Cyclopalladation of 2-[(Dimethylamino)methyl]-Substituted Naphthalenes: 1- *vs* 3-Palladation. Crystal Structures of [Hydrotris(pyrazolyl)borato][2-[(dimethylamino)methyl]-3-naphthyl]palladium and *trans*-[4,4-Dimethyl-2-(2-naphthyl)oxazoline]palladium Dichloride

Jean-Marc Valk,[†] Fida Maassarani,[†,‡] Paul van der Sluis,[§] Anthony L. Spek,[*,§] Jaap Boersma,[†] and Gerard van Koten[*,†]

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Bijvoet Center for Biomolecular Research, Laboratory of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received January 13, 1994[⊗]

In the course of a study directed toward the selective metal-mediated oxidation of naphthalenes to 1,4-naphthoquinones, the palladation of 2-[(dimethylamino)methyl]naphthalene and 4,4-dimethyl-2-(2-naphthyl)oxazoline was investigated. Direct palladation of 2-[(dimethylamino)-methyl]naphthalene with Li_2PdCl_4 showed a clean selectivity for position 3 instead of the earlier reported preference for position 1. This finding was confirmed by the crystal structure of [hydrotris(pyrazolyl)borato][2-[(dimethylamino)methyl]-3-naphthyl]palladium. The complex $C_{22}H_{24}N_7BPd{\cdot}0.5CH_3OH$ crystallizes as triclinic in space group $P\bar{1}$ with a = 13.170(1) Å, b = 13.413(1) Å, c = 14.112(1) Å, α = 109.34(1)°, β = 95.60(1)°, γ = 97.38(1)°, and Z = 4. Final R = 0.025 for 8181 observed reflections with $I > 2.5\sigma(I)$. The second ligand, 4,4-dimethyl-2-(2-naphthyl)oxazoline, was also cyclopalladated on position 3. The fastest reaction was obtained when palladium acetate was employed. Reaction with Li_2PdCl_4 yielded the cyclopalladated complex as the minor product and the intermediate coordination complex *trans*-[4,4-dimethyl-2-(2-naphthyl)oxazoline]palladium dichloride as the major product. This latter complex $C_{30}H_{30}Cl_2N_2O_2Pd$ crystallizes in orthorhombic space group *Pbca* with a = 20.221(1) Å, b = 16.000(1) Å, c = 8.516(1) Å, and Z = 4. Final R = 0.039 for 2479 reflections with $I > 2.5\sigma(I)$.

Introduction

The oxidation of substituted naphthalenes is an important process, because some of the oxidation products are of interest for pharmaceutical applications. For example, 2-methyl-1,4-naphthoquinone (menadione) is the starting material for the synthesis of vitamin K. However, like most oxidation reactions, the conversion of 2-methylnaphthalene into menadione suffers from several disadvantages. In the industrial process, 2-methylnaphthalene is oxidized by chromium(VI) in a strongly acidic mixture of concentrated sulfuric acid and acetic acid. The high reactivity of this oxidizing system results in a low selectivity. Apart from menadione (<70%), a large number of byproducts are formed, *i.e.* the regio-isomer 6-methyl-1,4-naphthoquinone, as well as 2-naphthaldehyde, phthalic acid, 4-methylphthalic acid, and the corresponding phthalic acid anhydrides.[1] Moreover, the process requires a large excess of chromium, thereby creating a severe environmental problem. Typically, in this reaction 18 kg of waste is produced for every 1 kg of menadione. Both the low selectivity and the waste problem indicate that new routes for the oxidation of aromatic hydrocarbons are needed.

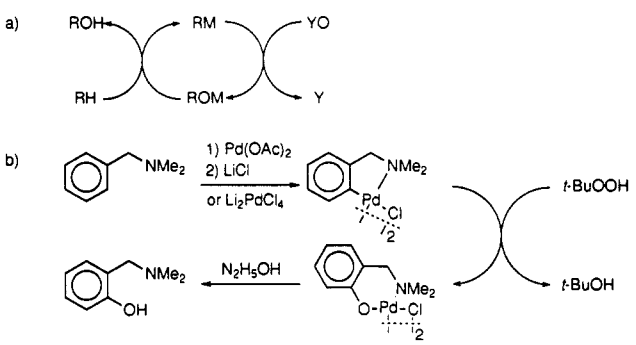


Figure 1. (a) Strategy studied for the metalation and oxidation of aromatic compounds exemplified by (b) metallation and subsequent oxygenation of [(dimethylamino)-methyl]benzene.

In a recent study[2] we explored the reaction, shown in Figure 1a, for the regioselective hydroxylation of aromatic systems involving (i) C–H bond activation by cyclopalladation, (ii) selective oxygenation of the Pd–C bond, and

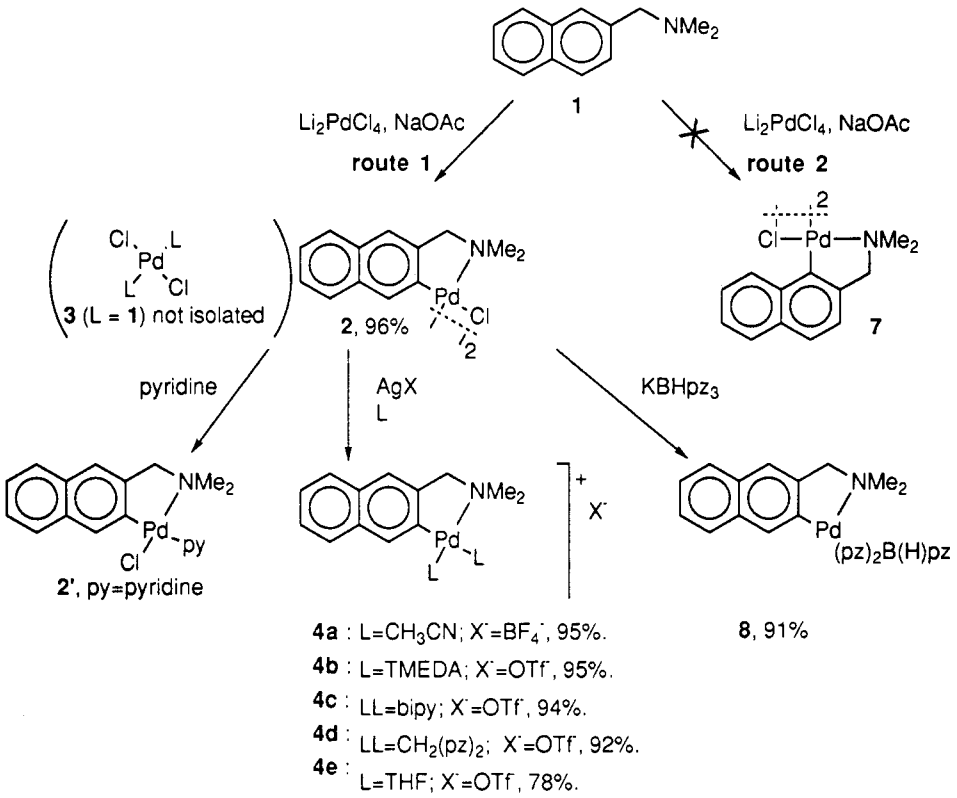
* To whom correspondence should be addressed: G.v.K., all noncrystallographic matters; A.L.S., crystallographic matters.
† Debye Institute.
‡ On leave from The Lebanon University, Tripoli, The Lebanon.
§ Bijvoet Center for Biomolecular Research.
⊗ Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) (a) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Hafner, K., Rees, C. W., Trost, B. M., Lehn, J. M., von Ragué Schleyer, P., Zahradnik, R., Eds.; Springer: Berlin, 1984; pp 93–96. (b) *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 57–59.

(2) Alsters, P. L.; Teunissen, H. T.; Boersma, J.; van Koten, G. *Recl. Trav. Chim. Pays-Bas*, **1990**, *109*, 487; *Organometallics* **1993**, *12*, 4691.

0276-7333/94/2313-2320$04.50/0

Scheme 1



(iii) reductive removal of the hydroxylated arene, ROH. The feasibility of this cycle was demonstrated by the selective vanadium-catalyzed oxygenation of bis(μ-chloro)-bis{2-[(dimethylamino)methyl]phenylpalladium} by *tert*-butyl hydroperoxide.[2] The starting material is obtained via the well-established cyclopalladation reaction of *N,N*-dimethylbenzylamine (DMBA-H).[3] This route allows the preparation of 2-hydroxy-*N,N*-dimethylbenzylamine in >90% yield starting from DMBA-H (see Figure 1b). Although this sequence does not yet represent a catalytic process, we recently set out to study whether the above approach could be applied to the selective hydroxylation of 2-substituted naphthalenes.

2-[(Dimethylamino)methyl]naphthalene (**1**) was chosen as the model system because it was reported that the CH_2-NMe_2 moiety directs cyclometalation to the 1 position[4] (Scheme 1, route 2), with the 3-cyclometalated species **7** being formed as a minor product (route 1). The 1- and 3-palladated naphthalenes were reported to be formed in a 2/1 ratio.

As alternative ligands, 2-(2-naphthyl)oxazolines (**11** and **12**) can be employed (see Scheme 3). The imine moiety present in these compounds is also capable of directing cyclometalation[5] but has the advantage that the oxazoline fragment in the hydroxylated product may subsequently be converted into either a carboxylate[6] or a methyl group.[7]

(3) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(4) Julia, M.; Duteil, M.; Lallemand, J. Y. *J. Organomet. Chem.* **1975**, *102*, 239.
(5) (a) Gschwend, H. W.; Hamdan, A. *J. Org. Chem.* **1975**, *40*, 2008. (b) Meyers, A. I.; Mihelich, E. D. *J. Org. Chem.* **1975**, *40*, 3158.
(6) (a) Meyers, A. I.; Temple, D. L.; Haidukewych D.; Mihelich, E. D. *J. Org. Chem.* **1974**, *39*, 2787. (b) Meyers, A. I.; Slade, J. *J. Org. Chem.* **1980**, *45*, 2785. (c) Levin, J. I.; Weinreb, S. M. *Tetrahedron Lett.* **1982**, *23*, 2347.
(7) Meyers, A. I.; Himmelsbach, R. J.; Reuman, M. *J. Org. Chem.* **1983**, *48*, 4053.

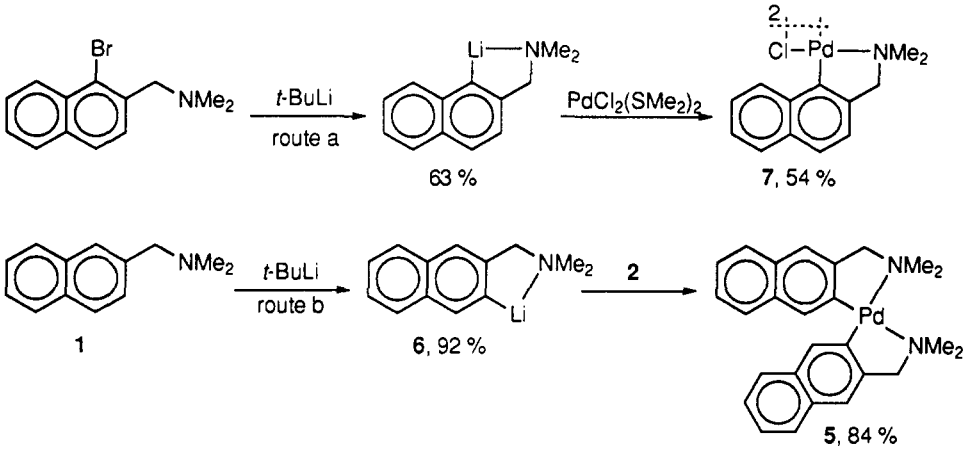
In this paper we report the results of our studies on the regioselectivity of the cyclopalladation of 2-substituted naphthalenes. Moreover, since oxidation of cyclopalladated complexes has been found to be highly dependent on the charge density of the palladium center,[2] several derivatizations leading to various RPdX species will be described.

Results

Palladation of 2-[(dimethylamino)methyl]naphthalene. The reaction of Li_2PdCl_4 with 2-[(dimethylamino)methyl]naphthalene (**1**) was carried out in methanol using either excess **1** or NaOAc as a base to remove the HCl formed during the reaction. When **1** was used as a base, the yield of 3-palladated chlorine-bridged dimer **2** was 80%, while about 10% of the nonmetalated precursor complex $PdCl_2(C_{10}H_7CH_2NMe_2\text{-}2)_2$ (**3**) was still present after 20 h (Scheme 1, route 1). When NaOAc was used as a base, **2** was formed quantitatively as the sole organometallic product (96% isolated yield) and the required reaction time was reduced from 20 to 3 h.

The $PdCl_2$ coordination complex **3** could be easily distinguished from the cyclopalladation product **2** by NMR spectroscopy. The ^1H NMR spectrum of the 3-palladated compound **2** in $CDCl_3$ shows two patterns in a 2:3 ratio, each having one singlet arising from the NCH_3 group and a singlet from the benzylic protons. Furthermore, the proton in the 1-position appears as a single singlet, while two singlets are found for proton 4. These observations are compatible with the presence of a 2:3 *cis*- and *trans*-isomer mixture. Upon the addition of pyridine, the spectrum collapses into one, new pattern, as a result of cleavage of the chlorine bridge to form the mononuclear pyridine complex $PdCl(3\text{-}C_{10}H_6CH_6NMe_2\text{-}2)(C_5H_5N)$ (**2'**) (Scheme 1). The $PdCl_2$ complex **3** shows only one pattern

Scheme 2



for the CH_2 and CH_3 protons, as well as for the aromatic protons 1 and 4 (*i.e.* one singlet for proton 1, while proton 4 appears as part of an AB pattern). In this case, the addition of excess pyridine to **3** yielded free ligand **1** and $PdCl_2(pyridine)_2$.

The occurrence of 3-palladation is surprising because a previous report claimed the formation of the 1-palladated product **7** under the same reaction conditions (Scheme 1, route 2), with the 3-palladated product only being formed as a minor product.[4,8]

To establish the identities of both **2** and **7**, the 1-palladated naphthalene **7** (Scheme 2a) was prepared in 54% yield by the 1:1 reaction of $PdCl_2(SMe_2)_2$ with [2-(dimethylamino)methyl-1-naphthyl]lithium[9] in Et_2O.

A derivative of **2**, *viz.* [hydrotris(pyrazolyl)borato][2-[(dimethylamino)methyl]-3-naphthyl]palladium (**8**) (see Scheme 1) was obtained from **2** with potassium hydrotris(pyrazolyl)borate in THF (90% yield), analogous to that described by Onishi *et al.*[10] Crystallization of **8** from methanol yielded crystals suitable for X-ray diffraction. The unit cell contains two sets of two independent molecules, which differ by the presence or absence of a methanol molecule coordinating to N-7 of the pyrazolyl group that does not coordinate to the palladium (type 1 and type 2, respectively; the molecular structure of both types of **8** in the solid state is shown in Figure 2). Relevant bond distances and bond angles are presented in Table 1. Crystal data are shown in Table 4.

The crystal structure of complex **8** conclusively shows that 3-palladation has occurred. In both type 1 and 2 molecules, the metal center in **8** is almost perfectly planar, while the deviations of the angles between the substituents from 90° are small. The metal plane is not coplanar with the plane of the naphthalene system, which is reflected in the value found for the dihedral angle C(2)–C(1)–Pd–N(4) [15.30(20)° in type 1; 20.40(20)° in type 2]. Although in the solid state two pyrazolyl groups are attached to the palladium, ^1H NMR spectra at 25 °C show only one kind of pyrazolyl groups indicating fast exchange on the NMR time scale. This rapid *intra*molecular exchange contrasts with the behavior of the corresponding 2-[(dimethylamino)methyl]phenyl (DMBA) complex, which was reported to show two different kinds of pyrazolyl groups.[10] The reason for these differences remains unclear, as also molecular models show no obvious differences in the steric requirements of the pyrazolyl groups in either the naphthyl (**8**) or the DMBA compound.

The corresponding bis(3-naphthyl)palladium (**5**) was prepared by reacting the naphthylpalladium chloride **2** with the 3-lithiated derivative **6** at −78 °C in THF (Scheme 2). The latter was obtained from the reaction of **1** with *t*-BuLi in pentane at −78 °C in 92% yield.

The cationic complexes **4a–e** were prepared by reacting naphthylpalladium chloride (**2**) with silver tetrafluoroborate or silver triflate in the presence of the appropriate mono- or bidentate ligands (see Scheme 1). Their ^1H NMR data are summarized in Table 2.

Palladation of 4,4-Dimethyl-2-(2-naphthyl)oxazoline. 4,4-Dimethyl-2-(2-naphthyl)oxazoline (**11**) reacts very slowly with Li_2PdCl_4 to give a mixture of two products, *viz.* the palladium dichloride complex $PdCl_2(L)_2$ (**9**) (>94% yield) and the 3-palladated product **10** (<5% yield) (Scheme 3). When the reaction was run for periods shorter than 1 week, the only observable product was **9**, present as a mixture of *cis* and *trans* isomers. Cyclometalated **10** was formed in high yield when $Pd(OAc)_2$ in HOAc was employed instead of Li_2PdCl_4.[11] After workup with LiCl in acetone, **10** was isolated in 70% yield.

As in the case of the palladation of 2-[(dimethylamino)methyl]naphthalene (**1**) (vide supra), the 3-palladated complex **10** exists as a mixture of *cis* and *trans* isomers, again in a 2:3 molar ratio. In contrast, the precursor complex **9** of $PdCl_2$ with 4,4-dimethyl-2-(2-naphthyl)oxazoline shows two singlets for H(1), as well as for the OCH_2 and N–C–CH_3 protons, which can only be explained by the formation of a *cis*/*trans* isomer mixture. Complex **9** was crystallized by slow distillation of Et_2O into a concentrated solution of **9** in CH_2Cl_2, and its crystal structure was solved (the molecular structure of **9** is shown in Figure 3). The crystal data are presented in Table 4. Selected bond distances and bond angles are presented in Table 3. The palladium center is nearly perfectly square planar surrounded with the two organic ligands *trans* and in an *anti*-fashion. The *trans* structure points to preferential crystallization of one of the geometrical isomers. When the crystals are dissolved in $CDCl_3$, the ^1H NMR

(8) The original paper describes the reaction of 2-[(dimethylamino)methyl]naphthalene with K_2PdCl_4. The fact that the results were independent of the cation present in this palladating species was established when we found that K_2PdCl_4 and Li_2PdCl_4 gave similar results.

(9) Gay, R. L.; Hauser, C. R. *J. Am. Chem. Soc.* **1967**, *89*, 2297.

(10) Onishi, M.; Ohama, Y.; Sugimura, K.; Hiraki, K. *Chem. Lett. Chem. Soc. Jpn.* **1976**, *955*.

(11) Izumi, T.; Watabe, H.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1711.

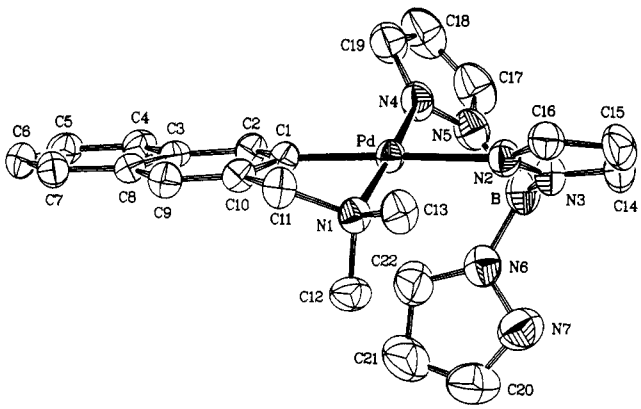


Figure 2. ORTEP drawing (50% probability level) of the molecular structure of **8** together with the adopted numbering scheme. (MeOH molecule and H-atoms are omitted for clarity).

spectrum of the solution again shows the *cis* and *trans* isomer mixture.

2-(2-Naphthyl)oxazoline (**12**) (Scheme 3) was prepared to investigate the steric influence of the methyl groups in **11** on cyclopalladations. Compound **12** reacted with Li_2PdCl_4 to yield the $PdCl_2$ coordination complex *trans*-**14** (Scheme 3); this reaction proceeded to completion in 91% isolated yield in a period of one day at 25 °C.

Addition of NaOAc to **12** did not convert **14** into 3-palladated **13** as was observed for the formation of the 3-palladated 2-naphthyloxazoline (**10**). The reaction of **12** with $Pd(OAc)_2$ gave an undefined mixture containing metallic palladium. Probably the oxazoline ring is destroyed by $Pd(OAc)_2$.

NMR Spectra. On N-coordination with the palladium center in cyclopalladated complexes, a puckered 5-membered ring is formed. When the Pd–N coordination is inert on the NMR time scale, this puckering will affect the resonance pattern of the protons in the ring. Since the barrier to ring inversion is generally believed to be small,[12] the benzylic protons as well as the NCH_3 protons will usually appear as one singlet in the ^1H NMR spectrum. However, when the inversion is slow on the NMR time scale, the CH_2 protons will be diasterotopic and will therefore appear as AB or AX patterns, while the $N(CH_3)_2$ protons will be present as two singlets. The ring inversion will cause a concomitant movement of the other substituents attached to palladium and therefore the bulkiness of the substituent, as well as the strength of the Pd–N coordination may be expected to influence the rate of inversion. These arguments can be used to explain the NMR spectra of cationic complexes **4a–e**. Both MeCN and TMEDA (in **4a,b**) are too small to prevent ring inversion. Surprisingly, even bpy is unable to fix the ring, although models show that one of its β-protons is very close to H(4) of the naphthyl ring *ortho* to the Pd–C bond in **4c**. As **4a–c** show singlets for the CH_2 and NCH_3 protons, no choice can be made between a rapid on–off movement of the NMe_2 group or fast ring inversion on the NMR time scale. However, [bis(pyrazolyl)methane]-palladium (**4d**) behaves differently. Although the distance between the proton *ortho* to palladium in the naphthyl system in **4d** and H(3) in one of the pyrazolyl rings is approximately equal to the distance mentioned above for **4c**, the ring inversion in **4d** is accompanied by a concomitant inversion of the six-membered ring formed on coordination of the $CH_2(pz)_2$ ligand to palladium. Obviously, this extra factor is enough to fix the conformation in the five-membered ring and to explain the NMR behavior. High-temperature ^1H NMR measurements show that the CH_2 and NMe_2 protons coalesce at the same temperature. The barrier to inversion in **4d** was calculated to be 62.3 kJ/mol.[12]

The ^1H NMR spectrum of the bis(THF)palladium complex (**4e**) in CD_3CN is identical to that of the bis-(MeCN)palladium complex **4a**, apart of course from the presence of free THF and the absence of MeCN. However, when the spectrum of **4e** was recorded in CD_2Cl_2 or $CDCl_3$, an AB pattern and two singlets were found for the CH_2 and the $N(CH_3)$ protons, respectively, pointing to a higher barrier to inversion for the chelate ring in **4e** as compared with this barrier in **4a**. Two factors may be responsible for this difference. THF is bulkier than MeCN, and it is a much weaker donor toward palladium.[13] This would imply that the barrier for inversion is comparable or smaller in **4e**; however, as a result of the smaller *trans* influence of oxygen (compared to that of nitrogen in acetonitrile) the bidentate C,N-coordination of the naphthylamine fragment in **4e** is enhanced. A combination of this stronger Pd–N coordination and the size of THF appears to be sufficient to prevent fast inversion at room temperature.

The ^1H NMR spectrum of the neutral bis(3-naphthyl)-palladium (**5**) shows singlets for the CH_2 and $N(CH_3)_2$ protons. Apparently, although **5** is expected to exist in a *cis*-configuration,[14] there is only a small barrier to ring inversion. The neutral tris(pyrazolyl)palladium (**8**) shows broad singlets for the CH_2 and $N(CH_3)_2$ protons; because of fast intramolecular exchange of the pyrazolyl groups, the five-membered ring-inversion is too fast on the NMR time scale.

Discussion

Although position 2 of a naphthalene is the thermodynamically favored site for electrophilic attack,[15] the 1-position is kinetically favored.[16] The more effective delocalization of the positive charge in the Wheland intermediate, formed on attack at C(1) of a naphthalene system, usually outweighs the unfavorable steric interaction of the electrophile with H(8), thereby directing the reaction kinetically to the 1-position. Nevertheless, in the palladation of 2-[(dimethylamino)methyl]naphthalene (**1**), only the 3-metalated **2** is formed. Three factors may play a role in the formation of this product, *i.e.* Pd–N coordination of the substrate to the Pd salt, formation of a chelate ring by interaction of the Pd center with the C–H bond, and, finally, steric constraints during these two processes. A separate role is played by the anion. It was noted that in the presence of chloride anions incom-

(12) Van der Poel, H.; van Koten, G. *J. Organomet. Chem.* **1981**, *217*, 129 and references cited therein. Conformational stable six-membered stannacycles have been observed. See for example: van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 6593.

(13) Russell, M. J. H.; Barnard, C. F. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 5, pp 1112–1115.

(14) (a) Maassarani, F.; Pfeffer, M. *Organometallics* **1987**, *6*, 1111. (b) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D.; Le Borgne, G.; Jastrzebski, J. T. B. H.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

(15) (a) Cerfontain, H. *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*; Interscience: New York, 1968; pp 68–69. (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984; Part B, pp 413.

(16) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Interscience: New York, 1985; p 461.

Table 1. Selected Bond Lengths and Bond Angles of $Pd(3\text{-}C_{10}H_6CH_2NMe_2\text{-}2)[BH(C_3H_3N_2)_3]$ (8) with Esd's in Parentheses

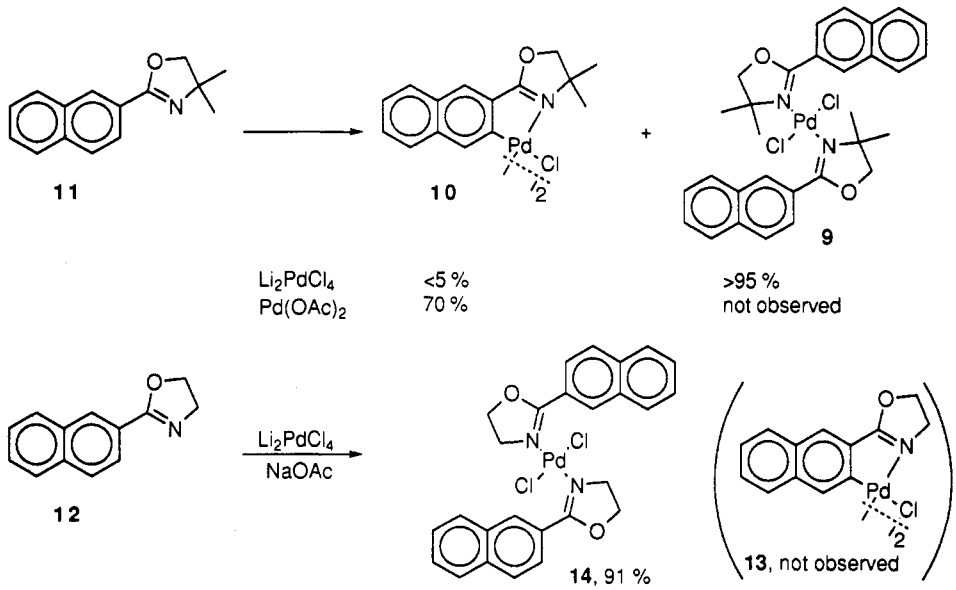
	mol 1	mol 2		mol 1	mol 2
		Bond Lengths (Å)			
C(1)–Pd	1.984(2)	1.989(2)	N(2)–Pd	2.145(2)	2.128(2)
N(1)–Pd	2.087(2)	2.080(2)	N(4)–Pd	2.011(2)	2.026(2)
		Bond Angles (deg)			
C(1)–Pd–N(1)	81.77(9)	81.74(9)	N(1)–Pd–N(2)	99.67(8)	98.49(8)
C(1)–Pd–N(2)	178.06(8)	177.52(8)	N(1)–Pd–N(4)	174.35(8)	174.68(8)
C(1)–Pd–N(4)	93.00(8)	93.58(9)	N(2)–Pd–N(4)	85.52(8)	86.07(8)
C(10)–C(1)–Pd	114.3(2)	113.6(2)			
		Dihedral Angle (deg)			
C(2)–C(1)–Pd–N(4)	15.30(20)	20.40(20)			

Table 2. Selected ^1H NMR Data for the Cationic Complexes 4a–e

cmpd (L)	yield (%)	$ArCH_2$	NCH_3	ArH
4a[a] (MeCN)	95	4.06	2.81	7.71 (m, 2 H), 7.42 (m, 3 H), 7.31 (s, 1 H)
4b[b] (tmeda)	95	4.14	2.90	7.85 (m, 1 H), 7.73 (m, 1 H) 7.61 (s, 1 H), 7.51 (m, 1 H) 7.40 (m, 2 H)
4c[b] (bpy)	94	4.35	2.91	7.78 (m, 4 H), 7.60 (s, 1 H), 7.52 (s, 1 H)
4d[b,c] (CH_2pz_2)	92	4.67 (bs) 3.92 (bs)	2.98 (bs) 2.80 (bs)	7.77 (m, 1 H), 7.65 (m, 1 H) 7.60 (s, 1 H), 7.40 (m, 2 H) 7.14 (s, 1 H)
4e[d] (THF)	78	5.28 (d, J = 14.2) 3.68 (d, J = 14.2)	3.00, 2.90	8.15 (d, 1 H, J = 8.00 Hz), 7.71 (m, 4 H), 7.42 (m, 1 H)

[a] Recorded in CD_2Cl_2. [b] Recorded in CD_3CN. [c] For reasons of clarity the data are given as observed on a 200-MHz spectrometer. At 300 MHz all broad singlets arising from pyrazolyl protons appear as doublets or triplets: 8.14 (d, 1 H, ^2J = 2.65 Hz), 8.10 (d, 1 H, ^2J = 2.53 Hz), 7.92 (d, 1 H, ^2J = 2.30 Hz), 7.79 (d, 1 H, ^2J = 2.29 Hz), 6.55 (dd, 1 H, ^2J = 2.65 Hz, ^2J = 2.29 Hz), 6.52 (dd, 1 H, ^2J = 2.53 Hz, ^2J = 2.30 Hz). [d] Recorded in $CDCl_3$.

Scheme 3



plete (in the case of 1) or no (in the case of 2) cyclopalladation occurred.

Coordination complexes like 3 and 9 are known intermediates in cyclopalladation reactions.[17,18] In such complexes, the arylamine ligand is brought close to the palladium center by Pd–N coordination. After initial coordination, it is presumably Pd–X (X = Cl, OAc) bond dissociation[19] which produces the kinetically active 14e cationic PdX^+ entity that ultimately carries out the electrophilic attack at the C–H bond. For the coordinated PdX^+ moiety, this can equally well be at the 1- or the 3-position of the naphthalene ring since both sites 1 and 3 are equally accessible as regards the steric and conformational restraints of the connecting chain between C_{ipso} and the N-donor group. This chain flexibility will play an important role in attaining the oblique, above-plane approach of the *ortho*-C–H bond toward the Pd center, which initiates the necessary ligand dissociation in the 16e complex, as we proposed earlier.[19] This will be more difficult for the more rigid $C(sp^2)$–$C(sp^2)$–$C(sp^2)$–$N(sp^2)$ chain in the oxazoline complex than for the more flexible $C(sp^2)$–$C(sp^2)$–$C(sp^3)$–$N(sp^3)$ chain. The solid-state structure of 9 shows that the C(1)–H bond is close to the palladium. Comparable weak, linear Pt–H–C interactions have been identified by Pregosin et al.[20]

(17) For recent reviews on cyclometalation, see: (a) Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 250. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(18) Yatsimirskii, A. K. *Zh. Neorg. Khim.* **1979**, *24*, 2711; *Chem. Abstr.* **1979**, *91*, 217478a.

(19) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831.

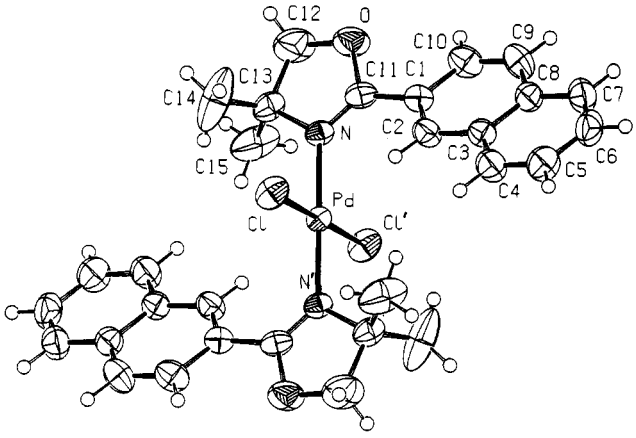


Figure 3. ORTEP drawing (50% probability level) of the molecular structure of **9** together with the adopted numbering scheme.

Table 3. Selected Bond Lengths and Bond Angles of Bis[4,4-dimethyl-2-(2-naphthyl)oxazoline]palladium Dichloride (9) with Esd's in Parentheses

	Bond Lengths (Å)		
Cl–Pd	2.3026(8)	N–Pd	2.0354(19)
	Bond Angles (deg)		
Cl–Pd–N	91.056	N–Pd–N	180
Cl–Pd–Cl	180		

On attack of the metal center, a σ-complex (Wheland arenonium intermediate) is formed leading to a chelate ring.[21a] For 2-[(dimethylamino)methyl]naphthalene (**1**), both positions C(1) and C(3) are equally reactive, as far as the Wheland intermediate is concerned. However, when the reaction proceeds further along the reaction coordinate in the direction of proton release, the ligand *trans* to the coordinated amine functionality starts to interfere sterically with H(8) for the 1-metalated transition state, whereas, for the 3-metalated intermediate, no interference with neighboring substituents is obvious (cf. Figure 4). It is this difference in steric constraints that may explain why clean 3-palladation for the present 2-substituted naphthalenes has been observed.

In addition to prior coordination of the substrate arene rendering the electrophilic attack of the metal center an intramolecular process, another role of the nitrogen donor atom may be considered at this stage, *i.e.* accelerating the reaction by acting as an intermediate proton acceptor. We have found evidence for this possibility in the [(dimethylamino)naphthyl]platinum complex $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$, in which a protonated tertiary amine shares its proton with a Pt center in a 3-center–4-electron bond.[21b] Also in the formation of (phenylnorbornyl)palladium complex $Pd(C_7H_{11}\text{-Ph-}o)$(pmdta)OTf ($C_7H_{11}$ = 2-*exo*-norbornyl, pmdta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) an intramolecular electrophilic attack of Pd(II) at the aryl group is thought to occur in which a noncoordinated nitrogen atom accepts the proton.[21c] In a subsequent step, this proton is used in the protonolysis of the Pd–norbornyl bond; see Figure 5. A similar rate enhancement by proton abstraction was also achieved by the addition of NaOAc. This has been observed earlier in the cyclometalation of [(dimethylamino)methyl]benzene[22] and azobenzene.[23]

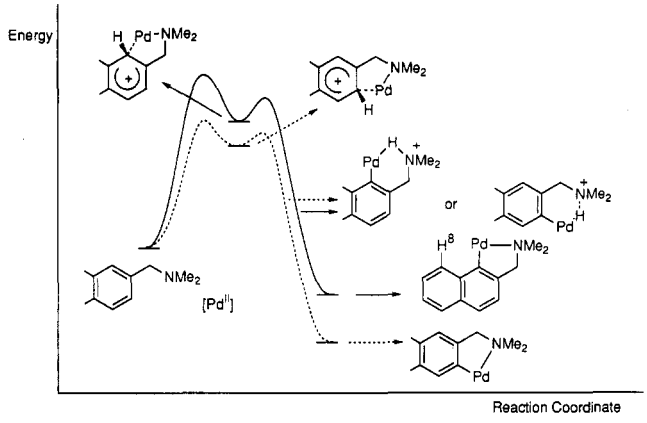


Figure 4. Qualitative energy diagram in which 1- and 3-cyclopalladations of ligand **1** are compared. All energy levels are located on relative positions.

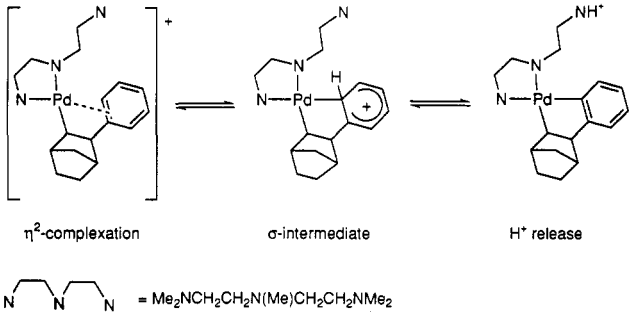


Figure 5. Part of the reaction of Pd(Ph)(pmdien) with norbornene showing the intramolecular palladation by a 14e Pd cation of the arene ring and the proposed role of the amine substituent in the proton release step.

The question remains whether or not **2** is formed by a rearrangement of an intermediate 1-palladated product to a 3-palladated species, in other words whether 1- or 3-palladation is kinetically preferred. This question was investigated by carrying out the cyclopalladation of 2-[(dimethylamino)methyl]naphthalene with Li_2PdCl_4 in CD_3OD. After a reaction time of 3 h, we found no deuteration of position 1, indicating that reversible 1-palladation does not occur. Furthermore, when 1-palladated **7** was suspended in a solution of Li_2PdCl_4 in CH_3OH, no rearrangement to **2** was found. This supports the view that, in the reaction of **1** with Li_2PdCl_4, palladium is never attached to position 1 but attacks directly and irreversibly at position 3, confirming that attack at position 3 in **1** is kinetically preferred.

Experimental Section

General Methods. Reactions performed in an atmosphere of nitrogen were conducted using standard Schlenk techniques. All solvents, except MeOH and acetone, were dried prior to use. THF and Et_2O were distilled from sodium–benzophenone ketyl. MeCN was distilled from CaH_2 and stored on 4-Å molecular sieves. CH_2Cl_2 was dried on CaH_2 or anhydrous $CaCl_2$. 2-(Bromomethyl)naphthalene (97%) and $AgBF_4$ (both purchased from Janssen Chimica) were used without purification. AgOTf (Janssen Chimica) was dried by azeotropic distillation of its solution in

(20) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812 and references cited therein.
(21) (a) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1367. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916. (c) Markies, B. A.; Wijkens, P.; Kooijman, H.; Spek, A. L.; Boersma, J.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1420.
(22) Ekardt, W. *Phys. Rev. Lett.* **1984**, *52*, 1925.
(23) Yatsimirski, A. K. *Zh. Neorg. Khim.* **1979**, *24*, 2711.

benzene. Precipitation with an excess of pentane yielded the $AgOTf{\cdot}C_6H_6$ complex. ^1H- and ^{13}C-NMR spectra were recorded in $CDCl_3$, except when noted, on a Bruker AC-200 or a AC-300 MHz spectrometer. Elemental analyses were carried out by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands, and by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

2-[(Dimethylamino)methyl]naphthalene (1). 2-(Bromomethyl)naphthalene (7.2 g, 32.6 mmol) was dissolved in THF (20 mL). To this solution was added Me_2NH (0.20 mol) in a mixture of absolute EtOH (35 mL) and THF (150 mL). After it was stirred for 18 h, the mixture was treated with a 20% NaOH solution in H_2O (50 mL) and a further amount of 200 mL of H_2O was added. The layers were separated. The aqueous phase was extracted twice with 150 mL of Et_2O. The collected organic layer was dried ($MgSO_4$) and concentrated in vacuo to give an oily liquid, which was distilled in vacuo (0.5 mmHg, 89 °C) and gave 5.24 g of colorless product (28.1 mmol, 85%). ^1H NMR (300 MHz): δ 7.89–7.85 (m, 3 H, ArH), 7.78 (s, 1 H, ArH), 7.55 (d, 1 H, J = 8.4 Hz), 7.52–7.48 (m, 2 H, ArH), 3.60 (s, 2 H, CH_2), 2.31 (s, 6 H, NCH_3). ^{13}C NMR (75.5 MHz): δ 136.9, 133.6, 133.0, 128.1, 127.9, 127.9, 127.6, 127.5, 126.1, 125.7, 64.6 (CH_2), 45.6 (NCH_3).

4,4-Dimethyl-2-(2-naphthyl)oxazoline (11) and 2-(2-Naphthyl)oxazoline (12). The ligands 11 and 12 were synthesized by following the three-step procedure described for phenyloxazolines[24] and crystallized from hexane (−18 °C) in 40% and 80% isolated yield, respectively, based on 2-naphthoic acid. ^1H NMR (11, 200 MHz): δ 8.45 (s, 1H, ArH^1), 8.05–7.49 (m, 6 H, ArH), 4.17 (s, 2 H, CH_2), 1.43 (s, 6 H, CH_3). ^1H NMR (12, 200 MHz): δ 8.42 (s, 1 H, ArH^1), 8.03 (d, 1 H, J = 10.0 Hz), 7.91–7.82 (m, 3 H, ArH), 7.56–7.45 (m, 2 H, ArH), 4.46 (t, 2 H, ^3H = 9.8 Hz, CH_2), 4.09 (t, 2 H, ^3J = 9.8 Hz, CH_2). ^{13}C NMR (12, 75.5 MHz): δ 164.7 (C=N), 134.7, 131.7, 128.9, 128.7, 128.1, 127.8, 127.5, 126.5, 125.1, 124.8, 67.6 (OCH_2), 55.0 (NCH_2).

$\{PdCl[3\text{-}C_{10}H_6CH_2NMe_2\text{-}2]\}_2$ (2). To a solution of Li_2PdCl_4 (1.18 mmol) in MeOH (5 mL) was added a solution of 1 (0.22 g, 1.18 mmol) and anhydrous NaOAc (97 mg, 1.18 mmol) in MeOH (10 mL). After the solution was stirred at 25 °C for 3 h, the solvent was removed by decantation. The yellow precipitate was washed with MeOH (50 mL) and Et_2O (100 mL) and dried in vacuo. Yellow 2 was obtained (96%) as a 2:3 *cis* and *trans* isomer mixture. When the reaction was carried out in the absence of NaOAc for 1 night at 25 °C, non-cyclopalladated $PdCl_2(C_{10}H_7\text{-}CH_2NMe_2\text{-}2)_2$, 3, also was formed (approximately 10% yield) and could not be separated from 2. Reaction of 2 with pyridine yielded the monomeric complex $PdCl(3\text{-}C_{10}H_6CH_2NMe_2\text{-}2)(C_5H_5N)$, 2′, which was crystallized from CH_2Cl_2 and Et_2O. ^1H NMR (2, 200 MHz) (mixture of isomers): δ 7.80–7.60 (m, 2 H, ArH), 7.63 and 7.53 (2 s, ArH^4), 7.50–7.30 (m, 2 H, ArH), 7.35 (s, 1 H, ArH^1), 4.09 (s, 2 H, CH_2), 2.92 and 2.87 (2 s, 3 H, NCH_3). ^{13}C NMR (2, 50.3 MHz) (mixture of isomers): δ 145.3, 131.6, 131.1, 129.7, 128.4, 127.9, 127.5, 127.4, 127.0, 125.2, 125.2, 124.7, 119.7, 73.1 (CH_2), 73.1 and 72.9 (CH_2), 52.8 and 52.5 (NCH_3). Several signals of both isomers are coinciding. Anal. Calcd for $C_{26}H_{28}Cl_2N_2Pd_2$: C, 47.87; H, 4.30; N, 4.30. Found: C, 47.54; H, 4.33; N, 4.09. ^1H NMR (3, 200 MHz): δ 8.36 (s, 1 H, ArH^1), 8.18 (d, 1 H, ^3J = 7.0 Hz, ArH^3 or H^4), 7.90–7.80 (m, 3 H, ArH), 7.54–7.49 (m, 2 H, ArH), 4.09 (s, 2 H, CH_2), 3.48 (s, 6 H, NCH_3). ^1H NMR (2′, 200 MHz): δ 8.96 (d, 2 H, J = 5.0 Hz, $H_{pyridine}$), 7.86–7.78 (m, 2 H, ArH), 7.68 (d, 1 H, ^3J = 9.8 Hz, ArH), 7.47–7.25 (m, 5 H, ArH), 6.36 (s, 1 H, ArH), 4.13 (s, 2 H, CH_2), 2.94 (s, 6 H, NCH_3). Anal. Calcd for $C_{18}H_{19}ClN_2Pd$: C, 53.35; H, 4.73; N, 6.91. Found: C, 54.12; H, 4.85; N, 6.71.

$\{PdCl[1\text{-}C_{10}H_6CH_2NMe_2\text{-}2]\}_2$ (7). A solution of *tert*-butyllithium (42 mmol) in pentane was added to a solution of 1-bromo-2-[(dimethylamino)methyl]naphthalene (11.1 g, 42 mmol) in pentane (30 mL) at −78 °C. The stirred mixture was allowed to slowly reach 25 °C overnight. The solvent was removed by decantation. The white precipitate was washed with two 100-mL portions of pentane and dried in vacuo. The yield of [2-[(dimethylamino)methyl]-1-naphthyl]lithium was 5.0 g (26 mmol, 63%).

A solution of $PdCl_2(SMe_2)_2$ (0.68 g, 2.3 mmol) in Et_2O (30 mL) was cooled to −78 °C. To this solution was added a solution of 2-[(dimethylamino)methyl]-1-naphthyllithium (0.43 g, 2.2 mmol) in Et_2O (40 mL) over a period of 30 min. After stirring at 0 °C for 1 h, the mixture was allowed to reach 25 °C. The solvent was decanted, and the yellow solid washed with two 50-mL portions of Et_2O and dried in vacuo to give 7 (0.39 g. 24 mmol) as crystals which were obtained by diffusion of Et_2O into a solution of 7 in CH_2Cl_2. ^1H NMR (300 MHz) (mixture of isomers): δ 8.73 (d, ^3J = 6.8 Hz, H^8 of major isomer), 8.61–8.58 (m, H^8 of minor isomer), 7.64–7.60 (m, 2 H, ArH), 7.51–7.47 (m, 2 H, ArH), 7.39–7.30 (m, 2 H, ArH), 7.20 (d, ^3J = 8.0 Hz, 1 H, ArH^3 or H^4), 4.29 and 4.28 (s, 2 H, CH_2), 2.75 (s, 6 H, NCH_3). ^{13}C NMR (50.3 MHz) (mixture of isomers): δ 144.1, 142.8 and 142.6, 137.2 and 137.0, 132.3 and 132.1, 130.6 and 130.4, 127.8 and 127.6, 125.7, 125.0, 124.8, and 124.5, 119.7, 74.6 and 74.5 (CH_2), 53.0 and 52.6 (NCH_3). Several signals from both isomers are coinciding. Anal. Calcd for $C_{26}H_{28}N_2Pd_2Cl_2$: C, 47.88; H, 4.33; N, 4.29. Found: C, 47.79; H, 4.22; N, 4.27.

Bis[4,4-dimethyl-2-(2-naphthyl)oxazoline]palladium Dichloride (9). A solution of 11 (2.70 g, 12 mmol) in MeOH (5 mL) was added to a stirred solution of Li_2PdCl_4 (12 mmol) in a mixture of MeOH (12 mL) and water (4 mL). After the mixture was stirred at 25 °C for 2 days, the yellow solid was collected by centrifugation, washed with two 15-mL portions of MeOH and two 10-mL portions of Et_2O, and dried in vacuo, to yield 3.54 g (94%) of 9, which was crystallized by diffusion of pentane into a solution of 9 in CH_2Cl_2. ^1H NMR (300 MHz) (major isomer): δ 9.38 (s, 1 H, ArH), 9.02 (dd, 1 H, J_1 = approximately 9.0 Hz, J_2 = 1.6 Hz, ArH), 8.06 (d, 2 H, J = 8.6 Hz, ArH), 7.69–7.57 (m, 2 H, ArH), 7.29–7.27 (m, 1 H, ArH), 4.28 (s, 2 H, CH_2), 1.72 (s, 6 H, CH_3). ^1H NMR (300 MHz) (minor isomer): 9.03 (s, 1 H, ArH), 8.75 (dd, 1 H, J_1 = 8.6 Hz, J_2 = 1.7 Hz, ArH), 7.95 (d, 2 H, J = 7.5 Hz, ArH), 7.60–7.51 (m, 2 H, ArH), 7.27–7.24 (m, 1 H, ArH), 4.31 (s, 2 H, CH_2), 1.95 (s, 6 H, CH_3). ^{13}C NMR (50.3 MHz): δ 166.9 (N=C, major isomer), 166.7 (N=C, minor isomer), 135.4, 135.0, 132.3, 132.2, 132.0, 131.9, 129.4, 129.3, 128.4, 128.3, 128.2, 128.0, 127.7, 126.9, 126.6, 126.0, 125.7, 124.0, 123.2, 80.1 (OCH_2 major isomer), 79.6 (OCH_2 minor isomer), 70.1 [$C(CH_3)_2$ minor isomer], 69.5 [$C(CH_3)_2$ major isomer], 28.7 (CH_3 minor isomer), 28.4 (CH_3 major isomer). The twentieth aromatic carbon was not resolved. Anal. Calcd for $C_{30}H_{30}O_2N_2PdCl_2$: C, 57.38; H, 4.78; N, 4.46. Found: C, 57.28; H, 4.81; N, 4.54.

Bis(μ-chloro)bis{[[2-(4,4-dimethyloxazolino)naphthyl]palladium} (10). A solution of 1.00 g (4.5 mmol) of 11 and $Pd(OAc)_2$ (1.00 g, 4.5 mmol) in HOAc (40 mL) was stirred at 60 °C for 1.5 h. After cooling of the solution of 25 °C, the metallic palladium was removed by centrifugation. The solvent was removed under reduced pressure. The orange residue was dissolved in 20 mL of acetone. To this solution was added a solution of LiCl (0.56 g, 13 mmol) in a mixture of 25 mL of acetone and 5 mL of H_2O. After the mixture was stirred at 25 °C for 3 h, the yellow precipitate was collected by centrifugation and washed successively with two 10-mL portions of MeOH and two 20-mL portions of Et_2O. After the solid was dried in vacuo, 0.87 g (2.37 mmol, 70%) of 10 remained. Crystals were obtained by diffusion of Et_2O into a solution of 10 in CH_2Cl_2. ^1H NMR ($CDCl_3$, 300 MHz) (mixture of isomers): δ 7.82 (s, 1 H, ArH), 7.75–7.71 (m, 2 H, ArH), 7.66 (s, 1 H, ArH), 7.46–7.37 (m, 23 H, ArH), 4.44 (s, 2 H, CH_2 major isomer), 4.42 (s, 2 H, CH_2 minor isomer), 1.64 (s, 6 H, CH_3 major isomer), 1.59 (s, 6 H, CH_3 minor isomer). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.2 (N=C, minor isomer), 173.1 (N=C, major isomer), 136.2, 135.9, 134.8, 134.7, 131.1, 131.0, 130.7, 129.7, 128.8, 128.0, 127.9, 127.7, 126.7, 125.3, 82.3 (OCH_2 minor isomer), 82.2 (OCH_2 major isomer), 66.5 [$C(CH_3)_2$ minor isomer], 66.1 [$C(CH_3)_2$ major isomer], 27.7 (CH_3 major isomer), 27.6 (CH_3 minor isomer). Several ^{13}C signals for the aromatic region are coalescent. Anal. Calcd for $C_{30}H_{28}Cl_2N_2O_2Pd_2$: C, 49.20; H, 3.85; N, 3.83. Found: C, 49.30; H, 3.89; N, 3.97.

(24) Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837.

Bis[2-(2-naphthyl)oxazoline]palladium Dichloride (14). A solution of **12** (0.30 g, 1.52 mmol) and Li_2PdCl_4 (0.76 mmol) in MeOH (30 mL) was stirred overnight at 25 °C. The yellow precipitate was collected and washed with two 20-mL portions of MeOH and two 30-ml portions of Et_2O. After the solid was dried in vacuo, 0.40 g of product remained (0.70 mmol, 91% yield). Crystallization was achieved by slow distillation of Et_2O into a concentrated solution of **14** in CH_2Cl_2. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.30 (s, 1 H, ArH), 8.97 (d, 1 H, J = 8.5 Hz, ArH), 7.84–7.67 (m, 3 H, ArH), 7.60 (t, 1 H, J = 7.1 Hz, ArH), 7.46–7.41 (m, 1 H, ArH), 4.69 (t, 2 H, ^3J = 9.4 Hz, OCH_2), 4.42 (t, 2 H, ^3J = 9.5 Hz NCH_2). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 168.1 (C=N), 135.4, 132.2, 131.9, 129.4, 128.5, 128.3, 127.8, 126.8, 125.4, 122.1, 68.2 (CH_2O), 55.6 (CH_2N).

[Pd(3-$C_{10}H_6CH_2NMe_2$-2)x]y, x = $(MeCN)_2$, tmeda, 2,2′-bpy, CH_2pz_2; y = BF_4, OTf (4a–d). To a solution of $AgBF_4$ (570 mg, 2.92 mmol) or AgOTf·C_6H_6 (0.98 g, 2.92 mmol) in CH_2Cl_2 (20 mL) was added MeCN (5 mL) or 2.92 mmol of the appropriate bidentate species. The resulting solution was added to a stirred suspension of **2** (0.95 g, 1.46 mmol) in 50 mL of CH_2Cl_2. After being stirred at 25 °C for 10 min, the solution was decanted and concentrated in vacuo to give an oil which solidified after addition of 50 mL of pentane. See Table 1 for yields and selected ^1H NMR data.

4a: Attempts to crystallize **4a** were unsuccessful. ^1H NMR (300 MHz, CD_2Cl_2): δ 2.45 (s, 3 H, MeCN), 2.12 (s, 3 H, MeCN). ^{13}C NMR (75.5 MHz, CD_3CN): δ 147.3, 142.0, 133.1, 132.8, 132.5, 128.3, 128.1, 126.6, 126.5, 121.4, 73.3 (CH_2), 53.2 (CH_3). No satisfactory analytical data were obtained.

4b: Crystallization was by slow distillation of Et_2O into a solution of **4b** in CH_2Cl_2. ^1H NMR (tmeda fragment, 300 MHz, CD_3CN): δ 2.79 (m, 2 H, CH_2), 2.69 (s, 2 H, CH_2), 2.69 (s, 6 H, NCH_3), 2.60 (s, 6 H, NCH_3). ^{13}C NMR (75.5 MHz): δ 144.50, 143.27, 131.77, 131.59, 127.12, 127.05, 125.58, 125.50, 73.93 ($ArCH_2$), 64.32 (CH_2CH_2), 60.59 (CH_2CH_2), 51.92 (NCH_3), 51.53 (NCH_3), 49.31 (CH_3). Anal. Calcd for $C_{20}H_{30}F_3N_3O_3PdS$: C, 43.21; H, 5.44; N, 7.56. Found: C, 44.39; H, 5.48; N, 7.51.

4c: Crystallization by diffusion of Et_2O into a solution of **4c** in CH_2Cl_2. ^1H NMR (bpy fragment, 300 MHz): δ 8.89 (d, 2 H, J = 5.3 Hz), 8.40 (d, 2 H, J = 8.0 Hz), 8.27 (ddd, 2 H, J_1 = 7.8 Hz, J_2 = 7.8 Hz, J_3 = 1.5 Hz), 7.43 (dd, 2 H, J_1 = 6.2 Hz, J_2 = 3.3 Hz). ^{13}C NMR (75.5 MHz, CD_3CN): δ 156.4, 152.8, 151.3, 141.6 (2 C), 133.4, 133.0, 128.6 (2 C), 128.4, 128.1, 126.6, 126.4, 124.8, 121.1, 75.5 (CH_2), 52.2 (NCH_3). Anal. Calcd for $C_{24}H_{22}F_3N_3O_3PdS$: C, 48.37; H, 3.72; N, 7.05. Found: C, 48.32; H, 3.80; N, 7.01.

4d: Crystallization was by diffusion of Et_2O into a solution of **4d** in CH_2Cl_2. ^1H NMR (CH_2pz_2 fragment, 200 MHz, CD_3CN): δ 8.14 (bs, 1 H, pzH), 8.10 (bs, 1 H, pzH), 7.92 (bs, 1 H, pzH), 7.79 (bs, 1 H, pzH), 7.02 (bs, 1 H, CH*H*), 6.82 (bs, 1 H, C*H*H), 6.55 (bs, 1 H, pzH), 6.52–6.45 (m, 1 H, pzH). ^{13}C NMR (75.5 MHz, CD_3CN): δ 147.1, 146.3, 145.3, 144.5, 134.7, 133.0, 132.7, 128.2, 128.0, 126.5, 126.3, 121.3, 109.8, 108.9, 73.5 ($ArCH_2$), 64.8 (CH_2-pz), 53.8–52.4 (NCH_3). Several signals are not resolved. Anal. Calcd for $C_{21}H_{22}F_3N_5O_3PdS$: C, 42.90; H, 3.77; N, 11.91. Found: C, 42.95; H, 3.85; N, 11.97.

Pd(OTf)[3-$C_{10}H_6(CH_2NMe_2$-2)](THF) (4e). A solution of AgOTf·C_6H_6 (1.08 g, 3.23 mmol) in THF (20 mL) was added to a suspension of **2** (1.0 g) in THF (20 mL). After being stirred for 40 h at 25 °C the red solution was filtrated and concentrated in vacuo. Extremely hygroscopic, red **4e** remained (1.43 g, 2.91 mmol, 90%). It proved to be impossible to obtain product containing a well-defined amount of THF. A ^1H NMR spectrum recorded in CD_3CN gave the same spectrum obtained for **4a**, apart from the signals arising from MeCN. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.73–7.70 (m, 2 H, ArH), 7.42–7.39 (m, 4 H, ArH), 5.27 (d, 1 H, ^2J = 14.2 Hz, CH_AH_BN), 3.73 (bs, 4 H, CH_2, THF), 3.68 (d, 1 H, ^2J = 14.2 Hz, CH_AH_BN), 2.99 (s, 3 H, NCH_3), 2.90 (s, 3 H, NCH_3), 1.90 (bs, 4 H, CH_2, THF). No satisfactory analytical data were obtained.

Pd[BH(pz)$_3$](3-$C_{10}H_6CH_2NMe_2$-2) (8). To a solution of **2** (1.51 g, 2.3 mmol) in THF (40 mL) was added a solution of KHB(pz)$_3$ (1.16 g, 4.6 mmol) in THF (20 mL). After the solution was stirred at 60 °C for 2 h, the solvent was removed in vacuo. After extraction with 50 mL of CH_2Cl_2 and removal of the solvent, 2.1 g (4.2 mmol, 91%) of white **8** remained. Crystals suitable X-ray analysis were obtained from a concentrated MeOH solution. After 30 min at 25 °C crystals separated. By means of elemental analysis it was found that the crystals consisted of **8** and 0.5 equiv of MeOH. ^1H NMR (300 MHz): δ 7.81 (bs, 3 H, pzH), 7.76–7.68 (m, 2 H, ArH), 7.66 (bs, 3 H, pzH), 7.47 (s, 1 H, ArH), 7.41–7.39 (m, 2 H, ArH), 7.18 (s, 1 H, ArH), 6.27 (bs, 3 H, pzH, CC(H)C), 4.04 (bs, 2 H, CH_2), 3.48 (s, 1.5 H, CH_3OH, only observed when the product was crystallized from MeOH), 2.52 (bs, 6 H, NCH_3), hydride not resolved. ^{13}C NMR (75.5 MHz): δ 146.2, 145.5, 141.8 (bs, pz-C), 135.9 (bs, pz-C), 133.0, 131.9, 131.6, 127.3, 127.1, 125.1, 124.7, 119.5, 105.1 (bs, pz-C), 73.4, 51.9. Anal. Calcd for $C_{22.5}H_{28}BN_7O_{0.5}Pd$: C, 52.00; H, 5.43; N, 18.88; O, 1.54. Found: C, 51.83; H, 5.18; N, 18.29; O, 1.50.

Pd(3-$C_{10}H_6CH_2NMe_2$-2)$_2$ (5). To a solution of 2-[(dimethylamino)methyl]naphthalene (**1**) (0.61 g, 3.3 mmol) in pentane (10 mL) was added at −78 °C 2.1 mL of a 1.6 M solution of *tert*-butyllithium (3.3 mmol) in pentane. After the solution was stirred at 25 °C for 10 h, the solvent was removed by decantation. The white precipitate was washed with two portions of pentane (15 mL). After drying in vacuo 0.58 g of **6** remained (3.0 mmol, 92%). The lithiated derivative **6** (0.58 g, 3.0 mmol) was dissolved in 15 mL of THF and added to a suspension of **2** (0.44 g, 0.68 mmol) in 20 mL of THF on which a clear brown solution was formed. After the solution was stirred at 25 °C for 2 h, the solvent was removed in vacuo and the product washed with two portions of 20 mL of pentane. After extraction with CH_2Cl_2, filtration over Celite to remove formed metallic palladium, and evaporation

Table 4. Crystal Data for the Complexes Pd[BH(pz)$_3$](3-$C_{10}H_6CH_2NMe_2$-2] (8) and Bis[4,4-dimethyl-2-(2-naphthyl)oxazoline]palladium Dichloride (9)

	Crystal Data	
formula	$C_{22}H_{24}N_7BPd$·CH_3OH (8)	$C_{30}H_{30}N_2O_2PdCl_2$ (9)
mol wt	519.73	627.91
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a (Å)	13.170(1)	20.221(1)
b (Å)	13.413(1)	16.000(1)
c (Å)	14.112(1)	8.516(1)
α (deg)	109.34(1)	
β (deg)	95.60(1)	
γ (deg)	97.38(1)	
V (Å^3)	2306.4(3)	2755.2(4)
Z	4	4
D_{calc} (g cm^{-3})	1.497	1.514
F(000)	1060	1280
μ (cm^{-1})	8.2	8.9
cryst size (mm)	0.8 × 0.3 × 0.3	0.25 × 0.45 × 0.50
	Data Collection	
temp (K)	295	295
θ_{max} (deg)	27.5	27.5
radiation, λ (Å)	Mo Kα (Zr-filtered), 0.710 73	Mo Kα (Zr-filtered), 0.710 73
scan type	$\omega/2\theta$	$\omega/2\theta$
Δω (deg)	0.70 + 0.35 tan θ	0.65 + 0.35 tan θ
hor and vert aperture (mm)	3.0, 6.0	3.0, 4.0
ref reflcns	304, 042, 420	406, 006
data set	h, 0:17; k, −17:17, l, −18:18	−26:26; 0:20; −11:11
tot. data	11 390	13 140
tot. no. of unique data	10 559	3154
obsd data [$I > 2.5\sigma(I)$]	8481	2479
	Refinement	
no. of refined params	591	177
weighting scheme	$w = 1.0/[\sigma^2(F)]$	$w = 1.0/[\sigma^2(F)]$
final R, R_w, S	0.025, 0.036, 0.86	0.039, 0.029, 1.29
$\Delta/\sigma)_{av}$ in final cycle	0.008	0.04
min and max resd dens (e/Å^3)	−0.43, 0.31	−0.48, 0.69

Table 5. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for $Pd[BH(pz)_3](3\text{-}C_{10}H_6CH_2NMe_2\text{-}2]$ (8)

atom	x	y	z	U(eq)[a] (Å²)
		(a) Residue 1		
Pd(1)	0.18968(1)	0.13256(1)	0.49752(1)	0.0331(1)
N(11)	0.1823(2)	0.1049(2)	0.6340(1)	0.0444(7)
N(12)	0.2186(2)	0.3046(2)	0.5539(1)	0.0448(6)
N(13)	0.2879(2)	0.3563(2)	0.5134(2)	0.0448(6)
N(14)	0.2004(2)	0.1447(1)	0.3604(1)	0.0354(5)
N(15)	0.2796(2)	0.2116(2)	0.3459(1)	0.0400(6)
N(16)	0.4356(2)	0.2497(2)	0.4834(2)	0.0490(7)
N(17)	0.5199(2)	0.3186(3)	0.5444(3)	0.094(1)
B(1)	0.3546(2)	0.2983(2)	0.4352(2)	0.0452(8)
C(11)	0.1664(2)	−0.0265(2)	0.4422(2)	0.0366(7)
C(12)	0.1830(2)	−0.0931(2)	0.3493(2)	0.0390(7)
C(13)	0.1664(2)	−0.2060(2)	0.3214(2)	0.0411(7)
C(14)	0.1813(2)	−0.2740(2)	0.2249(2)	0.0510(8)
C(15)	0.1682(2)	−0.3822(2)	0.2003(3)	0.062(1)
C(16)	0.1397(3)	−0.4288(2)	0.2705(3)	0.068(1)
C(17)	0.1221(3)	−0.3664(2)	0.3636(3)	0.063(1)
C(18)	0.1348(2)	−0.2533(2)	0.3922(2)	0.0479(8)
C(19)	0.1174(2)	−0.1851(2)	0.4873(2)	0.0519(9)
C(110)	0.1321(2)	−0.0765(2)	0.5115(2)	0.0423(7)
C(111)	0.1126(2)	−0.0004(2)	0.6100(2)	0.0502(9)
C(112)	0.2884(2)	0.0977(3)	0.6727(2)	0.058(1)
C(113)	0.1425(3)	0.1863(3)	0.7132(2)	0.062(1)
C(114)	0.2810(3)	0.4616(2)	0.5442(2)	0.062(1)
C(115)	0.2057(3)	0.4781(3)	0.6060(3)	0.071(1)
C(116)	0.1684(2)	0.3789(2)	0.6095(2)	0.0569(9)
C(117)	0.2655(2)	0.2043(2)	0.2478(2)	0.0485(8)
C(118)	0.1785(2)	0.1314(2)	0.1980(2)	0.0459(8)
C(119)	0.1400(2)	0.0967(2)	0.2712(2)	0.0392(7)
C(120)	0.5768(3)	0.2552(4)	0.5740(3)	0.095(1)
C(121)	0.5343(3)	0.1513(4)	0.5330(3)	0.084(2)
C(122)	0.4441(3)	0.1494(3)	0.4745(3)	0.067(1)
		(b) Residue 2		
Pd(2)	0.56158(1)	0.35532(1)	0.05458(1)	0.0339(1)
N(21)	0.5109(2)	0.4757(1)	0.1661(1)	0.0384(6)
N(22)	0.7231(2)	0.4168(2)	0.0906(2)	0.0434(6)
N(23)	0.7886(2)	0.3475(2)	0.0957(2)	0.0464(7)
N(24)	0.5997(2)	0.2286(2)	−0.0529(2)	0.0450(6)
N(25)	0.6769(2)	0.1792(2)	−0.0271(2)	0.0482(7)
N(26)	0.6943(2)	0.2113(2)	0.1607(2)	0.0506(8)
N(27)	0.7492(2)	0.2413(2)	0.2558(2)	0.070(1)
B(2)	0.7506(2)	0.2273(3)	0.0754(3)	0.051(1)
C(21)	0.4114(2)	0.2939(2)	0.0246(2)	0.0342(6)
C(22)	0.3644(2)	0.1889(2)	−0.0238(2)	0.0349(6)
C(23)	0.2558(2)	0.1571(2)	−0.0367(2)	0.0320(6)
C(24)	0.2067(2)	0.0489(2)	−0.0872(2)	0.0382(7)
C(25)	0.1013(2)	0.0203(2)	−0.1004(2)	0.0433(7)
C(26)	0.0397(2)	0.0992(2)	−0.0651(2)	0.0460(8)
C(27)	0.0842(2)	0.2039(2)	−0.0159(2)	0.0438(8)
C(28)	0.1927(2)	0.2351(2)	0.0011(2)	0.0346(6)
C(29)	0.2425(2)	0.3425(2)	0.0556(2)	0.0394(7)
C(210)	0.3470(2)	0.3704(2)	0.0671(2)	0.0364(7)
C(211)	0.4045(2)	0.4825(2)	0.1241(2)	0.0436(7)
C(212)	0.5062(2)	0.4399(2)	0.2552(2)	0.0515(9)
C(213)	0.5747(2)	0.5848(2)	0.2023(2)	0.0519(8)
C(214)	0.8867(2)	0.3990(3)	0.1132(2)	0.060(1)
C(215)	0.8858(2)	0.5016(3)	0.1173(2)	0.064(1)
C(216)	0.7820(2)	0.5098(2)	0.1030(2)	0.0497(8)
C(217)	0.6815(3)	0.0923(2)	−0.1065(3)	0.066(1)
C(218)	0.6079(3)	0.0842(3)	−0.1844(3)	0.072(1)
C(219)	0.5582(2)	0.1713(2)	−0.1485(2)	0.0577(9)
C(220)	0.6825(3)	0.2170(3)	0.3122(3)	0.082(1)
C(221)	0.5871(3)	0.1710(3)	0.2573(3)	0.082(2)
C(222)	0.5971(3)	0.1679(3)	0.1610(3)	0.066(1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j a_i^* a_j^* \bar{a}_i \bar{a}_j$.

of the solvent, 0.49 g of light gray **5** remained (1.03 mmol, 84%). The product was crystallized from CH_2Cl_2 and Et_2O. ^1H NMR (**6**, 300 MHz, C_6D_6): δ 8.97 (s, 1 H ArH), 7.79–7.76 (m, 1 H, ArH), 7.66–7.64 (m, 1 H, ArH), 7.56 (s, 1 H, ArH), 7.38–7.35 (m, 2 H, ArH), 7.16 (s, 1 H, ArH), 4.48 (d, 1 H, ^2J = 12.8 Hz, CH_AH_B), 3.03 (d, 1 H, ^2J = 12.8 Hz, CH_AH_B), 1.71 (s, 3 H, NCH_3), 0.98 (s, 3 H, NCH_3). ^1H NMR (**5**, 200 MHz): δ 8.05 (s, 1 H, H^1), 7.74–7.67 (m, 2 H, ArH), 7.57 (s, 1 H, H^4), 7.38–7.31 (m, 2 H, ArH), 4.06 (s, 2 H, CH_2), 2.66 (s, 6 H, NCH_3). ^{13}C NMR (**5**, 50.3 MHz): δ 154.8, 146.4, 138.4, 133.4, 131.1, 127.3, 126.9, 124.4, 123.7, 119.4, 72.1 (CH_2), 49.2 (NCH_3). Anal. Calcd for $C_{26}H_{28}N_2Pd$: C, 65.77; H, 5.90; N, 5.90. Found: C, 65.65; H, 5.86; N, 5.89.

Table 6. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for Bis[4,4-dimethyl-2-(2-naphthyl)oxazoline]palladium Dichloride (9)

atom	x	y	z	U(eq)[a] (Å²)
Pd	0	0	0	0.0319(1)
Cl	0.05401(4)	0.09966(5)	0.14698(9)	0.0521(3)
O	−0.11010(11)	−0.09209(14)	0.3805(3)	0.0647(9)
N	−0.03860(11)	−0.05247(13)	0.1975(2)	0.0365(8)
C(1)	−0.14835(14)	0.01659(17)	0.2183(3)	0.0406(10)
C(2)	−0.13513(14)	0.09281(18)	0.1530(3)	0.0453(10)
C(3)	−0.18614(14)	0.15112(18)	0.1225(3)	0.0416(10)
C(4)	−0.17375(17)	0.2311(2)	0.0602(4)	0.0563(11)
C(5)	−0.22312(17)	0.2871(2)	0.0380(4)	0.0620(12)
C(6)	−0.28830(17)	0.2656(2)	0.0776(4)	0.0600(14)
C(7)	−0.30211(15)	0.1898(2)	0.1373(4)	0.0561(11)
C(8)	−0.25197(14)	0.12991(19)	0.1615(3)	0.0439(10)
C(9)	−0.26429(15)	0.0506(2)	0.2283(4)	0.0570(12)
C(10)	−0.21446(15)	−0.0042(2)	0.2570(4)	0.0542(11)
C(11)	−0.09525(15)	−0.04218(18)	0.2578(3)	0.0427(10)
C(12)	−0.0547(2)	−0.1458(3)	0.4036(4)	0.0880(17)
C(13)	−0.00204(16)	−0.11945(17)	0.2861(3)	0.0466(10)
C(14)	0.0572(2)	−0.0828(3)	0.3683(6)	0.116(2)
C(15)	0.0158(2)	−0.1904(2)	0.1821(4)	0.0900(16)

[a] U(eq) = $^1/_3$ of the trace of the orthogonalized U.

Structure Determinations. General Methods. Neutral-atom scattering factors were taken from ref 25 and corrected for anomalous dispersion.[26] All calculations were performed on a Micro-VAX cluster. The program PLATON[27] was used for geometrical calculations and illustrations.

Structure Determination and Refinement of 8. A yellowish rod-shaped crystal was mounted on a glass fiber and transferred to an Enraf-Nonius CAD4-F diffractometer for data collection. Unit cell parameters were determined from a least-squares fit of the SET4 setting angles of 25 reflections with 14.1 < θ < 17.9°. The unit cell parameters were checked for the presence of higher lattice symmetry.[28] Data were corrected for Lp, for a linear decay (2%) of the intensities during the 160 h of X-ray exposure time, and for absorption (*ABSORB*;[29] correction range 1.20–1.33). Four low-order reflections were left out of the final refinement in view of experimental difficulties. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the three reference reflections.[30] $\sigma^2(I) = \sigma^2_{cs}(I) + (0.038I)^2$. The structure was solved with automated Patterson interpretation followed by peak optimization (SHELXS86[31]). Refinement on *F* was carried out by full-matrix least-squares techniques (SHELX76[32]). Hydrogen atoms were introduced on calculated positions (B–H, C–H = 0.98 Å) and included in the refinement riding on their carrier atoms, except for the MeOH hydroxyl hydrogen atom, which was located from a difference Fourier map and refined with a distance restraint. Disorder was found in the orientation of the methyl hydrogens of the MeOH molecule and in the MeOH molecule orientation and handled in the refinement with a disorder model. The solvent molecule with minor occupation (*p*

(25) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.
(26) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(27) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, A46, C34.
(28) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
(29) Spek, A. L. ABSORB. Program for absorption Correction. Utrecht University, The Netherlands, ECM Abstract Book, p 283, 1983.
(30) McCandlish, L. E., Stout, G. H.; Andrews, L. C. *Acta Crystallogr., Sect. A.* **1975**, *31*, 245.
(31) Sheldrick, G. M. SHELXS86. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany, 1986.
(32) Sheldrick, G. M. SHELX76. Program for crystal structure determination. Univ. of Cambridge, U.K., 1976.

= 0.142(7)) was refined isotropically. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with two isotropic thermal parameters, one for the hydrogens of the MeOH molecule (U = 0.099(9) Å^2) and one common to all other hydrogen atoms (U = 0.067(1) Å^2). Weights were introduced in the final refinement cycles; convergence was reached at R = 0.025. Crystal data and numerical details of the structure determination are given in Table 4. Data on the geometry are given in Table 1. Final atomic parameters for the non-hydrogen atoms are listed in Table 5.

Structure Determination and Refinement of 9. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer for a orange crystal glued on top of a glass fiber. Unit cell parameters were derived from the 25 SET4 setting angles in the range $10 < \theta < 17°$. A total of 13 140 reflections were scanned and corrected for Lp and a 3% linear decay, resulting in a unique set of 2479 reflections with $I > 2.5\sigma(I)$. The structure was solved by Patterson methods (SHELXS-86[31]) and refined by full-matrix least-squares techniques on F (SHELX-76[32]) to a final R = 0.039. Hydrogen atoms were taken into account at calculated positions with two common isotropic thermal parameters and refined riding on their carrier atoms. Numerical details have been collected in Table 4. Final atomic parameters for the non-hydrogen atoms are listed in Table 6.

Acknowledgment. The authors wish to thank the Innovation Oriented Research Program on Catalysis, Solvay-Duphar BV, the Netherlands Foundation for Chemical Research (SON, A.L.S.), and the Netherlands Organisation for Scientific Research (NWO) for financial support.

Supplementary Material Available: Tables of anisotropic thermal parameters, H-atom positions and thermal parameters, and bond distances and angles involving H-atoms for **8** and **9** (10 pages). Ordering information is given on any current masthead page.

OM940028H