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The Template Effect of Palladium(II): Synthesis, Characterization, and Crystal Structures of 2,4-Substituted 1,3,5-Triazapentadienatopalladium(II) Complexes

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The reaction of $LiN(SiMe_3)_2$ with two equivalents of 2-, 3-, or 4-cyanopyridine followed by the addition of half an equivalent of $[PdCl_2(PhCN)_2]$ gives neutral 1,3,5-triazapentadienato complexes of the general formula [Pd{HNC(Py)NC(Py)NH}$_2$] (Py = 2-pyridyl **1**, 3-pyridyl **2**, 4-pyridyl **3**). When the above reaction was carried out with benzonitrile and then 3- or 4-cyanopyridine was added followed by half an equivalent of $[PdCl_2(PhCN)_2]$ neutral unsymmetrical 1,3,5-triazapentadienato complexes of the general formula [Pd{HNC(Ph)NC(Py)NH}$_2$] (Py = 3-pyridyl **4**, 4-pyridyl **5**) were obtained. When $LiN(SiMe_3)_2$ was treated with one equivalent of benzonitrile in THF, followed by the addition of a quarter of an equivalent of anhydrous palladium chloride and workup in air, the trinuclear complex tetrakis(benzamidinato)bis(2,4-diphenyl-1,3,5-triazapentadienato)tripalladium(II) (**6**) was obtained as yellow crystals in 19 % yield. All complexes were fully characterized by elemental analysis, ^1H NMR spectroscopy, and mass spectrometry. The solid-state structures of compounds **2**, **3**, and **6** were determined by X-ray crystallography. Structural analyses revealed that the 2,4-bis(pyridyl)-1,3,5-triazapentadienyl ligands in **2** and **3** behave as didentate ligands to form six-membered rings with the metal ion. For **6**, the 2,4-diphenyl-1,3,5-triazapentadienyl ligands also behave as didentate ligands to form six-membered rings with the metal ion, whereas the amidinato ligands behave as bridging didentate ligands.

Introduction

Didentate, monoanionic, nitrogen-based L–X$^-$ ligands and their complexes are one of the subjects of intense study in the field of amidinates.[1] Among this class of compounds, the coordination chemistry and potential application in catalysis of β-diketiminato ligands and their metal complexes have received significantly increasing attention recently. A series of β-diketiminate complexes have been synthesized by the nucleophilic addition reaction of α-hydrogen-free nitriles to substituted methyllithiums, and the catalytic properties of some of these complexes have been investigated.[2,3] Similar diimine ligands, namely *N*-phosphanyl-β-diimine ligands,[4] sterically demanding aromatic diimine ligands,[5] and their complexes have also been developed. Many metal β-diiminate complexes, such as magnesium,[6] aluminum,[7] nickel and palladium,[8] zirconium,[9] rhodium,[10] gallium,[11] and scandium[12] etc. have been reported. Moreover, these diimine and similar complexes have been found to be effective catalysts for the polymerization of ethylene.[8,13]

However, there are very few reports on the isoelectronic 1,3,5-triazapentadienato ligands and their complexes. Transition metal complexes with chelating 1,3,5-triazapentadienato ligands have been isolated by (i) evaporating a methanol solution of nickel chloride hexahydrate and acetamidine,[14] (ii) treating lithium benzamidinate with $[PtCl_2(PhCN)_2]$,[15] (iii) treating acetonitrile with the dinuclear nickel complex $[Ni_2(\mu\text{-}OH)_2(tpa)_2](ClO_4)_2$ [tpa = tris(2-pyridylmethyl)amine],[16] (iv) treating triazine with copper acetate,[17] and (v) a coupling reaction between amidine and ligated nitriles.[18] Bis(perfluoroalkyl)triazapentadiene and its transition metal complexes have also been synthesized.[19,20]

We have synthesized the complex bis[2,4-bis(*n*-pyridyl)-1,3,5-triazapentadienato]nickel(II) (*n* = 3 or 4) in about 30% yield by the reaction of anhydrous nickel(II) chloride with the addition product of cyanopyridine with $LiN(SiMe_3)_2$.[21] We have since extended our study to $[PdCl_2(PhCN)_2]$ and the results are described here. Depending on the nature of the aryl group, $[PdCl_2(PhCN)_2]$ reacts with the addition product of lithium *N*,*N*′-bis(trimethylsilyl)arylamidinate, $[(Me_3Si)N(Li)C(Ar)N(SiMe_3)]$ (Ar = phenyl, 2-pyridyl, 3-pyridyl, 4-pyridyl) and an aryl nitrile to give the neutral mononuclear triazapentadienyl complexes bis(2-Ar-4-Ar′-1,3,5-triazapentadienato)palladium(II) (Ar = Ar′ = 2-pyridyl **1**; Ar = Ar′ = 3-pyridyl **2**; Ar = Ar′ = 4-pyridyl **3**; Ar = Ph, Ar′ = 3-pyridyl **4**; Ar = Ph, Ar′ = 4-pyridyl **5**) and trinuclear triazapentadienyl complex tetrakis(benzamidinato)bis(2,4-diphenyl-1,3,5-triazapentadienato)tripalladium(II) (**6**; Scheme 1). This is in contrast to the reaction of $[MCl_2(PhCN)_2]$ (M = Pd or Pt) with lithium *N*,*N*′-diphenylbenzamidinate [PhN(Li)C(Ph)NPh],

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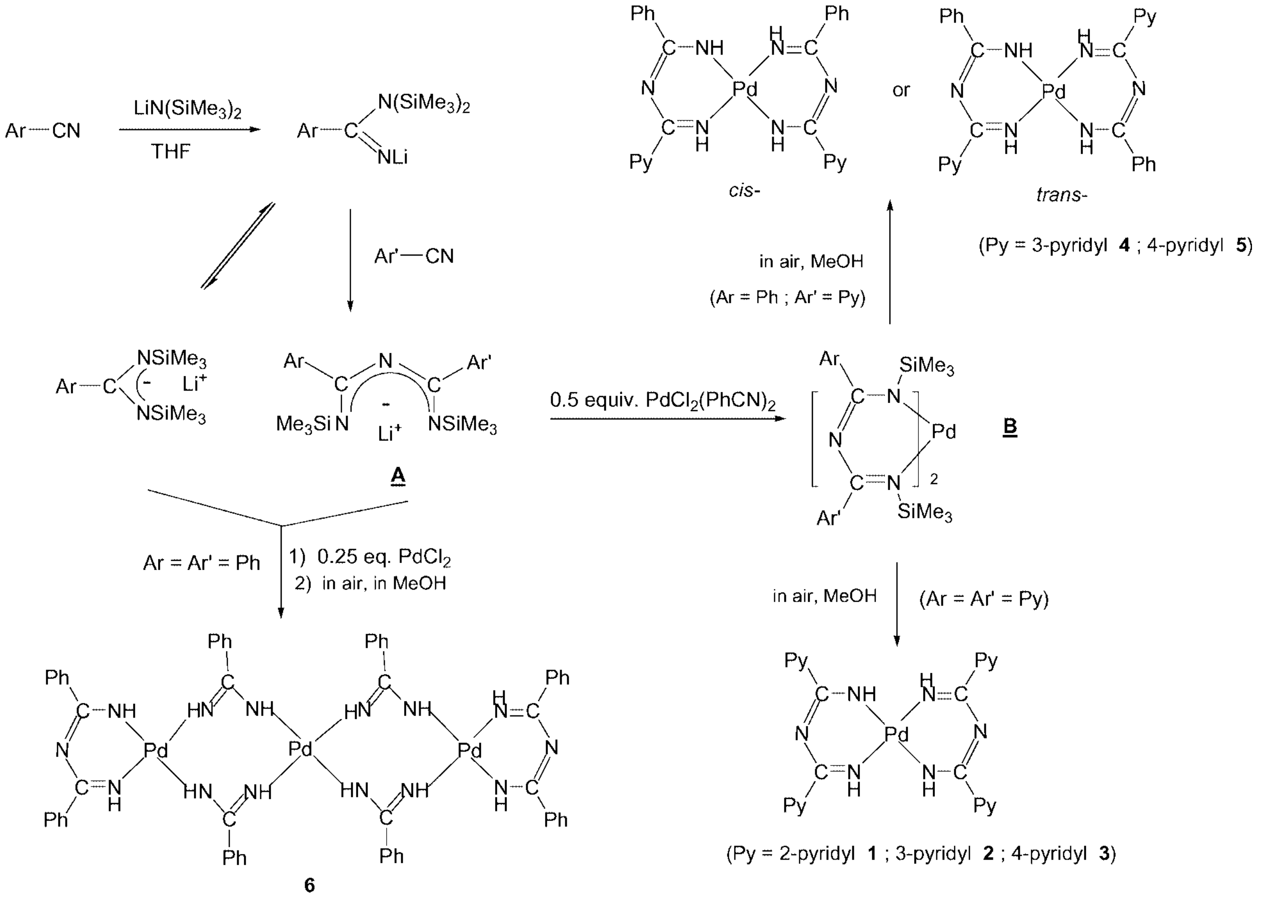

Scheme 1.

which gives the bis(amidinato) complexes [M{PhNC(Ph)-NPh}$_2$].[22] The fact that the palladium complexes are isolated with higher yields than the related nickel complexes and the formation of compound **6** suggest that palladium plays a more evident template role in the synthesis of 1,3,5-triazapentadienato metal complexes. In other words, palladium may be specially suited to stabilizing the six-membered ring formed by palladium and the 1,3,5-triazapentadienato ligand.

Result and Discussion

Synthesis and Structural Characterization

Yellow crystals of the neutral, symmetrical 2,4-disubstituted 1,3,5-triazapentadienato complexes [Pd{HNC(Py)-NC(Py)NH}$_2$] (Py = 2-pyridyl **1**; 3-pyridyl **2**; 4-pyridyl **3**), were obtained in good yields (71, 70, and 71 %, respectively) when LiN(SiMe$_3$)$_2$ was treated with two equivalents of 2-, 3-, or 4-cyanopyridine in THF, followed by the addition of half an equivalent of [PdCl$_2$(PhCN)$_2$] and workup in air. Elemental analyses and electrospray ionization high resolution mass spectroscopic (ESI-HRMS) data confirmed the formulation of the compounds. The ESI mass spectra (positive mode) of **1**–**3** exhibit the [M + 1]$^+$ peak at *m/z* 555.0947, 555.0944, and 555.1032, respectively, which deviate less than 10 ppm from the theoretical value of 555.0985 for the elemental composition $C_{24}H_{21}N_{10}Pd$. The observed isotopic distribution patterns of these peaks also match the expected theoretical signals.

Compounds **1**–**3** should have a similar structure. The solid-state structures of **2** and **3** were ascertained by X-ray crystallography. Perspective drawings of **2** and **3** are shown in Figures 1 and 2, respectively; selected bond lengths and angles are given in Table 1.

The structural analyses of **2** and **3** revealed that their structures are similar to the corresponding nickel(II) complexes [Ni{HNC(Py)NC(Py)NH}$_2$][21] and the analogous Pt complex [Pt{HNC(Ph)NC(Ph)NH}$_2$].[15] Both **2** and **3** are centrosymmetric with the palladium(II) ion adopting a square-planar geometry. The palladium(II) ion in **2** is located at the center of the plane defined by the four nitrogen atoms of the two didentate 1,3,5-triazapentadieno ligands [HNC(3-Py)NC(3-Py)NH]$^-$, with Pd–N distances of 1.980(3) [Pd(1)–N(1)] and 1.974(3) Å [Pd(1)–N(2)], and an N(1)–Pd(1)–N(2) angle of 87.12(12)°. Each didentate 1,3,5-triazapentadienato ligand forms a six-membered metallacycle with the metal ion. This six-membered ring is nearly planar with a mean deviation of 0.0278 Å from the plane. Within the 1,3,5-triazapentadieno ligand, the N(1)–C(1) [1.299(5) Å], C(1)–N(3) [1.353(5) Å], N(3)–C(7) [1.344(4) Å], and C(7)–N(2) [1.307(4) Å] distances are very

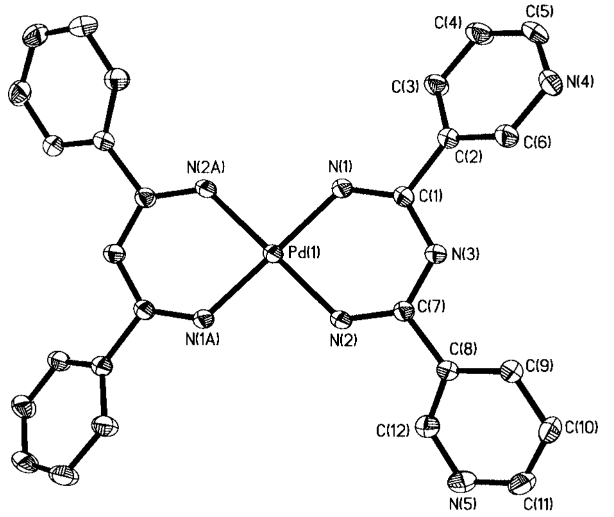

Figure 1. ORTEP drawing (30% probability level) of the molecular structure of **2**. Hydrogen atoms have been omitted for clarity.

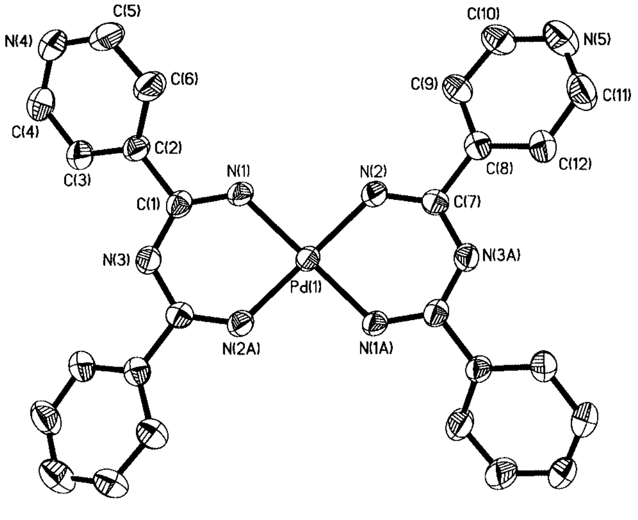

Figure 2. ORTEP drawing (30% probability level) of the molecular structure of **3**. Hydrogen atoms have been omitted for clarity.

similar, thereby indicating complete delocalization within the N–C–N–C–N framework. The plane of the six-membered ring forms dihedral angles of 37.8° and 30.7° with the N(4)- and N(5)-pyridyl planes, respectively, thus indicating that the N(4)-pyridyl and N(5)-pyridyl rings are not coplanar with the metal-containing six-membered ring.

Figure 2 shows the palladium(II) ion of **3** positioned at the center of the N(1)N(2)N(1A)N(2A) plane, with Pd–N distances of 1.980(4) [Pd(1)–N(1)] and 1.971(4) Å [Pd(1)–N(2)], and an N(1)–Pd(1)–N(2) angle of 92.38(16)°. Each didentate 1,3,5-triazapentadienato ligand forms a six-membered metallacycle with the metal ion. This six-membered ring is almost planar, with a mean deviation of 0.0086 Å from the plane. Within the 1,3,5-triazapentadienato ligand, the similarity between the N(1)–C(1) [1.316(6) Å], C(1)–N(3) [1.339(6) Å], N(3)–C(7A) [1.339(6) Å], and C(7A)–N(2A) [1.304(3) Å] distances shows complete delocalization within the N–C–N–C–N framework. The planes of the N(4)-pyridyl and N(5A)-pyridyl rings are not coplanar with the metal six-membered ring; they form a dihedral angle of 27.1° and 26.8° with the plane of the six-membered metallacycle, respectively.

When $LiN(SiMe_3)_2$ was treated with one equivalent of benzonitrile, then one equivalent of 3- or 4-cyanopyridine in THF, followed by the addition of half an equivalent of $[PdCl_2(PhCN)_2]$ and workup in air, the unsymmetrical complexes $[Pd\{HNC(Ph)NC(Py)NH\}_2]$ (Py = 3-pyridyl **4**; 4-pyridyl **5**) were obtained as yellow crystals in 31 and 27% yields, respectively. The formulation of the compounds was confirmed by elemental analyses and ESI-HRMS data. The ESI mass spectra (positive mode) of both compounds in methanol exhibit the corresponding $[M+1]^+$ peak at *m/z* 553.1106 for **4** and 553.1049 for **5**, both of which deviate by less than 10 ppm from the theoretical value of 553.1080 for the elemental composition $C_{26}H_{23}N_8Pd$. The observed isotopic distribution patterns of the $[M+1]^+$ peak also match the expected theoretical signals. It is clear that the lithium benzamidinate undergoes a nucleophilic addition reaction with 3-cyanopyridine or 4-cyanopyridine

Table 1. Selected bond lengths [Å] and bond angles [°] for compounds **2**, **3**, and **6**.

2		**3**		**6**			
Pd(1)–N(1)	1.980(3)	Pd(1)–N(1)	1.980(4)	Pd(1)–N(4)	1.986(10)	N(4)–Pd(1)–N(6)	88.5(4)
Pd(1)–N(2)	1.974(3)	Pd(1)–N(2)	1.971(4)	Pd(1)–N(6)	2.067(9)	N(1)–Pd(2)–N(2)	88.3(4)
N(1)–C(1)	1.299(5)	N(1)–C(1)	1.316(6)	Pd(2)–N(1)	1.998(9)	N(5)–Pd(2)–N(7)	86.8(4)
C(1)–N(3)	1.353(5)	C(1)–N(3)	1.339(6)	Pd(2)–N(2)	1.931(8)	Pd(1)–N(4)–C(15)	131.9(9)
N(3)–C(7)	1.344(4)	N(3)–C(7A)	1.339(6)	Pd(2)–N(5)	2.022(9)	N(4)–C(15)–N(5)	120.0(12)
C(7)–N(2)	1.307(4)	C(7)–N(2)	1.304(6)	Pd(2)–N(7)	2.044(8)	C(15)–N(5)–Pd(2)	125.9(9)
C(1)–C(2)	1.497(5)	C(1)–C(2)	1.487(6)	N(1)–C(1)	1.360(13)	Pd(1)–N(6)–C(22)	130.2(9)
C(7)–C(8)	1.498(5)	C(7)–C(8)	1.489(6)	C(1)–N(3)	1.238(15)	N(6)–C(22)–N(7)	125.9(11)
N(1)–Pd(1)–N(2)	87.12(12)	N(1)–Pd(1)–N(2)	92.38(16)	N(3)–C(8)	1.306(15)	C(22)–N(7)–Pd(2)	121.2(9)
Pd(1)–N(1)–C(1)	127.9(3)	Pd(1)–N(1)–C(1)	126.7(3)	C(8)–N(2)	1.391(12)	Pd(2)–N(1)–C(1)	124.4(9)
Pd(1)–N(2)–C(7)	128.3(3)	Pd(1)–N(2)–C(7)	128.4(4)	C(1)–C(2)	1.445(17)	N(1)–C(1)–N(3)	128.0(12)
N(1)–C(1)–N(3)	127.4(3)	N(1)–C(1)–N(3)	128.2(4)	C(8)–C(9)	1.500(17)	C(1)–N(3)–C(8)	127.9(11)
C(1)–N(3)–C(7)	121.7(3)	C(1)–N(3)–C(7A)	122.0(4)	N(4)–C(15)	1.332(15)	N(3)–C(8)–N(2)	122.9(12)
N(3)–C(7)–N(2)	127.0(3)	N(3A)–C(7)–N(2)	127.0(5)	C(15)–N(5)	1.305(15)	C(8)–N(2)–Pd(2)	128.2(9)
N(1)–C(1)–C(2)	119.8(3)	N(1)–C(1)–C(2)	117.8(4)	N(6)–C(22)	1.239(14)		
N(2)–C(7)–C(8)	118.8(3)	N(2)–C(7)–C(8)	119.6(4)	C(22)–N(7)	1.336(15)		
				C(15)–C(16)	1.504(15)		
				C(22)–C(23)	1.448(14)		

and $[PdCl_2(PhCN)_2]$ to form the respective palladium(II) complex. Attempts to grow crystals of **4** and **5** suitable for an X-ray diffraction study were unsuccessful. However, the structures of **4** and **5** are expected to be similar to those of **2** and **3**. Compounds **4** and **5** could adopt either a *cis* or a *trans* configuration (Scheme 1). Unfortunately, the existing spectroscopic data cannot distinguish between these two configurations.

When $LiN(SiMe_3)_2$ was treated with an excess amount of benzonitrile followed by addition of a quarter of an equivalent of $PdCl_2$, the neutral trinuclear palladium complex $[Pd_3\{[HNC(Ph)NC(Ph)NH]_2[\mu_2\text{-}HNC(Ph)NH]_4\}]$ (**6**) was isolated in low yield (19%). This contrasts with the reaction with anhydrous $NiCl_2$, which gave the ionic salt $[Ni\{H_2NC(Ph)NH\}_4]Cl_2$.[21] The solid-state structure of **6** was ascertained by X-ray crystallography; a perspective drawing is shown in Figure 3. Selected bond lengths and angles are also given in Table 1. This structural analysis revealed that **6** is centrosymmetric, with Pd(1) at the inversion center. There are two kinds of coordinated anions – benzamidinato and 2,4-diphenyl-1,3,5-triazapentadienato – and three palladium atoms in the molecule of **6**. All three palladium(II) ions adopt a square-planar geometry. The distance between two neighboring palladium atoms is 2.933 Å, which is too long for any significant interaction between the two metal centers. The N(2)–Pd(2)–N(1) and N(5)–Pd(2)–N(7) angles are 88.3(4)° and 86.8(4)°, respectively, and the N(4)–Pd(1)–N(6) angle is 88.5(4)°. The lengths of the bonds between palladium and the coordinated nitrogen atoms of the 2,4-bis(phenyl)-1,3,5-triazapentadienato ligand are 1.998(9) [Pd(2)–N(1)] and 1.931(8) Å [Pd(2)–N(2)], respectively. The Pd–N bond lengths between the palladium atoms and the coordinated nitrogen atoms of benzamidinato are 2.022(9) [Pd(2)–N(5)], 2.044(8) [Pd(2)–N(7)], 1.986(10) [Pd(1)–N(4)], and 2.067(9) Å [Pd(1)–N(6)], which are similar to the Pd–N distance [2.038(3) Å] in $[Pd\{PhNC(Ph)NPh\}_2]$.[22] The didentate 1,3,5-triazapentadienato ligand forms a six-membered metallacycle with the metal ion. This six-membered ring is nearly planar, with a mean deviation of 0.0224 Å from the plane. Within the 1,3,5-triazapentadieno ligand, the N(1)–C(1) [1.360(13)], C(1)–N(3) [1.238(15)], N(3)–C(8) [1.306(15)], and C(8)–N(2) [1.391(12) Å] distances are similar, thus indicating delocalization within the N–C–N–C–N framework. The plane of the six-membered ring forms dihedral angles of 35.1° and 2.5° with the C(2)–C(7) and C(9)–C(14) phenyl planes, respectively, presumably due to solid-state packing effects. This indicates that the C(9)–C(14) phenyl plane is coplanar with the metal six-membered ring.

There are two benzamidinato anions in half a molecule of **6**. Each of them forms a five-membered ring with two palladium ions. The five-membered rings Pd(1)N(4)C(15)N(5)Pd(2) and Pd(1)N(6)C(22)N(7)Pd(2) are nearly planar with a mean deviation of 0.0615 and 0.0399 Å from the plane, respectively. The N(4)–C(15) [1.332(15) Å] and C(15)–N(5) [1.305(15) Å] bond lengths are indicative of delocalization within the N–C–N framework, which is also the case for the N(6)–C(22) [1.239(14) Å] and C(22)–N(7) [1.336(15) Å] bonds. The Pd(1)N(4)C(15)N(5)Pd(2) and Pd(1)N(6)C(22)N(7)Pd(2) planes form a dihedral angle of 36.3° and 53.0° with the C(16)–C(21) and C(23)–C(28) phenyl planes, respectively. The dihedral angle between the two five-membered planes is 87.9°.

Template Effect of Palladium(II) for the Formation of 1,3,5-Triazapentadienato Complexes

The above discussion can be summarized as follows: (1) Under the same reaction conditions, the yields of compounds **2** (70%) and **3** (71%) are much higher than those

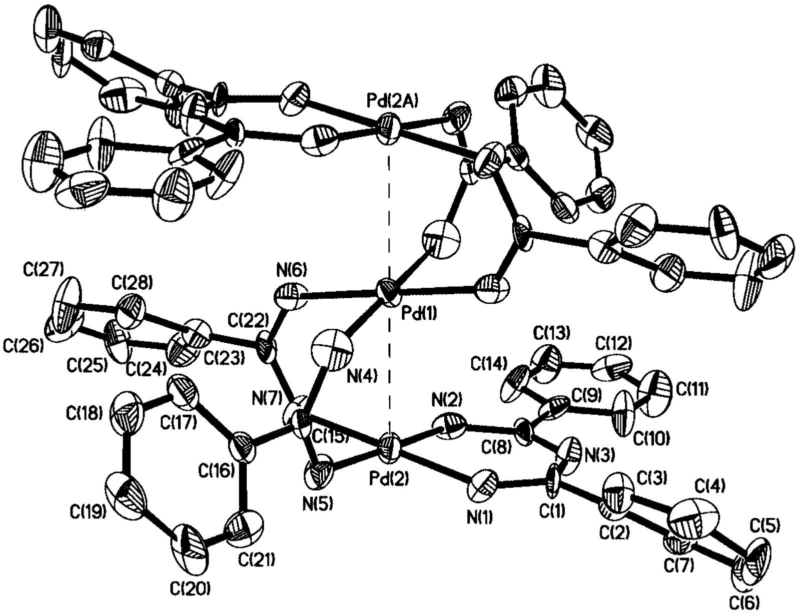

Figure 3. ORTEP drawing (30% probability level) of the molecular structure of **6**. Hydrogen atoms have been omitted for clarity.

for the corresponding nickel complexes (28 and 30%, respectively).[21]

(2) If $[PdCl_2(PhCN)_2]$ is replaced by $ZnCl_2$, under the same reaction conditions as for the preparation of compound **3**, the product is 4-pyridylamidinatozinc chloride instead of bis[2,4-bis(pyridyl)-1,3,5-triazapentadienato]zinc.[23]

(3) The ligand 2,4-bis(pyridyl)-1,3,5-triazapentadiene [HN=C(4-Py)N=C(4-Py)-NH_2] is not stable in air as it could not be isolated from the hydrolysis products obtained from the hydrolysis of the intermediate derived from reaction of lithium 4-pyridylamidinate with 4-cyanopyridine. If the hydrolysis product was analyzed very quickly after the hydrolysis, the $[M+1]^+$ peak (226.1198) could be found in the ESI spectra. Moreover, MS-MS analysis of the $[M+1]^+$ peak showed that [HN=C(4-Py)N=C(4-Py)NH_2] is cleaved into 4-cyanopyridine and 4-pyridylamidine.

(4) Rapid mass spectral analysis of the hydrolysis products derived from reaction of lithium benzamidinate with benzonitrile did not locate the $[M+1]^+$ peak of the ligand 2,4-diphenyl-1,3,5-triazapentadiene [HN=C(Ph)–N=C(Ph)-NH_2]. This indicates that the ligand cannot exist in air.

(5) Under the same reaction conditions as for compound **6**, but with nickel chloride instead of palladium chloride, the product was tetrakis(benzamidine)nickel chloride rather than the analogous nickel complex.[21]

From the observations mentioned above it is clear that the nickel or palladium center plays a key role in the formation of 1,3,5-triazapentadienato complexes. The lithium arylamidinate attacks another aryl nitrile followed by a 1,3-silyl shift to produce the 1,3,5-triazapentadienatolithium intermediate **A** (see Scheme 1). When palladium chloride is added to the reaction system, the 1,3,5-triazapentadienato metal intermediate complexes **B** are produced, and these are hydrolyzed during work up in air to give the stable bis(2,4-aryl-1,3,5-triazapentadienato)-coordinated metal complexes. It is clear that the square-planar geometry of nickel and palladium ions leads to a template effect in the synthesis. Moreover, the high yield of palladium complexes and the formation of compound **6** indicate that palladium is a very effective template for the formation of bis(2,4-aryl-1,3,5-triazapentadienato)palladium complexes.

Conclusions

We have developed a simple and effective method for the synthesis of symmetric and unsymmetrical 1,3,5-triazapentadienyl-based transition metal complexes. The 1,3,5-triazapentadienyl ligands, which are generated in situ by the interaction of amidinate with aryl nitrile, react with palladium and nickel ions to form a six-membered planar metallacycle. Structural analyses have revealed that the N–C–N–C–N framework within the 1,3,5-triazapentadienyl ligand is completely delocalized.

Experimental Section

General Procedures: All reactions were carried out under nitrogen in flame-dried Schlenk-type glassware on a dual manifold Schlenk line unless otherwise stated. Solvents were pre-dried prior to use. All chemicals used were of reagent grade and obtained from Aldrich or Fisher Scientific Chemical Company. NMR spectra were measured in [D_6]DMSO either on a Varian INOVA 400 MHz FT-NMR or a Bruker DRX-300 spectrometer. Fast atom bombardment (FAB) mass spectra were recorded with a Finnigan MAT SSQ710 mass spectrometer, and electrospray ionization high resolution mass spectra (ESI-HRMS) with a quadrupole time-of-flight (Q-TOF) mass spectrometer equipped with a turbo ionspray source (PE SCIEX API QSTAR Pulsar i, Applied Biosystem). IR spectra (KBr pellets) were recorded with a Perkin–Elmer Paragon 1000PC or Nicolet Nagan-IR 550 Series II FTIR spectrometer. Elemental analyses were performed with a Vario EL-III instrument.

Preparation of Bis[2,4-bis(2-pyridyl)-1,3,5-triazapentadienato]palladium(II) (1): 2-Cyanopyridine (0.416 g, 4.0 mmol) and $LiN(SiMe_3)_2$ (0.334 g, 2.0 mmol) were placed in THF (20 mL) at 0 °C. The resultant red solution was warmed to room temperature and stirred for an additional 2 h before cooling down to –78 °C. Anhydrous $[PdCl_2(PhCN)_2]$ (0.383 g, 1.0 mmol) was then added to the reaction mixture which was stirred at –78 °C for an hour before warming up to room temperature and allowed to react overnight. Solvent was then removed in vacuo. The reaction system was exposed to air, methanol (20 mL) was added to the residue and the solution was filtered. Slow evaporation of the methanol solution gave yellow crystals of **1**. Yield: 0.392 g (0.708 mmol, 71%); m.p. > 300 °C. MS (FAB, +ve): *m/z* 554.4 $[M]^+$. ESI-HRMS (in methanol, +ve) calcd. for $C_{24}H_{21}N_{10}Pd$: 555.0985; found 555.0947 $[M+H]^+$. ^1H NMR ([D_6]DMSO): NH protons: δ = 9.31 (s, 4 H); 2-pyridyl protons: δ = 8.79 (dd, *J* = 5.6 and 1.6 Hz, 4 H), 8.65 (d, *J* = 7.6 Hz, 4 H), 8.04 (td, *J* = 7.6 and 1.6 Hz, 4 H), 7.62 ppm (ddd, *J* = 7.6, 5.6 and 1.6 Hz, 4 H). IR (KBr): $\tilde{\nu}$ = 3448 m, 3286 s, 3057 w, 1576 s, 1550 vs, 1483 m, 1431 vs, 1265 w, 1241 w, 1057 m, 1997 m, 813 mm, 751 s, 708 s cm^{-1}. See also Table 2. $C_{24}H_{20}N_{10}Pd{\cdot}2H_2O$ (590.94): calcd. C 48.78, H 4.09, N 23.70; found C 48.65, H 4.14, N 23.50.

Table 2. Characteristic ^1H NMR and IR data for compounds **1**–**6**.

	^1H NMR NH protons [ppm]	IR [cm^{-1}] ν_{N-H}	$\nu^{[24]}$ for the 1,3,5-triazapentadienyl skeleton
1	9.31 (s, 4×1 H)	3448, 3286	1483, 1431 and 1265
2	8.81 (s, 4×1 H)	3406, 3299	1462, 1411 and 1302
3	9.01 (s, 4×1 H)	3327, 3283	1464, 1410 and 1301
4	9.26 (d, 2×1 H) 8.76 (s, 2×1 H)	3299	1472, 1421 and 1285
5	8.85 (s, 2×1 H) 8.79 (s, 2×1 H)	3430, 3317, 3231	1452, 1402 and 1295
6	8.22 (s, 2×1 H) 8.03 (m, 2×2 H) 7.75 (m, 2×2 H) 6.83 (s, 2×1 H)	3404, 3375, 3357	1472, 1445 and 1273

Preparation of Bis[2,4-bis(3-pyridyl)-1,3,5-triazapentadienato]palladium(II) (2): Compound **2** was prepared under the same reaction conditions as **1** from 3-cyanopyridine (0.416 g, 4 mmol), $LiN(SiMe_3)_2$ (0.334 g, 2.0 mmol), and anhydrous $[PdCl_2(PhCN)_2]$ (0.383 g, 1 mmol). Yellow crystals of **2** were obtained. Yield: 0.389 g (0.702 mmol, 70%); m.p. > 300 °C. MS (FAB, +ve): *m/z*: 554 $[M]^+$. ESI-HRMS (in methanol, +ve) calcd. for $C_{24}H_{21}N_{10}Pd$: 555.0985; found 555.0944 $[M+H]^+$. ^1H NMR ([D_6]DMSO): NH protons: δ = 8.82 (s, 4 H); 3-pyridyl protons: δ = 9.23 (s), 8.67 (d, *J* = 6.0 Hz, 4 H), 8.42 (d, *J* = 9.0 Hz, 4 H), 7.51 ppm (dd, *J* = 9.0 and 6.0 Hz, 4 H). IR (KBr): $\tilde{\nu}$ = 3576 w, 3406 w, 3299 s, 3061 m, 1589 s, 1548 s, 1462 s, 1411 s, 1302 s, 1196 w, 1028 m, 827 m, 732 s, 697 s cm^{-1}. See also Table 2. $C_{24}H_{20}N_{10}Pd{\cdot}2H_2O$ (590.94): calcd. C 48.78, H 4.09, N 23.70; found C 48.93, H 3.93, N 23.39.

Preparation of Bis[2,4-bis(4-pyridyl)-1,3,5-triazapentadienato]palladium(II) (3): Compound **3** was prepared under the same reaction conditions as **1** from 4-cyanopyridine (0.416 g, 4 mmol), LiN$(SiMe_3)_2$ (0.334 g, 2.0 mmol), and anhydrous $[PdCl_2(PhCN)_2]$ (0.383 g, 1 mmol). Yellow crystals of **3** were obtained. Yield: 0.392 g (0.708 mmol, 71%); m.p. > 300 °C. MS (FAB, +ve): *m/z* 554.4 [M]$^+$. ESI-HRMS (in methanol, +ve) calcd. for $C_{24}H_{21}N_{10}Pd$: 555.0985; found 555.1032 [M+H]$^+$. ^1H NMR ([D$_6$]DMSO): NH protons: δ = 9.02 (s, 4×1 H); 4-pyridyl protons: δ = 8.76 (d, *J* = 4.8 Hz, 8 H) and 8.02 (d, *J* = 4.8 Hz, 8 H). IR (KBr): $\tilde{\nu}$ = 3327 s, 3283 s, 3037 m, 1605 s, 1581 s, 1540 s, 1464 s, 1410 s, 1301 s, 1062 w, 1043 w, 1004 m, 841 m, 749 m, 704 s cm^{-1}. See also Table 2. $C_{24}H_{20}N_{10}Pd{\cdot}2H_2O{\cdot}0.5CH_3OH$ (606.96): calcd. C 48.48, H 4.32, N 23.08; found C 48.48, H 4.28, N 22.31.

Preparation of Bis[2-phenyl-4-(3-pyridyl)-1,3,5-triazapentadienato]-palladium(II) (4): Compound **4** was prepared under similar reaction conditions to **1**. Benzonitrile (0.26 mL, 2.5 mmol) and LiN$(SiMe_3)_2$ (0.418 g, 2.5 mmol) were placed in THF (20 mL) at 0 °C. The resultant yellow solution was warmed to room temperature and stirred for an additional 2 h. 3-Cyanopyridine (0.26 g, 2.5 mmol) was then added at room temperature and allowed to react overnight. Anhydrous $[PdCl_2(PhCN)_2]$ (0.479 g, 1.25 mmol) was then added to the reaction mixture at –78 °C which was stirred at this temperature for an hour before warming up to room temperature and allowed to react overnight. Solvent was then removed under vacuum. The reaction mixture was exposed to air, saturated with methanol (20 mL), and filtered. Slow evaporation of the methanol filtrate gave yellow crystals of **4**. Yield: 0.189 g (0.34 mmol, 27%); m.p. > 300 °C. ESI-HRMS (in methanol, +ve) calcd. for $C_{26}H_{23}N_8Pd$: 553.1080; found 553.1106 [M+H]$^+$. ^1H NMR ([D$_6$]DMSO): δ = 9.26 (d, *J* = 2.4 Hz, 2×1 H, NH) 8.76 (s, 2×1 H, NH), 8.69 (m, 2×2 H), 8.43 (m, 2×1 H), 8.08 (m, 2×2 H), 7.52 (m, 2×4 H). IR (KBr): $\tilde{\nu}$ = 3299 bm, 3062 w, 1593 m, 1544 vs, 1473 s, 1421 s, 1285 s, 1029 m, 822 w, 720 s cm^{-1}. See also Table 2. $C_{26}H_{22}N_8Pd{\cdot}0.5H_2O$ (561.94): calcd. C 55.58, H 4.13, N 19.93; found C 55.53, H 4.11, N 19.51.

Preparation of Bis[2-phenyl-4-(4-pyridyl)-1,3,5-triazapentadienato]-palladium(II) (5): Compound **5** was prepared under the same reaction conditions as compound **4** from benzonitrile (0.41 mL, 4.0 mmol), LiN$(SiMe_3)_2$ (0.67 g, 4.0 mmol), 4-cyanopyridine (0.41 g, 4.0 mmol), and anhydrous $[PdCl_2(PhCN)_2]$ (0.77 g, 2.0 mmol). Slow evaporation of the methanol filtrate gave yellow crystals of **5**. Yield: 0.34 g (0.62 mmol, 31%); m.p. > 300 °C. ESI-HRMS (in methanol, +ve) calcd. for $C_{26}H_{23}N_8Pd$: 553.1080; found 553.1049 [M+H]$^+$. ^1H NMR ([D$_6$]DMSO): NH protons: δ = 8.85 (s, 2×1 H), 8.79 (s, 2×1 H, NH); 4-pyridyl protons: δ = 8.74 (m, 2×2 H), 8.08 (m, 2×2 H), 8.01 (m, 2×2 H), 7.52 (m, 2×3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 121.7, 127.6, 128.3, 130.2, 138.4, 145.7, 150.1, 158.5, 160.7 ppm. IR (KBr): $\tilde{\nu}$ = 3430 bw, 3317 bm, 3231 bm, 3042 bw, 1602 w, 1585 m, 1565 m, 1535 vs, 1453 s, 1403 vs, 1295 s, 1064 m, 844 w, 825 w, 712 s, 530 w cm^{-1}. See also Table 2. $C_{26}H_{22}N_8Pd{\cdot}H_2O$ (570.95): calcd. C 54.70, H 4.24, N 19.62; found C 54.69, H 4.04, N 19.08.

Preparation of Tetrakis(benzamidinato)bis(2,4-diphenyl-1,3,5-triazapentadienato)tripalladium(II) (6): Benzonitrile (0.412 mL, 4 mmol) and LiN$(SiMe_3)_2$ (0.67 g, 4 mmol) were placed in THF (20 mL) at 0 °C. The resultant red solution was warmed to room temperature and stirred for an additional 2 h before cooling down to –78 °C. Anhydrous $PdCl_2$ (0.177 g, 1 mmol) was then added to the reaction mixture, which was stirred at –78 °C for an hour before warming up to room temperature and allowed to react overnight. Solvent was then removed under vacuum. The mixture was exposed to air, dichloromethane (20 mL) was added to the residue, and the solution was filtered. The solvent of the filtrate was removed in vacuo to give a dark-red oily product. The product was dissolved in THF (10 mL) and the solvent was allowed to evaporate slowly in air to afford yellow crystals of **6**. Yield: 0.12 g (0.097 mmol, 19%), m.p > 300 °C. ^1H NMR ([D$_6$]DMSO): NH protons, δ = 8.22 (s, 2×1 H), 8.03 (m, 2×2 H), 7.75 (m, 2×2 H), 6.83 (s, 2×1 H); phenyl protons: 7.66–7.45 ppm (m, 2×20 H). IR (KBr): $\tilde{\nu}$ = 3404 m, 3375 s, 3357 m, 3057 w, 3021 w, 1648 w, 1559 vs, 1540 vs, 1472 s, 1445 s, 1273 m, 1218 w, 1028 w, 783 w, 697 vs, 651 m cm^{-1}. See also Table 2. $C_{56}H_{52}N_{14}Pd_3{\cdot}0.5H_2O$ (1247.2): calcd. C 53.88, H 4.28, N 15.72; found C 53.85, H 4.14, N 15.33.

X-ray Crystallography: Crystals of **2**·$2CH_3OH$, **3**·$2CH_3OH$, and **6** suitable for X-ray diffraction were grown by slow evaporation of the respective methanol solution of these compounds in air. The intensity data were collected with a Bruker AXS SMART 1000 CCD area-detector diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The collected frames were processed with the proprietary software SAINT[25] and an absorption correction was applied (SADABS[26]) to the collected reflections. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL.[27] Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective carbon atoms. Pertinent crystallographic data and other experimental details are summarized in Table 3.

Table 3. Crystal data and refinement for compounds **2**, **3** and **6**.

	2·$2CH_3OH$	**3**·$2CH_3OH$	**6**
Empirical formula	$C_{26}H_{28}N_{10}O_2Pd$	$C_{26}H_{28}N_{10}O_2Pd$	$C_{56}H_{52}N_{14}Pd_3$
Molecular mass	618.98	618.98	1240.32
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	7.518(2)	5.5416(9)	9.6938(8)
b [Å]	7.865(3)	18.296(3)	10.5983(8)
c [Å]	12.645(4)	13.962(2)	25.0385(19)
α [°]	86.156(6)	90	95.411(2)
β [°]	78.994(5)	97.950(3)	96.251(2)
γ [°]	63.959(5)	90	96.4450(10)
V [Å^3]	659.4(4)	1401.9(4)	2526.1(3)
Z	1	2	2
$F(000)$	316	632	1248
$D_{calcd.}$ [g cm^{-3}]	1.559	1.466	1.631
μ(Mo-K_α) [mm^{-1}]	0.749	0.704	1.111
Rflns. collected	3249	8182	12876
Unique rflns.	2629	3159	8860
Obsd. rflns.	2294	1790	3374
GOF on F^2	1.002	0.917	0.999
R_1, wR_2 [$I > 2\sigma(I)$]	0.0448, 0.1050	0.0526, 0.1309	0.0434, 0.1043
R_1, wR_2 (all data)	0.0523, 0.1087	0.0973, 0.1497	0.1345, 0.1362

CCDC-602853 (for **2**), -602854 (for **3**) and -602855 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] L. Bourget-Merie, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3066 and references cited therein.

[2] a) P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Chem. Soc., Chem. Commun.* **1994**, 1699–1700; b) P. B. Hitchcock, M. F. Lappert, M. Layh, D.-S. Liu, R. Sablong, T. Shun, *J. Chem. Soc., Dalton Trans.* **2000**, 2301–2312; c) P. B. Hitchcock, M. F. Lappert, M. Layh, *J. Chem. Soc., Dalton Trans.* **2001**, 2409–2416.

[3] B.-J. Deelman, M. F. Lappert, H.-K. Lee, T. C. W. Mak, W.-P. Leung, P.-R. Wei, *Organometallics* **1997**, *16*, 1247–1252.

[4] A. Maraval, D. Arquier, A. Igau, Y. Coppel, B. Donnadieu, J.-P. Majoral, *Organometallics* **2001**, *20*, 1716–1718.

[5] S. Nückel, P. Burger, *Organometallics* **2000**, *19*, 3305–3311.

[6] V. C. Gibson, J. A. Segal, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 7120–7121.

[7] a) C. E. Radzewich, I. A. Guzei, R. F. Jordan, *J. Am. Chem. Soc.* **1999**, *121*, 8673–8674; b) C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 1885–1887; *Angew. Chem. Int. Ed.* **2000**, *39*, 1815–1817.

[8] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514–1516.

[9] B. Qian, W. J. Scanlon, M. R. Smith, D. H. Motry, *Organometallics* **1999**, *18*, 1693–1698.

[10] P. H. M. Budzelaar, R. Gelder, A. W. Gal, *Organometallics* **1998**, *17*, 4121–4123.

[11] N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.* **2000**, 1991–1992.

[12] L. W. M. Lee, W. E. Piers, M. R. J. Elsegood, W. Clegg, M. Parvez, *Organometallics* **1999**, *18*, 2947–2949.

[13] a) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268; b) B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050; c) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849–850.

[14] R. Norrestam, *Acta Crystallogr., Sect. C* **1984**, *40*, 955–957.

[15] J. Barker, M. Kilner, M. M. Mahmoud, S. C. Wallwork, *J. Chem. Soc., Dalton Trans.* **1989**, 837–841.

[16] S. V. Kryatov, M. B. Smith, E. V. Rybak-Akimova, A. Y. Nazarenko, *Chem. Commun.* **2001**, 1174–1175.

[17] T. Kajiwara, A. Kamiyama, T. Ito, *Chem. Commun.* **2002**, 1256–1257.

[18] a) M. N. Kopylovich, A. J. L. Pombeiro, A. Fischer, L. Kloo, V. Yu. Kukushkin, *Inorg. Chem.* **2003**, *42*, 7239–7248; b) N. A. Bokach, T. V. Kuznetsova, S. A. Simanova, M. Haukka, A. J. L. Pombeiro, V. Yu. Kukushkin, *Inorg. Chem.* **2005**, *44*, 5152–5160.

[19] a) A. R. Siedle, R. J. Webb, F. E. Behr, R. A. Newmark, D. A. Weil, K. Erickson, R. Naujok, M. Brostrom, M. Mueller, S.-H. Chou, V. G. Young Jr, *Inorg. Chem.* **2003**, *42*, 932–934; b) A. R. Siedle, R. J. Webb, M. Brostrom, R. A. Newmark, F. E. Behr, V. G. Young Jr, *Organometallics* **2004**, *23*, 2281–2286.

[20] H. V. R. Dias, S. Singh, *Inorg. Chem.* **2004**, *43*, 5786–5788.

[21] J. Guo, W.-K. Wong, W.-Y. Wong, *Eur. J. Inorg. Chem.* **2004**, 267–275.

[22] a) J. Barker, M. Kilner, R. O. Gould, *J. Chem. Soc., Dalton Trans.* **1987**, 2687–2693; b) J. Barker, N. Cameron, M. Kilner, M. M. Mahoud, S. C. Wallwork, *J. Chem. Soc., Dalton Trans.* **1986**, 1359–1365.

[23] J. Guo, W.-K. Wong, unpublished work.

[24] D. Lin-Vien, N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Inc., **1991**.

[25] *SAINT*, *Reference manual*, Siemens Energy and Automation, Madison, WI, **1994–1996**.

[26] G. M. Sheldrick, *SADABS*, *Empirical Absorption Correction Program*, University of Göttingen, Germany, **1997**.

[27] G. M. Sheldrick, *SHELXTL*™, *Reference manual*, version 5.1, Siemens, Madison, WI, **1997**.

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