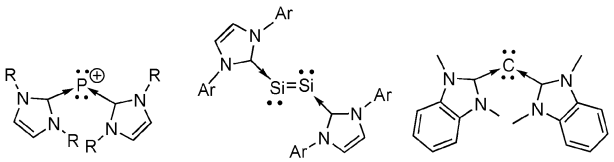
Diazabutadiene complexes of selenium as Se^{2+} transfer reagents†

Jason L. Dutton, Taylor L. Battista, Michael J. Sgro and Paul J. Ragogna*

Received (in Cambridge, UK) 1st September 2009, Accepted 2nd December 2009
First published as an Advance Article on the web 23rd December 2009
DOI: 10.1039/b917841d

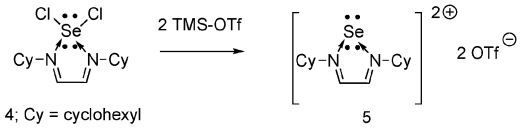
Alkyl and aryl substituted diazabutadiene ligands are shown to support a highly electrophilic "Se^{2+}" synthon, which can be utilized in ligand exchange reactions to generate Se centred dicationic coordination complexes.

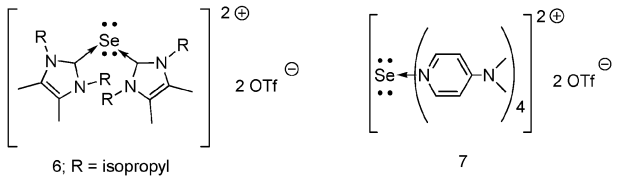
The isolation of new main group element synthons is critical to the development of highly novel structure, bonding and reactivity for the p-block elements. At the forefront of current efforts is the study of low-oxidation state species, where recent examples include the synthesis of stable P(I),[1,2] P(0),[3–5] As(I),[1,6] Si(II),[7,8] Si(0),[9–11] Ge(II),[12,13] B(I),[14] S(II),[15] Te(II),[16,17] and C(0)[18,19] complexes (*e.g.* **1–3**).



The common theme for these achievements is the use of a formally neutral 2-electron donor ligands to stabilize otherwise highly transient species. Although a variety of donors can be utilized (*i.e.* phosphine, imine), a universal player is the N-heterocyclic carbene, as it has been utilized in a large majority of the examples cited above. Once stabilized, the compounds can, in principle, be stored for later use, while still retaining the unique reactivity of a low-oxidation state central core. In this context, we report the isolation and comprehensive characterization of an electrophilic Se^{2+} synthon (**5**) supported by a diazabutadiene (DAB) ligand.‡ The Se(II) centre can be forced from the chelate using NHC or 4-DMAP to generate trapped Se^{2+} dications (**6**, **7**). These transformations indicate that the central element in **5** is uniquely available for further chemistry and can be utilized as the synthetic equivalent of a naked Se^{2+}.

The 1 : 1 stoichiometric reaction between dicyclohexyldiazabutadiene (Cy_2DAB) and $SeCl_2$ (generated *in situ* from $SeCl_4$ and $SbPh_3$)[20] in THF resulted in the immediate precipitation of a yellow powder. The supernatant was decanted and the powder washed with Et_2O to remove the $SbPh_3Cl_2$ byproduct. The isolated material was found to be highly insoluble in all organic solvents, precluding NMR spectroscopy, and the growth of single crystals. Nevertheless, based on studies of the reaction of $SeCl_2$ with aryl substituted





diazabutadiene ligands, as well as results from combustion analysis, the powder was assigned as being the Cy_2DAB chelate of $SeCl_2$ (**4**).[21] The addition of two stoichiometric equivalents of TMS–OTf to a CH_2Cl_2 slurry of **4** resulted in a colour change from yellow to nearly colourless within 40 minutes. The supernatant was then decanted and the colourless powder washed with Et_2O and dried *in vacuo*. A sample of the powder was dissolved in CD_3CN for ^1H NMR spectroscopy, which revealed a set of resonances consistent with a single product containing the Cy_2DAB framework. The singlet arising from the protons on the ligand backbone was shifted far downfield (δ = 9.82 ppm) from the free ligand (δ = 7.92 ppm), which is a typical feature when a large positive charge is imparted onto the ring.[22] X-Ray diffraction studies on single crystals grown from the bulk powder revealed the dicationic Se–Cy_2DAB chelate paired with two triflate anions (**5**) (Fig. 1). The metrical parameters of the five

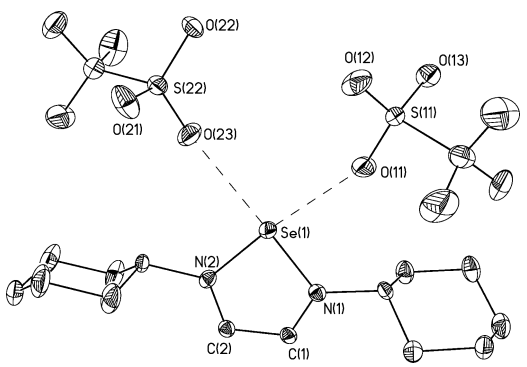


Fig. 1 Solid state structure of **5**. One of the two formula units within the asymmetric unit is represented. Ellipsoids are drawn to 30% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Se(1)–N(1) 1.843(3), Se(1)–N(2) 1.845(3), N(1)–C(1) 1.294(5), C(1)–C(2) 1.415(5), Se(1)–O(11) 2.570(3), Se(1)–O(23) 2.711(3), S(11)–O(11) 1.432(3), S(11)–O(12) 1.433(3), S(11)–O(13) 1.429(3), N(1)–Se(1)–N(2) 84.2(1).

Department of Chemistry, The University of Western Ontario, 1151 Richmond St., London, Ontario, Canada. E-mail: pragogna@uwo.ca; Fax: +1-519-661-3022; Tel: +1-519-661-2111 ext. 87048

† CCDC 738651–738653. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b917841d

membered ring are in almost perfect agreement with previously calculated values.[23] The Se–N bonds average 1.84 Å, and the N–C bonds average 1.30 Å, reflecting retainment of the diimine framework. Long Se–O contacts of 2.57–2.71 Å are observed in the solid state; in solution the compound is distinctly ionic, based on the $^{19}F\{^{1}H\}$ chemical shift of the triflates (δ = −78.4 ppm, *cf.* MeOTf δ = −75.4 ppm; $[NOct]_4[OTf]$ δ = −79.0 ppm).[24]

We have previously synthesized a related Se dication, with diisopropylphenyl R-groups on the DAB ligand.[22] However, this dication was paired with the highly reactive $[SnCl_6]$ dianion, precluding our ability to study the chemistry. Having the dication in hand paired with inert triflate anions, we sought to demonstrate that the Se^{2+} centre is labile, therefore we explored its reactivity in ligand exchange reactions. The 2 : 1 stoichiometric reaction of **5** with the NHC 2,5-diisopropylimidazole-3,4-dimethyl-2-ylidene ($^{i}Pr_2NHC$) in THF resulted in a yellow solution. After workup a light yellow powder was obtained. A sample of the solid was redissolved in $CDCl_3$ for ^{1}H NMR spectroscopy, which revealed a set of resonances indicative of a single product containing the $^{i}Pr_2NHC$ and the absence of Cy_2DAB. Single crystals were grown from a CH_2Cl_2 solution of the bulk powder *via* vapour diffusion of *n*-pentane at 30 °C, and subsequent X-ray diffraction experiments revealed a Se centred dication bound by two $^{i}Pr_2NHC$ ligands (**6**) (Fig. 2).

The Se–C bonds are 1.915(3) Å and 1.920(3) Å for Se(1)–C(10) and Se(1)–C(20), respectively, and the C(10)–Se(1)–C(20) bond angle is 96.3(1)°. These two pieces of data point to purely single Se–C bonds, unlike the partial allene character observed in the C(0) analogue **3** (C–C–C = 134°), similar to the cationic P(I) species (**1**) (C–P–C = 97.4°), and our work with the dicationic Te(II) congener (C–Te–C = 91.5°).[2,16,18] Unlike our tellurium work the addition of two further equivalents of NHC does not give a square planar complex, but rather results in decomposition.

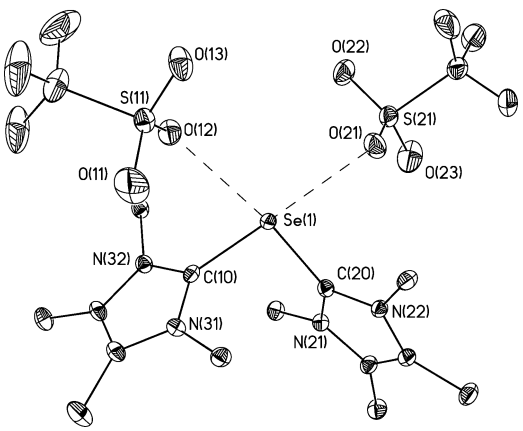


Fig. 2 Solid state structure of **6**. Ellipsoids are drawn to 30% probability hydrogen atoms and methyl groups on the isopropyl substituents are omitted for clarity. Selected bond lengths (Å) and angles (°): Se(1)–C(10) 1.915(3), Se(1)–C(20) 1.920(3), Se(1)–O(12) 2.969(2), Se(1)–O(21) 2.755(3), C(10)–Se(1)–C(20) 96.3(1).

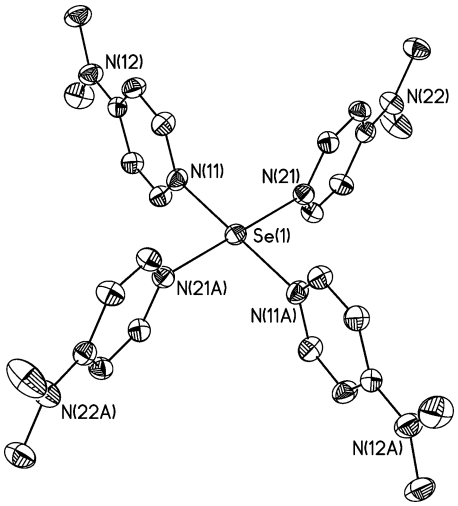
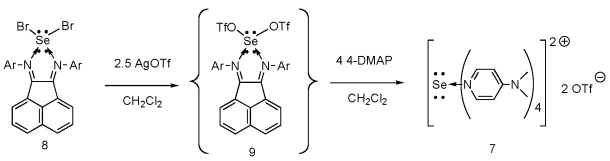


Fig. 3 Solid state structure of **7**. Ellipsoids are drawn to 30% probability. Triflate anions, hydrogen atoms and CH_2Cl_2 solvate are omitted for clarity. One of the two independent dications within the asymmetric unit is represented. The Se atom sits on an inversion centre. Selected bond lengths (Å) and angles (°): Se(1)–N(11) 2.149(5), Se(1)–N(21) 2.159(5), N(11)–Se(1)–N(21) 85.4(2), N(11)–Se(1)–N(21A) 94.6(2).

The reaction of a Se(II) synthon supported by the aryl substituted $Dipp_2BIAN$ ligand (**8**) with an excess of AgOTf and four equivalents of 4-DMAP (4-methylaminopyridine) resulted in a yellow slurry.[21,25] Upon removal of the silver salts and precipitation with *n*-pentane a nearly colourless powder was obtained, the ^{1}H NMR spectrum showed only signals arising from a 4-DMAP derivative. Single crystals were grown from a CH_2Cl_2 solution of the bulk powder *via* vapour diffusion of Et_2O at −30 °C. X-Ray diffraction studies revealed a Se centred dication (**5**) bearing four 4-DMAP substituents in a pinwheel motif, approaching D_{4h} symmetry (Fig. 3). The closest Se–OTf contact is 4.02 Å, well outside the sum of the van der Waals radii for Se and O (3.4 Å). The presence of the $Dipp_2BIAN$ ligand is critical to the reaction for the stabilization of the N-chelated $Se(OTf)_2$ intermediate (**9**); the same reaction using free $SeBr_2$ does not give **7** as the product.



We have shown that it is possible to stabilize a highly electrophilic Se(II) source utilizing diazabutadiene ligands. The Se centre is sufficiently labile to allow for the delivery of the Se^{2+} fragment in ligand exchange reactions, and we are currently exploring its reactivity in small molecule activations.

We thank Natural Sciences and Engineering Research Council (NSERC), The Canada Foundation for Innovation, and The University of Western Ontario for their financial support.

Notes and references

‡ All manipulations were performed under an N_2 atmosphere in a glovebox. Synthesis of **4**: a solution of Ph_3Sb (0.160 g, 0.455 mmol; THF 3 mL) was added to a solution of $SeCl_4$ (0.100 g, 0.455 mmol; THF 5 mL) giving an orange solution. A solution of Cy_2DAB (0.100 g, 0.455 mmol; THF 3 mL) was added resulting in the immediate generation of a yellow slurry. The mixture was centrifuged and the supernatant was decanted. The precipitate was washed with Et_2O (3 × 5 mL) and dried *in vacuo* giving **4** as a yellow powder. Yield 0.134 g, 80%; dp 130–131 °C; FT-Raman (cm^{-1}, ranked intensity ()): 85(2), 123(1), 213(6), 252(3), 330(9), 410(8), 513(13), 587(12), 796(15), 1297(7), 1445(14), 1483(10), 2854(5), 2940(4), 3014(11); FT-IR (cm^{-1}, ranked intensity ()): 435(13), 520(5), 583(14), 869(8), 894(15), 1009(11), 1027(10), 1059(7), 1277(9), 1298(12), 1445(6), 1481(2), 2853(4), 2932(1), 3014(3); elemental analysis, found (calcd): C 45.79 (45.40), H 6.28 (6.54), N 7.19 (7.57)%. Synthesis of **5**: neat TMS–OTf (91 μL, 0.500 mmol) was added to a slurry of **4** (0.099 g, 0.250 mmol; CH_2Cl_2 5 mL) resulting in a colour change from yellow to nearly colourless over 40 minutes. Diethyl ether (10 mL) was added and the solids were allowed to settle. The supernatant was decanted and the powder washed with Et_2O (3 × 5 mL). The solid was then dried *in vacuo* giving **5** as a colourless powder. Yield 0.147 g, 95%; dp 141–143 °C; ^{1}H NMR (CD_3CN, δ ppm): 9.82 (s, 2H), 5.18 (m, 2H, cyclohexyl C-H), 2.31–1.28 (cyclohexyl CH_2); $^{13}C\{^1H\}$ NMR (CD_3CN, δ ppm): 156.7, 71.1, 35.0, 25.0, 24.0; $^{19}F\{^1H\}$ NMR (CH_3CN, δ ppm): −78.4; $^{77}Se\{^1H\}$ NMR (CD_3CN, δ ppm): 1335; FT-Raman (cm^{-1}, ranked intensity ()): 111(2), 252(1), 349(9), 521(14), 645(15), 761(6), 799(7), 1034(3), 1147(8), 1224(11), 1250(12), 1356(13), 1482(4), 2870(10), 2953(5); FT-IR (cm^{-1}, ranked intensity ()): 515(8), 576(12), 640(5), 752(14), 875(15), 1029(3), 1172(4), 1237(1), 1280(2), 1430(13), 1455(9), 1481(10), 2870(11), 2952(7), 3068(6); elemental analysis, found (calcd): C 32.05 (32.16), H 3.56 (4.05), N 4.12 (4.69)%; ESI-MS (m/z^+): [M − H] 299, [M − C_6H_{11}] 217. Crystal data: $C_{16}H_{24}F_6N_2O_6S_2Se_1$, M = 597.45 g mol^{-1}, monoclinic, $C2/c$, a = 20.755(4), b = 20.753(4), c = 22.493(5) Å, β = 102.06(3)°, V = 9474(3) Å^3, T = 150(2) K, Z = 16, D_C = 1.675 Mg m^{-3}, measured reflections = 20 705, unique = 10 832 (R_{int} = 0.0655), refined parameters = 596, $R[I > 2\sigma(I)]$ = 0.0551, w$R_2(F^2)$ = 0.1208, R_1 (all data) = 0.1213, wR_2 (all data) = 0.1456. CCDC 738651. Synthesis of **6**: a solution of NHC (0.102 g, 0.565 mmol; THF 5 mL) was added dropwise at −30 °C to a slurry of **5** (0.175 g, 0.283 mmol; THF 5 mL) resulting in a light yellow solution. *n*-Pentane (3 mL) was added resulting in the deposition of an orange gel. The supernatant was decanted and a further 10 mL of *n*-pentane was added resulting in the precipitation of a light yellow powder. The mixture was cooled to –30 °C and the supernatant decanted. The powder washed with Et_2O (3 × 5 mL). The solids were dried *in vacuo* giving **6** as a light yellow powder. Yield 0.104 g, 50%; dp 102–105 °C; ^{1}H NMR (CD_3CN, δ ppm): 5.13 (sept, $^3J_{H-H}$ 6.8 Hz, 4H), 2.45 (s, 12H), 1.60 (d, $^3J_{H-H}$ 6.8 Hz, 24H); $^{19}F\{^1H\}$ NMR (CH_2Cl_2, δ ppm): −78.4; FT-Raman (cm^{-1}, ranked intensity ()): 112(12), 146(11), 253(13), 313(3), 347(10), 573(15), 753(7), 886(14), 1031(1), 1278(4), 1367(9), 1406(5), 1450(8), 1615(6), 2947(2); FT-IR (cm^{-1}, ranked intensity ()): 516(15), 571(11), 752(14), 781(4), 903(8), 1221(9), 1380(6), 1400(7), 1453(13), 1616(12), 2305(1), 2354(3), 2944(5), 2988(10), 3446(2); ESI-MS (m/z^+): $[M]_2[OTf]_3$ 1327, [M][OTf] 588, [M − ^{i}Pr] 398. Crystal data: $C_{24}H_{40}F_6N_4O_6S_2Se_1$, M = 737.68 g mol^{-1}, monoclinic, $P2_1/c$, a = 12.181(2), b = 17.678(4), c = 15.178(3) Å, β = 95.10(3)°, V = 3256(1) Å^3, T = 150(2) K, Z = 4, D_C = 1.505 Mg m^{-3}, measured reflections = 12 210, unique = 6449 (R_{int} = 0.0326), refined parameters = 400, $R[I > 2\sigma(I)]$ = 0.0423, w$R_2(F^2)$ = 0.0930, R_1 (all data) = 0.0616, wR_2 (all data) = 0.1022. CCDC 738652. Synthesis of **7**: a solution of **8** (0.139 g, 0.188 mmol; CH_2Cl_2 5 mL) was added to solid AgOTf (0.120 g, 0.469 mmol; CH_2Cl_2 5 mL) and was allowed to stir for 10 minutes, giving a dark orange mixture. A solution of 4-DMAP (0.091 g, 0.752 mmol; CH_2Cl_2 3 mL) was added giving a light orange slurry. The mixture was centrifuged and the supernatant decanted. *n*-Pentane (15 mL) was added resulting in a light yellow precipitate. The supernatant was decanted and the precipitate washed with Et_2O (3 × 5 mL), then dried *in vacuo* giving **7** as a beige powder. Yield 0.070 g, 43%; dp 135–138 °C; ^{1}H NMR ($CDCl_3$, δ ppm): 8.40 (d, $^3J_{H-H}$ 6.8 Hz, 2H), 6.55 (d, $^3J_{H-H}$ 7.2 Hz, 2H), 3.05 (s, 6H); $^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ ppm): 155.1, 148.0, 107.0, 39.0; $^{19}F\{^1H\}$ NMR (CH_2Cl_2, δ ppm): −78.6; FT-Raman (cm^{-1}, ranked intensity ()): 111(3), 253(2), 312(11), 348(8), 571(12), 655(13), 760(1), 947(5), 1032(4), 1058(6), 1222(7), 1444(15), 1611(9), 1563(14), 2932(10); FT-IR (cm^{-1}, ranked intensity ()): 520(12), 572(14), 636(7), 755(15), 808(11), 1002(5), 1031(4), 1052(8), 1154(6), 1219(3), 1269(2), 1396(9), 1444(13), 1561(10), 1616(1). Crystal data: $C_{31.5}H_{43}Cl_3F_6N_8O_6S_2Se_1$, moiety formula $[Se_1N_8C_{28}H_{40}][CF_3S_1O_3]_2{\cdot}1.5CH_2Cl_2$; M = 993.16 g mol^{-1}, triclinic, $P\bar{1}$, a = 11.951(2), b = 13.706(3), c = 14.440(3), α = 67.84(3)°, β = 86.92(3)°, γ = 78.47(3)°, V = 2145.8(7) Å^3, T = 150(2) K, Z = 2, D_C = 1.536 Mg m^{-3}, measured reflections = 14 477, unique = 7641 (R_{int} = 0.0380), refined parameters = 536, $R[I > 2\sigma(I)]$ = 0.0815, w$R_2(F^2)$ = 0.2215, R_1 (all data) = 0.1191, wR_2 (all data) = 0.2526. CCDC 738653.

1 B. D. Ellis, M. Carlesimo and C. L. B. Macdonald, *Chem. Commun*., 2003, 1946–1947.
2 B. D. Ellis, C. A. Dyker, A. Decken and C. L. B. Macdonald, *Chem. Commun*., 2005, 1965–1967.
3 Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc*., 2008, **130**, 14970–14971.
4 J. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc*., 2007, **129**, 14180–14181.
5 J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed*., 2007, **46**, 7052–7055.
6 G. Reeske and A. H. Cowley, *Chem. Commun*., 2006, 1784–1786.
7 A. C. Filippou, O. Chernov and G. Schnakenburg, *Angew. Chem., Int. Ed*., 2009, **48**, 5687–5690.
8 R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, *Angew. Chem., Int. Ed*., 2009, **48**, 5683–5686.
9 Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. R. Schleyer and G. H. Robinson, *Science*, 2008, **321**, 1069–1071.
10 S. Ishida, T. Iwamoto, C. Kabuto and M. Kira, *Nature*, 2003, **421**, 725–727.
11 N. Takagi, T. Shimizu and G. Frenking, *Chem.–Eur. J*., 2009, **15**, 3448–3456.
12 P. A. Rupar, V. N. Staroverov, P. J. Ragogna and K. M. Baines, *J. Am. Chem. Soc*., 2007, **129**, 15138–15139.
13 P. A. Rupar, V. N. Staroverov and K. M. Baines, *Science*, 2008, **322**, 1360–1363.
14 Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. I. Schaefer, P. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc*., 2007, **129**, 12412–12413.
15 C. D. Martin, M. C. Jennings, M. J. Ferguson and P. J. Ragogna, *Angew. Chem., Int. Ed*., 2009, **48**, 2210–2213.
16 J. L. Dutton, H. M. Tuononen and P. J. Ragogna, *Angew. Chem., Int. Ed*., 2009, **48**, 4409–4413.
17 G. Reeske and A. H. Cowley, *Chem. Commun*., 2006, 4856–4858.
18 C. A. Dyker, V. Lavallo, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed*., 2008, **47**, 3206–3209.
19 R. Tonner and G. Frenking, *Angew. Chem., Int. Ed*., 2007, **46**, 8695–8698.
20 P. Del Bel Belluz, A. W. Cordes, E. M. Kristof, P. V. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc*., 1989, **111**, 9276–9278.
21 J. L. Dutton, G. J. Farrar, M. J. Sgro, T. L. Battista and P. J. Ragogna, *Chem.–Eur. J*., 2009, **15**, 10263–10271.
22 J. L. Dutton, H. M. Tuononen, M. C. Jennings and P. J. Ragogna, *J. Am. Chem. Soc*., 2006, **128**, 12624–12625.
23 H. M. Tuononen, R. Roesler, J. L. Dutton and P. J. Ragogna, *Inorg. Chem*., 2007, **46**, 10693–10706.
24 L. Huang and X. Huang, *Electronic Encyclopedia of Reagents in Organic Synthesis*, 2005, RM226M, Wiley, New York.

25 Attempts at utilizing compound **5** for this reaction gave protonated 4-DMAP as the main product owing to the acidic protons found on the ligand "backbone". Use of the BIAN ligand circumvents this problem. For the synthesis of **8**, see ref. 21.