Synthesis of a Dirhodium(I) Bisimidazolium Carbene Complex and Catalytic Activity toward Hydroformylation of Olefins. High-Pressure NMR Spectroscopy of the Catalyst under Catalytic Conditions

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Received July 16, 2002

A new dirhodium(I) bisimidazolium-carbene complex has been obtained and fully characterized by means of NMR spectroscopy and single-crystal X-ray diffraction. The complex has been used as catalyst in hydroformylation reactions, showing selectivity on the branched aldehyde. High-pressure NMR spectroscopy provides evidence that the dinuclear unit is maintained under catalytic conditions.

Introduction

During the past decade, the use of heterocyclic carbene ligands of the imidazolium type has emerged as an alternative to the use of phosphines in the design of new organometallic catalysts. The easy access to a large variety of imidazolium precursors has widen the variety of catalysts where the steric and electronic properties conferred by the ligand can be easily modulated. Since the first paper reporting catalytic results using a heterocyclic carbene appeared in 1995,[1] many approaches regarding catalytic applications have been reported, such as C−C couplings (Heck, Suzuki, Sonogahira, Stille, etc.), hydrosilylation, olefin metathesis, C−H activation, hydroformylation, and cyclopropanation, among many others.[2]

Among all the imidazolium-derived carbene ligands obtained, those of the pincer type have appeared as an attractive new type of system, probably due to the stability that they confer to their complexes as a consequence of the combination of a high chelate entropic effect and the strength of the M−C bonds in low-valent late transition metals.[3−8] The ready accessibility of 2,6-bis(1-alkylimidazolium-3-yl)pyridine salts has widened the library of new precursors to tridentate CNC biscarbenes providing a series of complexes where steric and electronic properties can be smoothly modulated. Although in most cases the activation of the imidazolium salts requires the use of strong (*t*-BuOK, BuLi, LDA) or weak (NEt_3, NaOAc, Na_2CO_3) bases, there are examples where oxidative addition of the imidazolium C−H bond to Pd(0) can provide the desired heterocyclic carbene.[9]

Since most of the pincer N-heterocyclic carbenes reported to date are Pd-based, we decided to extend the study to other metals. In this work, we describe the preparation and characterization of a new Rh(I) dinuclear biscarbene complex, where the ligand is bridging the two metal fragments. To study the catalytical properties of this new compound, we performed a series of hydroformylation reactions, with the aim to determine whether a dinuclear phosphine-free precursor of catalyst could provide stable enough bimetallic intermediates.

Results and Discussion

The reaction of $[(COD)RhCl]_2$ with 2,6-bis(1-butylimidazolium-3-yl)pyridine bromide, **1**-Br_2, in CH_3CN in the presence of NEt_3, yields the dirhodium(I) complex **2** (Scheme 1) in high yield (72%). NMR spectroscopy and elemental analysis allowed the identification of **2** at the first stage. The ^1H NMR spectrum of **2** shows a typical pattern of a metalated biscarbene ligand, where the 2-fold symmetry is maintained. The signals due to the pyridine ring appear at higher frequencies (8.2, t; 10.1, d) than those shown for other complexes in which this ligand is coordinated in the pincer form,[5−8] suggesting that the pyridine ring is not coordinated to the metal atom. The imidazolium rings display their H signals at 7.0 and 7.8 ppm, in the region where this type of metalated rings appear. The integration of the aromatic signals compared to those corresponding to the COD

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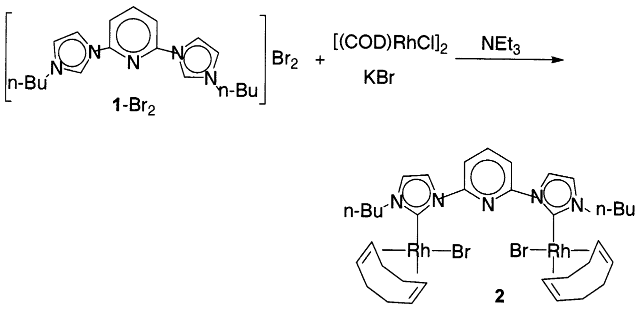
10.1021/om0205748 CCC: $25.00

Scheme 1



ligand suggests that two rhodium atoms are bound to the bisimidazolium ligand. The ^{13}C NMR spectrum of this complex confirms that a Rh−C has been formed ($^1J_{\mathrm{Rh-C}} = 43$ Hz, $\delta = 184.2$ ppm).

The structure of **2** was unequivocally confirmed by X-ray diffraction. Figure 1 shows the molecular structure of **2** with the selected bond distances and angles. The compound consists of a dirhodium structure bridged by the 2,6-bis(1-butylimidazolylidene-3-yl)pyridine, with the nitrogen atom of the pyridine unbound. The Rh(1)−Rh(2) distance of 7.9 Å discards any possible M−M bonding interaction, although it cannot be excluded that in solution the two Rh atoms may approach each other due to the ligand flexibility (see below). The geometry about each rhodium atom is pseudo-square-planar, with a Rh−C$_{\mathrm{imid}}$ distance of 2.03 Å, suggesting that the bond has a major σ contribution with very little back-donation. However, the coordination of the ligand by the carbene end, instead of the nitrogen end, may be due to its better ability to release electron density from the low valence metal by back-donation. It has been suggested that the preferential C-binding versus N-binding in imidazolyl ligands depends on the metal fragment involved.[10] In this sense, C-bound imidazoles are predicted to be thermodynamically more stable than the conventional N-bound forms for several second- and third-row transition metals. In any case, the synthesis of this complex argues against the idea that the pyridine unit acts as the initial binding site for the ligand, bringing the imidazolium rings into the vicinity of the metal in those cases where the pincer coordination is obtained.

Compound **2** seemed a good candidate for catalyzing hydroformylation reactions. The fact that the bridging unit resisted high temperatures (the compound is stable during several hours at 150 °C) suggested that it could resist harsh catalytic conditions. In addition, it may also shed some light on the possible cooperative effect of having two metal atoms in the catalyst, since the bridging ligand is flexible enough to approach the two Rh atoms in order to cooperate (the rotation about the C−N bond of the ligand may cause the Rh atoms to approach each other at a distance of ca. 4 Å). To check the catalytic activity of **2**, we decided to try hydroformylation reactions. The rhodium-catalyzed hydroformylation reaction is considered a useful tool for the preparation of organic compounds.[11,12] The development of new catalytic systems that enable the study of the hydroformylation of alkenes through phosphine-free rhodium complexes has become one of the most important aims of our study, since the use of phosphine ligands seems to afford a route to catalyst deactivation by induced ligand fragmentation. In addition, the number of bimetallic catalysts that are active and actually operating via a bimetallic mechanism in the hydroformylation of alkenes is extremely limited.[13−15]

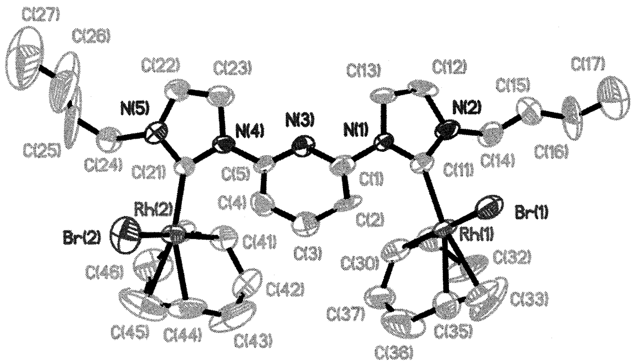


Figure 1. ORTEP diagram of **2** (50% probability, hydrogen atoms and two molecules of solvent CHCl$_3$ have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−C(11) 2.027(15), Rh(1)−C(30) 2.117(18), Rh(1)−C(31) 2.145(19), Rh(1)−C(34) 2.185(16), Rh(1)−C(35) 2.235(19), Rh(1)−Br(1) 2.521(2), Rh(2)−C(21) 2.010(15), Rh(2)−C(40) 2.114(18), Rh(2)−C(41) 2.118(17), Rh(2)−C(44) 2.163(19), Rh(2)−C(45) 2.22(2), Rh(2)−Br(2) 2.500(3), C(11)−Rh(1)−Br(1) 88.3(4), C(21)−Rh(2)−Br(2) 90.9(5), Rh(1)−Rh(2) 7.9.

Table 1. Hydroformylation of Styrene with [(COD)RhBr]$_2$(CNC-Bu$_2$), 2[a]

entry	solvent	T (°C)	P (atm)	conv[b] (%)	TOF[c]	ald[b] (%)	iso[b] (%)
1	toluene	25	30	4	1.2	96	100
2	toluene	40	30	11	3.2	99	98
3	toluene	40	80	30	8.7	98	98
4	toluene	80	80	100	29.1	99	86
5	toluene[d]	40	80	100	16.7	99	97
6	CH$_2$Cl$_2$ [d]	40	50	94	15.7	100	97

[a] Standard conditions: substrate/Rh = 700, time 24 h. [b] Conversion, selectivity on aldehydes, and regioselectivity on the branched aldehyde have been determined by GC in a Ultra-2-column (5% diphenylmethyl silicone and 95% dimethylsilicone). [c] TOF = turnovers per hour. [d] Substrate/Rh = 400.

Table 1 shows the catalytic activity of **2** in the hydroformylation of styrene, this being the most widely investigated alkene of the vinyl-arene family. Although **2** provides high percentages of chemio- and regioselectivity on the branched aldehyde in toluene, a quantitative conversion of the substrate is achieved only when 80 °C and 80 bar (subs/Rh = 700; CO/H$_2$ = 1/1) are used as reaction conditions (Table 1, entries 1−4). The ratio of branched versus linear aldehyde isomers is clearly diminished by the temperature. Higher amounts of

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Table 2. Hydroformylation of Alkenes with $[(COD)RhBr]_2(CNC\text{-}Bu_2)$, 2[a]

entry	alkene	conv[b] (%)	TOF[c]	ald[b] (%)	branched[b] (%)
1	*p*-(MeO)-styrene	74	12.3	100	96
2	*p*-(F)-styrene	69	11.5	100	96
3	1-octene	70	11.6	92	43
4	2,5-dihydrofuran	90	15	98	63[d]

[a] Standard conditions: substrate/Rh = 400, time 24 h, 40 °C, 50 atm ($CO/H_2 = 1/1$). [b] Conversion, selectivity on aldehydes, and regioselectivity on the branched aldehyde have been determined by GC in a column Ultra-2-(5%diphenylmethyl silicone and 95%dimethylsilicone). [c] TOF = turnover frequency per hour. [d] 63% on the tetrahydrofuran-3-carbaldehyde.

catalyst (subs/Rh = 400) allows quantitative conversions at 40 °C (Table 1, entry 5). Moderate pressure and temperature (50 atm and 40 °C) were used when the solvent was the more polar CH_2Cl_2, yielding quantitative conversions without loss of chemio- and regioselectivity on the required product with a TOF = 15.6 turnover/h (Table 1, entry 6). The use of NEt_3 has provided better TOFs for previously reported hydroformylation reactions with halogen-containing precursors,[16] although we did not see any improvement for our system by addition of this base. Complex **2** provides a higher reactivity on hydroformylation of styrene than the analogue carbene-rhodium monomer complex reported in the literature,[17] which in addition requires the presence of triphenylphosphine as ligand.

A variety of other alkenes were hydroformylated, yielding the corresponding aldehydes (Table 2). Also, a large predominance of the branched isomer (96%) over the linear one is obtained with electron-withdrawing and electron-donating aryl substituents on the substrate (Table 2, entries 1 and 2). Hydroformylation of aliphatic substrates such as 1-octene showed no significant isomerization of the starting substrate, the percentage of the branched aldehyde being relatively low, 43%. This value is similar to those found for the hydroformylation of linear 1-alkenes with unmodified rhodium complexes.[18] Hydroformylation of more hindered alkenes such as 2,5-dihydrofurane was also carried out, yielding a mixture of tetrahydrofuran-3-carbaldehyde (63%) and tetrahydrofuran-2-carbaldehyde (37%), but no hydrogenation products were formed.

To determine the nature of the catalytic species during the hydroformylation process, we performed in situ high-pressure (HP) NMR spectroscopy. The ^{13}C (HP) NMR spectrum was obtained from a solution of **2** in $CDCl_3$, heating at 40 °C for 72 h under 30 atm CO/H_2 (1/1) (Figure 2). Two important features deserve to be mentioned in comparison with the spectrum of the starting material. First, the coordinated 1,5-cyclooctadiene is replaced by carbonyl ligands, on the basis of the doublet observed at $\delta = 190.6$ ppm ($J_{C-Rh} = 64$ Hz) attributed to the symmetric carbonyl moieties coordinated to rhodium and the appearance of the signals due to free 1,5-cyclooctadiene. More significant is the shift of the doublet due to the carbene from $\delta = 184.2$ ppm in the starting dirhodium complex to $\delta = 177.6$ ppm ($J_{C-Rh} = 38$ Hz) in the new metal-carbonyl species. This indicates that the carbene moiety is stable under the hydroformylation conditions. The other signals in the ^{13}C NMR spectrum are readily assigned as the primary, secondary, and tertiary carbon nuclei of the biscarbene ligand according to a DEPT experiment carried out under the same reaction conditions. The number of signals observed indicates that the ligand maintains its 2-fold symmetry. Both the ^{13}C and ^{1}H NMR spectra indicate that the pyridine ring remains uncoordinated in this newly formed complex, thus discarding the possibility of a pincer coordination of the ligand. The same spectrum is observed for the catalyst under 30 atm of CO. The IR spectrum of this rhodium-carbonyl species shows three bands at 2098.9, 2053.2, and 1992.1 cm^{-1}, which are characteristic of dinuclear tetracarbonylated complexes.[19,20] When the in situ (HP) NMR spectrum was carried out under CO/H_2 (30 atm) and in the presence of 1 equiv of styrene, the signal due to the carbene and the 2-fold symmetry of the ligand is still maintained. The absence of detectable signals due to mononuclear rhodium(I) species such as $RhH(CO)_4$ discards that the catalytic activity may be due to these species, although we cannot exclude the possible formation of traces of $RhH(CO)_4$.[21] As a result of these experimental data, we suggest that the dinuclearity of the dirhodium complex is maintained under the hydroformylation conditions.

To compare the catalytic results of our compound with a phosphine-free Rh(I) carbene complex, we decided to use compound **3** (Scheme 2) in the hydroformylation of styrene under similar conditions as those used for **2**. Compound **3** was obtained by a procedure similar to that used for **2**, and the detailed experimental procedure, reactivity, and structural details are described in a new manuscript in preparation.[22] Under all the reaction conditions used, the activity of **3** in the hydroformylation of styrene was negligible even using drastic reaction conditions (80 atm and 80 °C). This result, together with the comparison with the catalytic activity of Crudden's catalyst,[17] supports the idea of a catalytical dinuclear species being involved, although a more detailed study must be carried out.

In conclusion, we have reported a new Rh(I) dinuclear biscarbene complex which has been fully characterized using spectroscopic and crystallographic studies. The compound has shown to be active in hydroformylation catalysis, giving selectivities for the branched isomer when vinylarenes are used as substrates. (HP) NMR spectroscopic experiments have revealed that the complex keeps its dinuclearity along the catalytic reaction, since the carbene unit remains present in the metallic species involved under CO/H_2 pressure. Our work starts a new series of dirhodium(I) complexes whose properties can be modulated by the great variety of possibilities that offer the synthesis of imidazolium ligand precur-

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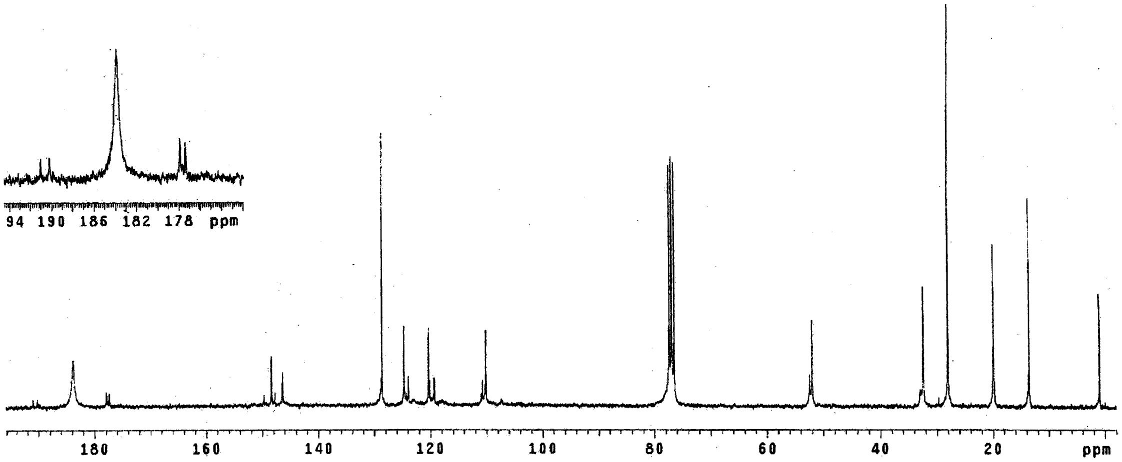
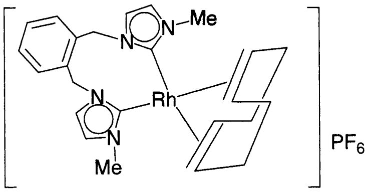


Figure 2. ^{13}C (HP) NMR spectrum obtained after 72 h of reaction of **2** under 30 atm CO/H_2 (1/1), 40 °C, in $CDCl_3$ as solvent.

Scheme 2



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sors. Further studies to establish a plausible cooperative mechanism through bimetallic species are under way.

Experimental Section

General Procedures. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using $CDCl_3$ and DMSO-d_6 as solvents. (HP) NMR spectra were recorded on a 300 Gemini NMR spectrometer. The ligand precursor **1**-Br_2 was prepared according to literature methods.[8] All other reagents are commercially available and were used as received.

Synthesis of [(COD)RhBr]$_2$(CNC-Bu$_2$), 2. A mixture of $[(COD)RhCl]_2$ (200 mg, 0.41 mmol), **1**-Br_2 (400 mg, 0.82 mmol), KBr (300 mg), and NEt_3 (0.5 mL, 3.5 mmol) was heated at 45 °C for 12 h in CH_3CN. The reaction mixture was filtered, and the solvent was eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2, and the solution was transferred to a column for chromatography. Elution with CH_2Cl_2 separated a minor yellow band that contained $[(COD)RhCl]_2$. Further elution with a gradient of CH_2Cl_2/acetone (10/1) afforded the separation of a major yellow band that contained **2** (yield 72%).

[(COD)RhBr]$_2$(CNC-Bu$_2$), 2. ^{1}H NMR ($CDCl_3$, 300 MHz): 10.05 (d, $^2J_{H-H} = 8.1$ Hz, pyridine-H), 8.32 (t, $^2J_{H-H} = 8.2$ Hz, pyridine-H), 7.82 (d, $^2J_{H-H} = 2.1$ Hz, imidazole-H), 7.03 (d, $^2J_{H-H} = 2.0$ Hz, imidazole-H), 4.32 (t, 4H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 1.90 (quintet, 4H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.37 (sextuplet, 4H, $\mathrm{NCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 0.92 (t, 6H, $\mathrm{NCH_2CH_2CH_2C}\mathit{H}_3$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 184.2 (d, $^2J_{Rh-C} = 43$ Hz, N*C*N), 149.9 (C_{ipso}), 139.8 (C_{ortho}), 121.3 (im-C), 120.8 (C_{meta}), 116.5 (im-C), 98.6, 97.3, 70.6, 70.0 (COD), 52.4 ($\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 32.6 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 29.3 (COD), 20.4 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 14.1 ($\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$).

Standard Hydroformylation Catalytic Experiments. Hydroformylation reactions were carried out in a specially designed autoclave with magnetic stirring and electrical heating. The catalytic solution was contained in a glass vessel. The inside part of the cover was made from Teflon to protect the solution from direct contact with the stainless steel. A solution of the substrate (4 mmol), the rhodium complex **2** (0.01 mmol), and the solvent (8 mL) were placed in the evacuated autoclave. The gas mixture (CO/H_2) was introduced, the system was heated, and the stirring was initiated when the thermal equilibrium was reached. Conversion and selectivities were determined by GC analysis of the crude sample.

Table 3. Crystal Data and Structure Refinement for 2

empirical formula	$C_{37}H_{51}Br_2Cl_6N_5Rh_2$
fw	1144.17
temperature	293(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 9.974(2)$ Å, $\alpha = 79.931(6)°$
	$b = 14.356(3)$ Å, $\beta = 80.763(6)°$
	$c = 16.959(4)$ Å, $\gamma = 80.892(6)°$
volume	2338.7(9) Å^3
Z	2
density (calcd)	1.625 Mg/m^3
abs coeff	2.788 mm^{-1}
$F(000)$	1140
cryst size	0.09 × 0.11 × 0.28 mm^3
θ range for data collection	1.23 to 20.82°
index ranges	$-9 \le h \le 9$, $-14 \le k \le 12$,
	$-16 \le l \le 16$
no. of reflns collected	8926
no. of ind reflns	4879 [R(int) = 0.0780]
completeness to $\theta = 20.82°$	100.0%
abs corr	Bruker SADABS
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4879/0/458
goodness-of-fit on F^2	1.034
final R indices [$I > 2\sigma(I)$]	R1 = 0.0743, wR2 = 0.1724
R indices (all data)	R1 = 0.1380, wR2 = 0.2112
largest diff peak and hole	1.385 and −0.849 e Å^{-3}

In Situ HP NMR Experiments. In a typical experiment, the in situ HP NMR experiments were carried out in a sapphire tube ($\phi = 10$ mm). Complex **2** (0.02 mmol) was dissolved in $CDCl_3$ (2 mL) under nitrogen, and the sample tube was closed. After pressurizing the mixture with CO/H_2 the tube was placed in the NMR spectrometer and the spectra were recorded.

X-ray Diffraction Studies. Single crystals of **2** were grown by slow diffusion of MeOH into concentrated CH_2Cl_2 solutions and mounted on a glass fiber in a random orientation. Crystal data are summarized in Table 3. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected based on three ω-scans runs (starting $\omega = -28°$) at values $\phi = 0°$, 90°, and 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435, and 230) were collected at 0.3° intervals and 30 s per frame.

Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package.[23] All non-hydrogen 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 3. The diffraction frames were integrated using the SAINT[24] package and corrected for absorption with SADABS.[25]

Acknowledgment. We thank the DGESIC (PB98-1044) and BANCAIXA (P1.1B2001-03) for financial support and Generalitat Valenciana for a fellowship (J.A.M.). We would also like to thank Ramón Guerrero for his valuable help in the (HP) NMR experiments.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, bond lengths and angles, thermal parameters, and hydrogen atom positional parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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