Migratory Insertion at Gold

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Cationic Gold(III) Alkyl Complexes: Generation, Trapping, and Insertion of Norbornene**

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Abstract: *Migratory insertion of alkenes into gold–carbon bonds, a fundamental yet unprecedented organometallic transformation, has been investigated from a discrete (P,C) cyclometalated gold(III) dimethyl complex. Methide abstraction by* $B(C_6F_5)_3$ *is shown to generate a highly reactive cationic* Au^{III} *complex that evolves spontaneously by* C_6F_5 *transfer from boron. In the presence of norbornene, migratory insertion into the Au−C bond proceeds readily. The resulting norbornyl complex is efficiently trapped with pyridines or chloride to give stable four-coordinate adducts.*

Migratory insertion of alkenes into metal–carbon bonds is a key organometallic reaction at the basis of several major catalytic transformations, including the Ziegler–Natta type polymerization of olefins and the Mirozoki–Heck cross-coupling reaction.[1] This elementary step has been extensively documented and thoroughly investigated with early to late transition metals, but strikingly it is unprecedented with gold.

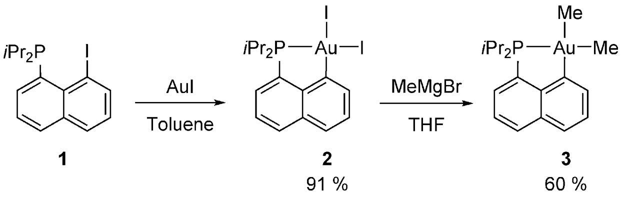
Over the last decade, our knowledge of gold(III) chemistry has tremendously progressed. A variety of highly reactive gold(III) complexes including π adducts of alkenes,[2,3] hydride,[4] hydroxide[5]/peroxide[6]/oxo,[7] and vinyl[8]/allenyl[9] species have been isolated as stable compounds. Important insights have also been gained in terms of reactivity. In particular, the insertion of alkenes into gold(III)–oxygen bonds has attracted much attention,[3,7,10] and a recent thorough mechanistic study has shown that the insertion of ethylene into a gold(III)–oxygen bond proceeds by addition of the *O*-based nucleophile to the π-coordinated alkene.[10]

Our interest for new reactivity patterns of gold complexes[11] prompted us to investigate the insertion of alkenes into gold(III)–carbon bonds.[12] Despite the fact that gold(III) complexes are excellent catalysts for the activation and functionalization of alkenes,[13] insertion into Au^{III}–carbon bonds remains unknown. This situation is in stark contrast with the well-known ability of the isoelectronic Ni, Pd, and Pt^{II} alkyl complexes to readily insert olefins.[14] Tilset and coworkers recently reported the reaction between an Au^{III} alkyl complex and an olefin,[2] but no insertion reaction was observed. Instead, a very rare example of a gold(III) alkene complex was isolated.

To study the insertion of alkenes into gold(III)–carbon bonds, it is crucial to identify well-suited precursors and to be able to generate gold(III) alkyl complexes with a free coordination site. To this end, we envisioned that the (P,C) cyclometalated gold(III) complexes we recently prepared by C_{Ar}–X (X = I, Br) oxidative addition to gold(I)[11e] might be ideal candidates. As discussed hereafter, this strategy was exploited to prepare a discrete (P,C) dimethyl gold(III) complex. Abstraction of a methyl group from gold is described and the ensuing cationic gold(III) methyl complex is shown to display versatile reactivity, including migratory insertion of norbornene.

The (P,C) cyclometalated gold(III) dimethyl complex **3** was prepared following a two-step procedure (Scheme 1). First, the 8-iodonaphthyl phosphine **1**[15] was reacted with AuI at 50 °C to obtain the gold(III) di-iodide complex **2** (91% yield of isolated product) after coordination of the phosphorus atom to gold and oxidative addition of the C_{Ar}–I bond. Methylation with MeMgBr (3 equiv) then afforded the desired complex **3** (isolated as a stable beige solid in 60% yield). The structure of **3** was deduced from multinuclear NMR spectroscopy and confirmed by X-ray diffraction analysis.[16] The two inequivalent Me groups at gold are clearly distinguished by ^1H and ^{13}C NMR. Most diagnostic are the H−P and C−P coupling constants which are substantially larger for the Me group in *trans* vs. *cis* position to phosphorus ($J_{H\text{-}P} = 15.5/5.9$ Hz, $J_{C\text{-}P} = 111.3/5.7$ Hz).

Aiming at generating a cationic gold(III) methyl species with a free coordination site, complex **3** was reacted with



Scheme 1. Synthesis of the (P,C) cyclometallated gold(III) dimethyl complex **3**.

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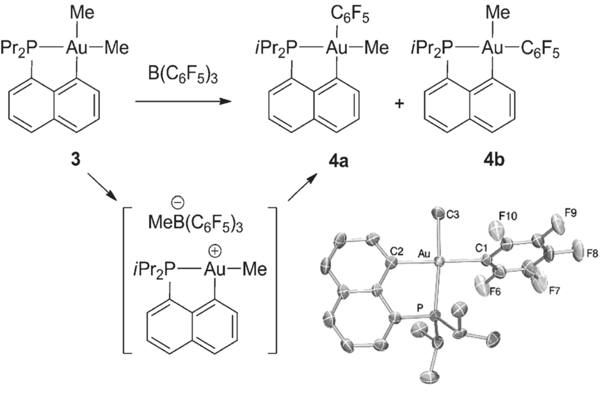
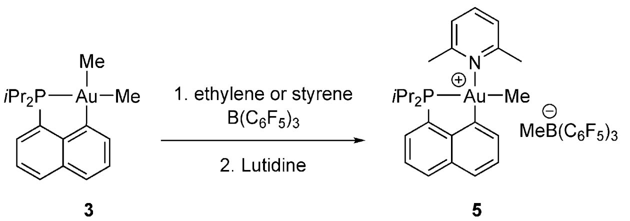
trifluoromethane sulfonic acid (HOTf) to cleave one of the Au−Me bonds. Regardless of the reaction conditions, only intractable mixtures were obtained, and ^{1}H NMR monitoring indicated that protonolysis of the Au−$C_{naphthyl}$ bond occurred to a significant extent. Despite the stabilizing effect of (P,C) chelation, the Au−C_{sp^2} bond is preferentially protonated over the Au−C_{sp^3} bonds under these conditions.[2,3,17] As an alternative strategy, we envisioned to abstract a methide from complex **3** with a strong Lewis acid, namely tris(pentafluorophenyl)borane $B(C_6F_5)_3$.[3,18] The reaction was much cleaner and afforded two stable species **4a** and **4b** in approximately 1:1 ratio according to ^{31}P NMR (δ 71.2 and 68.5 ppm). ^{11}B and ^{19}F NMR analyses indicate concomitant formation of $MeB(C_6F_5)_2$. The spectroscopic data of **4a** and **4b** are very similar, suggesting the formation of two closely related isomers. Column chromatography on silica gel enabled the two compounds to be separated and isolated. Based on spectroscopic data, they were assigned to the neutral complexes [(P,C)AuMe(C_6F_5)] with *cis* and *trans* arrangement of the P atom and C_6F_5 group, respectively (Scheme 2).[19] The two isomers **4a**/**4b** are unambiguously distinguished by the ^{1}H and ^{13}C NMR signals of the Me group at gold and the associated coupling constants to phosphorus.[16] Furthermore, the molecular structure of complex **4b** was confirmed by X-ray diffraction analysis.



Scheme 2. Formation of the neutral gold(III) complexes **4a** and **4b** by Me/C_6F_5 redistribution between **3** and $B(C_6F_5)_3$. Molecular structure of complex **4b.** Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.[32]

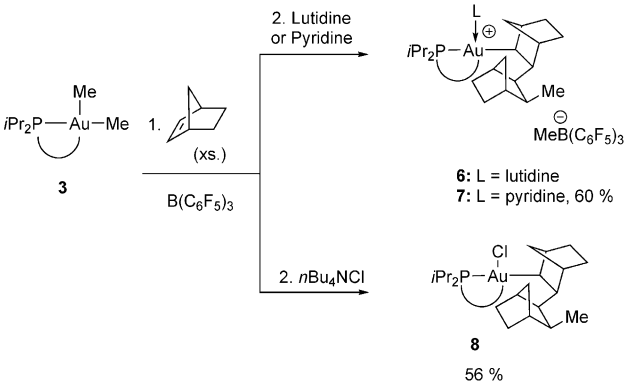
Thus, complex **3** reacts with $B(C_6F_5)_3$ by Me/C_6F_5 redistribution between gold and boron. Such a transfer of aryl groups from boron to gold is relatively rare.[5,18b,20] By analogy with that known for alkyl zirconocenes and related species,[21] the formation of complexes **4a**/**4b** probably involves an ion pair intermediate formed of a tricoordinate cationic gold(III) methyl complex and a borate counteranion. At this point, we wondered if this cationic gold complex could react with olefins before a C_6F_5 group is transferred from boron. However, the instability of three-coordinate gold(III) species[22] represents an inherent bottleneck here and therefore, we envisioned to stabilize the complexes of interest by coordination of Lewis bases. Four-coordinate gold(III) complexes are generally much more stable than the corresponding three-coordinate species,[23] and Lewis bases, in particular pyridines, have been shown to stabilize efficiently electrophilic gold(III) complexes.[24]

We first investigated this approach by reacting complex **3** with $B(C_6F_5)_3$ at −80 °C in the presence of an excess of ethylene (5 bars) or styrene (10 equiv), followed by trapping with 2,6-lutidine. NMR monitoring indicated that ethylene and styrene did not react under these conditions. Instead, the cationic gold(III) methyl complex **5** stabilized by lutidine coordination was formed as major product (70% spectroscopic yield) (Scheme 3).[25] This result confirms the ability of $B(C_6F_5)_3$ to abstract a methyl group from complex **3** to generate a tricoordinate cationic gold(III) complex, which is trapped in situ by lutidine to give complex **5**.



Scheme 3. Formation of the tetracoordinate cationic gold(III) complex **5** by reaction of **3** with $B(C_6F_5)_3$ and lutidine.

We then tested the same reaction with a more reactive olefin, norbornene (NB), and gratifyingly, a different outcome was observed. The reaction of complex **3** with $B(C_6F_5)_3$ at −80 °C in the presence of an excess (3 equiv) of NB, followed by addition of lutidine or pyridine (1 equiv), afforded the norbornyl gold(III) complexes **6** and **7** (Scheme 4).[26] Complex **7** was isolated as a light yellow powder by precipitation with pentane (60% yield). It was characterized by high-resolution mass spectrometry (HRMS) and multinuclear NMR spectroscopy. The ESI mass spectrum of complex **7** shows one peak at *m*/*z* 722.3194 amu corresponding to the mass of [(P,C)AuMe(Py)]$^+$ augmented by two norbornene molecules. This suggests the insertion of two NB units in the Au−Me bond, something which is corroborated by



Scheme 4. Formation of the gold(III) norbornyl complexes **6**–**8** upon insertion of norbonene into the Au−Me bond of **3** (the naphthyl moiety is simplified for clarity).

the relative integration of the aliphatic and naphthyl signals in the ^1H NMR spectrum (37 vs. 6 H). Double insertion of NB in the Au−Me bond parallels what was observed previously with Pd^{II}−Me species,[27] and indicates that the gold–norbornyl species generated after the first insertion is more reactive than the gold–methyl complex. All of the ^1H and ^{13}C NMR resonance signals of complex **7** were assigned thanks to 2D HSQC and HMBC NMR experiments.[16] The most salient NMR data are the ^1H and ^{13}C signals observed at δ 3.26 and 81.1 ppm for the NB C−H unit directly linked to the cationic gold center. Both signals display large coupling constants to phosphorus ($J_{HP} = 7.8$ Hz and $J_{CP} = 87.5$ Hz), indicating that the norbornyl fragment is located *trans* to phosphorus.

Despite significant efforts, single crystals of complex **6** or **7** could not be obtained to analyze their structure by crystallographic means. Having in mind that the ionic character of the complexes and the $[MeB(C_6F_5)_3]$ counteranion may complicate the crystallization process, we decided to quench the tricoordinate norbornyl species with $n\mathrm{Bu_4NCl}$ so as to obtain a neutral gold(III) complex. The reaction worked well and afforded complex **8** in 56 % yield of isolated product. NMR data closely parallel those of complex **7**,[16] and in this case, crystals suitable for X-ray diffraction analysis were obtained by layering a saturated dichloromethane solution of **8** with pentane at −30 °C (Figure 1). Accordingly, double insertion of NB into the Au−Me bond was unambiguously confirmed.[28] The gold atom sits in a square-planar environment formed by the (P,C) chelate ligand, the chlorine atom and the norbornyl moiety which is located *trans* to the phosphorus atom. The stereochemistry of the norbornyl units deserves comment. Insertion of the two NB units occurred on the *exo* face and in a *syn* manner, consistent with a coordination–insertion process. Such an inner-sphere migratory insertion is extremely rare for gold,[29] and contrasts with the outer-sphere *anti* addition process commonly encountered.[10,30]

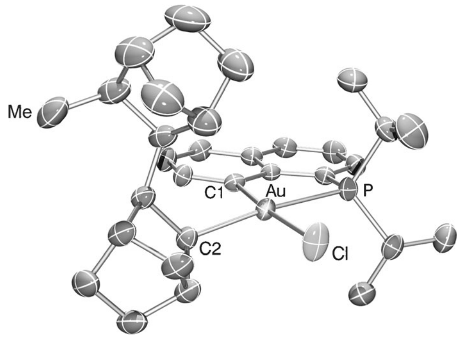


Figure 1. Molecular structure of complex **8**. Ellipsoids are set at 50 % probability; hydrogen atoms omitted for clarity.[32]

In conclusion, the first example of olefin insertion into gold–carbon bonds has been disclosed. Norbornene was found to readily insert into the Au−Me bond of a (P,C) cyclometalated gold(III) alkyl complex. The reaction proceeds in a *syn* manner, consistent with an inner-sphere migratory insertion process. It most likely occurs via a highly reactive tricoordinate cationic Au^{III}−Me intermediate, which is generated by methide abstraction with $B(C_6F_5)_3$. An original Me/C_6F_5 redistribution between gold and boron has also been observed, and found to be competitive with olefin insertion. These results substantiate the feasibility of olefin insertion into Au−C bonds, and pave the way for the development of new gold-mediated transformations based on migratory insertion, in particular olefin polymerization processes.[31] Future work from our group will seek to generate new cationic gold(III) alkyl complexes and to study their reactivity towards other olefins to extend the scope of migratory insertion.

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[1] J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, Universtity Science Books, Sausalito, CA, **2009**.

[2] E. Langseth, M. L. Scheuermann, D. Balcells, W. Kaminsky, K. I. Goldberg, O. Eisenstein, R. H. Heyn, M. Tilset, *Angew. Chem. Int. Ed.* **2013**, *52*, 1660 – 1663; *Angew. Chem.* **2013**, *125*, 1704 – 1707.

[3] N. Savjani, D. Roşca, M. Schormann, M. Bochmann, *Angew. Chem. Int. Ed.* **2013**, *52*, 874 – 877; *Angew. Chem.* **2013**, *125*, 908 – 911.

[4] a) D. A. Roşca, D. A. Smith, D. L. Hughes, M. Bochmann, *Angew. Chem. Int. Ed.* **2012**, *51*, 10643 – 10646; *Angew. Chem.* **2012**, *124*, 10795 – 10798; b) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12935 – 12936; *Angew. Chem.* **2012**, *124*, 13109 – 13110.

[5] D. A. Roşca, D. A. Smith, M. Bochmann, *Chem. Commun.* **2012**, *48*, 7247 – 7249.

[6] D. A. Roşca, J. A. Wright, D. L. Hughes, M. Bochmann, *Nat. Commun.* **2013**, *4*, 2167 – 2171.

[7] M. A. Cinellu, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, *Angew. Chem. Int. Ed.* **2005**, *44*, 6892 – 6895; *Angew. Chem.* **2005**, *117*, 7052 – 7055.

[8] O. A. Egorova, H. Seo, Y. Kim, D. Moon, Y. M. Rhee, K. H. Ahn, *Angew. Chem. Int. Ed.* **2011**, *50*, 11446 – 11450; *Angew. Chem.* **2011**, *123*, 11648 – 11652.

[9] A. Johnson, A. Laguna, M. C. Gimeno, *J. Am. Chem. Soc.* **2014**, *136*, 12812 – 12815.

[10] E. Langseth, A. Nova, E. A. Tråseth, F. Rise, S. Øien, R. H. Heyn, M. Tilset, *J. Am. Chem. Soc.* **2014**, *136*, 10104 – 10115.

[11] a) P. Gualco, S. Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2011**, *50*, 8320 – 8324; *Angew. Chem.* **2011**, *123*, 8470 – 8474; b) P. Gualco, S. Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Organometallics* **2012**, *31*, 6001 – 6004; c) M. Joost, P. Gualco, S. Mallet-Ladeira, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2013**, *52*, 7160 – 7163; *Angew. Chem.* **2013**, *125*, 7301 – 7304; d) M. Joost, P. Gualco, Y. Coppel, K. Miqueu, C. E. Kefalidis, L. Maron, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 747 – 751; *Angew. Chem.* **2014**, *126*, 766 – 770; e) J. Guenther, S. Mallet-Ladeira, L. Estevez, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 1778 – 1781; f) M. Joost, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 10373 – 10382; g) M. Joost, A. Zeineddine, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 14654 – 14657.

[12] Recent calculations have been performed on gold(I) complexes. A prohibitively high activation barrier was predicted for the

insertion of ethylene into (L)Au−H bonds (L = NHC, PR_3); see: a) G. Klatt, R. Xu, M. Pernpointner, L. Molinari, T. Quang Hung, F. Rominger, A. S. Hashmi, H. Köppel, *Chem. Eur. J.* **2013**, *19*, 3954–3961; b) A. Comas-Vives, G. Ujaque, *J. Am. Chem. Soc.* **2013**, *135*, 1295–1305.

[13] a) H. Schmidbaur, A. Schier, *Arab. J. Sci. Eng.* **2012**, *37*, 1187–1225; b) A. S. K. Hashmi, F. D. Toste, *Modern Gold Catalyzed Synthesis*, Wiley-VCH, Weinheim, **2012**.

[14] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204.

[15] S. Bontemps, M. Devillard, S. Mallet-Ladeira, G. Bouhadir, K. Miqueu, D. Bourissou, *Inorg. Chem.* **2013**, *52*, 4714–4720.

[16] See the Supporting Information for details.

[17] For selective cleavage of Au−C_{aryl} over Au−C_{alkyl} bonds with proton sources, see: a) J. K. Jawad, R. J. Puddephatt, M. A. Stalteri, *Inorg. Chem.* **1982**, *21*, 332–337; b) K. E. Roth, S. A. Blum, *Organometallics* **2010**, *29*, 1712–1716.

[18] Generation of cationic gold species using $B(C_6F_5)_3$ abstraction has been scarcely explored; see: a) B. M. Wile, R. J. Burford, R. McDonald, M. J. Ferguson, M. Stradiotto, *Organometallics* **2006**, *25*, 1028–1035; b) M. M. Hansmann, F. Rominger, M. P. Boone, D. W. Stephan, A. S. Hashmi, *Organometallics* **2014**, *33*, 4461–4470.

[19] A. Luquin, E. Cerrada, M. Laguna, *Gold chemistry: Applications and future directions in the life sciences* (Ed.: F. Mohr), Wiley-VCH, Weinheim, **2009**, pp. 93–181.

[20] a) S. G. Weber, D. Zahner, F. Rominger, B. F. Straub, *Chem. Commun.* **2012**, *48*, 11325–11327; b) D. A. Smith, D. A. Rosca, M. Bochmann, *Organometallics* **2012**, *31*, 5998–6000; c) M. Hofer, E. Gomez-Bengoa, C. Nevado, *Organometallics* **2014**, *33*, 1328–1332; d) M. D. Levin, F. D. Toste, *Angew. Chem. Int. Ed.* **2014**, *53*, 6211–6215; *Angew. Chem.* **2014**, *126*, 6325–6329.

[21] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015–10031.

[22] a) S. Komiya, T. A. Albright, R. Hoffmann, J. K. Kochi, *J. Am. Chem. Soc.* **1976**, *98*, 7255–7265; b) W. J. Wolf, M. S. Winston, F. D. Toste, *Nat. Chem.* **2014**, *6*, 159–164.

[23] Bis(silyl)gold(III) complexes were isolated as stable crystalline compounds upon coordination of two phosphines, whereas related monophosphine species could only be spectroscopically characterized at low temperature; see references [11a,d].

[24] Coordination of DMAP was used to stabilize tricationic Au^{III} complexes; see: R. Corbo, T. P. Pell, B. D. Stringer, C. F. Hogan, D. J. D. Wilson, P. J. Barnard, J. L. Dutton, *J. Am. Chem. Soc.* **2014**, *136*, 12415–12421.

[25] Treatment of complex **3** with the frustrated Lewis pair $B(C_6F_5)_3$/lutidine (see: S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476–3477) cleanly gives complex **5**, which was isolated in 46% yield after workup; see also reference [16].

[26] Since the ^1H and ^{13}C NMR signals for the methyl groups of lutidine overlap with those of the norbornyl skeleton, in-depth characterization was carried out on the pyridine complex **7**.

[27] M. D. Walter, P. S. White, M. Brookhart, *Chem. Commun.* **2009**, 6361–6363.

[28] A Cambridge database search revealed only two norbornyl gold(III) complexes previously characterized by XRD; see references [3,7].

[29] We recently reported the *syn* insertion of alkynes into Au−Si bonds of gold(I) silyl complexes; see references [11c,f].

[30] For representative references, see: a) R. L. LaLonde, J. Brenzovich, D. Benitez, E. Tkatchouk, K. Kelley, I. I. I. Goddard, F. D. Toste, *Chem. Sci.* **2010**, *1*, 226–233; b) Z. J. Wang, D. Benitez, E. Tkatchouk, W. A. Goddard III, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 13064–13071; c) G. Kovács, A. Lledós, G. Ujaque, *Angew. Chem. Int. Ed.* **2011**, *50*, 11147–11151; *Angew. Chem.* **2011**, *123*, 11343–11347; d) A. Zhdanko, M. E. Maier, *Angew. Chem. Int. Ed.* **2014**, *53*, 7760–7764; *Angew. Chem.* **2014**, *126*, 7894–7898.

[31] For rare examples of gold-catalyzed olefin polymerization involving cationic species, see: a) J. Urbano, A. J. Hormigo, P. de Fremont, S. P. Nolan, M. M. Diaz-Requejo, P. J. Perez, *Chem. Commun.* **2008**, 759–761; b) M. A. Cinellu, L. Maiore, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, C. Manassero, *Organometallics* **2009**, *28*, 7015–7024; c) R. A. Sanguramath, S. K. Patra, M. Green, C. A. Russell, *Chem. Commun.* **2012**, *48*, 1060–1062.

[32] CCDC 1025240 (**4b**) and CCDC 1025241 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.