Ruthenium Janus-Head Complexes with a Triazolediylidene Ligand. Structural Features and Catalytic Applications

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The use of the ligand triazolediylidene (ditz), has afforded the preparation of two new complexes of Ru in which the ligand is bridging two metal fragments in a facially opposed (Janus-head) disposition. One of the complexes is dinuclear (**2**) and the other tetranuclear (**3**). The tetranuclear compound displays interesting structural features, as shown by the X-ray diffraction studies. The two complexes have been tested in the catalytic β-alkylation of secondary alcohols with primary alcohols, providing high activities when both aliphatic and aromatic alcohols are used.

Introduction

Since the first use of N-heterocyclic carbenes in the preparation of homogeneous catalysts,[1] and the recognition that this type of ligands may provide enhanced catalytic activities, a great effort has been made in the design of new NHC-based ligands with a wide variety of topological architectures. Now, we can find an extense library of compounds containing monodentate,[2] bischelate,[3,4] and pincer[4,5] NHC ligands, which can also combine chirality for asymmetric catalysis purposes.[6] Despite some efforts having been made in order to tune the electronic properties of NHC ligands and some experimental and theoretical studies having been carried out to rationalize these factors,[7] it is well recognized that NHCs are more electron-donating than phosphines, and the modulation of their basicity is not as easily achieved as for the latter ligands.

The easy preparation of NHC-precursors, has allowed an almost infinite access to new organometallic topologies, in which the only limitation seems to be the imagination of the researchers. On many occasions NHCs have allowed coordination abilities that were unknown for other traditional ligands. In a series of recent works, Bielawski and co-workers prepared a series of benzobis(imidazolylidene)s (**A** and **B**, Scheme 1) that show facially opposed coordination abilities (Janus-head type).[8−11]

Scheme 1
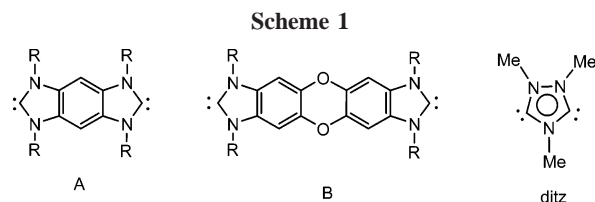
The coordination of these ligands to metallic fragments has provided a series of discrete and polymeric structures of Rh,[10] Pd,[8,9] Pt,[9] and Ag.[9] A large number of applications to these new types of ligands can be envisaged, including the preparation of multitopic tandem catalysts, conducting polymers, and nonlinear optical materials, among others.

We recently used the simple triazolediylidene unit (ditz, Scheme 1) as a synthon to the preparation of dinuclear homo−heterometallic species of Rh and Ir.[12] The same ligand had previously been used for the preparation of polymeric carbenes of silver.[13,14] In our preliminary results, we observed that the products obtained showed improved catalytic performances comparable to some other related homometallic complexes with analogous NHC ligands. The connection of two catalytically active metal fragments through an aromatic linker may provide interesting implications in their catalytic cooperativity, thus facilitating the improvement of their performances. Besides, the electronic donor power of ditz is one of the lowest for other NHC ligands, ranging among those shown for the successful phosphine set. On the basis of these results, we now report the preparation of two new Ru compounds with the triazole-dicarbene ditz ligand. The full structural characterization of an unprecedented tetraruthenium species is described. The complexes show excellent catalytic activity toward the β-alkylation of secondary alcohols with primary alcohols.

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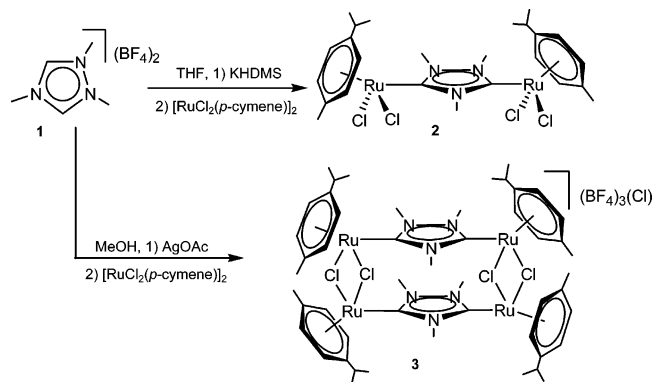(10) Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186.

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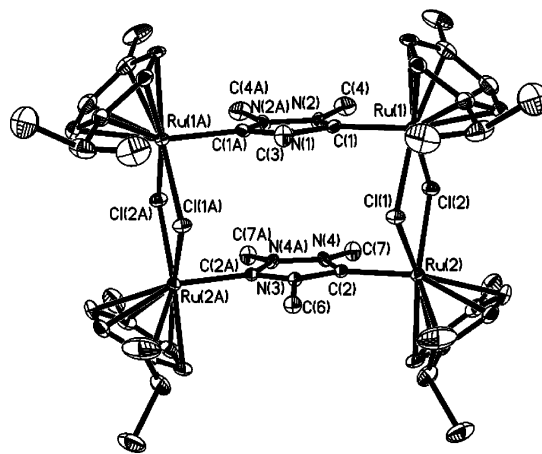
Scheme 2

Figure 1. Molecular diagram of compound **3**. Hydrogen atoms and anions (3 BF_4^- and 1 Cl^-) have been omitted for clarity. Ellipsids at 30% probability. Selected bond distances (Å) and angles (deg): Ru(1)−C(1) 2.080(8), Ru(2)−C(2) 2.051(8), Ru(1)−Cl(1) 2.428(2), Ru(1)−Cl(2) 2.452(2), Ru(2)−Cl(1) 2.433(2), Ru(2)−Cl(2) 2.453(2), C(1)−Ru(1)−Cl(1) 88.5(2), C(1)−Ru(1)−Cl(2) 89.7(2), Cl(1)−Ru(1)−Cl(2) 78.91(7), C(2)−Ru(2)−Cl(1) 89.2-(2), C(2)−Ru(2)−Cl(2) 89.2(2), Cl(1)−Ru(2)−Cl(2) 78.78(7).

Results and Discussion

The trimethyltriazolium salt **1** reacted with [RuCl₂(*p*-cymene)]₂ in the presence of potassium hexamethyldisilazide (KHDMS), affording the dinuclear compound **2** in moderate yield (63%), as shown in Scheme 2. When the activation of the ligand precursor **1** was performed by transmetalation from a silver carbene (not isolated) obtained by addition of AgOAc, the tetranuclear compound **3** was obtained as the only isolable product (yield, 57%). Compounds **2** and **3** were characterized by NMR spectroscopy and mass spectrometry, and gave satisfactory elemental analysis.

The ¹H NMR of **2** shows that the signal due to the acidic NC*H*N protons has disappeared, thus providing the first evidence of the metalation of the ligand. The room temperature spectrum shows broad signals, probably due to a dynamic fluxional equilibrium, implying the rotation of the *p*-cymene ligand, so the accurate chemical shifts for the resonances were recorded at −10 °C. The resonances assigned to the protons of the *N*-methyl groups appear as two separate signals at 4.40 and 4.26 ppm, in a 3:6 ratio, which in fact suggests that the compound has a twofold symmetry. The clearest evidence of the metalation of the ligand arises from the evaluation of the ¹³C NMR spectrum that shows a signal at 185.1 ppm due to the Ru−C$_{carbene}$ bond. The dimetallic nature of the compound is supported by the data resulting from the electrospray mass spectrometry (ESI-MS), which shows a main peak at *m/z* 688.2, due to [M − Cl] ⁺ (see the Supporting Information for more details).

The ¹H NMR spectrum of **3** shows the two resonances due to the *N*-methyl groups at 4.03 and 3.65 ppm (12:6 ratio, respectively), also implying a symmetry related structure. The ¹³C NMR shows a signal at 185.5 ppm due to the metalated carbene-carbon. The tetranuclear nature of the complex is supported by the ESI-MS spectrum, which displays peaks at *m/z* 739.6 ([M + 2BF₄]²⁺), 464.4 ([M + BF₄]³⁺), 347.3 ([M + 2CH₃CN]⁴⁺), 336.8 ([M + CH₃CN]⁴⁺), and 335.5 ([M]⁴⁺) (see the Supporting Information for more details). The elemental analysis fits well for a mixture of counteranions (3 BF₄⁻, and 1 Cl⁻) present in the compound, as confirmed by the X-ray diffraction studies (see below).

The structure of **3** was determined by means of X-ray diffraction studies, and confirmed that the compound contained a mixture of BF₄ (3) and Cl (1) as counterions. Figure 1 shows the molecular diagram of **3**. The compound can be seen as the sum of two dinuclear structures with one ditz bridging ligand, bridged by four chlorine ligands, thus forming a tetranuclear structure. Two perpendicular symmetry planes are defined by the four chlorine bridging ligands and the bisecting C−CH₃ axis

of the two azole rings, respectively. A C_2 axis defined by the intersection of the two perpendicular symmetry planes would be relating the two imidazolediylidene ligands. The two azole rings show a relative eclipsed disposition, according to the orientation of the *N*-methyl substituents. The Ru−C$_{carbene}$ distance is 2.065 Å (average). The Ru−C distances of the *p*-cymene significantly differ depending on their relative orientation to the carbene ligand, with longer distances for the trans carbons (average: $d_{Ru−C(trans)} = 2.26$ Å; $d_{Ru−C(cis)} = 2.16$ Å), as a clear consequence of the trans influence of the NHC ligand. The Cl−Ru−C$_{carbene}$ angles are almost perpendicular (av. 89.3°), thus affording an almost orthogonal cavity inside the tetranuclear structure.

To test the catalytic activity of **2** and **3**, we decided to study the β-alkylation of secondary alcohols with primary alcohols.[15,16] The catalytic version of this type of reaction has important beneficial implications compared to the traditional multistep processes, especially considering the economical benefits that a high-yielding one-pot procedure implies, together with the use of an environmentally friendly process. Despite these obvious important implications, we just found four examples of this catalytic reaction described in the literature, three referred to Ru complexes[17−19] and one referred to Ir.[20] Mechanistically, the reaction is believed to involve oxidation of both alcohols to form a ketone and an aldehyde, which undergo an aldol condensation giving an α,β-unsaturated ketone, which is further reduced to give the saturated alcohol.[15,20] The process would then imply the formation of a metal hydride, at the stage of the oxidation of the alcohols. We thought that our complexes **2** and **3** may be good candidates for the study of this reaction because Ru−NHC complexes have proven as excellent catalysts

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Table 1. β-Alkylation of Secondary Alcohols with Primary Alcohols[a]
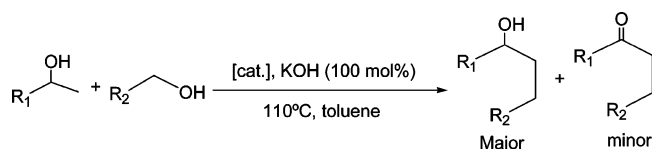
entry	catalyst	R1	R2	t (h)	% conv	% alcohol	% ketone
1	[Ru(p-cymene)Cl$_2$]$_2$	Ph	Pr	20	11	100	0
2	**2**	Ph	Pr	20	80	87	13
3	**2**	Ph	iPr	20	61	100	0
4				90	91	100	0
5[b]	**2**	Ph	Pr	20	73	100	0
6[b]				100	90	88	12
7	**2**	Ph	3-Cl(C$_6$H$_4$)	20	92	100	0
8				50	>99	100	0
9	**2**	Ph	4-Cl(C$_6$H$_4$)	20	76	100	0
10				36	80	100	0
11	**2**	Ph	Ph	20	75	100	0
12				36	80	100	0
13	**2**	CH$_3$(CH$_2$)$_4$	Ph	20	87	100	0
14				36	>99	100	0
15	**3**	CH$_3$(CH$_2$)$_4$	Ph	20	90	100	0
16[b]	**3**	Ph	Pr	20	62	94	6
17[b]				100	85	89	11
18	**3**	Ph	Pr	20	60	99	1
19				65	85	90	10
20[b]	**3**	Ph	3-Cl(C$_6$H$_4$)	20	2	100	0
21[b]				100	96	100	0
22	**3**	Ph	3-Cl(C$_6$H$_4$)	20	58	100	0
23				52	98	100	0
24	**3**	Ph	4-Cl(C$_6$H$_4$)	20	98	64	36
25				40	>99	49	51
26				20	88	100	0
27	**3**	Ph	Ph	40	95	100	0
28[b]				20	80	100	0
29	**3**	Ph	iPr	20	85	100	0
30				90	>99	100	0

[a] 2.5 mmol of primary and secondary alcohol, 2.5 mmol (100 mol %) of KOH, 0.3 mL of toluene, 1 mol % cat. (referred to metal). Temperature: 110 °C. Conversions determined by ^{1}H NMR spectroscopy. [b] Solvent: dioxane.

for the hydrogen transfer reactions between alcohols and ketones,[21] and also because NHC ligands have been shown to efficiently activate catalysts toward C−H activation processes.[22]

The reactions were performed by using different primary and secondary alcohols in a 1:1 molar ratio (Table 1), and a fixed catalyst loading of 1 mol % (referred to the amount of metal) in the presence of KOH in toluene. We also changed the solvent (dioxane) and the base (Na$_2$CO$_3$, NaOAc), but all these changes resulted in a lowering of the reaction yields. A wide variety of primary alcohols and two different secondary alcohols (1-

phenylethanol and 2-heptanol) were tested. Table 1 shows the catalytic results obtained when using catalysts **2** and **3**. The data reflect the conversions obtained after 20 h of reaction, and the time for which a maximum conversion was achieved. For comparison purposes we first studied the catalytic activity of [RuCl$_2$(p-cymene)]$_2$ (entry 1) and observed that this species gave very low conversions to the desired alkylated alcohol, compared to the performances shown by **2** and **3**. Both complexes showed similar efficiencies if we compare the conversions provided. For most of the reactions, the process is very selective in the production of the alkylated alcohols, although in some cases small amounts of the alkylated ketones were obtained as secondary products. The production of the ketone is significantly more important when 4-chlorobenzyl alcohol is used (entries 24 and 25), which provides an almost equimolar ratio between the alkylated alcohol and ketone.

Both compounds, **2** and **3**, gave excellent conversions to the alcohols in shorter reaction times than previously reported catalysts for the same reaction.[17−20] This result is even more significant if we take into account that a lower catalyst loading (1 mol %) was used compared to previously reported studies

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with other Ru catalysts (2−5 mol %). It is noteworthy to point out that both catalysts provided excellent conversions when 2-heptanol was used (entries 13, 14, and 15), even for relatively short reaction times (20 h). This result clearly contrasts with previously reported results that found that the same aliphatic alcohol gave very low chemical yields (<5 mol %).[19] Aliphatic primary alcohols have also been reported to provide very low yields in this coupling reaction.[19] In our case, isobutyl alcohol afforded very high conversions after 4 days of reaction (entries 4 and 30). The fact that **2** and **3** can effectively provide the coupling of both aliphatic and aromatic alcohols has important synthetic implications, since it widens the scope of this reaction.

Conclusions

With this work we have widened the scope of the ligand ditz in the preparation of discrete molecules with transition metals.[12] The preparation of complexes **2** and **3** provides new evidence of the coordination versatility of ditz. Depending on the activation of the ligand precursor the dinuclear (**2**) or tetranuclear (**3**) compounds were obtained. The interesting structural features of the tetranuclear complex **3** have been described.

The catalytic performances of both **2** and **3** toward the β-alkylation of secondary alcohols with primary alcohols have shown that these two species are very active, especially when compared to previously reported catalysts for the same reaction. These results are even more significant if we take into account that the reactions were carried out in the optimal conditions for a maximum atomically efficient process, which is with both alcohols in a 1:1 molar ratio and with 100 mol % of base. The activity of both species is also much higher than that shown for [RuCl$_2$(*p*-cymene)]$_2$, which may imply that the introduction of the basic NHC ligand has some implications in the yield of this C−H activation process. Also, taken into account that each pair of metal fragments connected by ditz are electronically communicated, we cannot discard that some cooperativity may enhance the catalytic performance of the system. Further studies to elucidate this point are underway.

Experimental Section

NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers, using CDCl$_3$, acetone-d_6, and acetonitrile-d_3 as solvents. Elemental analyses were carried out on an Euro EA 3000 CHN Eurovector analyzer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, with nitrogen employed as drying and nebulizing gas. 1,2,4-Trimethyl-1,2,4-triazolium tetrafluoroborate[14] (**1**) and [RuCl$_2$(*p*-cymene)]$_2$[23] were synthesized according to literature procedures. All other reagents are commercially available and were used as received.

Synthesis of [RuCl$_2$(*p*-cymene)]$_2$(μ-ditz), 2. A 0.5 M solution of KHMDS in toluene (1.28 mL, 0.65 mmol) was added to **1** (94 mg, 0.33 mmol) in 10 mL of dry THF at 0 °C. The mixture was stirred for 10 min at room temperature. This solution was added via a cannula to a mixture of [RuCl$_2$(*p*-cymene)]$_2$ (200 mg, 0.32 mmol) in 5 mL of CH$_2$Cl$_2$ under inert atmosphere. The initial red suspension was stirred 1 h at 45 °C, and it progressively turned orange. After 1 h, the orange suspension was refluxed for 20 min. Then the mixture was filtered through Celite and the solvent was removed on a rotatory evaporator. Washing the residue with acetone and drying in vacuo afforded product **2** as a brownish solid. Yield:

150 mg, 63%. ^{1}H NMR (CDCl$_3$, 500 MHz, −10 °C): δ 5.52 (d, 2H, $^3J_{H-H}$ = 5.00 Hz, CH$_{pcym}$), 5.47 (d, 2H, $^3J_{H-H}$ = 4.50 Hz, CH$_{pcym}$), 5.39 (d, 2H, $^3J_{H-H}$ = 5.00 Hz, CH$_{pcym}$), 5.21 (d, 2H, $^3J_{H-H}$ = 4.50 Hz, CH$_{pcym}$), 4.40 (s, 3H, NCH$_3$), 4.26 (s, 6H, NCH$_3$), 2.92 (m, 2H, CH$_{isop\ pcym}$), 2.12 (s, 6H, CH$_{3isop\ pcym}$), 1.30 (t, 12H, $^3J_{H-H}$ = 7.50 Hz, CH$_{3\ isop\ pcym}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz, 0 °C): δ 185.10 (C−Ru), 110.53, 98.11 (Cq$_{pcym}$), 86.79, 85.86, 85.21, 85.12 (CH$_{pcym}$), 43.21, 39.74 (NCH$_3$), 31.30 (CH$_{isop\ pcym}$), 23.02, 22.94 (CH$_{3isop\ pcym}$), 19.30 (CH$_{3pcym}$). Assignment of ^{13}C{^{1}H} NMR signals is confirmed by ^{13}C−^{1}H inverse correlation at 0 °C. Electrospray MS (10V, *m/z*): 347.2 [M − 2Cl + CH$_3$CN]$^{2+}$, 367.7 [M − 2Cl + 2CH$_3$CN]$^{2+}$, 688.2 [M − Cl]$^+$, 729.3 [M − Cl − CH$_3$CN]$^+$. Anal. Calcd for C$_{25}$N$_3$Ru$_2$Cl$_4$H$_{37}$(CH$_2$Cl$_2$) (mol wt 808.47): C, 38.63; H, 4.86; N, 5.20. Found: C, 38.37; H, 4.80; N, 5.11.

Synthesis of {[RuCl(*p*-cymene)]$_2$(μ-ditz)}$_2$(BF$_4$)$_3$(Cl), 3. A mixture of **1** (46 mg, 0.16 mmol) and AgOAc (60 mg, 0.34 mmol) was stirred in CH$_3$OH (10 mL) at room temperature for 90 min. Then, [RuCl$_2$(*p*-cymene)]$_2$ (100 mg, 0.16 mmol) was added. The mixture was refluxed for 24 h, then filtered through Celite, and the solvent was evaporated. Washing of the residue with CHCl$_3$ and drying in vacuo afforded product **3** as an orange-brownish solid. Yield: 75 mg (57%). ^{1}H NMR (CD$_3$CN-d_3, 300 MHz): δ 6.20 (d, $^3J_{H-H}$ = 6.00 Hz, 4H, CH$_{pcym}$), 6.15 (d, $^3J_{H-H}$ = 6.00 Hz, 4H, CH$_{pcym}$), 6.00 (d, $^3J_{H-H}$ = 6.30 Hz, 4H, CH$_{pcym}$), 5.93 (d, $^3J_{H-H}$ = 6.00 Hz, 4H, CH$_{pcym}$) 4.03 (s, 12H, NCH$_3$), 3.65 (s, 6H, NCH$_3$), 2.77 (m, 4H, CH$_{isop\ pcym}$), 2.06 (s, 12H, CH$_{3isop\ pcym}$), 1.45 (d, $^3J_{H-H}$ = 4.80 Hz, 12H, CH$_{3iso\ pcym}$), 1.43 (d, $^3J_{H-H}$ = 4.80 Hz, 12H, CH$_{3isop\ pcym}$). ^{13}C{^{1}H} NMR (CD$_3$CN-d_3, 125 MHz): δ 185.50 (C−Ru), 109.14, 99.48 (Cq$_{pcym}$), 86.70, 86.43, 86.07, 85.96 (CH$_{pcym}$), 41.76, 39.12 (NCH$_3$), 31.68 (CH$_{isop\ pcym}$), 22.22, 21.83 (CH$_{3isop\ pcym}$), 17.61 (CH$_{3pcym}$). Assignment of ^{13}C{^{1}H} NMR signals is confirmed by ^{13}C−^{1}H inverse correlation at room temperature. Electrospray QTOF-MS (25V, *m/z*): 739.6 [M + 2BF$_4$]$^{2+}$, 464.4 [M + BF$_4$]$^{3+}$, 347.3 [M + 2CH$_3$CN]$^{4+}$, 336.8 [M + CH$_3$CN]$^{4+}$, 335.5 [M]$^{4+}$. Anal. Calcd for C$_{50}$H$_{74}$B$_3$Cl$_5$F$_{12}$N$_6$Ru$_4$ (mol wt 1601.1): C, 37.51; H, 4.66; N, 5.25. Found: C, 37.55; H, 4.53; N, 5.18.

β-Alkylation of Secondary Alcohols with Primary Alcohols: Typical Procedure. The reaction was carried out with secondary alcohol (2.5 mmol), primary alcohol (2.5 mmol), 1 mol % of catalyst, and base, KOH (2.5 mmol) in toluene (0.3 mL) at 110 °C. The reaction was monitored by ^{1}H NMR spectroscopy, by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of CDCl$_3$. The evolution was determined by integration, using ferrocene as internal standard. The signals due to reagents and products were taken from the literature.[18,19]

X-ray Diffraction Studies. Crystals for X-ray diffraction of **3** were obtained by slow diffusion of CH$_2$Cl$_2$ in a concentrated solution of the compound in acetonitrile. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer with use of graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction frames were integrated with the SAINT package.[24] 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 refined with the SHELXTL 6.1 software package.[25] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were assigned to ideal positions and refined by using a riding model.

X-ray crystal structure data: C$_{50}$H$_{74}$B$_3$Cl$_5$F$_{12}$N$_6$Ru$_4$, monoclinic, space group *Cm*, *a* = 20.6064(11) Å, *b* = 15.2933(8) Å, *c* = 11.5848(6) Å, β = 111.0560(10)°, *V* = 3407.1(3) Å,^{3} *Z* = 2, P_{calcd} = 1.561 g cm^{-3}, crystal dimensions 0.22 × 0.16 × 0.13 mm^3;

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Supporting Information Available: Crystallographic data of compound **3** in the form of CIF files and electrospray ionization mass spectrometry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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