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Preparation and structural characterization of tetracoordinated tungsten(II) diazadiene complexes

Thouraya Turki [a], Taha Guerfel [b], Faouzi Bouachir [a,*]

[a] *Laboratoire de Chimie de Coordination, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia*
[b] *Laboratoire de Chimie du Solide, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia*

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Abstract

Reduction in situ of $WCl_4(MeCN)_2$ with zinc in the presence of diazadiene ligands **1b–f** is reported and produces a series of diamagnetic complexes $(DAD)WCl_2$ **2b–f**. All complexes were characterized by ^1H, ^{13}C NMR and IR spectroscopic data. The crystal structures of complexes **2b** and **2e** were solved by X-ray diffraction methods.

Keywords: Tungsten; Chemical reduction; Tungsten(II) diazadiene complexes; α-Diimine; X-ray crystallographic determination

1. Introduction

Diazadienes (DAD, **1**) exhibit a rich coordination chemistry [1]. In fact, they can formally act as 2-, 4-, 6- or 8-electron donors. Metal coordination of the heterodiene is possible in different conformations. The most frequent case is the chelation of two imine nitrogens by one metal.

Late transition metal complexes of 1,4-diaza-1,3-diene (DAD, **1**) ligands have recently received renewed attention, primarily due to their usefulness as homogenous polymerization catalysts [2]. As a result, the reaction chemistry of this class of diimine ligand with a variety of transition metals has become well established [1,3–8]. Lately, the interest in early transition metal chemistry has focused on group 6 complexes that contain chelating diazadiene ligands [9–15].

Coordination of these diazadiene ligands to low-valent Pt(0) and Pd(0) metal centers was shown to stabilize the imine functionality towards hydrolysis. Despite a growing interest in the chemistry of water-soluble organometallic complexes and their potential application as recoverable "green" catalysts [16,17], the use of diimine complexes in this area of research has remained relatively unexplored.

Only few examples of divalent chromium and molybdenum containing diazadiene ligands are known [18,19]. Herein, we describe the preparation of divalent tungsten compounds with diazadiene ligand as well as the structure of W(II) species in the solid-state by X-ray crystallography. The diazadiene derivatives **1b–f** used in this study are shown in Table 1.

2. Results and discussion

The reduction of $WCl_4(MeCN)_2$ with zinc in the presence of diazadiene ligand, using dichloromethane as solvent, resulted in the formation of the tungsten complexes $WCl_2(DAD)$ **2b–f**.

The divalent tungsten(II) compounds containing diazadiene ligands have been isolated as green crystals for **2b–c**, orange for **2d–e** and yellow for **2f** in good yields after recrystallization in a mixture of CH_2Cl_2/n-hexane. All of them are readily soluble in polar organic solvents such as DMSO, DMF, CH_3CN but are insoluble in water. They have been characterized by ^1H, ^{13}C NMR and IR spectroscopy. Single crystals of **2b** and **2e** suitable for X-ray

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[*] Corresponding author. Tel.: +216 98 503 997; fax: +216 71 704 329.
E-mail address: bouachirf@yahoo.de (F. Bouachir).

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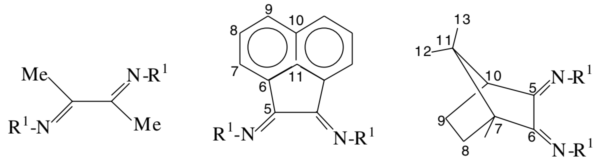
Table 1
Diazadiene derivatives used



DAD : 1b-c 1d-e 1f

Compound	R^1
1b	2,4,6-Me_3–C_6H_2
1c	2,6-Me_2–C_6H_3
1d	2,6-*i*Pr_2–C_6H_3
1e	2-Me–C_6H_4
1f	C_6H_5

analysis have been obtained from CH_2Cl_2/*n*-hexane at ambient temperature.

The new complexes exhibit spectroscopic data in agreement with the proposed structures. ^{13}C NMR spectra of complexes **2b**–**f** at ambient temperature show the presence of the expected number of carbon atoms. The substituents on the aryl groups of the diazadiene ligand are all equivalent as indicated for the C_{2v} and C_2-symmetric isomer which is in accord with the proton NMR spectra. The iminic carbon appears at the range between 159 and 173 ppm, which is slightly shielded in comparison to the free ligands (4 ppm). This result is similar to those observed with other complexes (DAD)MCl_2 [M = Cr, Mo] [18,19] and (DAD)$M(CO)_4$ [20].

In the IR spectra of **2b**–**f** (as KBr pellets), the C=N stretching vibration is observed at 1600–1660 cm^{-1}, i.e., shifted by 10–30 cm^{-1} to lower frequency in comparison to the free ligands.

The analysis of the structure of both complexes, **2b** and **2e,** has been conducted using single-crystal X-ray diffraction. In each case, a single crystal has been grown from a mixture of CH_2Cl_2/*n*-hexane solution at room temperature.

The ORTEP diagrams of **2b** and **2e** are shown in Figs. 1 and 2, with details of the structure determination including unit cell data, data collection parameters, as well as refinement information that is summarized in Table 2. Relevant bond distances and bond angles, for both structures, are presented in Tables 3 and 4, respectively.

The N1–W–N2 angle of 78.57(17)° and 81.3(6)° for compounds **2b** and **2e**, respectively, reflects a slightly distorted tetrahedral coordination sphere. These angles are consistent with known literature values for related complexes [21]. The α-diimine plane ($N{=}C{-}C{=}N$) is essentially planar (torsion angle N1–C19–C20–N2 = −0.06° and N1–C1–C12–N2 = 0.40° for compounds **2b** and **2e**, respectively); a result that is very similar to other platinum(II) complexes [22].

Comparison with other diazadiene complexes [18,19] in the literature indicates that as the steric bulk of the aryl *ortho* substituents increases, the *N*-aryl rings tend to lie more perpendicular to the α-diimine plane ($N{=}C{-}C{=}N$).

The N1–C19 (N1–C1), N2–C20 (N2–C12) and C19–C20 (C1–C12) bond distances are equal to 1.25(7), 1.26(7) and 1.51(7) in **2b** and 1.22(19), 1.27(2) and 1.59(2) in **2e**, respectively, confirming the conjugated diimine nature of this ligand [11].

There are no significant differences observed in the W–Cl and W–N bond distances between the two complexes. The W–Cl bonds are equal to 2.21(19) and 2.27(2) for **2b** and 2.17(7) and 2.17(6) for **2e** while for the W–N bonds we obtained 2.06(4) and 2.03(4) for **2b** and 2.09(13) and 2.06(14) for **2e**, respectively.

3. Conclusion

A novel synthetic procedure for divalent tungsten(II) complexes with α-diimine ligands was described. The new

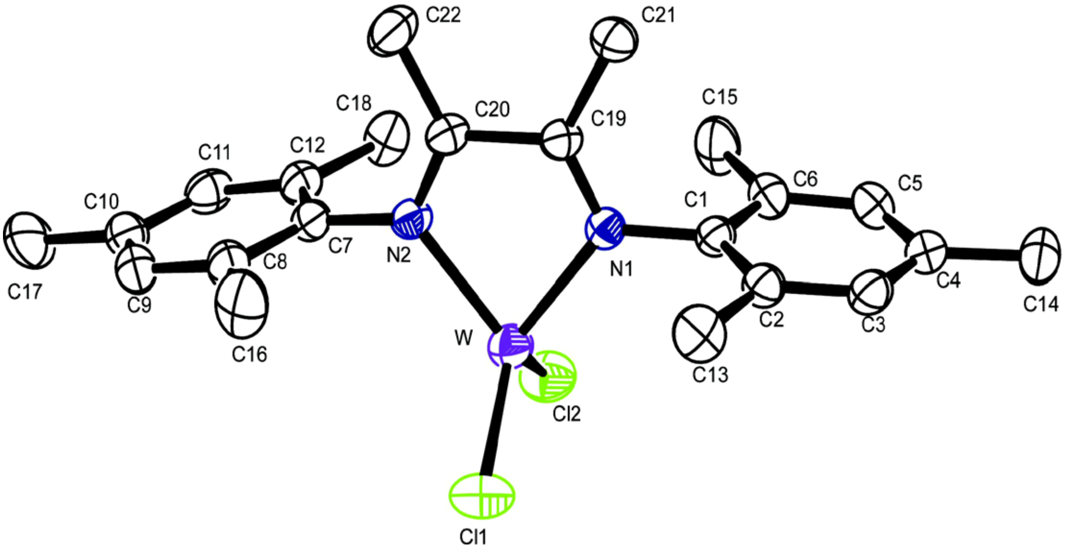


Fig. 1. ORTEP diagram of **2b** · CH_2Cl_2. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.

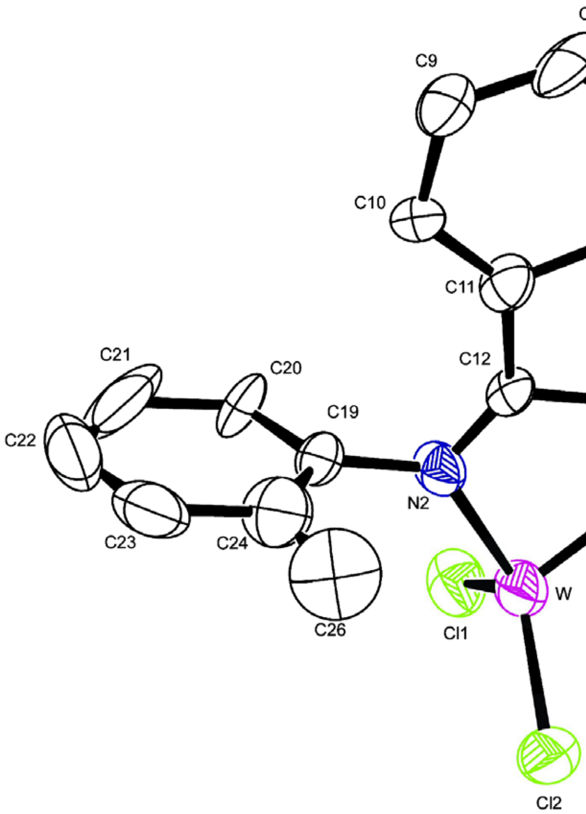


Fig. 2. ORTEP diagram of **2e**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for the sake of clarity.

complexes (DAD)WCl_2 **2b**–**f** display a slightly distorted tetrahedral coordination geometry around tungsten.

The reactivities of these complexes in polymerisation reactions are currently under investigation and the result will be reported in subsequent publications.

4. Experimental

All manipulations are carried out under an atmosphere of dry and oxygen-free argon with standard schlenk techniques. Diethylether was purified by reflux over sodium benzophenone ketyl and distilled under argon prior to use. Methylene chloride and *n*-hexane were purified from P_2O_5 and distilled under argon.

The diazadiene ligands: dab (**1b**–**c**) [23], Ar–BIAN (**1d**–**e**), Ph–BIC (**1f**) [24]; $WCl_4(MeCN)_2$ [25] were obtained according to literature procedures.

All routine NMR experiments were carried out on a Bruker AM 300 and infrared spectra on a BioRad FTS-6000 spectrophotometer.

General procedure for the preparation of (DAD)WCl₂. In an inert atmosphere, $WCl_4(MeCN)_2$ (1 equiv.) was added to diazadiene ligand (3 equiv.) in 20 ml of anhydrous CH_2Cl_2. Zinc powder was added (5 equiv.) as a reducing agent. The solution was stirred at room temperature for two days. The supernatant was separated by filtration, and the solvent was removed under vacuum until 3 ml. The product was precipitated by addition of hexane. Pure compound was isolated as a solid by crystallization from methylene chloride/hexane solution at ambient temperature. Yields ranged from 65% to 80%.

4.1. Synthesis of [2,4,6-$(CH_3)_3$–C_6H_2-NC(Me)C(Me)NC_6H_2-2,4,6-$(CH_3)_3$] WCl_2 (2b)

Following general procedure, from $WCl_4(MeCN)_2$ (0.49 mmol, 0.20 g), [2,4,6-$(CH_3)_3$–C_6H_2NC(Me)C(Me)N-C_6H_2-2,4,6-$(CH_3)_3$] (1.4 mmol, 0.471 g). Zinc (2.4 mmol, 0.160 g) in 20 ml of methylene chloride was obtained 0.226 g (yield 80%) of **2b** as a green solid after crystallization from a mixture of *n*-hexane/CH_2Cl_2 (9/1). Decomposition = 346 °C; IR ($\upsilon_{C=N}$ = 1647; 1595 cm^{-1}).

^1H NMR (300 MHz, CD_3CN, 25 °C, δ [ppm]): δ = 2.11–2.15 (m, 18H, *o*–*o*′-CH_3, CH_3—C=N); 2.38 (s, 6H, *para*-CH_3); 6.87 (s, 4H, Har).

^{13}C NMR (75.5 MHz, CD_3CN, 25 °C, δ [ppm]): δ = 18.81 (CH_3—C=N); 19.33 (*ortho*, *ortho*′-CH_3); 21.22 (*para*-CH_3); 129.97 (C_{ortho}); 130.29 (C_{meta}); 137.08 (C_{para}); 141.07 (C_{ipso}); 173.03 (C=N).

4.2. Synthesis of [2,6-Me_2–C_6H_3NC(Me)C(Me)NC_6H_3-2,6-Me_2] WCl_2 (2c)

Following general procedure, from $WCl_4(MeCN)_2$ (0.46 mmol, 0.190 g), [2,6-Me_2–C_6H_3NC(Me)C(Me)N-C_6H_3-2,6-Me_2] (1.39 mmol, 0.764 g). Zinc (2.3 mmol, 0.150 g) in 20 ml of methylene chloride was obtained 0.192 g (yield 76%) of **2c** as a brown solid after crystalliza-

Table 2
Summary of crystallographic data and X-ray experimental details for **2b**

	2b · CH_2Cl_2	**2e**
Empirical formula	$C_{23}H_{30}Cl_4N_2W$	$C_{26}H_{20}Cl_2N_2W$
Formula weight	660.14	615.19
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/b$	$P2_12_12_1$
Z	4	4
a (Å)	12.810(3)	11.733(3)
b (Å)	14.552(4)	12.003(3)
c (Å)	14.349(3)	16.332(5)
α (°)	90	90
β (°)	90.68(3)	90
γ (°)	90	90
V (Å)^3	2674.6(11)	2300.1(11)
ρ_{calc} (g cm^{-3})	1.639	1.777
Crystal dimensions (mm)	$0.15 \times 0.38 \times 0.59$	$0.18 \times 0.25 \times 0.29$
Temperature (K)	293(2)	293(2)
Radiation, λ (Å)	Mo, 0.71073	Mo, 0.71073
F(000)	1296	1192
2θ Range (°)	1.59–27.47	2.11–27.02
Limiting indices	$-16 \leqslant h \leqslant 16$; $-13 \leqslant k \leqslant 0$; $-2 \leqslant l \leqslant 18$	$-8 \leqslant h \leqslant 14$; $-1 \leqslant k \leqslant 15$; $-3 \leqslant l \leqslant 20$
Number of scanned reflections	6335	3930
Number of independent reflections	5249	3446
Number of observed reflections	3161	1136
Number of parameters varied	272	215
Absorption correction	Empirical (DIFABS)	Empirical (DIFABS)
Data reductions programs	XCAD4	XCAD4
Programs used	SHELX-97	SHELX-97
R_1 (F_o), wR_2(F_o^2) ($I > 2\sigma(I)$) (%)	6.97, 21.10	8.81, 24.03
Goodness-of-fit on F^2	1.021	1.004

Table 3
Selected bond distances (Å) for complexes **2b** and **2e**

Compound ***2b***			
W–N1	2.066(4)	W–N2	2.038(4)
W–Cl1	2.2138(19)	W–Cl2	2.227(2)
N1–C19	1.255(7)	N2–C20	1.264(7)
N1–C1	1.442(6)	N2–C7	1.434(6)
C6–C15	1.518(9)	C12–C18	1.527(9)
C2–C13	1.519(9)	C8–C16	1.518(10)
C4–C14	1.474(9)	C10–C17	1.517(9)
C19–C20	1.511(7)		
Compound ***2e***			
W–N1	2.099(13)	W–N2	2.063(14)
W–Cl1	2.173(7)	W–Cl2	2.178(6)
N1–C1	1.227(19)	N2–C12	1.27(2)
N1–C13	1.47(2)	N2–C19	1.396(16)
C18–C25	1.42(3)	C20–C26	1.201(12)
C1–C12	1.59(2)		

tion from a mixture of n-hexane/CH_2Cl_2 (9/1). Decomposition = 340 °C; IR ($\upsilon_{C=N}$ = 1644; 1602 cm^{-1}).

^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, δ [ppm]): δ = 1.76 (m, 18H, o,o'-CH_3, CH_3—C=N); 6.69–6.89 (m, 6H, Har).

^{13}C NMR (75.5 MHz, DMSO-d_6, 25 °C, δ [ppm]): δ = 16.31 (CH_3—C=N); 18.05 ($ortho$–$ortho'$-CH_3); 123.75 (C_{ortho}); 124.73 (C_{para}); 128.49 (C_{meta}); 148.68 (C_{ipso}); 168.29 (C=N).

Table 4
Selected bond angles (°) for complexes **2b** and **2e**

Compound ***2b***			
N1–W–N2	78.57(17)	Cl1–W–Cl2	117.44(8)
N2–W–Cl1	113.01(14)	N1–W–Cl1	112.86(14)
N2–W–Cl2	115.88(14)	N1–W–Cl2	112.98(14)
C20–N2–W	115.0(4)	C19–N1–W	115.0(4)
C20–N2–C7	122.5(5)	C19–N1–C1	119.7(5)
C7–N2–W	122.4(3)	C1–N1–W	125.1(4)
C8–C7–N2	119.6(5)	C2–C1–N1	117.9(5)
C12–C7–N2	117.1(5)	C6–C1–N1	118.3(5)
N2–C20–C19	116.1(5)	N1–C19–C20	115.1(5)
Compound ***2e***			
N1–W–N2	81.3(6)	Cl1–W–Cl2	120.5(3)
N2–W–Cl1	111.9(5)	N1–W–Cl1	116.6(5)
N2–W–Cl2	111.6(5)	N1–W–Cl2	108.4(5)
C12–N2–W	112.6(11)	C1–N1–W	112.6(10)
C12–N2–C19	118.5(13)	C1–N1–C13	118.8(15)
C19–N2–W	128.9(10)	C13–N1–W	126.5(12)
C20–C19–N2	116.3(8)	C14–C13–N1	123 (2)
C24–C19–N2	123.7(8)	C18–C13–N1	114.4(17)
N2–C12–C1	116.2(14)	N1–C1–C12	117.0(14)

*4.3. Synthesis of [2,6-iPr$_2$–C_6H_3-acenaphtene] WCl_2 (**2d**) {Ar–BIAN,Ar = 2,6-iPr$_2$–C_6H_3}*

Following general procedure, from $WCl_4(MeCN)_2$ (0.42 mmol, 0.172 g), [(2,6-iPr$_2$-acenaphtene)] (1.26 mmol, 0.605 g). Zinc (2.1 mmol, 0.137 g) in 20 ml of methylene chloride was obtained 0.225 g (yield 73%) of **2d** as orange brown solid after crystallization from a mixture of n-hexane/CH_2Cl_2 (9/1). Decomposition = 375 °C; IR ($\upsilon_{C=N}$ = 1635; 1601 cm^{-1}).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): δ = 0.79 (d, 12H, CH_3-iPr, J_{HH} = 6.6 Hz); 1,30 (d, 12H, CH_3-iPr, J_{HH} = 6,6 Hz); 3.21 (sept, 2H, CH–iPr, J = 6.9 Hz); 6.65 (d, 2H, H_7, J = 7.2 Hz); 7.51–7.19 (m, 8H, 6Har + 2H_8); 8.08 (d, 2H, H_9, J = 8.4 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): δ = 24.91, 24.63 (CH_3–iPr); 29.19 (CH–iPr); 125.38 (C_7); 126.16 (C_{meta}); 127.29 (C_{para}); 128.32 (C_8); 129.22 (C_9); 131.36 (C_6); 133.00 (C_{10}); 139.91 (C_{ortho}); 140.82 (C_{11}); 144.83 (C_{ipso}); 165.31 (C=N).

*4.4. Synthesis of [o-Me–C_6H_4-acenaphtene] WCl_2 (**2e**) {Ar–BIAN, Ar = o-Me–C_6H_4}*

Following general procedure, from $WCl_4(MeCN)_2$ (0.49 mmol, 0.202 g), [o-Me-acenaphtene] (1.4 mmol, 0.535 g). Zinc (2.45 mmol, 0.160 g) in 20 ml of methylene chloride was obtained 0.206 g (yield 68%) of **2e** as orange solid after crystallization from a mixture of n-hexane/CH_2Cl_2 (9/1). Decomposition = 336 °C; IR ($\upsilon_{C=N}$ = 1669, 1636 cm^{-1}).

^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, δ [ppm]): δ = 2.10 (s, 6H, CH_3); 6.64 (d,2H, H_7, J = 6 Hz); 7.01 (d, 2H, H_{meta}, J = 7.5 Hz); 7.25 (d, 2H, $H_{meta'}$, J = 7.2 Hz); 7.45–7.32 (m, 4H, $H_{ortho,para'}$); 7.56 (d, 2H, H_8); 8.14 (d, 2H, H_9, J = 10.5 Hz).

^{13}C NMR (75.5 MHz, DMSO-d_6, 25 °C, δ [ppm]): $\delta = 16.31$ (o-CH_3); 121.83 (C_{ortho}); 123.52 (C_7); 124.56 (C_{para}); 125.76 (C_{ortho}); 126.16 ($C_{meta'}$); 127.29 (C_8); 128.62 (C_9); 129.64 (C_{10}); 129.94 (C_{meta}); 132.65 (C_6); 147.97 (C_{11}); 149.17 (C_{ipso}); 159.03 (C=N).

4.5. Synthesis of [Ph–BIC] WCl_2 (**2f**)

Following general procedure, from $WCl_4(MeCN)_2$ (0.39 mmol, 0.16 g), [Ph–BIC] (1.17 mmol, 0.371 g). Zinc (1.95 mmol, 0.127 g) in 20 ml of methylene chloride was obtained 0.145 g (yield 65%) of **2f** as green solid after crystallization from a mixture of n-hexane/CH_2Cl_2 (9/1). Decomposition = 318 °C; IR ($\upsilon_{C=N} = 1634, 1609\ cm^{-1}$).

^{1}H NMR (300 MHz, acetone-d_6, 25 °C, δ [ppm]): $\delta = 0.69$, 0.87, 1.08 (s, 3H chacun, $H_{12,13,14}$); 1.85–1.95 (m, 4H, $H_{8,9}$) 3.15 (d, 1H, H_{10}); 6.52–7.27 (m, 10H, Har).

^{13}C NMR (75.5 MHz, acetone-d_6, 25 °C, δ [ppm]): $\delta = 11.59$, 17.72, 20.45 ($C_{12,13,14}$); 24.09 ($C_{8,9}$); 45.28 (C_7); 50.66 (C_{10}), 55.28 (C_{11}); 118, 119 (C_{ortho}); 122.73, 124.37 (C_{para}); 128.72, 129.29 (C_{meta}); 150.07, 151.64 (C_{ipso}); 168.59, 171.36 ($C_{5,6}$).

X-ray structure determination. Crystals of **2b** and **2e** suitable for X-ray intensity data collection were selected. X-ray intensity data were collected on a MACH3 Enraf Nonius diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Accurate unit cell parameters and orientation matrix were determined from 25 reflections in the range 13–15° for **2b** and 12–15° for **2e**. Intensity data were collected by using the ω–2θ scan mode with a range of $1.6° < \theta < 27.5°$ and $2° < \theta < 27°$ for **2b** and **2e**, respectively. All the intensity data were corrected for Lorentz and polarization effects. The crystal structure solution was carried out with direct methods from the SHELXS-97 permitting the location of all non-Hydrogen atoms. After anisotropic least-squares refinement, Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding atoms with isotropic thermal parameters. Final refinement based on the reflections [$I > 2\sigma(I)$] converged at $R_1 = 0.0697$, $wR_2 = 0.2110$ and at $R_1 = 0.0881$, $wR_2 = 0.2403$ for **2b** and **2e**, respectively. The experimental conditions of data collection, strategy followed for the structure determination, and final results are given in Table 2.

Supporting information available. Crystallographic data for the structural analysis of complexes **2b** and **2e** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 276433 and 272719, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk).

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