New Ruthenium(II) CNC-Pincer Bis(carbene) Complexes: Synthesis and Catalytic Activity

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$Ru(CNC)(CO)Br_2$ and $[Ru(CNC)_2](PF_6)_2$ complexes (CNC = 2,6-bis(butylimidazol-2-ylidene)-pyridine) are accessible via a simple synthesis. The crystal structures of both complexes have been determined by means of X-ray diffractometry. The catalytic activity of the $Ru(CNC)(CO)Br_2$ precursor toward hydrogen transfer from alcohols to ketones and oxidation of olefins confirms the versatility of this new phosphine-free Ru catalyst.

Introduction

Arduengo-type carbenes[1,2] have recently been attracting great attention as alternatives to phosphines in homogeneous catalysts.[3−6] Carbenes show a higher trans effect than N- or P-donor ligands, conferring different electronic properties on the metal and thus modifying its catalytic behavior. While chelate and pincer-type[7] phosphine and amine ligands are well-known, their carbene analogues are rare, probably because they are usually obtained from ligand precursors that need to be activated (i.e. deprotonation by a strong base) prior to coordination to the metal. This implies the use of harsher experimental conditions for bis- than for mono(carbenes). Chelate and pincer carbene ligands are among the most challenging compounds to obtain, because they combine the stability of late-transition-metal carbenes with a high entropic chelate effect, thus providing a new family of highly stable compounds with interesting chemical properties.

On the other hand, the ready accessibility of 2,6-bis-(1-alkylimidazolium-3-yl)pyridine salts[8,9] provides a new source of tridentate CNC bis(carbenes) that we have satisfactorily used in the synthesis of several pincer palladium complexes.[10−18] The high stability of these complexes allowed us to use some of them in high-temperature catalytic C−C bond formation reactions, in which traditionally inert bonds (i.e. C−Cl) were readily activated.[10−12]

To extend the number of potential catalysts derived from these CNC-pincer type ligands, we decided to widen their use in the synthesis of new Ru complexes. The only Ru−CNC-pincer complex reported so far appeared very recently in the literature and was shown to be a good catalyst for reactions of hydrogen transfer.[19] On the basis of our previous results, we now report the synthesis of the pincer complexes $Ru(CNC)(CO)Br_2$ (**1**) and $[Ru(CNC)_2](PF_6)_2$ (**2**) (CNC = 2,6-bis(butylimidazol-2-ylidene)pyridine), which have been fully characterized by spectroscopic methods; in addition, their crystal structures have been determined by X-ray diffractometry. **1** has been satisfactorily used in catalytic hydrogen transfer from alcohols to ketones and oxidation of olefins.

Results and Discussion

1 can be obtained in moderate yield (25%) from direct reaction of $[(COD)RuCl_2]_n$ and 2,6-bis(1-*n*-butylimidazolium-3-yl)pyridine bromide in refluxing ethanol in the presence of NEt_3 (Scheme 1). We chose this ligand with the *n*-Bu wingtips, because we thought that the butyl wingtips would give the complex better solubility than we saw for our previously reported methyl analogues when coordinated to Pd.[11,12] We have observed that the

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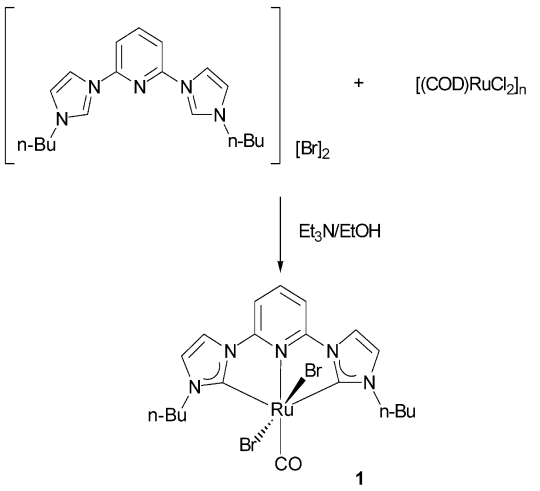
Scheme 1. General Procedure for the Synthesis of 1 (12 h Reflux)



use of NEt_3 provides much better results in the deprotonation of L, at least in this case, compared to other mild (NaOAc, Na_2CO_3) or stronger bases (NaH, *t*-BuOK). **1** crystallizes as an air-stable yellow compound, which does not decompose over 24 h in refluxing DMSO (196 °C). We believe that the CO source in this reaction may be the oxidative addition of CH_3CHO followed by CH_3 migration and reductive elimination of CH_4. The CH_3CHO may have been produced by oxidation of EtOH, which suggests that the low yield of **1** may be due to a partial reduction to low-valence-state compounds of Ru. A similar mechanism is operative in the well-known synthesis of $RuHCl(CO)(PPh_3)_3$.[20]

Evidence of the CNC chelating coordination of the ligand in **1** comes from NMR spectroscopy, which shows that the imidazole rings are symmetry-related. In the $^{13}C\{^1H\}$ NMR spectrum, the carbene signal appears at 197 ppm.

The structure of **1** was determined by X-ray diffraction methods (Figure 1). The pincer ligand occupies three meridional sites with the three rings in a quasi-planar disposition. The bite angle is 76.8°. The Ru−C(imidazole) distance is 2.06 Å, indicating that it is essentially single, with very little back-donation. These data are confirmed by the high frequency displayed by the CO stretching frequency observed in the IR spectrum (1922 cm^{-1}). The two bromides are mutually trans, and the CO is trans to the nitrogen atom of the pyridine ring.

To check whether **1** could also be obtained from the more easily accessible complex $RuCl_3$, we carried out reactions with $RuCl_3$ and 2,6-bis(1-*n*-butylimidazolium-3-yl)pyridine bromide in refluxing ethanol in the presence of NEt_3 (Scheme 2). After the crude product was purified by column chromatography (elution with CH_2Cl_2/acetone/KPF_6 afforded the source of the desired counteranion), a new compound was obtained, displaying NMR spectra virtually identical with those shown by **1**, with the only difference being that no CO signal was observed in the ^{13}C NMR spectrum. The IR spectrum did not show any signals due to CO coordinated to Ru. The compound so obtained, $[Ru(CNC)_2](PF_6)_2$ (**2**), is sparingly soluble in $CHCl_3$ and moderately soluble

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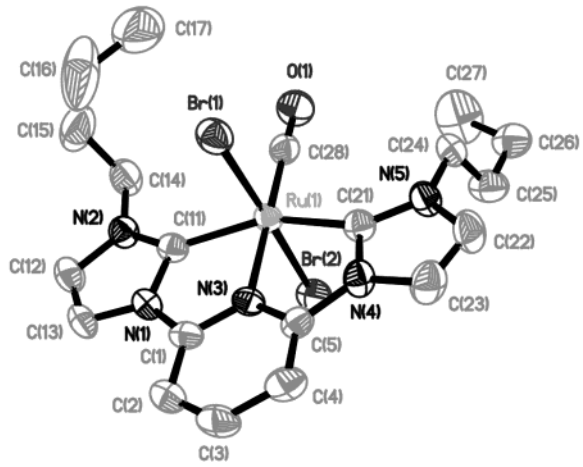
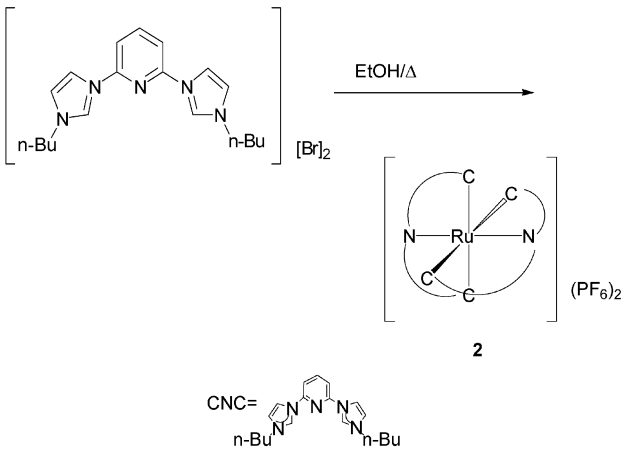


Figure 1. Ortep diagram of **1** (50% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru(1)−C(28) = 1.835(5), Ru(1)−C(21) = 2.056(5), Ru(1)−N(3) = 2.061(4), Ru(1)−C(11) = 2.062(5), Ru(1)−Br(1) = 2.5435(11), Ru(1)−Br(2) = 2.5444(11), O(1)−C(28) = 1.152(6); C(21)−Ru(1)−N(3) = 76.52(18), N(3)−Ru(1)−C(11) = 76.78(18).

Scheme 2



in CH_2Cl_2. The ^1H NMR spectrum was measured in DMSO-d_6 and suggests that the coordination of the ligand maintains the 2-fold rotation axis along the pyridine N−C direction, that is, with the two imidazole rings being symmetry-related. The loss of the two NC(*H*)N hydrogens suggests that the ligand has coordinated to the metal. The ^{13}C NMR spectrum shows a signal at 189 ppm, typical of a metalated carbon.

The molecular geometry of **2** was unequivocally confirmed by single-crystal structure analysis. Yellow crystals were obtained from slow evaporation of a solution of **2** in MeOH. The molecular structure (Figure 2) shows the ruthenium in a distorted-octahedral geometry. The two pincer ligands show a mutual perpendicular disposition, with a planar disposition of the imidazolyl and pyridyl rings on each ligand. The two *n*-butyl groups on each pincer ligand are pointing out of these planes. The NRuC bite angle is 76−77°. The Ru−C distances (2.05−2.07 Å) again indicate that the bond is essentially single, with very little back-donation and high mutual trans influence. The two pyridyl nitrogen atoms have a mutually trans disposition, with a NRuN angle of 179.8°.

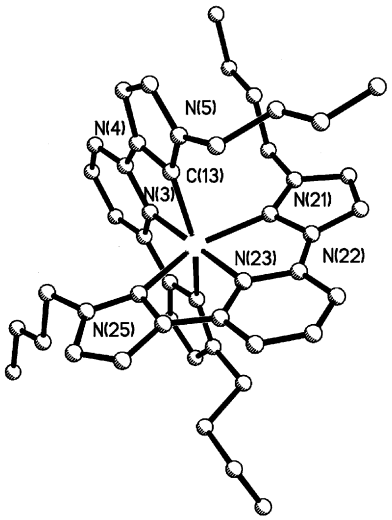


Figure 2. Molecular diagram of **2** (50% probability, hydrogen atoms and PF_6 omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru(1)−C(13) = 2.052(7), Ru(1)−C(5) = 2.057(7), Ru(1)−C(25) = 2.061(7), Ru(1)−C(33) = 2.068(7), Ru(1)−N(3) = 2.014(5), Ru(1)−N(23) = 2.020(5); N(3)−Ru(1)−C(13) = 76.6(3), N(3)−Ru(1)−C(5) = 76.7(5), C(13)−Ru(1)−C(25) = 90.4.

Table 1. Selected Results on Catalytic Hydrogenation Transfer of Ketones using 1 as Catalyst[a]

entry	substrate	time (h)	amt of cat. (mol %)	TON	TOF
1	cyclohexanone	3	0.07	1400	471
2	cyclohexanone	3	0.07	8800	2950
3	cyclohexanone	20	0.07	12600	630
4	cyclohexanone	3	0.0007	45700	15200
5	cyclohexanone	20	0.0007	126000	6300
6	methyl ethyl ketone	20	0.07	1400	70
7	benzophenone	3	0.07	1400	471
8	acetophenone	6	0.07	700	117

[a] Conditions: 2 mmol of substrate, 10 mL of 0.1 M KOH in *i*-PrOH, T = 80 °C. Yields were determined by ^{1}H NMR. TON = (mol of product)/(mol of catalyst). TOF = (mol of product)/((mol of catalyst) h).

Catalytic Measurements. Hydrogen Transfer. Complex **1** catalyzes the hydrogenation of the C=O groups of ketones via hydrogen transfer from *i*-PrOH/KOH at 80 °C.[21,22] Aryl and alkyl ketones are converted to the corresponding alcohols in quantitative yields (Table 1). The reactions were slow at room temperature but proceeded at very good rates at 80 °C. The high stability of **1** allowed us to do all the reactions in air, with solvents used as purchased and in the absence of any special precautions concerning moisture. For the reactions performed with 0.07 mol % catalyst, the conversions are very fast for cyclohexanone, benzophenone, and acetophenone (quantitative in 3−6 h), and slower for the methyl ethyl ketone case (20 h). The catalytic activity of our complex is higher than that reported by us for the Rh(III) chelate bis(carbene) complex, specially for the case of the aromatic ketones.[23] No aldol condensation byproducts from the acetone were observed. Incubation of the catalyst with KOH/*i*-PrOH at 80 °C prior to substrate addition did not improve the catalytic performance; therefore, we believe that the activation of the catalyst must be fast.[24] Remarkably, the conversion of cyclohexanone in cyclohexanol is quantitative even at catalyst concentrations as low as 7×10^{-3} and 7×10^{-4} mol %. Although the conditions have not yet been optimized, these results are among the best in terms of catalytic activity, comparable to other phosphine and amine pincer complexes of Ru.[21,22] Transfer hydrogenation to alkene C=C gave no significant amounts of the hydrogenated products, which in fact favors the use of this catalyst in the regioselective hydrogenation of conjugated enones.

Oxidation of Olefins. The oxidative cleavage of olefins to aldehydes is a synthetically important reaction to introduce oxygen into organic molecules. Some of the most important challenges in the research of this reaction are to produce selective and efficient catalysts, to avoid undesired byproducts (often obtained due to overoxidations of the olefin), and to avoid the safety problems derived from the use of the traditional ozonolysis. Among the most efficient catalysts reported so far, $RuCl_3$,[25,26] RuO_4,[26] and OsO_4[27,28] are the most widely used, although low selectivities and complicated workups make this reaction far from being fully developed. Direct oxidation of the olefins without the intermediacy of 1,2-diols has also become one of the most desirable objectives in order to achieve high selectivity in the synthesis of aldehydes, although the yields reported so far are rather low.[29,30]

Table 2 shows the catalytic results for the use of **1** in the oxidation of simple olefins to aldehydes. The reactions were performed at room temperature with 1 mol % of catalyst. In all the cases under study, the only products observed were the aldehydes derived from the cleavage of the olefins. Remarkably, no side products were observed from overoxidation reactions or from the presence of epoxidation or diolization processes. As seen from the data shown in Table 2, electron-deficient olefins (with aromatic substituents) react more slowly than aliphatic ones, the latter giving higher product yields. In the case of norbornene, the reaction was rapid, yielding the corresponding dialdehyde, and almost quantitative after 24 h (entries 5 and 6), probably due to the release of ring strain upon oxidation. We were slightly surprised that 1-methylcyclohexene reacted more quickly, offering better yields than cyclohexene due to the higher steric hindrance of the former (entries 9−12). In fact, we believe that the higher electron density of the double bond in 1-methylcyclohexene may have a predominant role in the reaction process. Interestingly, for the cleavage of 2-geraniol (entries 1 and 2), the reaction is regioselective on the double bond

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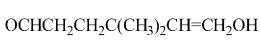
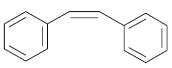
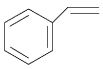
Table 2. Oxidative Cleavage of Olefins by 1 with $NaIO_4$[a]

Entry	Olefin	Product	Time(h)	Yield(%)
1			2	17
2			24	>99
3			2	5
4			24	58
5			2	63
6			24	>99
7			2	12
8			24	23
9			2	6
10			24	72
11			2	7
12			24	>99

[a] Reactions carried out in 1 mL of $CDCl_3$/0.1 mL of H_2O, with 1.25 mmol $NaIO_4$ vs substrate and 1 mol % catalyst. The product yield was determined by ^1H NMR.

located farther to the hydroxyl group. This fact may be due to a combination of both steric and electronic reasons.

Compound **2** was also tested in the two mentioned catalytic reactions (hydrogen transfer and oxidative cleavage of olefins), but it was completely inefficient. To check whether the pincer ligands remained coordinated to the Ru atom under the catalytic conditions, we took ^1H and ^{13}C NMR spectra of the reaction mixtures of both catalytic reactions with 15 mol % of **2**. As far as the resolution of the NMR spectra allowed, we observed that the 2-fold symmetry of the ligand remained unchanged, and the characteristic Ru−C bond (^{13}C NMR spectra) persisted. We strongly believe that even under the harsh conditions used in the reactions, the pincer ligand remains bound, blocking the coordination sites of the Ru atom. Similar studies for compound **1** revealed that the pincer ligand remains coordinated for this compound as well, which in fact explains the high thermal stability of this compound. We cannot exclude the partial decomposition of the catalyst precursor to produce carbene-free Ru−oxo species as the true catalyst, however.

In summary, two new pincer bis(carbene) complexes of Ru have been obtained and fully characterized. The catalytic activity of the ruthenium mono(pincer) complex has proved to be highly effective in the transfer hydrogenation of ketones from alcohols.

Experimental Section

General Considerations. NMR spectra were recorded on Varian Innova 300 and 500 MHz instruments, using $CDCl_3$ and DMSO-d_6 as solvents. The ligand precursor 2,6-bis(1-*n*-butylimidazoliumyl)pyridine dibromide was prepared according to literature methods.[12] All other reagents are commercially available and were used as received.

Synthesis of Ru(CNC)(CO)Br_2 (1). A mixture of $[(COD)RuCl_2]_n$ (400 mg, 1.42 mmol, Ru), 2,6-bis(1-*n*-butylimidazoliumyl)pyridine dibromide (696 mg, 1.4 mmol), and NEt_3 (0.8 mL, 5.6 mmol) were refluxed in EtOH for 14 h. The solvent was evaporated, and the crude solid was purified by column chromatography. Elution with CH_2Cl_2/acetone (9:1) afforded **1** as a yellow solid (yield 25%).

^1H NMR (DMSO-d_6, 500 MHz): δ 8.39 (s, 2H, imidazole *H*), 8.30 (t, 1H, $^3J_{HH}$ = 14.0 Hz, pyridine *H*), 7.91 (d, 2H, $^3J_{HH}$ = 13.5 Hz, pyridine *H*), 7.61 (s, 2H, imidazole *H*), 4.32 (t, 4H, *n*-Bu), 1.92 (quintet, 4H, *n*-Bu), 1.38 (sextet, 4H, *n*-Bu), 0.92 (t, 6H, *n*-Bu). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 208.9 (CO), 197.2 (N*C*N), 152.5 (C_{ipso}), 144.2 (C_{ortho}), 124.2 (imidazole C), 118.1 (C_{meta}), 106.8 (imidazole C), 51.5 (*n*-Bu), 33.4 (*n*-Bu), 20.2 (*n*-Bu), 14.5 (*n*-Bu). IR (cm^{-1}): 1922 (vs). Anal. Calcd for compound **1**, $C_{20}H_{25}Br_2N_5ORu$, M_w = 612.34: C, 39.19; H, 4.08; N, 11.43. Found: C, 39.32; H, 3.98; N, 11.81.

Synthesis of $[Ru(CNC)_2](PF_6)_2$ (2). A mixture of $RuCl_3 \cdot 3H_2O$ (200 mg, 0.77 mmol), 2,6-bis(1-*n*-butylimidazoliumyl)-pyridine dibromide (374 mg, 0.77 mmol), and NEt_3 (155 mg, 0.22 mL, 1.6 mmol) was stirred in EtOH (15 mL) at reflux for 12 h. A black precipitate appeared and was removed by filtration. After the mixture was cooled, the solvent was removed under vacuum and the crude solid was purified by column chromatography on silica gel. Elution with CH_2Cl_2/acetone/KPF_6 gave **2** as a yellow-orange solid (yield 17%). Analytically pure **2** was obtained by slow diffusion of acetonitrile into a solution of **2** and KPF_6 in CH_2Cl_2, which afforded crystals that were also suitable for a single-crystal structure determination.

^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.59 (d, 4H, $^3J_{HH}$ = 2.1, imidazole *H*), 8.40 (t, 2H, $^3J_{HH}$ = 7.5 Hz, pyridine *H*), 8.24 (d, 4H, $^3J_{HH}$ = 8.1 Hz, pyridine *H*), 7.44 (d, 4H, $^3J_{HH}$ = 1.8 Hz, imidazole *H*), 4.32 (t, 8H, *n*-Bu), 1.82 (quintet, 8H, *n*-Bu), 1.38 (sextet, 4H, *n*-Bu), 0.92 (t, 12H, *n*-Bu). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 188.65 (N*C*N), 151.6 (C_{ipso}), 139.5 (C_{ortho}), 124.52 (im-C), 117.92 (C_{meta}), 106.69 (imidazole C), 49.75 (*n*-Bu), 33.16 (*n*-Bu), 19.87 (*n*-Bu), 14.31 (*n*-Bu). Anal. Calcd for compound **2**, $C_{38}H_{50}F_{12}N_{10}P_2Ru$, M_w = 1037.89: C, 43.93; H, 4.82; N, 13.49. Found: C, 44.12; H, 4.95; N, 13.21.

Hydrogen-Transfer Catalysis. A typical procedure for the catalytic hydrogen-transfer reaction is as follows. A mixture of the ketone (2 mmol), KOH (10 mL, 0.2 M in *i*-PrOH), and a solution of **1** in CH_2Cl_2 (0.07, 0.007, or 0.0007 mol % vs substrate) was heated to reflux. At the desired reaction times, aliquots were extracted from the reaction vessel and added to an NMR tube with 0.5 mL of $CDCl_3$. Yields were determined by ^{1}HNMR.

Oxidative Cleavage of Olefins. A mixture of olefin (0.5 mmol) and **1** (5×10^{-3} mmol) were dissolved in 1 mL of $CDCl_3$. A solution of 0.1 mL of H_2O containing 0.625 mmol of $NaIO_4$ was added, and the resulting suspension was stirred at room temperature. At the desired times, 0.5 mL aliquots were collected and placed in a 5 mm NMR tube. Yields were determined by ^{1}H NMR.

X-ray Diffraction Studies. Single crystals of **1** and **2** were 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 (λ = 0.710 73 Å) with a nominal crystal to detector distance of 4.0 cm. A hemisphere of data was collected on the basis of three ω-scan runs (starting $\omega = -28°$) at values ϕ = 0, 90, and 180° with the detector at 2θ = 28°. During each of these runs, frames (606, 435, and 230) were collected at 0.3° intervals with 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.[31] 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 3. The diffraction frames were integrated using the SAINT[32] package and corrected for absorption with SADABS.[33]

Table 3. Crystallographic Data

	1	**2**
empirical formula	$C_{20}H_{25}Br_2N_5ORu$	$C_{38}H_{50}F_{12}N_{10}P_2Ru$
fw	612.34	1037.89
wavelength (Å)	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	12.563(4)	13.522(4)
b (Å)	11.196((3)	13.402(4)
c (Å)	16.440(4)	25.096(7)
α (deg)	90	90
β (deg)	103.999(6)	99.841(6)
γ (deg)	90	90
V (Å^3)	2243.5(11)	4481(2)
Z	4	4
calcd density (Mg/m^3)	1.813	1.538
abs coeff (mm^{-1})	4.282	0.513
no. of rflns collected	13 912	21 287
no. of indep rflns	4577 (R(int) = 0.046)	6420 (R(int) = 0.0603)
no. of data/restraints/params	4577/0/262	6420/0/553
goodness of fit on F^2	1.010	1.067
final R indices ($I > 2\sigma(I)$)	R1 = 0.0399, wR2 = 0.0912	R1 = 0.0622, wR2 = 0.1673
largest diff peak, hole (e Å^{-3})	0.686, −0.809	1.376, −0.708

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Supporting Information Available: For **1** and **2**, tables giving 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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