Coordinatively Unsaturated 16-Electron Ruthenium Allenylidene Complexes: Synthetic, Structural, and Catalytic Studies

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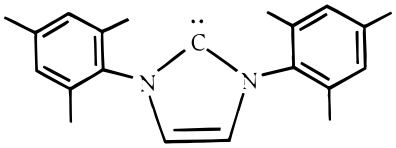
*Summary: The one-pot reactions of [(p-cymene)$RuCl_2$]$_2$ (**1**) or $(PPh_3)_4RuCl_2$ (**2**) with 2 equiv of PCy_3 and 3,3-diphenylpropyn-3-ol afford the novel 16-electron ruthenium allenylidene complex $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ (**3**) in high yields. Substitution of one PCy_3 ligand in **3** for one nucleophilic carbene ligand, IMes [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene], affords the novel complex $(PCy_3)(IMes)Cl_2Ru(=C=C=CPh_2)$ (**4**). Single-crystal X-ray structure analyses of complexes **3** and **4** were performed. Thermal stability of complexes **3** and **4** was investigated, and their catalytic activity promoting ring-closing metathesis (RCM) of various substrates was tested.*

Introduction

Ruthenium-based olefin metathesis catalysts have been the focus of considerable attention since they are relatively inert to air and moisture and show significant tolerance to functional groups.[1] Characteristic of these five-coordinated, distorted square-pyramidal complexes is the coordination of the ruthenium center, which is comprised of chlorides in trans arrangement and trans-phosphine ligands at the base of the pyramid with the carbene moiety at the apex. The nature of the phosphine ligation as well as that of the carbene moiety affects the catalytic activity of the complex.[1f]

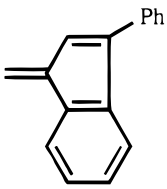
Widely used phosphine ligands are PCy_3 and PPh_3. However, these complexes suffer from significant decomposition at elevated temperatures.[2] Nucleophilic carbenes were found to mimic phosphines and were employed in several organometallic catalytic reactions.[3] Replacement of one phosphine ligand in these complexes by the sterically demanding imidazol-2-ylidene ligand IMes developed by Arduengo and co-workers[4] not only stabilizes the catalysts but also increases their activity in metathesis reactions.[5]



IMes

The nature of the carbene moiety has been proven to affect not only the initiation but also the progression of the catalytic process.[1f] Very common carbene moieties are benzylidene (=CHPh) and vinylmethylene (=CH−CH=CR_2, R = alkyl, aryl, H) groups. Due to their high catalytic activities, benzylidene complexes have drawn large attention and are commercially available.[1f] However, their synthesis from the hazardous diazoalkane derivative is of concern. Vinylmethylene complexes are less active, and their original preparation using cyclopropane derivatives is cumbersome.[1a] However, the most recent synthetic routes make use of propargyl chloride derivatives.[1l] Catalytically active vinylidene complexes (=C=CHR, R = alkyl, aryl) were successfully prepared by reaction of 1-alkynes with suitable precursors.[6]

Introducing an allenylidene moiety (=C=C=CR_2, R = Ph, Me) at the ruthenium center was successfully carried out by using 3,3-diphenylpropyn-3-ol as reagent, forming mostly cationic 18-electron complexes.[7] Recently, Hill and co-workers have reported a similar, straightforward route for the synthesis of 16-electron ruthenium allenylidene complexes by reacting $(PPh_3)_{3-4}RuCl_2$ with 3,3-diphenylpropyn-3-ol.[8] Recent investigations, however, have proven these complexes to be 3-phenyl-1-indenylidene complexes formed by intramolecular rearrangement (Scheme 1).[9] These complexes perform well in metathesis reactions and show a high thermal stability.[8,10]



3-phenyl-1-indenylidene

Recently, we have synthesized several imidazol-2-ylidene ruthenium 3-phenyl-1-indenylidene complexes starting from the reaction of $(PPh_3)_4RuCl_2$ with 3,3-diphenylpropyn-3-ol.[8,10] The addition was accompanied by a rearrangement reaction forming the indenylidene instead of the expected allenylidene moiety. We now

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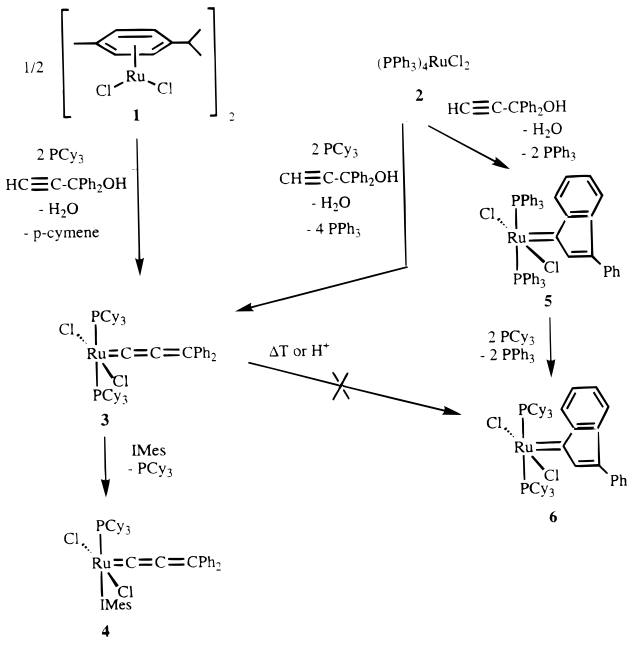
Scheme 1



wish to report the syntheses and catalytic activity of the first 16-electron ruthenium allenylidene complexes.

Results and Discussion

The reaction of $(PPh_3)_4RuCl_2$ (**2**) with 3,3-diphenylpropyn-3-ol results exclusively in the formation of the 3-phenyl-1-indenylidene complex **5**. Starting from complex **5**, the PPh_3 ligands can be substituted by the better donating ligand such as PCy_3, affording the analogous indenylidene complex **6**.[9] Carrying out this reaction under identical conditions with two additional equivalents of PCy_3, however, leads exclusively to the formation of the allenylidene complex **3**. The C_3 spine remains intact, although water is also liberated in this reaction. This can only be explained by the different ligation at the metal center. The better donating PCy_3 provides a higher electron density at the ruthenium center. Obviously the rearrangement reaction forming the indenylidene moiety is promoted by this lack of electron density. Complex **3** is also accessible from the reaction of $[(p\text{-cymene})RuCl_2]_2$ (**1**) with 3,3-diphenylpropyn-3-ol and 2 equiv of PCy_3 via loss of *p*-cymene. However, the product (85% of **3** based on ^{31}P NMR data) contains two side products, one identified as the 3-phenyl-1-indenylidene complex **6** (^1H and ^{31}P NMR data, 8%) and one unknown [7%, ^{31}P NMR (C_6D_6, 25 °C, 121.4 MHz): $\delta = 37.4$]. When 2 equiv of PPh_3 instead of PCy_3 were used, no carbene moiety was formed. All attempts to convert the allenylidene into the indenylidene by addition of protic acids or by subjecting the allenylidene to elevated temperatures were unsuccessful. The exchange of one PCy_3 ligand for IMes affords complex **4** in high yields. The reactions are summarized in Scheme 1.

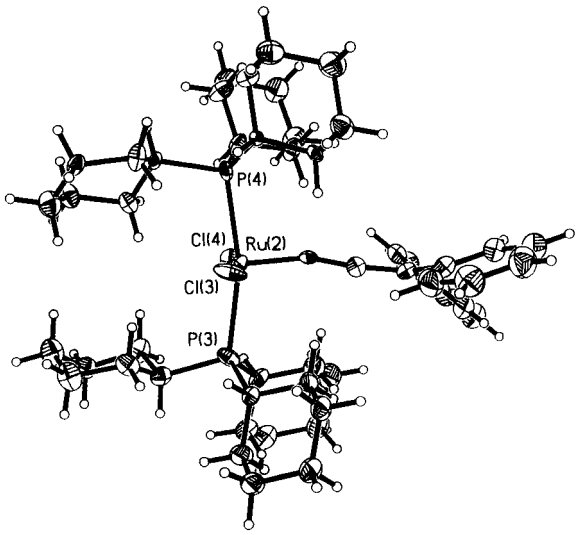


Figure 1. ORTEP diagram of $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$, **3**.

Single crystals of the complexes **3** and **4**, suitable for X-ray structure analysis, were obtained from slow diffusion of hexanes into a saturated toluene solution (ORTEP diagrams of **3**[11] and **4** are given in Figures 1 and 2). In both structures the five-coordinated ruthenium center is located at the bottom of a square pyramid. The allenylidene moiety is located at the apex, the trans chlorides and PCy_3 ligands (**3**), PCy_3 and IMes ligands (**4**), form the base. In both complexes the Ru−C_α bond distances are nearly identical (1.794(11) Å). This is in the usual range (1.76−1.84 Å) for carbene moieties in this kind of 16-electron ruthenium complexes.[5] However, these bond distances are much shorter than the bond lengths determined for cationic 18-

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(11) Crystals of compound **3** contain two conformers in the asymmetric unit cell, differing only in allynylidene−phenyl torsion angles. Only one is shown in Figure 1.

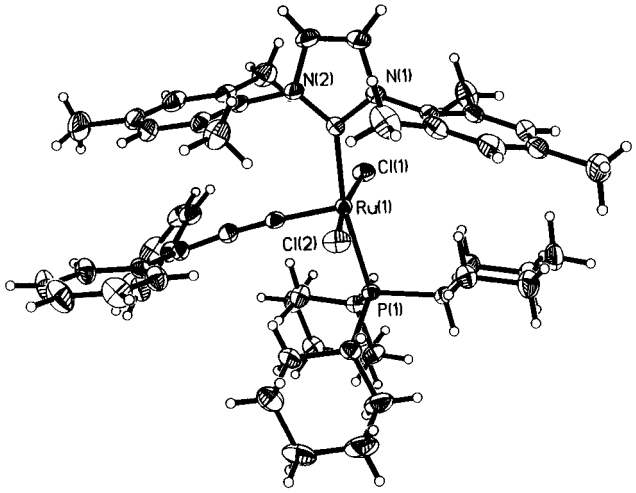

Figure 2. ORTEP diagram of (IMes)(PCy_3)$_2Cl_2Ru$(=C=C=CPh_2), **4**.

electron ruthenium allenylidene complexes (1.87−1.92 Å).[7a,d,i−k] This indicates a better overlap and a significantly higher bond strength of the carbene moiety to the metal center in complexes **3** and **4**. The comparable metal−ligand bond distances at the base also give very similar values, indicating no significant change for the electronic environment of the metal center, and these structural features may explain the similar catalytic properties of complexes **3** and **4** (see below). The bond angles in both complexes at the base do not deviate more than 4° from the ideal 90°. However, steric interference with the allenylidene moiety causes widening of one C_α−Ru−Cl angle [96.2 (5)° (**3**), 95.89(4)° (**4**)] and one C_α−Ru−P angle (101.4(5)°) in complex **3** and the C_α−Ru−C(IMes) angle (98.89(5)°) in complex **4**. The allenylidene chain is only slightly bent in complex **4** (Ru−C_α−C_β = 175.36(11)°, C_α−C_β−C_γ = 175.29(13)°). This indicates a strong conjugation along the spine excluding C−H π-interaction to neighboring hydrogen atoms, as observed in other complexes.[7j] Complex **3**, however, shows significantly stronger bending along the spine (Ru−C_α−C_β = 169.20(11)°, C_α−C_β−C_γ = 167.20(18)°). C−H π-interaction to hydrogen atoms of the PCy_3 ligands may be present. The bond distances along the spine [C_α−C_β = 1.27 Å (**3**), 1.26 Å (**4**) and C_β−C_γ = 1.35 Å (**3**), 1.34 Å (**4**)] are in the usual range for ruthenium allenylidene complexes.[7a,d,i−k] Selected bond distances and angles are given in Table 2.

Thermal Stability. Compounds **3** and **4** were subjected to elevated temperatures. The thermal stability studies have been performed in NMR tubes by dissolving 5 mg of each compound in 0.4 mL of toluene-d_8 and heating the solution to 80 °C. The onset of decomposition was noted by examining the ^{31}P NMR spectra taken at certain time intervals (2, 4, ..., 2^n h). Both compounds turned out to be relatively robust at this temperature. Even after 32 h of constant heating no signs of decomposition products were found. Initial signs of decomposition were noticed for complex **3** after 64 h and for complex **4** after 128 h. A similar increased thermal stability has been observed for the $Cl_2(PCy_3)$(IMes)Ru(=C(H)Ph complex compared to $Cl_2(PCy_3)_2$Ru(=C(H)Ph.[5]

Metathesis Reactions. The role of complexes **3** and **4** as catalyst precursors in the ring-closing metathesis (RCM) reactions was investigated. Three different diene substrates, diethyl diallylmalonate (**7**), diallyltosylamine (**8**), and diethyl di(2-methylallyl)malonate (**9**), were added to the NMR tubes containing a solution of 5 mol % of catalyst precursor in an appropriate deuterated solvent. The catalytic reactions are depicted in Scheme 2, and results of the RCM reactions are presented in Table 3.

Product formation and diene disappearance were

Table 1. Crystallographic Data for the Complexes ($PCy_3)_2Cl_2Ru$(=C=C=CPh_2) (3) and (PCy_3)(IMes)Cl_2Ru(=C=C=CPh_2) (4)

	3	4
formula	$C_{51}H_{76}Cl_2N_2PRu$	$C_{54}H_{67}Cl_2N_2PRu$
fw	923.02	947.04
color	purple-brown	purple-brown
space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
a, Å	31.391(3)	21.778(3)
b, Å	19.3287(16)	10.1794(12)
c, Å	16.2623(13)	23.736(3)
α, deg	90	90
β, deg	104.448(2)	111.978(12)
γ, deg	90	90
μ(Mo), cm^{-1}	5.40	5.01
Z	8	4
R^a	0.0740	0.0414
$R_w{}^a$	0.1484	0.0427
no. of refined params	1009	827
no. of data collected	159173	100274
no. of unique data, $I > 2\sigma$	27830	14220
R_{merge}	0.1385	0.0393

Table 2. Selected Bond Distances [Å] and Angles [deg] for the Complexes 3 and 4 (esd's are in parentheses)

	3	4
Ru−C_α	1.794(11)	1.7932(13)
Ru−C(IMes)		2.0893(14)
Ru−P	2.358(5), 2.413(5)	2.4107(4)
Ru−Cl	2.371(5), 2.382(5)	2.3640(4), 2.3916(4)
C_α−C_β	1.273(12)	1.2605(17)
C_β−C_γ	1.346(12)	1.3447(17)
C_α−Ru−C(IMes)		98.89(5)
C_α−Ru−P	91.4(4), 101.4(5)	92.19(4)
C_α−Ru−Cl	91.6(5), 96.2(5)	93.13(4), 95.89(4)
C(IMes)−Ru−Cl		88.94(3), 89.61(3)
P−Ru−Cl	86.44(17), 87.56(17), 91.62(17), 92.62(16)	88.056(14), 91.665(14)
Ru−C_α−C_β	169.20(12)	175.36(11)
C_α−C_β−C_γ	167.20(18)	175.29(13)

Scheme 2

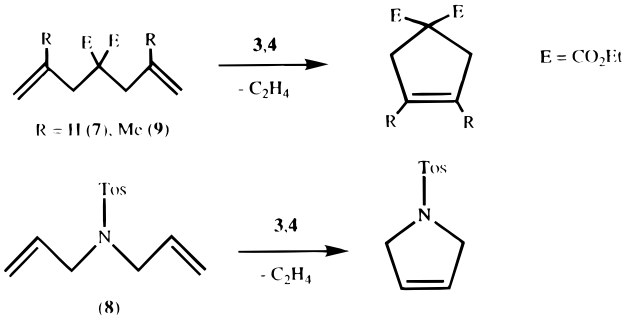

Table 3. Ring-Closing Metathesis Mediated by 3 and 4

entry no.	substrate	catalyst precursor	solvent	temp (°C)	time	yield (%)[a]
1	**7**	**3**	CD_2Cl_2	40	25 min	12
2	**7**	**4**	CD_2Cl_2	40	25 min	8
3	**8**	**3**	CD_2Cl_2	40	25 min	4
4	**8**	**4**	CD_2Cl_2	40	25 min	0
5	**9**	**3**	toluene-d_8	80	2 h	0
6	**9**	**4**	$d_8$toluene-d_8	80	2 h	0

[a] Monitored by ^{1}H NMR spectroscopy.

monitored by integrating the allylic methylene peaks in the ^{1}H NMR. Both complexes perform very poorly in these reactions compared to cationic 18-electron arene−ruthenium allenylidene complexes.[7h] The significantly higher bonding energy of the allenylidene moiety at the metal center as inferred from the single-crystal X-ray data may be at the origin of the lower catalytic activity displayed by **3** and **4**. The sterically hindered substrate diethyl di(2-methylallyl)malonate shows no sign of ring closing using either complex even after 2 h at 80 °C. To get detectable conversion of the other substrates, reaction mixtures were heated to 40 °C in CD_2Cl_2. The turnover rates after 25 min indicated slightly lower catalytic activity for the IMes-substituted complex **4** (diethyl diallylmalonate 8%, diallyltosylamine 0%) compared to complex **3** (diethyl diallylmalonate 12%, diallyltosylamine 4%).

Conclusions

The first coordinatively unsaturated 16-electron ruthenium allenylidene complex $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ (**3**) is easily available from the one-pot reaction of $[(p\text{-cymene})RuCl_2]_2$ (**1**) or $(PPh_3)_4RuCl_2$ (**2**) with 2 equiv of PCy_3 and 3,3-diphenylpropyn-3-ol. The higher electron density at the metal center provided by the PCy_3 ligands inhibits the rearrangement of the allenylidene backbone. $(PCy_3)(IMes)Cl_2Ru(=C=C=CPh_2)$ (**4**) can be obtained in high yields by simple ligand exchange reaction with IMes starting from complex **3**. Both complexes possess a high thermal stability at 80 °C, with complex **4** being slightly more stable to decomposition than complex **3**. The single-crystal X-ray data reveal very similar metal−ligand bond distances in the solid state, indicating a similar electronic environment at the metal center. Disappointingly low catalytic activities for ring-closing metathesis reactions were obtained for **3** and **4**.

Experimental Section

General Considerations. All synthesis and kinetic studies were performed under inert atmospheres of argon using standard high-vacuum or Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm oxygen and water. Solvents including deuterated solvents for NMR analysis were dried and distilled under nitrogen before use employing standard drying agents. Compounds **1**[12] and **2**[13] and the ligand IMes[4] were synthesized according to literature procedures. NMR spectra were recorded using a Varian Gemini 300 or Oxford 400 MHz spectrometer. IR spectra were performed with a Perkin-Elmer System 2000 FT-IR. Elemental analyses were performed by Desert Analysis, Tucson, AZ.

Synthesis of $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ 3. Method A. Bis(*p*-cymeneruthenium) tetrachloride (1.106 g/1.81 mmol) (**1**), PCy_3 (2.059 g/7.342 mmol), and 3,3-diphenylpropyn-3-ol (0.760 g/ 3.65 mmol) were dissolved in 50 mL of THF and heated under reflux for 16 h. After cooling to room temperature all volatiles were removed under reduced pressure and the residue was suspended in 20 mL of hexanes. After heating under reflux for an additional 3 h the suspension was filtered and the yellow-brown residue was washed with 3 × 5 mL of pentanes. Drying the residue in vacuo for 30 min afforded 1.465 g (44%) of compound **3**.

Method B. Tetrakis(triphenylphosphine)ruthenium dichloride (0.829 g/0.671 mmol) (**2**), PCy_3 (0.435 g/1.550 mmol), and 3,3-diphenylpropyn-3-ol (0.162 g/ 0.775 mmol) were dissolved in 30 mL of THF and heated under reflux for 16 h. After cooling to room temperature all volatiles were removed under reduced pressure and the residue was suspended in 15 mL of hexanes. After heating under reflux for an additional 3 h the suspension was filtered and the yellow-brown residue was washed with 3 × 5 mL of pentanes. Drying the residue in vacuo for 30 min afforded 0.448 g (72%) of compound **3**. ^{1}H NMR (300.1 MHz, 25 °C, C_6D_6): δ = 8.03 (d, 4 H), 7.25 (t, 2 H), 7.06 (m, 4 H, CPh_2), 2.83 (m, 6 H), 2.17 (m, 12 H), 1.65 (m, 30 H), 1.21 (m, 18 H, PCy_3). ^{31}P NMR (121.4 MHz, 25 °C, C_6D_6): δ = 40.9. IR (20 °C, CH_2Cl_2): ν (cm^{-1}) = 1925 (C=C=C). Anal. Calcd for $C_{51}H_{76}Cl_2P_2Ru$: C, 65.46; H, 8.52. Found: C, 65.10; H, 8.14.

Synthesis of $(IMes)(PCy_3)Cl_2Ru(=C=C=CPh_2)$, 4. $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ (**3**, 0.7460 g/ 0.808 mmol) and IMes (0.2610 g/0.857 mmol) were dissolved in 50 mL of toluene and stirred at 40 °C for a period of 16 h. After cooling to room temperature the reaction solution was filtered. The solvent of the filtrate was removed under reduced pressure, and the residue was suspended in 30 mL of hexanes. The mixture was heated under reflux for 3 h and filtered after cooling to room temperature. The residue was washed with pentanes (3 × 10 mL) and dried in vacuo for 30 min. Pure compound **4** was obtained as an orange-brown powder (0.602 g/79%). ^{1}H NMR (300.1 MHz, 25 °C, C_6D_6): δ = 7.89 (d, 4 H), 7.28 (t, 2 H), 7.06 (m, 4 H, CPh2), 6.85 (s, 2 H), 6.28 (s, 2 H), 6.20 (d, 1 H), 6.14 (d, 1 H), 2. 58 (s, 6 H), 2.32 (s, 6 H), 2.14 (s, 3 H), 1. 72 (s, 3 H, IMes), 2.50 (m, 3 H), 1.88 (m, 6 H), 1.47 (m, 9 H), 0.97−1.22 (m, 15 H, PCy_3). ^{31}P NMR (121.4 MHz, 20 °C, C_6D_6): δ = 39.4. IR (25 °C, CH_2Cl_2): ν (cm^{-1}) = 1924 (C=C=C). Anal. Calcd for $C_{54}H_{67}Cl_2N_2PRu$: C, 68.48; H, 7.13; N, 2.96. Found: C, 68.46; H, 7.04; N, 3.00.

General Procedure for Thermal Stability Experiments. In the drybox the catalyst precursor (5 mg) was accurately weighed in a Wiland screw-capped NMR tube and dissolved in toluene-d_8 (0.4 mL). The solution was heated to 80 °C. The onset of decomposition was noted by examining the ^{31}P NMR spectra taken at regular time intervals.

General Procedure for Ring-Closing Metathesis. In the drybox, the catalyst precursor (5.0 μmol/5 mol %) was accurately weighed in a Wilmad screw-capped NMR tube and dissolved in CD_2Cl_2 or toluene-d_8 (0.4 mL). Diethyl diallylmalonate (0.1 mmol), diethyl di(2-methyl)allylmalonate (0.1 mmol), or diallyltosylamine (0.1 mmol) was added to the solution, and the NMR tube was heated under argon. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks.[1k]

X-ray Crystallographic Studies. Deep red crystals of complexes **3** and **4** were obtained by slow diffusion of hexane into a saturated toluene solution. A single crystal of each compound was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo Kα radiation at 170 K. Cell dimensions were determined by least-squares refinements of the measured setting angles of 159 173 reflections with $2.50° < 2\theta < 60.00°$ for **3** and 100 274 reflections with $4.04° < 2\theta < 60.00°$ for **4**. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Crystallographic data for both compounds are given in Table 1.

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Supporting Information Available: Details of crystal structure determinations for **3** and **4** (PDF) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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