The Effect of the Trimethylsilyl Group on Electrophilic Cyclopalladation; A Study of $C_{aryl}-Si$ versus $C_{aryl}-H$ Selective Bond Activation with 2,6-$(Me_2NCH_2)_2C_6H_3R$ (R = H or $SiMe_3$)

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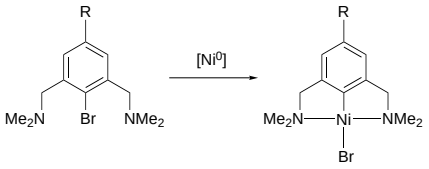
Abstract: The site selectivity of electrophilic palladation has been studied by using two bis(aminomethyl)-substituted benzenes 1,3-$(Me_2NCH_2)_2C_6H_4$ (**6**) and 2,6-$(Me_2NCH_2)_2C_6H_3(SiMe_3)$ (**7**) and $Li_2[PdCl_4]$ or $Pd(OAc)_2$ in solution in MeOH or CH_2Cl_2. The major product of direct palladation of **6** in both solvents is the polymeric cyclopalladated organometallic complex [1,5-{PdCl}$_2$-2,4-$(Me_2NCH_2)_2C_6H_2]_n$, which was characterized as its dinuclear pyridine derivative [1,5-{PdCl(C_5H_5N)}$_2$-2,4-$(Me_2NCH_2)_2C_6H_2$] (**9**). The effect of the trimethylsilyl group present at the 1-position in **7** leads to inversion of the site selectivity in comparison to that observed for **6**, and to activation of the C–Si bond when MeOH is used as solvent; the major product of this direct palladation is the known monomeric cyclopalladated complex [{PdCl}2,6-$(Me_2NCH_2)_2C_6H_3$] (**8**). However, using CH_2Cl_2 instead of MeOH in the palladation reaction of **7** leads to the major product arising from C–H rather than C–Si bond activation.

Keywords: C–H activation · C–Si activation · metalations · metallacycles · palladium · site selectivity

Introduction

A fundamental goal in synthetic organic chemistry is the activation of C–R (R = H, CR_3, SiR_3) bonds, and this area is currently attracting considerable interest.[1] Part of our research has been focussed on the activation of $C_{aryl}-R$ bonds by transition metals, with the aim of forming novel *ortho*-chelated organometallic compounds with useful synthetic and/or catalytic properties.[2,3] As part of this exploratory work, we have reported a number of methods that can be used to form $M-C_{aryl}$ bonds with a variety of metals. For example, in the development of organonickel(II) catalysts bearing a functionalized *N,C,N′*-terdentate coordinating ligand [2,6-$(Me_2NCH_2)_2$-4-R-$C_6H_2]^-$ (R = H, NO_2, NH_2, MeC(O)N(H), Cl, PhCH=N, MeO, MeC(O), $SiMe_3$ or a carbosilane dendritic core), we have introduced the metal center through oxidative addition of an $C_{aryl}-Br$ bond to a Ni^0 precursor [Eq. (1)].[3,4] In cases where oxidative addition cannot be used to form $M-C_{aryl}$ bonds (e.g., Ln^{III} chemistry), an alternative route involving a transmetallation reaction of the C–Li bond in $[Li_2(NCN)_2]$ (NCN = [2,6-$(Me_2NCH_2)_2C_6H_2]^-$) can be employed.[2a, 5] Unfortunately, many functional groups (such as NH_2) are not compatible with organolithium reagents. The most useful and economic technique to form $M-C_{aryl}$ bonds involves the activation of the $C_{aryl}-R$ bond by direct metallation,[1] that is substitution of R for the metal. This procedure would be most useful if it is synthetically straightforward and tolerant to the presence of a variety of functional groups.



(1)

In platinum group metal chemistry, direct metallation is often observed under mild conditions and examples of alkyl and aryl C–H bond activation by electrophilic substitution and oxidative addition are well known.[1,6] However, a problem in many of these metallations of hydrocarbons is the lack of site-(i.e., bond) selectivity. Fortunately, this can often be overcome by the introduction of an activating group such as the trimethylsilyl group. Recently, it has been reported that selective palladation of aminomethyl-substituted naphthalenes **1**, **2**, and **4** (Scheme 1) with a Pd^{II} salt can occur through C–H and C–Si bond activation,[6d, 7–9] and the site of metallation can be directed by the proper placement of the

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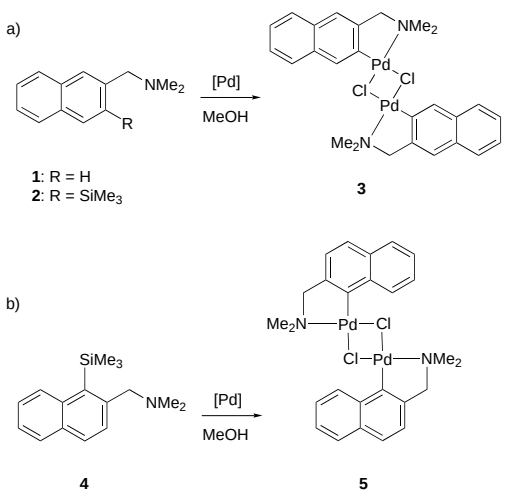

Scheme 1. The directional effect of a $SiMe_3$ substituent on the site of cyclopalladation of (dimethylamino)methyl-substituted naphthalenes. a) C–H and C–Si bond cleavage, b) selective C–Si bond cleavage. [Pd] = $Li_2[PdCl_4]$ or $Pd(OAc)_2$.

$SiMe_3$ group on the naphthalene backbone. Both the unsubstituted 2-[(dimethylamino)methyl]naphthalene **1** and its 3-trimethylsilyl analogue **2** can be palladated selectively at the carbon atom at the 3-position of the naphthyl group, thereby affording the dimeric organopalladium(II) complex **3**. However, it is only the 1-trimethylsilyl-substituted compound **4** that undergoes selective palladation at the 1-position (by C_{aryl}–Si bond cleavage) to yield complex **5** (Scheme 1); that is in this case palladation occurs preferentially through activation of the C_{aryl}–Si bond rather than the C_{aryl}–H bond.

Since a complete inversion of selectivity is obtained by the introduction of a trimethylsilyl group on naphthalene ligand precursors, we decided to investigate this effect in the precursor of our potentially terdentate ligand NCN.[1a,2a] Herein, we report the syntheses of three Pd^{II} complexes derived from 2,6-$(Me_2NCH_2)_2C_6H_3R$ (R = H (**6**), $SiMe_3$ (**7**)) that involve either electrophilic C_{aryl}–H or C_{aryl}–Si bond activation. The $SiMe_3$ group on the aromatic ring of an NCN ligand has an important directional effect on the site selectivity of these palladations. Furthermore, the nature of the solvent plays an interesting role in the metallation, and the selectivity for C–Si or C–H bond activation can be inverted by using CH_2Cl_2 in place of MeOH. The application of this work for the synthesis of mono- and dinuclear platinum group metal complexes using ligands such as 2,6-$(CH_2NMe_2)_2$-$C_6H_3(EMe_3)$ and 1,4-$(Me_3E)_2$-2,3,5,6-$(CH_2NMe_2)_4C_6$ (E = Si or Sn) has been recently reported.[10]

Abstract in Dutch: *De selectiviteit van electrofiele palladering van bis(aminomethyl)-gesubstitueerde benzeen-verbindingen 1,3-$(Me_2NCH_2)_2C_6H_4$, **6**, en 2,6-$(Me_2NCH_2)_2C_6H_3(SiMe_3)$, **7**, met $Li_2[PdCl_4]$ of $Pd(OAc)_2$ in MeOH of CH_2Cl_2 oplossing werd bestudeerd. Als hoofdprodukt van de directe cyclopalladering van **6** in beide oplosmiddelen wordt het polymere organometaalcomplex [1,5-{PdCl}$_2$-2,4-$(Me_2NCH_2)_2C_6H_2]_n$ gevormd, dat werd geïsoleerd en gekarakteriseerd als het overeenkomstige dinucleaire pyridinederivaat [1,5-{PdCl-(C_5H_5N)}$_2$-2,4-$(Me_2NCH_2)_2C_6H_2$], **9**. Het effect van de trimethylsilyl groep op de 1-positie in **7** draait, vergeleken met **6**, de selectiviteit van de plaats waar cyclopalladering optreedt geheel om en activering van de C-Si binding vindt plaats wanneer MeOH wordt gebruikt als oplosmiddel; het hoofdproduct van deze directe palladering is het bekende monomere gecyclopalladeerde complex [2,6-$(Me_2NCH_2)_2C_6H_3$[PdCl}], **8**. Wanneer CH_2Cl_2 in plaats van MeOH wordt gebruikt in de palladerings reactie van **7** is het hoofdproduct afkomstig van C-H in plaats van C-Si band activering.*

Results and Discussion

In this study, we have examined the site selectivity of electrophilic palladation using two known bis(aminomethyl)-substituted benzenes 1,3-$(Me_2NCH_2)_2C_6H_4$ (**6**), and 2,6-$(Me_2NCH_2)_2C_6H_3(SiMe_3)$ (**7**)[10] as the organic substrates with $Li_2[PdCl_4]$ or $Pd(OAc)_2$ as palladium(II) salts using MeOH or CH_2Cl_2 as the reaction medium. In these experiments a solution of the palladium(II) salt was added to a solution of one equivalent of the aryldiamine substrate with or without the presence of an organic base (Et_3N; about two equivalents) and the mixture was subsequently stirred for 18 h. After appropriate work-up, including addition of pyridine (see Experimental Section), the organometallic complexes resulting from the cyclopalladations were identified and quantified by ^1H NMR spectroscopy. Table 1 summarizes the results of these experiments and shows the relative ratios of the three organometallic products in the final product mixture. The numbers given represent relative selectivity and not absolute yield, although in most cases the total yield of cyclopalladated products was ≥ 90% (with respect to Pd). The three products identified are **8**,[11] which is formed by activation of the C_{aryl}–R bond (R = H, $SiMe_3$) of the substrates **6** and **7** (that is the C_{aryl}–R bond located in between the two CH_2NMe_2 groups), **9**, and its 3-trimethylsilyl analogue **10**. Complexes **9** and **10** both result from C–H activation[6a] at positions that are *ortho* to one of the CH_2NMe_2 groups of the substrates **6** and **7**,

Table 1. Results of the palladation reaction of the NCN ligand precursors 2,6-$(Me_2NCH_2)_2C_6H_3R$ (R = H (**6**) or $SiMe_3$ (**7**)) with Pd^{II} starting materials.[a]

Entry	R	Solvent	[Pd]	**8**	**9**	**10**
1	H	MeOH	$Li_2[PdCl_4]$	0	0	–
2	H	MeOH/Et_3N	$Li_2[PdCl_4]$	< 5	> 95	–
3	H	MeOH	$Pd(OAc)_2$	0	0	–
4	H	MeOH/Et_3N	$Pd(OAc)_2$	8	92	–
5	H	CH_2Cl_2	$Pd(OAc)_2$	45	55	–
6	H	CH_2Cl_2/Et_3N	$Pd(OAc)_2$	23	77	–
7	$SiMe_3$	MeOH	$Li_2[PdCl_4]$	95	–	5
8	$SiMe_3$	MeOH/Et_3N	$Li_2[PdCl_4]$	90	–	10
9	$SiMe_3$	MeOH	$Pd(OAc)_2$	95	–	5
10	$SiMe_3$	MeOH/Et_3N	$Pd(OAc)_2$	88	–	12
11	$SiMe_3$	CH_2Cl_2	$Pd(OAc)_2$	15	–	85
12	$SiMe_3$	CH_2Cl_2/Et_3N	$Pd(OAc)_2$	38	–	62
13	H	MeOH	$Pd(OAc)_2$[b]	55	45	–
14	$SiMe_3$	MeOH	$Pd(OAc)_2$[b]	34	–	66

[a] Ratio was determined by integration of relevant ^1H NMR resonances. Conditions: aryldiamine:Pd salt = 1:1; [Pd], [aryldiamine] ≈ 20 mM; [Et_3N] ≈ 40 mM; room temperature. [b] Excess $Pd(OAc)_2$ (5 equiv).

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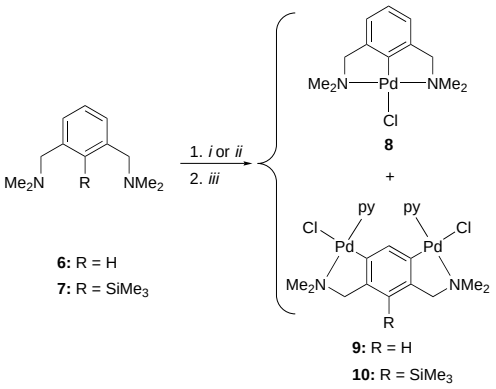
respectively; that is positions 4 and 6 for **6** and positions 3 and 5 for **7**. The reactions affording the cyclopalladated complexes **8**, **9,** and **10** are summarized in Scheme 2; the precursors of



Scheme 2. Direct palladation of NCN derivatives **6** and **7**; Conditions: *i*) $Li_2[PdCl_4]$/MeOH; *ii*) $Pd(OAc)_2$/MeOH or CH_2Cl_2; LiCl/MeOH; *iii*) pyridine (py).

products **9** and **10** are in fact polymers, that is $[1,5\text{-}\{PdCl\}_2\text{-}2,4\text{-}(Me_2NCH_2)_2\text{-}3\text{-}R\text{-}C_6H]_n$ (R = H or $SiMe_3$), and excess pyridine is added to break down the polymeric structure. It should be noted that Chakladar et al. recently reported the structural characterization of $[1,5\text{-}\{PdCl(PPh_3)\}_2\text{-}2,4\text{-}(Et_2NCH_2)_2C_6H_2]$, which is closely related to **9**.[11]

At this point it should be emphasized that bimetallic complexes **9** and **10** are the result of two successive palladations and this suggests that the initial monometallated intermediate is more susceptible to C–H activation than the organic substrates **6** and **7**. This point will be discussed later.

Product ratios and C_{aryl}–Si versus C_{aryl}–H bond chemoselectivity: The results depicted in Table 1 clearly show that there is little difference between the use of $Li_2[PdCl_4]$ or $Pd(OAc)_2$ as the palladium salts in 1:1 cyclometallations of compounds **6** and **7** (cf. entries 1, 2, 7 and 8 with entries 3, 4, 9 and 10, respectively). In two cases (entries 13 and 14) in which excess $Pd(OAc)_2$ was used, the change in product distribution is believed to result from the change in concentration ratios of the substrate and the palladium salt (vide infra).

It is well known that cyclometallations can often be promoted by the presence of a free nucleophile or base. Not unexpectedly, the results of the cyclometallations of **6** and **7**, depicted in Table 1, clearly show a strong influence of added base (Et_3N). For example, in the presence two equivalents of Et_3N compound **6** is susceptible to palladation in MeOH solution (entries 2 and 4), whereas omission of this base (entries 1 and 3) affords no cyclometallated materials, even under forcing conditions (MeOH, reflux temperature, 18 h). Since compound **6** (and **7**) is a strong organic base itself, the absence of reactivity when no additional nucleophile/base is present may indicate that all CH_2NMe_2 groups are coordinated to the palladium salts and are consequently not free to promote C–H activation processes.

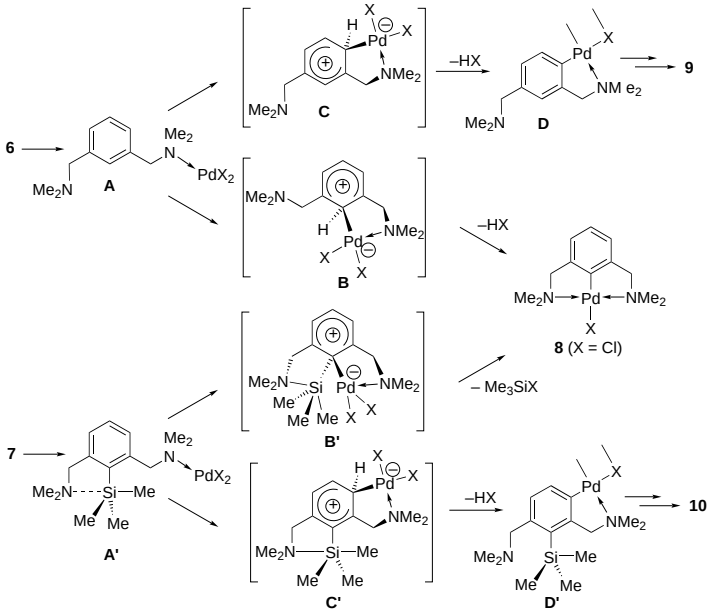
Interestingly, it was found that the 1:5 reaction mixture of either **6** or **7** and $Pd(OAc)_2$ (entries 13 and 14, respectively) does lead to cyclometallated products but the selectivity is poor. In the case of **6** there is C–H bond activation to afford **8** and **9** (55:45) and in the case of **7** there is C–Si and C–H bond cleavage affording **8** and **10** (34:66). These results indicate that OAc^-, like NEt_3, can promote the cyclopalladation of aryldiamines such as **6** and **7**. In this context it is evident that the relative concentration of substrates and reagents can have a significant effect on cyclopalladation processes involving arylamines. This and other related aspects of palladation chemistry have recently been discussed.[12]

The substituent positioned between the two CH_2NMe_2 groups in **6** and **7** (i.e., H and $SiMe_3$, respectively) has a dramatic influence on the reactivity. Whereas compound **6** can not be metallated in MeOH in the absence of base (entries 1 and 3), compound **7** cyclometallates readily (entries 7 and 9). Furthermore, substrates **6** and **7** show significant differences in the resulting product distributions, that is C_{aryl}–H versus C_{aryl}–Si bond activation selectivity. Compound **6** in MeOH in the presence of NEt_3 affords, with both palladium salts, mainly the dinuclear organopalladium(II) species **9** (entries 2 and 4); the latter is formed by a double C–H bond activation reaction (vide supra). In contrast, compound **7** gives under the same conditions primarily the product of a single C–Si bond cleavage, that is mononuclear complex **8** (entries 8 and 10). Note that addition of base in the reaction mixtures with **7** causes a minor decrease in the selectivity for **8** (entries 7 vs. 8 and 9 vs. 10 for $Li_2[PdCl_4]$ and $Pd(OAc)_2$, respectively); the other product is the bimetallic compound **10**. These results clearly show that the $SiMe_3$ group in **7** can, under the correct conditions, be used for the selective introduction of a palladium(II) center between two mutually *meta*-positioned aryl CH_2NMe_2 groups.

This directional influence of the $SiMe_3$ group of **7** in palladations performed in MeOH (entries 9 and 10) is much greater for monometallation, that is for **8**, than that found when CH_2Cl_2 is the solvent. In the latter solvent this reaction with or without added Et_3N gives much lower amounts of **8**, and the bimetallic complex **10** is now the major product (entries 11 and 12). This result indicates that C–H bond activation *ortho* to the CH_2NMe_2 substituent in **7** is preferred over C–Si bond cleavage, that is the $SiMe_3$ group acts as a protecting group for the position between the two CH_2NMe_2 substituents; in the presence of a base/nucleophile, this preference for bimetallic product **10** is decreased slightly (entry 12).

With substrate **6** the use of CH_2Cl_2 also affords a mixture of mono- and biscyclometallated products; again the bimetallated species (i.e., complex **9**) is the major product (entries 5 and 6). A more important result in the solvent-dependent reactivity of **6** with $Pd(OAc)_2$ is that in CH_2Cl_2 cyclometallation occurs readily, but not selectively, at room temperature even in the absence of a base (entry 5), whereas in MeOH (entry 3) no cyclometallated products are found at all. In general, the double palladation of **6** (or **7**) also resulted in the isolation of the unconverted ligand precursors after work-up.

Mechanistic aspects: The effects of variation of the organic substrate, solvent, and additional organic base on the outcome of palladations including C_{aryl}–H versus C_{aryl}–Si bond activation can be rationalized by a mechanism depicted in Scheme 3. In this mechanism, we assume that prior to



Scheme 3. Proposed reaction pathways for the electrophilic $C_{aryl}-H$ and $C_{aryl}-Si$ bond cleavage reactions of aryldiamines **6** and **7** ($PdX_2 = PdCl_2$ or $Pd(OAc)_2$).

metallation an intermediate coordination complex is probably formed.[13] This intermediate consists of organic substrate **6** or **7** coordinated with only one of the CH_2NMe_2 groups to the PdX_2 center, that is situation **A** and **A′**, respectively (see Scheme 3; $X^- = Cl^-$, OAc^-). In the next step, a Wheland-type intermediate (that is, an arenonium complex) is formed by electrophilic aromatic substitution. As a result, the metal is attached to an sp^3 carbon center with a M–C σ bond and therefore the former aromatic ring carries a positive charge and the metal center carries a negative charge. Since there is coordination of only one of the two CH_2NMe_2 groups to the metal center, there are two possible outcomes of this step, that is a M–C bond at the position between the two CH_2NMe_2 substituents (situation **B** and **B′**; see Scheme 3) or at the position *ortho* to one of these substituents (**C** and **C′**; see Scheme 3). If in this second step the two positions are equally activated for electrophilic attack, then the sterically least congested arenonium complex will be favored kinetically (that is, situations **C** and **C′**). However, if the position between the two substituents is activated, as in **7** by the presence of a $SiMe_3$ group, then metallation at this location is more favorable, that is, situation **B′**. In the final stage of cyclometallation, the cationic leaving group is released from the arenonium intermediate by combination with an appropriate nucleophile from the metal center (X^-) or from the solution (e.g., Cl^-, AcO^-, Et_3N or MeOH) to form the final products of metallation. Note that platinum(II) complexes of the NCN ligand are known to form stable arenonium complexes (Figure 1) that are structurally related to the species **B** and **B′**.[14]

An important consequence of this mechanistic scheme for compound **7** is that the product distributions will be influenced by the nature of the solvent. If the palladation is performed in MeOH, which can not only stabilize a polar transition state but can also be a source of nucleophilic MeO^- ions, then the pathway from arenonium species **B′** to the final products is more favorable. The result of the C–Si bond cleavage is the production of **8** and methoxytrimethylsilane. The latter product contains a strong Si–O bond. In the case of compound **6** and **7**, a C–H bond activation affords HX and the metallated product. When these reactions are performed in CH_2Cl_2, the only nucleophiles present in the reaction mixture are OAc^- or Cl^- and Et_3N, all of which can extract H^+. Therefore it can be expected that C–H bond cleavage processes will be more favorable in this solvent.[1b, 12]

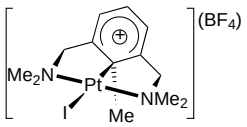


Figure 1. Example of a structurally characterized Wheland-type intermediate (arenonium complex) with a Pt–C σ bond.[14]

In the case of **7**, the situation is significantly different to that of **6** because one of the CH_2NMe_2 groups can associate with the silicon center. This association can cause polarization of the C–Si bond prior to coordination of the second group to palladium.[10,15] Such intramolecular interaction with silicon has recently been shown in closely related species both in the solid state and in solution.[10] As a result of this N→Si interaction, there is an increase in electron density at the $C_{aryl}-Si$ bond, and this situation (**B′**) will favor electrophilic attack of the Pd center at this bond. Thus, we can now understand the influence of nucleophiles such as MeO^-, Cl^- or OAc^-, which allow the $SiMe_3$ group to undergo an S_N2 type nucleophilic substitution where the metallated arenonium ring acts as the leaving group. This S_N2 mechanism is well-documented in silicon chemistry. The cleavage of $C_{aryl}-Si$ bonds in compounds similar to those shown in Scheme 3 was the subject of extensive study by Eaborn et al.[7a] many years ago. This work demonstrated that there is a major influence of the electronic character of aryl substituent(s) on the rate of $C_{aryl}-Si$ bond cleavage. In particular, $C_{aryl}-Si$ bonds of aromatic compounds with electron-donor substituents are cleaved at rates that are much greater than those containing electron-withdrawing groups.

Our mechanism can also be used to explain the lower selectivity for complex **8** in the cyclometallation of **7** when excess $Pd(OAc)_2$ is used. In this case, both CH_2NMe_2 groups are probably coordinated to a palladium atom and therefore are not available for interaction with silicon. This makes the $C_{aryl}-Si$ bond less susceptible to palladation. Thus, the $SiMe_3$ group now merely acts to sterically buttress[16] the aromatic ring and hence causes the C–H bond *ortho* to one the CH_2NMe_2 substituents to be more favored for activation. Therefore, silicon can play a dual role in this chemistry which is directly related to reagent concentration ratios. This results in the formation of a species related to **C′** in which the second CH_2NMe_2 group is coordinated to a palladium atom and thus does not interact with the silicon center.

Clear evidence that the monometallated products **D** and **D′** (Scheme 3) are much better nucleophiles than **6** or **7** is shown by the fact that the monometallated organic substrates can not be isolated and only dimetallated products are formed. Similar observations have also been previously reported by Trofimenko in closely related arylamine systems.[6a] We believe that following initial cyclopalladation at the 4-position in **6** or at the 3-position in **7**, the electron density on the

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aromatic ring is enhanced. This can be caused by either π-backdonation from a filled palladium d orbital or, more likely, by the polarization of the C_{aryl}–Pd bond in product **D** (**D′**) with respect to the former C–H bond in **6** (or **7**), which leaves relatively more negative charge on the arene ring in **D** (**D′**) than in **6** (or **7**). This enhanced electron density in the aromatic ring of the monometallated product **D** (**D′**) results in the ring being more susceptible to electrophilic substitution. Furthermore, there is still one potentially ligating CH_2NMe_2 group available. Overall, this situation makes the monometallated (intermediate) complex more susceptible to palladation then **6** or **7**.[6a] The second metallation reaction can then take place at two positions that are *ortho* to the non-coordinated CH_2NMe_2 substituent. However, one of these positions, the one between the two CH_2NMe_2 substituents, is sterically more hindered than the other[6a] and this property results in the selective palladation of the C–H bond at the position *ortho* to one of the CH_2NMe_2 substituents. In practice, products with palladium bonded at the 1- and the 3-positions have not been detected. Note that directly related 1,3-biscyclomanganated complexes can be formed if the aromatic group is η^6-bonded to a $Cr(CO)_3$ fragment.[17]

The bis-*ortho*-chelated complex **8** and the bispalladium(II) complexes **9** and **10** are not, under the conditions of our study, susceptible to further palladations of the remaining C–H (in **8** and **9**) or C–Si bonds (**10**). This implies that in these species the CH_2NMe_2 groups are effectively coordinated to the Pd^{II} centers and that a free amine unit may be an important prerequisite for a further palladation reaction to occur.[6a]

Conclusions

Several conclusions are immediately evident upon examination of Table 1. Variation of the Pd precursor seems to have little effect on the selectivity or product distribution in the cyclometallation of **6** or **7**. The addition of an external organic base in MeOH solution promotes the dimetallation of ligand precursor **6**. Note that this base is not required if CH_2Cl_2 is used as the solvent. The presence of the $SiMe_3$ group in compound **7** has a directional effect on the site selectivity of cyclopalladation (that is, C–Si bond cleavage is favored over C–H bond activation). This C–Si bond cleavage (with concurrent palladation) occurs to a much higher degree in the protic solvent MeOH but is inhibited in the less polar halocarbon solvent CH_2Cl_2. Moreover, bulky silicon groups have been shown to play a dual role as either an activating group for chemoselective palladation or conversely as a blocking group which promotes regioselective palladation.

The development of an alternative route to organopalladium(II) complexes, by means of an electrophilic C–Si bond cleavage, has been described. A direct consequence of this result is that a transmetallation involving highly reactive organolithium reagents can be avoided. Therefore, a synthetic protocol has been developed for organopalladium chemistry that will allow the use of functionalised bis(amino)aryl ligand precursors containing sensitive groups such as MeC=O and NO_2.[3,4]

Experimental Section

General comments: All organometallic syntheses were performed in a dry dinitrogen atmosphere using standard Schlenk techniques. The solvents MeOH and CH_2Cl_2 were dried and freshly distilled prior to use. NMR measurements were performed at 298 K with a Bruker AC200 spectrometer with chemical shifts referenced to external Me_4Si. The compounds **6**[10] and **7**[10] were prepared according to previously described methods. Palladium precursors were obtained from Degussa.

Electrophilic palladation reactions of the NCN ligand precursors 6 and 7 with the palladium(II) complexes $Li_2[PdCl_4]$ and $Pd(OAc)_2$: The following is a representative example of the experimental conditions used. In a typical experiment [2,6-bis(dimethylaminomethyl)phenyl]trimethylsilane (0.10 g, 0.38 mmol) and $Pd(OAc)_2$ (0.08 g, 0.38 mmol), each dissolved in MeOH (10 mL), and Et_3N (0.10 mL, 0.72 mmol) were mixed at room temperature, and the reaction mixture was then stirred for 18 h. A solution of LiCl (0.05 g, 1.14 mmol; excess) in MeOH (10 mL) was then added, and the mixture was stirred at room temperature for 30 min. After evaporation of the solvent in vacuo, a solution of pyridine (0.18 g, 2.28 mmol) in CH_2Cl_2 (10 mL) was added to the residue, and the mixture stirred for an additional 30 min at room temperature. Volatile components were then removed in vacuo and the residue washed with pentane (2×10 mL). The product mixture was redissolved in CH_2Cl_2 (10 mL), filtered through Celite, and then evaporated in vacuo. The resulting residue was then analyzed by NMR spectroscopy and the appropriate resonances were then used to determine the product ratio. NMR data of the products of the cyclopalladation reactions of **6** and **7** are collected below.

8: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.73$ (m, 1H; Ar), 6.71 (d, 2H, $^3J_{H,H} = 7.24$ Hz; Ar), 3.94 (s, 4H; CH_2), 2.87 (s, 12H; NMe_2).

9: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.62$ (d, 4H, $^3J_{H,H} = 4.9$ Hz; Ar), 7.57 (t, 2H, $^3J_{H,H} = 7.4$ Hz; Ar), 7.07 (t, 4H, $^3J_{H,H} = 7.0$ Hz; Ar), 6.65 (s, 1H; Ar), 4.81 (s, 1H; Ar), 3.86 (s, 4H; CH_2), 2.86 (s, 12H; NMe_2).

10: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.45$ (d, 4H, $^3J_{H,H} = 5.2$ Hz; Ar), 7.51 (t, 2H, $^3J_{H,H} = 7.2$ Hz; Ar), 6.98 (t, 4H, $^3J_{H,H} = 6.6$ Hz, Ar), 4.78 (s, 1H; Ar), 3.88 (s, 4H; CH_2), 2.82 (s, 12H; NMe_2), 0.34 (s, 9H; $SiMe_3$).

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