C−N Coupling Reactions of Allenes and Methylacetylenes with an Imidotitanium Complex

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Reaction of the imidotitanium complexes [(N$_2$Npy-κ^3N)Ti(=NtBu)(py)] (**1**) and [(N$_2$Npy-κ^3N)Ti(=NtBu)] (**1a**) (N$_2$Npy = (2-C$_5$H$_4$N)C(Me)(CH$_2$NSiMe$_3$)$_2$) with 2-butyne and 1-phenylpropyne led to C−N coupling with the imido ligand and yielded the four-membered titanaazetidines [(N$_2$Npy-κ^3N)Ti{N(tBu)C(CHCH$_3$)CH$_2$}] (**2**) and [(N$_2$Npy-κ^3N)Ti{N(tBu)C(CHC$_6$H$_5$)CH$_2$}] (**3**), respectively. The same reaction products were obtained in 2 + 2 cycloaddition reactions of **1** and **1a** with 1,2-butadiene and phenylallene. The four-membered metallacycle with an exocyclic C=C double bond was established by X-ray diffraction studies of both compounds. A mechanism to explain the observed products from both types of reactions is proposed. Whereas the reactions of **1** with CO$_2$, tBuNCO, and PhNCO were highly unspecific and did not lead to an isolable product, the conversion with the sterically encumbered isocyanate 2,6-iPr$_2$C$_6$H$_3$NCO yielded the product of 2 + 2 cycloaddition to the Ti=N bond, namely [(N$_2$Npy-κ^3N)Ti{N(tBu)C(N-2,6-C$_6$H$_3$$iPr_2$)O}(py)] (**4**), the structure of which was elucidated by NMR spectroscopy.

Introduction

Imido ligands (NR where R typically is an organic group) generally behave as *ancillary* or supporting groups in the chemistry of high-valent metal complexes of the group 5−group 7 transition metals.[1−3] However, recent investigations[4−10] of the chemistry of group 4 imides has uncovered a variety of novel transformations of the M=NR linkages themselves with examples ranging from the activation of C−H bonds to cycloaddition reactions with unsaturated C−C or C−X bonds.[11−13]

In a systematic study we have shown that the coordination to titanium of the diamidopyridine ligand system developed previously by us[14,15] leads to stable monomeric imidotitanium complexes such as **1** (Chart 1).[16,17] The *tert*-butylimido compound **1** possesses labile

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(1) (a) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2.

(2) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(3) For applications of imido complexes in olefin polymerization catalysis see: (a) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1709. (b) Chan, M. C. W.; Chew, K. C.; Dalby, C. I.; Gibson, V. C.; Kohlmann, A.; Little, I. R.; Reed, W. *Chem. Commun.* **1998**, 1673. For applications of imido complexes in ring opening metathesis polymerization see: (c) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (d) Gibson, V. C. *Adv. Mater.* **1994**, *6*, 37.

(4) Mountford, P. *Chem. Commun.* **1997**, 2127.

(5) (a) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (b) Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669.

(6) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Glueck, D. S.; Wu, J. X.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.

(7) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

(8) McGrane, P. L.; Jensen, M.; Livinghouse, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5459.

(9) (a) Dunn, S. C.; Batsanov, A. S.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2007. (b) Blake, A. J.; Collier, P.; Dunn, S. C.; Li, W.-S.; Mountford, P.; Shishkin, O. V. *J. Chem. Soc., Dalton Trans.* **1997**, 1549. (c) Collier, P. E.; Dunn, S. C.; Mountford, P.; Shishkin, O. V.; Swallow, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3743.

(10) Lewkebandra, T. S.; Sheridan, P. H.; Heeg, M. J.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1994**, *33*, 5879.

(11) (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (b) Bennet, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696.

(12) (a) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669. (b) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974.

(13) (a) Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F.; Wilson, D. J.; Mountford, P. *Chem. Commun.* **1999**, 661. (b) Thorman, J. L.; Guzei, I. A.; Young, V. G.; Woo, L. K. *Inorg. Chem.* **2000**, *39*, 2344. (c) Thorman, J. L.; Woo, L. K. *Inorg. Chem.* **2000**, *39*, 1301. (d) Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. *J. Organomet. Chem.* **1999**, *591*, 2. (e) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795. (f) Harlan, C. J.; Tunge, J. A.; Bridgewater, B. M.; Norton, J. R. *Organometallics* **2000**, *19*, 2365.

(14) (a) Friedrich, S.; Gade, L. H.; Edwards, A. J.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2861. (b) Friedrich, S.; Schubart, M.; Gade, L. H.; Scowen, I. J.; Edwards, A. J.; McPartlin, M. *Chem. Ber.* **1997**, *120*, 11751. (c) Galka, C. H.; Trösch, D. J. M.; Schubart, M.; Gade, L. H.; Radojevic, S.; Scowen, I. J.; McPartlin, M. *Eur. J. Inorg. Chem.* **2000**, 2577.

(15) Gade, L. H. *Chem. Commun.* **2000**, 173.

(16) Blake, A. J.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Schubart, M.; Scowen, I. J. *Chem. Commun.* **1997**, 1555.

(17) For a review of imido complexes with diamido donor ligands see: Gade, L. H.; Mountford, P. *Coord. Chem. Rev.*, in press.

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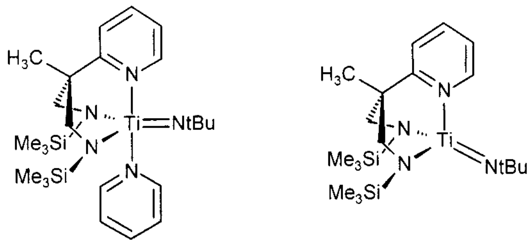
Chart 1



1 **1a**

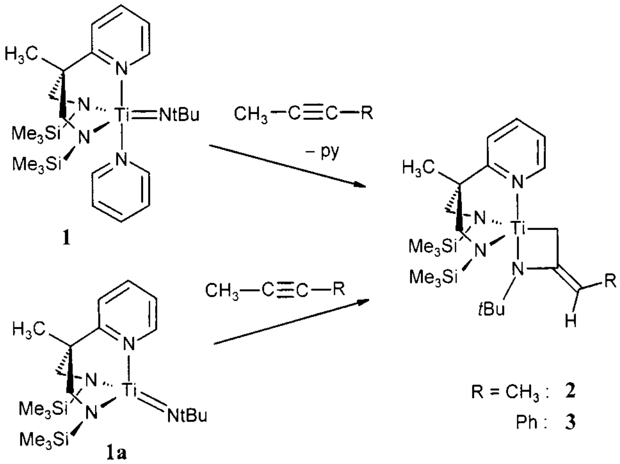
pyridine and pyridyl functionalities that, under appropriate reaction conditions, may dissociate to yield imido species of a type hitherto only accessible via irreversible thermolysis of suitable precursors.[7,11] In fact, sublimation of the pyridine adduct **1** under high vacuum quantitatively leads to the 14-valence-electron, four-coordinate complex **1a** in which the metal center is already fairly exposed.[18] The facile accessibility and stability of **1** and **1a** has allowed us to undertake a systematic investigation into their reactivity, in particular C−N coupling with unsaturated hydrocarbons or substrates containing polar functional groups.

In this paper we report the reactivity of complexes **1** and **1a** toward methylacetylenes, allenes, and heteroallenes.[19]

Results and Discussion

Reaction of 1 and 1a with Methylacetylenes. Heating compound **1** dissolved in neat 2-butyne or 1-phenylpropyne at 80 °C for 14 days in a sealed tube led to its complete conversion to the novel complexes [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHCH$_3$)CH$_2$}] (**2**) and [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHC$_6$H$_5$)CH$_2$}] (**3**) (Scheme 1), respectively, which were isolated by direct crystallization from the reaction mixture (yields: **2**, 73%; **3**, 70%).

Scheme 1. Reaction of Complexes 1 and 1a with Methylacetylenes To Give the Metallacycles 2 and 3



Neither of the reaction products **2** and **3** contain the auxiliary pyridine ligand present in the starting material, and the ^{1}H and ^{13}C NMR spectra indicate a transformation of a methyl group of the acetylene substrate. Thus, new singlet resonances for a metal-bound CH$_2$ group were observed (δ(^{1}H/^{13}C): **2**, 1.77/62.4; **3**, 2.03/63.6) as well as signals for an olefinic CH unit (δ(^{1}H/^{13}C): **2**, 4.76 (quartet)/86.7; **3**, 5.86 (singlet)/96.4). This led to the formulation of the reaction products as depicted in Scheme 1. The same reaction products were obtained in similar yields under virtually identical reaction conditions from the pyridine-free imido complex **1a**, which indicates that the auxiliary pyridine ligand does not play a direct role in the conversion of the methylacetylenes. As with all previously studied transformations of **1**,[17] the dissociation of the pyridine molecule appears to be the first step. This is supported by the observation that addition of 3−5 equiv of pyridine to a mixture of **1** and the methylacetylenes inhibits the reaction to the extent that virtually no conversion to the metallacycles is observed, even after 3 weeks at 80 °C. In contrast to the methylacetylenes, the homologues containing longer chain alkyl units attached to the C≡C triple bonds were found to be unreactive toward **1** or **1a**. Surprisingly, in none of these reactions was the direct addition of the acetylenic triple bond to the Ti═N*t*Bu linkage observed, in contrast to the situation found for the reaction of other terminal imides with acetylenes.[2] This is especially surprising, since certain phosphaalkynes (RCP) and azaalkynes (RCN) readily undergo 2 + 2 cycloaddition reactions with the Ti═N*t*Bu bond in **1**.[25b]

Reaction of 1 and 1a with Allenes. Compounds **2** and **3** are related to 2 + 2 cycloaddition products reported by Bergman and co-workers for the reaction of certain zirconocene imides with the C═C double bonds of alkenes[20] and allenes.[21] In particular, the reaction of a chiral imidozirconium derivative with racemic chiral allenes occurred stereoselectively and allowed a kinetic resolution of the racemate.[21] In these cases the reaction of an allene with the imido complex led to a metallaazetidine with an exocyclic double bond, as in complexes **2** and **3**. Both compounds may thus be viewed as formally derived from an analogous reaction of **1** or **1a** with 1,2-butadiene or phenylallene, respectively. In fact, heating the imidotitanium complexes with these allenes at 60 °C over a period of 14 days led to their complete and selective conversion to compounds **2** and **3** (Scheme 2), as established by comparison of the spectroscopic and analytical data of both products with the corresponding products derived from the methylacetylenes.

In contrast to the reaction of allenes with Bergman's zirconocene imido complex,[21] the conversion of compounds **1** to the products **2** and **3** is a slow reaction and is irreversible. The irreversible nature was established by a (null) crossover experiment of **2** with a large excess of phenylallene. Thus, heating the two compounds at 80 °C for over 14 days did not lead to any detectible generation of **3** or to the concomitant liberation of 1,2-butadiene. Furthermore, in all the reactions leading to

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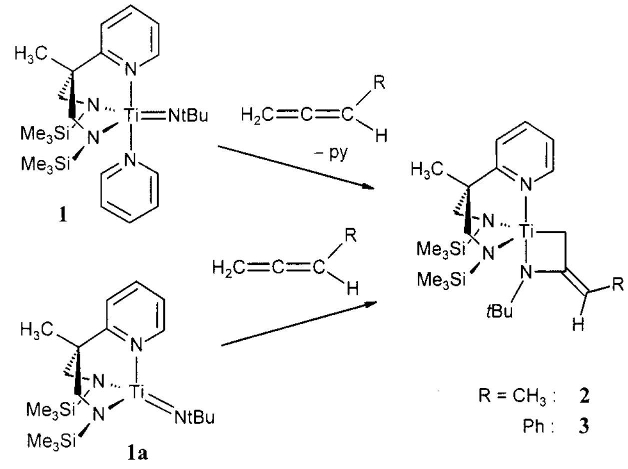
(18) Blake, A. J.; Collier, P. E.; Gade, L. H.; Lloyd, J.; Mountford, P.; Pugh, S. M.; Schubart, M.; Skinner, M. E. G.; Trösch, D. J. M. *Inorg. Chem.* **2001**, *40*, 870.

(19) Bashall, A.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Trösch, D. J. M. *Chem. Commun.* **1998**, 2555.

(20) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405.

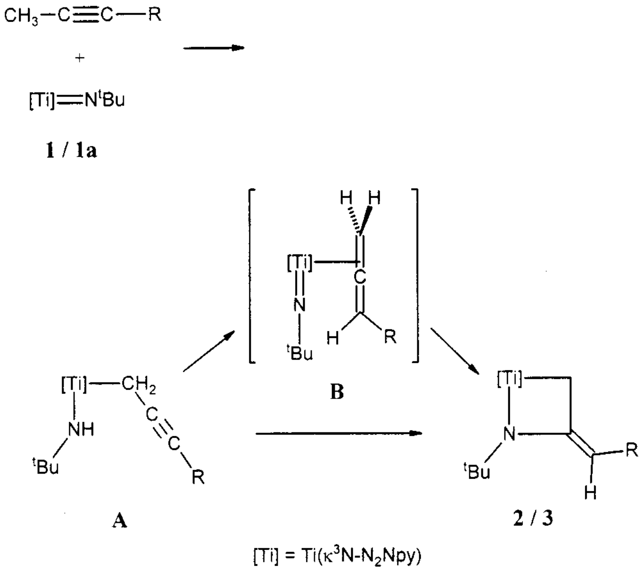
(21) Sweeney, Z. K.; Salsman, J. L.; Andersen, R. A.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 2339.

Scheme 2. Reaction of Complexes 1 and 1a with Allenes To Give the Metallacyclic Titanium Complexes 2 and 3



2 and **3** there was no detectible isomerization of the free methylacetylenes to the corresponding free allenes or vice versa. If such an acetylene-to-allene isomerization takes place, it presumably must therefore occur within the coordination sphere of the complex. It is thus probable that both reaction pathways involve the same intermediate, i.e., a metal π-bound allene complex, and that the 2 + 2 cycloaddition is the slow reaction step in the sequence of transformations leading to **2** and **3**. A mechanistic pathway which takes these observations into account is depicted in Scheme 3.

Scheme 3. Proposed Mechanism for the Formation of 2 and 3



In the first reaction step (formation of intermediate **A**) the CH_3 group of the methylacetylene adds across the Ti=NR bond, generating an R(H)N amido ligand and a Ti−alkyl unit. Prior coordination of the alkyne to Ti could render the alkyne Me group C−H atoms more acidic and amenable to deprotonation (activation) by the *tert*-butylimido group. We note that C−H bond activation reactions of transiently generated imido compounds have been studied extensively by Wolczanski and others in recent years.[11] In a proposed second step H atom transfer to an acetylene C atom leads to the re-formation of the imido unit and a π-bonded allene ligand (**B**). These fragments couple in the third and final step to give the four-membered azatitanacycle present in **2** and **3**. Alternatively, intermediate **A** may also be directly converted to the metallacycle. Note that since the reversible addition of alkynes to M=NR or M=O bonds is established, we cannot rule out the reversible formation of an azatitanacyclobutene intermediate prior to C−H bond migration.[6c] In addition, we cannot discount an alternative mechanism in which initial deprotonation of the Me group of a coordinated alkyne by an amido nitrogen occurs. This would give an amido−imido−diamido intermediate analogous to **A.** This then could, in turn, collapse to the imido−allene intermediate **B** and subsequently form **2**/**3**.

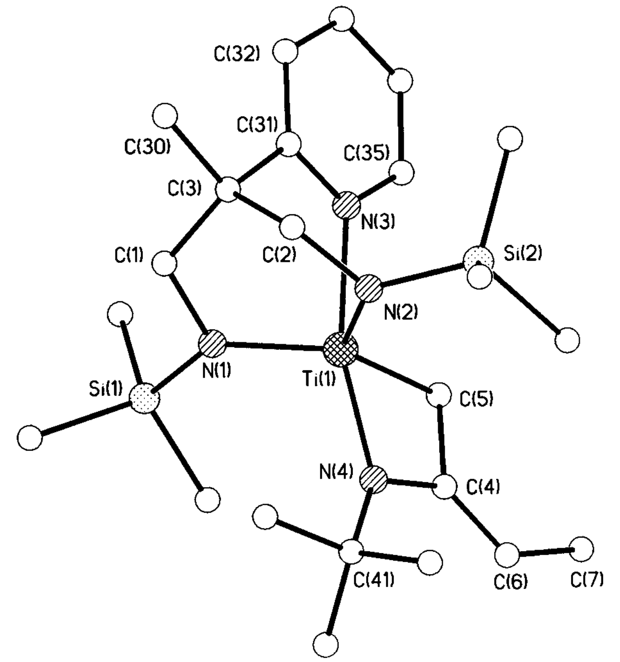


Figure 1. Molecular structure of [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C-(CHMe)CH$_2$}] (**2**).

X-ray Diffraction Studies of 2 and 3. Unambiguous evidence for the molecular structures of **2** and **3** was obtained from a single-crystal X-ray structure analysis of both compounds, which are observed to have the very similar structures depicted in Figure 1(for **2**) and Figure 2(for **3**). Both compounds have molecular structures of virtual C_s symmetry. Considerable disorder of the methyl groups in **3** led to poor diffraction by the crystals and consequently to relatively high esd's on the parameters. However, the main features are well-established, and the mean bond lengths and angles for **3** are in most cases equal within experimental error to those observed for **2**, with which they are compared in Table 1; the lengths for compound **2** will be used in the discussion. The coordination geometry of both molecules is distorted trigonal bipyramidal. The two amido functions N(1) and N(2) of the tripodal ligand as well as the alkyl C atom C(5) occupy the equatorial sites (mean Ti(1)−N$_{am}$ = 1.896(5) Å, Ti(1)−C(5) = 2.149(7) Å), while the pyridyl N atom (Ti(1)−N(3) = 2.232(6) Å) and the amido N atom (Ti(1)−N(4) = 1.949(6) Å) derived from the imido ligand form the axial set. The angle between the axial bonds, N(3)−Ti(1)−N(4) = 154.3(2)°, is distorted from the ideal

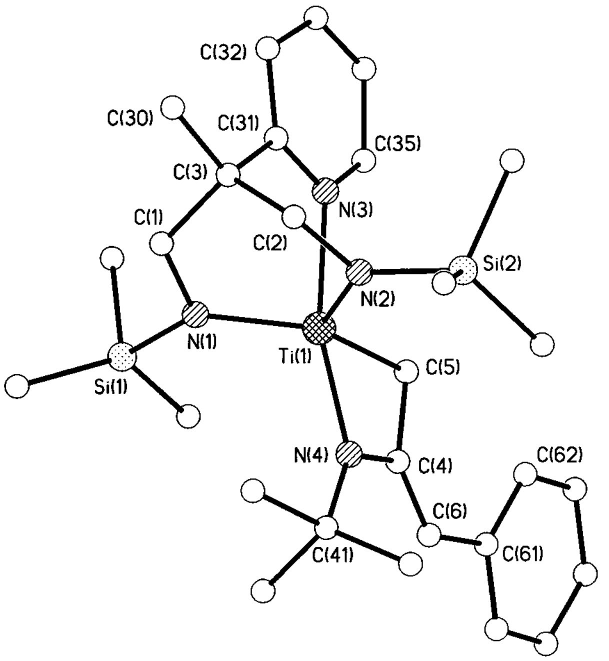


Figure 2. Molecular structure of [(N$_2$Npy-κ^3N)Ti{N(tBu)C(CHPh)CH$_2$}] (**3**).

Table 1. Selected Metric Parameters for 2 and Selected Mean Metric Parameters for the Two Independent Molecules of 3

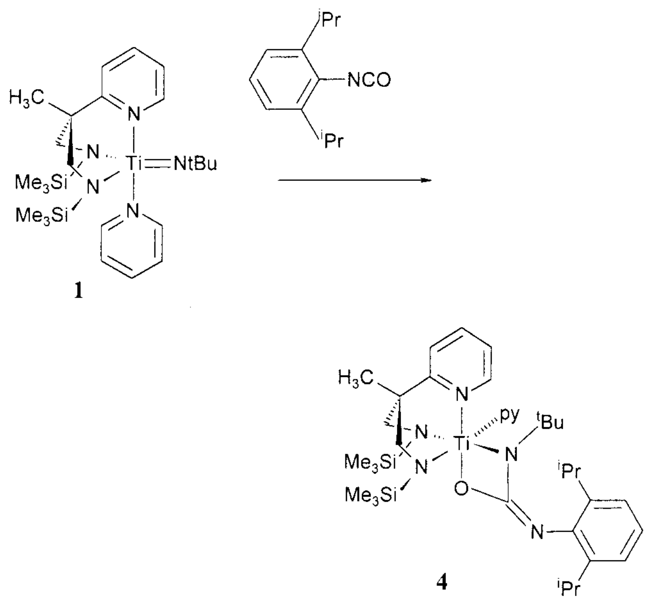
	2	3
(a) Bond Lengths (Å)		
Ti(1)−N(1)	1.890(5)	1.895(9)
Ti(1)−N(2)	1.903(5)	1.919(9)
Ti(1)−N(3)	2.232(6)	2.228(9)
Ti(1)−N(4)	1.949(6)	1.981(11)
Ti(1)−C(5)	2.149(7)	2.153(11)
N(4)−C(4)	1.404 (8)	1.39(2)
C(4)−C(5)	1.515(9)	1.51(2)
C(4)−C(6)	1.338(9)	1.35(2)
mean Si−N	1.741(6)	1.743(11)
(b) Bond Angles (deg)		
N(1)−Ti(1)−N(2)	110.5(3)	108.9(5)
N(1)−Ti(1)−N(3)	86.1(2)	84.7(5)
N(1)−Ti(1)−N(4)	107.3(3)	109.1(6)
N(2)−Ti(1)−N(3)	83.9(2)	82.6(6)
N(2)−Ti(1)−N(4)	106.3(2)	108.6(6)
N(3)−Ti1(1)−N(4)	154.3(2)	157.2(5)
C(5)−Ti(1)−N(1)	121.6(3)	125.3(6)
C(5)−Ti(1)−N(2)	127.1(3)	124.5(6)
C(5)−Ti(1)−N(3)	90.9(3)	90.8(6)
C(5)−Ti(1)−N(4)	67.6(2)	66.4(6)

linear value as a consequence of the small bite of the coordinated chelating metalla-enamine (N(4)−Ti(1)−C(5) = 67.6(2)°).

The bond lengths and interbond angles within the C−N-coupled organic fragment clearly support its interpretation as a metalated enamine, with C(4)−C(5) = 1.515(9) Å and C(4)−N(4) = 1.404(8) Å implying the presence of predominantly single bonds, and the exocyclic bond C(4)−C(6) (1.338(9) Å) being consistent with a C=C double bond. The {Ti(NtBu)C(=CHR)CH$_2$} metallaazetidine fragment in **2** and **3** is the first crystallographically authenticated example of this structural unit and is analogous to the metallacyclic structures characterized spectroscopically from the reaction of a zirconocene imide with allenes by the groups of Bergman and Anderson.[21] Related oxo−metallacyclic species (i.e., metallaoxetanes) have only recently been fully characterized, namely [Ti(η^5-C$_5$Me$_5$)$_2${OC(=CH$_2$)CH$_2$}],[22] [Mo(NtBu)$_2$Cl{OC(=CHPPh$_3$)CPh$_2$}],[23] and [Ru(PMe$_3$)$_4${OC(=CHtBu)CH$_2$}].[24] Interestingly, the last two complexes have a Z configuration for the exocyclic C=C bond, whereas the configuration in the zirconaazetidines referred to above as well as compounds **2** and **3** is E.

Reaction of 1 with Heteroallenes. We previously established an extensive reaction chemistry of compounds **1** and **1a** toward isocyanides and, thus, substrates possessing polar multiple bonds, giving products of multiple C−N and C−C coupling.[25] In view of the reactivity of allenes toward the titanium imido complexes, we reacted compound **1** with heteroallenes.[2,26] While upon exposure of **1** to stoichiometric amounts of CO$_2$, tBuNCO, and PhNCO immediate conversion of the starting material was observed, all reactions were highly unspecific and did not lead to an isolable product. Only upon reaction with the sterically encumbered isocyanate 2,6-C$_6$H$_3$$iPr_2$NCO did we observe a selective conversion to the product of 2 + 2 cycloaddition with the Ti=N bond, [(N$_2$Npy-κ^3N)Ti{N(tBu)C(N-2,6-C$_6$H$_3$-iPr$_2$)O}(py)] (**4**) (Scheme 4).

Scheme 4. Cycloaddition of 2,6-Diisopropylphenyl Isocyanate To Give Compound 4



The structure of compound **4** depicted in Scheme 3 is based on the ^{1}H and ^{13}C NMR spectra of the complex and ^{1}H−^{1}H and ^{13}C−^{1}H correlation spectra, as well as ^{1}H-NOE difference spectra. Coordination of the pyridine molecule is reflected in the chemical shifts of its protons (ortho, δ 9.35; para, 6.98; meta, 6.74) and reduces the molecular symmetry from C_s to C_1. This renders the CH$_2$

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[22] Schwartz, D. J.; Smith, M. R.; Andersen, R. A. *Organometallics* **1996**, *15*, 1446.

[23] Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344.

[24] Sundermeyer, J.; Weber, K.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 731.

[25] (a) Bashall, A.; Gade, L. H.; McPartlin, M.; Mountford, P.; Pugh, S. M.; Radojevic, S.; Schubart, M.; Scowen, I. J.; Trösch, D. J. M. *Organometallics* **2000**, *19*, 4784. (b) Pugh, S. M.; Trösch, D. J. M.; Wilson, D. J.; Bashall, A.; Cloke, F. G. N.; Gade, L. H.; Hitchcock, P. B.; McPartlin, M.; Nixon, J. F.; Mountford, P. *Organometallics* **2000**, *19*, 3205.

[26] See the following and references therein: Blake, A. J.; McInnes, J. M.; Mountford, P.; Nikonov, G. I.; Swallow, D.; Watkin, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 379.

protons in the N$_2$Npy ligand inequivalent, giving two AB systems at δ 3.72, 3.33 and δ 2.31, 2.21. The signals of the two Me$_3$Si groups overlap accidentally in the ^{1}H NMR spectrum (δ 0.40) but are clearly separated in the ^{13}C NMR spectrum (δ 1.9 and 3.1). The steric demand of the 2,6-C$_6$H$_3$*i*Pr$_2$ group is responsible for hindered rotation around the aryl−N bond, leading to two sets of signals for the inequvalent isopropyl groups.

Isocyanates can add M═NR bonds to give either N,N-bound or N,O-bound ureate derivatives.[2,26] The absence of a characteristic band attributable to a CO stretch in the region of 1620−1640 cm^{-1} of the infrared spectrum of **4** indicates the presence of an N,O-bound ureate ligand. In a series of NOE difference spectra cross relaxation between the *t*Bu group and the pyridyl H^6 proton, and to a lesser extent the pyridine ortho protons, suggests the structural arrangement represented in Scheme 4.

In contrast to the pronounced reactivity of **1** toward oxygen-containing heteroallenes, leading mostly to non-specific conversions, it proved to be unreactive to the sulfur analogues. Thus, no reaction was observed with either CS$_2$ or isothiocyanates.

Conclusions

The reaction of the imidotitanium complexes **1** and **1a** with 2-butyne and 1-phenylpropyne has led to the unusual transformation to the metallacycles **2** and **3**, which are equally accessible via 2 + 2 cycloaddition of the imido compounds with the respective allenes. The remarkable products of a C−N coupling reaction may be viewed as *di*metalated enamines, the reactivity of which will be the subject of future investigations. In contrast, the pronounced reactivity of the Ti═N double bond toward polar unsaturated substrates has set limits to the possibility of selective 2 + 2 cycloaddition of **1** with these types of substrates.

Experimental Section

All manipulations were performed under an inert-gas atmosphere of dried argon in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive “freeze−pump−thaw” cycles and dried over 4 Å molecular sieves. Solids were separated from suspensions by centrifugation, thus avoiding filtration procedures. The centrifuge employed was a Rotina 48 (Hettich Zentrifugen, Tuttlingen, Germany) which was equipped with a specially designed Schlenk tube rotor.[27]

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable-temperature unit (at 200.13, 50.32, and 39.76 MHz, respectively) with tetramethylsilane as references. Infrared spectra were recorded on Perkin-Elmer 1420 and Bruker IRS 25 FT spectrometers.

Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at the University of Würzburg or Nottingham. The imidotitanium complexes [(N$_2$Npy-κ^3*N*)Ti(═N*t*Bu)(py)] (**1**) and the complexes [(N$_2$Npy-κ^3*N*)Ti(═N*t*Bu)] (**1a**) were prepared as previously reported by us.[16,18] Phenylallene was prepared according to a synthetic procedure reported in the literature.[28] All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHCH$_3$)CH$_2$}] (2). Method A. The imido complex [(N$_2$Npy-κ^3*N*)Ti(═N*t*Bu)(py)] (**1**; 340 mg, 0.672 mmol), 0.5 mL of 2-butyne, and 2 mL of benzene were placed in a 30 mL pressure tube equipped with a Young tap and heated at 80 °C for 14 days. After the solution thus obtained was cooled, all volatile components were removed in vacuo and the residue washed with 5 mL of cold pentane. The yellow solid containd 236 mg of analytically pure [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHCH$_3$)CH$_2$}] (**2**). Yield: 73%.

Method B. The imido complex [(N$_2$Npy-κ^3*N*)Ti(═N*t*Bu)] (**2**; 200 mg, 0.435 mmol) and 1 mL of 1,2-butadiene were placed in a 30 mL pressure tube equipped with a Young tap and heated at 60 °C for 14 days. The workup was the same as above. Yield: 76%.

Anal. Calcd for C$_{23}$H$_{44}$N$_4$Si$_2$Ti (480.7): C, 57.47; H, 9.23; N, 11.66. Found: C, 57.45; H, 9.04; N, 11.86. IR (Nujol): ν 1587 vw, 1461 vs, 1377s, 1249 w, 918 w, 840 w, 743 vw, 723 vw cm^{-1}. ^{1}H NMR (200.1 MHz, C$_6$D$_6$, 295 K): δ 0.04 [s, 18 H, Si(CH$_3$)$_3$], 1.00 (s, 3 H, CCH$_3$), 1,77 (s, 2 H, CH$_2$), 1.81 [s, 9 H, C(C*H*$_3$)$_3$], 2.22 [d, ^4J(HH) = 6.3 Hz, 3 H, CHC*H*$_3$], 3.08 [d, ^3J(HH) = 12.3 Hz, C*H*HN], 3.70 (d, 2 H, CH*H*N), 4.76 (q, 1 H, C*H*CH$_3$), 6.51 (m, 1 H, H^5), 6.80 [d, ^3J(HH) = 17.9 Hz, 1 H, H^3), 7.03 [td, ^3J(H^{4}H^5) = 7.7, ^3J(H^{4}H^3) = 7.9, ^5J(H^{4}H^6) = 1.7 Hz, 1 H, H^4], 8.59 [d, ^3J(HH) = 5.4 Hz, 1 H, H^6]. ^{13}C{^{1}H} NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ 0.1 [Si(CH$_3$)$_3$], 13.6 (CH$_3$), 23.3 (CH$_3$), 30.4 (CH*C*H$_3$), 46.5 (*C*CH$_3$), 56.4 [*C*(CH$_3$)$_3$], 62.4 (CH$_2$), 63.5 (CH$_2$N), 86.7 (*C*HCH$_3$), 120.6 (C^3), 121.7 (C^5), 138.3 (C,^{4} 140.7 (*C*═CHCH$_3$), 145.7 (C^6), 159.8 (C^2).

Preparation of [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHC$_6$H$_5$)CH$_2$}] (3). Method A. The imido complex [(N$_2$Npy-κ^3*N*)Ti(═N*t*Bu)(py)] (**1**; 240 mg, 0.475 mmol), 0.5 mL of 3-phenylpropyne, and 2 mL of benzene were placed in a 30 mL pressure tube equipped with a Young tap and heated at 80 °C for 14 days. After the solution thus obtained was cooled, all volatile components were removed in vacuo and the residue washed with 5 mL of cold pentane. The yellow solid containd 180 mg of analytically pure [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHC$_6$H$_5$)CH$_2$}] (**3**). Yield: 70%.

Method B. The imido complex [(N$_2$Npy-κ^3*N*)Ti(═N*t*Bu)] (**2**; 200 mg, 0.435 mmol) and 1 mL of phenylallene were placed in a 30 mL pressure tube equipped with a Young tap and heated at 60 °C for 14 days. The workup was the same as above. Yield: 69%.

Anal. Calcd for C$_{28}$H$_{46}$N$_4$Si$_2$Ti (542.8): C, 61.96; H, 8.54; N, 10.32. Found: C, 61.89; H, 8.59; N, 10.28. IR (Nujol): ν 1575 w, 832 w, 1459 vs, 1377 s, 1249 s, 1050 w, 902 vw, 844 m, 774 vw, 750 m, 719 vw, 688 vw cm^{-1}. ^{1}H NMR (200.1 MHz, C$_6$D$_6$, 295 K): δ −0.03 [s, 18 H, Si(CH$_3$)$_3$], 0.97 (s, 3 H, CCH$_3$), 1.81 [s, 9 H, C(CH$_3$)$_3$], 2.03 (s, 2 H, CH$_2$), 3.03 [d, ^2J(HH) = 12.8 Hz, 2 H, C*H*HN], 3.71 (d, 2 H, CH*H*N), 5.86 [s, 1 H, C*H*(C$_6$H$_5$)], 6.50 [ddd, ^3J(H^{5}H^4) = 7.6 Hz, ^3J(H^{5}H^6) = 5.6 Hz, ^5J(H^{5}H^3) = 1.2 Hz, 1 H, H^5], 6.76 [dd, ^3J(H^{3}H^4) = 7.9 Hz, 1 H, H^3], 6.95−7.06 [m, 2 H, H^4 (C$_5$H$_5$N), H^4 (C$_6$H$_5$)], 7.37 [m, 2 H, H^3, H^5 (C$_6$H$_5$N)], 7.79 [m, 2 H, H^2, H^6 (C$_6$H$_5$)], 8.42 [ddd, H^6 (C$_5$H$_4$N)]. ^{13}C{^{1}H} NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ 0.0 [Si(CH$_3$)$_3$], 23.4 (C*C*H$_3$), 30.6 [C(*C*H$_3$)$_3$], 47.5 [*C*(CH$_3$)$_3$], 56.2 (*C*CH$_3$), 58.0 (CH$_2$), 63.6 (CH$_2$N), 96.4 [*C*H(C$_6$H$_5$)], 120.4 [C^3 (C$_5$H$_4$N)], 121.4 [C^4 (C$_6$H$_5$)], 122.0 [C^5 (C$_5$H$_4$N)], 127.9 [C^2, C^6 (C$_6$H$_5$)], 128.3 [C^3, C^5 (C$_6$H$_5$)], 138.7 [C^4 (C$_5$H$_4$N)], 144.23 [C^1 (C$_6$H$_5$)], 145.8 [C^6 (C$_5$H$_5$N)], 147.7 [*C*═CH(C$_6$H$_5$)], 159.5 [C^2 (C$_5$H$_5$N)].

Attempted Crossover Experiment of [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHCH$_3$)CH$_2$}] (2) with Phenylallene. [(N$_2$Npy-κ^3*N*)Ti{N(*t*Bu)C(CHCH$_3$)CH$_2$}] (30 mg, 0.0625 mmol) was dissolved in C$_6$D$_6$ (0.5 mL) in an NMR tube, and an excess of phenylallene (58 mg, 0.0 mmol) added to the solution. The reaction mixture was heated at 80 °C over a period of 3 weeks, during which time no reaction was observed.

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(27) Hellmann, K. W.; Gade, L. H. *Verfahrenstechnik* **1997**, *31*(5), 70.

(28) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, 1451.

Preparation of [(N_2Npy-κ^3*N*)Ti{N(*t*Bu)C(N-2,6-C_6H_3-*i*Pr_2)O}(py)] (4). The imido complex [(N_2Npy-κ^3N)Ti(=N*t*Bu)(py)] (**1**; 410 mg, 0.810 mmol) was dissolved in benzene (30 mL), and 2,6-diisopropylphenyl isocyanate was added via a syringe (165 mg, 173 μL, 0.81 mmol). The solution was stirred for 10 min before the volatile components were removed under pressure. The red solid was extracted into pentane (20 mL), and the extract was cooled to −25 °C. The product [(N_2Npy-κ^3N)Ti{N(*t*Bu)C(N-2,6-C_6H_3*i*Pr_2)O}(py)] (**4**) was isolated as a microcystalline red powder. Yield: 387 mg (67%). Anal. Calcd for $C_{37}H_{60}N_6OSi_2Ti$ (692.97): C, 62.7; H, 8.5; N, 11.9. Found: C, 60.5; H, 8.1; N, 11.5. IR (Nujol): 1600 m, 1540 m, 1348 w, 1332 w, 1288 w, 1236 m, 1212 w, 1172 m, 1103 w, 1082 w, 1070 w, 1064 w, 1039 w, 1012 w, 964 w, 952 w, 934 w, 903 w, 886 w, 858 m, 840 m, 801 w, 773 w, 755 w, 696 w, 681 w, 663 w, 634 w, 604 w, 582 w, 570 w, 545 w, 462 w, 440 w cm^{-1}. ^1H NMR (300.1 MHz, C_6D_6, 295 K): δ 0.40 [s, 18 H, Si(CH_3)$_3$], 0.45 (d, 3 H, CH*Me*Me, ^3J(HH) = 6.8 Hz), 0.69 (d, 3 H, CHMe*Me*, ^3J(HH) = 6.8 Hz), 0.78 (s, 3 H, CCH_3), 0.82 (d, 3 H, CH*Me*Me, ^3J(HH) = 6.9 Hz), 0.98 (d, 3 H, CHMe*Me*, ^3J(HH) = 6.9 Hz), 1,58 [s, 9 H, C(C*H*$_3$)$_3$], 2.21 [d, ^3J(HH) = 12.9 Hz, C*H*HN], 2.31 [d, ^3J(HH) = 12.9 Hz, CH*H*N], 2.67 [sept, 1H, C*H*Me$_2$, ^3J(HH) = 6.8 Hz], 2.77 [sept, 1H, C*H*Me$_2$, ^3J(HH) = 6.9 Hz], 3.33 [d, ^3J(HH) = 12.9 Hz, C*H*HN], 3.72 [d, ^3J(HH) = 12.9 Hz, CH*H*N], 6.69 (m, 1 H, H^5), 6.74 [t, 2H, ^3J(HH) = 6.3 Hz, *m*-C_5H_5N], 6.83−6.94 (m, overlapping *m*-C_6H_3*i*Pr_2 and H^3), 6.98 (m, 1 H, *p*-C_5H_5N), 7.01 (d, 1 H, ^3J(HH) 7.6 Hz, *p*-C_6H_3*i*Pr_2), 7.04 [td, 1 H, $^3J(H^4H^5)$ = 7.7, $^3J(H^4H^3)$ = 7.9, $^5J(H^4H^6)$ = 1.7 Hz, H^4], 9.35 [d, 2 H, $^3J(H^6H^5)$ = 4.3 Hz, *m*-C_5H_5N], 9.66 [d, 1 H, ^3J(HH) = 6.4 Hz, H^6]. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 295 K): δ 1.9, 3.1 [Si(CH_3)$_3$], 22.1 (CH_3C), 23.6 (CH*Me*Me), 23.7 (CHMe*Me*), 24.0 (CH*Me*Me), 25.1 (CHMe*Me*), 28.4(2 × overlapping *C*HMe$_2$), 33.5 [N*C*(CH_3)$_3$], 49.1 [*C*(CH_2N)$_2$], 56.3, 64.4 (CH_2N), 64.6 (N*C*Me$_3$), 119.8 (C^5), 122.1, 123.0 (*m*-C_6H_3*i*Pr_2), 123.3 (*m*-C_5H_5N), 136.8 (C^4), 139.9 (*p*-C_5H_5N), 137.4 (*ipso*-C_6H_3*i*Pr_2), 145.7, 156.9 (*o*-C_6H_3*i*Pr_2), 151.7 (*o*-C_5H_5N), 151.8 (C^6), 163.2 (C^2), 167.1 (O*C*=N).

X-ray Crystallographic Studies of 2 and 3. Data Collection for 2 and 3. Crystals of **2** and **3** were mounted on a quartz fiber in Lindemann capillaries under argon and in an inert oil. X-ray intensity data were collected with graphite-monochromated radiation, on a Siemens P4 four-circle diffractometer. The only crystals that could be obtained of **3** diffracted very weakly at high angle. Details of the data collection and refinement and crystal data are listed in Table 2. Lorentz−polarization and absorption corrections were applied to the data of both compounds.

Structure Solution and Refinement for 2 and 3. The positions of most of the non-hydrogen atoms were located by direct methods.[29] The remaining non-hydrogen atoms were revealed from subsequent difference Fourier sytheses. In the structure of **3** there were two independent molecules per equivalent position. Relatively high displacement parameters for the methyl groups in **3** were consistent with some rotational disorder, and some methyl carbon atoms were resolved into two components of ca. 50:50 occupancy. Refinement was based on *F*,[2,29] and chemically equivalent bond lengths within the molecules were constrained to be equal within an esd of 0.02. All hydrogen atoms were placed in calculated positions with displacement parameters set equal to 1.2 times the U_{eq} value of the parent carbon atoms for the methylene and aromatic carbon groups and 1.5 times the U_{eq} value for methyl groups. For **2** semiempirical absorption corrections were applied using ψ-scans.[29] After initial refinement with isotropic displacement parameters empirical absorption corrections[30] were applied to the data of **3**. All full-occupancy non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.

Table 2. Crystal Data and Structure Refinement for Complexes 2 and 3

	2	**3**
empirical formula	$C_{23}H_{44}N_4Si_2Ti$	$C_{28}H_{46}N_4Si_2Ti$
fw	480.70	542.77
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c* (No. 15)	$Pna2_1$ (No. 33)
unit cell dimens		
a/Å	28.721(7)	21.060(5)
b/Å	10.450(2)	10.250(4)
c/Å	18.886(4)	30.243(12)
β/deg	100.50(2)	
V/Å^3	5567(2)	6529(4)
Z	8	8
D_{calcd}/Mg m^{-3}	1.147	1.104
radiation (λ/Å)	Mo Kα (0.710 73)	Mo Kα (0.710 69)
μ/mm^{-1}	0.410	0.356
F(000)	2080	2336
cryst size/mm	0.38 × 0.38 × 0.22	0.45 × 0.44 × 0.44
θ range/deg	2.08−23.00	2.10−21.00
limiting *hkl* indices	−1 to 24, −11 to 1, −20 to 20	−21 to 1, −1 to 10, −1 to 30
no. of rflns collected	4176	4584
no. of indep rflns (R_{int})	3391 (0.0893)	3769 (0.1010)
max, min transmissn	0.799, 0.682	0.656, 0.560
no. of data/restraints/params	3391/22/271	3769/54/434
S on F^2	0.862	0.904
final *R* indices[a]		
$I > 2\sigma(I)$	R1 = 0.0665, wR2 = 0.0983	R1 = 0.0980, wR2 = 0.2162
all data	R1 = 0.1821, wR2 = 0.1221	R1 = 0.2633, wR2 = 0.2802
weights *a*, *b*[a]	0.0219, 0.0	0.1326, 0.0
max, min peaks in final diff map/e Å^{-3}	0.325, −0.294	0.819, −0.426

[a] $S = [\sum w(F_o{}^2 - F_c{}^2)^2/(n-p)]^2$, where n = number of reflections and p = total number of parameters. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]^2]^{1/2}$, where $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = [\max(F_o{}^2,0) + 2(F_c{}^2)]/3$.

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Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) SHELTXL, PC version 5.03; Siemens Analytical Instruments Inc., Madison, WI, 1994.

(30) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.