Carbon–Hydrogen and C–X (X = Cl or $SiMe_3$) Bond Activation. 1-Cyclopalladation and Oxidation of Some Derivatives of 2-[(Dimethylamino)methyl]naphthalene‡

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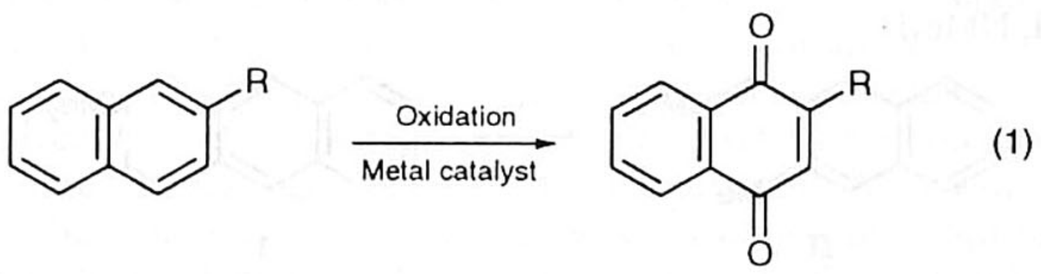
The regioselective palladation reactions of 3-substituted derivatives of 2-[(dimethylamino)methyl]-naphthalene, $C_{10}H_6(CH_2NMe_2)$-2-R-3 (R = Cl, $SiMe_3$ or $OSiMe_3$), were studied. For the substrate with R = Cl, no cyclopalladation at position 1 was observed and the co-ordination complex was isolated. The 3-palladated product was formed in 10% yield *via* C–Cl activation. The reaction of 2-[(dimethylamino)methyl]-3-methylnaphthalene with $Pd(O_2CMe)_2$ and work-up with LiCl did lead to palladation at position 1, the resulting complex being isolated in 96% yield. The crystal structure of bis(acetonitrile){2-[(dimethylamino)methyl]-3-methyl-1-naphthyl}palladium trifluoromethanesulfonate was solved. Monoclinic, space group $P2_1/n$, with a = 13.193(1), b = 11.801(1), c = 14.797(1) Å, β = 105.15(1)°, Z = 4. The structure was refined to R = 0.042 for 3455 reflections with $I > 2.5\sigma(I)$. Palladation at position 1 was also achieved by oxidative addition of 1-bromo-2-[(dimethylamino)methyl]-naphthalene to $[Pd(dba)_2]$ (dba = dibenzylideneacetone). Protection of C(3) with R = $SiMe_3$ resulted in quantitative replacement of the $SiMe_3$ group by palladium. Silicon–oxygen bond cleavage was observed when the substrate with R = $OSiMe_3$ was treated with $Pd(O_2CMe)_2$. Palladium bis{3-[(dimethylamino)methyl]-2-naphtholate} was obtained quantitatively. Oxidation of several arylpalladium complexes with Bu^tO_2H was achieved in the presence of $[VO(acac)_2]$ (acac = acetylacetonate) or $[\{RhCl(cod)\}_2]$ (cod = cycloocta-1,5-diene) as catalyst. The corresponding 1-naphthols were prepared in yields varying from 33 to 78%. In a number of cases the corresponding 1,4-naphthoquinones were prepared in yields varying from 18 to 38%.

The oxidation of naphthalenes to 1,4-naphthoquinones [see equation (1)] is a well known process in the synthesis of



(1)

certain pharmaceuticals. Since the product-to-waste ratio is often extremely unfavourable,[1] especially when oxidants like CrO_3 are applied, there is a need to design new reaction routes in which the naphthalene substrate is selectively oxidized to the desired naphthoquinone product.

Recently we set out to investigate the feasibility of a palladium-mediated reaction sequence leading to regioselective oxygenation of an aromatic substrate [see Scheme 1(*a*)].[2] An example of this reaction in which regioselective *ortho*-hydroxylation of [(dimethylamino)methyl]benzene was achieved with *tert*-butyl hydroperoxide is shown in Scheme 1(*b*). Crucial steps in this cycle, when this would be applied to the oxygenation of naphthalenes, are the selective palladation of the 1 position of naphthalene and subsequent oxygenation of the Pd–C bond.

Previously, we had found that direct palladation of 2-[(dimethylamino)methyl]naphthalene, a model ligand chosen for its ability to direct cyclometallation and to keep the metal centre in a well defined conformation, gave the 3-palladated product in almost quantitive yield.[3] Interestingly, a cationic derivative of this product reacts selectively with Bu^tO_2H in the presence of a catalytic amount of $[\{RhCl(cod)\}_2]$ (cod = cycloocta-1,5-diene) to give a product in which the positions 1, 2 and 4 are oxygenated [see Scheme 1(*c*)], thus demonstrating the feasibility of the approach shown in Scheme 1(*a*).[4] The fact that 2-[(dimethylamino)methyl]naphthalene undergoes clean palladation at position 3 is rather surprising, as position 1 in a naphthalene system would be kinetically preferred for electrophilic palladation.

In an attempt to direct palladation to the 1 position, we prepared several derivatives of 2-[(dimethylamino)methyl]-naphthalene, all containing a substituent in the 3 position, *i.e.* Cl **I**, Me **II**, $OSiMe_3$ **III** and $SiMe_3$ **IV** (see Scheme 2), and tested their regioselectivity in cyclopalladation reactions with $Pd(O_2CMe)_2$ or $Li_2[PdCl_4]$. The results of these experiments and of the subsequent oxidations of the obtained cyclopalladated naphthalenes by Bu^tO_2H are presented.

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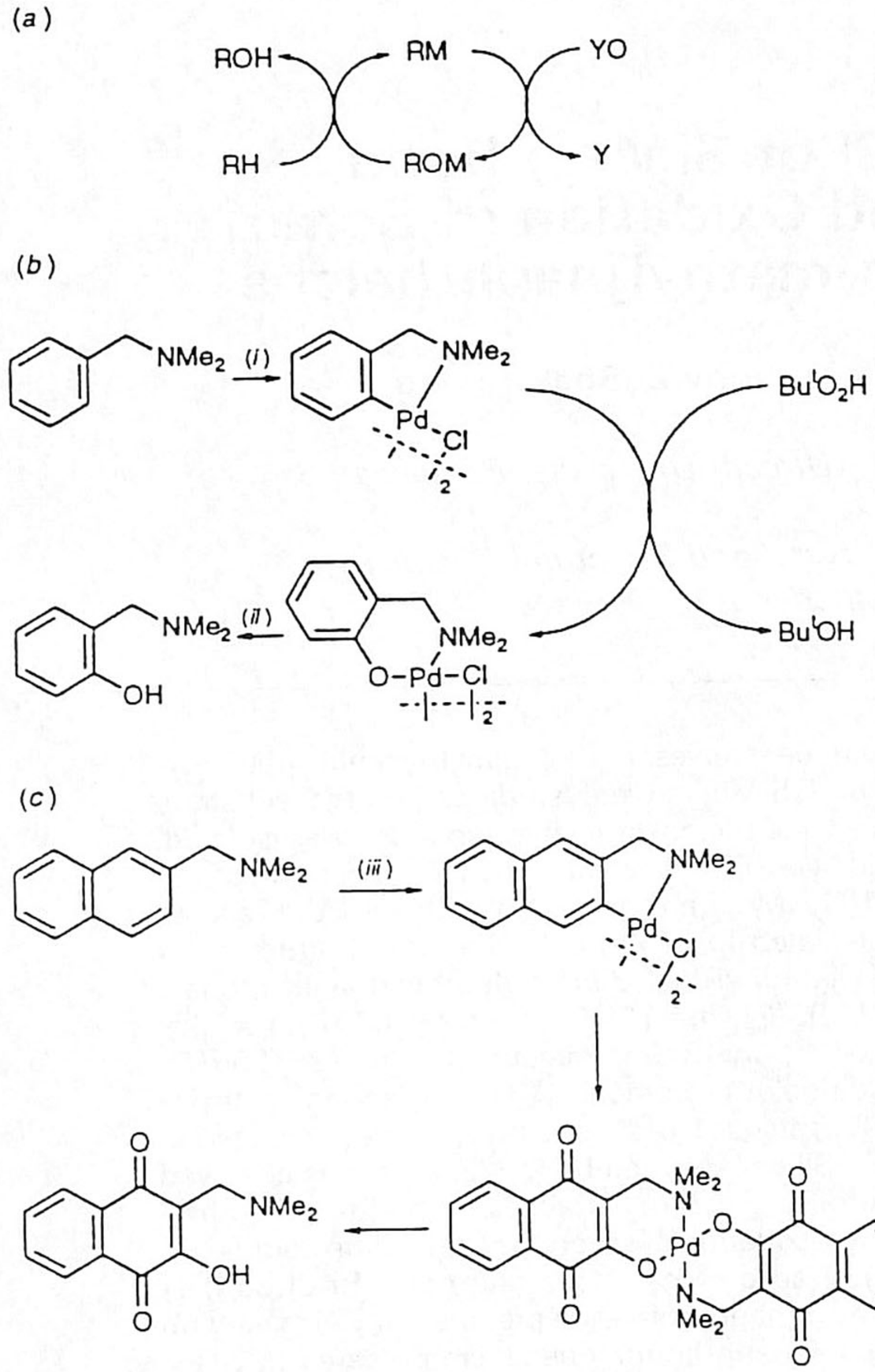
‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: mmHg ≈ 133 Pa.

Throughout the paper the (dimethylamino)methyl and chloro substituents in compound **I** have been assigned locant numbers 2 and 3, respectively, to enable comparison with the analogous compounds **II**–**IV**. However, the correct name according to IUPAC recommended nomenclature is 2-chloro-3-[(dimethylamino)methyl]naphthalene, where alphabetical ordering of substituents prevails.



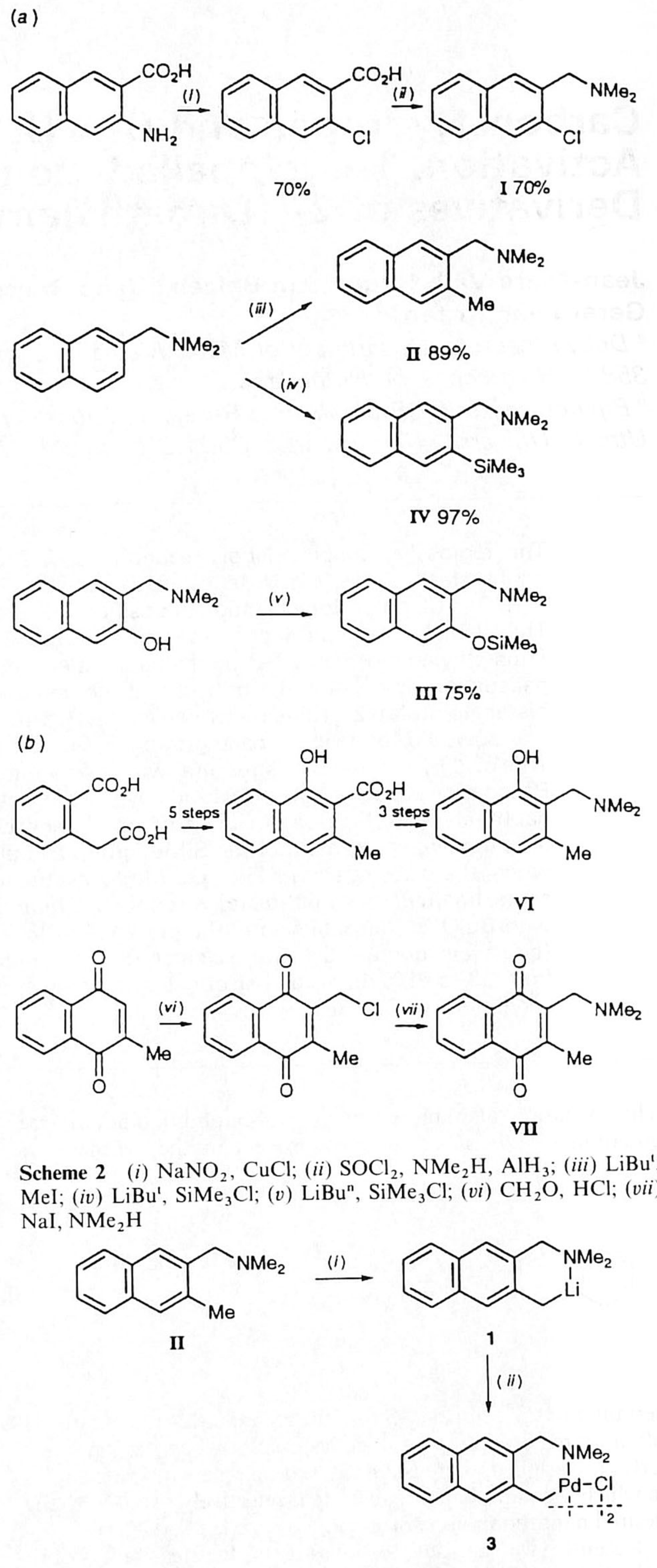
Scheme 1 (*a*) Metallation and oxidation of aromatic compounds (R = aryl group, M = metal, Y = oxygen carrier), exemplified by metallation and subsequent oxygenation of (*b*) [(dimethylamino)-methyl]benzene and (*c*) 2-[(dimethylamino)methyl]naphthalene. (*i*) $Pd(O_2CMe)_2$, LiCl or $Li_2[PdCl_4]$; (*ii*) N_2H_5OH; (*iii*) $Li_2[PdCl_4]$

Results

Syntheses of the Starting Compounds [*see Scheme* 2(a)].—3-Chloro-2-[(dimethylamino)methyl]naphthalene **I** was prepared from 3-amino-2-naphthoic acid in 50% overall yield, by replacing the amino group by a chloro-substituent,[5] converting the carboxylic group into its amide and reduction of the latter (47% overall yield).[6] The 3-methyl derivative **II** was prepared in 89% yield by reaction of 3-[(dimethylamino)methyl]-2-naphthyllithium[3] with MeI. Reaction of the same naphthyllithium compound with $SiMe_3Cl$ gave **IV** in 97% yield. 3-[(Dimethylamino)methyl]-2-naphthol was treated consecutively with *n*-butyllithium and $SiMe_3Cl$ to give **III** in 75% yield. The 1-naphthyl bromide derivative **V** (see Scheme 4) was prepared in three steps from 2-methylnaphthalene in 80% overall yield.[7]

2-[(Dimethylamino)methyl]-3-methyl-1-naphthol **VI** was prepared in seven steps in 33% overall yield from 2-carboxybenzeneacetic acid. We were unable to reproduce the synthesis of 1-hydroxy-3-methyl-2-naphthoic acid described by Marion and McRae,[8] and instead used a modified version of the procedure described by Rama Rao *et al.*[9] The so obtained 1-hydroxy-3-methyl-2-naphthoic acid was converted in two steps into **VI** [see Scheme 2(*b*)].[6,10]

2-[(Dimethylamino)methyl]-3-methyl-1,4-naphthoquinone **VII** [see Scheme 2(*b*)] was prepared in three steps from 2-methyl-1,4-naphthoquinone (menadione) and isolated as a slightly impure and unstable solid in approximately 50% yield. In this synthesis 2-methyl-1,4-naphthoquinone was chloromethylated in the 2 position of the quinone ring. When the chloromethylated product was treated with NMe_2H a very unselective reaction occurred, probably due to a competitive condensation reaction of NMe_2H and the carbonyl groups of the quinone system.[11] This problem was overcome by replacing the chloro- by an iodo-substituent.



Scheme 2 (*i*) $NaNO_2$, CuCl; (*ii*) $SOCl_2$, NMe_2H, AlH_3; (*iii*) LiBu^t, MeI; (*iv*) LiBu^t, $SiMe_3Cl$; (*v*) LiBu^n, $SiMe_3Cl$; (*vi*) CH_2O, HCl; (*vii*) NaI, NMe_2H

Scheme 3 (*i*) LiBu^n; (*ii*) $[PdCl_2(SMe_2)_2]$; (*iii*) LiBu^n (60%) or LiBu^t (90% yield)

Lithiation Reactions.—The 3-chloro derivative **I** surprisingly reacted with both $LiBu^n$ and $LiBu^t$ to give 3-[(dimethylamino)-methyl]-2-naphthyllithium *via* a chlorine–metal exchange reaction (see Scheme 3). No indications for lithiation at the 1 position were found. Quenching with D_2O and $SiMe_3Cl$ established that only lithiation at position 2 had occurred. Benzylic lithiation of the 3-methyl derivative **II** *via* hydrogen–lithium exchange gave **1** as a thermally stable yellow powder (81% yield, see Scheme 3). Its ^1H NMR spectrum in C_6D_6 gave no indications for a rearrangement of this compound to the aryllithium compound 2-[(dimethylamino)methyl]-3-methyl-1-naphthyllithium, even after heating to 80 °C. Lithiation of the 3-trimethylsilyloxy-substituted substrate **III** resulted in highly selective cleavage of the oxygen–silicon bond. After acidic work-up, 3-[(dimethylamino)methyl]-2-naphthol was isolated in almost quantitative yield.

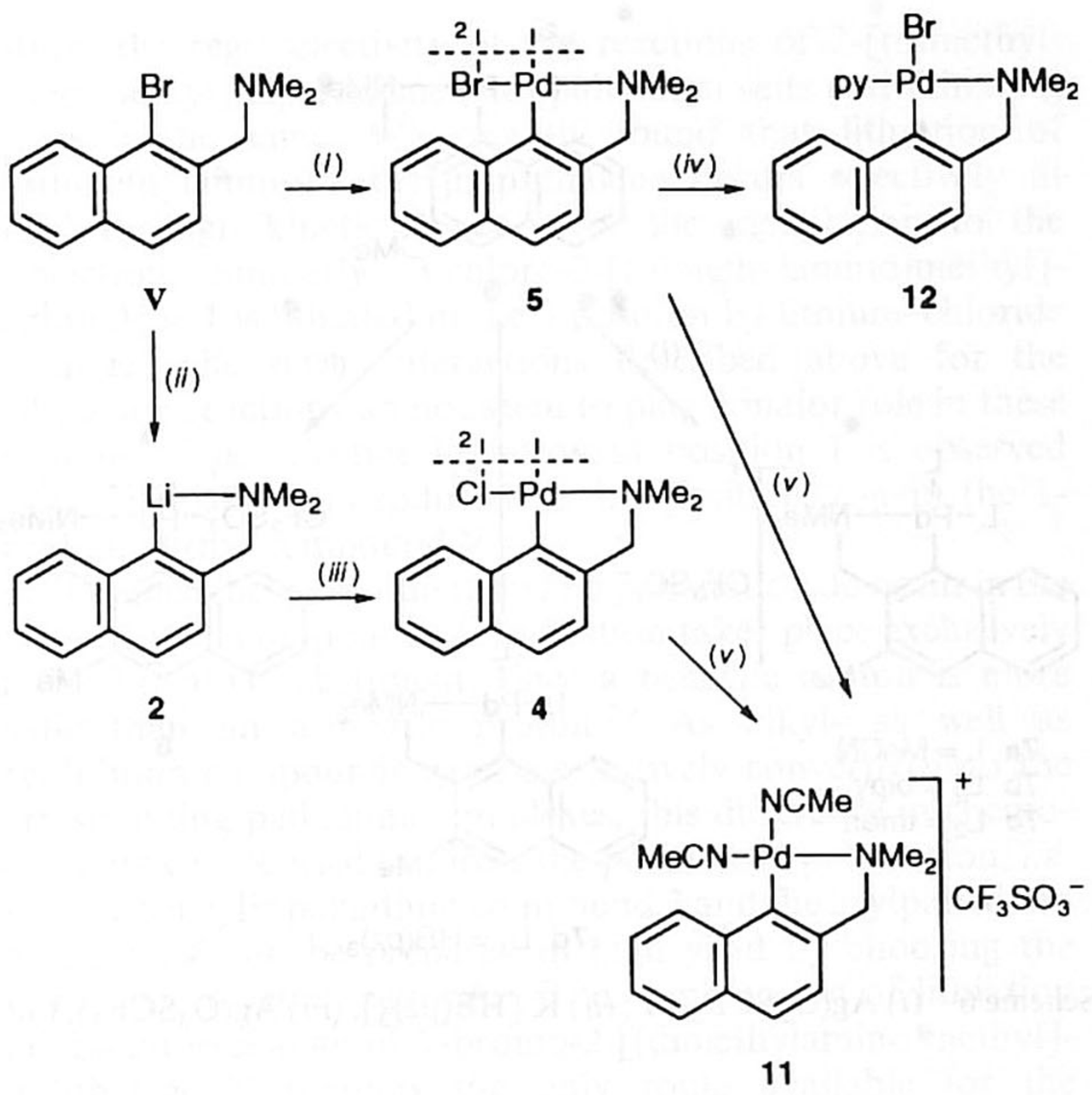
The 3-trimethylsilyl-substituted compound **IV** did not react at all, being recovered quantitatively from a mixture with $LiBu^t$. The 1-bromo derivative **V** could be converted directly into the 1-naphthyllithium compound **2** by the action of $LiBu^n$ (75% yield, see Scheme 4).

Palladation Reactions.—Both lithium derivatives $C_{10}H_6$-(CH_2NMe_2)-2-(CH_2Li)-3 **1** and $C_{10}H_6(CH_2NMe_2)$-2-Li-1 **2** reacted with $[PdCl_2(SMe_2)_2]$ to give the corresponding palladated derivatives **3** (85%, Scheme **3**) and **4** (80%, Scheme 4). Oxidative addition of the 1-bromo derivative **V** to $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in acetone yielded the bromide-bridged dimer **5** in 90% yield (Scheme 4). Cationic derivatives of **4** and **5** (see Scheme 4) were prepared by reaction with $Ag(O_3SCF_3)$ in the presence of acetonitrile. The bis(aceto-nitrile)palladium complex **11** was isolated in 92% yield, starting from **5**. The monomeric compound **12** was prepared by reaction of the 1-naphthylpalladium bromide **5** with pyridine (96%).

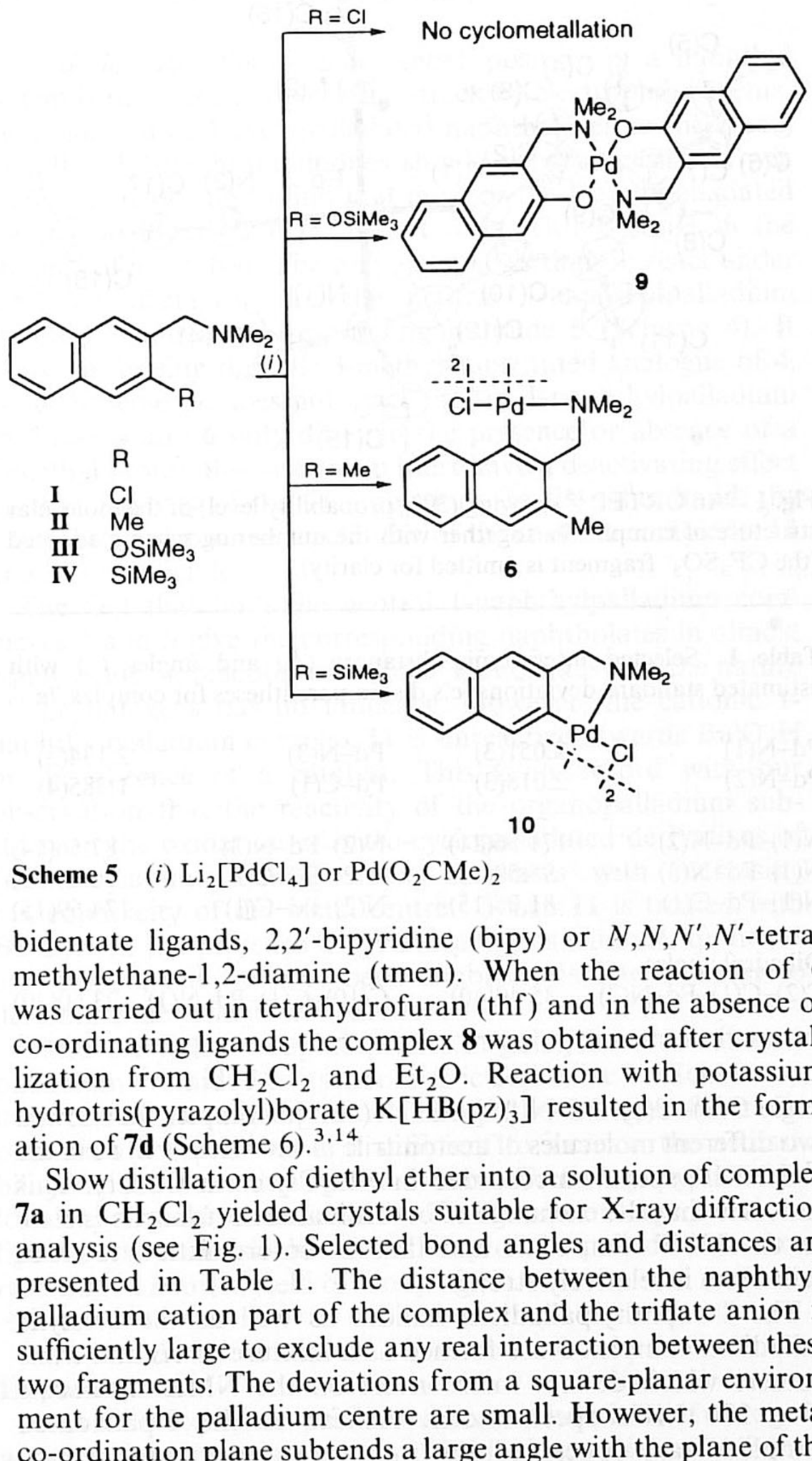
Direct palladation of compound **I** at the 1 position, involving reaction with $Pd(O_2CMe)_2$ or $Li_2[PdCl_4]$ did not occur (see Scheme 5). In the latter case, NMR spectra in $CDCl_3$ indicated the formation of a co-ordination complex after 3 h. Addition of a slight excess of deuteriated pyridine to the reaction mixture converted this complex into $[PdCl_2(py)_2]$ and the starting material **I**. The co-ordination complex reacted with $AgNO_3$ but did not give cyclopalladated products. The reaction of silver salts with this type of co-ordination complex was previously applied to induce cyclopalladation.[12] When the reaction of **I** with $Pd(O_2CMe)_2$ was carried out for 2 d the 2-naphthyl-palladium complex **10** was isolated in approximately 10% yield. Instead of C–H activation, C–Cl activation had occurred.

Reaction of the 2-naphthyl silyl ether **III** with $Pd(O_2CMe)_2$ resulted in cleavage of the oxygen–silicon bond. After work-up, the bis(2-naphtholate) complex **9** was isolated in quantitative yield (see Scheme 5).* Likewise, the carbon–silicon bond in 2-[(dimethylamino)methyl]-3-trimethylsilylnaphthalene **IV** was cleaved by reaction with $Pd(O_2CMe)_2$, leading to the formation of **10** which was isolated in 99% yield after work-up with LiCl.

The 3-methyl-substituted compound **II** reacted with Li_2-$[PdCl_4]$ in the presence of 1 equivalent of $Na(O_2CMe)$ or 1 equivalent excess of **II**, but much faster with $Pd(O_2CMe)_2$, to yield 1-palladated **6** in 96% yield after work-up with LiCl. A number of cationic derivatives of this complex, **7a**–**7c** (Scheme 6), were obtained in almost quantitative yield after reaction with $Ag(O_3SCF_3)$ in the presence of acetonitrile or one of the



Scheme 4 (*i*) $[Pd(dba)_2]$; (*ii*) $LiBu^n$; (*iii*) $[PdCl_2(SMe_2)]$; (*iv*) pyridine (py); (*v*) $Ag(O_3SCF_3)$, MeCN

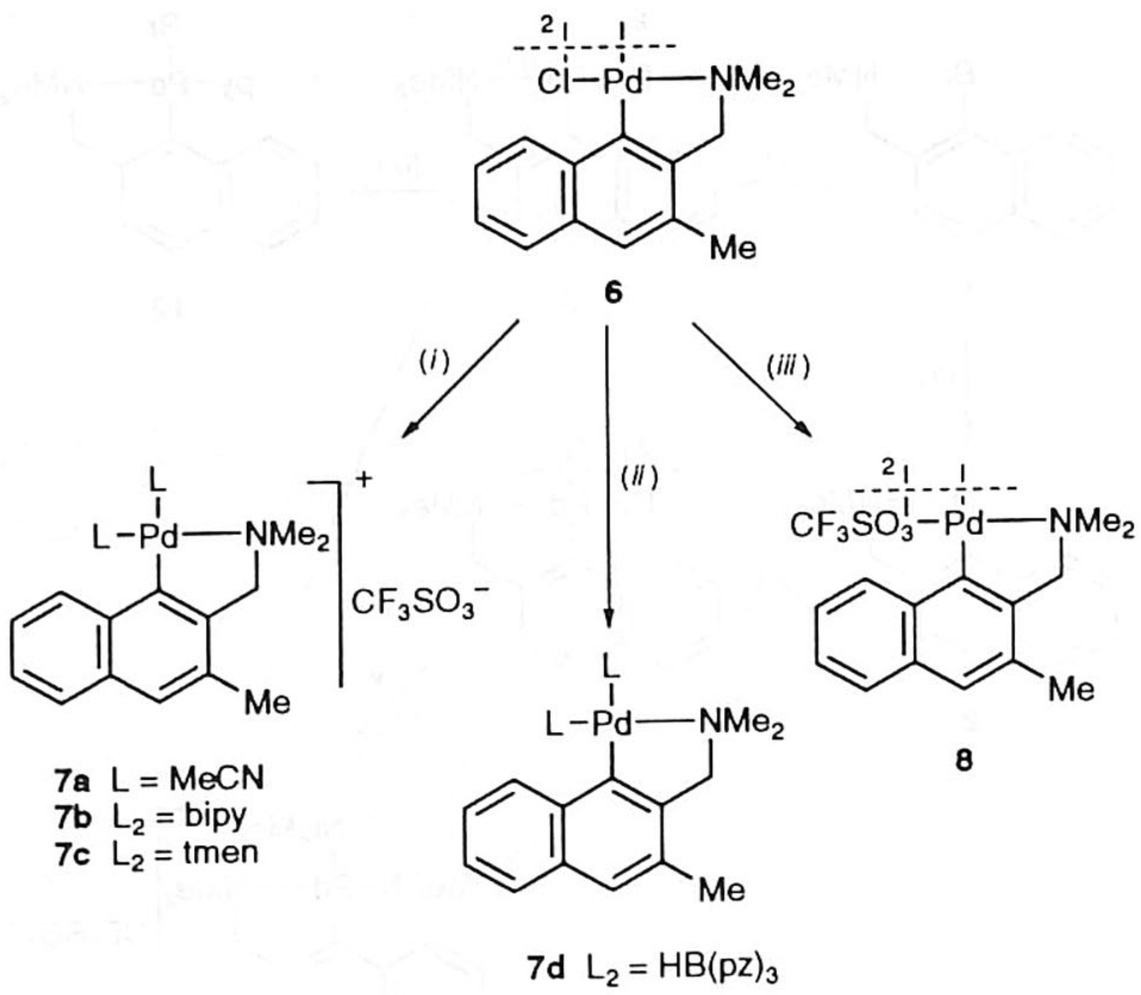


Scheme 5 (*i*) $Li_2[PdCl_4]$ or $Pd(O_2CMe)_2$

bidentate ligands, 2,2′-bipyridine (bipy) or *N*,*N*,*N*′,*N*′-tetra-methylethane-1,2-diamine (tmen). When the reaction of **6** was carried out in tetrahydrofuran (thf) and in the absence of co-ordinating ligands the complex **8** was obtained after crystal-lization from CH_2Cl_2 and Et_2O. Reaction with potassium hydrotris(pyrazolyl)borate $K[HB(pz)_3]$ resulted in the form-ation of **7d** (Scheme 6).[3,14]

Slow distillation of diethyl ether into a solution of complex **7a** in CH_2Cl_2 yielded crystals suitable for X-ray diffraction analysis (see Fig. 1). Selected bond angles and distances are presented in Table 1. The distance between the naphthyl-palladium cation part of the complex and the triflate anion is sufficiently large to exclude any real interaction between these two fragments. The deviations from a square-planar environ-ment for the palladium centre are small. However, the metal co-ordination plane subtends a large angle with the plane of the naphthalene system, as reflected in the large value of the torsion

* The isolation of *trans*-bis{3-[(dimethylamino)methyl]-2-naphtho-lato}palladium **9** after reaction of compound **III** with palladium salts, instead of the chloride bridged dimer of palladated 3-[(dimethylamino)-methyl]-2-naphtholate, *i.e.* di-μ-chloro-bis{3-[(dimethylamino)methyl]-2-naphtholato}palladium, is not unexpected. In a previous study the synthesis of the latter failed because of the high nucleophilicity of the oxygen centre, resulting in the formation of **9**.[13] This explains the formation of the latter product in the reaction of **III** with the palladium salts employed.



Scheme 6 (*i*) $Ag(O_3SCF_3)$, L; (*ii*) K [$HB(pz)_3$]; (*iii*) $Ag(O_3SCF_3)$, thf

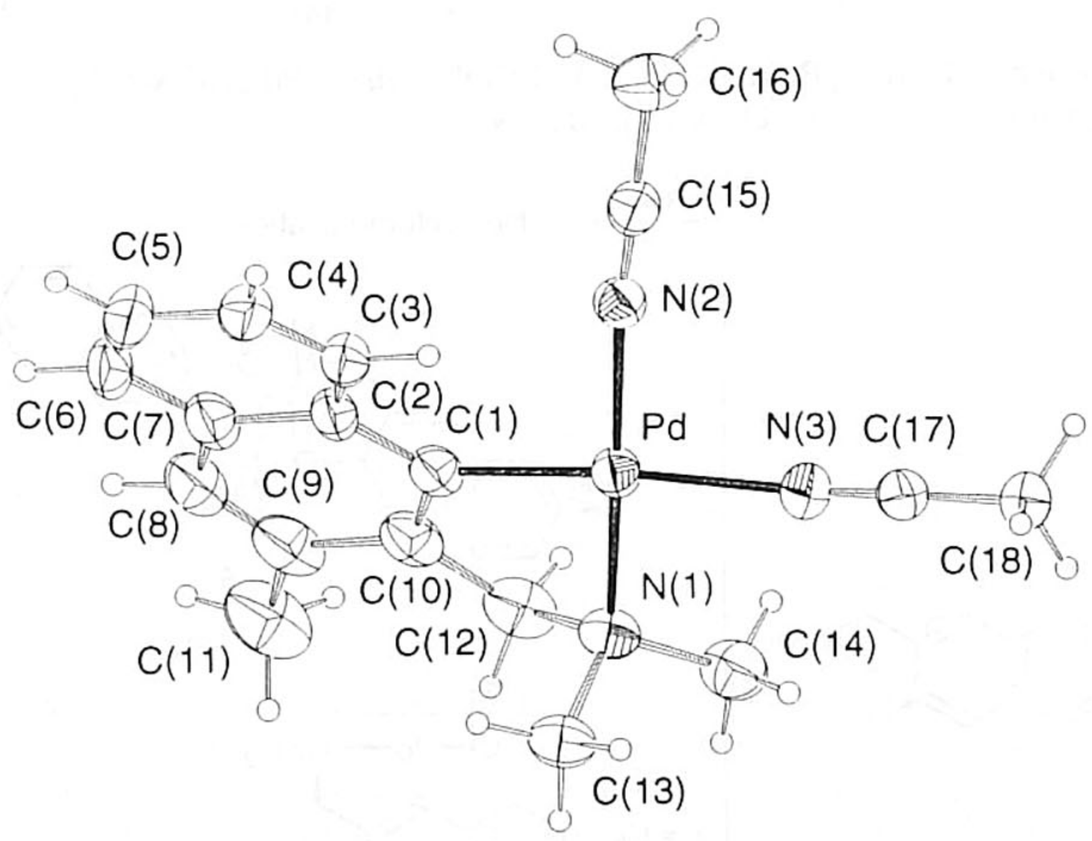


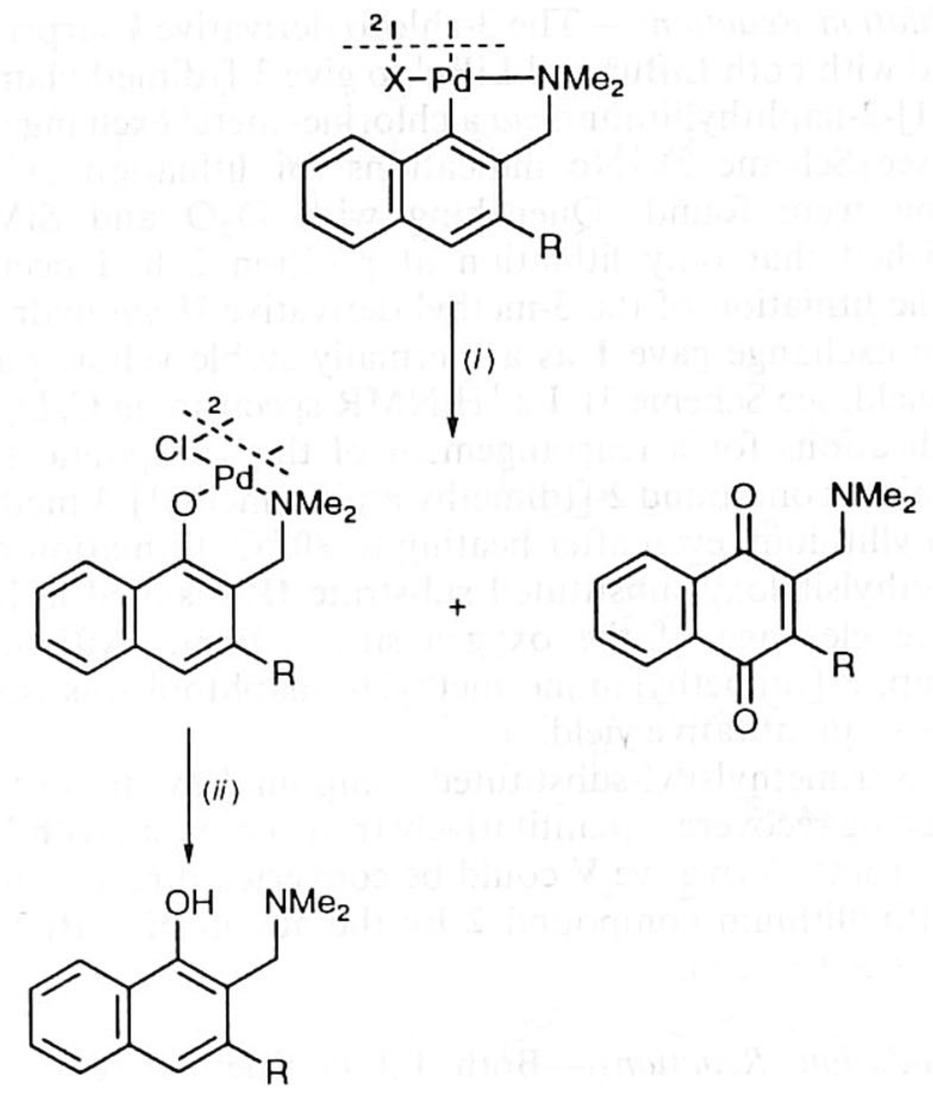
Fig. 1 An ORTEP[15] drawing (30% probability level) of the molecular structure of complex **7a** together with the numbering scheme adopted (the $CF_3SO_3^-$ fragment is omitted for clarity)

Table 1 Selected interatomic distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **7a**

Pd–N(1)	2.051(3)	Pd–N(3)	2.134(3)
Pd–N(2)	2.018(3)	Pd–C(1)	1.985(4)
N(1)–Pd–N(2)	171.56(11)	N(2)–Pd–N(3)	87.56(14)
N(1)–Pd–N(3)	95.59(14)	N(2)–Pd–C(1)	96.34(15)
N(1)–Pd–C(1)	81.06(15)	N(3)–Pd–C(1)	174.59(15)
Dihedral angles			
C(2)–C(1)–Pd–N(2)	−35.40(40)	C(10)–C(1)–Pd–N(1)	−23.60(30)

angle C(2)–C(1)–Pd–N(2) [−35.40(40)°]. Complex **7a** showed two different molecules of acetonitrile in the ^1H as well as in the ^{13}C NMR spectrum recorded in CD_2Cl_2 or in $CDCl_3$. This indicates that the exchange of co-ordinated acetonitrile is slow on the NMR time-scale and that its co-ordination towards palladium is relatively strong.

The 1-naphthylpalladium halides as well as the benzylic palladium complex **3** are formed as a mixture of *cis* and *trans* isomers which do not interconvert on the NMR time-scale of a 200 MHz spectrometer. As far as the 1-palladated complexes are concerned the isomers are not present in a 1:1 ratio (see Experimental section). Again, this is probably due



Scheme 7 (*i*) Bu^tO_2H; (*ii*) N_2H_5OH

Table 2 Products formed (%) in the oxidation of 1-palladated naphthalenes by Bu^tO_2H

	$[VO(acac)_2]$[a]		$[\{RhCl(cod)_2\}]$[a]	
Compound	Naphthol[b]	Quinone	Naphthol[b]	Quinone
4[c]	60	—	60	—
5[c]	60	—	60	—
11	68	n.d.	70	n.d.
12	74	—	78	—
6[d]	40	—	45	—
7a	70	18	68	28
7b	62	—	66	—
7c	45	—	48	—
7d	33	—	35	—
8	65	27	60	38

[a] 5 mol % was used as catalyst; n.d. = not determined. [b] Determined after reduction with hydrazine hydrate. [c] No catalyst was added. [d] 10% of 1-chloro-2-[(dimethylamino)methyl]-3-methylnaphthalene was also formed.

to steric effects. Model studies show that in the *cis* isomers the aromatic systems are partly overlapping, thereby destabilizing this isomer.

Oxidation Reactions.—All arylpalladium complexes described above reacted with *tert*-butyl hydroperoxide to yield the corresponding 1-naphthols or 1,4-naphthoquinones (see Table 2 and Scheme 7). With the exception of complexes **4** and **5**, a catalytic amount of $[VO(acac)_2]$ (acac = acetylacetonate) or $[\{RhCl(cod)\}_2]$ had to be added to induce reaction with the organometallic substrate.[4]

The yields of naphtholates were determined after liberation of the naphthols by reduction of the reaction mixture with hydrazine hydrate. The yield of naphthoquinone was determined prior to the reduction since it reacted with hydrazine hydrate to give intractable polymeric materials.[4] Attempts to remove the palladium by reaction with HCl,[4] $NaBH_4$ or $LiAlH_4$[16] in order to liberate the free 1,4-naphthoquinone or one of its reduced derivatives were not successful.

The oxidation of complex **6** with the alternative oxidant $[MoO(O_2)\{OP(NMe_2)_3\}(H_2O)]$[17] resulted in replacement of the palladium by a chloro-substituent and 1-chloro-2-[(dimethylamino)methyl]-3-methylnaphthalene was isolated in 42% yield. This reaction type was described earlier for a series of

cyclopalladated aryl and alkyl derivatives.[18] The same C–Cl coupling product was obtained as a minor product (*ca.* 10% yield) in the $[VO(acac)_2]$-catalysed oxidation of **6** by Bu^tO_2H, together with the main product, *i.e.* the 3-methyl-1-naphthol derivative **VI**.

Discussion

In the present study we have shown that naphthyl compounds carrying a dimethylaminomethyl substituent in the 2 position undergo selective palladation at position 1 when the 3 position is blocked by a methyl group. While this work was in progress,[4] Klaus and co-workers[19] reported that 2-arylazonaphthalenes react with $Na_2[PdCl_4]$ in methanol to give a mixture of two products in which either the phenyl or the naphthyl moiety is palladated. Also in that case 1-naphthyl palladation was observed when C(3) was substituted by a methyl group.

The direct metallation of aromatic as well as aliphatic carbon atoms is well documented. Generally, organolithium species used in metallation reactions react like nucleophiles,[20] while palladium salts tend to react like electrophiles.[21] These differences allow the tuning of the regio- as well as the chemoselectivity of the metallation of the substrates (see below). A complicating factor is that the kinetic reactivity of positions 1 and 3 in naphthalene differs notably due to steric interactions which accompany the metallation of position 1.[3]

The palladation reactions of the trimethylsilyloxy derivative **III** and the trimethylsilyl derivative **IV** show that the $SiMe_3$ and $OSiMe_3$ groups are unsuitable as blocking groups in palladation reactions. Electrophilic cleavage of the C–Si and the O–Si bonds by transition metals has been described earlier.[22] We believe that the efficiency and high selectivity of the palladations of **III** and **IV** are due to the neighbouring-group effect of the amino group which co-ordinates to the palladium centre and so directs it intramolecularly towards the aromatic system.

The observation that the 3-chloro-substituted substrate **I** does not react with palladium salts to give palladation at position 1 is most likely due to a combination of two factors. First, the aromatic ring is deactivated for electrophilic substitution by the presence of the chloro-substituent. Secondly, this substituent may co-ordinate with the palladium centre and so prevent the metal from attacking C(1).* This co-ordination brings the palladium in the proximity of C(3), which may lead to the formation of the 2-naphthylpalladium chloride **10** (Scheme 5) in low yield (10%).

The reaction of palladium with C–X bonds (X = halogen) is well known for palladium(0) species, but is rather rare for C–Cl bonds involving palladium(II) species.[24]

Unlike the chloro-substituent in **I**, the methyl group in 2-[(dimethylamino)methyl]-3-methylnaphthalene **II** has an activating effect on the aromatic ring, and leads to the formation of complex **7a** by reaction with silver triflate. The most remarkable structural feature in the crystal structure of **7a** is the large angle [33.1(1)°] between the square-planar co-ordination plane of the palladium centre and the plane of the naphthalene moiety. This angle is the result of severe steric interaction between the co-ordinating acetonitrile ligand, *trans* to the nitrogen ligand, and proton H(8). Such an interaction most likely prevents palladation at position 1 in the reaction between 2-[(dimethylamino)methyl]naphthalene and $Li_2[PdCl_4]$ and leads to the direct formation of the 3-palladated compound. This view is corroborated by the fact that the 1-palladated compound **4**, made independently *via* another route (Scheme 4), does not rearrange to its 3-palladated regioisomer **10**.

Although palladation and lithiation are very different in nature, the regioselectivity of the reactions of 2-[(dimethylamino)methyl]naphthalene with palladium salts and lithiating agents is the same. We recently found that lithiation of 2-[(dimethylamino)methyl]naphthalene occurs selectively at C(3)[3] through kinetic direction of the metallation to the 3 position. Similarly, 3-chloro-2-[(dimethylamino)methyl]-naphthalene **1** is lithiated in the 3 position by lithium–chloride exchange. The steric interactions described above for the palladation reactions do not seem to play a major role in these reactions, since selective lithiation at position 1 is observed when a halogen is introduced at this position, *e.g.* in the 1-bromonaphthyl compound **V**.

Differences between lithiation and palladation do occur in the reactions with compound **II**. Lithiation takes place exclusively at the 3-methyl substituent, since a benzylic proton is more acidic than an aromatic proton.[20] As alkyl- as well as aryl-lithium compounds can be selectively converted into the corresponding palladium complexes, this difference in chemoselectivity can be used to direct the position of palladation, *i.e.* both the benzylic palladium compound **3** and the arylpalladium compound **6** can be prepared in high yield by choosing the appropriate reaction sequence. The combination of lithiation and Li–Pd exchange of 1-bromo-2-[(dimethylamino)methyl]-naphthalene **V** presents the only route available for the preparation of the 1-naphthylpalladium chloride **4** since direct palladation as well as lithiation of 2-[(dimethylamino)methyl]-naphthalene occurs selectively at C(3).

Oxidation Reactions.—Since the 1 position in a naphthyl system is the preferred place for attack by electrophilic agents, the oxidation of 1-cyclopalladated naphthalenes to the corresponding 1,4-naphthoquinones should proceed easily. It was therefore surprising to find that most of the 1-cyclopalladated complexes described here do not react with Bu^tO_2H in the absence of a catalyst. The only complexes that do react under these circumstances are the neutral 1-naphthylpalladium chloride **4** and its corresponding bromide **5** (Scheme 4). It is also surprising that the 3-methyl-substituted analogue of **4**, *i.e.* **6** (Scheme 5), does not react. As the 1-naphthylpalladium chlorides **4** and **6** only differ in the presence or absence of a 3-methyl group, this last group must have a deactivating effect on the reactivity of the C(1) position. On the other hand, the difference between the reactivities of the cationic complexes **11** and **7a** is negligible.

The fact that both the neutral 1-naphthylpalladium complexes **4** and **5** give the corresponding naphtholates in almost equal yields on reaction with Bu^tO_2H indicates that the nature of the halogens has no influence. However, the cationic 1-naphthylpalladium complex **11** is unreactive towards Bu^tO_2H in the absence of a catalyst. This is in accord with our observation that the reactivity of the organopalladium substrate in the oxidation of *ortho*-cyclopalladated derivatives of [(dimethylamino)methyl]benzene increases with increasing nucleophilicity of the metal centre.[2] When **11** is treated with Bu^tO_2H in the presence of $[VO(acac)_2]$ as catalyst, quinones are formed, but we have been unable to isolate them or to determine the yield of this reaction.

Since the yield of naphthol rises in going from the dimeric palladium bromide **5** to its monomeric derivative **12** (Scheme 4), it is clearly not essential to remove the halogen from the palladium complex but it is sufficient to increase the accessibility of the palladium centre. This effect may explain the lowering in yield in the series **7a**–**7d**. The use of large spectator ligands will diminish the accessibility of the palladium centre, resulting in a lower yield of 1-naphthols.

Experimental

General.—Reactions performed in an atmosphere of nitrogen were carried out using standard Schlenk techniques. All solvents, except MeOH were dried prior to use: thf and Et_2O were

* This type of co-ordination has been observed for several organometallic compounds. For palladium this interaction is believed to be very weak.[23]

distilled from sodium–benzophenone, MeCN was distilled from CaH_2 and stored on 4 Å molecular sieves and CH_2Cl_2 was dried on CaH_2 or anhydrous $CaCl_2$. The synthesis of complex **4** has been described elsewhere.[3] 2-[(Dimethylamino)methyl]-1-naphthol was prepared according to a literature procedure.[26] Proton and ^{13}C NMR spectra were recorded on a Bruker AC-200 or AC-300 spectrometer, IR spectra on a Perkin-Elmer 283 spectrophotometer and mass spectra on a Kratos MS80 GC-MS combination apparatus, equipped with a CP-SIL5 column. Elemental analyses were carried out by the Institute of Applied Chemistry (TNO), Zeist, and by Dornis und Kolbe, mikroanalytisches laboratorium, Mülheim a. d. Ruhr.

Synthesis of Organic Compounds.—3-*Chloro*-2-[(*dimethylamino*)*methyl*]*naphthalene* **I**. Solid $NaNO_2$ (4.1 g, 59 mmol) was added over a period of 15 min to concentrated sulfuric acid (43 cm^3) while stirring.[5] The mixture was heated to 70 °C for 15 min. When the solution had cooled to room temperature a solution of 3-amino-2-naphthoic acid (10 g, 54 mmol) in acetic acid (100 cm^3) was added at such a rate that the temperature was kept below 40 °C. The mixture was stirred at 40 °C for an additional 30 min after which time it was carefully poured into an ice-cooled solution of CuCl (11.8 g, 127 mmol) in concentrated hydrochloric acid (100 cm^3). The temperature was not appreciably affected by this addition. After stirring at 80 °C for 30 min, water (300 cm^3) was added. The precipitated brown solid was filtered off over a Büchner funnel, and was purified by flash column chromatography (20 g of silica, eluted with Et_2O) to yield 7.7 g of off-white 3-chloro-2-naphthoic acid (37 mmol, 70%, m.p. 212 °C). 3-Chloro-2-naphthoic acid (5 g, 24 mmol) was stirred in $SOCl_2$ (20 cm^3) for 1 night. After carefully removing the excess of $SOCl_2$ *in vacuo*, the residue was dissolved in Et_2O (100 cm^3) and cooled to 0 °C. A solution of NMe_2H (10 cm^3) in Et_2O (100 cm^3) was added over a period of 30 min. After stirring at room temperature for 1 night, 10% $NaHCO_3$ solution (100 cm^3) was added. The layers were separated and the aqueous phase was extracted twice with Et_2O (50 cm^3). The collected organic layers were dried on $MgSO_4$, filtered and concentrated *in vacuo*. The yield of solid 3-chloro-*N*,*N*-dimethylnaphthalene-2-carboxamide was 4.7 g (20 mmol, 84%). The compound $LiAlH_4$ (3.1 g, 82 mmol) was suspended in thf (125 cm^3) and cooled to 5 °C.[6] To this mixture was carefully added concentrated sulfuric acid (3.7 g) in thf (15 cm^3). After stirring at 5 °C for 30 min, a solution of 3-chloro-*N*,*N*-dimethylnaphthalene-2-carboxamide (14.6 g, 63 mmol) in thf (200 cm^3) was added at such a rate that the temperature did not exceed 20 °C. The grey suspension was allowed to reach room temperature and was then stirred for 6 h after which time a mixture of water (15 cm^3) and thf (15 cm^3) was slowly added while stirring vigorously, followed by a solution of NaOH (2.9 g) in water (60 cm^3). The precipitated aluminium salts were filtered off over a Büchner funnel. Diethyl ether (100 cm^3) was added to the filtrate. The aqueous phase was separated and extracted with three portions of ether (100 cm^3), dried on $MgSO_4$, filtered and concentrated *in vacuo*. The remaining oil was distilled under reduced pressure (b.p. 93 °C, 0.3 mmHg). The yield was 11.2 g of 2-chloro-3-[(dimethylamino)methyl]-naphthalene **I** (51 mmol, 80%). ^1H NMR: 3-chloro-2-naphthoic acid [200 MHz, in $(CD_3)_2CO$], δ 8.52 (s, 1 H, aryl H), 8.09 (m, 2 H, aryl H) and 7.61 (m, 3 H, aryl H); 3-chloro-*N*,*N*-dimethylnaphthalene-2-carboxamide [200 MHz, $(CD_3)_2CO$], δ 8.06 (s, 1 H, aryl H), 8.01–7.92 (m, 2 H, aryl H), 7.89 (s, 1 H, aryl H), 7.65–7.55 (m, 2 H, aryl H), 3.11 (s, 3 H, NCH_3) and 2.88 (s, 3 H, NCH_3); compound **I** (300 MHz, $CDCl_3$), δ 7.87 (s, 1 H, aryl H), 7.84 (s, 1 H, aryl H), 7.80–7.74 (m, 1 H, aryl H), 7.70–7.62 (m, 1 H, aryl H), 7.44–7.41 (m, 2 H, aryl H), 3.68 (s, 2 H, CH_2) and 2.37 (s, 6 H, NCH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 134.2 (CCl), 133.2, 132.6, 132.0, 129.6, 127.7, 126.7, 126.5, 126.2, 61.2 (CH_2) and 45.6 (NCH_3).

2-[(*Dimethylamino*)*methyl*]-3-*methylnaphthalene* **II**. To a solution of 3-[(dimethylamino)methyl]-2-naphthyllithium[3] (36.3 g, 0.19 mol) in thf (200 cm^3) was added a solution of MeI (26.9 g, 0.19 mol) in thf (100 cm^3) at 0 °C over a period of 30 min. After stirring at room temperature for 4 h, water (50 cm^3) and Et_2O (100 cm^3) were added. The aqueous phase was separated and extracted with three portions of Et_2O (100 cm^3). The collected organic phases were dried on $MgSO_4$, filtered and concentrated *in vacuo*. The remaining oil was purified by vacuum distillation (b.p. 126 °C, 0.6 mmHg) yielding 33.8 g (0.17 mol, 89%) of a colourless oil which solidified upon standing, m.p. 37 °C. NMR ($CDCl_3$): ^1H (300 MHz), δ 7.81 (m, 2 H, aryl H), 7.74 (s, 1 H, aryl H), 7.65 (s, 1 H, aryl H), 7.44 (m, 2 H, aryl H), 3.55 (s, 2 H, CH_2), 2.57 (s, 3 H, CH_3) and 2.33 (s, 6 H, NCH_3); ^{13}C (75.5 MHz), δ 136.1, 135.8, 133.1, 132.1, 128.3, 127.5, 127.0, 125.6, 125.1, 62.7 (CH_2), 45.7 (NCH_3) and 19.5 (aryl CH_3) (Found: C, 83.00; H, 8.60; N, 6.60. Calc. for $C_{14}H_{17}N$: C, 84.35; H, 8.60; N, 7.05%).

2-[(*Dimethylamino*)*methyl*]-3-*trimethylsiloxynaphthalene* **III**. Sodium hydride (0.32 g of a 80% dispersion in mineral oil, 11 mmol) was washed with two portions (50 cm^3) of pentane. After the careful addition of a solution of 3-[(dimethylamino)methyl]-2-naphthol[10] (2.15 g, 11 mmol) in Et_2O (5 cm^3), the solvent was removed *in vacuo* and hexane (50 cm^3) was added. The mixture was heated to reflux for 2 h after which time the hexane was removed by decantation. The solid sodium naphtholate was washed with pentane (50 cm^3), dried *in vacuo* and suspended in Et_2O (30 cm^3). A solution of $SiMe_3Cl$ (1.15 g, 11 mmol) in Et_2O (10 cm^3) was added and the solution was stirred for 2 h. Precipitated NaCl was removed by centrifugation. The ether layer was concentrated under reduced pressure yielding 2.32 g of oily product (8.5 mmol, 75%). This was pure. When exposed to water the compound is slowly hydrolysed to give the starting naphthol. NMR ($CDCl_3$): ^1H (300 MHz), δ 7.82 (s, 1 H, aryl H), 7.79–7.70 (m, aryl H), 7.45–7.33 (m, 2 H, aryl H), 7.20 (s, 1 H, aryl H), 3.60 (s, 2 H, CH_2), 2.35 (s, 6 H, NCH_3) and 0.38 (s, 9 H, $SiCH_3$); ^{13}C (75.5 MHz), δ 152.6 (CO), 133.8, 131.0, 129.7, 129.3, 127.6, 126.3, 125.8, 123.8, 113.9, 58.7 (CH_2), 45.6 (NCH_3) and 0.54 ($SiCH_3$) (Found: C, 70.35; H, 8.45; N, 5.20. Calc. for $C_{16}H_{23}NOSi$: C, 70.30; H, 8.50; N, 5.10%).

2-[(*Dimethylamino*)*methyl*]-3-*trimethylsilylnaphthalene* **IV**. The compound $SiMe_3Cl$ (1.52 cm^3, 12 mmol) in thf (10 cm^3) was slowly added to an ice-cooled solution of 3-[(dimethylamino)methyl]-2-naphthyllithium (2.30 g, 12 mmol) in thf (40 cm^3). After stirring for 2 h at room temperature, thf was removed *in vacuo* and the oily residue was extracted twice with Et_2O (40 cm^3). After removal of Et_2O under reduced pressure, 3.0 g of oily product remained (12 mmol, 97%). It could be used without further purification. NMR ($CDCl_3$): ^1H (200 MHz), δ 7.99 (s, 1 H, aryl H), 7.80 (s, 1 H, aryl H), 7.77 (m, 2 H, aryl H), 7.42 (m, 2 H, aryl H), 3.63 (s, 2 H, CH_2), 2.22 (s, 6 H, NCH_3) and 0.35 (s, 9 H, $SiCH_3$); ^{13}C (50.3 MHz), δ 141.9, 137.6, 136.0, 133.8, 132.2, 128.0, 127.5, 127.0, 126.5, 125.6, 65.1 (CH_2), 45.5 (NCH_3) and 0.9 ($SiCH_3$).

2-[(*Dimethylamino*)*methyl*]-3-*methyl*-1-*naphthol* **VI**. Ethyl 1-hydroxy-3-methyl-2-naphthoate was prepared in four steps from 2-carboxybenzeneacetic acid.[9] The former compound (20.5 g, 89 mmol) was dissolved in EtOH (80 cm^3) and added to a solution of KOH (20.0 g, 0.36 mol) in a mixture of water (32 cm^3) and EtOH (16 cm^3). After stirring at 80 °C for 3 h the reaction mixture was poured into water (400 cm^3). The resulting solution was washed twice with CH_2Cl_2 (100 cm^3), and cooled to 0 °C and then carefully acidified with HCl (4 mol dm^{-3}) to pH 4. Significant decarboxylation occurred when the temperature was too high, when too much HCl was added or when the saponification reaction was carried out for longer periods of time. The aqueous phase was extracted with three portions (100 cm^3) of Et_2O. The collected organic layers were dried on $MgSO_4$, filtered and concentrated under reduced pressure at room temperature. The white solid consisted of 1-hydroxy-3-methyl-2-naphthoic acid (62 mmol, 70%) and 3-methyl-1-naphthol (15 mmol, 17%). Work-up of the collected CH_2Cl_2 layers gave 2.0 g of starting material (8.7 mmol, 10%). 1-

Hydroxy-3-methyl-2-naphthoic acid was converted into the corresponding dimethylamide[10] without separation from 1-hydroxy-3-methylnaphthalene since also in this reaction decarboxylation occurs. The product amide is thermally stable (55% yield, 40% decarboxylation during reaction) and was purified by treating an ethyl acetate solution with two portions (50 cm^3) of a 10% solution of NaOH in water, drying on $MgSO_4$ and removal of the solvent under reduced pressure. The product 1-hydroxy-*N*,*N*,3-trimethylnaphthalene-2-carboxamide can be used in the final step without further purification. The reduction of this amide was accomplished using a literature procedure.[6] The product, 2-[(dimethylamino)methyl]-3-methyl-1-naphthol **VI**, was obtained as yellowish crystals from dimethylformamide and water (m.p. 45 °C, 87% yield). ^1H NMR: 1-hydroxy-3-methyl-2-naphthoic acid [200 MHz, $(CD_3)_2CO$], δ 12.86 (s, 1 H, aryl OH), 8.31 (s, 1 H, J = 8.3), 7.72 (d, 1 H, J = 7.8), 7.61 (td, 1 H, J_1 = 7.4, J_2 = 1.4), 7.47 (td, 1 H, J_1 = 7.5, J_2 = 1.5 Hz), 7.16 (s, 1 H, aryl H^5) and 2.64 (s, 3 H, CH_3); compound **VI** (300 MHz, $CDCl_3$), δ 8.36–8.31 (m, 1 H, aryl H), 7.76–7.71 (m, 1 H, aryl H), 7.52–7.45 (m, 2 H, aryl H), 7.18 (s, 1 H, aryl H^4), 3.81 (s, 2 H, CH_2), 2.42 (s, 3 H, aryl CH_3) and 2.39 (s, 6 H, NCH_3); ^{13}C (75.5 MHz, $CDCl_3$), δ 154.4 (COH), 134.1, 133.6, 126.6, 126.1, 124.2, 124.0, 122.1, 118.6, 113.6, 58.9 (CH_2), 44.5 (NCH_3) and 20.7 (aryl CH_3) (Found: C, 77.00; H, 8.05; N, 6.35. Calc. for $C_{14}H_{17}NO$: C, 78.10; H, 7.95; N, 6.50%).

2-[(*Dimethylamino*)*methyl*]-3-*methyl*-1,4-*naphthoquinone* **VII**. To a solution of 2-(chloromethyl)-3-methyl-1,4-naphthoquinone[26] (1.50 g, 6.80 mmol) in acetone (20 cm^3) was added a solution of NaI (1.02 g, 6.8 mmol) in acetone (20 cm^3). A precipitate formed immediately. After stirring at room temperature for 3 h the yellow solution was decanted and concentrated under reduced pressure leaving yellow solid 2-(iodomethyl)-3-methyl-1,4-naphthoquinone (1.95 g, 6.3 mmol, 92%). This compound was used without further purification. To a solution of 2-(iodomethyl)-3-methyl-1,4-naphthoquinone (1.38 g, 4.6 mmol) in benzene (50 cm^3) was aded NMe_2H (10 mmol) in benzene (20 cm^3). After stirring at room temperature for 1 h the solution was concentrated *in vacuo* leaving impure red compound **VII**. Attempts to purify it by crystallization and column chromatography were unsuccessful. The estimated yield was 50%. ^1H NMR [300 MHz, $(CD_3)_2CO$]: 2-(iodomethyl)-3-methyl-1,4-naphthoquinone, δ 8.09–8.07 (m, 2 H, aryl H), 7.88–7.83 (m, 2 H, aryl H), 4.52 (s, 2 H, CH_2I) and 2.13 (s, 3 H, CH_3); compound **VII**, δ 8.13–8.09 (m, 2 H, aryl H), 7.40–7.36 (m, 2 H, aryl H), 3.84 (s, 2 H, CH_2), 2.35 (s, 6 H, NCH_3) and 2.22 (s, 2 H, CCH_3).

Lithiation Reactions.—Compound **I** was lithiated according to the procedure recently described for 2-[(dimethylamino)-methyl]naphthalene.[3] The yield of 3-[(dimethylamino)methyl]-2-naphthyllithium was approximately 60% when $LiBu^n$ and 90% when $LiBu^t$ was used.

3-[(*Dimethylamino*)*methyl*]-2-*naphthylmethyllithium* **1**. A 1.5 mol dm^{-3} solution of *n*-butyllithium in hexane (7.7 cm^3, 11.5 mmol) was added at 0 °C to a solution of 2-[(dimethylamino)-methyl]-3-methylnaphthalene (2.29 g, 11.5 mmol) in a mixture of hexane (50 cm^3) and Et_2O (5 cm^3). After stirring at room temperature for 1 night the yellow solid was separated by centrifugation, washed with two portions of hexane (50 cm^3) and dried *in vacuo* yielding 1.90 g (9.3 mmol, 81%) of pyrophoric yellow product. Owing to its extremely low solubility in C_6D_6 and [$^2H_8$] toluene, the product was analysed as its trimethylsilyl derivative (see synthesis of **IV**) 2-[(*dimethylamino*)*methyl*]-3-(*trimethylsilylmethyl*)*naphthalene*, 92% yield, b.p. 155 °C (1.0 mmHg). NMR ($CDCl_3$): ^1H (300 MHz), δ 7.90 (d, 1 H, J = 7.3 Hz), 7.85 (m, 2 H), 7.60 (s, 1 H), 7.50 (m, 2 H), 3.85 (s, 2 H, CH_2N), 2.61 (s, 2 H, CH_2Si), 2.42 (s, 6 H, NCH_3) and 0.21 (s, 9 H, $SiCH_3$); ^{13}C (75.5 MHz), δ 128.9, 127.6, 126.7, 126.7, 125.6, 124.5, 63.2 (CH_2N), 45.7 (CH_2Si), 23.1 (NCH_3) and −1.0 ($SiCH_3$) (Found: C, 75.05; H, 9.20; N, 5.20. Calc. for $C_{17}H_{25}NSi$: C, 75.20; H, 9.30; N, 5.15%).

2-[(*Dimethylamino*)*methyl*]-1-*naphthyllithium* **2**. 1-Bromo-2-[(dimethylamino)methyl]naphthalene (5.0 g, 18.9 mmol)[7] was dissolved in pentane (20 cm^3), cooled to −78 °C and $LiBu^n$ in hexane (19 mmol) added. A yellow-brown solid separated and was isolated by centrifugation after stirring at room temperature for 1 night. Repeated washings with pentane yielded a yellow product (2.71 g, 75%).

Palladation Reactions.—*Lithium–palladium exchange to give complex* **3**. A solution of 3-[(dimethylamino)methyl]-2-naphthylmethyllithium (1.10 g, 5.37 mmol) in thf (20 cm^3) was added at −78 °C to a suspension of $[PdCl_2(SMe_2)_2]$[27] (1.62 g, 5.37 mmol) in thf (10 cm^3). After stirring at room temperature for 1 h, MeOH (1 cm^3) was added carefully to destroy any lithium species still present. The solution was concentrated *in vacuo*. The green solid was extracted with two portions of CH_2Cl_2 (20 cm^3). After removal of the solvent, 1.55 g (2.28 mmol, 85%) of yellow-orange product remained. This was crystallized by diffusion of Et_2O into a solution in CH_2Cl_2. NMR: ^1H, mixture of isomers (200 MHz, $CDCl_3$), δ 7.92–7.39 (m, 6 H, aryl H), 3.34 (s, 2 H, CH_2N), 3.34 (s, 2 H, CH_2Pd), 2.72 (s, 6 H, NCH_3 of isomer **a**), 2.68 (s, 6 H, NCH_3 of isomer **b**); isomer **a** (200 MHz, C_6D_6), δ 7.95 (s, 1 H, aryl H), 3.65 (s, 2 H, CH_2N), 2.50 (s, 2 H, CH_2Pd) and 2.22 (s, 6 H, NCH_3); isomer **b**, δ 7.87 (s, 1 H, aryl H), 3.53 (s, 2 H, CH_2N), 2.56 (s, 2 H, CH_2Pd) and 2.29 (s, 6 H, NCH_3); both, δ 7.59–7.54 (m, 2 H, aryl H), 7.32–7.27 (m, 2 H, aryl H) and 6.97 (m, 1 H, aryl H); ^{13}C NMR (50.3 MHz, $CDCl_3$), δ 142.3 (CPd), 135.2, 133.7, 130.7, 129.9, 129.7, 128.4, 127.9, 124.5, 123.1 and 129.9, 65.7 (CH_2), 51.1 and 50.7 (NCH_3), 22.6 and 20.0 (CH_2Pd) (Found: C, 49.35; H, 4.80; N, 4.20. Calc. for $C_{28}H_{32}Cl_2N_2Pd_2$: C, 49.45; H, 4.75; N, 4.10%).

Oxidative addition[28] *to give complex* **5**. A mixture of $[Pd(dba)_2]$ (10 g, 19 mmol) and 1-bromo-2-[(dimethylamino)methyl]naphthalene (5.1 g, 19 mmol) in acetone (50 cm^3) was stirred at 50 °C for 2 h after which time the solvent was removed *in vacuo*. The solid residue was extracted with CH_2Cl_2 (50 cm^3). After removal of the solvent, 5.8 g (15 mmol, 90%) of bright yellow-orange product remained. It was crystallized by diffusion of Et_2O into a solution in CH_2Cl_2. NMR ($CDCl_3$): ^1H (200 MHz), δ 8.79–8.46 (m, 1 H, aryl H), 7.65–7.25 (m, 4 H, aryl H), 7.00 (d, 1 H, J = 4.0 Hz, aryl H), 4.31 (s, 2 H, CH_2) and 2.77 (s, 6 H, NCH_3); ^{13}C (75.5 MHz), δ 146.6, 142.5, 137.0, 132.0, 131.7, 127.4, 125.5, 124.8, 124.3, 124.0, 119.77 (10 C, aryl C), 74.4 (CH_2), 53.2 and 52.8 (NCH_3) (Found: C, 42.05; H, 3.90; N, 3.85. Calc. for $C_{26}H_{28}Br_2N_2Pd_2$: C, 42.15; H, 3.80; N, 3.80%).

Direct palladation to give complex **6**. A mixture of 2-[(dimethylamino)methyl]-3-methylnaphthalene (0.26 g, 1.31 mmol) and $Pd(O_2CMe)_2$ (0.34 g, 1.51 mmol) in MeOH (30 cm^3) was stirred overnight at room temperature. Some metallic palladium that had formed was removed by centrifugation. To the clear red solution was added a solution of LiCl (60 mg, 1.42 mmol) in MeOH (5 cm^3). Immediately a yellow solid precipitated. After stirring for 1 h the solid was collected by centrifugation and washed with two portions of MeOH (20 cm^3) and diethyl ether (30 cm^3). It was dried *in vacuo*, yielding 0.43 g (1.26 mmol, 96%) of product. Crystals were obtained by diffusion of Et_2O into a solution in CH_2Cl_2. NMR (200 MHz, $CDCl_3$): ^1H, δ 8.67 (m, 1 H, aryl H of isomer **a**), 8.53 (m, 1 H, aryl H of isomer **b**), 7.55 (m, 1 H, aryl H), 7.35–7.24 (m, 3 H, aryl H), 4.28 (s, 2 H, CH_2 of isomer **a**), 4.26 (s, 2 H, CH_2 of isomer **b**), 2.78 (s, 3 H, CH_3 of isomer **a**), 2.76 (s, 3 H, CH_3 of isomer **b**) and 2.34 (s, 3 H, aryl CH_3); ^{13}C NMR, δ 145.0 (CPd), 142.2 and 142.1, 135.9 and 135.8, 132.9 and 132.7, 130.4, 129.6, 127.0 and 126.8, 125.6, 125.0, 123.8 and 123.5, 72.6 and 72.4 (CH_2), 53.2 and 52.9 (NCH_3), and 21.1 (aryl CH_3) (Found: C, 49.30; H, 7.60; Cl, 10.30; N, 4.15. Calc. for $C_{28}H_{32}Cl_2N_2Pd_2$: C, 49.45; H, 7.75; Cl, 10.40; N, 4.10%).

Of compound **I**. This reaction was carried out using the above

procedure described for complex **6**. The reaction mixture was stirred at room temperature for 2 d. The yellow product consisted of a co-ordination complex of **I** with $PdCl_2$ in a 2:1 molar ratio (61%) and complex **10** (10%).[3] No satisfactory analytical data could be obtained for the former compound. Addition of [$^2H_5$]pyridine to this complex gave the spectrum of compound **I**. ^1H NMR (200 MHz, $CDCl_3$): first complex, δ 9.69 (s, 1 H, aryl H), 7.97–7.77 (m, 3 H, aryl H), 7.56–7.47 (m, 2 H, aryl H), 4.33 (s, 2 H, CH_2) and 2.73 (s, 6 H, NCH_3).

Of compound **III**. This reaction was carried out as described for complex **6**. The reaction mixture was stirred at room temperature for 3 h. The yield of complex **9** was 96%.[3] The use of $Li_2[PdCl_4]$ or 0.5 equivalent of palladium salt did not alter the outcome.

Of compound **IV**. This reaction was carried out as described for complex **6**. The reaction mixture was stirred at room temperature for 3 h. The yield of complex **10** was 99%. When $Li_2[PdCl_4]$ was employed instead the yield was 92%.

Derivatization Reactions.—Complex **7a**. A mixture of complex **6** (0.60 g, 0.88 mmol) and $Ag(O_3SCF_3)$ (0.45 g, 1.75 mmol) in CH_2Cl_2 (20 cm^3) was stirred at room temperature for 2 h. Silver chloride was removed by centrifugation and the yellow solution concentrated under reduced pressure yielding 0.87 g (1.62 mmol, 92%) of product. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into a concentrated solution in CH_2Cl_2. NMR ($CDCl_3$): ^1H (300 MHz), δ 7.93 (m, 1 H, aryl H), 7.57 (m, 1 H, aryl H), 7.32 (m, 2 H, aryl H), 7.28 (s, 1 H, aryl H^4), 4.19 (s, 2 H, CH_2), 2.75 (s, 6 H, NCH_3), 2.31 (s, 3 H, aryl CH_3) and 2.25 (s, 6 H, CH_3CN); ^{13}C (75.5 MHz), δ 143.2, 142.3, 135.0, 132.8, 130.4, 128.4, 127.6, 126.5, 125.3, 124.4, 123.0 (CH_3CN), 120.7 (q, J_{CF} = 321 Hz, CF_3), 119.0 (CN), 72.3 (CH_2), 52.9 (NCH_3), 20.8 (aryl CH_3), 3.2 (CH_3CN) and 2.5 (CH_3CN) (Found: C, 41.55; H, 4.15; N, 7.65. Calc. for $C_{19}H_{22}F_3N_3O_3PdS$: C, 42.60; H, 4.15; N, 7.85%).

Complexes **7b** *and* **7c**. These cationic complexes were prepared analogously to **7a**. Instead of acetonitrile, an equivalent of the bidentate ligand bipy or tmen was added. The complexes were obtained in 92 and 81% yield respectively. No satisfactory analytical data were obtained. ^1H NMR (CD_3CN): **7b** (300 MHz), δ 8.37 (d, 2 H, J = 8.0, aryl H), 8.28–8.12 (m, 2 H, aryl H), 7.80 (d, 1 H, J = 8.0, aryl H), 7.71 (d, 1 H, J = 8.2), 7.45 (s, 1 H, naphthyl H^4), 7.45 (t, 1 H, J = 8.1, aryl H), 7.12 (t, 1 H, J = 8.2 Hz, aryl H), 5.3–3.6 (br s, 2 H, CH_2), 2.87 (s, 6 H, NCH_3) and 2.44 (s, 3 H, aryl CH_3); the remaining aromatic protons were found by integration from 9.0 to 7.2; **7c** (200 MHz), δ 8.81 (d, 1 H, J = 7.2, aryl H), 7.67–7.63 (m, 1 H, aryl H), 7.55–7.30 (m, 3 H, aryl H), 4.81 (d, 1 H, J = 14.4, aryl C*H*HN), 4.04 (d, 1 H, J = 14.0 Hz, aryl CH*H*N), 2.76 (br s, 8 H, CH_3 and CH_2), 2.48 (s, 3 H, CH_3), 2.38 (s, 6 H, NCH_3) and 2.24 (br s, 8 H, CH_3 and CH_2).

Complex **8**. To a solution of $Ag(O_3SCF_3)$ (0.69 g, 2.1 mmol) in thf (20 cm^3) was added a solution of complex **6** (0.69 g, 2.0 mmol) in thf (30 cm^3). After stirring at room temperature for 3 h, AgCl was removed by centrifugation. The solution was concentrated under reduced pressure leaving an extremely hygroscopic yellow thf adduct. Crystallization from Et_2O yielded the thf-free product in 88% yield. NMR ($CDCl_3$): ^1H (300 MHz), δ 8.01 (d, 1 H, J = 8.1, aryl H), 7.60 (d, 1 H, J = 8.2 Hz), 7.37 (m, 2 H, aryl H), 7.31 (s, 1 H, aryl H^4), 4.19 (s, 2 H, CH_2), 2.78 (s, 6 H, NCH_3) and 2.34 (s, 3 H, aryl CH_3); ^{13}C (200 MHz), δ 143.0, 137.1, 134.9, 132.4, 129.9, 127.5, 126.3, 125.9, 125.3, 124.4, 120.0 (q, J_{CF} = 319 Hz, CF_3), 72.5 (CH_2), 53.0 (NCH_3) and 20.7 (aryl CH_3). The best reproducible analytical data were obtained from the crude product, which contained 1 equivalent of thf (Found: C, 40.75; H, 4.30; N, 2.85. Calc. for $C_{34}H_{40}F_6N_2O_7Pd_2S_2$: C, 41.70; H, 4.10; N, 2.85%).

Complex **7d**. To a solution of complex **6** (1 g, 2.94 mmol) in thf (40 cm^3) was added a solution of K[$HB(pz)_3$] (0.74 g, 2.94 mmol) in thf (20 cm^3). After stirring at 60 °C for 2 h the solvent was removed *in vacuo*. After extraction with CH_2Cl_2 (50 cm^3) and removal of the solvent *in vacuo* white **7d** (1.40 g, 92%) remained. Crystals were obtained by diffusion of ether into a concentrated solution of it in methylene chloride. NMR ($CDCl_3$): ^1H (200 MHz), δ 7.92–7.84 (m, 3 H), 7.54 (d, 1 H, J = 8.0), 7.30 (s, 1 H), 7.20 (t, 1 H, J = 7.1), 6.91 (t, 1 H, J = 7.6), 6.47 (d, 1 H, J = 8.5 Hz), 6.30–6.05 (m, 3 H), 4.33 (s, 2 H, CH_2), 2.77 (s, 6 H, NCH_3) and 2.42 (s, 3 H, aryl CH_3); the remaining protons occurred as an extremely broadened signal from 8.0 to 7.0; ^{13}C (75.5 MHz), δ 150.3, 141.8, 136.2, 135.8 (2 C), 133.1, 130.9, 129.2, 126.6, 125.3, 124.7, 123.0, 105.0 (pz), 72.6 (CH_2), 52.8 (NCH_3) and 20.9 (aryl CH_3).

Complex **11**. This hygroscopic compound was prepared using the same procedure described for **7a** using **5** as the starting palladium complex. The yield was 92%. Crystallization was achieved by diffusion of Et_2O into a concentrated solution of **11** in CH_2Cl_2. NMR ($CDCl_3$): ^1H (200 MHz), δ 8.03–7.98 (m, 1 H, aryl H), 7.70–7.66 (m, 1 H, aryl H), 7.54 (d, 1 H, J = 8.1, H^3 or H^4), 7.41–7.36 (m, 2 H, aryl H), 7.02 (d, 1 H, J = 8.1 Hz, H^4 or H^3), 4.19 (s, 2 H, CH_2), 2.72 (s, 6 H, NCH_3), 2.28 (s, 3 H, CH_3CN) and 2.04 (s, 3 H, CH_3CN); ^{13}C (50.3 MHz), δ 143.2, 139.7 136.3, 132.1, 128.7, 128.3, 126.6, 125.3, 123.3, 122.9, 120.1, 116.9, 73.8 (CH_2), 52.0 (NCH_3) and 3.4 (CH_3CN).

Complex **12**. To a solution of complex **5** (0.30 g, 0.81 mmol) in CH_2Cl_2 (10 cm^3) was added pyridine (0.5 cm^3, 5 mmol). After stirring at room temperature for 10 min the solvent was removed *in vacuo*. The residue was washed with Et_2O and crystallized by slow diffusion of Et_2O into a solution of it in CH_2Cl_2. The yield was 96%. NMR ($CDCl_3$): ^1H (200 MHz), δ 8.78 (dd, 2 H, J_1 = 1.4, J_2 = 6.6 Hz, pyridine H^2), 7.73–7.51 (m, 3 H, aryl H), 7.24–7.10 (m, 4 H, aryl H), 6.83–6.73 (m, 2 H, aryl H), 4.29 (s, 2 H, CH_2) and 2.69 (s, 6 H, NMe_2); ^{13}C (50.3 MHz), δ 155.0 (pyridine C^2), 152.4, 143.2, 137.7 (pyridine C^4), 136.6, 132.7, 128.3, 128.0, 125.5, 124.9 (pyridine C^3), 124.3, 124.2, 120.0, 75.0 (CH_2) and 54.1 (NCH_3).

Oxidation Reactions.—General procedure with Bu^tO_2H. *tert*-Butyl hydroperoxide (4 mmol) was added to a solution of the appropriate arylpalladium complex (1 mmol) in CH_2Cl_2 (10 cm^3). The reaction was carried out in the absence of catalyst, or in the presence of 5 mol % of [$VO(acac)_2$] or [{$RhCl(cod)$}$_2$] (see Table 2). After stirring at room temperature for 3 h a sample of 1 cm^3 was carefully concentrated under reduced pressure. The residue was dissolved in $CDCl_3$ and a ^1H NMR spectrum was recorded, using CH_2Cl_2 as an internal standard. The remaining solution was concentrated, taken up in MeOH (10 cm^3) and N_2H_5OH (10 mmol) was added. After stirring at room temperature for 3 h the solvent was removed *in vacuo*. The residue was analysed by ^1H NMR spectroscopy. The results are summarized in Table 2. See the syntheses of compound **VI** for analytical data. In the oxidation reaction of complex **6**, approximately 10% of 1-chloro-2-[(dimethylamino)methyl]-3-methylnaphthalene was formed. Separation from **VI** was achieved by prolonged evacuation under vacuum (0.1 mmHg, 8 h). Since the separation from **VII** is extremely difficult, the reaction was stopped after 15 min. NMR {for 1-chloro-3-methyl-2-[(dimethylamino)methyl]naphthalene, in $CDCl_3$}: ^1H (200 MHz), δ 8.32–8.27 (m, 1 H, aryl H), 7.67–7.60 (m, 1 H, aryl H), 7.57 (s, 1 H, aryl H^4), 7.54–7.47 (m, 2 H, aryl H), 3.78 (s, 2 H, CH_2), 2.61 (s, 3 H, aryl CH_3) and 2.32 (s, 6 H, NCH_3); ^{13}C (50.3 MHz), δ 137.3, 134.2, 133.7, 129.7, 127.5, 127.2, 126.4, 126.1, 125.0, 124.0, 58.0 (CH_2), 45.4 (NCH_3) and 20.3 (aryl CH_3). Mass spectrum: m/z 233 ($M^{\bullet+}$ = $C_{14}H_{16}{}^{35}ClN^{\bullet+}$), 198 ([$M$ − Cl]$^{\bullet+}$), 188 ([M − $NHMe_2$]$^{\bullet+}$) and 153 ([M − $NHMe_2$ − Cl]$^{\bullet+}$).

Complex **6** *with* [$MoO(O_2)${$OP(NMe_2)_3$}(H_2O)].[17] The complex [$MoO(O_2)${$OP(NMe_2)_3$}(H_2O)] (11.8 mmol) was added to a solution of **6** (1.0 g, 1.47 mmol) in CH_2Cl_2 (20 cm^3). After stirring at room temperature for 12 h the reaction mixture was concentrated *in vacuo* and dissolved in MeOH (20 cm^3). To this solution was added N_2H_5OH (15 mmol). After stirring at room temperature for 3 h the reaction mixture was filtered over

Table 3 Crystal data for complex **7a**

Formula	$C_{19}H_{22}F_3N_3O_3PdS$
M	535.88
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	13.193(1)
b/Å	11.801(1)
c/Å	14.797(1)
β/°	105.15(1)
U/Å^3	2223.7(3)
Z	4
D_c/g cm^{-3}	1.601
F(000)	1080
μ(Mo-Kα)/cm^{-1}	9.6
Crystal size (mm)	0.10 × 0.35 × 0.05
Minimum and maximum residual density/e Å^{-3}	−0.42, 0.62
T/K	295
λ(Mo-Kα) (Zr)/Å	0.710 73
Minimum, maximum θ/°	1.43, 28.5
Scan type	ω–2θ
Scan range/°	0.60 + 0.35 tan θ
Horizontal and vertical aperture/mm	3.00, 6.00
Reference reflections	1 0 3, −3 −3 0, 0 −4 4 (decay 2%)
hkl ranges	−17 to 16, −15 to 0, −18 to 19
Total, unique data	10 374, 5281
Observed data [$I > 2.5\sigma(I)$]	3455
N_{ref}, N_{par}	3455, 288
R, R', S*	0.042, 0.036, 1.17
Weighting scheme	$w^{-1} = \sigma^2(F)$
Maximum and average shift/error	0.77, 0.03

* $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w(|F_o|^2)]^{\frac{1}{2}}$, $S = [\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{\frac{1}{2}}$, n = no. of observations, m = no. of parameters.

Table 4 Final coordinates of the non-hydrogen atoms for complex **7a**

Atom	x	y	z
Pd	0.355 49(2)	0.008 86(2)	0.883 85(2)
N(1)	0.439 1(2)	0.088 9(3)	0.803 5(2)
N(2)	0.255 4(2)	−0.069 5(3)	0.945 8(2)
N(3)	0.352 1(3)	0.150 5(3)	0.972 7(2)
C(1)	0.373 2(3)	−0.120 8(3)	0.803 9(3)
C(2)	0.375 6(3)	−0.239 7(4)	0.827 0(3)
C(3)	0.375 4(3)	−0.282 8(3)	0.915 4(3)
C(4)	0.381 3(3)	−0.395 9(4)	0.933 5(4)
C(5)	0.388 6(4)	−0.472 4(4)	0.864 4(5)
C(6)	0.390 2(3)	−0.437 3(5)	0.778 6(5)
C(7)	0.385 2(3)	−0.319 1(5)	0.756 4(4)
C(8)	0.394 3(3)	−0.278 4(6)	0.669 2(4)
C(9)	0.400 0(3)	−0.167 4(6)	0.650 1(3)
C(10)	0.390 2(3)	−0.086 9(4)	0.720 5(3)
C(11)	0.416 1(4)	−0.124 9(6)	0.558 5(3)
C(12)	0.400 2(3)	0.037 8(4)	0.708 1(3)
C(13)	0.554 8(3)	0.068 4(4)	0.839 7(3)
C(14)	0.421 7(4)	0.214 8(3)	0.797 2(3)
C(15)	0.195 0(3)	−0.102 5(3)	0.979 4(3)
C(16)	0.120 2(4)	−0.149 1(5)	1.026 4(4)
C(17)	0.351 0(3)	0.216 6(3)	1.027 0(3)
C(18)	0.350 8(3)	0.302 0(4)	1.096 7(3)
S	0.135 84(12)	0.133 07(13)	0.172 32(11)
F(1)	0.180 0(4)	0.127 1(5)	0.351 0(3)
F(2)	0.313 0(4)	0.150 0(5)	0.293 1(3)
F(3)	0.240 7(5)	−0.009 7(5)	0.289 6(5)
O(1)	0.194 1(3)	0.097 2(3)	0.108 7(3)
O(2)	0.044 8(3)	0.070 6(5)	0.171 8(3)
O(3)	0.125 2(4)	0.251 6(3)	0.177 7(3)
C(19)	0.220 6(7)	0.097 0(8)	0.281 4(5)

Celite and concentrated under reduced pressure. The residue was dissolved in Et_2O (50 cm^3) and washed with two portions of water (100 cm^3). The organic layer was dried on $MgSO_4$ and concentrated *in vacuo* (0.1 mmHg, 8 h). The yield of 1-chloro-2-[(dimethylamino)methyl]-3-methylnaphthalene was 42%.

Crystal-structure Determination of Complex **7a**.—X-Ray data were collected on an Enraf–Nonius CAD4 diffractometer for a yellowish crystal glued on top of a glass fibre. Unit-cell parameters were derived from the 25 SET4[29] setting angles in the range $25 < 2\theta < 35°$. A total of 10 374 reflections were scanned, corrected for Lorentz polarization, a small linear decay (2%) and absorption/extinction (DIFABS;[30] correction range 0.84–1.11), resulting in a unique set of 3455 reflections with $I > 2.5\sigma(I)$. The structure was solved by direct methods (SHELXS 86[31]) and refined on F by full-matrix least squares to a final $R = 0.042$ (with SHELX 76[32]). Hydrogen atoms were taken into account at calculated positions with two common isotropic thermal parameters. Weights were based on counting statistics. Geometrical calculations and the ellipsoid plot were done with PLATON.[33] Scattering factors were taken from ref. 34, corrected for anomalous dispersion.[35] Numerical details are collected in Table 3, positional parameters for the non-hydrogen atoms in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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