

Nickel(II) Heterocyclic Carbene Complexes as Catalysts for Olefin Dimerization in an Imidazolium Chloroaluminate Ionic Liquid

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Received August 7, 2001

Nickel(II) heterocyclic carbene complexes of the formula NiI₂(carbene)₂ (carbene = 3-methyl-1-propylimidazolin-2-ylidene (**1**), 1-butyl-3-methylimidazolin-2-ylidene (**2**), 1-isopropyl-3-methylimidazolin-2-ylidene (**3**), 1,3-diisopropylimidazolin-2-ylidene (**4**)) have been prepared and fully characterized by both spectroscopic methods and single-crystal X-ray structure analysis. All complexes have “square-planar” nickel environments, with the donor atoms pairwise trans, all obligate, except for one of the two independent molecular types found in **2**, in which, with different substituents at the nitrogen atoms, the two rotamers are observed as independent molecules in the one crystal. Complexes **1–4** were tested as catalysts for propene and 1-butene dimerization in both toluene and an imidazolium–chloroaluminate ionic liquid. While the complexes are inactive to sparingly active in toluene, highly active catalysts are produced in the ionic liquid. In all cases the complexes are more active toward 1-butene dimerization than is NiCl₂(PCy₃)₂ in the ionic liquid. The results are interpreted in terms of catalyst stabilization by the imidazolium-based ionic liquid. In toluene the complexes decompose rapidly via reductive elimination of imidazolium cations, while in the ionic liquid no decomposition is observed. While reductive elimination of imidazolium is possible in the ionic liquid, a rapid reoxidation via addition of the solvent imidazolium cation seems possible and may prevent the formation of Ni⁰ deposits associated with catalyst deactivation.

1. Introduction

In recent years the use of transition-metal catalysts dissolved in room-temperature molten salts, or ionic liquids, has received increasing attention.^{1–6} These ionic liquids are typically highly polar and are good solvents for inorganic complexes (catalysts), while being immiscible with most hydrocarbons. As such, they provide a nonaqueous alternative for two-phase catalysis, in which the catalyst is immobilized in the ionic liquid and can be easily separated from the products and recycled.^{1–3} Furthermore, ionic liquid solvents eliminate the need to use volatile organic solvents. Among the different types of ionic liquids available, imidazolium salts are widely used, often in combination with halogeno-

alkylhalogenoaluminum(III) compounds.^{1–3} The use of these chloroaluminate imidazolium ionic liquids in the Ni-catalyzed dimerization of olefins has been studied.^{7–10} Chauvin et al. have used a slightly acidic ionic liquid composed of [imidazolium]Cl/AlCl₃/AlEtCl₂ in combination with Ni^{II} phosphine complexes for the selective dimerization of propene.^{7,8} The addition of AlEtCl₂ to the melt is found to inhibit the formation of higher oligomers due to a cationic side reaction. High activities were achieved along with high selectivity toward desirable 2,3-dimethylbutene, with the product easily separable from the catalyst solution by a simple decantation step. The dimerization of ethylene using a similar system was later reported.⁹ The dimerization of 1-butene using a buffered chloroaluminate–pyridinium ionic liquid has recently been reported.¹⁰ Using weak organic bases such as *N*-methylpyrrole to buffer the slightly acidic melt prevented the formation of higher oligomers by a cationic side reaction. In this way the addition of

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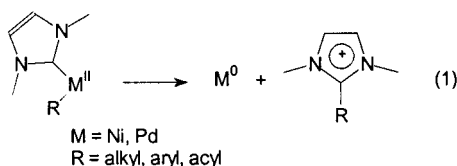
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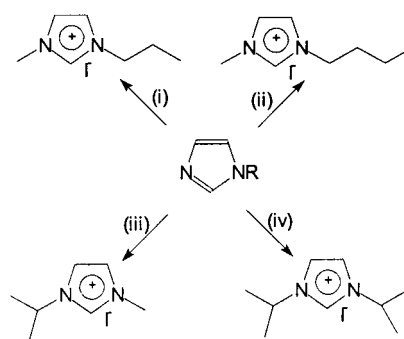
AlEtCl₂ to the melt, which was found to reduce selectivity toward linear dimers, could be avoided.

Deprotonation of 1,3-dialkylimidazolium salts yields stable heterocyclic carbenes.¹¹ The use of complexes of these ligands as catalysts for a number of reactions has been reported.¹² These include olefin metathesis (Ru),^{13–18} hydrosilylation and hydroformylation (Rh),^{19–24} and C–C coupling reactions (Pd, Ni).^{25–36} The expected affinity of heterocyclic carbene complexes for imidazolium-based ionic liquids makes them promising candidates for immobilization in these solvents. Furthermore, in several recent reports we have shown that heterocyclic carbene complexes of Pd^{II} and Ni^{II} which contain alkyl, aryl, and acyl groups may decompose via elimination of 2-organylimidazolium salts (reaction 1)^{29,30,32,37}



and that this reaction occurs via a concerted reductive elimination of the hydrocarbyl and carbene moieties.³⁸

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Scheme 1^a

^a Reagents and conditions: (i) R = Me, ^tPrI, 65 °C, 2 h; (ii) R = Bu, MeI, room temperature, 30 min. (iii) R = Me, ^tPrI, 65 °C, 2 h; (iv) R = H, 2 ^tPrI, KHCO₃, 70 °C, 2 days.

As this represents a route to catalyst deactivation, we were interested in developing methods by which the process could be controlled. It seemed possible that the energetics of this reaction could be modified so that oxidative addition of the imidazolium cation to M⁰ becomes favored over reductive elimination; it has recently been shown by experiment and theory that oxidative addition of imidazolium cations to Ni⁰, Pd⁰, and Pt⁰ is possible.^{39,40} These results suggest that using an imidazolium-based ionic liquid as solvent may limit catalyst decomposition via reductive elimination. While the catalyst may still reductively eliminate imidazolium ion, a large excess of this cation may be expected to favor reoxidation of the metal to give an active carbene complex. Hence, catalysts based on heterocyclic carbenes should be particularly suited to reactions in ionic liquids.³⁸ For this reason we decided to study catalysts based on Ni^{II} heterocyclic carbene complexes for olefin dimerization in an imidazolium-based ionic liquid. Here we report the synthesis and structures of Ni carbene precatalysts and investigations on their activity for olefin (propene, 1-butene) dimerization in both toluene and an ionic liquid.

2. Results and Discussion

2.1. Synthesis of Imidazolium Salts. A range of carbene ligand precursors were required to study the effect of the carbene ligand on activity, stability, and selectivity of the catalyst. Four imidazolium salts were prepared with different N-substituents, as shown in Scheme 1, the *n*-propyl and *n*-butyl imidazoliums being employed since salts of these cations are commonly used in ionic liquids, for which the resulting carbene ligand might be expected to have a good affinity. The ^tPr imidazolium salts were prepared so that the effect of steric bulk on the carbene could be investigated, with the expectation that increased out-of-plane bulk might lead to a greater stability of the catalyst and should affect its selectivity.

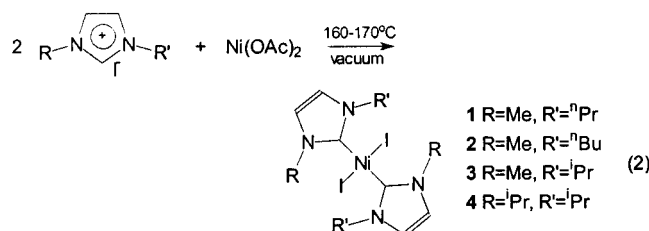
2.2. Synthesis and Structures of Ni Carbene Complexes. The preparation of Ni carbene complexes from Ni(OAc)₂ and 1,3-dimethylimidazolium salts has

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been previously reported.⁴¹ The use of this procedure and workup for the present substituted imidazolium salts resulted in a large amount of unreacted imidazolium salt containing only a very small amount of the expected complex. To get satisfactory yields of the pure complexes, more forcing conditions and an improved workup were introduced. Two equivalents of the imidazolium salt was mixed with Ni(OAc)₂, and the mixture was heated to 160–170 °C under vacuum for periods of 2–18 h. Under these conditions the imidazolium salts melt, dissolving the Ni(OAc)₂. After cooling, the resulting dark residues were triturated with water to remove unreacted imidazolium salt and Ni(OAc)₂. In each case red powders were obtained corresponding to complexes **1–4** (reaction 2).



The ¹³C NMR spectra of **1**, **2**, and **4** show the C_{carbene} resonances between 170.5 and 174.6 ppm (not observed for **3** due to signal broadening). Comparison with the values found for other NiI₂(carbene)₂ complexes^{30,41} suggested a trans arrangement of the ligands. The ¹H NMR spectra display broad signals, and in the case of **2** and **3** some peak splitting is observed (see Experimental Section), suggesting restricted rotation around the Ni–C bond giving different rotamers. This is manifest in the ¹³C NMR spectra of **1–3**, which also show peak splitting.

Single-crystal X-ray structures were obtained for all four complexes. Crystals were grown from DCM (dichloromethane)/ether by vapor diffusion (**1–3**) or from straight DCM by slow evaporation (**4**), representative molecular structures being shown in Figure 1 with selected bond lengths and angles listed in Table 1. The results of low-temperature (ca. 153 K) single-crystal X-ray structure determinations of **1–4** (and **5**, the tetramethyl-substituted analogue³⁰) are consistent, in terms of stoichiometry and connectivity, with their description as unsolvated “square-planar” *trans*-NiI₂L₂ arrays, obligate in all cases (except one molecule of **2**), the molecules being disposed with their metal atoms on crystallographic inversion centers. Where there is unsymmetrical substitution at the carbene ligand nitrogen atoms, the substituent disposition is also trans, except in one molecule of **2**, as below. Half of one molecule comprises the asymmetric unit of the structure in both **1** and **3** (and also **5**³⁰), and two halves of each of two molecules comprise the asymmetric unit in **4**; in **2** half of one molecule also has this status, but an independent molecule, devoid of crystallographic symmetry, completes the asymmetric unit of the structure, and, although of the form *trans*-NiI₂L₂ also, the (unsymmetrical) ligand substituents lie cis, so that here the two rotamers coexist in the crystal in 1:2 *trans*:*cis*

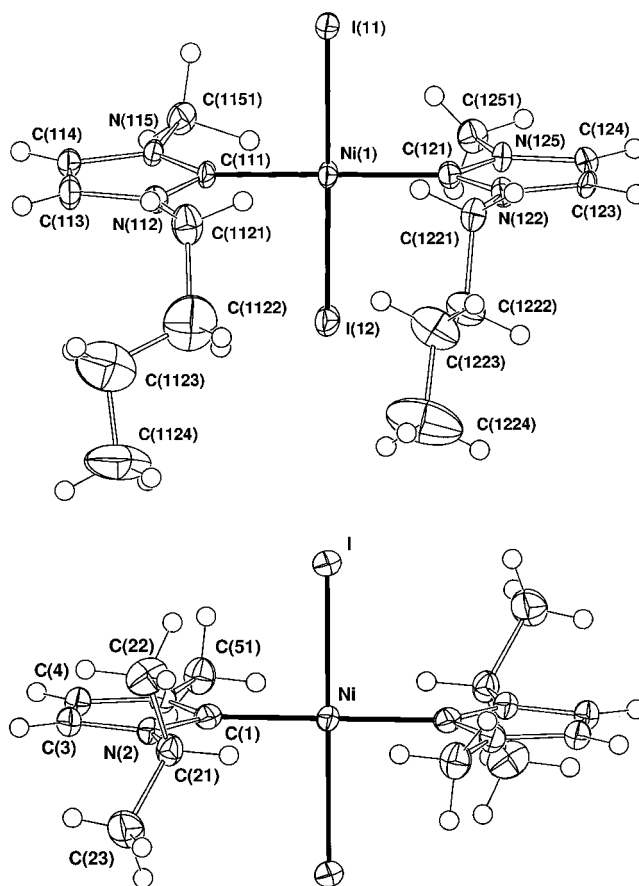


Figure 1. Single molecules of (a, top) **2** (molecule 1) and (b) **3**, projected normal to their coordination planes and showing *cis*- and *trans* rotamers (see text). Thermal ellipsoids at the 50% level are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

stoichiometry. The ligand donor atom dispositions about all nickel atoms (inclusive of **5**) are closely orthogonal (overall *cis* I–Ni–C ranging between 89.21(8) and 90.79(8)° and *trans* between 178.21(5) and 180°); the distances overall are also in a tight range (Ni–I = 2.4952(9)–2.5149(1) Å; Ni–C = 1.895(6)–1.909(1) Å). The exocyclic angles at the carbene carbon are essentially symmetrical, regardless of asymmetry of the N-substituents; the range overall for **2–4** is 127.3(2)–129.2(6)° and is rather greater in **1** (125.8(9), 130.8(8)°). This is also the case at the nitrogens (122.4(10)–126.0(2)°). The carbene ligand C₃N₂ planes lie essentially normal to the coordination plane (minimum dihedral angle 79.91(5)° (**4**, molecule 2)); where substituted by isopropyl, the tertiary hydrogen of the latter is quasi-coplanar with the ligand, directed toward the nickel atom. A further example of the *trans*-NiI₂(carbene)₂ array, essentially similar to the present case with respect to its metal atom environment, has been reported recently.⁴²

2.3. Catalytic Studies. Catalysis in Toluene. To provide a comparison, and to highlight any effect due to an imidazolium based ionic liquid in catalysis, initial catalytic testing of **1–4** was conducted in toluene with 1-butene as the substrate. Results of the tests are shown in Table 2. Complex **1** was first tested with AlEt₂Cl as

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Table 1. Selected Bond Lengths (Å), Bond Angles (deg) and Interplanar Angles (deg) in Complexes 1–4^a

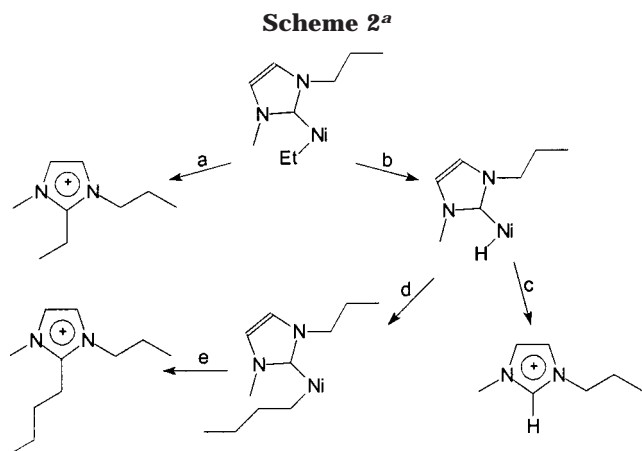
param	1	2 (molecules 1; 2)	3	4 (molecules 1; 2)
Ni–C	1.899(11)	1.905(4), 1.905(5); 1.895(6)	1.913(3)	1.904(1); 1.909(1)
Ni–I	2.4952(8)	2.508(1), 2.510(1); 2.5030(7)	2.5182(3)	2.4960(2); 2.5149(1)
C _{carbene} –N	1.326(14), 1.391(13)	1.351(7)–1.355(8)	1.349(4), 1.359(3)	1.354(2)–1.358(2)
C–Ni–C	180(–)	179.5(2); 180(–)	180(–)	180(–) (×2)
C–Ni–I	89.7(3), 90.3(3)	89.2(2)–90.5(2)	89.46(8)	89.38(4)–90.62(4)
I–Ni–I	180(–)	179.21(5); 180(–)	180(–)	180(–) (×2)
NiC ₂ I ₂ /carbene dihedral	84.4(4)	82.0–89.6(2)	83.68(9)	82.70(5); 79.91(5)

^a Esds given in parentheses.

Table 2. Attempted 1-Butene Dimerization with Complexes 1–4 in Toluene^a

run no.	catalyst	activator (equiv)	temp (°C)	remarks
1	1	AlEt ₂ Cl (100)	20	Ni ⁰ forms immediately after AlEt ₂ Cl added; no dimers or oligomers detected; only imidazolium salts detected (see text)
2	1	AlCl ₃ (40)	20	no butene dimers or oligomers detected; co-oligomers of butene–toluene formed
3	1	AlCl ₃ (35.2), pyrrole (34.2)	20	no products formed
4	3	MAO (50)	20	rapid decomposition once MAO added; no products formed
5	2	MAO (50)	–20	complex decomposed, but more slowly than at 20 °C
6	4	AlEt ₂ Cl (100)	–15	Ni ⁰ forms shortly after AlEt ₂ Cl added; 5 mmol of isomeric butene dimers formed (TON = 50)

^a Conditions: 0.1 mmol of Ni, 15 mL of toluene, 1 bar of 1-butene, 30 min.



^a Counteranions (presumably chloroaluminates) are excluded.

the cocatalyst (run 1). Upon addition of the Al–alkyl solution immediate decomposition to Ni⁰ took place. After 30 min the reaction was stopped and quenched with methanol. Analysis of the toluene phase by GC showed that no dimers or oligomers had formed. To gain insight into the catalyst decomposition process, the resinous phase formed by addition of methanol (mostly reacted Al–alkyl) was extracted with DCM and allowed to evaporate. This left a small amount of yellow oil, which, when analyzed by MS (LSIMS), was found to yield cations composed predominantly of 3-methyl-1-propylimidazolium (*m/z* 125) along with traces of both 2-ethyl-3-methyl-1-propylimidazolium (*m/z* 153) and 2-butyl-3-methyl-1-propylimidazolium (*m/z* 181, ca. 5% by ion count) species. The formation of these can be accounted for by the reactions shown in Scheme 2. Reaction of **1** with AlEt₂Cl would first give an ethyl–Ni species through metathesis, which could decompose via reductive elimination of 2-ethylimidazolium cation (path a). The ethyl–Ni species could also form a Ni hydride by β -hydride elimination (path b), either from the ethyl group or after insertion of butene), which could either reductively eliminate 2-H imidazolium (path c)

or insert butene to give a butyl–Ni complex (path d). The butyl–Ni species could then decompose by reductive elimination (path e), accounting for the formation of the 2-butylimidazolium cation. This result shows that although the required reactions are taking place to create a potentially active catalyst (i.e. formation of ethyl and hydrido Ni species), the resulting species are decomposing via reductive elimination too rapidly for chain growth to occur.

The activity of complex **1** in toluene was tested with AlCl₃ as an activator (runs 2 and 3). When AlCl₃ alone was used (run 2), no Ni⁰ was observed, and no butene dimers or oligomers were formed. Instead, coreaction of butene and toluene took place to give isomeric butyl-, dibutyl-, and tributyltoluenes. A control run was thus conducted using only AlCl₃ without a Ni complex. A similar amount and distribution of products was formed, showing coreaction of toluene and butene to be catalyzed by Lewis acidic AlCl₃, and not a Ni carbene species. In run 3 the organic base pyrrole was added to buffer excess AlCl₃,¹⁰ and although this stopped the formation of toluene–butene oligomers, no butene dimers were formed either. In run 4 complex **3** was tested with MAO as the activator. As with run 1, Ni⁰ formed immediately after the Al solution was added and no oligomeric products were obtained. The same activator was tested along with complex **2** at –20 °C (run 5). In this case, although decomposition was slightly slower than at 20 °C, no products were obtained. In the final run the diisopropylcarbene complex **4** was tested at –15 °C with AlEt₂Cl as activator. Again decomposition occurred, but more slowly than in other runs and approximately 5 mmol of isomeric butene dimers were formed, corresponding to a TON of 50. This last result shows that, although Ni carbene complexes are capable of dimerizing olefins, decomposition via reductive elimination of the carbene is rapid and leads to a low conversion. The slight activity of **4** may result from some protection against decomposition by the bulky isopropyl groups.³⁸

Catalysis in an Ionic Liquid. Catalytic testing in an imidazolium-based ionic liquid was conducted in a

Table 3. 1-Butene Dimerization in Ionic Liquid with 1–4^a

run no.	catalyst	yield (%)	TON	TOF (h ⁻¹)
1	1	56.3	2815	5630
2	2	70.2	3510	7020
3	3	38.2	1910	3820
4	4	50.7	2535	5070
5	NiCl ₂ (PCy ₃) ₂	29.5	1475	2950

^a Conditions and reagents: 0.1 mmol of Ni, 0.5 mol of 1-butene, 30 min, room temperature.

Table 4. Selectivity of Propene Dimerization (after Hydrogenation)^a

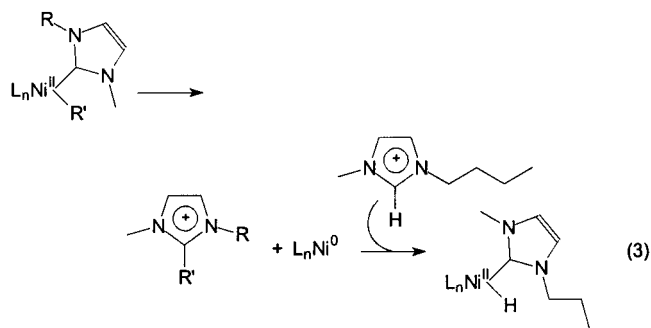
catalyst	2,3-dimethylbutane	2-methylpentane	hexane
1	6.9	71.1	22.0
NiCl ₂ (PCy ₃) ₂	49.8	41.1	9.1
1 + 2 PCy ₃	7.6	69.1	23.3

^a Conditions and reagents: 0.1 mmol of Ni, 0.25 mol of propene, 2 min, room temperature.

buffered melt composed of a mixture of 1-butyl-3-methylimidazolium chloride, AlCl₃, and *N*-methylpyrrole (0.45:0.55:0.1 molar ratio) at room temperature, as previously used for olefin dimerization.¹⁰ For comparison NiCl₂(PCy₃)₂ was tested under the same conditions. With a reaction time of 2 min, 0.1 mmol of Ni catalyst, and 0.25 mol of propene, all carbene complexes gave 100% conversion to propene dimers, corresponding to a TOF of 75 000 h⁻¹. No Ni⁰ was observed. NiCl₂(PCy₃)₂ led to the same conversion of propene under the same conditions, whereupon 1-butene dimerization was tested to differentiate the relative activities of the carbene and phosphine complexes. Table 3 shows that all Ni carbene complexes were active for dimerization of 1-butene, with TONs ranging from 1910 to 3510 after 30 min (runs 1–4). In comparison, NiCl₂(PCy₃)₂ gave a TON of 1475 after the same time (run 5), indicating greater olefin dimerization activity for the carbene complexes. Interestingly, the most active catalyst was **2** (run 2, *n*-butyl substituent), followed by **1** (run 1, *n*-propyl substituent). The isopropyl-substituted complexes **3** and **4** were somewhat less active (runs 3 and 4). The reason for this is unclear but may be related to steric effects of the ligands. The selectivity toward different isomeric butene dimers was relatively unaffected by the ligand, whether carbene or tricyclohexylphosphine. The isomer proportions, after hydrogenation, obtained with complex **1** were 11.5% octane, 56.8% 3,4-dimethylhexane, and 31.7% 3-methylheptane. A similar distribution was obtained with the other carbene complexes, and NiCl₂(PCy₃)₂ gave 14.1% octane, 58.8% 3,4-dimethylhexane, and 26.8% 3-methylheptane.

The selectivity of complex **1** toward different isomers in the dimerization of propene is shown in Table 4, along with that for NiCl₂(PCy₃)₂. In contrast to butene dimerization, the selectivity toward desirable highly branched propene dimers is low for **1**. In comparison NiCl₂(PCy₃)₂ gives a high proportion of 2,3-dimethylbutane after hydrogenation. This may be attributed to the low steric demand of the planar carbene ligand relative to PCy₃. This is evident from the crystal structure of **1**. Changes in the organic side chain of the carbene did not lead to an increase in branching, possibly due to the formation of a common active species early in the reaction. If the active complexes reductively eliminate imidazolium cations reversibly during the reaction, the ionic liquid

solvent (1-butyl-3-methylimidazolium cation) would become incorporated into the complex (reaction 3). There-



fore, early in the reaction any selectivity resulting from a bulky carbene would disappear as 1-butyl-3-methylimidazolium-2-ylidene replaces the bulky carbene at the Ni center. The diverse activities observed for the different catalyst systems may simply reflect varying induction periods for conversion of the catalyst precursors into the common active species. If this is the case, to achieve selectivity toward branched dimers, a sterically demanding substituent on the ionic liquid imidazolium species or a precatalyst containing a carbene that better resists reductive elimination may be required. Further studies to delineate the reaction pathway are currently underway.

The selectivity of **1** has also been tested in the presence of added PCy₃ (Table 4). The selectivity remained virtually unaffected by PCy₃, indicating that the phosphine does not coordinate to the Ni center and that Ni remains ligated by carbene ligands during catalysis. If the carbene ligands were not coordinated to the Ni center, it would be expected that highly basic PCy₃ would be coordinated and that this would be reflected in the dimer distribution. The fact that the carbene complexes are much more active than the phosphine complex is also indicative that the Ni center remains ligated by carbenes.

3. Conclusions

The above results show that Ni carbene complexes give rise to active catalysts for Ni-catalyzed dimerization when used in an imidazolium-based ionic liquid. The activity in one case is over twice that of NiCl₂(PCy₃)₂, although selectivity toward branched dimers is disappointing. Importantly, the change from toluene, in which the complexes are almost inactive, to ionic liquid results in high catalytic activity with good stability. Several other groups have also recently shown imidazolium based ionic liquids to be noninnocent solvents.^{43,44} While further mechanistic information is desirable, these results show that predictions proposing carbene complexes would be especially suited to use in ionic liquids were well founded^{38,40} and again highlight the advantages of buffered chloroaluminate ionic liquids for olefin dimerization.¹⁰ Further work on this catalytic system would involve testing the effect of carbene ligands with even greater steric requirements, such as those with mesityl, 2,6-diisopropylphenyl, and adaman-

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Table 5. Crystal Data and Collection and Refinement Parameters for Complexes 1–4

	1	2	3	4
	Crystal Data			
formula	C ₁₄ H ₂₄ I ₂ N ₄ Ni	C ₁₆ H ₂₈ I ₂ N ₄ Ni	C ₁₄ H ₂₄ I ₂ N ₄ Ni	C ₁₈ H ₃₂ I ₂ N ₄ Ni
mol wt	560.9	588.9	560.9	617.0
cryst size (mm)	0.37 × 0.28 × 0.07	0.44 × 0.32 × 0.15	0.45 × 0.18 × 0.08	0.40 × 0.30 × 0.18
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P1</i>	<i>P2₁/n</i>	<i>C2/c</i>
	Cell Parameters			
<i>a</i> (Å)	12.896(2)	8.0659(8)	8.427(1)	32.052(2)
<i>b</i> (Å)	9.091(1)	8.3373(8)	9.180(1)	9.1587(5)
<i>c</i> (Å)	16.684(4)	27.188(3)	12.841(2)	17.4316(9)
α (deg)	90	83.618(3)	90	90
β (deg)	90	83.010(4)	107.005(2)	111.257(1)
γ (deg)	90	62.557(2)	90	90
<i>V</i> (Å ³)	1956.0(6)	1607.4(3)	949.9(2)	4769(2)
<i>Z</i>	4	3	2	8
ρ _c (g cm ⁻³)	1.90 ₅	1.82 ₅	1.96 ₁	1.71 ₈
	Data Collection and Refinement Parameters			
μ (cm ⁻¹)	41.2	37.9	42.7	34.1
2θ _{max} (deg)	52	75	58	75
<i>N</i> _i	5743	32159	9093	45319
<i>N</i> (<i>R</i> _{int})	1918 (0.15)	16553 (0.031)	2318	11921
<i>N</i> _o	1080	11696	2155	9715
" <i>T</i> " (min, max)	0.55, 0.99	0.46, 0.70	0.49, 0.80	0.45, 0.70
<i>R</i> , <i>R</i> '	0.068, 0.153 (wR2)	0.072, 0.085	0.029, 0.039	0.022, 0.031
Δρ _{max} (e Å ⁻³)	2.0	4.2	1.7	1.2

tyl substituents, and studying the effect of different imidazolium-based ionic liquids on selectivity. The in situ formation of Ni carbene complexes from Ni⁰ precursors should also be possible.⁴⁰ Furthermore, it would be of value to carry out catalyst recycling experiments in order to determine the long-term stability of the catalysts, and the degree to which they are immobilized in the ionic liquid. The extension of this methodology to other reactions in which the catalyst may decompose via reductive elimination—for example, olefin polymerization and CO/olefin copolymerization—seems promising, given the remarkable increase in activity gained in olefin dimerization.

4. Experimental Section

4.1. General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox. All solvents were purified and dried by standard procedures and distilled under nitrogen immediately before use. Nuclear magnetic resonance spectra were recorded at ambient temperature, and peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Elemental analysis and MS were carried out by the Central Science Laboratory, University of Tasmania, Australia.

4.2. Structure Determinations. For **1**, a unique data set was measured at 213 K using an Enraf-Nonius CAD-4 diffractometer and refined with SHELXL-97 on intensities. For **2–4** full spheres of data were measured at ca. 153 K using a Bruker AXS CCD area detector instrument, with monochromatic Mo Kα radiation ($\lambda = 0.710\ 7_3$ Å) being employed in both contexts, as also were "empirical"/multiscan absorption corrections. *N*(total) reflections were obtained, merging to *N*(unique) (*R*_{int} quoted), with *N*_o with *F* > 4σ(*F*) being considered "observed" and used in the full-matrix least-squares refinements. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H being included constrained at estimates (except for **3**, where those parameters were refined). Conventional residuals *R* and *R*_w (statistical weights) are quoted at convergence, neutral atom complex scattering factors being employed. Pertinent results are given in the figures and tables and in the Cambridge Crystal-

lographic Data Base depositions (#167439–167442). Crystal data and collection and refinement parameters are given in Table 5.

Variata. Substituent strings in molecule 2 of **2** were modeled as disordered over two sets of sites, set at equal occupancies after trial refinement.

4.3. Catalysis. In Toluene. Catalysis attempts were carried out in 100 mL glass Schlenk flasks so that the solution could be observed. In a typical run, complex **1** (0.1 mmol) was put under N₂ and dissolved/suspended in toluene (15 mL). The flask was charged with 1-butene (1 bar) before AlEt₂Cl (4.8 mL of 25% solution in toluene, 100 equiv) was added. After 30 min the 1-butene was bled off and the reaction quenched with MeOH followed by water. The toluene phase was analyzed for products by GC.

In Ionic Liquid. Catalysis was conducted in a 75 mL steel autoclave at room temperature. The Ni complex (0.1 mmol) and ca. 7.2 g of chloroaluminate ionic liquid (3-butyl-1-methylimidazolium chloride/AlCl₃/*N*-methylpyrrole, 0.45/0.55/0.1) were added to the autoclave, which was then charged with propene or 1-butene. After the desired time the reaction was stopped by depressurizing the autoclave. The organic phase was then collected by decantation and analyzed by GC using a heptane internal standard. Dimer selectivity was in all cases over 95%.

4.4. Synthesis. 1-Propyl-3-methylimidazolium Iodide. Propyl iodide (2.5 mL, 26 mmol) and methylimidazole (2 mL, 25 mmol) were taken up in 20 mL of THF and refluxed for 2 h. The cooled solution was decanted and the oil washed with THF (4 × 20 mL) before being dried in vacuo to give a thick oil. Yield: 4.2 g (67%). ¹H NMR (200 MHz, CDCl₃): δ 9.91 (s, 1H, NC(*H*)N), 7.59 (m, 1H, HC=CH), 7.54 (m, 1H, HC=CH), 4.27 (t, *J* = 8 Hz, 2H, NCH₂), 4.08 (s, 3H, NCH₃), 1.93 (m, 2H, NCH₂CH₂), 0.95 (t, *J* = 7 Hz, 3H, NCH₂CH₂CH₃).

1-Butyl-3-methylimidazolium Iodide. This was prepared in a manner similar to that for propylimidazolium from 1-butylimidazole (5.14 g, 41.4 mmol) and MeI (3 mL, 47 mmol) to yield an oil. Yield: 7.46 g (68%). ¹H NMR (200 MHz, CDCl₃): δ 10.11 (s, 1H, NC(*H*)N), 7.48 (m, 1H, HC=CH), 7.42 (m, 1H, HC=CH), 4.33 (t, *J* = 7 Hz, 2H, NCH₂), 4.12 (s, 3H, NCH₃), 1.92 (m, 2H, NCH₂CH₂), 1.40 (m, 2H, NCH₂CH₂CH₂), 0.97 (t, *J* = 7 Hz, 3H, NCH₂CH₂CH₂CH₃).

1-Isopropyl-3-methylimidazolium Iodide. This compound was prepared as above from isopropyl iodide (2.5 mL,

25 mmol) and methylimidazole (2 mL, 25 mmol) to yield a white powder. Yield: 1.30 g (21%). ¹H NMR (200 MHz, CDCl₃): δ 10.00 (s, 1H, NC(H)N), 7.54 (m, 2H, HC=CH), 4.80 (m, 1H, NCH), 4.09 (s, 3H, NCH₃), 1.60 (d, *J* = 7 Hz, 6H, NC(CH₃)₂). ¹³C NMR (50 MHz, CDCl₃): δ 136.1 (NCN), 124.4 (NC=CN), 120.9 (NC=CN), 53.9 (NC(CH₃)₂), 37.6 (NCH₃), 23.8 (NC(CH₃)₂).

1,3-Diisopropylimidazolium Iodide. Isopropyl iodide (4.14 g, 24.4 mmol) and 1*H*-imidazole (1.63 g, 24.0 mmol) were heated to 70 °C in THF (20 mL) for 24 h, after which time the THF was decanted off; the oil that formed was washed with a further 10 mL of THF. The oil was taken up in DCM (30 mL) and KHCO₃ was added along with ca. 3 mL of water. The mixture was stirred until CO₂ evolution ceased and a large excess of KHCO₃ added to absorb the water. The DCM was decanted off, and the H₂O/KHCO₃/KI mass was washed several times with more DCM. The DCM was removed in vacuo, the remaining oil taken up in THF (10 mL), and a further 1 equiv of isopropyl iodide added. After the solution was heated to 70 °C for 18 h, it was cooled and the THF was decanted off the oil. The product was washed with ether and dried in vacuo to leave an oil. Yield: 2.9 g (43%). ¹H NMR (200 MHz, CDCl₃): δ 10.22 (s, 1H, NC(H)N), 7.45 (2, 2H, HC=CH), 4.96 (m, 2H, NCH), 1.65 (d, *J* = 7 Hz, 12H, NC(CH₃)₂).

Ni Carbene Complexes. The general procedure for the synthesis of **1–4** was as follows. The imidazolium iodide (0.5–1 g, 2 equiv) and anhydrous Ni(OAc)₂ (1 equiv) were thoroughly mixed and heated to 160–170 °C under vacuum. After 2–18 h (longer times were required for more sterically demanding imidazoliums) the residue was cooled and water was added (in air). After trituration the product was collected by filtration and washed with more water followed by ether before drying in vacuo.

NiI₂(3-methyl-1-propylimidazolin-2-ylidene)₂ (1). Yield: 14%. Anal. Calcd for C₁₄H₂₄N₄I₂Ni: C, 29.98; H, 4.31; N, 9.99. Found: C, 29.96; H, 4.39; N, 10.01. MS (LSIMS): *m/z* 560 [M]⁺ (12%), 433 [M – I]⁺ (40%), 306 [M – 2I]⁺ (100%). ¹H NMR (200 MHz, CDCl₃): δ 6.77 (s, 4H, HC=CH), 4.71 (t, br, *J* = 8 Hz, 4H, NCH₂), 4.27 (s, br, 6H, NCH₃), 2.24 (m, br, 4H, NCH₂CH₂), 1.12 (t, br, *J* = 7 Hz, 6H, NCH₂CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 173.1 (NCN), 123.1 (HC=CH), 121.6 (HC=CH), 52.7, 52.6 (NCH₂), 38.1, 37.9 (NCH₃), 23.4, 23.3 (NCH₂CH₂), 11.7 (NCH₂CH₂CH₃).

NiI₂(1-butyl-3-methylimidazol-2-ylidene)₂ (2). Yield: 33%. Anal. Calcd for C₁₆H₂₈N₄I₂Ni: C, 32.63; H, 4.79; N, 9.51. Found: C, 32.74; H, 4.86; N, 9.43. MS (LSIMS): *m/z* 589 [M]⁺

(10%), 461 [M – I]⁺ (40%), 334 [M – 2I]⁺ (100%). ¹H NMR (300 MHz, CDCl₃): δ 6.70 (s, 4H, HC=CH), 4.65 (m, 4H, NCH₂), 4.21, 4.20 (two overlapping singlets, 6H, NCH₃), 2.10 (m, 4H, NCH₂CH₂), 1.48 (m, 4H, NCH₂CH₂CH₃), 1.00 (m, 6H, NCH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 174.6 (NCN), 124.6 (HC=CH), 122.9 (HC=CH), 52.4, 52.3 (NCH₂), 39.7, 39.5 (NCH₃), 33.5, 33.4 (NCH₂CH₂), 21.9 (NCH₂CH₂CH₂), 15.5 (NCH₂CH₂CH₂CH₃).

NiI₂(1-isopropyl-3-methylimidazol-2-ylidene)₂ (3). Yield: 48%. Anal. Calcd for C₁₄H₂₄N₄I₂Ni: C, 29.98; H, 4.31; N, 9.99. Found: C, 29.90; H, 4.41; N, 9.89. MS (LSIMS): *m/z* 560 [M]⁺ (7%), 433 [M – I]⁺ (30%), 306 [M – 2I]⁺ (100%). ¹H NMR (200 MHz, CDCl₃): δ 6.81 (m, 4H, HC=CH), 6.26 (m, 2H, NCH), 4.27, 4.26 (two singlets, 6H, NCH₃), 1.63, 1.60 (two doublets, *J* = 3 Hz, 12H, NC(CH₃)₂). ¹³C NMR (100 MHz, CDCl₃): δ 123.7 (HC=CH), 117.2 (HC=CH), 52.4 (NC(CH₃)₂), 38.1 (NCH₃), 22.9 (C(CH₃)₂).

NiI₂(1,3-diisopropylimidazol-2-ylidene)₂ (4). Yield: 24%. Anal. Calcd for C₁₈H₃₂N₄I₂Ni: C, 35.04; H, 5.23; N, 9.08. Found: C, 35.20; H, 5.04; N, 9.21. MS (LSIMS): *m/z* 615 [M – H]⁺ (5%), 487 [M – HI]⁺ (10%). ¹H NMR (200 MHz, CDCl₃): δ 6.87 (s, br, 4H, HC=CH), 6.32 (m, br, 4H, NCH), 1.62 (d, br, *J* = 6 Hz, 24H, NC(CH₃)₂). ¹³C NMR (50 MHz, CDCl₃): δ 170.5 (NCN), 117.6 (HC=CH), 52.4 (NC(CH₃)₂), 22.8 (C(CH₃)₂).

Acknowledgment. We are indebted to the Australian Research Council for financial support and for providing an Australian Postgraduate Award for D.S.M. P.W. and W.M. thank BP Amoco for financial support. D.S.M. also thanks the Institut für Technische Chemie und Makromolekulare Chemie for funding a research visit to this institution, and the British Council and British Foreign and Commonwealth Office for a Chevening Scholarship, which made this visit possible. The staff of the Central Science Laboratory (University of Tasmania) are gratefully acknowledged for their assistance in a number of instrumental techniques.

Supporting Information Available: Crystallographic data, in CIF format, for the structure analyses of **1–4** and figures giving thermal ellipsoid plots of complexes **1**, **2** (molecule 2), and **4** (molecules 1 and 2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM010717A