

Table 1 Compounds 2–6

Compound	<i>n</i>	R ^a	Yield (%) ^b
2a	2	Ph	70
2b	2	c-C ₃ H ₅	75
2c	2	2-thienyl	71
2d	3	2-thienyl	77
2e	3	Ph	70
3	3	c-C ₆ H ₁₁	66
4	3	Ph	61
6a	—	Ph	55(76)
6b	—	c-C ₆ H ₁₁	71(90)

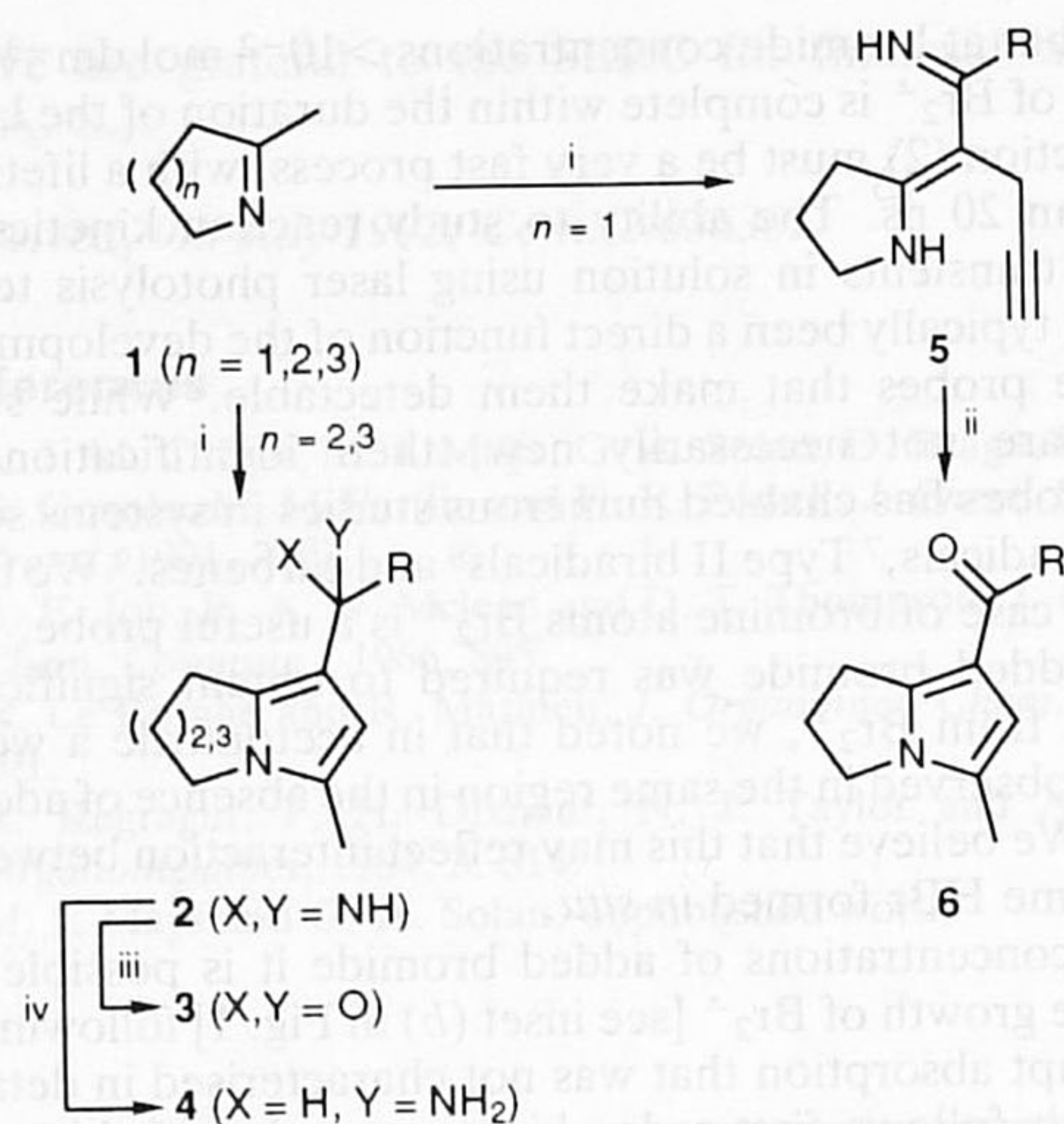
^a c-C₃H₅ = cyclopropyl; c-C₆H₁₁ = cyclohexyl. ^b Overall yields from 1. In parentheses, yield of 6 from 5. Yields are not optimized.

bromide and final cycloamination.⁷ The imino moiety (X, Y = NH) can be hydrolysed quantitatively (1 mol dm⁻³ HCl, THF) to 3 (X, Y = O) or reduced (NaBH₄, MeOH, 20 °C) to the corresponding primary amine function 4 (X = H, Y = NH₂) in 87% yield. Treatment of methylpyrrolines 1 (*n* = 1) as above resulted in the formation of the prop-2-ynylated derivatives 5 in 80–90% yield, after being chromatographed on silica gel (ethyl acetate–hexane, 1:1). Then, heating an ethanolic solution (100 °C, sealed tube) of 5 in the presence of triethylamine followed by aqueous work-up and column chromatography on silica gel (CH₂Cl₂–MeOH, 5:1) led to pyrrolizidine derivatives 6 in 76–90% yield.

In summary, different types of 1-functionalized *N*-bridgehead heterocycles, e.g. pyrrolizidines, indolizidines and azaazulenes, are straightforwardly synthesized from readily available, cheap starting materials in good overall yields; the whole process comprises four steps (metallation of an imine, addition to a nitrile, propynylation, and intramolecular *N*–H addition to an alkyne function) and is achieved in one-pot in most instances. The reaction seems to be of wide scope, as aromatic, heteroaromatic and aliphatic, in particular cyclopropyl,⁸ nitriles can be used.

This work was supported in part by the Dirección General de Investigación Científica y Técnica (DGICYT, PB88-0500). V. K. and E. R. thank the Ministerio de Educación y Ciencia for fellowships.

Received, 17th June 1992; Com. 2/03170A



Scheme 1 Reagents and conditions: i, lithium diisopropylamide (LDA)–tetrahydrofuran (THF) (–78 °C, 30 min), RCN (–78 °C, 3 h), prop-2-ynyl bromide (–78 to 25 °C, 14 h); ii, EtOH–Et₃N, 100 °C, 6 h; iii, 1 mol dm⁻³ HCl, THF, 2 h, 20 °C; iv, NaBH₄, MeOH, 20 °C

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Insertion of Norbornene into Aryl–Palladium(II) Bonds: Mechanistic Aspects of the Subsequent C–H Activation

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The insertion of norbornene into the Pd–C bond of the cationic phenylpalladium(II) complex [PdPh(pmdien)]OTf (2, pm dien = *N,N,N',N',N''*-pentamethyldiethylenetriamine, OTf = trifluoromethanesulfonate) yields a 1:1 enantiomeric mixture of an *ortho* 2-*exo*-norbornyl-substituted phenylpalladium(II) compound via selective, intramolecular C–H activation of the phenyl ring.

The activation of relatively unreactive C–H bonds via metallation reactions is a very useful reaction in transition-metal catalysed organic synthesis as it provides a facile route to the functionalization of alkanes and arenes. When the metallating agent is a palladium(II) centre attacking an arene the ensuing

reaction can be regarded as an electrophilic substitution.¹ Such reactions are well known and studied for arenes which contain an intramolecularly coordinating group that directs the metal to its *ortho* site(s) for C–H activation.¹ We here report a mechanistic study on a reversible phenyl C–H

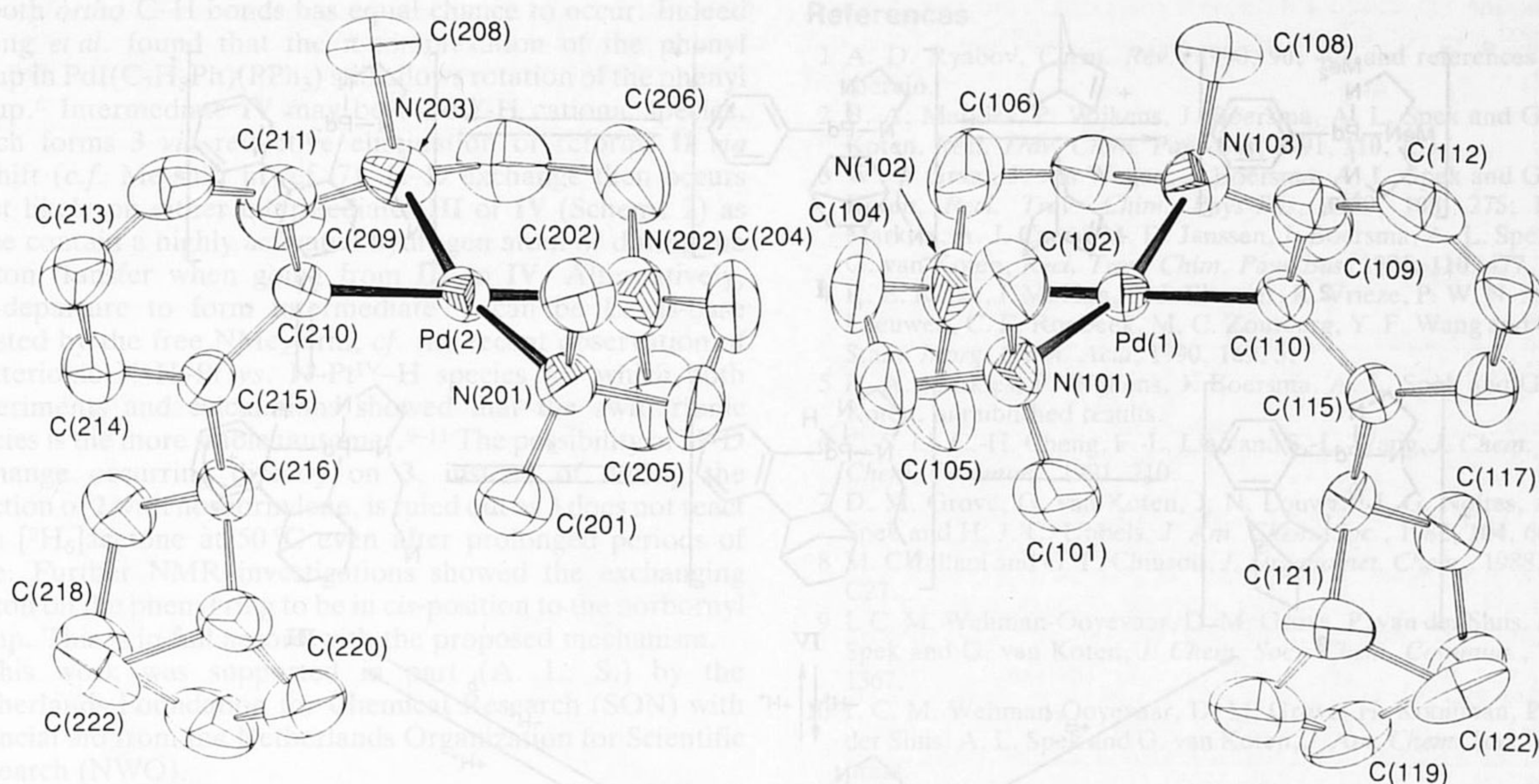
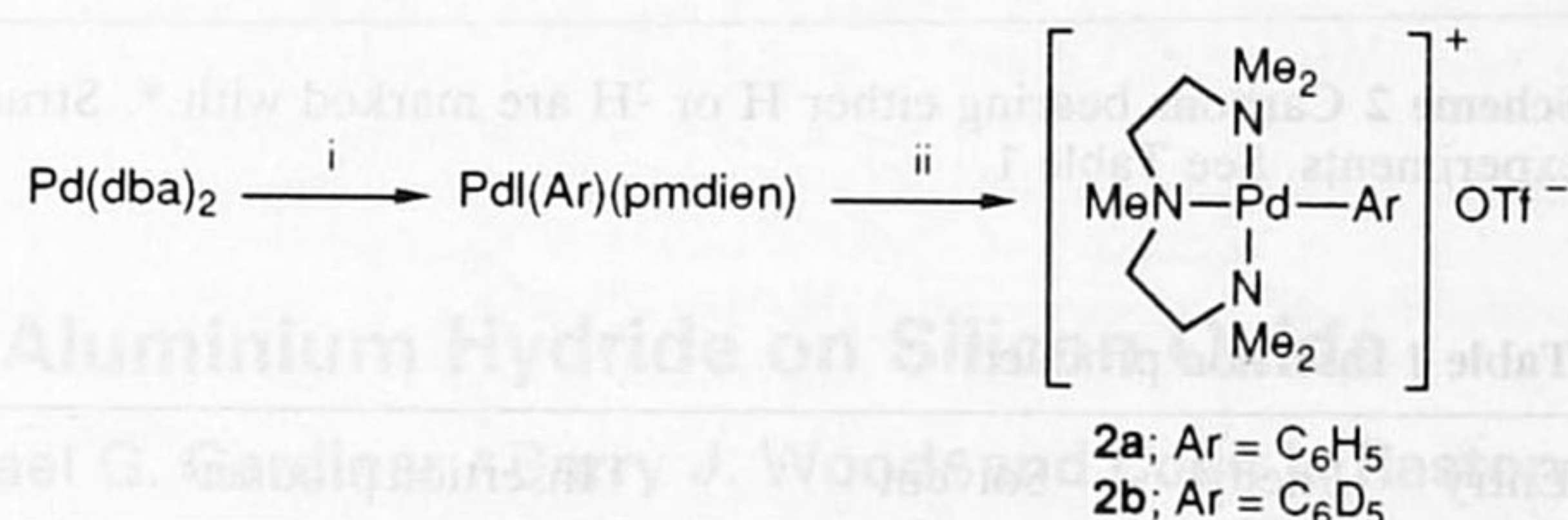


Fig. 1 ORTEP drawing (50% probability level) of both residues of the cation $[\text{Pd}(\text{C}_7\text{H}_8\text{-Ph-}o)(\text{pmdien})]^+$ **3a** with the adopted numbering system. Selected bond distances (\AA) and angles ($^\circ$): Pd(1)–N(101) 2.101(6), Pd(1)–N(102) 2.126(6), Pd(1)–N(103) 2.093(6), Pd(1)–C(110) 2.000(6), N(101)–Pd(1)–N(103) 164.7(2); Pd(2)–N(201) 2.093(6), Pd(2)–N(202) 2.119(6), Pd(2)–N(203) 2.094(6), Pd(2)–C(210) 1.999(6), N(201)–Pd(2)–N(203) 165.5(2).

activation that takes place after a norbornene molecule has inserted into the Pd–C bond of a cationic phenylpalladium(II) complex containing the terdentate coordinating triamine ligand pmdien.

Recently, we reported a facile route for the synthesis of cationic monoorganopalladium(II) compounds containing a terdentate nitrogen-donor ligand, *viz.* $[\text{PdR}(\text{NN}'\text{N})]\text{OTf}$ (**1**, R = Me or aryl; NN'N = 2,6-bis[(dimethylamino)methyl]pyridine; OTf = trifluoromethanesulfonate).² The new cationic complexes $[\text{Pd}(\text{Ar})(\text{pmdien})]\text{OTf}$ (Ar = C_6H_5 **2a** or C_6D_5 **2b**) were obtained similarly in 84% (**2a**) and 82% (**2b**) yield (Scheme 1).[†] Reaction of **2a** with 1.5 equiv. of norbornene in acetone for 24 h at 50 °C afforded the insertion product $[\text{Pd}(\text{C}_7\text{H}_{11}\text{-Ph-}o)(\text{pmdien})]\text{OTf}$ (**3a**, C_7H_{11} = 2-*exo*-norbornyl in 1:1 mixture of enantiomers) in 84% yield after recrystallization from methanol–diethyl ether.[†] The complex $[\text{PdPh}(\text{NN}'\text{N})]\text{OTf}$ **1** reacted with norbornene to give a product analogous to **3a**. We were, however, unable to obtain this product in pure form.



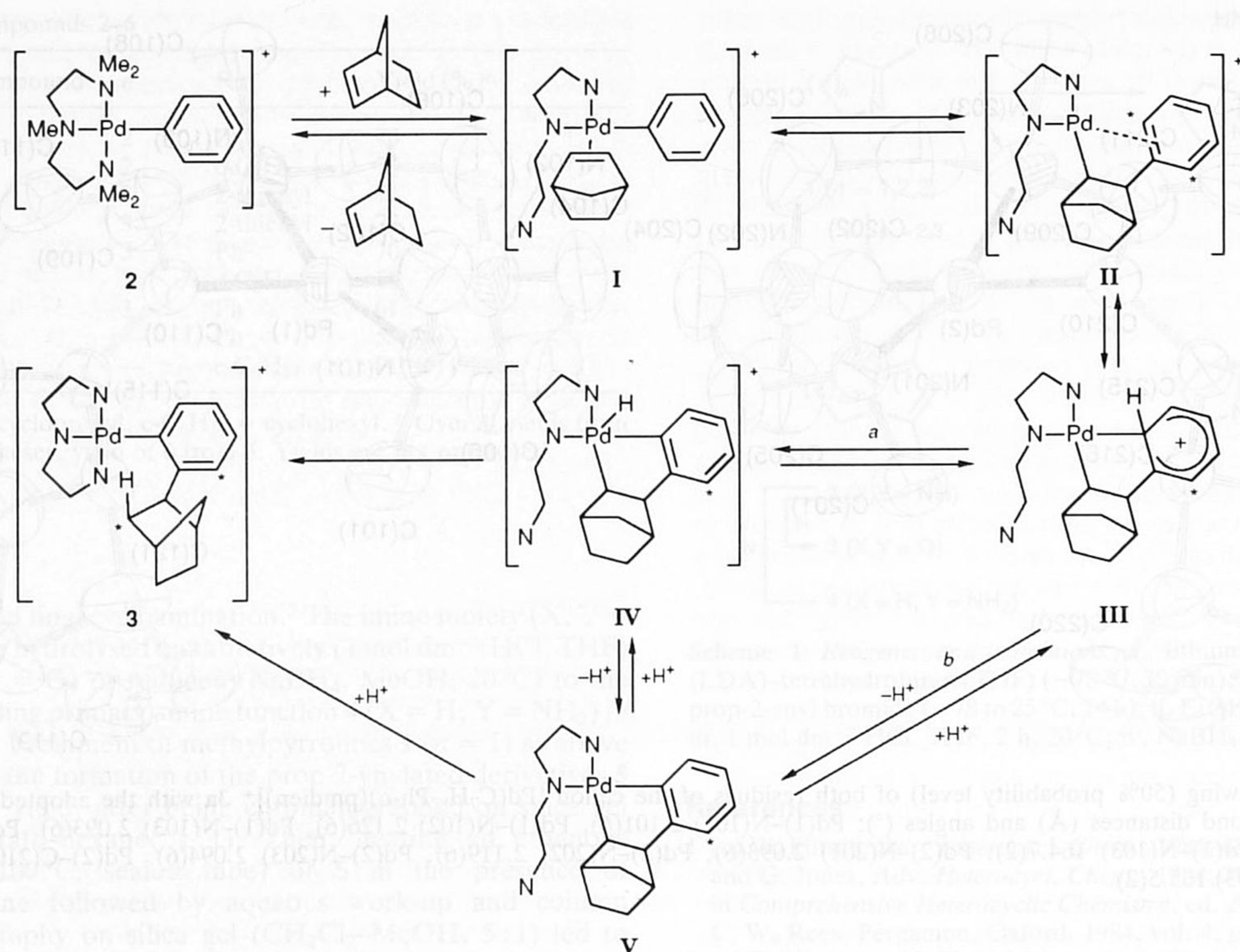
Scheme 1 Reagents and conditions: i, $\text{C}_6\text{H}_5\text{I}$ or $\text{C}_6\text{D}_5\text{I}$, pmdien, 40 °C, 1 h, C_6H_6 ; ii, AgOTf, 20 °C, acetone, (dba = dibenzylideneacetone)

The molecular structure of **3a** has been established by an X-ray crystal structure determination[‡] and ORTEP representations of the two crystallographically independent cations in the unit cell are shown in Fig. 1. These surprising structures are enantiomers and contain a phenyl group which is σ -bonded to the palladium centre and is *ortho* substituted with a 2-*exo*-norbornyl group. As normally found in arylpalladium(II) compounds,³ the phenyl ring in both residues is almost perpendicular to the coordination plane [the angles between the least-square planes are 84.5(3) and 87.4(3)°, respectively]. The N(101)–Pd(1)–N(103) and N(201)–Pd(2)–N(203) bond angles [164.7(2) and 165.5(2)°] and the Pd(1)–N(102) and Pd(2)–N(202) bond lengths [2.126(6) and 2.119(6) \AA] deviate less from the expected values than is found in similar complexes.^{2,4,5} Apparently, because of its greater flexibility, the pmdien ligand is more suited for *mer*-coordination modes

[‡] *Crystal data* for **3a**: $\text{C}_{22}\text{H}_{38}\text{N}_3\text{Pd}.\text{CF}_3\text{SO}_3$, $M = 600.05$, triclinic, space group $P\bar{1}$, $a = 10.5617(6)$, $b = 13.8168(8)$, $c = 18.8383(9)$ \AA , $\alpha = 78.616(4)$, $\beta = 80.496(4)$, $\gamma = 89.283(4)^\circ$, $U = 2657.4(3)$ \AA^3 , $Z = 4$, $D_c = 1.500$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 8.1$ cm^{-1} , $F(000) = 1240$. Data were collected for a block-shaped crystal (0.2 \times 0.3 \times 0.5 mm) on an Enraf-Nonius CAD4 diffractometer using Mo-K α (Zr-filtered) radiation ($\lambda = 0.71073$ \AA), $T = 295$ K. Of a total of 12 177 independent reflections ($\theta < 27.5^\circ$) 7055 with $I > 2.5\sigma(I)$ were used to solve (direct methods, SHELXS86) and refine (full-matrix, SHELX76) the structure (final $R = 0.050$, $R_w = 0.057$, $w^{-1} = [\sigma^2(F) + 0.00052 F^2]$, $S = 2.08$). H-atoms were placed at calculated positions. The number of refined parameters was 644 and the maximum residual electron density was 0.76 $\text{e}\text{\AA}^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] *Spectroscopic data* (^1H and ^{13}C NMR in CD_3COCD_3 , δ rel. to SiMe_4 , J/Hz) for **2a**: ^1H NMR, 2.38 (s, 3H, NMe_2), 2.74 (ddd, 2H, 3J 13.1, 4J 3.0, 5J 0.9, CH_2NMe_2), 2.85 (s, br, 7H, $\text{NMe}_2 + \text{CH}_2\text{NMe}_2$), 2.88 (d, 1H, 4J 3.4, CH_2NMe_2), 2.90 (s, 3H, NMe), 3.59 (td, 2H, 3J 13.8, 4J 3.0, CH_2NMe), 3.79 (td, 2H, 3J 13.4, 4J 3.2, CH_2NMe), 6.93 (tt, 1H, 3J 7.1, 4J 1.3, *p*-Ph), 7.00 (m, 2H, *m*-Ph), 7.42 (d, 1H, 3J 7.9, *o*-Ph), 7.64 (d, 1H, 3J 7.0, *o*-Ph); ^{13}C NMR, 41.33 (NMe), 51.00 (NMe₂), 53.24 (NMe₂), 57.74 ($-\text{CH}_2-$), 67.53 ($-\text{CH}_2-$), 124.45 (Ph-C4), 127.61, 127.68 (Ph-C3,5), 134.92 (Ph-C2,6), 159.89 (Ph-C1).

For **3a**: ^1H NMR, 1.30 (m, 1H, norb), 1.49 (m, 1H, norb), 1.66 (m, 4H, norb), 1.95 (m, 1H, norb), 2.12 (m, 1H, norb), 2.20 (m, 1H, norb), 2.30 (s, 3H, NMe), 2.40 (4H, NMe + norb), 2.79 (m, 4H, $-\text{CH}_2-$), 2.88 (s, 3H, NMe), 2.98 (s, 6H, NMe), 3.71 (m, 4H, $-\text{CH}_2-$), 4.48 (m, 1H, norb), 6.87 (td, 1H, 3J 7.2, 4J 1.6, Ph-H4), 6.96 (td, 1H, 3J 7.4, 4J 1.3, Ph-H5), 7.05 (dd, 1H, 3J 7.7, 4J 1.5, Ph-H6), 7.33 (td, 1H, 3J 7.4, 4J 1.4, Ph-H3); ^{13}C NMR, 28.84 (norb), 33.27 (norb), 37.26 (norb), 37.76 (norb), 41.09 (NMe), 43.78 (norb), 46.29 (norb), 50.98 (NMe), 51.02 (NMe), 52.23 (norb), 53.97 (NMe), 54.36 (NMe), 57.63 ($-\text{CH}_2-$, 2C), 67.43 ($-\text{CH}_2-$), 67.56 ($-\text{CH}_2-$), 125.11 (Ph-C4), 125.18 (Ph-C5), 125.77 (Ph-C6), 134.39 (Ph-C3), 152.95 (Ph-C2), 158.33 (Ph-C1, *ipso*).



Scheme 2 Carbons bearing either H or ²H are marked with *. Structures I-V are proposed intermediates on the basis of deuterium-labelling experiments. See Table 1.

Table 1 Insertion products

Entry	Phenyl	Solvent	Insertion product ^a
1	C ₆ H ₅	[H ₆]acetone ^b	C ₇ H ₁₁ -C ₆ H ₄ 3a
2	C ₆ H ₅	[² H ₆]acetone	C ₇ H ₁₀ ² H-C ₆ H ₃ ² H 3b
3	C ₆ ² H ₅	[H ₆]acetone	C ₇ H ₁₁ -C ₆ H ² H ₃ 3c
4	C ₆ ² H ₅	[² H ₆]acetone	C ₇ H ₁₀ ² H-C ₆ ² H ₄ 3d

^a Carbons bearing either H or D are marked with * in Scheme 2.

^b Non-deuteriated.

than other terdentate ligands that also contain five-membered chelate rings.^{2,4}

We believe that the first step in the formation of **3a** is the insertion of norbornene into the Pd-aryl bond. This should then be followed by C-H activation of the aryl ring to give **3a**. The full reaction sequence would be as presented in Scheme 2 for one of the two possible coordination sites for the norbornene molecule. The first step in Scheme 2 is the dissociation of one of the Pd-NMe₂ bonds followed by coordination of a norbornene to the open in-plane coordination site to give intermediate I. Although the NMe group is a prochiral group becoming chiral on dissociation of an NMe₂ group, thereby influencing the coordination mode of the norbornene, a 1:1 enantiomeric mixture of the 2-*exo* insertion compound **3** will always be obtained as both NMe₂-groups have equal possibilities to dissociate. We consider it unlikely that insertion of norbornene occurs from a five-coordinate intermediate, which would also result in a 1:1 mixture of enantiomers, as the strongly σ -donating N-donors render the metal centre only weakly electrophilic. Subsequently, intermediate II is formed *via* insertion of the norbornene molecule in the Pd-C bond and subsequent π -complexation of the arene ring to the palladium-centre. Recently, the formation of such π -complexes of η_2 -arene species was confirmed by X-ray crystallography for the complex PdI(C₇H₈Ph)(PPh₃) by

Cheng and coworkers.⁶ Electrophilic attack of the palladium on the *ortho*-position of the phenyl group then gives III, a Wheland-type intermediate. Only one organometallic example of this type of arenonium intermediate has been structurally characterized, *viz.* [PtI(MeC₆H₃(CH₂NMe₂)₂-*o,o'*)]BF₄.⁷ The palladium(IV) species IV (route *a* in Scheme 2) is formed by a shift of the hydrogen from the phenyl to the metal. Reductive coupling of the hydride and the norbornyl group followed by reformation of the Pd-NMe₂ bond then forms **3a**. Alternatively, deprotonation of III (route *b* in Scheme 2) affords a neutral palladium(II) metallacycle V which, *via* external attack by a proton, reacts to form either **3a**, III or IV. Catellani and Chiusoli have reported the synthesis of an analogous metallacycle containing 1,10-phenanthroline as a ligand.⁸ Attempts to isolate metallacycle V under the strongly basic conditions described by Catellani and Chiusoli have failed so far.

Conclusive experimental evidence for the proposed intramolecular reaction sequence, was obtained by using a pentadeuteriophenyl group in the starting material **2b** to trace the fate of the transferred proton. A signal corresponding to one aryl-proton in the ¹H NMR spectrum of the product (**3c**, see Table 1) was found when using acetone as a solvent while no deuterium was incorporated in the norbornyl group. This implies that during the course of the reaction not only reversible C-H activation of the phenyl ring takes place but that also a H-D exchange with the solvent occurs. This was corroborated by the results obtained in [²H₆]acetone. A list of the obtained insertion products is presented in Table 1. From this table it is clear that H-D exchange occurs both on the phenyl and on the norbornyl group. To explain this, we assume that the C-H activation process itself is a fast equilibrium and that interconversion between II and III occurs several times before collapse to intermediate IV or V and product **3** takes place. As there is rotational freedom of the phenyl ring around the connecting C-C bond between the phenyl and the norbornyl group in the π -complex II activation

of both *ortho* C–H bonds has equal chance to occur. Indeed Cheng *et al.* found that the π -complexation of the phenyl group in PdI(C₇H₈Ph)(PPh₃) still allows rotation of the phenyl group.⁶ Intermediate **IV** may be a Pd^{IV}-H cationic species, which forms **3** *via* reductive elimination or reforms **II** *via* H-shift (*c.f.* Me-shift in ref. 7). H–D exchange then occurs most likely on either intermediates **III** or **IV** (Scheme 2) as these contain a highly activated hydrogen atom or during the proton transfer when going from **III** to **IV**. Alternatively, H⁺-departure to form intermediate **V** can be Lewis-base assisted by the free NMe₂-arm, *cf.* the recent observation of zwitterionic N–H–Pt *vs.* N–Pt^{IV}–H species for which both experiments and calculations showed that the zwitterionic species is the more stable tautomer.^{9–11} The possibility of H–D exchange occurring directly on **3**, instead of during the reaction of **2** with norbornylene, is ruled out as **3** does not react with [²H₆]acetone at 50 °C even after prolonged periods of time. Further NMR investigations showed the exchanging proton on the phenyl ring to be in *cis*-position to the norbornyl group. This is in full accord with the proposed mechanism.

This work was supported in part (A. L. S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Received, 29th June 1992; Com. 2/03438G

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Adsorption of the Trimethylamine Adduct of Aluminium Hydride on Silicon Oxide

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X-Ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS) studies of surface adsorbed H₃AlNMe₃ on a SiO₂ substrate support molecular adsorption, most likely as a five coordinate species, H₃AlNMe₃(O=), and an aluminium rich species (Al : N 2 : 1) sensitive to the amount of exposure to the vapour; *ab initio* molecular orbital calculations on H₃AlNH₃ and H₂O gave formation of H₃AlNH₃(OH₂) as energetically favoured by 4.53 kcal mol⁻¹, and fragmentation of H₃AlNH₃(OH₂) to H₃AlOH₂ and NH₃ requiring 13.16 kcal mol⁻¹ (1 cal = 4.184 J).

The trimethylamine adduct (TMAA) of aluminium hydride, H₃AlNMe₃, **1** is a highly volatile solid, which is monomeric in the gas phase,¹ yet weakly associated *via* unsymmetrical bridging hydrides in the solid state.² It has application in delivering metal to surfaces, as in electroless^{3,4} and electro-solution⁵ aluminium plating, chemical beam epitaxy (CBE),^{6,7} metal-organic vapour-phase epitaxy (MOVPE),^{8,9} and laser-induced chemical vapour deposition (LICVD)¹⁰ technology. The absence of direct metal–carbon interactions in this compound avoids the formation of carbonaceous material, which is a problem when using organometallic compounds for conventional thermolytic chemical vapour deposition.¹¹ The adsorption and degradation of the compound on silicon, aluminium and gallium arsenide have been reported,^{6–8} although a detailed understanding of the nature of the adsorbed species is lacking. Herein, we report studies on the adsorption of **1** on thermally grown silicon oxide on a silicon wafer, which shows two exposure dependent adsorption processes. We also report a theoretical study on H₃AlNMe₃(OH₂) as a model for the adsorption of **1** onto surface oxygen centres.

Compound **1** was prepared from lithium aluminium hydride and trimethylamine hydrochloride¹² and purified by sublima-

tion at 40 °C. Dosing experiments[†] were performed on a silicon wafer with an oxide layer thermally grown to *ca.* 5000 Å. The surface was cleaned by washing in acetone prior to ion-beam etching (Ar⁺ or Xe⁺) for 20 min, 3 μA cm⁻² in the vacuum chamber. A SSIMS survey of the cleaned surface suggested a trace of hydroxy groups (SiOH, M⁺ 45) and XPS analysis gave an adventitious carbon level of <3 atom%. After 15 min in the vacuum chamber (*ca.* 10⁻⁸ Torr; 1 Torr = 133.3 Pa), there was substantial build up of hydroxy groups, along with carbonaceous material, thus dosing was carried out

[†] The experiments were performed in ultrahigh vacuum using a Perkin-Elmer PHI Model 560 surface analysis system. This system contains a double pass CMA (Model 25-270AR) with a perpendicularly mounted dual anode (Mg/Al), X-ray sources operated at 500 W. Two Mg-K α X-ray sources were operated, each at 250 W. The maximum energy resolution of the CMA was 1.2 eV operated for XPS analysis in the fixed analyser transmission (FAT) mode with a pass energy of 25 eV for the Ag 3d_{5/2} emission. The electron binding energies (*E*_B) were calibrated against the Au 4f_{7/2} emission at *E*_B 84 eV.¹⁷ The exposure rate was measured in langmuirs (L); 1 L = 1 second exposure at 1 × 10⁻⁶ Torr. Charging was referenced to the Si 2p photoelectron peak from SiO₂ at 103.8 eV.¹⁸