DOI: 10.1002/ejic.201000906

A Simple Route to Chelating, Structurally Different Triazole-Based Bis(Nheterocyclic carbene) Ligands and Their Coordination to Pt^{II}

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Keywords: Platinum / Hydrosilylation / Homogeneous catalysis / N-Heterocyclic carbenes

Two new bis(triazolium) salts have been prepared and used as N-heterocyclic carbene (NHC) precursors. The structure of the salts is highly dependent on the synthetic route, which implies the sequential alkylation of two of the three N atoms at the triazole rings. This method allows the easy preparation of bistriazolium salts with the bridge at the 1,1' or 4,4' posi-

Introduction

Despite the large library of chelating N-heterocyclic carbene (NHC) ligands available in the literature,^[1] there is a relatively scarce number of such ligands containing triazolebased rings.^[2-4] Triazolylidenes are an interesting class of NHCs because the presence of the three nitrogen atoms in the azole ring provides asymmetry, reduces the electron donation of the ligand, and allows the trisalkylation of the three nitrogen atoms,^[5] which potentially facilitates the preparation of monoazole-based dicarbenes.^[6] Specifically. 1,2,4-triazoles are interesting building blocks to bis(chelating) triazoles because the asymmetric distribution of the nitrogens in the azole ring allows two different topologies only by exchanging the positions of the linkers between the azole rings and the terminal wingtips. Because we have been long interested in the chemistry of chelating NHC ligands,^[7] we thought that the introduction of a simple method to modify the topology of bis(triazolylidene) ligands may be of interest for the design of new complexes with fine tuned catalytic properties. With this in mind, we herein report the preparation of three different triazole-based bis(chelating) NHC complexes of Pt^{II}.

To test the catalytic activities of the new complexes we chose to try the catalytic hydrosilylation of terminal alkynes as, during the last decade, platinum complexes have appeared as widely used catalysts in this type of reaction.^[8–11] Some of the most active platinum catalysts for hydrosilylation are those functionalized with NHC ligands;^[8,9,12–14] a family of complexes that have been vastly

tions. The two bis(triazolium) salts have been used for the preparation of three different $bis(NHC)Pt^{II}$ complexes that have been fully characterized and the molecular structures of all three new complexes have been determined. The new Pt compounds have been tested in the hydrosilylation of terminal alkynes.

studied after the excellent catalytic results obtained by the [Pt(dvtms)(NHC)] (dvtms = divinyltetramethyldisiloxane) complexes reported by Markó and co-workers.^[13] Probably one of the main drawbacks of such Pt⁰ complexes is that their preparation requires strict air- and moisture-free reaction conditions, and the use of a strong base. As an alternative, several Pt^{II}-NHC complexes have been prepared and used as hydrosilylation catalysts.^[8,11,14] As a way to improve the stability of the Pt^{II} catalysts, Lu and co-workers have recently used polydentate-NHC ligands,^[8] thus widening the vast number of applications that chelating NHC ligands provide in homogeneous catalysis.^[1] As a part of our research,^[7] we focused our attention on the preparation of M-NHC complexes as hydrosilvlation catalysts,^[15,16] and also studied the mechanism of the process by means of electrospray mass spectroscopy.^[16]

Results and Discussion

The ligand precursors 1 and 2 were prepared in high yield according to the general methods previously described by Crabtree and co-workers.^[2,3] Because 1,2,4-triazole undergoes alkylation first at the 1 position and then at the 4 position,^[17] we were able to prepare the two distinct ligands with the linker between the 1,1' (1) or 4,4' (2) positions (Scheme 1). It is important to point out that this simple synthetic procedure leads to subtle but interesting differences in the NHC ligand precursors, which may have interesting consequences, as we will discuss below.

The reactions of 1 and 2 with PtI_2 in refluxing acetonitrile in the presence of NaOAc afforded the bis(NHC)Pt complexes 3 and 4 in high (4, 73%) and moderate (3, 30%) yields (Scheme 2). For the preparation of 3, addition of an excess of KI was needed to ensure the presence of the iodide ligand in the final complex. To obtain the *N*-*n*Bu-substi-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000906.



Scheme 1.



Scheme 2.

tuted 1,1'-linked analogue of 3, we tried to bisalkylate *o*-xylene-1,1'-bis(triazole) using 1-bromobutane and 1-iodobutane, but we always obtained highly hygroscopic oils that were difficult to treat and their coordination to PtI_2 always yielded mixtures of compounds that we could not identify. The Pd-compound of this ligand would have provided us more accurate data for the comparison with the structural features and reactivity of compound 4.

Compound **3** was characterized by means of NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. We previously reported the spectroscopic data of complex $4^{[18]}$ and will use some its characterization data to compare with **3**. The ¹H and ¹³C NMR spectra of the two complexes exhibit signals that are diagnostic for metal complexes having mutually *cis* NHCs linked by an *ortho*-xylyl spacer.^[19] Probably, the most representative NMR spectroscopic signals are those observed in the expected range of the ¹³C NMR spectra at $\delta = 142.9$ (**3**) and 143.5 ppm (**4**), assigned to the C_{carbene}–Pt carbon atoms. As seen for other Pt-NHC complexes, no Pt-satellites were observed for the signals assigned to the metalated carbon atoms in the ¹³C NMR spectra of **3** and **4**.^[8,20]

The addition of silver trifluoroacetate to a suspension of **4** in acetonitrile allowed the removal of the two iodide li-

gands and afforded the bis(trifluoroacetate) platinum adduct **5** in high yield. The ¹³C NMR spectrum of compound **5** displays the representative signal due to the C_{carbene}–Pt carbon atom at δ = 142.8 ppm.

Once we had our three new complexes 3-5 fully characterized, we decided to study their structural and reactivity properties to determine if the 1,1'- or 4,4'-bridged bis(triazolylidenes) present any significant structural and catalytic differences.

The molecular structures of compounds **3**, **4**, and **5** were unambiguously confirmed by means of X-ray diffraction studies. Figures 1, 2 and 3 show the molecular diagrams of **3**, **4**, and **5**, respectively. The molecular structure of compound **3** (Figure 1) contains the chelating bis(NHC) and two iodide ligands about the Pt^{II} center. The average Pt– $C_{carbene}$ distance is 1.961 Å. The average Pt–I distance is 2.652 Å. The chelating bis(NHC) bite angle [C(2)–Pt(1)– C(1)] is 87.8° and the planes of the azole rings are at an average angle of 84.2° with respect to the plane of the molecule.

Compound 4 (Figure 2) is quasi-isostructural to 3 with all distances and angles lying in the same range. The average $Pt-C_{carbene}$ distance is 1.967 Å. The ligand bite angle is 91.2° as measured by the C(2)–Pt(1)–C(1) angle. The azole



Figure 1. Molecular diagram of complex **3**. Hydrogen atoms and solvent (CH_2Cl_2) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–C(1) 1.973(10), Pt(1)–C(2) 1.950(10), Pt(1)–I(1) 2.6538(8), Pt(1)–I(2) 2.6501(9), C(2)–Pt(1)–C(1) 87.8(4), C(2)–Pt(1)–I(1) 176.9(3), C(1)–Pt(1)–I(1) 89.5(3), C(2)–Pt(1)–I(2) 87.8(3), C(1)–Pt(1)–I(2) 175.3(3), I(1)–Pt(1)–I(2) 94.89(3), N(1)–C(1)–Pt(1) 128.8(8), N(3)–C(1)–Pt(1) 128.6(8), N(6)–C(2)–Pt(1) 127.5(7), N(4)–C(2) Pt(1) 127.5(7).



Figure 2. Molecular diagram of complex 4. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–C(1) 1.971(5), Pt(1)–C(2) 1.963(6), Pt(1)–I(1) 2.6440(5), Pt(1)–I(2) 2.6502(4), C(2)–Pt(1)–C(1) 91.2(2), C(2)–Pt(1)–I(1) 177.81(15), C(1)–Pt(1)–I(1) 86.83(16), C(2)–Pt(1)–I(2) 89.37(15), C(1)–Pt(1)–I(2) 178.89(17), I(1)–Pt(1)–I(2) 92.654(16), N(1)–C(1)–Pt(1)–129.1(4), N(3)–C(1)–Pt(1) 127.6(4), N(6)–C(2)–Pt(1) 128.4(4), N(4)–C(2) Pt(1) 129.0(5).

rings are quasi-perpendicular with respect to the coordination plane with an average angle of 84.4°. All other distances and angles are unexceptional.

The average Pt– $C_{carbene}$ distance in **5** is 1.941 Å, slightly shorter than in **4**. The chelating ligand bite angle is 89.7°. The angle between the azole rings and the plane of the molecule is 83.6°, very close to that shown in **4**.

We have screened the catalytic properties of 3–5 in the hydrosilylation reaction of terminal alkynes; we also tested



Figure 3. Molecular diagram of complex **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–C(1) 1.934(10), Pt(1)–C(2) 1.948(9), Pt(1)–O(3) 2.061(7), Pt(1)–O(1) 2.065(6), C(2)–Pt(1)–C(1) 89.7(4), C(2)–Pt(1)–O(3) 93.2(3), C(1)–Pt(1)–O(1) 95.6(3), C(2)–Pt(1)–O(1) 174.5(3), O(3)–Pt(1)–O(1) 81.5(3), C(21)–O(1)–Pt(1) 124.6(7), N(1)–C(1)–Pt(1) 129.0(7), N(3)–C(1)–Pt(1) 128.7(7), N(6)–C(2)–Pt(1) 126.0(7), N(4)–C(2)–Pt(1) 129.8(8).

the activity of PtI₂ under the same reaction conditions for comparative purposes. In this reaction, four different silvlated products can be formed as depicted in Scheme 3. The three products resulting form the hydrosilylation of the alkyne are the α , the β -*E*, and the β -*Z* isomers. Product B results from the dehydrogenative silvlation process and is always accompanied by the formation of styrene. Interestingly, the products resulting from the dehydrogenative silvlation are difficult to detect if reactions are followed by ¹H NMR spectroscopy since the products are very easy to miss.^[16] The formation of styrene as a hydrogen-trapping agent is the clearest indication that this process is occurring. For this reason, it is important to present the catalytic results in a manner in which the yields of each of the final products are clearly specified because the presentation of the catalytic data based on conversions and isomer ratios may lead to misinterpretations. Following the same argument, the use of an internal reference to quantify product formation is an important protocol that is sometimes forgotten because many times unidentified products can be formed that may lead to an apparent disagreement between conversions and yields. This is the case in the data shown in Table 1, where the sum of the yields of the three products formed does not match with the overall conversion as a consequence of the formation of other minor unidentified products. The reactions were carried out using toluene with equimolecular amounts of the alkyne and hydrosilane at different temperatures, with a fixed catalyst loading of 3 mol-%. The first analysis of the data shown in Table 1 is that the subtle modifications in the nature of catalysts 3-5 lead to important catalytic differences.

For the catalyst screening we chose a model reaction involving the hydrosilylation of phenylacetylene with dimethylphenylsilane. As can be seen from the data shown in Table 1, the most active catalyst from all those we used is R₃Si-H

Ph-C=C-H



dehydrogenative silylation

products

Scheme 3.

Table 1. Hydrosilylation of alkynes.^[a]

	Silane	Alkyne	Cat.[c]	<i>t</i> [h]	<i>T</i> [°C]	Conv. [%] ^[b]	α ^[b]	$E^{[b]}$	$Z^{[b]}$	B[p]
1	HSiMe ₂ Ph	PhC≡CH	4	2	100	> 95	6	8	18	56
2	HSiMe ₂ Ph	PhC≡CH	4	4	80	> 95	9	31	30	14
3	HSiMe ₂ Ph	PhC≡CH	3	48	r.t.	85	67	_	5	_
4	HSiMe ₂ Ph	PhC≡CH	3	10	100	> 95	60	_	20	_
5	HSiMe ₂ Ph	PhC≡CH	5	20	100	5	1	1	1	_
6	HSiMe ₂ Ph	PhC≡CH	5	20	60	0	-	_	_	_
7	HSiMe ₂ Ph	nBuC≡CH	5	5	100	10	_	_	7	1
8	HSiMe ₂ Ph	PhC≡CH	PtI_2	10	100	> 95	26	_	_	40
9	HSiMe ₂ Ph	PhC≡CH	PtI_2	24	60	> 95	26	5	_	32
10	HSiMe ₂ Ph	<i>n</i> BuC≡CH	4	5	100	> 95	12	11	10	45
11	HSiMe ₂ Ph	nBuC≡CH	4	48	r.t.	> 95	14	4	5	65
12	HSiEt ₃	nBuC≡CH	4	5	100	> 95	9	10	23	40
13	HSiEt ₃	<i>n</i> BuC≡CH	4	12	60	> 95	6	10	29	36
14	HSiEt ₃	<i>n</i> BuC≡CH	4	48	r.t.	> 95	4	5	22	50

hydrosilylation

products

SiR

β–Ε

[a] Reaction conditions: alkyne (0.36 mmol), hydrosilane (0.37 mmol), anisole as internal reference (0.36 mmol) in toluene (1 mL). The solution was heated under aerobic conditions. [b] Conversions and yields determined by GC chromatography. The sum of yields may not match with the conversion due to the formation of minor unidentified products. [c] Catalyst loading: 3%.

compound 4 because it achieved the highest conversions to the four possible reaction products (compare entries 1-10). As seen from the product distribution, however, compound **4** is a rather unselective catalyst because the formation of the silvlated/hydrosilvlated products seems to proceed in a quite random manner. Catalyst 3 is far less active than 4 in terms of conversions, but it proved to be very selective in the formation of the hydrosilylated products (the dehydrogenative silvlated product was not detected) and also very selective in the formation of the α isomer (entries 3 and 4), with α/β -Z ratios of up to 13 (entry 3) for the reaction run at room temperature. Under the same reaction conditions, the trifluoroacetate complex 5 showed negligible activity in this reaction (entries 5–7), whereas the activity of raw PtI_2 is very poor in terms of product yield, with a slight tendency to form the dehydrogenative silvlated product.

Catalyst 4 was also tested in the hydrosilylation using further combinations of the silanes $HSiMe_2Ph$, $HSiEt_3$, and the acetylenes phenylacetylene and 1-hexyne. Under the same reaction conditions all combinations showed a moderate selectivity to the dehydrogenative silylated product B.

Conclusion

We have prepared three different bis(NHC)Pt^{II} complexes with two new triazolium-based NHC ligands. The route to the bis(triazolium) salt determines whether the linker is between the 1,1' or 4,4' positions of the triazole rings. The three new complexes have been tested in the hydrosilylation reaction of terminal alkynes and show very different catalytic behaviors, although the intrinsic topological properties of all three catalysts may seem rather similar, as shown by the study of their X-ray molecular structures. Catalyst 4 is very active although very unselective, whereas 3 is very selective in the formation of the α -hydrosilylated product. On the other hand, catalyst 5 is a rather inactive catalyst. We believe that the differences in the catalytic activities of 3 and 4 may arise from the different steric bulk of the terminal N-substituents, with the benzyl group affording higher steric hindrance than the *n*Bu group. This would lower the activity of the benzyl-functionalized complex 3, but may also favor its selectivity.

Experimental Section

General Procedures: Ligand precursor o-xylene-4,4'-bis(1-n-butyltriazolium) diiodide (2)^[3] and complex 4^[18] were prepared according to literature procedures. All other reagents and solvents were used as received from commercial suppliers. Synthetic and catalytic experiments were carried out under aerobic conditions and without solvent pretreatment. NMR spectra were recorded on Varian spectrometers operating at 300 or 500 MHz (¹H NMR) and 75 or 125 MHz (¹³C NMR) and referenced to SiMe₄ (δ in ppm and J in Hertz). NMR spectra were recorded at room temperature in CDCl₃ unless otherwise stated. A QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, UK) was used. The drying and the nebulizing gas was nitrogen at flows of 400 and 80 L/h, respectively. The temperature of the source block was set to 120 °C and the desolvation temperature to 150 °C. A capillary voltage of 3.5 kV was used in the positive scan mode and the cone voltage was set

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to 30 V. Mass calibration was performed using a solution of sodium iodide in 2-propanol/water (50:50) from m/z 150 to 1000 a.m.u. Sample solutions (ca. 1×10^{-4} M) in dichloromethane/methanol (50:50) were infused through syringe pump directly connected to the interface at a flow of 10 µL/min. A 1 µg/mL solution of 3,5diiodo-L-tyrosine was used as lock mass. Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer. Gas chromatograph GC-2010 (Shimadzu) equipped with a FID and a Teknokroma (TRB-5MS, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) column. Gas chromatograph/Mass spectrometer GC-MS-OP2010 (Shimadzu) equipped with Teknokroma (TRB-5MS, а $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) column.

Synthesis of *o*-**Xylene-1,1**′-**bis(triazole):** This compound was prepared according to literature procedures.^[17] ¹H NMR (500 MHz, CDCl₃): δ = 7.99 (s, 2 H, C*H*), 7.89 (s, 2 H, C*H*), 7.33–7.31 (m, 2 H, Ph), 7.20–7.17 (m, 2 H, Ph), 5.39 (s, 4 H, -C*H*₂-) ppm. ¹³C NMR (125 MHz, CD₃Cl): δ = 152.9, 143.9, 134.0, 131.0, 130.4, 51.4 ppm. ESI-TOF-MS (positive mode): [L + H]⁺ 241.1205; calcd. 241.1202; ε_r = 1.2 ppm.

Synthesis of 1: A mixture of *o*-xylene-1,1'-bis(triazole) (1.0 g, 4.2 mmol) and benzyl chloride (1.32 g, 10.4 mmol) was refluxed for 15 h in acetonitrile (20 mL). Pure compound 1 was obtained as a white crystalline solid after recrystallization from dichloromethane/ diethyl ether; yield 2.05 g (88%). ¹H NMR (500 MHz, [D₆]DMSO): $\delta = 10.71$ (s, 2 H, NCHN), 9.33 (s, 2 H, NCHN), 7.53–7.41 (m, 14 H, Ph), 5.89 (s, 4 H, -*CH*₂-), 5.57 (s, 4 H, -*CH*₂-) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): $\delta = 144.9$, 143.1, 135.4, 133.6, 132.2, 131.2, 129.8, 129.1, 128.9, 51.9, 50.6 ppm. ESI-TOF-MS (positive mode): [L – H]⁺ 421.2147; calcd. 421.2141; $\varepsilon_{\rm r} = 0.9$ ppm.

Synthesis of 3: A mixture of 1 (231.9 mg, 0.47 mmol), PtI₂ (210 mg, 0.47 mmol), and NaOAc (77 mg, 0.94 mmol) was refluxed for 2 h in acetonitrile (5 mL). The reaction mixture was filtered through Celite and the solvent was removed under vacuum. Pure compound 3 was obtained as a white crystalline solid after recrystallization from acetone/hexane; yield 95 mg (25%). ¹H NMR (500 MHz, CD₃Cl): δ = 7.77 (s, 2 H, NC*H*), 7.6 (m, 2 H, Ph), 7.46 (m, 2 H, Ph), 7.40 (m, 6 H, Ph), 7.21 (m, 4 H, Ph), 6.83 (d, ²J_{H,H} = 14.5 Hz,

2 H, CH₂) 5.86 (d, ${}^{2}J_{H,H}$ = 15.0 Hz, 2 H, N-CH₂-), 5.18 (d, ${}^{2}J_{H,H}$ = 14.5 Hz, 2 H, CH₂), 4.84 (d, ${}^{2}J_{H,H}$ = 14.5 Hz, 2 H, N-CH₂-) ppm. 13 C NMR (125 MHz, CD₃Cl): δ = 158.7 (C_{carbene}-Pt), 142.9 (NCH), 133.7, 133.6, 133.3, 130.4, 129.8, 129.6, 128.9 (Ph), 53.3 (CH₂), 52.1 (CH₂) ppm. ES-MS (25 V): *m*/*z*: 783.1 [M - I + CH₃CN]⁺. ESI-TOF-MS (positive mode): *m*/*z* calcd. (monoisotopic peak): 783.1022; found 783.1033; $\epsilon_{\rm r}$ = 1.4 ppm. C₂₆H₂₄I₂N₆Pt (869.4): calcd. C 35.9, H 2.78, N 9.67; found C 36.2, H 3.05, N 9.87.

Synthesis of 5: A mixture of 4 (150 mg, 0.19 mmol) and AgO₂CCF₃ (83.9 mg, 0.38 mmol) was suspended in acetonitrile (40 mL) and stirred at 60 °C for 2 h shielded from light. The resulting brownish suspension was filtered from the precipitated AgI over celite and the acetonitrile was removed in vacuo to give the crude product as an off-white solid. Pure compound 2 was obtained as a white crystalline solid after recrystallization from dichloromethane/hexane; yield 90 mg (61%). ¹H NMR (500 MHz, CD₃CN): δ = 8.47 (s, 2 H, NCH), 7.80 (m, 2 H, Ph), 7.50 (m, 2 H, Ph), 6.93 (d, ${}^{2}J_{H,H}$ = 15.0 Hz, 2 H, CH₂), 5.24 (d, ${}^{2}J_{H,H}$ = 15.0 Hz, 2 H, CH₂), 4.86 (m, 2 H, CH₂, nBu), 4.21 (m, 2 H, CH₂, nBu), 1.86 (m, 2 H, CH₂, *n*Bu), 1.40 (m, 4 H, CH₂, *n*Bu), 0.95 (t, ${}^{3}J_{H,H}$ = 7.5 Hz, 6 H, CH₃, *n*Bu) ppm. ¹³C NMR (125 MHz, CD₃CN): $\delta = 162.3$ [q, ²J_{C,F} = 36 Hz, COO], 143.9 (NCH), 142.8 (Ccarbene-Pt), 135.9, 132.8, 131.2 (Ph), (CF₃) not observed, 53.1 (CH₂), 50.36, 31.9, 20.3, 13.9 (nBu) ppm. ¹⁹F NMR (282.31 MHz CD₃CN): δ = -75.55 (s, CF₃) ppm. ES-MS (25 V): $m/z = 701.2 [M - CF_3COO + CH_3CN]^+$. ESI-TOF-MS (positive mode): m/z calcd. (monoisotopic peak): 701.2141; found 701.2142; $\epsilon_r = 0.1$ ppm.

Hydrosilylation of 1-Alkynes and Olefins with Silanes. General Procedure: A typical procedure is performed as follows. An oven-dried tube containing a stirrer bar was charged with nBuC=CH or PhC=CH (0.36 mmol), silane (HSiEt₃ or HSiMe₂Ph, 0.37 mmol), catalyst (3 mol-%, 1.08×10^{-3} mmol), and anisole as internal standard (0.36 mmol) in toluene (1 mL). The mixture was kept at the selected temperature by immersion in an oil bath. The progress of the reaction was monitored by GC chromatography. The products

Table 2. Crystallographic data and structure refinement for complexes 3, 4 and 5.^[a]

	3	4	5
Empirical formula	C ₂₆ H ₂₄ I ₂ N ₆ Pt	$C_{20}H_{28}I_2N_6Pt \cdot CH_2Cl_2$	$C_{24}H_{28}F_6N_6O_4Pt$
Formula weight	869.4	886.30	773.61
Radiation		Mo- K_{α} (monochr.), 0.71073	λ [Å]
<i>T</i> [K]	293(2)	293(2)	293(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	$P\bar{1}$	ΡĪ
a [Å]	18.5754(18)	8.2651(4)	9.1290(7)
b [Å]	22.280(2)	12.3512(5)	12.8667(10)
c [Å]	14.6262(15)	14.6978(6)	13.3938(10)
	90.00	97.0990(10)	77.271(2)
β ^[°]	104.259(2)	92.4990(10)	70.729(2)
y [°]	90.00	107.3670(10)	81.928(2)
$V[Å^3]$	5866.7(10)	1415.89(11)	1444.67(19)
Z	8	2	2
$D_{\rm calcd}$ [Mgm ⁻³]	1.969	2.079	1.778
$\mu(Mo-K_{\alpha})$ [mm ⁻¹]	6.912	7.344	4.935
Number of total / unique reflections	5118 / 4147	5704 / 5065	5036 / 3638
R _{int}	0.0520	0.0250	0.0463
Number of parameters / restraints	316 / 0	289 / 0	370 / 0
$R / R_{w}^{[b]} [I > 2\sigma(I)]$	0.0608 / 0.0469	0.0250 / 0.0448	0.0479 / 0.0830
GOF	1.054	1.081	1.035
Min. / max. electron density [e·Å ⁻³]	-2.484 / 3.623	-1.953 / 1.254	-0.753 / 1.363

[a] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, for all $I > 3\sigma(I)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.



were characterized according to the NMR spectroscopic data obtained from the literature. $\ensuremath{^{[21]}}$

X-ray Diffraction Studies: Single crystals of compounds **3**, **4**, and **5** were mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package.^[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 2. The diffraction frames were integrated using the SAINT package.^[23]

CCDC-790376 (for 3), -790377 (for 4) and -790378 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Experimental and theoretical isotopic distribution of **3** and **5** (ESI-TOF-MS).

Acknowledgments

We thank the financial support from the Spanish Ministerio de Ciencia e Innovación (MICINN) (CTQ2008-04460) and Bancaixa (P1.1B2007-04 and ref. number P1.1B2008-16). We would also like to thank the "Generalitat Valenciana" for a fellowship (to A. Z.). The authors are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC) of the Universitat Jaume I for providing spectroscopy and crystal structure determination facilities.

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Received: August 25, 2010 Published Online: December 13, 2010