รายงานวิจัยฉบับสมบูรณ์

โครงการ Synthesis and Electrochemical Studies of Nickel and Cobalt Paddlewheel complexes

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สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

บทคัดย่อ

รายงานฉบับสมบูรณ์กล่าวถึงรายละเอียดการสังเคราะห์และการพิสูจน์เอกลักษณ์ของไตรอะซีนลิแกนด์ชนิดใหม่ 2 ชนิดคือ [RNNNHR] {R = 3,5-dimethylphenyl (3,5-dmp) หรือ 3,5-bistrifluoromethylphenyl (3,5-btfm)} และอะมิดีนลิแกนด์ [RNC(Me)NHR] (R = 3,5-dmp) ซึ่งในส่วนของสารประกอบชนิดหลังนี้ได้มีการศึกษาโดยเทคนิคเอกซเรย์คริสตัลโลกราฟฟี นอกจากนี้ยังมีการเตรียมชุดของสารประกอบเชิงซ้อนนิกเกิล(II)ไตรอะซีไนด์ $[NiX_2(RNNNHR)_2]\cdot 2H_2O$ (R = 3,5-dmp, X = Cl, Br and NO_3) จากการการศึกษาเคมีไฟฟ้าของสารประกอบเชิงซ้อนพบว่าเมื่อ X = NO_3 สารประกอบจะมีสมบัติทางรีดอกซ์ นอกจากกนั้นยังได้ทำการสังเคราะห์สารประกอบเชิงซ้อนแบบไบนิวเคลียร์ $[(PPh_3)ClPd(\mu\text{-}RNNNR)_2PdCl(PPh_3)]$ (R = 3,5-dmp หรือ 3,5-dichlorophenyl) ซึ่งได้มีการแยกสารซึ่งเป็นผลพลอยได้จากปฏิกิริยา *trans*-$[PdCl_2(NEt_3)(PPh_3)]$ และทำการศึกษาโครงสร้างของสารประกอบเชิงซ้อน

Abstract

The following report details the synthesis and characterization of novel triazene ligands [RNNNHR] {R = 3,5-dimethylphenyl (3,5-dmp) or 3,5-bistrifluoromethylphenyl (3,5-btfm)}, amidine ligand [RNC(Me)NHR] (R =3,5- dmp) the latter of which have been studied by X-ray crystallography. In addition, a series of Ni(II) triazenide complexes, $[NiX_2(RNNNHR)_2]\cdot 2H_2O$ (R = 3,5-dmp, X = Cl, Br and NO_3) have been prepared. The electrochemical studies show that when X = NO_3 the complex is redox-active. Furthermore, two new binuclear complexes, $[(PPh_3)ClPd(\mu\text{-}RNNNR)_2PdCl(PPh_3)]$ (R = 3,5-dmp or 3,5-dichlorophenyl), have been synthesized. The isolation of the byproduct, *trans*-$[PdCl_2(NEt_3)(PPh_3)]$, and X-ray structural studies are also included.

Acknowledgements

I wish to acknowledge the various people who have helped throughout this project. Firstly, I would like to thank my mentor Associate Professor Dr Sujittra Youngme who has been a support and suggested many ideas for this project.

The support of two research groups abroad namely, Professor Neil Connelly, the University of Bristol, who has provided rapid and free CHN and mass spectroscopic analysis and Pd starting materials, and Harry Adams, the University of Sheffield, who solved the amidine structures.

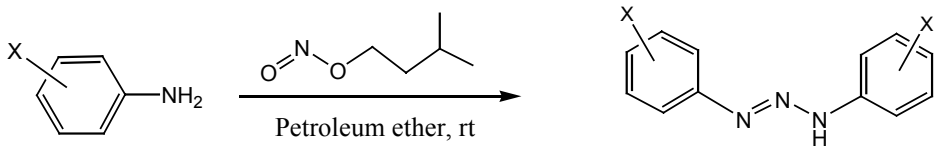
Associate Professor Dr Chaveng Pakawatchai (Prince of Songkla University) is also thanked for the structure of *trans*-[$PdCl_2(NEt_3)(PPh_3)$]. Many thanks to Assistant Professor Dr Apinpus Rujiwatra (Chiang Mai University) and Assistant Professor Dr Weerachai Phutdhawong (Maejo University) for generous access to the solvothermal apparatus and microwave oven respectively. Furthermore, the staff at Instrument centre, Walailak University for the 24 hours access to all equipment required for this project.

Finally, I would like to acknowledge Assistant Professor Dr David J. Harding for support and encouragement throughout the failures and the successes of this project and also for correcting the English in this report and also the manuscripts.

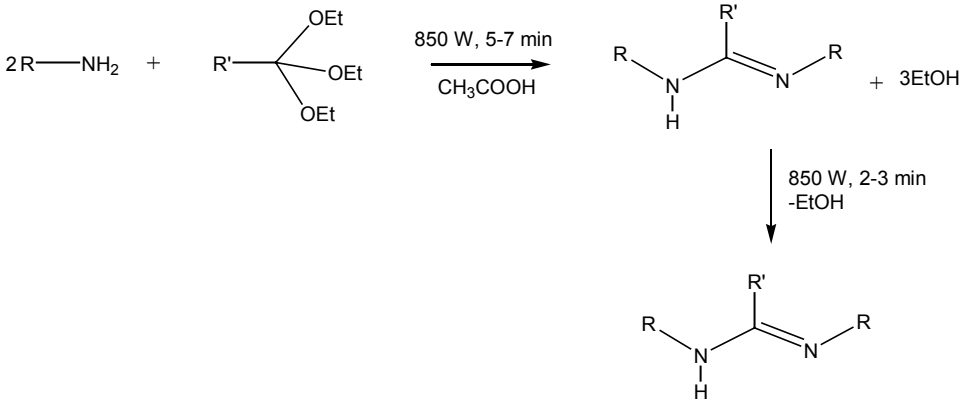
List of contents

Executive summary

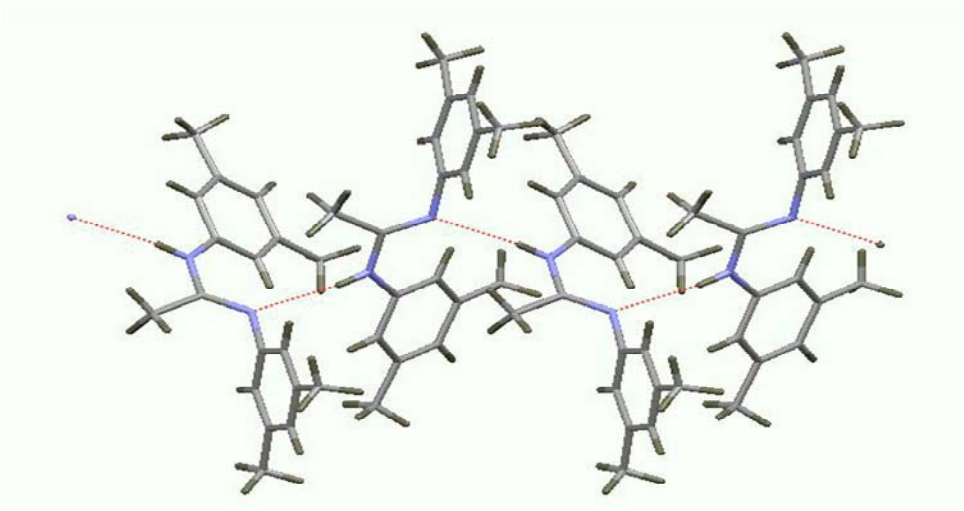
In this project we successfully prepared two new triazene ligands namely, RNNNHR when R = 3,5-dimethylphenyl (3,5-dmp) or 3,5-bistrifluoromethylphenyl (3,5-btfm) in very good yield.



Another achievement has been the synthesis of amidine ligand, RNC(Me)NHR (R = 3,5-dmp) by both conventional and microwave methods. The microwave assisted synthesis proved superior allowing rapid isolation of the amidine in high yield.

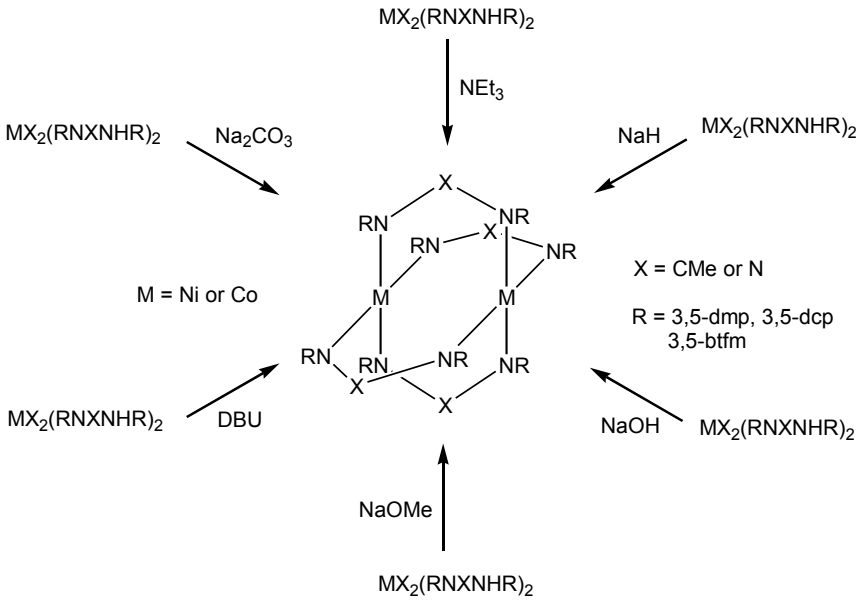


Structural and NMR studies of RNC(Me)RHR (R = 3,5-dmp and *p*-tolyl) reveal that the electron density on the N-C-N backbone is localized. Furthermore, a novel intramolecular H-bonding structural motif is observed forming a zigzag polymeric chain.

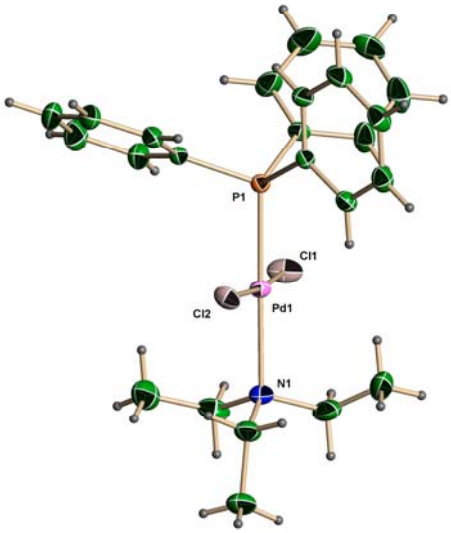


The reaction between the new triazene (RNNNHR) when R = 3,5-dmp with $NiX_2 \cdot xH_2O$ in EtOH gives a series of $[NiX_2(RNNNHR)_2]$ $2H_2O$ (X = Cl, Br, NO_3) complexes. These represent the first nickel(II) triazene complexes ever isolated. As expected all of these complexes are paramagnetic. Electrochemical studies of the complexes show that only $[Ni(NO_3)_2(RNNNHR)_2]$ $2H_2O$ is redox active with two irreversible oxidation waves at 0.65 and 1.17 V and one irreversible reduction wave at -0.19 V. Interestingly, the Co analogue $[CoCl_2(RNNNHR)_2]$ $2H_2O$ (R = 3,5-dichlorophenyl) exhibits solvatochromic behaviour.

Attempts were made to synthesize paddlewheel complexes using a variety of different bases including NEt_3, NaOMe, DBU and NaH. Using the conventional method we unable to prepare or isolate the paddlewheel complexes. Microwave assisted and solvothermal techniques have been applied in the hope of preparing paddlewheel complexes but have sadly proved unsuccessful.



Lastly, the reaction between $\{PdCl(PPh_3)(\mu\text{-}Cl)\}_2$ and RNNNHR in CH_2Cl_2 with an excess of NEt_3 to deprotonate the ligand resulted in $[Cl(PPh_3)Pd(\mu\text{-}RNNNR)_2PdCl(PPh_3)]$ and *trans*-$[PdCl_2(NEt_3)(PPh_3)]$. The latter has been characterized by X-ray diffraction.



1. Objectives

1.1. Investigate efficient methods for the preparation of new triazenide and amidine ligands for synthesis of novel complexes.

1.2. Synthesise triazenido, amidinido bridged Co and Ni paddlewheel complexes, molecular wires.

1.3. Study physical, chemical, electrochemical and magnetic properties of Co and Ni complexes.

2. Introduction

2.1. Triazene and triazenide complexes

1,3-Diaryltriazenes, RN=N-NHR′ (R and R′ = aryl), were first prepared by Griess in 1859[1] and are generally believed to adopt a *trans* configuration (Figure 1), as confirmed in several cases by X-ray diffraction studies, *e.g.* R = R′ = Ph[2] and R = C_6H_4Br-*p* and R′ = Ph.[3]

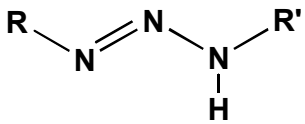


Figure 1 Structure of free triazenes (R = C_6H_4X-*p*; X = H, Me, Et, OMe, F, *etc*.).

Triazenide anions, $[RN{=}N\text{-}NR']^-$, form a variety of metal complexes which may involve monodentate (a), chelating (b) or bridging (c) arrangements (Figure 2), as found for the isoelectronic acetate and formamidinate ligands.[4]

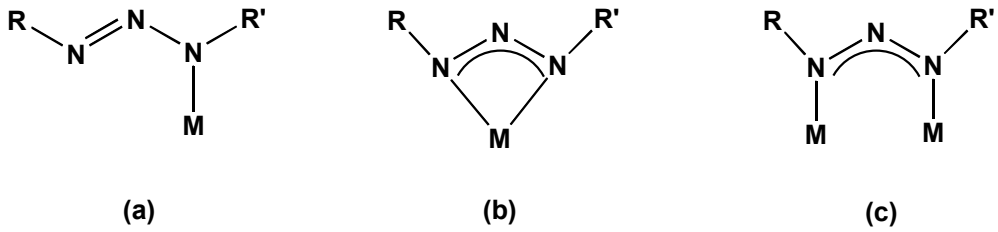


Figure 2 Bonding modes of the triazenide anion.

IR and NMR spectroscopy, and X-ray structural studies, showed that the monodentate triazenide ligand in complexes such as *cis*-$[Pt(PhNNNPh)_2(PPh_3)_2]$,[5] $[PtH(p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p)(PPh_3)_2]$[6] and $[PdCl(p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p)(PPh_3)_2]$[6] is bonded through a single nitrogen, as in Figure 2 (a), with the N-N bond nearer to the metal being shorter. This is in contrast to the monodentate triazene complex $[\{PhNNN(H)Ph\}Rh(\mu\text{-}O_2CMe)_4Rh\{PhNNN(H)Ph\}]$,[7] where the bond nearer the metal is longer.

Several complexes, such as $[Ir(PhNNNPh)(CO)(PPh_3)_2]$,[8] $[Rh(PhNNNPh)L_2]$ $\{L_2 = cod \text{ or } (PPh_3)_2\}$[8] and $[Rh(PhNNNPh)_3]$,[9] contain chelating triazenide ligands; both terminal N atoms are coordinated to the same metal to form a four-membered chelating ring in which the π-electrons are delocalised [Figure 2 (b)].

The bridging mode of bonding leads to face-to-face binuclear complexes with d^8 metals, *e.g.* $[Rh(\mu\text{-}PhNNNPh)_4Rh]$,[9] $[(CO)_2M(\mu\text{-}p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p)_2M(CO)_2]$ (M = Rh or Ir) and $[Cl(PR_3)M(\mu\text{-}p\text{-}MeC_6H_4NNNC_6H_4Me\text{-}p)_2M(PR_3)Cl]$ (M = Pd, $PR_3 = PBu_3$; M = Pt, $PR_3 = PEt_3$).[10,11] Extensive electron transfer series, where the complexes contain $[Rh_2]^{z+}$ (z = 2, 3 or 4) or $[Ir_2]^{z+}$ (z = 2 or 3) cores, are described below.

Most triazenide complexes that have been reported are Pt group metals. There are few examples of first row transition metal triazenide complexes, let alone paddlewheel triazenido bridged complexes. So far, there are only two paddlewheel triazenido complexes of first row transition metals, $[LNi(\mu\text{-}PhNNNPh)_4NiL]$ (Ar = arene; L = pyridine or quinolene) and $[Co_2(\mu\text{-}p\text{-}tolylNNN\text{-}p\text{-}tolyl)_4]$.

In the case of nickel, the three complexes, $[LNi(\mu\text{-}O_2CPh)_4NiL]$,[12,13] $[LNi(\mu\text{-}ArNC(H)NAr)_4NiL]$ and $[LNi(\mu\text{-}PhNNNPh)_4NiL]$ (Ar = arene; L = pyridine or quinolene) have

two Ni(II) centres and are also redox active giving access to $[Ni_2L_4]^n$ (n = 0-2). Surprisingly, theoretical calculations have shown that there is no Ni-Ni bond. Unlike the other complexes, $[BrNi(naphy)_4NiBr]^+$ (naphy = 1,8-naphthyridine) is paramagnetic with one Ni(I) and one Ni(II) centre. Although the two nickel centres do not appear to interact the magnetic properties are unusual and have yet to be fully explained.

Cobalt complexes are similarly scarce with only four dimers currently reported namely, $[LCo(\mu\text{-}O_2CPh)_4CoL]$ (L = quinolene),[14] $[Co_2(\mu\text{-}ArNC(R)NAr)_4]$ (R = H or benzyl) and $[Co_2(\mu\text{-}p\text{-tolylNNN-}p\text{-tolyl})_4]$. As before the two metal centres are Co(II) and are redox active. In this instance, studies have shown that there is a single metal-metal bond between the two metal centres. Indeed, further work has shown that some of these dimers may be oxidised to yield complexes with a $[Co_2]^{5+}$ core.

2.2. Amidine and amidinate complexes

Amidines have been known for many years, the first synthesis reported in 1858 by reaction of *N*-phenylbenzimidylchloride with aniline.[15] The amidinate ligand is a monoanionic nitrogen-donor ligand that is characterized by π-delocalization of the negative charge over the N-C-N backbone (Figure 3). This resembles the related triazenide ligand.

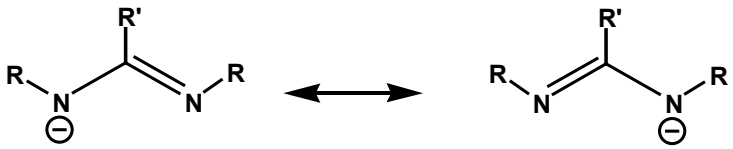


Figure 3 General form of the amidinate ligand.

Electronic and steric properties of an amidine ligand can be modified by varying the organic substituents on the nitrogen atoms and the central carbon atom. The anion acts in a monodentate, bidentate chelating or bridging fashion and help to stabilize metal-metal bonds in a manner similar to the isoelectronic 1,3-disubstituted triazenido. The amidinate complexes are usually obtained either by the reaction of $[RNC(R')NR]^-$ with metal salts or by deprotonation of a coordinated neutral amidine in a precursor [M(RNC(R′)NHR)]. The neutral amidines have two possible bonding sites, via the amine-N or the imine-N. However, coordination through the latter is usually observed.

Recently, Cotton and coworkers reported the synthesis of $[M(\mu\text{-}(RNC(R')NR)_4M]$ (R = R′ = Ph, M = Mn, Co, Ni or Fe) from the precursor $[MCl_2(RNC(R')NHR)_2]$.[16] This route is more efficient than the molten reaction between excess amidine ligand and metal

salt. A further development, reported by Cotton, has been the utilization of 1,3,4,6,7,8-hexahydro-*2H*-pyrimido[1,2-*a*]pyrimidine (hpp).[17] This electron rich amidinate has allowed the isolation of a number of transition metal complexes with unique chemistry and redox-activity.[18]

A wide range of diruthenium amidinato [Ru_2(amidinato)$_4L_2$] complexes have been synthesized by Ren *et al*. These complexes all show rich redox chemistry and also have been used to prepare short molecular wires.[19]

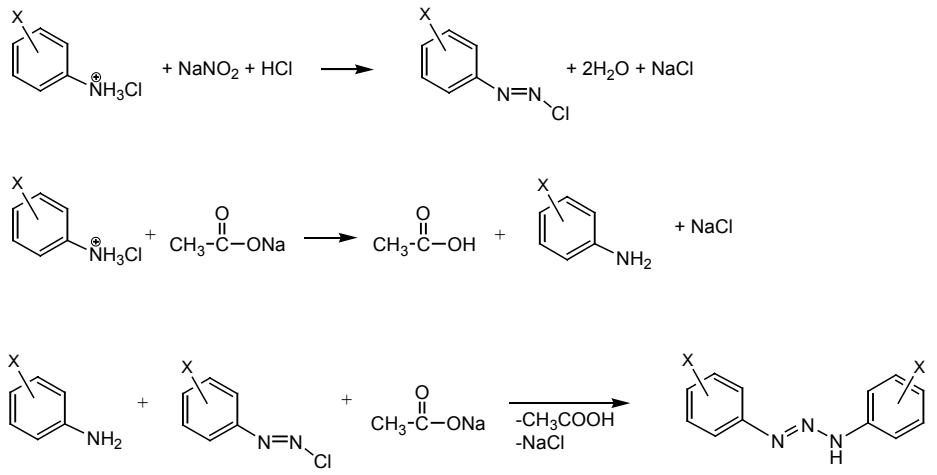
Finally, amidinate chemistry has received something of a revival with the synthesis of bulky amidinates. These have allowed the preparation of a number of intriguing compounds such as Cu(I) tetramers and dimers,[20] highly unusual Au(II) dimers,[21] Ni(II) catalysts[22] and first row transition metal monomers, [M(amidinato)$_2$] (M =Cr, Mn, Fe, Co, and Ni).[23]

3. Results and discussion

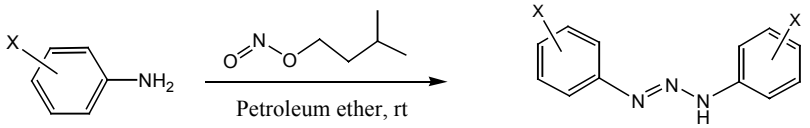
3.1. Synthesis and characterization of triazene ligands

There are two methods to synthesize triazene ligands (RNNNHR) as shown in Scheme 1. The preferred method depends on the substituent groups *e.g.* when R = *p*-tolyl **1** or 3,5-dimethylphenyl (3,5-dmp) **2** method A is more effective than method B while when R = 3,5-dichlorophenyl (3,5-dcp) **3** or 3,5-bistrifluoromethylphenyl (3,5-btfm) **4** method B is superior.

Method A



Method B



Scheme 1 Synthesis of triazene ligands.

We have made two new triazene ligands. All ligands have been fully characterized by CHN analysis, MS, IR and NMR spectroscopy. The IR and ^{1}H NMR spectroscopic data of ligands **1**-**4** show in Table 1.

Table 1 IR and ^{1}H NMR spectroscopic data for triazene ligands (RNNNHR).

Compound	R	% Yield	Colour	IR (ν_{NH})[a]	^{1}H NMR[b]
1	*p*-tolyl	42	Yellow	3202	7.32 (d, 4H, *H*-Ar), 7.19 (d, 4H, *H*-Ar), 2.37 (s, C*H*$_3$, 6H)
2	3,5-dmp	50	Orange	3206	7.45 (s, 2H, *H*-Ar), 7.07 (s, 2H, *H*-Ar), 6.43 (s, 2H, *H*-Ar), 2.47 (s, C*H*$_3$, 6H), 2.42 (s, C*H*$_3$, 6H)
3	3,5-dcp	72	Brown-yellow	3301	7.32 (d, 4H, *H*-Ar), 7.20 (t, 2H, *H*-Ar) or 8.45 (d, 4H, *H*-Ar), 8.20 (t, 2H, *H*-Ar) in acetone
4	3,5-btfm	44	Pale orange	3330	8.18 (s, 4H, *H*-Ar), 7.91 (s, 2H, *H*-Ar)

[a] Weak absorptions in KBr, [b] in $CDCl_3$, chemical shift is in ppm.

The ν_{NH} vibrations of **1-4** increase in accordance with the increasing electron withdrawing ability of the R groups. The yield of **4** is low because the ligand dissolves reasonably well in *n*-hexane. Interestingly, **4** is only lightly coloured suggesting that the CF_3 groups significantly decrease the electron density within the N-N=N unit thereby reducing the intensity of the $\pi \rightarrow \pi^*$ transition.

Synthesis of RNNNHR (R = 3,5-dmp) 1

A mixture of ice (100 g), water (150 cm^3), conc. HCl (3.8 cm^3) and 3,5-dimethylaniline (3.75 cm^3, 0.03 mol) were stirred together at room temperature. A solution of $NaNO_2$ (1.03 g in 5 cm^3 of water) was added drop-wise and the resulting mixture stirred for 10 minutes. A solution of CH_3COONa (4.24 g in 10 cm^3 of water) was then added and the orange solution was stirred in an ice bath for 40 minutes. The oily

red-orange solid was extracted from the solution by CH_2Cl_2 (5 x 30 cm^3) and dried over Na_2SO_4. The solution was filtered and the solvent removed to give a deep red-orange solid. The solid was dissolved in hot hexane and filtered through filter paper. Red-orange needle crystals precipitated from the solution overnight. (1.75 g, 50%)

m.p. 97-98 °C. Found: C, 76.2; H, 8.1; N, 16.7. $C_{16}H_{19}N_3$. Calcd.: C, 75.9; H, 7.6; N, 16.6.

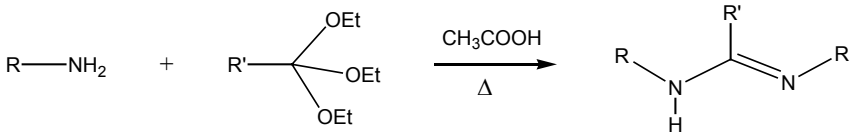
Synthesis of RNNNHR (R = 3,5-btfm) 2

3,5-bistrifluoromethylanaline (3.6 cm^3, 22.5 mmol) was dissolved in petroleum ether (30 cm^3). Isoamyl nitrite (4.6 cm^3, 34.4 mmol) was added to the yellow solution. The orange solution was stirred for 1.5 hour then the solvent was reduced to a small volume. *n*-Hexane (20 cm^3) was added and the mixture was stored at -20 °C overnight. The solid was filtered and washed with cold *n*-hexane (10 cm^3). The pale orange crystalline solid was dried in air. (2.36 g, 44%)

m.p. 132-134 °C. Found: C, 41.1; H, 1.5; N, 9.1. $C_{16}H_7N_3F_{12}$. Calcd.: C, 41.0; H, 1.5; N, 9.0.

1.1. Synthesis and characterization of amidine

A new amidine ligand namely [RNC(Me)NHR] (R = 3,5-dmp) **5** has been made by the route shown in Scheme 2. The IR and ^1H NMR spectroscopic data are shown in Table 2.



Scheme 2 Synthesis of amidine ligands.

Table 2 IR and ^{1}H NMR spectroscopic data for amidine ligands [RNC(Me)NHR].

Compound	R	% Yield	Colour	IR (ν_{NH})[a]	^{1}H NMR[b]
5	3,5-dmp	47	Light yellow	3281	6.78 (s, 3H, *H*-Ar), 6.68 (s, 3H, *H*-Ar), 2.28 (d, 12H, *CH*$_3$), 1.98 (s, 3H, *CH*$_3$)
7[c]	*p*-tolyl	70	Off-white	3301	7.14-7.05 (m, 8H, *H*-Ar), 2.32 (s, 6H, *CH*$_3$), 2.00 (s, 3H, *CH*$_3$)

[a] Weak absorptions in KBr, [b] in $CDCl_3$, chemical shift is in ppm, [c] synthesis by microwave radiation.

An attempt to synthesize ligand **5** by using the same mole ratio of starting materials as that of the known amidine [PhNC(Me)NHPh] gave a very poor yield. However, the yield can be improved by varying the amount of CH_3COOH which is a catalyst for this reaction and by increasing the reaction time. We found that the amount of CH_3COOH as a catalyst plays an important role in obtaining high yields of the compound. We tried to use the same method to prepare RNC(Me)NHR (R = 3,5-btfm **6**), however, the ^{1}H NMR spectrum shows that more than one product is formed in the reaction. Moreover, longer reaction times seem to be required to form **6**.

Given the difficulties encountered in the above reaction we have determined to investigate the synthesis of amidines using microwave technology. The modified commercial domestic microwave oven shown in Figure 4.

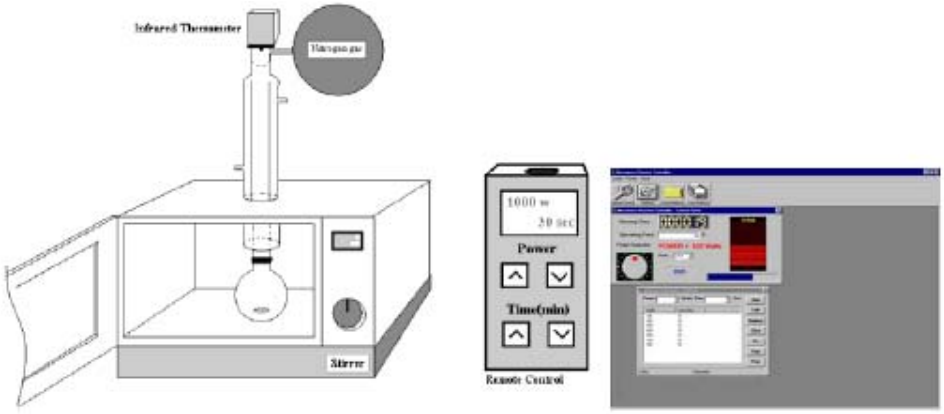
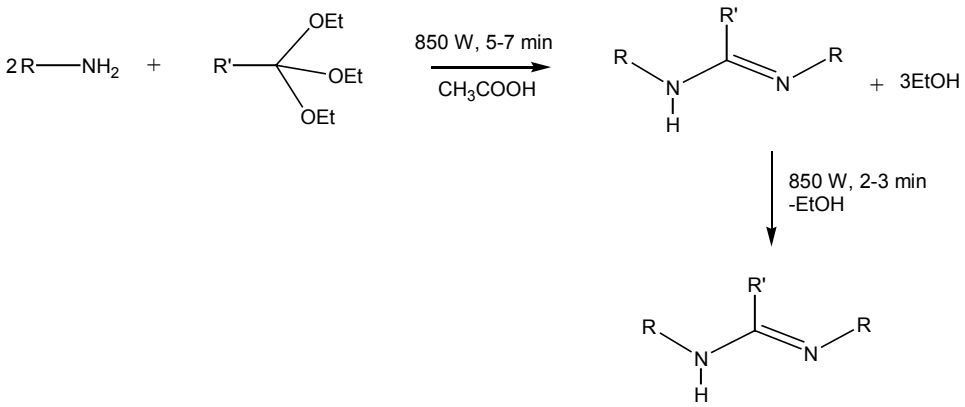


Figure 4 A modified commercial domestic microwave oven, control box and software (details of the microwave reactor are available at http://www.science.mju.ac.th/chemistry/research/weerachai/reactor_eng.htm).

Reflux of triethylorthoacetate and the desired aniline in the presence of acetic acid as a catalyst under microwave irradiation at 850 W for 5-7 min yields N,N′-disubstituted acetamidine, [RNC(Me)NHR] (R = 3,5-dimethylphenyl **5** and *p*-tolyl **7**), shown in scheme 3. The byproduct, EtOH, is easily removed by placing a receiver between the round bottom flask and the condenser and heating under microwave conditions at 850 W for a further two or three minutes. The complete removal of EtOH is the key to high yield and purity of the product. In general yields are increased by 10-20% and reaction times are shortened to minutes rather than hours with pure products obtained in most cases in under an hour.



Scheme 3 Synthesis of amidine ligands using microwave radiation.

IR spectra of **5** and **7** show ν_{NH} at 3281 and 3301 cm^{-1} respectively. Additional bands are observed for aromatic C=C and C-H stretches and are comparable with other reported amidines.

Even though, the microwave technique proves to be more efficient for preparing amidine ligands there are still difficulties in synthesizing RNC(Me)NHR (R = 3,5-btfm **6**). There are many products from the reaction and by the time the products have passed through a column the yield of the desired ligand was very low.

Crystals suitable for X-ray diffraction studies of compounds **5** and **7** were obtained by diffusion of *n*-hexane into the concentrated crude reaction mixture. The X-ray structures of **5** and **7** are shown in Figures 5 and 6, respectively.

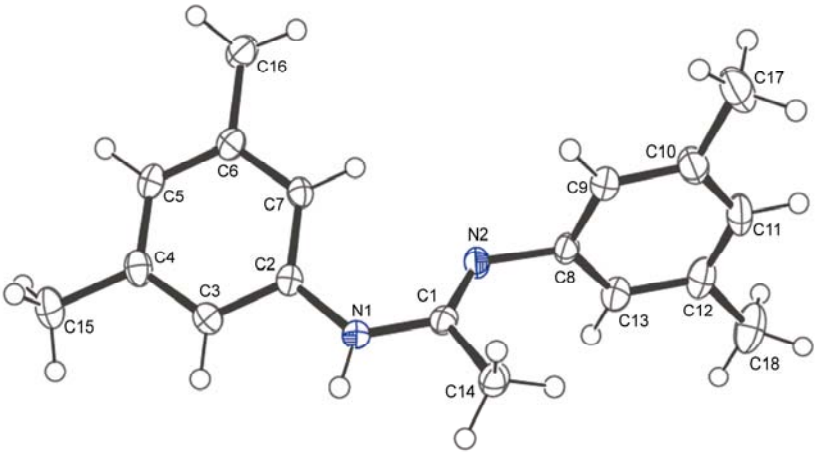


Figure 5 X-ray structure of [RNC(Me)NHR] when R = 3,5-dmp **5**.

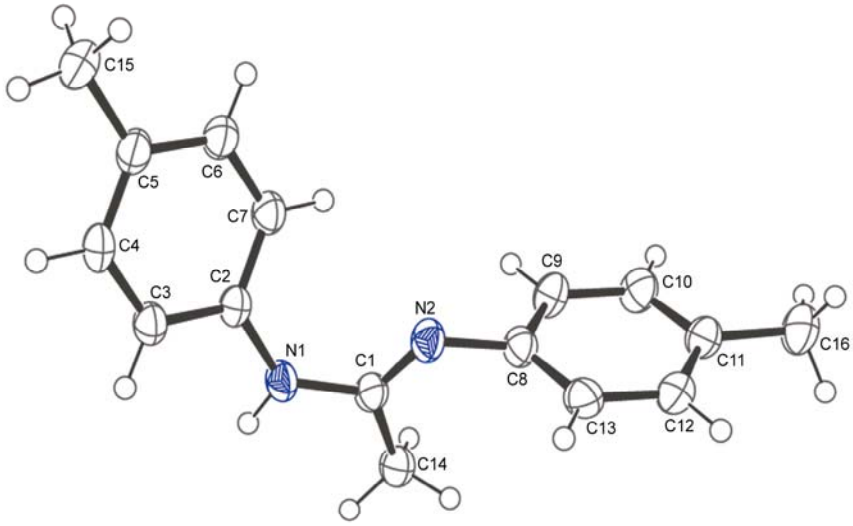


Figure 6 X-ray structure of [RNC(Me)NHR] when R = *p*-tolyl **7**.

Both compounds are orthorhombic and crystallize in the Pbca space group. Selected bond lengths and angles are shown in Table 3. As expected the two structures exhibit similar bond lengths and angles. However, N(1)-C(1), N(1)-C(2), N(2)-C(8) and C(1)-C (14) of **5** are slightly longer than those of **7** and N(2)-C(1) of **5** is a little bit shorter than that of **7**. The difference in bond lengths of these two compounds is due to the substituent groups on the aromatic rings. The amidine molecules adopt a *trans*-configuration with one of the aromatic rings orthogonal to the plane of the acetamidine core (see Figures 5 and 6). This arrangement is preferred because of the presence of a weak intramolecular hydrogen bond between the H-atom on N(1) and the imine nitrogen, N(2) on a

neighbouring molecule. The H-bond length is 2.26(4) and 2.25(6) Å for **1** and **2** respectively. In contrast to other reported amidines the H-bond forms a zigzag chain, in which neighbouring amidines are almost orthogonal to one another, and *not* a dimer of molecules.

Table 3 Selected Bond lengths (Å) and bond angles (°) of **5** and **7**.

	5	**7**
N(1)-C(1)	1.3727(18)	1.363(3)
N(1)-C(2)	1.4122(18)	1.416(3)
N(1)-H(1)	0.8800	0.8800
N(2)-C(1)	1.2906(18)	1.295(3)
N(2)-C(8)	1.4293(18)	1.422(3)
C(1)-C(14)	1.505(2)	1.499(3)
C(1)-N(1)-C(2)	129.46(12)	126.87(18)
C(1)-N(1)-H(1)	115.3	116.6
C(2)-N(1)-H(1)	115.3	116.6
C(1)-N(2)-C(8)	118.61(12)	118.63(18)
N(2)-C(1)-N(1)	121.42(13)	120.58(19)
N(2)-C(1)-C(14)	125.55(13)	124.65(19)
N(1)-C(1)-C(14)	113.03(12)	114.76(19)
C(3)-C(2)-N(1)	123.90(13)	119.40(18)
C(7)-C(2)-N(1)	116.46(13)	122.07(17)
C(13)-C(8)-N(2)	120.05(14)	120.3(2)
C(9)-C(8)-N(2)	120.66(14)	120.9(2)

Synthesis of N,N'-Bis(3,5-dimethylphenyl)acetamidine 5

Method A

A mixture of triethylorthoacetate (2.0 cm^3, 10.4 mmol), 3,5-dimethylaniline (1.6 cm^3, 20 mmol) and acetic acid (0.5 cm^3) was placed in a microwave oven equipped with a reflux condenser and heated at 850 W for 7 minutes. A receiver was placed between

the flask and the condenser and then heated under microwave conditions at 850 W for a further two or three minutes. The volume was reduced under vacuum to yield a thick oil and *n*-hexane (10 cm^3) was added. The solution was stored at 0°C overnight, resulting in colourless crystals (1.21 g, 45%)

Method B

Triethylorthoacetate (1 cm^3, 5.2 mmol), 3,5-dimethylaniline (0.78 cm^3, 10 mmol) and acetic acid 40 μL was refluxed at 135 °C for 2 hours. The orange solution was distilled at 140 °C *in vacuo* to remove EtOH and unreacted starting material. The orange crystals were washed with cool *n*-hexane to give colourless crystals and an orange solution. The mixture was stored at -20 °C overnight. The colourless crystals were filtered and dried in air, yield 0.62 g (47%).

m.p. 160-161.5 °C. Found: C, 81.5; H, 8.3; N, 10.6. $C_{18}H_{22}N_2$. Calcd.: C, 81.2; H, 8.3; N, 10.5.

Synthesis of N,N′-Bis(p-tolyl)acetamidine 7

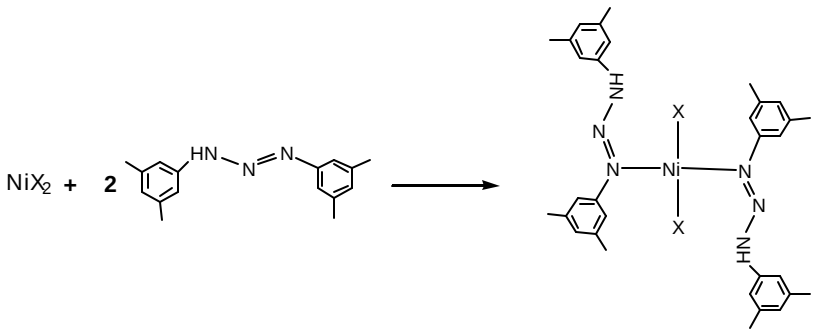
A mixture of triethylorthoacetate (2.0 cm^3, 10.4 mmol), *p*-toluedine (2.12 g, 19.8 mmol) and acetic acid (0.5 cm^3) was placed in a microwave oven equipped with a reflux condenser and heated at 850 W for 5 minutes. A receiver was placed between the flask and the condenser and then heated under microwave conditions at 850 W for a further two or three minutes. The volume was reduced under vacuum to yield a thick oil and *n*-hexane (10 cm^3) was added. The solution was stored at 0°C overnight, resulting in off-white crystals (1.66 g, 70%)

m.p. 102-103 °C. Found: C,76.4; H, 7.4; N, 10.4. $C_{16}H_{18}N_2 \cdot 0.75H_2O$. Calcd.: C, 74.6; H, 7.8; N, 11.1.

1.1. Synthesis and characterization of precursors, [$NiX_2(RNNNHR)_2$]

Oro and coworkers reported that the isolated precursors [$MX_2(RNNNHR)_2$] proved to be a key to the high yield synthesis of dimeric metal complexes. Therefore, we investigated the possibility of isolating and characterizing [$NiX_2(RNNNHR)_2$].

The reaction between $NiX_2.xH_2O$ in EtOH or *iso*-propanol and triazene yields a precursor namely [$NiX_2(RNNNHR)_2$] (R = 3,5-dmp, X = Cl **8**, Br **9** or NO_3 **10**, R = 3,5-dcp; X = Br **11** and X = Cl, R = 3,5-btfm **12**) as shown in Scheme 4.



Scheme 4 Synthesis of $[NiX_2(RNNNHR)_2]$.

The broad ^1H NMR spectra of **8**-**11** indicate that these precursors are paramagnetic as one would expect for Ni(II) complexes. Indeed, in the NMR spectrum of **11** the peaks are so broad that integration is unreliable. However, the change in the chemical shift of the ligands in the complexes compared with the free ligand suggest that the triazene ligands are bound to a Ni(II) metal centre (Table 4). Moreover, the shift in the ν_{NH} stretch, of the triazene ligand, to higher wavenumber confirms that the ligand is bound and in addition, shows that the ligand remains protonated. Even though, the ν_{NH} stretch of **11** does not shift as we would expect the change in the chemical shift in the NMR confirms that the triazene is bound to the Ni^{2+} ion. CHN analysis and mass spectroscopy suggest that the stoichiometry of these triazene complexes is $[NiX_2(RNNNHR)_2].2H_2O$ showing that the complexes readily absorb water. Unfortunately, attempts to grow crystals of $[NiX_2(RNNNHR)_2]$ for an X-ray crystallographic study proved unsuccessful providing no support for the above formulation. Interestingly, the precursor $[NiBr_2(RNNNHR)_2]$ **13** (R = *p*-tolyl) cannot be isolated due to decomposition in air. This confirms that the methyl groups on the aryl group of the triazene ligand in 3,5-dmp play an important role in stabilizing Ni(II) complexes

Table 4 IR and ^{1}H NMR spectroscopic data for $[NiX_2(RNNNHR)_2]$.

Compound	R	X	% Yield	Colour	IR (ν_{NH})[a]	^{1}H NMR[b]
8	3,5-dmp	Cl	70	Yellow-orange	3267	7.48 (m, 4H, *H*-Ar), 7.05 (m, 2H, *H*-Ar), 2.39 (s, C*H*$_3$,12H)
9	3,5-dmp	Br	56	Yellow-orange	3254	7.43 (s, 4H, *H*-Ar), 7.08 (s, 2H, *H*-Ar), 2.46 (s, C*H*$_3$,12H)
10	3,5-dmp	NO_3	74	Orange	3269	7.26 (s, 4H, *H*-Ar), 6.91 (s, 2H, *H*-Ar), 2.45 (s, C*H*$_3$,12H)
11	3,5-dcp	Br	19	Golden-yellow	3300	7.63 (s, *H*-Ar), 7.44 (s, *H*-Ar), 7.22 (s, *H*-Ar)

[a] Weak absorptions in KBr, [b] in acetone, chemical shift is in ppm.

The electrochemical studies of **8**, **9** and **11** indicate that these three complexes are not redox-active while that of **10** shows two irreversible oxidation waves at 0.65 and 1.17 V and one irreversible reduction wave at -0.19 V (Figure 7). At lower scan rates we found that the second oxidation wave became more reversible (Figure 8); this remains unexplained. The difference in the electrochemical properties of **10** compared with that of **8**, **9** and **11** suggest that **10** might have a different structure upon oxidation. Thus, the nitrate ligand may go from being monodentate in **10** and hence tetrahedral to chelating in $\mathbf{10}^{+/2+}$ and therefore octahedral.

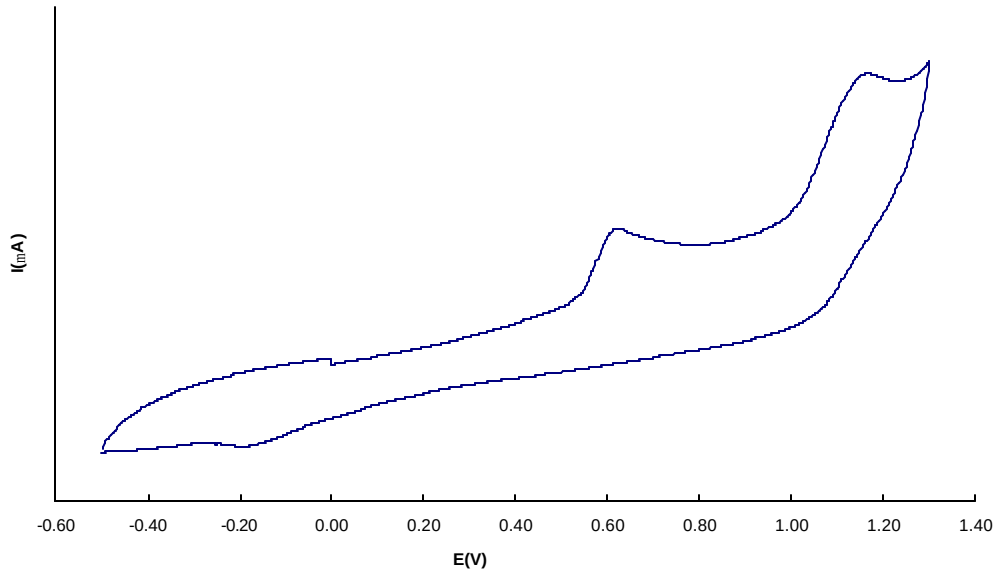


Figure 7 The cyclic voltammogram of **10** in CH_2Cl_2.

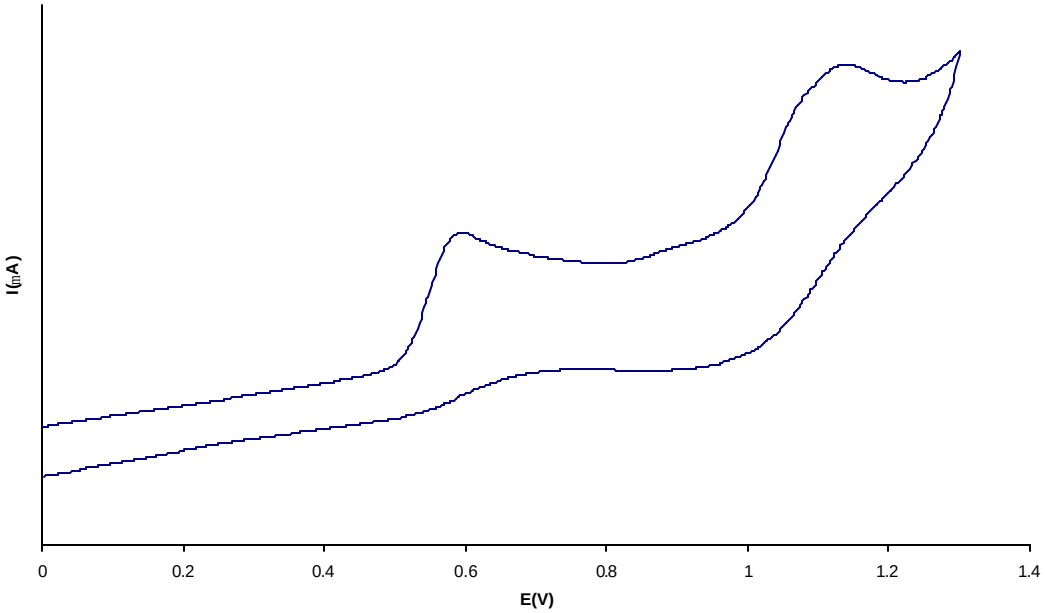


Figure 8 The cyclic voltammogram of **10** in CH_2Cl_2 at lower scan rates.

The reaction of the triazenes (R = 3,5-dcp and 3,5-btfm) and $Ni(NO_3)_2.6H_2O$ give red-orange and light green solids respectively. However, the CHN analysis shows that the product is not pure and further purification by recrystallization or column chromatography has been unsuccessful. Consequently, we can not compare the electrochemical properties of these two complexes with their analogue, $[Ni(NO_3)_2(RNNNHR)_2]\cdot 2H_2O$ **10**.

Synthesis of [$NiCl_2$(RNNNHR)$_2$]·2H_2O (R = 3,5-dmp) 8

$NiCl_2.6H_2O$ (61.8 mg, 0.26 mmol) was dissolved in EtOH (5 cm^3) to give a green solution. RNNNHR (130.1 mg, 0.51 mmol) was dissolved in CH_2Cl_2 (1 cm^3), the orange solution was added drop-wise to the Ni^{2+} solution. An orange solid precipitated. *n*-Hexane (30 cm^3) was added. The mixture was stirred for 30 min. The orange solid was filtered then washed with cold *n*-hexane (5 cm^3). (0.12 g, 70%)

Found: C, 56.6; H, 6.5; N, 12.4. $C_{32}H_{42}N_6O_2Cl_2Ni$. Calcd.: C, 57.2; H, 6.3; N, 12.5.

Synthesis of [$NiBr_2$(RNNNHR)$_2$]·2H_2O (R = 3,5-dmp) 9

$NiBr_2.2H_2O$ (100.4 mg, 0.50 mmol) was dissolved in EtOH (5 cm^3) to give a green solution. RNNNHR (232.4 mg, 0.92 mmol) was dissolved in CH_2Cl_2 (1 cm^3), the orange solution was added drop-wise to the Ni^{2+} solution. The red-orange solution was stirred for 15 min. *n*-Hexane (40 cm^3) was added and the solution was stored at 0 °C overnight. The solid was filtered then washed with cold *n*-hexane (10 cm^3). The yellow-orange solid was dried *in vacuo*. (0.21 g, 57%)

Found: C, 50.7; H, 5.9; N, 11.0. $C_{32}H_{42}N_6O_2Br_2Ni$. Calcd.: C, 50.5; H, 5.6; N, 11.0.

Synthesis of [Ni(NO_3)$_2$(RNNNHR)$_2$]·2H_2O (R = 3,5-dmp) 10

$Ni(NO_3)_2.6H_2O$ (72.6 mg, 0.25 mmol) was dissolved in EtOH (5 cm^3) to give a lime green solution. RNNNHR (127.5 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (1 cm^3), the orange solution was added drop-wise to the Ni^{2+} solution. The red-orange solution was stirred for 15 min. *n*-Hexane (30 cm^3) was added. The mixture was stirred for 1 hour. The solvent was reduced to small volume. The solution was stored at 0 °C overnight. The solid was filtered then washed with cold *n*-hexane (5 cm^3). The yellow solid was dried *in vacuo*. (0.13 g, 74%)

Found: C, 53.6; H, 6.0; N, 15.7. $C_{32}H_{42}N_8O_8Ni$. Calcd.: C, 53.0; H, 5.8; N, 15.5.

Synthesis of [NiBr$_2$(RNNNHR)$_2$]$\cdot$2H$_2$O (R = 3,5-dcp) 11

$NiBr_2.2H_2O$ (65.5 mg, 0.26 mmol) was dissolved in EtOH (1 cm^3) to give a green solution. RNNNHR (170.7 mg, 0..51 mmol) was dissolved in a mixture of *iso*-propanol (4 cm^3) and acetone (1 cm^3), the orange solution was added drop-wise to the Ni^{2+} solution. The red-orange solution was stirred for 15 min. *n*-Hexane (40 cm^3) was added and the solution was stored at 0 °C overnight. The solid was filtered and then washed with cold *n*-hexane (10 cm^3). The dark brown micro crystals were dried *in vacuo*. (175.1 mg, 77%)

Found: C, 35.5; H, 2.1; N, 10.8. $C_{24}H_{14}N_6Cl_8Br_2Ni$. Calcd.: C, 32.4; H, 1.6; N, 9.4.

Synthesis of [NiCl$_2$(RNNNHR)$_2$] (R = 3,5-btfm) 12

$NiCl_2.2H_2O$ (23.7 mg, 0.10 mmol) was dissolved in EtOH (1 cm^3) to give a green solution. RNNNHR (94.0 mg, 0.20 mmol) was dissolved in *iso*-propanol (2 cm^3), a yellow solution was added drop-wise to the Ni^{2+} solution. The yellow-green solution was stirred for 15 min. *n*-Hexane (40 cm^3) was added and the solution was stored at 0 °C overnight. The solid was filtered and then washed with cold *n*-hexane (10 cm^3). The yellow-green solid was dried *in vacuo*. (65 mg, 61%)

Found: C, 36.3; H, 0.9; N, 8.1. $C_{32}H_{14}N_6F_{24}Cl_2Ni$. Calcd.: C, 36.0; H, 1.3; N, 7.9.

1.1. Synthesis and characterization of precursors, [CoX$_2$(RNNNHR)$_2$]

The synthesis of [$CoCl_2$(RNNNHR)$_2$] is similar to that of [NiX_2(RNNNHR)$_2$]. The reaction between $CoCl_2.6H_2O$ and the triazene in EtOH gives a green solid, [$CoCl_2$(RNNNHR)$_2$] when R = 3,5-dmp **14**. The very broad ^{1}H NMR spectrum indicates that the complex is strongly paramagnetic. The green colour of complex **14** is typical of a tetrahedral Co(II) metal complex. After storage at room temperature and in air for a few weeks, complex **14** changes from green to orange. The CHN analysis fits with the complex [$CoCl_2$(RNNNHR)$_2$].$2H_2O$ where two water molecules are now present. Whether these water molecules are bound to the metal or are merely present in the lattice remains unclear. Despite repeated attempts we have been unable to obtain crystals of sufficient quality for an X-ray diffraction study.

Table 5 ^{1}H NMR spectroscopic data for $[CoCl_2(RNNNHR)_2]$.

Compound	R	% Yield	Colour	IR (ν_{NH})[a]	^{1}H NMR[b]
14	3,5-dmp	50	Green	3266	7.30, 6.50, 2.50 in $CDCl_3$
15	3,5-dcp	87	Golden brown	3300	7.54, 7.29

[a] Weak absorptions in KBr, [b] in acetone, chemical shift is in ppm.

In contrast, when R = 3,5-dcp **15**, we found that the precursor changes from green to orange after drying in *vacuo* for a few hours. Solutions of complex **15** vary from green to orange depending on the solvents used. Strongly coordinating solvents such as DMSO give green solutions while non-coordinating solvents *e.g.* acetone give orange solutions. The solvatochromism has been examined by UV-Vis spectroscopy (see Figure 9).

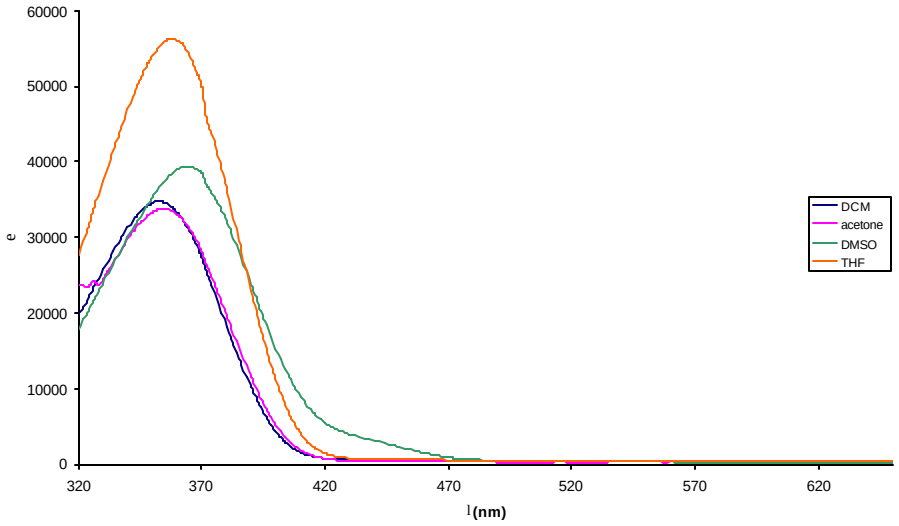


Figure 9 UV-Vis spectra of **15** in DMSO, acetone, THF and CH_2Cl_2.

The spectra all show a very intense band at ~ 350 nm due to a $\pi \rightarrow \pi^*$ ligand based charge transfer. The band is also very broad masking all the very much weaker d-d transitions.

In section 4.3, $[Ni(NO_3)_2(RNNNHR)_2]\cdot H_2O$ **10** is redox active. Therefore, we tried to synthesise the Co(II) analogue by reacting $Co(NO_3)_2\cdot 6H_2O$ with RNNNHR (R = 3,5-dmp or 3,5-btfm) in EtOH. However, the orange red product

decomposed before we managed to isolate it. The decomposition might be due to the presence of water from the starting materials.

The reaction between $Co(OAc)_2 \cdot 4H_2O$ with RNNNHR (R = 3,5-dmp or 3,5-btfm) in EtOH at 40 °C yielded an orange and yellow solid respectively. Analysis of these compounds is currently underway.

Synthesis of $[CoCl_2(RNNNHR)_2]\cdot 2H_2O$ (R = 3,5-dmp) 14

$CoCl_2.6H_2O$ (117.3 mg, 0.49 mmol) was dissolved in EtOH (5 cm^3) to give a deep blue solution. The solution of RNNNHR (249.9 mg, 0.99 mmol) in CH_2Cl_2 (1 cm^3) was added drop-wise to Co^{2+} solution. The brown green solution was stirred for 5 min before the solid precipitated. *n*-Hexane (20 cm^3) was added and the solution was stirred for 10 min. The green solid was filtered and dried *in vacuo* for 3 days during which time the green solid turned to golden yellow. (0.16 g, 50%)

Found: C, 56.9; H, 6.7; N, 12.6. $C_{32}H_{42}N_6O_2Cl_2Co$. Calcd.: C, 57.0; H, 6.2; N, 12.5.

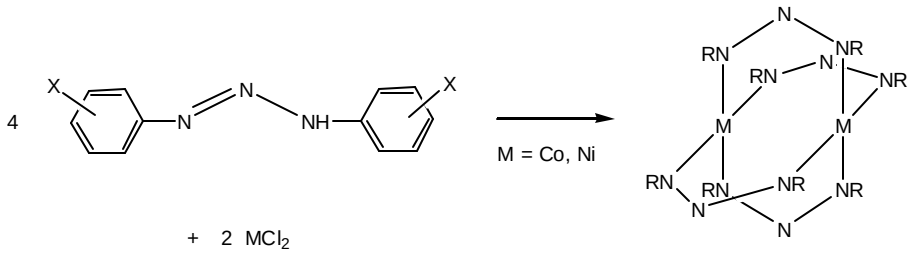
Synthesis of $[CoCl_2(RNNNHR)_2]\cdot 2H_2O$ (R = 3,5-dcp) 15

$CoCl_2.6H_2O$ (116.5 mg, 0.49 mmol) was dissolved in EtOH (5 cm^3) to give deep blue solution. The solution of RNNNHR (324.0 mg, 0.97 mmol) in a mixture of CH_2Cl_2: acetone (5 cm^3, 2:3 ratio) was added drop-wise to a Co^{2+} solution. The deep green solution was stirred for 5 min before the solid precipitated. The green solid was filtered and dried *in vacuo* for 3 hr during which time the green solid turned to golden yellow. (0.34 g, 87%)

Found: C, 30.6; H, 3.2; N, 8.8. $C_{24}H_{14}N_6Cl_{10}Co$. Calcd.: C, 36.0; H, 1.8; N, 10.5.

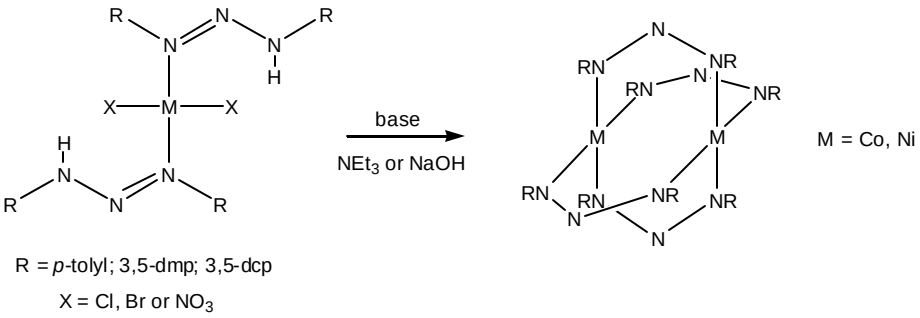
1.2. Synthesis and characterization of Ni(II) and Co(II) paddlewheel complexes [M(μ-RNNNR)$_4$M]

The above complexes, $[MX_2(RNNNHR)_2]$ (M = Ni, R = 3,5-dmp, X = Cl **8**, Br **9** and NO_3 **10**, R = 3,5-dcp and X = Br **11**; M = Co, X = Cl, R = 3,5-dmp **14**, 3,5-dcp **15**), were designed to act as precursors in the synthesis of novel paddlewheel complexes (see Scheme 5).



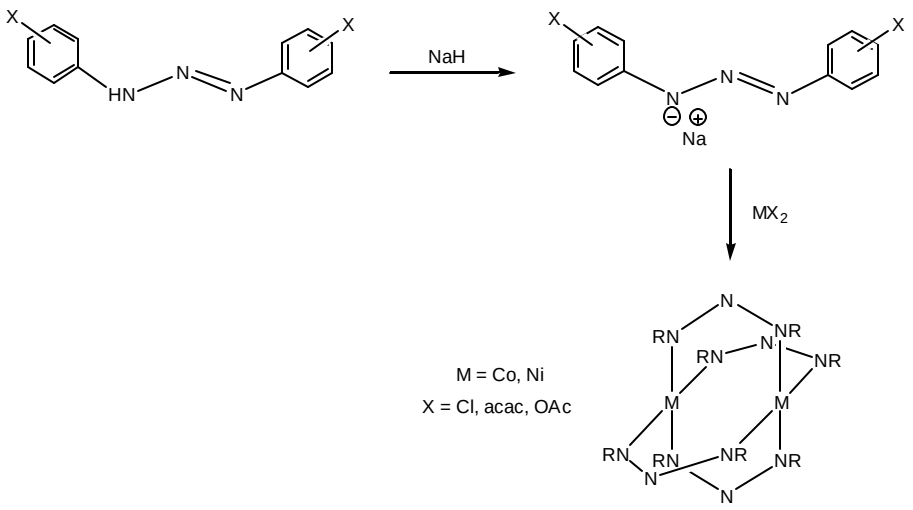
Scheme 5 Proposed synthetic method for the preparation of [M(μ-RNNNR)$_4$M].

Initially, we simply took the freshly prepared complexes and added NEt_3 acting as base to deprotonate the triazene. While this synthetic methodology is successful for Rh, Ir and Pd triazene complexes it doesn't appear to work for their Ni and Co counterparts. The reason for the failure of these reactions may be the presence of water in the precursor. We further reasoned that a stronger base may be required. Thus, the reaction was repeated replacing NEt_3 with a solution of NaOH in EtOH. In all cases an orange-red solid was the only product. Analysis by NMR spectroscopy indicated that this was the free triazene. The complete list of reactions tried with a base is given in Scheme 6.



Scheme 6 Attempted synthesis of [M(μ-RNNNR)$_4$M] with a base.

Deprotonation of the triazene was finally achieved by reacting the free triazene with NaH in dry THF. Subsequent addition of a suitable metal precursor, such as $Ni(acac)_2$ which exists as water free trimers, was intended to yield the paddlewheel complex (see Scheme 7). Unfortunately, the compounds formed tend to be very air sensitive and exposure results in formation of the free triazene and metal salts, probably $M(OH)_2$. Thus, characterization of these compounds has proved impossible.



Scheme 7 Attempted synthesis of [M(μ-RNNNR)$_4$M] with NaH.

Another approach involved taking the water free complex Ni(acac)$_2$ and reacting it with the free triazene under reflux for 24 hours. When the triazene is 3,5-dmp, red microcrystals are formed. The ^{1}H NMR of this solid shows aromatic protons at δ 7.16 (2H), 6.78 (1H) and a Me signal at δ 2.31 (6H). The resonances are broad indicative of a paramagnetic complex but are different from both the free ligand and the starting material. A similar reaction with *p*-tolyl triazene gives a dark brown solid. The ^{1}H NMR of this solid is so broad that it is difficult to know what the product may be. Both products decompose upon recrystallization in Schlenk flasks. In contrast, when the triazene is 3,5-dcp a red-orange solid is isolated which may be [Ni(acac)$_2$(RNNNHR)$_2$]. Similar reactions have been attempted using Ni(OAc)$_2$ as the source of the nickel metal. Irrespective of whether the triazene was *p*-tolyl or 3,5-dmp the only isolated product was the free triazene.

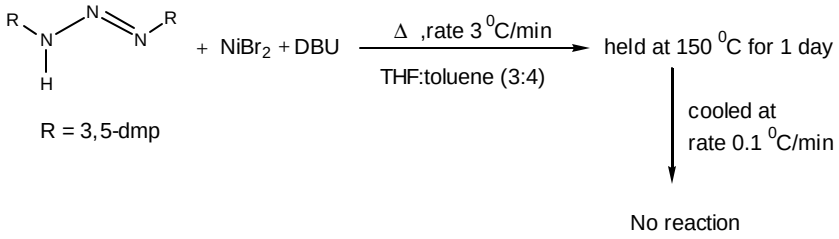
Utilization of $NiBr_2(PPh_3)_2$ as a metal precursor instead of Ni(OAc)$_2$ or [NiX_2(RNNNHR)$_2$] (X = Cl, Br) and subsequent addition of the triazene (R = *p*-tolyl or 3,5-dmp) results in a colour change from green to red-orange (R = 3,5-dmp) or from green to yellow-brown (R = *p*-tolyl). Attempts to recryatallize the solid in a Schlenk flask led to decomposition of the complexes.

Synthesis of the Co analogues have been undertaken using Co(OAc)$_2$ instead of Ni(acac)$_2$. Reluxing the free triazene (R = 3,5-dmp) with Co(OAc)$_2$ in MeOH in the presence of a base (NaOH) or not gives a red-orange solid in both cases.

The ^{1}H NMR spectrum suggests that only the free triazene is present. Replacing 3,5-dmp with *p*-tolyl results in the formation of a purple solid of unknown composition.

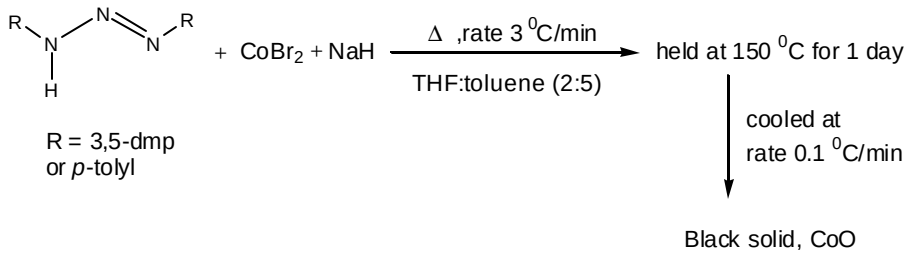
Synthesis of [M(μ-RNNNR)$_4$M] by solvothermal technique

Recently, many metal complexes have been synthesized by a solvothermal technique including paddlewheel complexes. After many failures in the preparation of paddlewheel Ni(II) or Co(II) complexes by conventional methods, we decided to try the solvothermal method. The mixture of RNNNHR (R = 3,5-dmp or *p*-tolyl), $NiBr_2 \cdot 2H_2O$ and DBU in THF:Toluene (3:4) was heated from room temperature to 150 °C at rate 3 °C/min. The mixture was held at 150 °C for 1 day before cooling to room temperature with rate 0.1 °C/min (Scheme 8). The result for R = 3,5-dmp was an unreacted green solid, $NiBr_2$, and a deep red solution (RNNNHR solution). In the case of R = *p*-tolyl, there was black oil from the decomposed product.



Scheme 8

We also varied the base in the reaction from DBU to Na_2CO_3 or NaH but were still unsuccessful. We applied the same condition for Co(II) and found that the decomposed product was a black solid, CoO (Scheme 9)

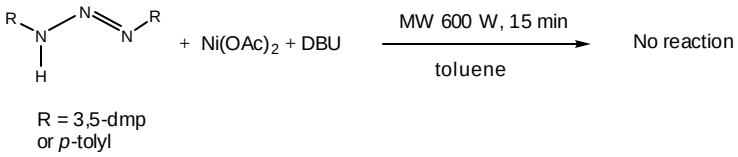


Scheme 9

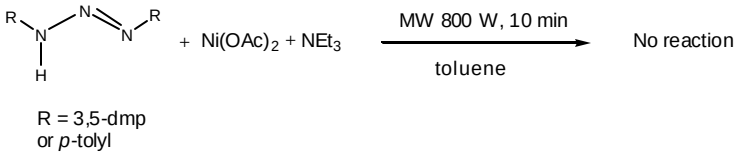
Synthesis of [M(μ-RNNNR)$_4$M] by microwave technique

Most of the paddlewheel complexes of Ni(II) and Co(II) were prepared by refluxing the triazene ligand with Ni(II) or Co(II) salt in toluene for a few days or under molten conditions. As the ligand synthesis shows the microwave technique speeds up the reaction time. Therefore, we explored the possibility of yielding the [M(μ-RNNNR)$_4$M] by using a microwave assisted synthesis (Scheme 10). We varied the strength of the base, the power of the microwave irradiation from 600 – 800 W and also the reaction time but we found that the formation of paddlewheel complex did not occur. The reaction time may not be long enough but for safety we can not continue to irradiate the sample longer than 10-15 min.

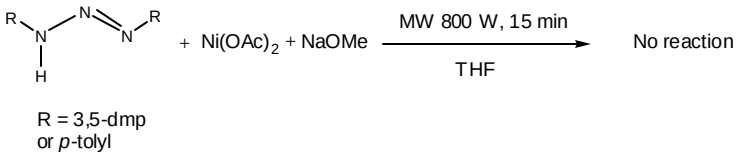
Experiment 1



Experiment 2



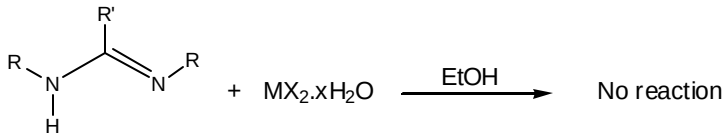
Experiment 3



Scheme 10

1.3. Synthesis and characterization of [MX$_2$(RNC(Me)NHR)$_2$] and [M(μ-(RNC(Me)NR)$_4$M]

We applied the same method of preparing the [NiX$_2$(RNNNHR)$_2$] series to the amidine ligands (Scheme 11). As with the triazene series no reactions were observed.



Scheme 11

Attempts to make the paddlewheel complex directly from the amidine and metal salts in the presence of base by using conventional, solvothermal and microwave assisted techniques proved to be impossible as well.

1.4. Synthesis and characterization of [Cl(PPh$_3$)Pd(m-RNNNR)$_2$PdCl(PPh$_3$)]

After a long series of unsuccessful attempts to synthesize the Ni(II) and Co(II) paddlewheel complexes we sought to investigate the route to these complexes by testing the reaction conditions (most especially the base) with a less reactive metal namely, palladium. Comparatively, weak bases such as NEt_3 have been shown to be successful at deprotonating *p*-substituted triazenes with rhodium, iridium and palladium.[24]

The reaction between $\{PdCl(PPh_3)(\mu\text{-}Cl)\}_2$ and RNNNHR in CH_2Cl_2 and addition of excess NEt_3 to deprotonate the ligand resulted in a yellow solid upon removal of the solvent. The solid is thought to contain the compounds [Cl(PPh$_3$)Pd(μ-RNNNR)$_2$PdCl(PPh$_3$)] (R = 3,5-dmp **16** and R = 3,5-dcp **17**). The ^{1}H NMR spectra of complexes **16** (δ at 8.00, 7.30, 6.80 and 6.75 ppm) and **17** (δ at 7.35-7.75 ppm) confirm the formation of triazenido binuclear complexes. There were also signals at δ 3.12 and 1.40 ppm due to NEt_3. Complex **16** was recrystallized from CH_2Cl_2/*n*-hexane yielding a yellow solid and dark orange square crystals. The X-ray structure of the orange crystals reveals the structure of *trans*-[$PdCl_2(NEt_3)(PPh_3)$] **18** (Figure 10).

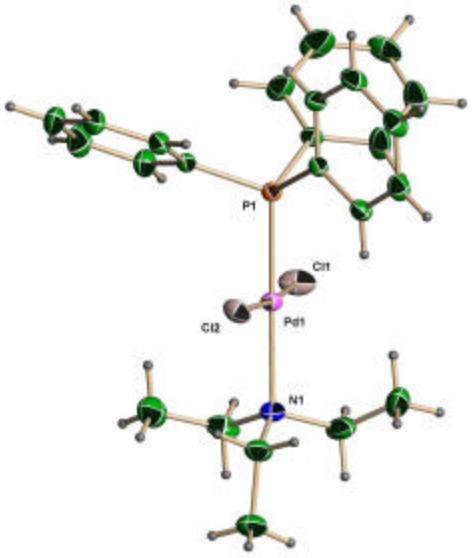
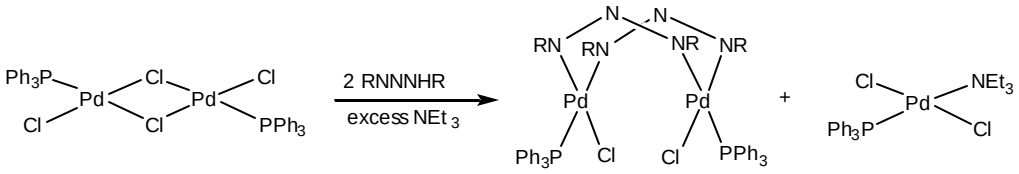


Figure 10 X-ray structure of *trans*-[$PdCl_2(NEt_3)(PPh_3)$] **18**.

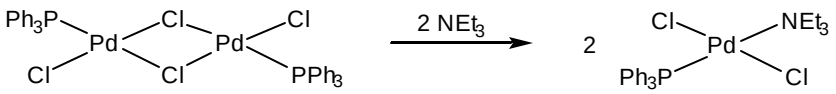
The X-ray crystallographic results indicate that controlling the amount of NEt_3 is essential for the successful synthesis of this compound. Too much NEt_3, clearly results in competition between NEt_3 and triazene leading to a lower yield of the desired compound and a greater amount of impurity (Scheme 12).



16 **18**

Scheme 12

Even though complex **18** is not what we intended to make, according to the CCDC database it is the first palladium-tertiary amine complex to be structurally characterized. A rational synthesis of **18** was devised (Scheme 13). The selected bond lengths and angles are given in Table 6.



18

Scheme 13

Table 6 Bond lengths (Å) and bond angles (°) of *trans*-[$PdCl_2(NEt_3)(PPh_3)$] **18**.

Pd(1)-N(1)	2.236(4)	P(1)-C(13)	1.821(4)
Pd(1)-P(1)	2.2463(12)	P(1)-C(1)	1.833(4)
Pd(1)-Cl(1)	2.2982(14)	N(1)-C(23)	1.484(7)
Pd(1)-Cl(2)	2.2959(12)	N(1)-C(21)	1.493(6)
P(1)-C(7)	1.812(5)	N(1)-C(19)	1.500(7)
N(1)-Pd(1)-P(1)	178.29(11)	C(13)-P(1)-Pd(1)	109.48(15)
N(1)-Pd(1)-Cl(2)	93.81(11)	C(13)-P(1)-Pd(1)	115.04(15)
P(1)-Pd(1)-Cl(2)	84.83(4)	C(1)-P(1)-Pd(1)	118.10(16)
N(1)-Pd(1)-Cl(1)	90.91(11)	C(23)-N(1)-C(21)	110.6(4)
P(1)-Pd(1)-Cl(1)	90.53(5)	C(23)-N(1)-C(19)	108.6(4)
Cl(2)-Pd(1)-Cl(1)	173.32(6)	C(21)-N(1)-C(19)	109.8(4)
C(7)-P(1)-C(13)	108.2(2)	C(23)-N(1)-Pd(1)	108.3(3)
C(7)-P(1)-C(1)	106.5(2)	C(21)-N(1)-Pd(1)	112.9(3)

2. Conclusions

In summary we can now prepare complex triazenes with the range of electron withdrawing and electron donating substituents. The application of microwave synthesis has allowed the preparation of bulky amidines in high yield with much reduced reaction times. This discovery may lead to the isolation of metal complexes with unusual reactivities.

The use of bulky triazenes has allowed the isolation of the first nickel(II) triazene complexes, $[NiX_2(RNNNHR)_2]\cdot 2H_2O$. Electrochemical studies show that even one of the precursors is redox-active. The synthesis of the Ni(II) and Co(II) paddlewheel complexes have proved extremely difficult and despite trying several different bases of varying strength and varying the reaction conditions we have been unable to

prepare the lantern complexes hoped for. There is either no reaction or the product formed quickly decomposes. The synthesis of the paddlewheel complexes may be achieved in a glove box under N_2 or Ar to help to stabilize the compound.

The formation of $[Cl(PPh_3)Pd(\mu\text{-}RNNNR)_2PdCl(PPh_3)]$ suggests that NEt_3 is strong enough to deprotonate the new triazene ligand when it reacts with a less reactive metal. In the course of preparing the palladium dimer we also isolated the first example of a palladium tertiary amine complex, *trans*-$[PdCl_2(NEt_3)(PPh_3)]$.

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Research output

- Poster presentation at the 30th Congress on Science and Technology of Thailand, Bangkok. (Appendix I)
- Poster presentation at the Thailand Research Fund Meeting, Cha-um. (Appendix II)
- Poster presentation at the 31th Congress on Science and Technology of Thailand, Nakhonrachasima. (Appendix III)
- International publication, Acta Crystallographica Section E, 2006, E62, m1616-m1617. (Appendix IV)
- Manuscript submitted to Synthetic Communications. (Appendix V)

Appendix I

Poster presentation at the 30th Congress on Science and Technology of Thailand, Bangkok, 19th - 21st October 2004

Poster presented at STT 30

19th – 21st October 2004

การสังเคราะห์ไตรอะซีนลิแกนด์ชนิดใหม่ และพรีเคอร์เซอร์สำหรับการสังเคราะห์สารประกอบเชิงซ้อนแบบกงล้อนิกเกิล (II) ไตรอะซีไนโด

Synthesis of a new triazene ligand and a precursor for the paddlewheel Ni(II) triazenido complex.

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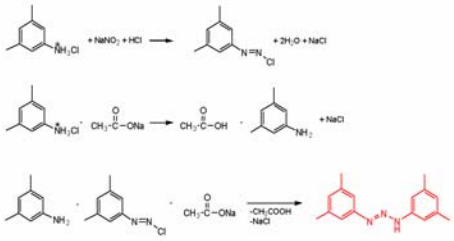
Abstract: The new triazene ligand (RNNNHR; R = 3,5-dimethylphenyl) **1** was made by an adaptation of the synthetic method for RNNNHR when R = *p*-tolyl. The reaction between this ligand and $NiBr_2$ yielded a paramagnetic complex namely $[NiBr_2(RNNNHR)_2]$ **2**. This complex may be a useful precursor in the synthesis of the new paddlewheel complex $[Ni(RNNNR)_4Ni]$ (R = 3,5-dimethylphenyl).

Methodology:

Preparation of RNNNHR (R = 3,5-dimethylphenyl) 1

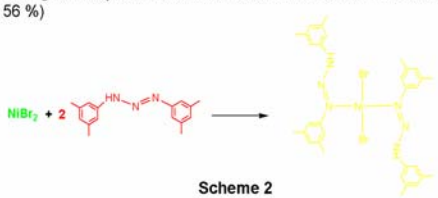
A mixture of ice, water, conc. HCl and 3,5-dimethylaniline were stirred together at room temperature. A solution of $NaNO_2$ was added drop-wise and the resulting mixture was stirred for 10 minutes. A solution of CH_3COONa was then added and the orange solution was stirred in an ice bath for 40 minutes. The oily red-orange solid was extracted from the solution by CH_2Cl_2 and dried over Na_2SO_4. The solution was filtered and the solvent was removed to give a deep red-orange solid. The solid was dissolved in hot hexane and filtered through filter paper. Red-orange needle crystals precipitated from the solution overnight. (Yield 50 %)



Scheme 1

Preparation of $[NiBr_2(RNNNHR)_2]$ (R = 3,5-dimethylphenyl) 2

$NiBr_2.2H_2O$ was dissolved in ethanol. A solution of RNNNHR in CH_2Cl_2 was added drop-wise. The red-orange solution was stirred for 10 minutes. Hexane was added, there was solid precipitated. The solution was stored at 0 °C overnight. The yellow solid was filtered and washed with cold hexane. (Yield 56 %)



Scheme 2

Results and Discussion:

An adaptation of the synthetic method for RNNNHR (R = *p*-tolyl) gives orange microcrystalline RNNNHR (R = 3,5-dimethylphenyl) **1** in good yield. The purity of the triazene **1** was checked by TLC. The IR spectrum (ν_{NH} = 3,200 cm-1) was in agreement with the data reported for other triazenes in the literature. The ^1H NMR spectrum shows two methyl signals at δ 2.42 and 2.47, a broad NH signal at δ 3.83 and aromatic protons signals at 6.43, 7.07 and 7.45.

The broadness of the ^1H NMR spectrum of **2** indicates that complex **2** is paramagnetic. Moreover, the change in the chemical shifts of the triazene ligand in **2** compared with those of the free ligand, **1** suggest that the triazene ligands are indeed bound to Ni(II) atom. Oro *et al.* have reported the synthesis of similar monomeric triazene metal complexes and have used them as effective precursors in the formation of metal dimers.

Conclusion:

We have synthesized a new triazene ligand namely RNNNHR (R = 3,5-dimethylphenyl) **1** and a paramagnetic complex $[NiBr_2(RNNNHR)_2]$ **2**.

Further Work:

Further Work will include the synthesis of the Co analogues of these complexes. These will be compared with their Ni counterparts and conclusions drawn.

The synthesis of the paddlewheel complexes will also be attempted as follows

Scheme 3

References:

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Acknowledgements:
The financial support from Thailand Research Fund (MRG4780116) is gratefully acknowledged.

Appendix II

Poster presentation at the Thailand Research Fund Meeting, Cha-um, 13th – 15th October 2005

Poster presented at TRF meeting

13th – 15th October 2005

Synthesis and characterization of triazenide Ni(II) complexes

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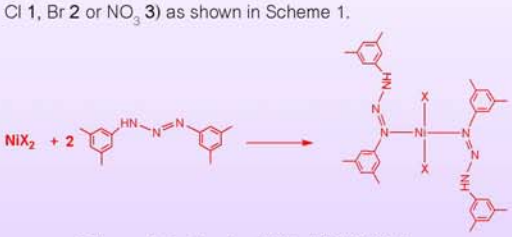
Abstract- The new triazene, RNNNHR (R = 3,5-dimethylphenyl) was used to synthesize a series of Ni(II) complexes namely $[NiX_2(RNNNHR)_2]$ (X = Cl 1, Br 2 or NO_3 3). Characterization by NMR and IR Spectroscopy, mass spectrometry and CHN analysis suggest that the stoichiometry of 1-3 is $[NiX_2(RNNNHR)_2].2H_2O$. Cyclic voltammetric studies of 1-3 found that only 3 is redox-active with irreversible oxidation waves at 0.65 and 1.17 V and an irreversible reduction wave at -0.19 V.

Experimental:

The reaction between $NiX_2.xH_2O$ in EtOH and triazene yields a complex namely $[NiX_2(RNNNHR)_2]$ (R = 3,5-dimethylphenyl, X = Cl **1**, Br **2** or NO_3 **3**) as shown in Scheme 1.



Scheme 1 Synthesis of $[NiX_2(RNNNHR)_2]$.

Results and Discussion:

The broad ^{1}H NMR spectra of **1-3** indicate that these complexes are paramagnetic as we would expect for Ni(II) complexes. However, the change in the chemical shift of the ligands in the complexes compared with the free ligand suggest that the triazene ligands are bonding to Ni(II) as shown in Table 1. Moreover, the shift in the ν_{NH} stretch, of the triazene ligand, to higher wavenumber confirms that the ligand is bound and that it remains protonated.

Table 1 IR and ^{1}H NMR spectroscopic data for $[NiX_2(RNNNHR)_2]$.

Compound	X	% Yield	IR (ν_{NH})[a]	^{1}H NMR[b]
1	Cl	70	3267	7.48 (m, ArC*H*, 4H), 7.05 (m, ArC*H*, 2H), 2.39 (s, CH_3,12H)
2	Br	56	3254	7.43 (s, ArC*H*, 4H), 7.08 (s, ArC*H*, 2H), 2.46 (s, CH_3,12H)
3	NO_3	74	3269	7.26 (s, ArC*H*, 4H), 6.91 (s, ArC*H*, 2H), 2.45 (s, CH_3,12H)

[a] in KBr, [b] in d^6-acetone, chemical shift is in ppm.

Electrochemical studies:

Electrochemical studies of **1-3** indicate that only **3** is redox-active with two irreversible oxidation waves at 0.65 and 1.17 V and one irreversible reduction wave at -0.19 V (Figure 1). The difference in the electrochemical properties of **3** compared with that of **1** and **2** suggest that **3** might have a different structure upon oxidation. Thus, the nitrate ligand may go from being monodentate in **3** and hence tetrahedral to chelating in $\mathbf{3}^{+/2+}$ and therefore octahedral.

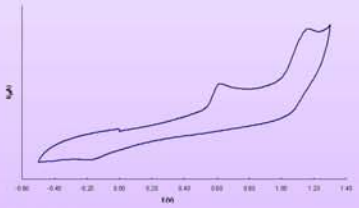


Figure 1 The cyclic voltammogram of **3** in CH_2Cl_2.

Conclusion:

In conclusion, the air stable Ni(II) complexes $[NiX_2(RNNNHR)_2]$ are readily synthesized in a simple one-step procedure. They have been fully characterized, revealing in one case an unusual redox-active Ni(II) complex.

Acknowledgements:

We gratefully thank the Thailand Research Fund (MRG4780116) for financial support and School of Chemistry, University of Bristol, UK for microanalysis and mass spectroscopic services.

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Appendix III

Poster presentation at the 31th Congress on Science and Technology of Thailand, Nakhonrachasima, 18th – 20th October 2005

Poster presented at STT 31

18th – 20th October 2005

สารประกอบเชิงซ้อนเพลเลเดียมไตรอะซีไนโดไดเมอร์ชนิดใหม่

NOVEL PALLADIUM TRIAZENIDO DIMERS

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บทคัดย่อ: ปฏิกิริยาระหว่างคลอโร-บริดจ์เพลเลเดียมไดเมอร์กับไตรอะซีน {RN=NNHR; R = 3,5-dimethylphenyl (3,5-dmp), 3,5-dichlorophenyl (3,5-dcp)} ทำให้เกิดมอนอเมอร์ $[PdCl_2(PPh_3)(RN=NNHR)]$ (R = 3,5-dmp; 3,5-dcp) ซึ่งเมื่อทำการดึงโปรตอนออกจะได้สารประกอบเชิงซ้อนไตรอะซีไนด์บริดจ์ $[Cl(PPh_3)Pd(\mu\text{-}RNNNR)_2Pd(PPh_3)Cl]$ (R = 3,5-dmp **1** and 3,5-dcp **2**) การศึกษาสารประกอบด้วย ^{1}H-NMR สเปกโทรสโกปีช่วยให้ทราบถึงการเกิดไดเมอร์ของสารประกอบดังกล่าว

Abstract: The reaction between chloro-bridged palladium dimers and triazene {RN=NNHR; R = 3,5-dimethylphenyl (3,5-dmp), 3,5-dichlorophenyl (3,5-dcp)} yields the monomers, $[PdCl_2(PPh_3)(RN=NNHR)]$ (R = 3,5-dmp; 3,5-dcp) which may be deprotonated to give triazenide bridged complexes $[Cl(PPh_3)Pd(\mu\text{-}RNNNR)_2Pd(PPh_3)Cl]$ (R = 3,5-dmp **1** and 3,5-dcp **2**). 1H-NMR studies are consistent with a dimeric formulation for these complexes.

Introduction: Our recent work on triazenes has lead to the synthesis of several new triazenes namely, 3,5-dimethylphenyl (3,5-dmp) and 3,5-trifluoromethylphenyl-1,3-triazene (3,5-tfmp) as well as the known 3,5-dichlorophenyl-1,3-triazene (3,5-dcp) (RN=NNHR). The coordination chemistry of these triazenes remains unexplored and we were interested to see how their chemistry may differ from simpler derivatives. To this end we have begun an investigation into their chemistry with palladium as palladium is known to catalyze a wide variety of organic reactions and previous palladium triazenido complexes have proved to be redox active.

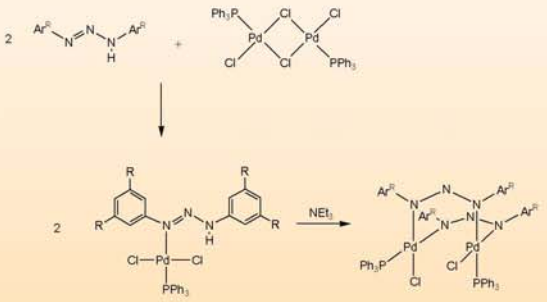

Figure 1 Synthetic route for $[Cl(PPh_3)Pd(\mu\text{-}RNNNR)_2Pd(PPh_3)Cl]$ complexes.

Methodology: $(PPh_3)ClPd(\mu\text{-}Cl)_2PdCl(PPh_3)$ was suspended in dry CH_2Cl_2 (15 mL) giving an orange suspension and stirred for 5 minutes. RNNNHR (R = 3,5-dmp, 3,5-dcp) was added with a further 10 mL of dry CH_2Cl_2 resulting in a darkening of the orange suspension. The suspension was stirred for 10 minutes and then NEt_3 was added. The suspension became immediately clear yielding a dark orange solution. This was stirred for a further hour and then reduced to dryness *in vacuo*. The solid was washed with dry *n*-hexane (3 × 10 mL) and then dissolved in dry toluene (15 mL) and filtered. Subsequent layering with *n*-hexane (50 mL) gave dark orange crystals.

Results and Discussion: The reaction of $[(PPh_3)ClPd(\mu\text{-}Cl)_2PdCl(PPh_3)]$ with triazene and subsequent deprotonation with a mild base (NEt_3) gives dark orange solids formulated as $[Cl(PPh_3)Pd(\mu\text{-}RNNNR)_2Pd(PPh_3)Cl]$ (R = 3,5-dmp **1** and 3,5-dcp **2**). ^{1}H-NMR spectroscopic studies reveal the presence of two multiplets between 7.35 -7.75 ppm characteristic of PPh3. In addition, there are several other aromatic protons at 8.00, 7.30, 6.80 and 6.75 ppm in a ratio of 4:2:4:2 indicative of four distinct aromatic environments consistent with a dimeric palladium complex (R = 3,5-dcp). In the case of R =3,5-dmp further peaks are observed for the aromatic methyl groups again supporting a dimeric formulation.

Conclusion: In conclusion, palladium triazenido bridged compounds are readily synthesized by a simple one-pot reaction from readily available palladium and triazene starting materials.

Acknowledgements: This work has been supported by the Thailand Research Fund (MRG4780116).

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Appendix IV

International Publication

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trans-Dichloro(triethylamine-κN)(triphenylphosphine-κP)palladium(II)

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trans-Dichloro(triethylamine-κN)(triphenylphosphine-κP)palladium(II)

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The Pd atom in the title compound, *trans*-[$PdCl_2(C_6H_{15}N)(C_{18}H_{15}P)$], is in an approximately square-planar environment, coordinated by one triethylamine, one triphenylphosphine and two *trans* Cl ligands.

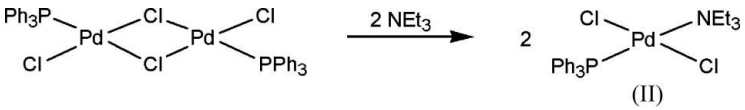
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.052
wR factor = 0.106
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The chemistry of palladium(II) complexes containing nitrogen donor ligands continues to be of interest, in part due to the role of such compounds in C—N bond formation (Hartwig, 1998; Müller & Beller, 1998). In this work, we report the synthesis and structural characterization of the first palladium–tertiary amine complex containing a *trans*-dichloro(triphenylphosphine) structural unit.



(II)

A one-pot reaction of [{Pd(μ-Cl)Cl(PPh_3)}$_2$] and *R*NNNH*R* (*R* = 3,5-dimethylphenyl) with excess NEt_3, for deprotonation of the triazene ligand, yielded not only the new Pd^{II} triazenide-bridged complex, [$(PPh_3)ClPd(\mu$-RNNNR)$_2$PdCl(PPh_3)], (I), but also a by-product, *viz.* *trans*-[$PdCl_2\{N(C_2H_5)_3\}\{P(C_6H_5)_3\}$], (II) (Harding & Harding, 2006). Subsequently, a rational synthesis of (II) was devised (see scheme) and the compound was studied by single-crystal X-ray crystallography.

Complex (II) consists of a Pd^{II} metal centre bound to one triethylamine, one triphenylphosphine and two *trans* Cl ligands (Fig. 1). The Pd—Cl and Pd—P bond distances (Table 1) are in good agreement with other structurally related compounds, such as *trans*-[$PdCl_2(NHCy_2)(PPh_3)$] (Cy is cyclohexyl; Parvez *et al.*, 2004), *trans*-[$PdCl_2(MeNHCH_2Ph)(PPh_3)$] (Jones *et al.*, 2000) and *trans*-[$PdCl_2$(indoline-κN)(PPh_3)] (Chen *et al.*, 1997). In contrast, the Pd—N bond distance is 2.236 (4) Å, far longer than that observed in palladium(II) complexes with secondary amines (Pd—N = 2.121–2.166 Å; Parvez *et al.*, 2004; Jones *et al.*, 2000; Chen *et al.*, 1997; Albinati *et al.*, 1992). The coordination of palladium has an approximately square-planar geometry (Table 1).

Experimental

NEt_3 (40 µl, 0.29 mmol) was added to a yellow suspension of [{Pd(μ-Cl)Cl(PPh_3)}$_2$] (0.0910 g, 0.1 mmol) in CH_2Cl_2 (10 ml). The resulting clear orange solution was stirred for 15 min, then *n*-hexane (15 ml) was added. The solvent was removed *in vacuo* until an orange solid started to precipitate. The mixture was stored at 253 K overnight,

yielding an orange solid (0.0670 g, 62%). Suitable orange plate-shaped crystals were obtained by allowing *n*-hexane to diffuse into a concentrated solution of the complex in CH_2Cl_2 at 253 K.

Crystal data

$[PdCl_2(C_6H_{15}N)(C_{18}H_{15}P)]$	$Z = 4$
$M_r = 540.76$	$D_x = 1.465$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 16.6260$ (14) Å	$\mu = 1.05$ mm^{-1}
$b = 10.7341$ (9) Å	$T = 293$ (2) K
$c = 14.9916$ (13) Å	Plate, orange
$\beta = 113.628$ (2)°	0.21 × 0.20 × 0.01 mm
$V = 2451.2$ (4) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	17249 measured reflections
	4312 independent reflections
ω scans	3639 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$R_{int} = 0.045$
	$\theta_{max} = 25.0°$
$T_{min} = 0.804$, $T_{max} = 0.990$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 1.5049P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.052$	
$wR(F^2) = 0.106$	
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
4312 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
265 parameters	$\Delta\rho_{min} = -0.78$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pd1—N1	2.236 (4)	Pd1—Cl2	2.2957 (12)
Pd1—P1	2.2459 (12)	Pd1—Cl1	2.2979 (14)
N1—Pd1—P1	178.30 (11)	N1—Pd1—Cl1	90.91 (11)
N1—Pd1—Cl2	93.80 (11)	P1—Pd1—Cl1	90.53 (5)
P1—Pd1—Cl2	84.83 (4)	Cl2—Pd1—Cl1	173.33 (6)

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95–0.98 Å and with U_{iso}(H) values set equal to 1.2 times U_{eq} of the carrier atom for sp^2 H atoms and methylene CH_2 groups, and to 1.5 times U_{eq} of the carrier atom for the methyl H atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSHELL* (Bruker, 1997); software used to prepare material for publication: *XSHEL*L.

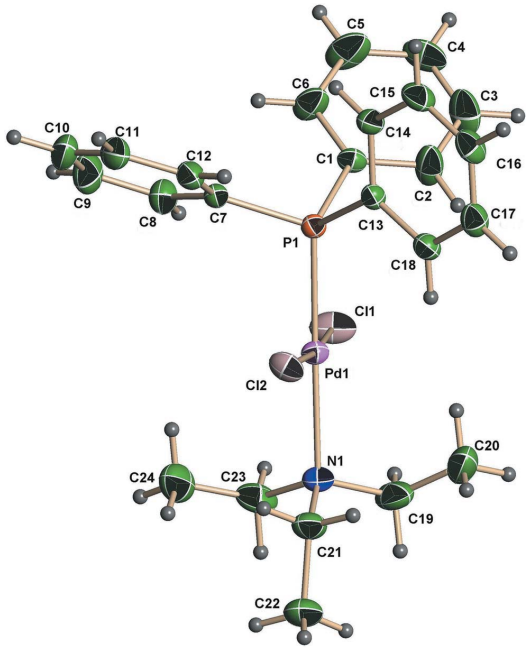


Figure 1
The molecular structure of (II), showing 50% probability displacement ellipsoids.

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Appendix V

Manuscript submitted to

Synthetic Communications

Microwave-Assisted Synthesis of N,N′-Disubstituted Acetamidine Ligands

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ABSTRACT

Under microwave activation, triethylorthoacetate reacts with the substituted anilines in the presence of acetic acid as a catalyst producing acetamidine in moderate to high yields. The X-ray structures of the new amidine, *N*,*N*′-bis(3,5-dimethylphenyl)-acetamidine and *N*,*N*′-bis(*p*-tolyl)acetamidine are also reported revealing polymeric chains supported by intramolecular H-bonds.

Keywords: amidine; microwave-assisted synthesis, one-pot.

COMMENT

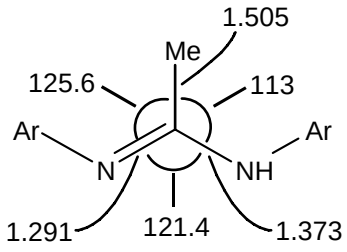
Recently, amidines have been used as bridging ligands for the preparation of transition metal complexes, especially paddlewheel complexes.[1-4] Rapid synthesis of increasingly complex amidines is therefore of prime importance. Taylor and Ehrhart reported an efficient synthesis of N,N′-disubstituted formamidines and acetamidines by refluxing ethyl orthoformate with alkylamines in the presence of acetic acid as a catalyst at high temperature and subsequent distillation at 80-150 °C under low pressure to remove the by-product, ethanol, and excess starting material. However, this method is time consuming requiring lengthy refluxing and extensive work-up to isolate the product.[5] In this communication we report a novel method for the synthesis of N,N′-disubstituted acetamidines by using a modified domestic microwave oven.[6-7]

Reflux of triethylorthoacetate and the desired aniline in the presence of acetic acid as a catalyst under microwave irradiation at 850 W for 5-7 min yields N,N′-disubstituted acetamidine, [RNC(Me)NHR] (R = 3,5-dimethylphenyl **1** and *p*-tolyl **2**), shown in scheme 1. The byproduct, EtOH, is easily removed by placing a receiver between the round bottom flask and the condenser and heating under microwave conditions at 850 W for a further two or three minutes. The complete removal of EtOH is the key to high yield and purity of the product. In general yields are comparable or increased by 10-20% and reaction times are shortened to minutes rather than hours with isolated pure products obtained in most cases in under an hour.

IR spectra of **1** and **2** show ν_{NH} at 3281 and 3301 cm^{-1} respectively. Additional bands are observed for the aromatic C=C and C-H stretches and are comparable with other reported amidines.[5] The ^{1}H NMR of the new amidine, **1** reveals two singlets in the aromatic region and a doublet for the aromatic methyl groups slightly downfield

of a singlet for the central amidine methyl group. The presence of two peaks for the aromatic methyl groups suggests that the acetamidine is asymmetric on the NMR timescale. The amino hydrogen is not observed in the NMR spectrum presumably due to broadening.

Single crystal X-ray diffraction studies of compounds **1** and **2** were undertaken and the molecular structures are shown in Figures 1 and 2 respectively with selected bond lengths and angles given in Table 1. The structures closely resemble one another differing only in the substitution on the aromatic ring and consequently the following discussion will be limited to the structure of **1**. The amidine molecules adopt a *trans*-configuration with one of the aromatic rings orthogonal to the plane of the acetamidine core (see Figures 1 and 2). This arrangement is preferred because of the presence of a weak intramolecular hydrogen bond between the H-atom on N(1) and the imine nitrogen, N(2) on a neighbouring molecule. The H-bond length is 2.26(4) and 2.25(6) Å for **1** and **2** respectively. In contrast to other reported amidines the H-bond forms a zigzag chain, in which neighbouring amidines are almost orthogonal to one another, and *not* a dimer of molecules.[8] The N(2)-C(1) bond is considerably shorter than the N(1)-C(1) bond (1.291 *cf.* 1.373 Å) consistent with double and single carbon-nitrogen bonds respectively.



In conclusion, we have successfully synthesized N,N′-disubstituted acetamidine ligands by microwave activation reducing reaction times to a matter of minutes rather than hours. X-ray crystal structures reveal that the acetamidine

molecules form polymeric chains through intramolecular hydrogen bonds. The synthesis of more complex acetamidines is currently underway in these laboratories.

EXPERIMENTAL

A modified domestic microwave oven with a computer controller and infrared thermometer was used for all experiments (details of the microwave reactor are available at http://www.science.mju.ac.th/chemistry/research/weerachai/reactor_eng.htm). Melting points were determined on a Stuart SMP3. Infrared spectra (as KBr discs) were recorded on a Perkin-Elmer Spectrum One infrared spectrophotometer in the range 400-4000 cm^{-1}. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in $CDCl_3$ with $SiMe_4$ as an internal standard. Elemental analyses and ESI MS were carried out by the staff of the School of Chemistry, University of Bristol, UK.

Synthesis of N,N′-Bis(3,5-dimethylphenyl)acetamidine (1)

Method A

A mixture of triethylorthoacetate (2.0 cm^3, 10.4 mmol), 3,5-dimethylaniline (1.6 cm^3, 20 mmol) and acetic acid (0.5 cm^3) was placed in a microwave oven equipped with a reflux condenser and heated at 850 W for 7 minutes. A receiver was placed between the flask and the condenser and the mixture heated under microwave conditions at 850 W for a further two or three minutes. The volume was reduced under vacuum to yield a thick oil and *n*-Hexane (10 cm^3) was added. The solution was cooled to 0°C resulting in colourless crystals (1.21 g, 45%)

Method B

Triethylorthoacetate (1 cm^3, 5.2 mmol), 3,5-dimethylaniline (0.78 cm^3, 10 mmol) and acetic acid 40 μL was reflux at 135 °C for 2 hours. The orange solution was distilled at 140 °C under *vacuo* to remove EtOH and starting material. The orange crystals were washed with cool *n*-hexane gives colourless crystals and orange solution. The mixture was stored at -20 °C overnight. The colourless crystals was filtered and dried in air, yield 0.619 g (47%).

m.p. 160-161.5 °C. IR (KBr, cm^{-1}) 3301 w, 3270 w, 3152 w, 3096 w, 2917 w, 2861 w, 1636 s, 1567 s, 1467 s, 1344 s, 1157 s, 1047 m, 846 s, 691 s, 654 s. ^{1}H NMR [$CDCl_3$], δ 6.78 (s, 3H, *H*-Ar), 6.68 (s, 3H, *H*-Ar), 2.28 (d, 12H, Ar-CH_3), 1.98 (s, 3H, CH_3). Found: C, 81.5; H, 8.3; N, 10.6. $C_{18}H_{22}N_2$. Calcd.: C, 81.2; H, 8.3; N, 10.5.

Synthesis of N,N′-Bis(p-tolyl)acetamidine (2)

A mixture of triethylorthoacetate (2.0 cm^3, 10.4 mmol), *p*-toluedine (2.12 g, 19.8 mmol) and acetic acid (0.5 cm^3) was placed in a microwave oven equipped with a reflux condenser and heated at 850 W for 5 minutes. A receiver was placed between the flask and the condenser and the mixture heated under microwave conditions at 850 W for a further two or three minutes. The volume was reduced under vacuum to yield a thick oil and *n*-Hexane (10 cm^3) was added. The solution was cooled to 0°C resulting in off-white crystals (1.66 g, 70%)

m.p. 102-103 °C. IR (KBr, cm^{-1}): 3281br, 3021 w, 2922 w, 2856 w, 1639 s, 1595 s, 1514 s, 1375s, 1219 s, 1016 w, 817 s, 655 m, 506 s. ^{1}H NMR [$CDCl_3$], δ. 7.14-7.05 (m, 8H, *H*-Ar), 2.32 (s, 6H, CH_3), 2.00 (s, 3H, CH_3). Found: C, 74.6; H, 7.4; N, 10.4. $C_{16}H_{18}N_2 \cdot 0.75H_2O$. Calcd.: C, 74.6; H, 7.8; N, 11.1.

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Table 1 Crystal and intensity data for RNC(Me)NHR (R = 3,5-dmp **1** and *p*-tolyl **2**).

	1		**2**	
Empirical formula	$C_{18}H_{22}N_2$		$C_{16}H_{18}N_2$	
Formula weight	266.38		238.32	
Temperature	100(2) K		100(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Orthorhombic		Orthorhombic	
Space group	Pbca		Pbca	
Unit cell dimensions	a = 8.5708(9) Å	α = 90°.	a = 12.390(3) Å	α = 90°.
	b = 15.7448(16) Å	β = 90°	b = 9.1300(18) Å	β = 90°
	c = 23.201(2) Å	γ = 90°	c = 23.950(5) Å	γ = 90°
Volume	3130.8(6) $Å^3$		2709.2(9) $Å^3$	
Z	8		8	
Density (calculated)	1.130 Mg/m^3		1.169 Mg/m^3	
Absorption coefficient	0.066 mm^{-1}		0.069 mm^{-1}	
F(000)	1152		1024	
Crystal size	0.32 x 0.18 x 0.14 mm^3		0.32 x 0.10 x 0.09 mm^3	
Theta range for data collection	1.76 to 27.53°		1.70 to 30.98°	
Index ranges	-11<=h<=11, -19<=k<=17, -30<=l<=29		-16<=h<=17, -13<=k<=13, -29<=l<=34	
Reflections collected	38695		53317	
Independent reflections	3545 [R(int) = 0.0706]		4217 [R(int) = 0.1169]	
Completeness to θ = 27.53°	98.2 %		100.0 %	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	0.9908 and 0.9791		0.9938 and 0.9782	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data / restraints / parameters	3545 / 0 / 186		4217 / 0 / 167	
Goodness-of-fit on F^2	1.048		1.032	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0491, wR2 = 0.1134		R1 = 0.0875, wR2 = 0.1903	
R indices (all data)	R1 = 0.0733, wR2 = 0.1250		R1 = 0.1884, wR2 = 0.2347	
Largest diff. peak and hole	0.266 and -0.294 e. $Å^{-3}$		0.026(3)	

Table 2 Selected Bond lengths (Å) and bond angles (°) of **1** and **2**.

	1	**2**
N(1)-C(1)	1.3727(18)	1.363(3)
N(1)-C(2)	1.4122(18)	1.416(3)
N(1)-H(1)	0.8800	0.8800
N(2)-C(1)	1.2906(18)	1.295(3)
N(2)-C(8)	1.4293(18)	1.422(3)
C(1)-C(14)	1.505(2)	1.499(3)
C(1)-N(1)-C(2)	129.46(12)	126.87(18)
C(1)-N(1)-H(1)	115.3	116.6
C(2)-N(1)-H(1)	115.3	116.6
C(1)-N(2)-C(8)	118.61(12)	118.63(18)
N(2)-C(1)-N(1)	121.42(13)	120.58(19)
N(2)-C(1)-C(14)	125.55(13)	124.65(19)
N(1)-C(1)-C(14)	113.03(12)	114.76(19)
C(3)-C(2)-N(1)	123.90(13)	119.40(18)
C(7)-C(2)-N(1)	116.46(13)	122.07(17)
C(13)-C(8)-N(2)	120.05(14)	120.3(2)
C(9)-C(8)-N(2)	120.66(14)	120.9(2)

Scheme 1 Synthesis of acetamidine.

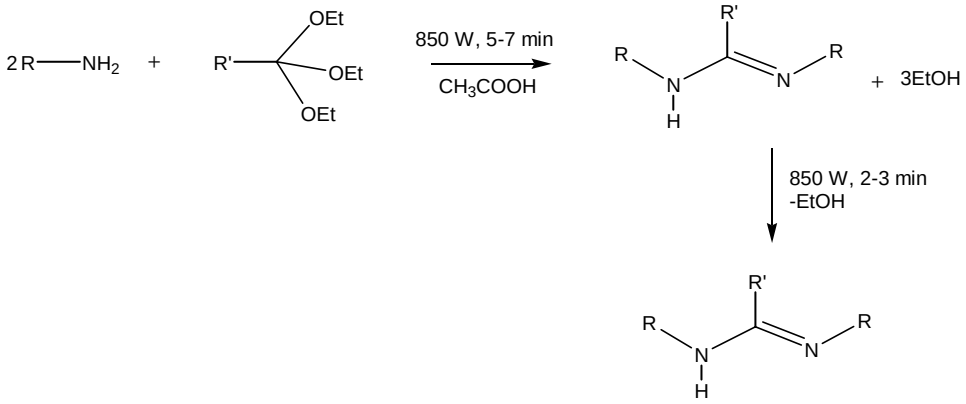

Figure 1 Molecular structure of **1** with thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity.

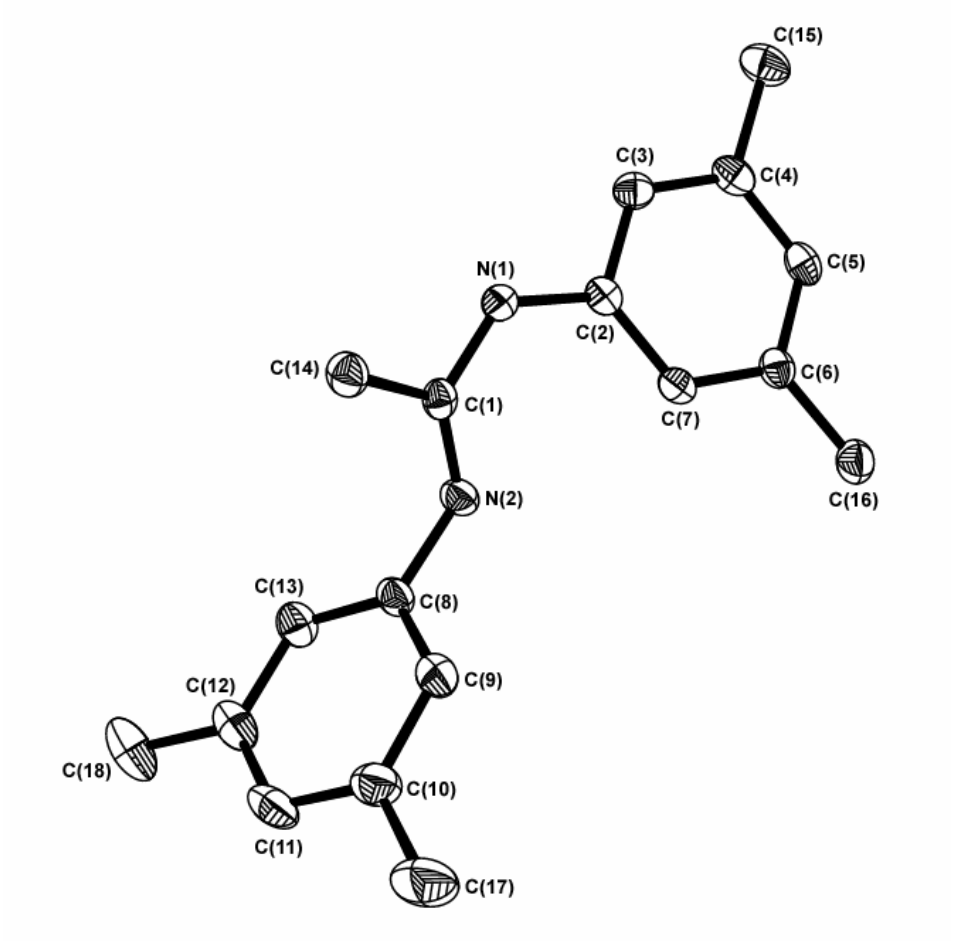

Figure 2 Molecular structure of **2** with thermal ellipsoids at 50% probability.

Hydrogen atoms have been omitted for clarity.