrogen atoms of the N-heterocyclic ring. Various complexes of donor-functionalized NHCs and their use in catalysis have been explored and recently reviewed.[2] Toward this point, N-functionalization with N-, O-, and P-donor groups is relatively common, whereas NHCs bearing S-donors are still rare. So far, only a few thiolato-NHCs,[3] thioether-NHCs,[4] and thiophene-NHCs[5] have been reported. Among these, we are particularly interested in the first type due to the versatile and diverse coordination chemistry of the soft and electron-rich thiolato ligands in general.[6] The monoanionic thiolato function also forms stronger M−S bonds compared to the neutral thioether or thiophene moieties. Current methodologies employed to prepare thiolato-NHC complexes include either (i) oxidative addition across a C−S bond using low-valent metal presursors[3b,c] or (ii) the reaction with free thiols.[3a] Both methods suffer from the limitation that air-sensitive precursors, such as metal(0) complexes or free thiols, are required. Furthermore, method (i) is restricted to ligand precursors with C2−S bonds. In addition, all reported examples are based on a saturated five- or six-membered N-heterocyclic ring system, while those based on benzimidazole remain to be explored. In relation to our research on benzimidazole-derived NHCs and their functionalization, we herein present the synthesis of the thiolato-bridged Pd(II) benzimidazolin-2-ylidene complex **1** from a benzimidazolium salt with a thiol function. More conveniently, **1** can also be synthesized from an air-stable thioester-functionalized benzimidazolium salt via in situ hydrolysis under aerobic conditions. Reactivity studies of this complex toward Ag salts and electrophiles led to the isolation of the carboxylato derivative **2** and the tetranuclear $[Pd_4S_4]$ molecular square **3**. The isolation of the latter demonstrates an unusual reactivity of

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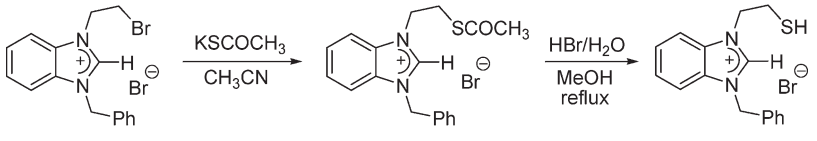
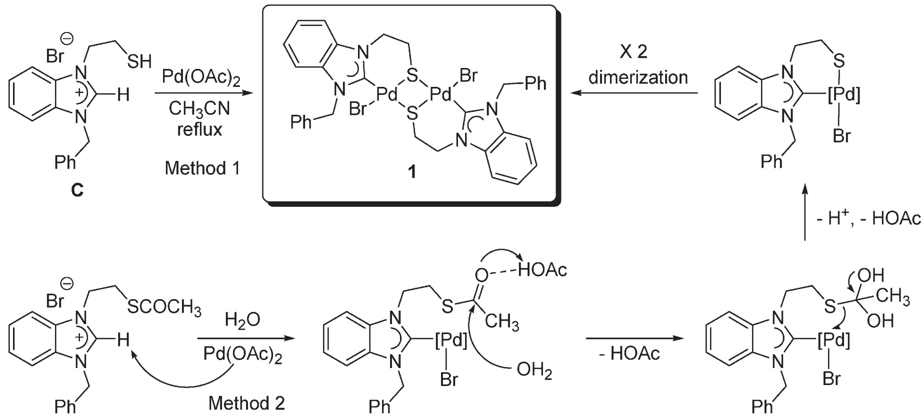
Scheme 1. Preparation of Sulfur-Functionalized Ligand Precursors B and C



Scheme 2. Two Synthetic Pathways to Dinuclear Complex 1



Me_3OBF_4 as a halide abstraction reagent, which represents a very useful metal-free alternative to the commonly used Ag- and toxic Tl-based reagents. The catalytic activities of all these thiolato-functionalized NHC Pd(II) complexes in the Suzuki–Miyaura coupling reaction have also been investigated and compared.

Results and Discussion

Synthesis of the Ligand Precursors. Recently, we have reported the synthesis of the bromo-functionalized benzimidazolium salt **A** from N-alkylation of *N*-benzylbenzimidazole, which offered access to CSC-pincer ligands.[4e] In a similar way, **A** can undergo nucleophilic substitution with 1 equiv of $KSCOCH_3$ in CH_3CN to afford the thioester-functionalized benzimidazolium salt **B** in a yield of 75% (Scheme 1).

The formation of the ligand precursor **B** is supported by a base peak in the ESI mass spectrum at m/z 311 for the molecular cation $[M - Br]^+$. Moreover, the ^1H NMR spectrum in DMSO-d_6 of **B** shows two triplets at 4.75 and 3.44 ppm assignable to the two inequivalent CH_2 groups in the ethylene chain of the N-substituent and a singlet at 2.27 ppm corresponding to the methyl thioester protons. In comparison to precursor **A**, the signals for the ethylene protons shifted upfield due to the replacement of the bromide with a less electron withdrawing thioester group. The ^{13}C NMR spectrum of **B** shows signals for the procarbene and carbonyl carbon atoms at 142.7 and 194.7 ppm, respectively.

The thioester group of **B** was easily hydrolyzed by aqueous HBr to form the thiol-functionalized salt **C** (Scheme 1). In the ^1H NMR spectrum of salt **C** in CD_3CN, the absence of the singlet assignable to the methyl thioester group of **B** and the appearance of a new signal at 2.72 ppm for the free thiol function corroborate the successful hydrolysis. Furthermore, a base peak in the ESI mass spectrum at m/z 269 for the molecular cation $[M - Br]^+$ also supports the formation of **C**.[7]

Synthesis of Pd(II) Complexes. The reaction of thiol-functionalized salt **C** with 1 equiv of $Pd(OAc)_2$ in degassed CH_3CN under reflux overnight yielded the thiolato-bridged dimeric Pd(II) benzimidazolin-2-ylidene complex **1** in a good yield of 76% (Scheme 2, method 1). In this case, the solvent CH_3CN was chosen over the commonly used DMSO to avoid oxidation of the free thiol function to disulfide. Complex **1** is insoluble in CH_3CN and can be readily isolated by filtration.

More straightforwardly, we found that the direct reaction of thioester salt **B** with 1 equiv of $Pd(OAc)_2$ in DMSO at 80 °C overnight also yielded complex **1** in a similar yield of 74% (Scheme 2, method 2). Isolation of **1** from this reaction is also easy, involving only a simple filtration step due to its low solubility in DMSO. Column chromatography of the saturated filtrate afforded a second crop of the yellow product. Apparently, the methyl thioester function undergoes in situ hydrolysis, probably assisted by free HOAc liberated from the deprotonation of **B** with $Pd(OAc)_2$. The resulting thiolate coordinates the Pd(II) center, and subsequent dimerization affords the desired thiolato-bridged Pd(II) carbene complex **1**. In this reaction, the thioester function acts as a thiol-protecting group, simplifying the synthesis of thiolato complexes to a great extent. Method 2 is preferred over method 1, since it shortens the reaction sequence and also eliminates the requirement of working under an inert atmosphere.

Complex **1** is soluble in CH_2Cl_2, $CHCl_3$, DMSO, and DMF, but insoluble in less polar solvents such as hexane and diethyl ether. Its formation is supported by ESI mass spectrometry, which shows a base peak at m/z 829 for the $[M - Br]^+$ complex fragment. In the ^1H NMR spectrum, the benzylic protons become diastereotopic upon complexation and resonate as two doublets centered at 6.63 and 5.58 ppm, respectively, with a coupling constant of $^2J(H-H) = 15.6$ Hz. All four methylene protons of each ethanethiolato bridge are also diastereotopic but give rise to two pseudodoublets and

(7) In addition, a strong peak at m/z 617 was observed, which can be assigned to the oxidized disulfide compound associated with one bromide counteranion.

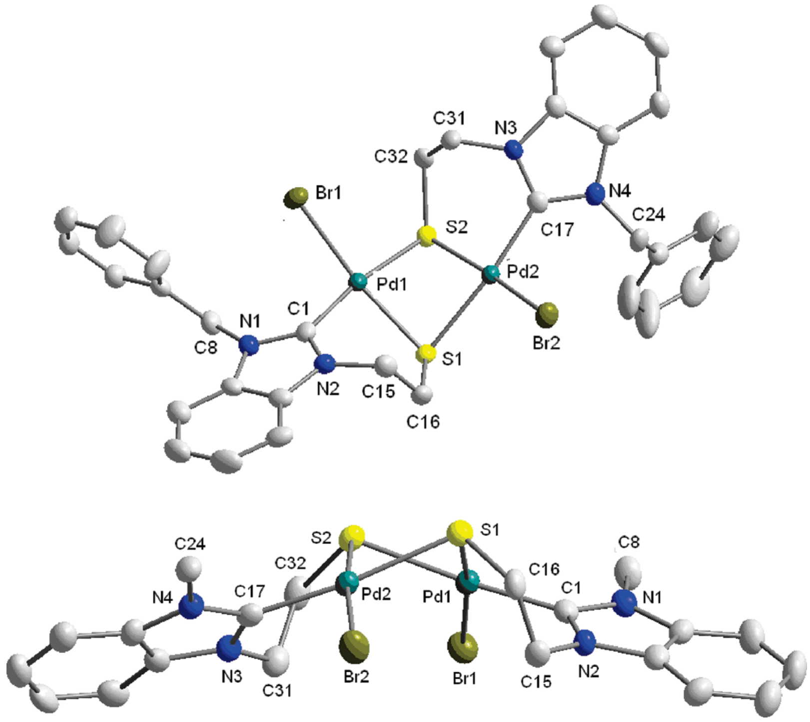


Figure 1. Molecular structure of **1** showing 50% probability ellipsoids: (top) top view; (bottom) side view. Hydrogen atoms and one part of the disordered phenyl ring are omitted for clarity. The phenyl rings of the benzyl substituents have been omitted in the side view for clarity as well. Selected bond lengths (Å) and bond angles (deg): Pd1−C1 1.977(4), Pd1−S1 2.2952(11), Pd1−S2 2.3705(10), Pd1−Br1 2.4401(5), Pd2−C17 1.997(4), Pd2−S2 2.2941(10), Pd2−S1 2.3721(10), Pd2−Br2 2.4652(5); C1−Pd1−S1 91.17(11), S1−Pd1−S2 80.32(4), S2−Pd1−Br1 97.46(3), Br1−Pd1−C1 91.44(11), C1−Pd1−S2 170.93(11), S1−Pd1−Br1 170.26(3), C17−Pd2−S2 90.75(12), S2−Pd2−S1 80.31(4), S1−Pd2−Br2 96.33(3), Br2−Pd2−C17 92.65(11), C17−Pd2−S1 171.01(12), S2−Pd2−Br2 171.21(3), Pd1−S1−Pd2 82.49(3), Pd1−S2−Pd2 82.55(3).

two pseudotriplets ranging from 4.88 to 2.10 ppm due to insufficient resolution and accidental overlap. In the ^{13}C NMR spectrum, the two equivalent carbene carbon atoms resonate at 175.4 ppm.

Single crystals of **1** were grown from CH_2Cl_2, and the molecular structure determined by X-ray diffraction analysis is shown in Figure 1. The two Pd(II) centers are coordinated and bridged by two μ-thiolato-functionalized carbene ligands in a chelating fashion. The square-planar coordination sphere at each Pd(II) is completed by one terminal bromido ligand. The dihedral angles between this [$PdCS_2Br$] coordination plane and the carbene ring planes amount to 55.07(9) and 54.21(9)°, respectively, which deviate substantially from the favored perpendicular orientation (90°) due to the chelating binding mode of the S-functionalized carbene ligand. There are two types of Pd−S bonds in the complex, of which the Pd1−S2 bond (2.3705(10) Å) trans to the carbene is significantly longer than the Pd1−S1 bond (2.2952(11) Å) trans to the bromido ligand due to the strong trans influence of the NHC. The [Pd_2S_2] core of **1** is significantly bent with a hinge angle of ca. 119.26(3)°, which is much smaller than the reported value of 144.7(2)° for a similar but dicationic dimeric complex bearing S-functionalized saturated NHCs and terminal phosphine ligands.[3b]

In order to investigate the robustness of the [Pd_2S_2] core, attempts were made to abstract the bromido ligands or to alkylate the thiolato bridges. The metathesis reaction of mixed halo/NHC Pd(II) complexes with Ag carboxylates is an established method to synthesize mixed carboxylato−carbene complexes as potentially useful catalyst precursors.[8] However, this methodology has not been extended to sulfur-functionalized NHCs, due to the potential interaction of the soft sulfur donor with the soft Ag(I) ion, which would compete with the desired halide abstraction. On the other hand, the bridging mode of the thiolato donor reduces the number of lone pairs available at sulfur, which may prevent or lower the interference with silver. To test this hypothesis, complex **1** was reacted with 2 equiv of AgO_2CCF_3 in CH_3CN, as depicted in Scheme 3. Indeed, this reaction cleanly afforded the dinuclear mixed carbene−carboxylato Pd(II) complex **2** in quantitative yield without affecting the [Pd_2S_2] core. The reaction mixture, initially a yellow suspension, turned greenish yellow with the precipitation of AgBr after stirring overnight. Complex **2** shows an improved solubility as compared to its precursor complex **1**, which is a common phenomenon observed for mixed carbene−carboxylato Pd(II) complexes.[8] It is soluble in most organic solvents, with the exception of hexane. In the ^{13}C NMR spectrum, the resonance for the $C_{carbene}$ in **2** amounts to 171.4 ppm, which is shifted upfield due to the stronger shielding effect of the trifluoroacetato ligand compared to that of the bromido ligand in the precursor **1**. Furthermore, the identity of **2** was also supported by a base peak in the ESI mass spectrum at m/z 861 for the monocation $[M - O_2CCF_3]^+$ and a less intense peak at m/z 373 for the dication $[M - 2\,O_2CCF_3]^{2+}$ due to stepwise loss of trifluoroacetato ligands.

Single crystals of **2** suitable for X-ray diffraction analysis were grown from a concentrated CH_2Cl_2 solution. There are

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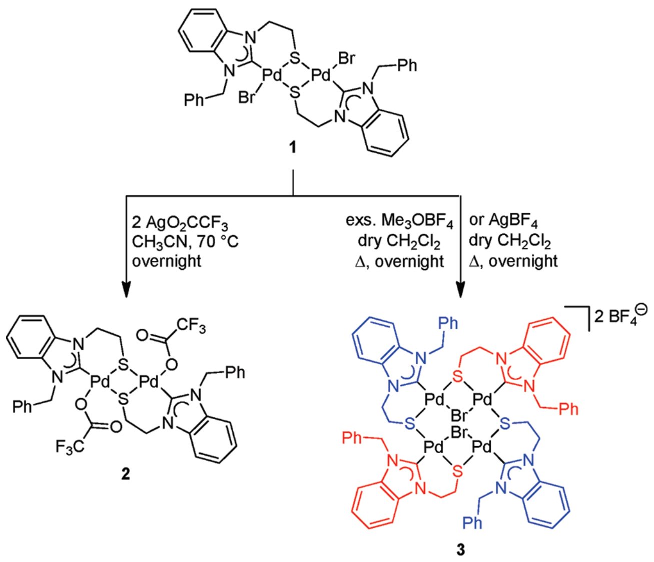
Scheme 3. Formation of Complexes 2 and 3



two independent molecules of complex **2** in the unit cell. Due to the similarities, the parameters of only one molecule of **2** are discussed. Its molecular structure depicted in Figure 2 shows the successful replacement of the bromido ligands in **1** by monodentate trifluoroacetato ligands. The dihedral angles between the carbene ring planes and the [$PdCS_2O$] coordination planes have further decreased to 45.1(1) and 49.7(1)° compared to those in the precursor **1**. The Pd−O bond distances of 2.080(3) Å are quite comparable with reported values for other mixed Pd−carboxylato/NHC complexes.[8a−e] More important, the halo−carboxylato exchange leads to a notable shortening of the trans-disposed Pd−S bonds to 2.2754(11) and 2.2689(11) Å, respectively. Presumably, this ligand substitution leads to more Lewis acidic metal centers, which in turn results in a higher electron donation of the thiolato functions and consequently strengthening of the Pd−S bonds. The stronger binding of the thiolato donors may also explain the aforementioned decrease in dihedral angles. Other parameters, including the hinge angle (117.89(4)°), remain largely unaffected.

The successful S-alkylation of thiolato-bridged complexes of type **1** would allow for a convenient template-directed synthesis of thioether-functionalized NHC complexes. Thus, a series of electrophiles, including iodomethane and dimethyl sulfate, has been used in an attempt to alkylate the sulfur atoms of dimer **1**; however, this was to no avail, and only starting materials were reisolated. Again, the lower electron density at the sulfur atoms as a result of the bridging mode may be the reason they cannot be alkylated. Unexpectedly, the reaction of **1** with an excess of the strong alkylating agent Me_3OBF_4 led to the formation of the novel tetranuclear complex **3** (Scheme 3). Apparently, electrophilic attack occurred preferably at the bromido ligand, supposedly liberating CH_3Br and resulting in a rearrangement of the unsaturated complex fragments to tetranuclear **3**.

To verify the unusual role of Me_3OBF_4 as a halide-abstracting agent, **1** was treated with 1 equiv of $AgBF_4$. Indeed, this reaction furnished complex **3** as well. Consequently, Me_3OBF_4 can be regarded as a very useful metal-free alternative to the commonly used Ag-based and toxic Tl-based reagents. A dicationic base peak at *m/z* 827 corresponding to the [$M - 2BF_4$]$^{2+}$ fragment in the ESI spectrum confirms

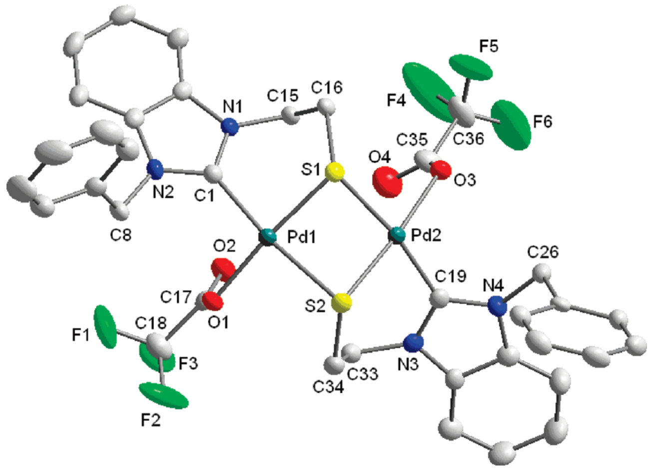


Figure 2. Molecular structure of one independent molecule of **2** showing 50% probability ellipsoids; hydrogen atoms and the CH_2Cl_2 molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd1−C1 1.988(4), Pd1−S1 2.2754(11), Pd1−S2 2.3611(11), Pd1−O1 2.080(3), Pd2−C19 1.980(4), Pd2−S2 2.2689(11), Pd2−S1 2.3709(11), Pd2−O3 2.080(3); C1−Pd1−S1 91.52(12), S1−Pd1−S2 81.23(4), S2−Pd1−O1 94.42(9), O1−Pd1−C1 92.67(14), C1−Pd1−S2 172.39(12), S1−Pd1−O1 174.44(9), C19−Pd2−S2 90.06(13), S2−Pd2−S1 81.15(4), S1−Pd2−O3 94.96(9), O3−Pd2−C19 93.72(15), C19−Pd2−S1 170.95(13), S2−Pd2−O3 175.26(9), Pd1−S1−Pd2 81.00(3), Pd1−S2−Pd2 81.34(4).

the formation of **3**. Its ^{1}H NMR spectrum shows a complicated pattern consisting of 11 signals for all methylene groups, indicating the presence of inequivalent chelating thiolato-NHC ligands in the complex. In line with this proposal, two carbene peaks appear in the ^{13}C NMR spectrum at 168.1 and 166.0 ppm, respectively.

The solid-state molecular structure of **3** was finally confirmed by X-ray diffraction analysis on single crystals obtained by diffusing ether into a concentrated DMF solution (Figure 3). Each of the four Pd(II) centers is coordinated by one carbene, one μ-bromido, and two μ-thiolato ligands in a square-planar fashion. As found in solution, there are two types of thiolato-NHC ligands in the molecule. The removal of one bromido ligand in **1** leads to the cleavage of one Pd−S bond and subsequent rearrangement/aggregation to form tetrameric **3**. An interesting feature of complex **3** is an eight-membered square consisting of alternating four palladium and four sulfur atoms with dimensions of 4.653(5) Å × 4.662(5) Å. The sulfur atoms form the corners of this [Pd_4S_4] macrocycle, which resembles a Pd_4 system bearing remote dicarbene ligands reported recently.[9] Two carbene moieties are each found above and below the plane spanned by this square. As a consequence, the two bridging bromido ligands trans to these carbenes are found on opposite sides. The presence of two pairs of inequivalent carbenes is reflected in the significantly different orientation of their ring planes with respect to the [$PdCS_2Br$] coordination (56.6(4) and 51.0(3)°) and the [Pd_4S_4] macrocyclic planes (59.5(3) and 55.1(4)°). The Pd−Br bonds of 2.5382(15) and 2.5268(16) Å, respectively, are as expected elongated compared to those in **1** (2.4401(5) and 2.4652(5) Å), since the μ-bromido ligands experience the trans influence of two carbenes.

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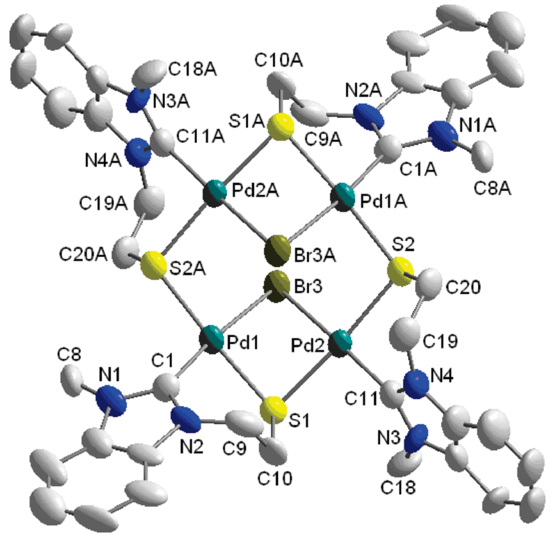
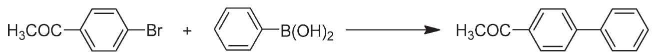


Figure 3. Molecular structure of **3** showing 50% probability ellipsoids; hydrogen atoms, BF_4^- counteranions, DMF molecules, H_2O molecules, and phenyl rings are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd1−C1 1.956(12), Pd1−S2A 2.334(4), Pd1−Br3 2.5382(15), Pd1−S1 2.321(4), Pd2−S1 2.318(3), Pd2−Br3 2.5268(16), Pd2−S2 2.350(4), Pd2−C11 1.986(13); C1−Pd1−S1 90.5(4), C1−Pd1−S2A 91.6(4), S2A−Pd1−Br3 94.60(9), Br3−Pd1−S1 83.26(9), Br3−Pd2−S1 83.58(9), Br3−Pd2−S2 94.79(10), S2−Pd2−C11 88.5(4), C11−Pd2−S1 93.9(4), Pd1−Br3−Pd2 76.48(4), Pd1−S1−Pd2 85.02(12), Pd1−S2A−Pd2A 103.31(13).

Catalysis. Despite often being regarded as catalyst poisons,[10] sulfur-containing compounds have become versatile donors in transition-metal chemistry. Nevertheless, some complexes of thioether-functionalized phosphite, phosphine, and NHC ligands have shown catalytic activities in reactions, such as allylic alkylations,[11] hydroformylations,[12] hydrogenations,[13] and Suzuki−Miyaura[4d] and Mizoroki−Heck reactions.[4e] More recently, dimeric phosphino−thiolato Pd(II) complexes were also reported to be highly active in the catalytic Suzuki−Miyaura coupling reaction at low catalyst loading.[14] For example, using 0.001 mol % catalyst, 91% yield was achieved with 4-bromoacetophenone and phenylboronic acid in dioxane at 140 °C in the presence of K_2CO_3 after 6 h. Encouraged by this finding, dimeric **1** was tested for its catalytic activity under the same reaction conditions, affording a quantitative yield (Table 1, entry 1) and showing the superiority of NHC complex **1** over its phosphine analogue. Further investigation revealed that the temperature can be lowered to 120 °C (entry 2) and even to 100 °C without compromising the yield when the reaction time was prolonged to 22 h (entry 3).

Table 1. Suzuki−Miyaura Coupling Reactions[a] Catalyzed by Complexes 1−3



entry	catalyst	temp (°C)	solvent	t (h)	yield (%)[b]	TON	TOF (h^{-1})
1	**1**	140	dioxane	6	>99	100 000	16 667
2	**1**	120	dioxane	6	>99	100 000	16 667
3	**1**	100	dioxane	22	>99	100 000	4 545
4	**1**	100	H_2O	22	>99	100 000	4 545
5	**1**	80	dioxane	24	48	48 000	2 000
6	**1**	80	H_2O	24	>99	100 000	4 167
7	**1**	60	dioxane	24	0	0	0
8	**1**	60	H_2O	24	84	84 000	3 500
9	**1**	40	H_2O	48	4	4 000	83
10	**2**	60	H_2O	24	>99	100 000	4 167
11	**3**[c]	60	H_2O	24	48	96 000	4 000

[a] Reaction conditions: 1 mmol of 4-bromoacetophenone; 1.4 mmol of phenylboronic acid; 1.4 mmol of K_2CO_3; 1 mL of solvent; 0.001 mol % of precatalyst. [b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs. [c] 0.0005 mol % of **3**.

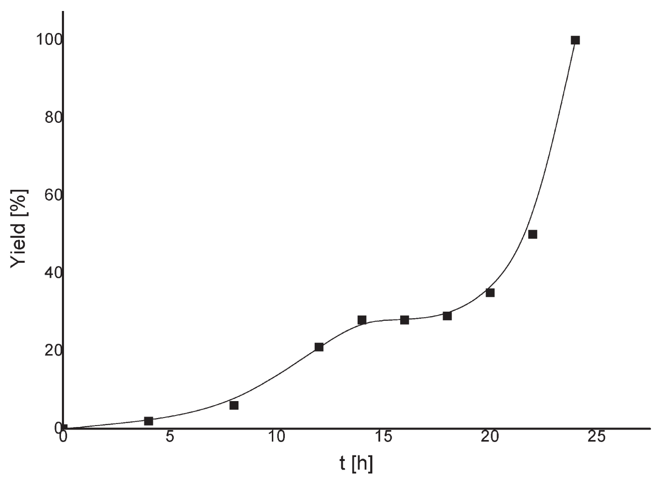


Figure 4. Concentration/time diagram (yield (%), time (h)) for the Suzuki−Miyaura coupling reaction of 4-bromoacetophenone and phenylboronic acid catalyzed by **2**.

Since water has been reported to be beneficial for the Suzuki−Miyaura coupling reaction,[15] we also tested its suitability as an environmentally benign solvent. Indeed, the coupling at 100 °C gave quantitative yield (entry 4). At a lower temperature of 80 °C, H_2O proves to be a superior solvent, as the yield remained quantitative (entry 6), while a drop to 48% was observed in dioxane (entry 5). When the temperature was further decreased to 60 °C, no coupling reaction was detected in dioxane (entry 7), while a good yield of 84% was still obtained in H_2O (entry 8). At temperatures below 60 °C, the yield dropped dramatically in H_2O as well (entry 9).

A comparative study on the activities of all three thiolato-NHC complexes **1−3** (entries 8, 10, and 11) under these mild reaction conditions revealed that **2** is the best precatalyst. Apparently, the replacement of the bromido ligands in **1** with more labile trifluoroacetato ligands results in enhanced

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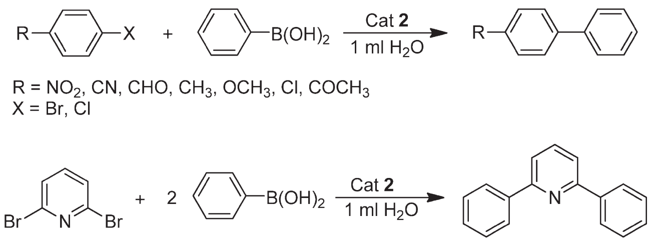
Table 2. Suzuki−Miyaura Coupling Reactions[a] Catalyzed by Complex 2



entry	aryl halide	catalyst load (mol %)	temp (°C)	t (h)	yield (%)[b]	TON	TOF (h^{-1})
1	4-bromobenzonitrile	0.001	60	24	> 99	100 000	4 167
2	1-bromo-4-nitrobenzene	0.001	60	42	90	90 000	2 143
3	4-bromobenzaldehyde	0.001	80	23	> 99	100 000	4 348
4	2,6-dibromopyridine[c]	0.0025	100	48	> 99	20 000	417
5	4-bromotoluene	0.0025	100	20	97	38 800	1 940
6	4-bromoanisole	0.0025	100	24	86	34 400	1 433
7	1-bromo-4-chlorobenzene	0.0025	100	24	72[d]	28 800	1 200
8	4-chlorobenzaldehyde	0.1	100	72	41[e]	410	5.7

[a] Reaction conditions: 1 mmol of aryl halide; 1.4 mmol of phenylboronic acid; 1.4 mmol of K_2CO_3; 1 mL of H_2O; the desired amount of precatalyst. [b] Yields were determined by ^1H NMR spectroscopy for an average of two runs. [c] 0.5 mmol of 2,6-dibromopyridine. [d] Isolated yield. [e] With addition of 1.0 equiv of $[N(n\text{-}C_4H_9)_4]Br$.

activities of **2**.[8] The lability of such ligands allows an easier ligand displacement, which in turn facilitates the formation of catalytically active species and, thus, promotes catalyst initiation. The poor performance of the higher aggregate **3**, on the other hand, is probably due to the strongly bridging bromido and thiolato ligands hampering the formation of active Pd(0) species.

Having identified the best precatalyst, **2**, a more detailed kinetic study was carried out on the coupling of 4-bromoacetophenone and phenylboronic acid at 0.001 mol % catalyst loading (Figure 4) to gain more insights into its catalytic behavior. The concentration/time profile shows that the reaction rate is rather low during a long period of about 22 h, after which the reaction exponentially completes within 2 h. Although the exact reason for the sluggish reaction at the beginning is not known yet, it may be due to a complicated dimer−monomer equilibrium[14,16] prior to catalyst initiation. Furthermore, the shape of the reaction profile suggests the involvement of various catalytically active species prior to the formation of the most active catalyst. It is commonly agreed that catalytically active species are generally monomeric,[16] which would also indirectly explain the poor performance observed for the tetranuclear complex **3**. The latter can be regarded as a tetramer, in which a tetramer−monomer dissociation is greatly hampered due to multiple strong bridging ligands.

To further test its efficiency, precatalyst **2** was subjected to the coupling of other aryl halides in pure water, and the results are summarized in Table 2. Generally, complex **2** showed good activities with activated bromo substrates (entries 1−3) at low loading (0.001 mol %) and under mild reaction conditions (60 or 80 °C). The coupling of 2 equiv of phenylboronic acid with 2,6-dibromopyridine was equally successful, giving quantitative yield (entry 4). For deactivated aryl bromides, the catalyst load and temperature were raised to 0.0025 mol % and 100 °C, respectively, to obtain good yields (entries 5−7). The catalyst, however, shows its limitation in the coupling with aryl chlorides. The best yield of 41% was obtained when 0.1 mol % of **2** was employed in the presence of 1 equiv of TBAB as a promoter (entry 8).

Conclusion

We have reported two methods (1 and 2) for synthesis of the new thiolato-bridged dimeric Pd(II) benzimidazolin-2-ylidene complex **1**, of which the pathway through in situ hydrolysis of a thioester (method 2) is more desirable due to its ease and convenience. Subsequent reaction of **1** with AgO_2CCF_3 gave rise to the mixed carboxylato−thiolato carbene complex **2**. The treatment of **1** with excess Me_3OBF_4 or 1 equiv of $AgBF_4$ led to the abstraction of one bromido ligand and subsequent rearrangement/dimerization to afford the tetranuclear species **3** featuring a macrocyclic $[Pd_4S_4]$ square. The unusual reactivity of Me_3OBF_4 as a halide-abstracting agent is remarkable and is believed to be of great synthetic use in cases where soft Ag^+ and toxic Tl^+ ions are interfering and are undesirable. All complexes have been fully characterized and their molecular structures determined by X-ray diffraction analyses. Catalytic studies reveal that dimeric complexes **1** and **2** show good activities at low loadings toward aqueous Suzuki−Miyaura couplings despite carrying thiolato functions, which are usually regarded as catalyst poisons. Research in our laboratory is ongoing to extend the straightforward and versatile coordination chemistry of thiolato-functionalized NHCs to other transition metals and also to aim at bigger thiolato-bridged aggregates as an entry to metallo-NHC-based supramolecular chemistry. We are also further exploring the feasibility of Meerwein's salts as alternative halide-abstracting agents.

Experimental Section

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. Salt **A** was prepared according to a previously reported method.[4e] ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^1H, ^{13}C) or

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Table 3. Selected X-ray Crystallographic Data for Complexes 1, 2·CH_2Cl_2 and 3·2DMF·O[a]

	1	2·CH_2Cl_2	3·2DMF·O[a]
formula	$C_{32}H_{30}Br_2N_4Pd_2S_2$	$C_{36}H_{30}F_6N_4O_4Pd_2S_2\cdot CH_2Cl_2$	$C_{64}H_{60}B_2Br_2F_8N_8Pd_4S_4\cdot C_6H_{14}N_2O_3$
fw	907.34	1058.49	1990.67
color, habit	yellow, block	yellow, block	yellow, needle
cryst size (mm)	0.40 × 0.12 × 0.10	0.36 × 0.36 × 0.06	0.60 × 0.07 × 0.06
temp (K)	223(2)	100(2)	100(2)
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	*Pbca*	$P2_1/n$
a (Å)	9.6224(3)	20.9496(7)	12.922(3)
b (Å)	15.5833(5)	21.0979(7)	13.527(3)
c (Å)	21.3048(7)	36.6305(13)	23.326(5)
α (deg)	90	90	90
β (deg)	90	90	91.314(5)
γ (deg)	90	90	90
V (Å^3)	3194.63(18)	16 190.4(10)	4076.4(14)
Z	4	16	2
D_c (g cm^{-3})	1.887	1.737	1.622
radiation used	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	3.787	1.196	2.018
θ range (deg)	1.62−27.50	1.11−27.50	1.74−25.00
no. of unique data	7216	18 607	7177
max, min transmissn	0.7032, 0.3126	0.9317, 0.6727	0.8885, 0.3772
final R indices ($I > 2\sigma(I)$)	R1 = 0.0322, wR2 = 0.0621	R1 = 0.0490, wR2 = 0.1094	R1 = 0.0869, wR2 = 0.2116
R indices (all data)	R1 = 0.0376, wR2 = 0.0636	R1 = 0.0667, wR2 = 0.1163	R1 = 0.1525, wR2 = 0.2448
goodness of fit on F^2	1.000	1.083	1.027
peak/hole (e Å^{-3})	1.060/−0.389	1.478/−0.827	1.089/−0.711

[a] No hydrogen atoms were added to this water molecule.

externally to CF_3CO_2H (^{19}F NMR). ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin−Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Thioester-Functionalized Benzimidazolium Bromide B. A mixture of salt **A** (792 mg, 2 mmol) and $KSCOCH_3$ (274 mg, 2.4 mmol) in CH_3CN (20 mL) was stirred at ambient temperature overnight. The resulting suspension was filtered, and the solvent of the filtrate was removed in vacuo. The resulting solid was washed with THF (3 × 20 mL) to give the product as an off-white solid (584 mg, 1.49 mmol, 75%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.11 (s, 1 H, NCHN), 8.17 (d, ^3J(H,H) = 8.1 Hz, 1 H, Ar H), 7.97 (d, ^3J(H,H) = 8.1 Hz, 1 H, Ar H), 7.68 (m, 2 H, Ar H), 7.52 (d, 2 H, Ar H), 7.40 (m, 3 H, Ar H), 5.84 (s, 2 H, NCH_2Ph), 4.75 (t, ^3J(H,H) = 6.3 Hz, 2 H, NCH_2), 3.44 (t, ^3J(H, H) = 6.3 Hz, 2 H, CH_2S), 2.27 (s, 3 H, $COCH_3$). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): 194.7 (s, CO), 142.7 (s, NCHN), 134.0, 131.2, 130.7, 128.9, 128.6, 128.1, 126.7, 113.9, 113.8 (s, Ar C), 49.8 (s, NCH_2Ph), 46.2 (s, NCH_2), 30.4 (s, CH_3), 27.8 (s, CH_2S). MS (ESI): m/z 311 [M − Br]$^+$.

Thiol-Functionalized Benzimidazolium Bromide C. To a MeOH (5 mL) solution of salt **B** (82 mg, 0.21 mmol) was added aqueous HBr solution (2 mL, 2 M). The mixture was degassed and heated to reflux under nitrogen overnight. The mixture was cooled to ambient temperature, and all the volatiles were removed in vacuo to give the product as a white solid (67 mg, 0.19 mmol, 92%). ^{1}H NMR (500 MHz, CD_3CN): δ 9.69 (s, 1 H, NCHN), 7.97 (d, ^3J(H,H) = 8.2 Hz, 1 H, Ar H), 7.81 (d, ^3J(H,H) = 8.2 Hz, 1 H, Ar H), 7.68 (m, 2 H, Ar H), 7.51 (m, 2 H, Ar H), 7.46 (m, 3 H, Ar H), 5.71 (s, 2 H, NCH_2Ph), 4.67 (t, ^3J(H,H) = 6.3 Hz, 2 H, NCH_2), 3.07 (t, ^3J(H,H) = 6.3 Hz, 2 H, CH_2S), 2.72 (br s, 1 H, SH). ^{13}C{^{1}H} NMR (125.77 MHz, CD_3CN): 142.7 (s, NCHN), 134.0, 132.4, 132.2, 130.0, 129.9, 129.3, 127.96, 127.95, 114.59, 114.57 (s, Ar C), 51.6 (s, NCH_2Ph), 50.4 (s, NCH_2), 24.4 (s, CH_2S). MS (ESI): m/z 269 [M − Br]$^+$.

Dinuclear Complex 1. **Method 1.** A mixture of salt **C** (67 mg, 0.19 mmol) and $Pd(OAc)_2$ (43 mg, 0.19 mmol) was heated under reflux in degassed CH_3CN under nitrogen overnight. The resulting brown solid was filtered and dissolved in CH_2Cl_2 (10 mL). The mixture was filtered, the residue was washed with CH_2Cl_2 (2 × 10 mL), and the filtrate was collected and dried under vacuum to give the product as a yellow solid (66 mg, 0.073 mmol, 76%).

Method 2. A mixture of salt **B** (117 mg, 0.3 mmol) and $Pd(OAc)_2$ (67 mg, 0.3 mmol) in DMSO (5 mL) was stirred at 80 °C overnight. The resulting yellow solid product was filtered and washed with H_2O (3 × 20 mL). A second crop of the product can be isolated from the filtrate after vacuum distillation, washing with H_2O (3 × 20 mL), and subsequent purification by chromatography on a short plug of silica using ethyl acetate (101 mg, 0.111 mmol, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.40 (m, 6 H, Ar H), 7.36−7.19 (m, 12 H, Ar H), 6.63 (d, ^2J(H,H) = 15.6 Hz, 2 H, NC*H*HPh), 5.58 (d, ^2J(H,H) = 15.6 Hz, 2 H, NCH*H*Ph), 4.88 (ps-d, 2 H, NC*H*H), 4.63 (ps-t, 2 H, NCH*H*), 3.90 (ps-d, 2 H, C*H*HS), 2.10 (ps-t, 2 H, CH*H*S). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 175.4 (s, NCN), 136.4, 134.9, 134.3, 129.5, 128.7, 128.3, 124.44, 124.40, 112.7, 111.2 (s, Ar H), 53.9 (s, NCH_2Ph), 52.3 (s, NCH_2), 26.8 (s, CH_2S). Anal. Calcd for $C_{32}H_{30}Br_2N_4Pd_2S_2$: C, 42.36; H, 3.33; N, 6.17. Found: C, 42.50; H, 3.50; N, 6.06. MS (ESI): m/z 829 [M − Br]$^+$.

Dinuclear Complex 2. A mixture of **1** (87 mg, 0.096 mmol) and AgO_2CCF_3 (42 mg, 0.192 mmol) was suspended in CH_3CN (10 mL) and heated at 70 °C overnight shielded from light. The reaction mixture was filtered over Celite, and the solvent of the filtrate was evaporated off to afford the product quantitatively as a yellow solid (94 mg, 0.096 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43−7.30 (m, 14 H, Ar H), 7.23 (m, 4 H, Ar H), 5.95 (d, ^2J(H,H) = 15.8 Hz, 2 H, NC*H*HPh), 5.56 (d, ^2J(H,H) = 15.8 Hz, 2 H, NCH*H*Ph), 4.87 (ps-t, 2 H, NC*H*H), 4.77 (ps-d, 2 H, NCH*H*), 2.69 (ps-d, 2 H, C*H*HS), 2.01 (ps-t, 2 H, CH*H*S). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 171.4 (s, NCN), 161.5 (q, ^2J(C,F) = 35.7 Hz, COO), 135.1, 133.6, 133.2, 128.9, 128.2, 127.2, 124.1, 124.0 (s, Ar H), 115.7 (q, ^1J(C,F) = 291.4 Hz, CF_3), 112.1, 110.7 (s, Ar H), 51.4 (s, NCH_2Ph), 50.6 (s, NCH_2), 24.9 (s, CH_2S). ^{19}F NMR (282.37 MHz, $CDCl_3$): 2.02 (s, CF_3). Anal. Calcd for $C_{36}H_{30}F_6N_4O_4Pd_2S_2$: C, 44.41; H, 3.11; N, 5.75. Found: C, 44.35; H, 3.05; N, 5.59. MS (ESI): m/z 861 [M − O_2CCF_3]$^+$, 373 [M − $2O_2CCF_3$]$^{2+}$.

Tetranuclear Complex 3. **Method 1.** A mixture of **1** (91 mg, 0.1 mmol) and Me_3OBF_4 (44 mg, 0.3 mmol) in dry CH_2Cl_2 (10 mL) was heated under reflux overnight. The resulting mixture was filtered, and the product was obtained as a yellow powder (52 mg, 0.028 mmol, 57%).

Method 2. A mixture of **1** (91 mg, 0.1 mmol) and $AgBF_4$ (19.5 mg, 0.1 mmol) in dry CH_2Cl_2 (10 mL) was heated under reflux overnight shielded from light. The precipitate was filtered and washed with CH_2Cl_2 (2 × 10 mL). The residue was triturated with DMF (3 × 10 mL) and the DMF solutions filtered through Celite. The solvent of the filtrate was removed under vacuum to afford the product as a yellow solid (62 mg, 0.034 mmol, 68%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.06 (d, 2 H, Ar H), 7.80−7.74 (m, 4 H, Ar H), 7.55−7.26 (m, 30 H, Ar H), 6.17 (d, ^2J(H,H) = 15.8 Hz, 2 H, C*H*HPh), 5.96 (d, ^2J(H,H) = 15.8 Hz, 2 H, CH*H*Ph), 5.85 (br s, 4 H, CH_2Ph), 5.61 (ps-d, 2 H, NC*H*H), 5.32 (ps-d, 2 H, NC*H*H), 5.24 (ps-t, 2 H, NCH*H*), 4.92 (ps-t, 2 H, NCH*H*), 3.96 (ps-d, 2 H, C*H*HS), 2.64 (ps-t, 2 H, C*H*HS), 2.21 (ps-t, 2 H, CH*H*S), 1.91 (ps-d, 2 H, CH*H*S). $^{19}F\{^1H\}$ NMR (282.37 MHz, DMSO-d_6): −72.28 (s, $^{10}BF_4$), −72.33 (s, $^{11}BF_4$). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): 168.1 (s, NCN), 166.0 (s, NCN), 135.7, 135.6, 134.3, 133.8, 133.4, 129.4, 129.2, 128.8, 128.5, 128.0, 127.8, 127.3, 125.3, 125.2, 125.0, 112.9, 112.7 (s, Ar H), 52.4 (s, CH_2Ph), 51.7 (s, CH_2Ph), 51.6 (s, NCH_2), 51.3 (s, NCH_2), 33.3 (s, CH_2S), 33.1 (s, CH_2S). Anal. Calcd for $C_{64}H_{60}B_2Br_2F_8N_8Pd_4S_4$: C, 42.04; H, 3.31; N, 6.13. Found: C, 41.92; H, 3.30; N, 6.09. MS (ESI): *m*/*z* 827 $[M - 2BF_4]^{2+}$, 1136 $[M - BF_4]^+$.

Suzuki−Miyaura Catalysis. In a typical run, a reaction tube was charged with a mixture of aryl halide (1.0 mmol for monohalides, 0.5 mmol for dihalides), K_2CO_3 (1.4 mmol), phenylboronic acid (1.4 mmol), precatalyst, and solvent (1 mL). The reaction mixture was stirred at elevated temperature. After the desired reaction time, the mixture was cooled to ambient temperature, and dichloromethane (10 mL) was added. The organic layer was then washed with water (6 × 8 mL) and dried over Na_2SO_4. The solvent was allowed to evaporate, and the residue was analyzed by ^{1}H NMR spectroscopy.

X-ray Diffraction Studies. X-ray data for **1**, **2**·CH_2Cl_2, and **3**·2DMF·O were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 223(2) K (for **1**) or at 100(2) K (for **2**·CH_2Cl_2 and **3**·2DMF·O) with the SMART suite of programs.[17] Data were processed and corrected for Lorentz and polarization effects with SAINT[18] and for absorption effects with SADABS.[19] Structural solution and refinement were carried out with the SHELXTL suite of programs.[20] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H atoms were put at calculated positions with exception of the water molecule in **3**·2DMF·O. A summary of the most important crystallographic data is given in Table 3.

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Supporting Information Available: CIF files giving crystallographic data for **1**, **2**·CH_2Cl_2 and **3**·2DMF·O. This material is available free of charge via the Internet at http://pubs.acs.org.

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