Functionalized Homoleptic *cis*- and *trans*-*C,N*-*ortho*-Chelated Aminoaryl Platinum(II) Complexes

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For the synthesis of corner building blocks with a 90° angle, to be used for the construction of larger structures, several homoleptic platinum(II) complexes [Pt(η^2-C,N)$_2$] (**10**−**14**), as both *cis*- and *trans*-isomers, have been prepared starting from newly synthesized *ortho*-lithiated (dimethylamino)methyl arene ligands. The aryl groups of these arylplatinum(II) complexes contain additional substituents such as halides or methyl, naphthyl, or (dimethylamino)methyl groups. With these functionalities on the aryl rings the *cis*/*trans* ratio could be tuned. The presence of steric groups *ortho* to the metal center (methyl or naphthyl) favors the formation of planar-chiral *cis*-isomers. The *trans*-isomers isomerize irreversibly to the thermodynamically favored *cis*-isomers upon heating. The arylplatinum(II) complexes were used in various substitution reactions. Addition of a stronger coordinating ligand changes the denticity of the *C,N*-attached ligands. The halide functionalities were exploited for chemoselective lithiation and subsequent transmetalation reactions in order to synthesize the $SnMe_3$-functionalized [Pt(C,N)$_2$] complexes. A Suzuki−Miyaura C−C coupling reaction on one of these complexes was also performed, resulting in the preparation of a mixed trinuclear palladium/platinum complex (**25**). The crystal structure determinations of four functionalized *cis*-[Pt(C,N)$_2$] complexes, *cis*-**12**·Et_2O, *cis*-**14**·*x*C_6H_6, **19**, and **25**·*x*CH_2Cl_2, are reported. With these structures it is shown that depending on the substituents, the degree of planarity around the platinum center can be tuned.

Introduction

Two important factors for a rational design of coordination-based supramolecular entities are the symmetry and the shape of the assembly. These two factors are determined solely by the type and properties of the building blocks. For two-dimensional structures two types of building blocks are required: (1) linear ditopic units, which contain reactive sites with a 180° orientation relative to each other, and (2) angular ditopic units, possessing reactive sites with other desirable angles. Generally, building blocks consist of either an electron-deficient metal center as an acceptor or an organic ligand with Lewis-base functionalities (often pyridine) as donor. Square-planar platinum(II) and palladium(II) centers with coordination angles of approximately 180° or 90° are frequently used as linear or corner acceptor units, respectively. Only in a few cases have organometallic complexes been used as donor building blocks. In these cases, the metal center itself is not used as an acceptor unit, but instead the metal center directs the orientation of the donor units via the attached ligands. The advantage of such complexes is that they have predefined structures, e.g., linear or angular in the case of square-planar complexes, as well as high stability as compared to coordination complexes. It should be noted that especially the 90° angle is rarely observed in entirely organic donor compounds. Examples of right-angled structures are complexes **A** and **B** (Chart 1) reported by Stang and co-workers.[1] For our research, we have chosen to use the homoleptic platinum(II) complex [Pt(dmba)$_2$] (dmba = [$C_6H_4(CH_2NMe_2)$-2]$^-$) (**C**, X = R = H (**1**), Chart 1)[2] as a corner building block with a predefined 90° angle. The choice for this system is motivated by the possibility to introduce donor functionalities on both the two arene rings[3] and the nitrogen donor substituents.[2,4] Our strategy has been to prepare the organometallic precursor complexes [Pt(C,N)$_2$] (C,N = *C,N*-*ortho*-chelating ligand) and to functionalize these in subsequent reactions. This reaction sequence starts with the synthesis of various *C,N*-chelating ligands

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(1) (a) Manna, J.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 8731−8732. (b) Müller, C.; Whiteford, J. A.; Stang P. J. *J. Am. Chem. Soc.* **1998**, *120*, 9827−9837. (c) Stang, P. J. *Chem. Eur. J.* **1998**, *4*, 19−27.
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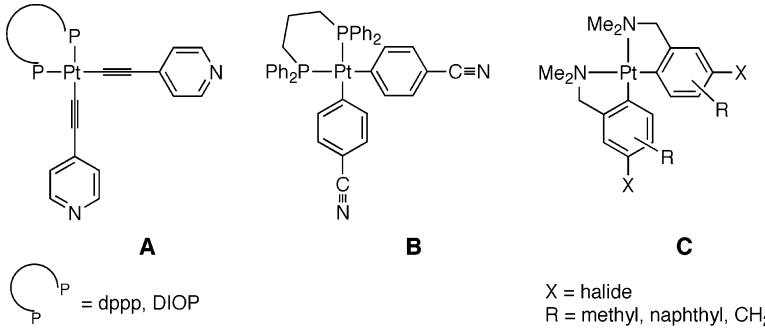
Chart 1. Organoplatinum Corner Complexes



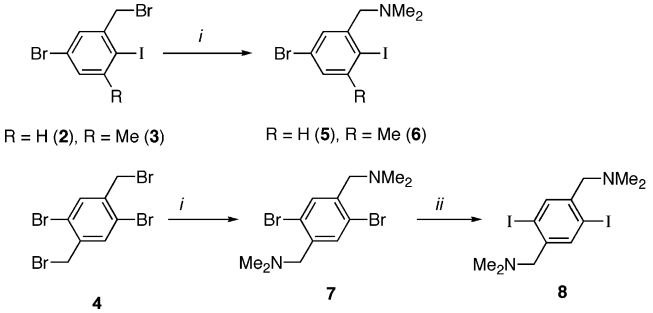
having a halide substituent on the arene ring, which allows further functionalization by C−C bond formation reactions such as Suzuki−Miyaura reactions. In this paper we describe the synthesis and characterization of various types of [Pt(C,N)$_2$] (**C**, X = Br, I, R = H, Me, CH_2NMe_2) complexes and their use in subsequent lithiation and transmetalation reactions. It was demonstrated that C−C coupling reactions on these organometallic complexes without affecting the metal−carbon bond are possible as well. We also describe the synthesis of [Pt(C,N)$_2$] complexes with planar chirality, which is induced by introduction of steric bulk on the aryl rings.

Results and Discussion

Synthesis of [Pt(C,N)$_2$] Complexes. The commonly applied route for the synthesis of homo- and heteroleptic bis-cyclometalated [M(C,N)$_2$] complexes is the introduction of the metal center via a transmetalation reaction. Previous reports showed that homoleptic compounds can be prepared via reaction of an organolithium or Grignard reagent with either a *cis*- or *trans*-[PtX$_2$L$_2$] salt (X = Br, Cl, L = cod, SEt_2, SMe_2),[2,5] while the synthesis of heteroleptic complexes involved reaction of a dinuclear, halide-bridged, complex [MX(C,N)]$_2$ (M = Pt, Pd, X = Br, Cl) with an organolithium,[6] -mercury,[7,8] or -zinc[9] complex. Various new 2,5-bis{(dimethylamino)methyl}-arene ligands (C,N), which are functionalized at the 1- and 4-positions with halide substituents, were designed for the synthesis of the platinum complexes (Scheme 1). The choice of halide, bromide or iodide, *ortho* to the potentially chelating (dimethylamino)methyl group, was made in such way that regioselective metalation would occur at that position. The second halide would thereby be unaffected, as a C−I bond is more reactive than the C−Br bond in both oxidative addition and halide−lithium exchange reactions.

The various amine ligands were prepared starting from their methyl analogues by benzylic bromination (Scheme 1). The synthesis of the starting compounds **2**−**4** was carried out following a new, highly efficient procedure.[10] Nucleophilic substitution of **2**−**4** with $HNMe_2$ yielded the benzylic amines **5**, **6**, and **7**, respectively. The preparation of 1,4-diiodo-2,5-bis{(dimethylamino)-methyl}benzene (**8**) was achieved via double lithiation of **7** followed by quenching of the dilithio compound with 1,2-diiodoethane.

Scheme 1. Ligand Synthesis[a]



[a] (*i*) $HNMe_2$, Et_2O, 2 h; (*ii*) *n*-BuLi, Et_2O, −78 °C → RT, 1 h, $C_2H_4I_2$.

Lithiation of benzylamines **5**−**8** with 1 equiv of *n*-BuLi in Et_2O occurred in all cases at the desired *ortho* C-halide position, without any trace of C−H activation. Quenching of the respective reaction mixtures with S_2Me_2 and subsequent analysis of the *ortho*-MeS products by ^{1}H NMR and GC-MS spectroscopy showed a unique chemoselectivity for lithiation at the C−I bond for both **5** and **6**.

Ligands **5**−**8** and 1-bromo-2-{(dimethylamino)methyl}-naphthalene (**9**)[11] were used to synthesize the corresponding [Pt(C,N)$_2$] complexes by sequential chemoselective lithiation and transmetalation reactions. The transmetalation reactions were performed by reacting the in situ prepared lithium complexes with 0.5 equiv of *trans*-[$PtCl_2(SMe_2)_2$] (Scheme 2). Full conversion to the respective homoleptic complexes **10**−**14** was obtained within 3 h. The complexes were obtained as a mixture of *cis*- and *trans*-isomers (see Table 1), except for **11**, for which only the formation of the *cis*-isomer was observed. This is in accordance with results reported by Longoni et al., who showed that upon reacting the lithium complex [Li(dmba)] with *trans*-[$PtCl_2(SMe_2)_2$], a mixture of *cis*- and *trans*-isomers of the nonfunctionalized [Pt(dmba)$_2$] (**1**) was obtained (Table 1, entry 1).[2]

A mechanism for the formation of homoleptic platinum complexes was proposed by von Zelewsky and co-

(5) 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*, 9916−9924.
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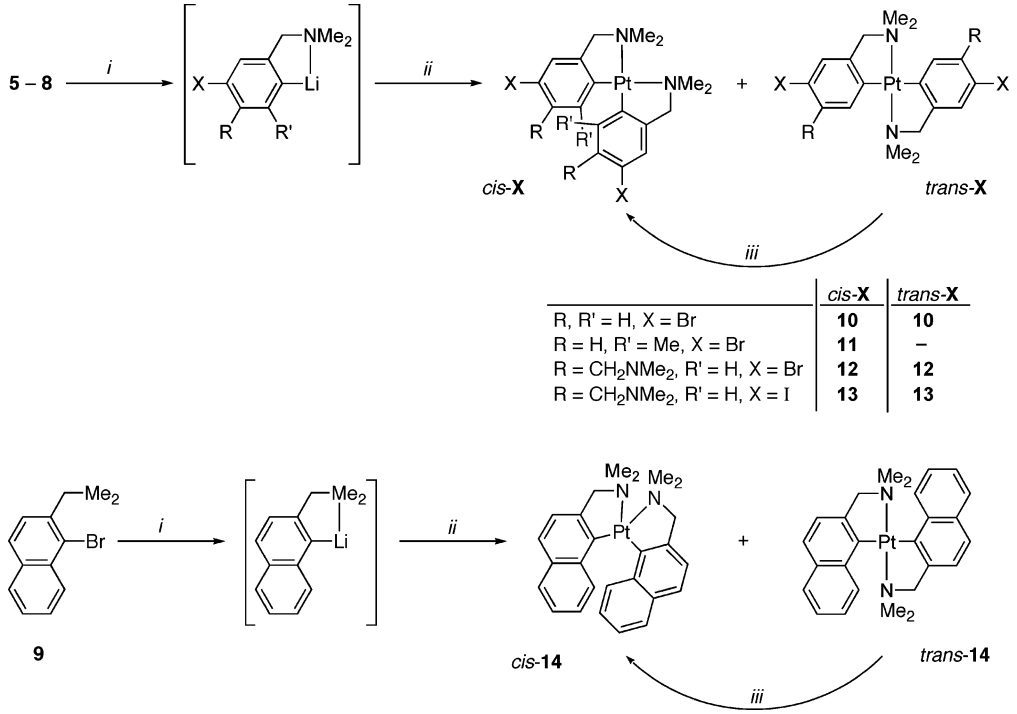
(8) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155−174.
(9) Valk, J.-M.; Boersma, J.; van Koten, G. *Organometallics* **1996**, *15*, 4366−4372.
(10) Amijs, C. H. M.; van Klink, G. P. M.; van Koten, G. *Green Chem.* **2003**, *5*, 470−474.
(11) Gay, R. L.; Hauser, C. R. *J. Am. Chem. Soc.* **1967**, *89*, 2297−2303.

Scheme 2. Synthesis of *cis*- and *trans*-[Pt(C,N)$_2$][a]



	cis-**X**	*trans*-**X**
R, R' = H, X = Br	**10**	**10**
R = H, R' = Me, X = Br	**11**	–
R = CH_2NMe_2, R' = H, X = Br	**12**	**12**
R = CH_2NMe_2, R' = H, X = I	**13**	**13**

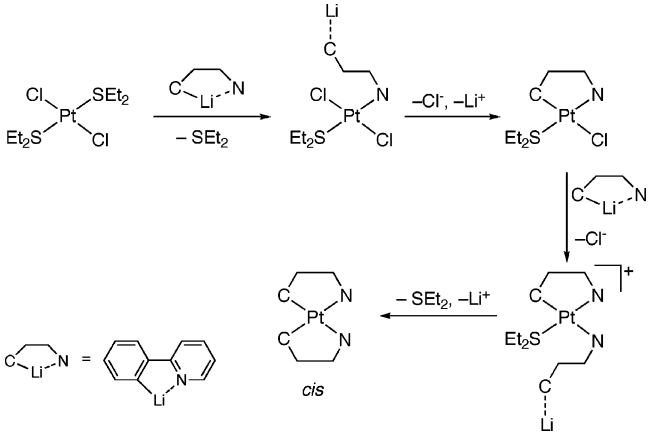
[a] (*i*) *n*-BuLi, Et_2O, −78 °C, 10 min; (*ii*) 0.5 equiv [$PtCl_2L_2$] (L_2 = cod, 2(SMe_2)), Et_2O, −78 °C → RT, 3 h; (*iii*) toluene, Δ*T*, 3−16 h.

Table 1. Observed *cis*/*trans* Ratios When Using Either *cis*-[$PtCl_2$(cod)] or *trans*-[$PtCl_2(SMe_2)_2$] as Starting Reagent

	Pt complex	substituents	ratio *cis*/*trans*[a]		
entry	[Pt(C,N)$_2$]	R, R′, X[b]	[*trans*-$PtCl_2(SMe_2)_2$]	[*cis*-$PtCl_2$(cod)]	ref
1	**1**	H, H, H	75/25		2
2	**10**	H, H, Br	85/15	100/0	*c*
3	**11**	H, Me, Br	100/0	100/0	*c*
4	**12**	CH_2NMe_2, H, Br	40/60[d]	100/0	*c*
5	**13**	CH_2NMe_2, H, I	45/55[d]	100/0	*c*
6	**14**	naphthyl	85/15[d]	100/0	*c*
7	**15**[e]	H, H, H[e]		100/0	5

[a] After analysis of the reaction mixtures by ^{1}H NMR spectroscopy in $CDCl_3$. [b] Substituents as depicted in Scheme 2. [c] This work. [d] C_6D_6 solutions. [e] C,N = [C_6H_4(CH(Me)NMe_2)-2-(*R*)]$^-$.

Scheme 3. Mechanism for the Formation of Homoleptic Platinum Complexes as Proposed by von Zelewsky et al.[12]



workers (Scheme 3), who obtained only *cis*-isomers of [Pt(C,N)$_2$] even when starting from *trans*-[$PtCl_2(SEt_2)_2$].[12] This mechanism is based on the *trans*-effect of bound ligands. According to this mechanism, in the first step one lithiated *C,N*-ligand is bound to the metal center by its nitrogen atom, causing liberation of a diethyl sulfide molecule. The chelation is completed with the formation of a metal−carbon bond and is followed by elimination of one chloride anion. The strong *trans*-effect of the bonded carbon atom directs the coordination of the second nitrogen atom into the *trans*-position, and formation of the second metal−carbon bond yields *cis*-[Pt(C,N)$_2$].

Although it is likely that the *trans*-effect does play an important role in the reaction mechanism, the present results show that other factors also affect the *cis*/*trans*-preference during the formation of these complexes. Most likely, the difference lies in the nature of the used *C,N*-ligands. Whereas von Zelewsky used rigid arylpyridine ligands, we and others used the more flexible dmba-type ligands. We found that the presence of substituents on the arene rings strongly influences the *cis*/*trans* ratio. As compared to parent complex **1**, a slightly higher ratio was observed for the *para*-bromo-substituted complex **10** (Table 1, entry 2). Interestingly,

(12) Jolliet, P.; Gianni, M.; von Zelewsky, A.; Bernardelli, G.; Stoeckli-Evans, H. *Inorg. Chem.* **1996**, *35*, 4883−4888.

the presence of a *meta* substituent in addition to the *para* halide group favors the formation of the *trans*-isomers (entries 4 and 5). In contrast, substituents at the *ortho*-positions favored the formation of *cis*-isomers (entries 3 and 6), most likely due to steric hindrance. Apparently, the steric interference between the *ortho*-substituents and the Me_2N groups in *trans*-**11** and *trans*-**14** destabilizes the *trans*-complexes with respect to the *cis*-complexes. This is in accordance with earlier observations for complexes with substantial sterically interacting ligands. Also in these cases, only *cis*-isomers were formed.[2,12,13] For example, the *N,N*-ethyl substituents on the benzylamine group in the closely related complex *cis*-[Pt(deba)$_2$] (deba = [$C_6H_4(CH_2NEt_2)$-2]$^-$) are sufficiently large to direct the reaction toward the complete formation of only the *cis*-isomer using reaction conditions similar to those applied for the synthesis of **1**.[2]

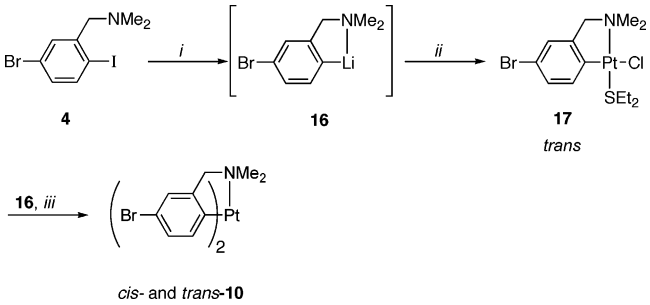
The formation of **10** and **12** was monitored by taking samples of the reaction mixture at regular intervals. ^{1}H NMR spectra of these samples showed that the *cis*/*trans* ratio did not change during the reaction.

When the transmetalation reactions were performed with *cis*-[$PtCl_2$(cod)], only *cis*-isomers were obtained without any trace of *trans*-complexes, as was already observed by Wehman-Ooyevaar et al., for the synthesis of *cis*-[Pt{C_6H_4(CH(Me)NMe_2)-2-(*R*)}$_2$] (**15**, Table 1, entry 7).[5] In the mechanism, starting from a *cis*-complex, in the first step one *C,N*-ligand is bound to the metal center by its nitrogen atom, thereby replacing one of the coordinated olefinic groupings of the initially η^2-bidentate-bonded cod ligand. Subsequently, the metal−carbon bond is formed and the strong *trans*-effect of the carbon atom directs the coordination of the second nitrogen atom to the *trans*-position. This nitrogen atom replaces the η^1-monodentate-bonded cod ligand, resulting in the formation of *cis*-[Pt(C,N)$_2$].

Separation of the *cis*- from the *trans*-isomers was possible due to the considerable solubility differences. The *trans*-complexes are generally more soluble in various solvents such as benzene, toluene, and THF. A convenient method for getting the pure *cis*-complex involved washing of the reaction mixture with THF or precipitation of the *cis*-product from a CH_2Cl_2/Et_2O mixture. Unfortunately, it was not possible to obtain completely pure *trans*-isomers, as small amounts of the *cis*-isomers remained present in the THF washing layers.

The synthesis of homoleptic complexes via a two-step procedure was also investigated. If successful, this would create new opportunities for the synthesis of both homo- and heteroleptic complexes and would provide insight in the mechanism of the reaction. The first step would result in the formation of [PtCl(C,N)L] (L = coordinating ligand), which after isolation and purification could be reacted in a second step with additional bidentate *C,N*-lithium complexes to form either a homoleptic [Pt(C,N)$_2$] or heteroleptic [Pt(C′,N′)(C,N)] complex. We tested this procedure for the synthesis of **10**. The in situ generated lithium complex **16** was reacted with 0.95 equiv of [$PtCl_2(SEt_2)_2$] (*cis*/*trans* = 1:1) in Et_2O (Scheme 4). The conversion to the *trans*-complex **17** was complete in 3 h. On the basis of the $^3J_{Pt-H}$ coupling constants, which are consistent with other *trans*-complexes ($^3J_{Pt-H}$ = 35 and 42 Hz for NMe_2 and CH_2N, respectively, see Table 4),[2] complex **17** was assigned to be the *trans*-isomer with the anionic groups (aryl and chloride) positioned *trans* to each other. NMR analysis of the product showed the presence of **17** and a small amount of *cis*-**10** (5%), which could be removed by column chromatography.[14] In the second step, pure **17** was reacted with **16** in Et_2O. This led to a complete conversion of **17** to homoleptic **10** in a *cis*/*trans* ratio of 80:20. It is interesting to note that the *cis*/*trans* ratio is in accordance with that found for the single-step procedure, thus showing that **17** is the intermediate in that reaction.

Scheme 4. Synthesis of 10 in a Two-Step Procedure[a]



[a] (*i*) *n*-BuLi, Et_2O, −78 °C, 10 min; (*ii*) [$PtCl_2(SEt_2)_2$], Et_2O, −78 °C → RT, 3 h; (*iii*) Et_2O, O °C → RT, 3 h.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for *cis*-12·Et_2O

Interatomic Distances			
Pt−C(1)	1.992(4)	Pt−C(13)	1.991(4)
Pt−N(1)	2.202(3)	Pt−N(3)	2.202(4)

Interatomic Angles and Torsion Angles			
C(1)−Pt−C(13)	97.38(16)	N(1)−Pt−N(3)	102.53(14)
N(1)−Pt−C(1)	80.25(14)	N(3)−Pt−C(13)	80.95(16)
N(1)−Pt−C(13)	171.40(14)	N(3)−Pt−C(1)	171.84(14)
N(1)−Pt−C(1)−C(2)	−15.4(3)	N(3)−Pt−C(13)−C(14)	−13.9(3)
C(1)−Pt−C(13)−C(18)	−29.3(4)	C(13)−Pt−C(1)−C(6)	−30.6(3)

It should be noted that the in situ prepared lithium reagents contain either LiI (reaction of **5**, **6**, and **8** with *t*-BuLi) or *n*-BuI (reaction with *n*-BuLi) in the reaction mixtures. Workup of the reaction mixtures of **10**, **11**, and **13** revealed that these bisaryl platinum(II) complexes are prone to further reacting to platinum(IV) derivatives; that is, under these conditions these platinum(II) compounds undergo oxidation by reaction with electrophiles.[15] For example, during the synthesis of *cis*-**10**, in the presence of LiI, a rapid, subsequent conversion of *cis*-**10** to the Pt^{IV} compound *trans,cis*-[PtI_2{C_6H_3-Br-4-(CH_2NMe_2)-2}$_2$] (**18**) was observed.[16] In this complex, the bidentate ligands are in their original position,

(13) Deuschel-Cornioley, C.; Stoeckli-Evans, H.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1990**, 121−122.

(14) In the ^{1}H NMR spectra $^3J_{Pt-H}$ couplings of 35 and 42 Hz were observed for the NMe_2 and CH_2 groups, respectively. This is in line with values found for the closely related *trans*-[PtCl(C,N)(DMSO)] complexes (32−34 and 39−40 Hz, respectively). (a) Meijer, M. D.; de Wolf, E.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2001**, *20*, 4198−4206. (b) Kleij, A. W.; Klein Gebbink, R. J. M.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *621*, 190−196.

(15) (a) van Beek, J. A. M.; van Koten, G.; Wehman-Ooyevaar, I. C. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 883−893. (b) Wehman, E.; van Koten, G.; Knaap, C. T.; Ossor, H.; Pfeffer, M.; Spek, A. L. *Inorg. Chem.* **1988**, *27*, 4409−4417.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for *cis*-14·*x*C_6H_6

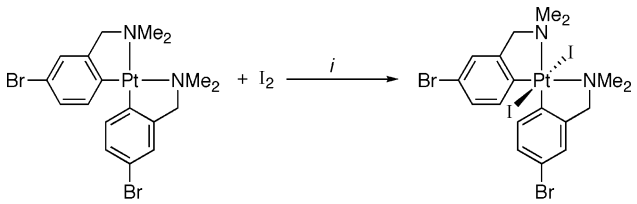
	Interatomic Distances		
Pt(1)−C(11)	2.008(3)	Pt(1)−C(12)	2.002(3)
Pt(1)−N(1)	2.196(2)	Pt(1)−N(2)	2.203(2)
	Interatomic Angles and Torsion Angles		
C(11)−Pt(1)−C(12)	100.82(11)	N(1)−Pt(1)−N(2)	101.53(8)
N(1)−Pt(1)−C(11)	79.57(9)	N(2)−Pt(1)−C(12)	79.86(10)
N(1)−Pt(1)−C(12)	169.45(9)	N(2)−Pt(1)−C(11)	170.49(9)
N(1)−Pt(1)−C(11)−C(21)	−22.18(18)	N(2)−Pt(1)−C(12)−C(22)	−20.6(2)
C(11)−Pt(1)−C(12)−C(92)	−41.7(2)	C(12)−Pt(1)−C(11)−C(91)	−40.9(2)

Table 4. Selected ^{1}H, ^{13}C, and ^{195}Pt NMR Data for Complexes 10−14, 17, 19, 20, 24, and 25[a]

	NMe_2 ($^3J_{Pt-H}$)		CH_2N ($^3J_{Pt-H}$)		C_{ipso} ($^1J_{Pt-C}$)		Pt	
complex	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
10[b]	2.80 (11)	3.02 (43)	3.58 (18)	3.96 (40)	137.4 (1182)	167.6[e]	−3388	−2872
11[b]	2.37 (18), 2.94 (12)		3.28/4.48[c,e]		138.9 (1215)		−3470	
12[d]	1.98 (19), 2.23	2.59 (44), 2.29	3.20 (13), 3.64	3.33 (40), 3.76	139.5[e]	168.8[e]	−3384	−2865
13[d]	1.96 (10), 2.22	2.58 (45), 2.28	3.18 (17), 3.55	3.31 (40), 3.67	140.9[e]	169.9[e]	−3391	−2880
14[d]	1.93, 2.20[e]	2.44, 2.47[e]	3.08/4.46[c,e]	3.03/ 4.69[c,e]	143.9 (1133)	174.4[e]	−3440	−2827
17		2.98 (35)		3.90 (42)		133.3 (1077)		−3700
19[b]	2.08[e]		2.73−3.88[c,e]		155.7[e,f]		−447[g]	
20[d]	2.06, 2.13[e]		3.44, 3.51[e]		140.5[e]		−3412	
24[b]	2.85[e]		3.96[e]		139.2[e]		−3386	
25[b]	2.84[e]		3.94[e]		139.2[e]		−3382	

[a] Chemical shifts in ppm, coupling in hertz, singlet resonances unless stated otherwise, 25 °C. [b] In $CDCl_3$ solutions. [c] AX pattern. [d] In C_6D_6 solutions. [e] $^3J_{Pt-H}$ or $^1J_{Pt-C}$ coupling not observed. [f] Double doublet, $^2J_{P-C}$ = 98 Hz (*trans*), $^2J_{P-C}$ = 15 Hz (*cis*). [g] Doublet, $^1J_{Pt-P}$ = 1744 Hz.

Scheme 5. Synthesis of Platinum(IV) Complex 18[a]



cis-**10** **18**

[a] (*i*) CH_2Cl_2, 1 h.

while the new iodide ligands were placed *trans* to each other, above and below the coordination plane.[15a] Independent synthesis of **18** by adding 1 equiv of I_2 to a solution of *cis*-**10** in CH_2Cl_2 afforded immediately a bright orange-colored solid (Scheme 5). This solid, which is insoluble in the greater part of the common solvents, had the correct elemental analysis based on the proposed composition for **18**. ^{1}H NMR analysis was carried out on an in situ prepared solution of **18** in $CDCl_3$ and confirmed the proposed structure.[17]

Isomerization of *trans*-[Pt(C,N)$_2$] Complexes. All *trans*-complexes of **10** and **12**−**14** can be isomerized quantitatively into the corresponding *cis*-isomers by heating a solution of *cis*−*trans* mixture to reflux for several hours in toluene. Geometrical isomerization by heating solid *trans*-**1** for 5 h at 150 °C, which resulted in the quantitative formation of *cis*-**1**, has already been reported.[8] Complete isomerization of *trans*-**12** and *trans*-**13** into the corresponding *cis*-isomers occurred within a few hours, whereas full isomerization of *trans*-**10** and *trans*-**14** needed 16 h of reaction time (all reactions were monitored by ^{1}H NMR analysis of samples taken from the reaction mixtures at regular intervals). All isomerization reactions were irreversible.

The reaction mechanism for *trans*−*cis* isomerization of the platinum group organometallic complexes has been the subject of considerable debate. Five-coordinate intermediates have been assumed to be involved in isomerization reactions, either catalyzed by the solvent or by addition of an extra ligand.[18] For *trans*−*cis* isomerization in the absence of free ligands a dissociative pathway through three-coordinate intermediates and coordination of a solvent molecule has been proposed.[19] It was found that electron-donating *para* and *meta* substituents in [PtX(C_6H_4R)(PEt_3)$_2$] (R = OMe, Me) enhanced the rate of isomerization.[19a] The relatively fast isomerization of complexes **12** and **13** can be ascribed to the presence of the potentially chelating 5-CH_2NMe_2 substituents. These groups can enhance the thermal isomerization reaction both due to their electron-donating properties and via intermolecular coordination in an associative pathway.

Structural Aspects of [Pt(C,N)$_2$] Complexes 10−14. Solid-State Structures of *cis*-12 and *cis*-14·*x*C_6H_6. Slow distillation of Et_2O to a saturated solution of *cis*-**12** in CH_2Cl_2 afforded single crystals of *cis*-**12**·Et_2O, which were suitable for X-ray crystal structure determination. The molecular structure is depicted in Figure 1 (see Table 2 for relevant bond lengths, bond angles, and torsion angles). The structure shows that the metal center is bonded to two bidentate, *C,N*-bonded amino aryl ligands in the *cis*-configuration and has a slightly distorted square-planar geometry. The two *meta*-amino substituents are not coordinated. The distorted square-planar geometry is reflected by the acute bite angles of the two *C,N*-ligands at the platinum

(16) I^- is in equilibrium with I_2, which upon formation immediately reacts with the platinum(II) complex ($I_3^- + 2e^- \leftrightarrow 3I^-$ (+0.53 V) and $I_2 + 2e^- \leftrightarrow 2I^-$ (+0.62 V).

(17) Since the isolated Pt^{IV} complex was insoluble in common organic solvents, its ^{1}H NMR spectrum was obtained from a $CDCl_3$ solution of the Pt^{II} complex to which a known amount of I_2 had been added.

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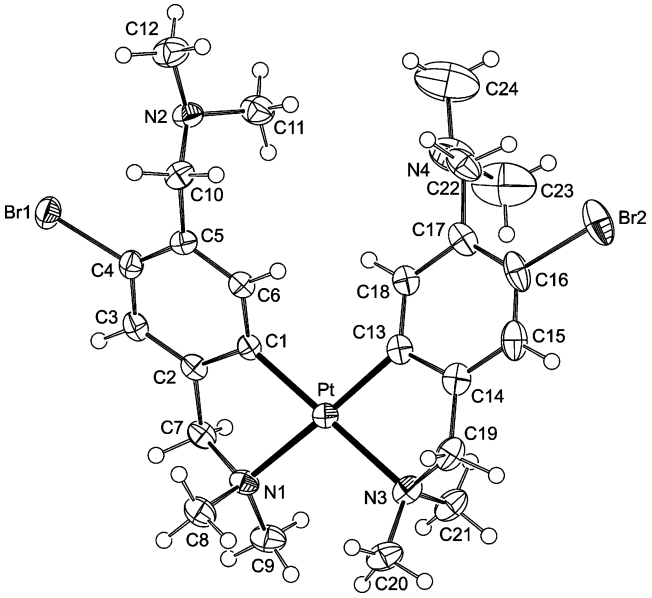


Figure 1. Displacement ellipsoid plot (50% probability level) of the molecular structure of *cis*-**12**·Et_2O, with the adopted labeling scheme. The Et_2O solvent molecule has been omitted for clarity.

center, 80.25(14)° (N(1)−Pt−C(1)) and 80.95(16)° (N(3)−Pt−C(13)). The two five-membered metallacycles are puckered, which is shown by angles between the platinum coordination plane and the aryl plane of −15.4(3)° and −13.9(3)° (N(1)−Pt−C(1)−C(2) and N(3)−Pt−C(13)−C(14), respectively). The C−Pt and N−Pt bond lengths fall in the range of other platinum(II) complexes with chelate-bonded *C,N*-ligands (C−Pt: 2.000−2.025 Å, N−Pt: 2.139−2.164 Å).[13,14,20,21]

Crystals of *cis*-**14**·*x*C_6H_6 suitable for single X-ray crystal structure determination were obtained from a saturated solution of *cis*-**14** in benzene/pentane (9:1). The molecular structure of *cis*-**14** (Figure 2) reveals a platinum(II) center that is ligated by two bidentate *C,N*-bonded amino naphthyl ligands in a *cis*-fashion, with C−Pt and N−Pt bond lengths that are comparable to those of *cis*-**12** (Table 3). The mutual steric intramolecular interference of the hydrogen atoms on C(81) and C(82) (H(81)···H(82) = 3.33 Å) causes the ligands to distort in a unilateral anti-twist fashion. As the crystal is centrosymmetric, both Δ and Λ enantiomers are present in a 1:1 ratio (Figure 3). The torsion angles of

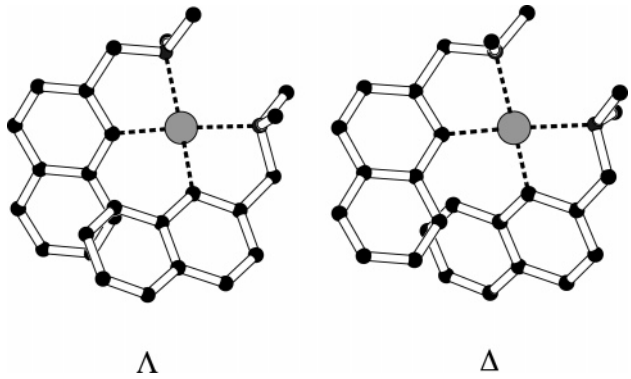


Figure 3. PLUTON plot of the two enantiomers of racemic *cis*-**14**·*x*C_6H_6, Λ, left-handed helicity, and Δ, right-handed helicity.

the platinum coordination plane with the aryl plane are considerably larger than for *cis*-**12**, −41.7(2)° and −40.9(2)° for C(11)−Pt−C(12)−C(92) and C(12)−Pt−C(11)−C(91), respectively. Similar values for these torsion angles were found for related planar chiral palladium(II) and platinum(II) complexes (38.3−44.5°).[12,22] The C−Pt−N bite angles (79.57(9)° and 79.86(10)° for N(1)−Pt−C(11) and N(2)−Pt−C(12), respectively) are similar to those of *cis*-**12** and are in the range of angles found for related homo- and heteroleptic [M(η^2-C,N)] (M = Pt, Pd) complexes (78.5−80.9°).[13,22,23]

NMR Analysis of Complexes 10−14. Complexes **11** and **14** showed two singlet signals for the dimethylamino protons and an AX pattern for the benzylic protons for *cis*-**11**, *cis*-**14**, and *trans*-**14** (Table 4). The

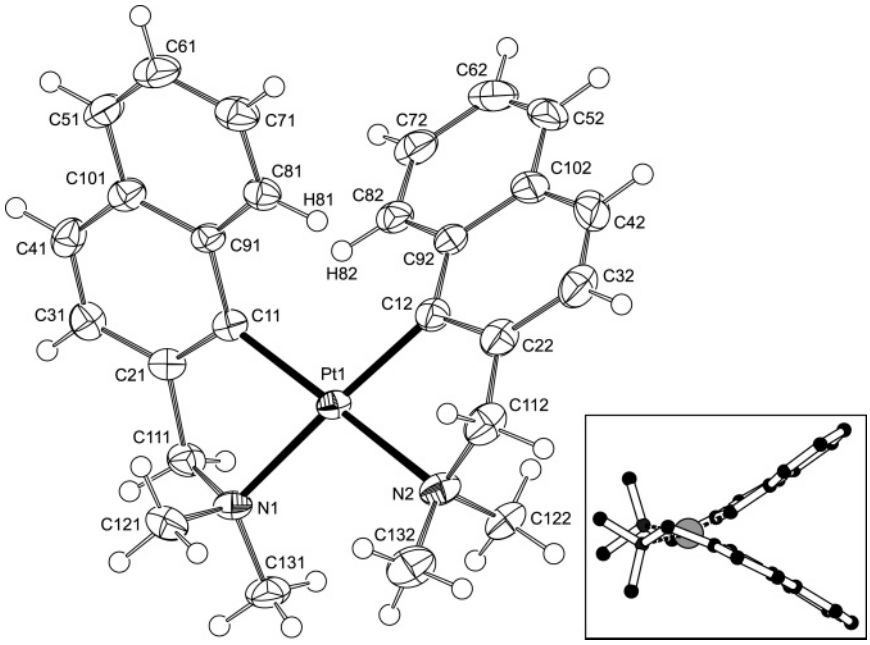


Figure 2. Displacement ellipsoid plot (50% probability level) of the molecular structure of *cis*-**14**·*x*C_6H_6, with the adopted labeling scheme. Disordered solvent molecules are not shown. The inset shows a side view of *cis*-**14**·*x*C_6H_6.

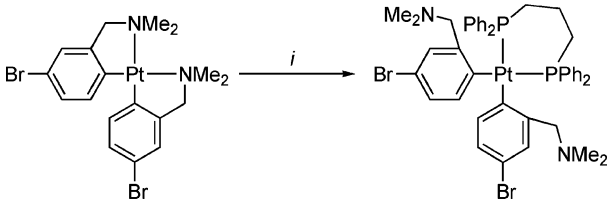
resonances of *trans*-**14** have distinct downfield shifts with respect to those of *cis*-**14**. The presence of AX patterns indicates that under these conditions there is no apparent molecular symmetry plane containing the benzylic carbon and nitrogen centers. This arises from the asymmetric environment that is created by the presence of steric bulk, which prevents a twist of the arene rings with respect to each other and thus induces planar chirality. The asymmetric environment was already observed for **14** in solid state. Both *cis*- and *trans*-isomers have a C_2 symmetry in solution. Variable-temperature ^{1}H NMR experiments of **11** and *cis*-**14** from −95 to +95 °C in toluene-d_8 did not reveal changes in the spectra. Interconversion of the two diastereoisomers, Δ and Λ, is not observed on the NMR time scale.

Singlet signals for the methyl protons and benzylic protons of the coordinated methylene amino substituents of the *cis*- and *trans*-isomers of **10**, **12**, and **13** were observed. Similar downfield shifts of the signals for the *trans*-compounds with respect to the corresponding *cis*-isomers were observed ($\Delta\delta$(H) = 0.13−0.64 ppm, Table 4). The benzylic protons showed the $^3J_{Pt-H}$ coupling constants of 18 (*cis*) and 40 (*trans*) Hz, while the methyl signals displayed coupling constants of 11 and 44 Hz for the *cis*- and *trans*-isomers, respectively. These differences point to a different Pt−N bond strength, as a result of the different *trans*-ligands, either aryl (*cis*) or amine (*trans*). In the *trans*-complexes, the *trans*-influence is weaker, giving rise to larger platinum couplings.[2] The *cis*-complexes have C_{2v} symmetry, whereas the *trans*-complexes exert a C_{2h} symmetry.

Variable-temperature ^{1}H NMR experiments were carried out to study the dynamic aspects of the *cis*-isomers. Low-temperature ^{1}H NMR spectra were recorded in CD_2Cl_2. Lowering the temperature resulted in broadening of the proton resonances of the CH_2NMe_2 groups coordinated to the platinum center. For complexes *cis*-**12** and *cis*-**13**, the NMe_2 and CH_2N singlet signals decoalesced into two broad singlets at −93 °C ($\Delta G^{\ddagger}$ = 35 kJ·mol^{-1}).[24] The decoalescence of these resonances for *cis*-**10** was not observed at temperatures down to −110 °C. This indicates that for *cis*-**12** and *cis*-**13** at low temperatures the interconversion process between the two diastereoisomers Δ and Λ is sufficiently slow. In contrast, this process is not observed for *cis*-**10** at low temperatures. This is probably caused by the absence of *meta*-substituents, whose steric interference can hamper twisting of the arene rings.

Ligand Displacement. Previous reports have shown that the hard donor amine ligands in cyclometalated aminoaryl platinum complexes can be replaced by phosphine ligands, as the soft platinum center favors coordination to the softer phosphine ligands.[3,25,26] In our case a partial ligand displacement, i.e., substitution of the chelating amine groups, should result in the formation of monodentate η^1-*C*-bonded aminoaryl ligands with a dangling CH_2NMe_2 base functionality. Reaction of *cis*-**10** with 1 equiv of the bidentate 1,3-(diphenylphosphino)propane (dppp) ligand in CH_2Cl_2 resulted in the rapid conversion to *cis*-[Pt(η^1-$C_6H_3(CH_2NMe_2)$-2-Br-4)$_2$(η^2-dppp)] (**19**), which contains a chelate-bonded dppp ligand (Scheme 6). The results of ^{1}H and ^{31}P NMR analysis of a solution of **19** excluded the possibility that the dppp ligand was either η^1-*P* monodentate or μ^2-η^2-*P,P′* bridge bonded. To study whether the dppp ligand could induce *trans*-to-*cis* isomerization, the synthesis of **19** was attempted starting from a *cis*/*trans*-**10** isomeric mixture. Mixing of 1 equiv of dppp with 1 equiv of a 1:1 molar mixture of pure *cis*-**10** and *trans*-**10** isomers in $CDCl_3$ at room temperature for 7 days did not result in complete conversion to **19**. Although the *cis*/*trans* ratio was increased to 3:1 (75% of *cis*-complex **19**, 25% of *trans*-complex [Pt(η^1-C,N)(η^2-C,N)(η^1-dppp)]), indicating that 50% *trans*-to-*cis* isomerization was achieved, the presence of dppp did not enhance the isomerization reaction to a great extent.

Scheme 6. Reaction of *cis*-10 with dppp[a]



cis-**10** **19**

[a] (*i*) dppp, CH_2Cl_2, RT, 5 min.

Structural Aspects of [Pt(η^1-C,N)$_2$(η^2-dppp)] (19). Solid-State Structure. Single crystals of **19** were obtained by cooling a saturated solution of **19** in CH_2Cl_2 at 4 °C. A molecular plot of the molecular structure is depicted in Figure 4, while Table 5 shows a selection of bond lengths, bond angles, and torsion angles. The structure has an exact, crystallographic C_2 symmetry. The molecular structure shows a square-planar platinum(II) complex, which possesses two monodentate η^1-*C*-bonded *C,N*-ligands in *cis*-configuration and an η^2-*P,P′*-bidentate-bonded dppp ligand. The *C,N*-aryl planes are oriented perpendicular to the coordination plane of the platinum center, which contrasts with the almost coplanar situation in, for example, *cis*-**12**. The Pt−C(1) bond is slightly elongated from 1.992(4) Å in *cis*-**12** to 2.065(4) Å in **19**. The noncoordinating *ortho*-amino groups are directed away from the metal center, in an *E*-conformation.[27] Only the *E*-stereoisomer is present in the crystal, whereas a mixture of *E*- and *Z*-conformers is present in solution. The P(1)−Pt−P(1)^i bite angle (89.69(6)°) has a lower value than the P−Pt−P bite angles observed in related complexes (94.63−97.02(8)°),

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(24) Calculated with formula $\Delta G^{\ddagger} = RT_c \ln\{(\sqrt{2})k_bT_c)/h\pi(\Delta\nu)\}$ from: Drago, R. S. *Physical Methods in Inorganic Chemistry*; Reinhold Publishing Corporation: New York, 1965.

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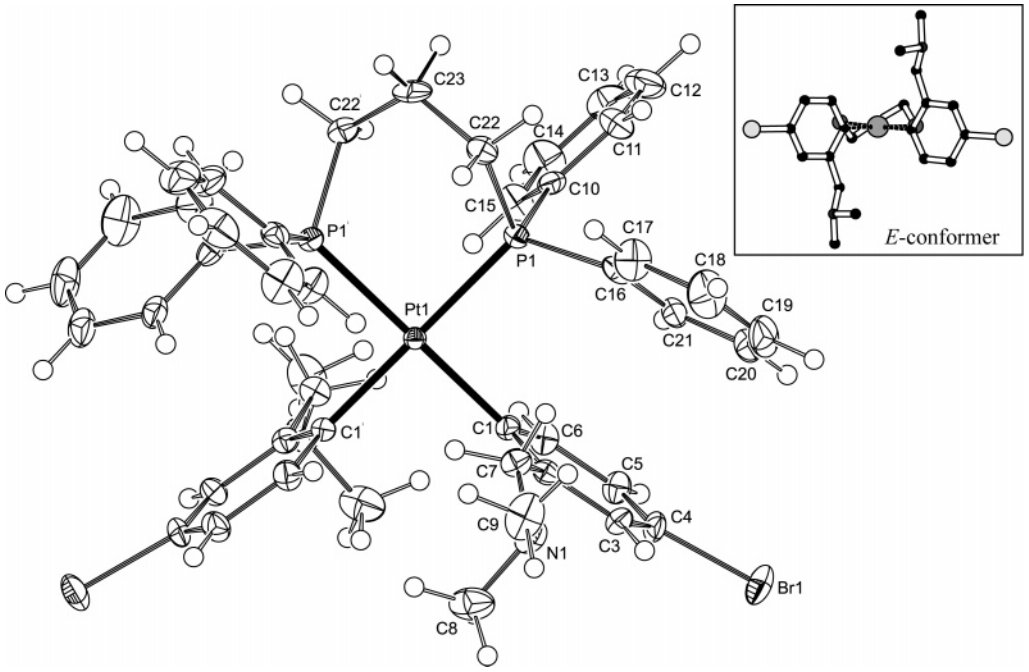

Figure 4. Displacement ellipsoid plot (50% probability level) of the molecular structure of **19**, with the adopted labeling scheme. Disordered solvent molecules have been omitted for clarity. Symmetry operation i: $1-x, y, 0.5-z$. The inset shows a view along the 2-fold axis of **19** with the *E*-conformation.

Table 5. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 19

Interatomic Distances			
Pt(1)−C(1)	2.065(4)	Pt(1)−P(1)	2.2998(11)
P(1)−C(10)	1.829(5)	P(1)−C(16)	1.828(5)
P(1)−C(22)	1.833(5)		

Interatomic Angles and Torsion Angles			
C(1)−Pt(1)−C(1)^{i}	89.7(2)	P(1)−Pt(1)−P(1)^{i}	89.69(6)
P(1)−Pt(1)−C(1)	90.34(12)	P(1)−Pt(1)−C(1)^{i}	179.00(13)
P(1)−Pt(1)−C(1)−C(2)	85.8(3)	C(1)^{i}−Pt(1)−C(1)−C(2)	−95.2(4)

while the Pt−P distance (2.2998(11) Å) lies within the range found for these complexes (2.271−2.305 Å).[28]

Structure in Solution. The ^{1}H NMR spectrum of **19** in CD_2Cl_2 reveals an AX pattern for the benzylic protons with platinum couplings. This shows that **19** lacks a symmetry plane containing the benzylic carbon atoms. ^{31}P and ^{195}Pt NMR analysis showed that the *cis*-configuration is retained. The coupling constant $^{1}J_{Pt-P}$ is 1721 Hz, which is in accordance with values found for related *cis*-complexes (1669−1748 Hz).[29] The presence of one sharp phosphor signal at −4.46 ppm points to one single complex in solution, i.e., a complex with an intramolecularly coordinated dppp ligand. The NMR spectra did not reveal the presence of the two *E*- and *Z*-conformers. Most likely, this indicates that the barrier for rotation of the aryl rings about the Pt−C_{ipso} axis is very low, and therefore fast interchange between the two conformers on the NMR time scale occurs. The alternate possibility, i.e., a high rotation barrier for the *E*−*Z* interconversion process, can be excluded because this would lead to two resonance patterns, one for the *E*- and one for the *Z*-conformer, whereas one resonance pattern is observed over a wide temperature range (−85 to +50 °C in CD_2Cl_2). Apparently, the presence of the *ortho*-CH_2NMe_2 substituents does not cause enough steric interference for the rotation or wagging process to become slow on the NMR time scale.

Functionalization of [Pt(C,N)$_2$] Complexes. As mentioned above, the [Pt(C,N)$_2$] complexes were designed as such that they would allow further functionalization, for example by displacement of the chelate-bonded amine ligands by addition of a stronger coordinating phosphine ligand (vide supra). Furthermore, the halide groups at the aryl rings can be used for substitution reactions, via either lithiation or metal-catalyzed C−C bond formation reactions. These kinds of nucleophilic substitution reactions are rarely performed on organometallic complexes, and only a few examples have been reported.[30,31] We have performed two types of functionalization reactions with the *cis*-isomers of **10** and **12**, i.e., lithiation and subsequent transmetalation reactions and C−C coupling reactions.

Lithiation and Transmetalation Reactions. Lithiation of the bromide substituents of *cis*-**10** and *cis*-**12**, respectively, was carried out by reaction with either *n*- or *t*-BuLi, followed by quenching the in situ prepared 4,4′-bis(lithio-aryl) platinum complex with [$SnBrMe_3$]. Double lithiation and subsequent transmetalation of *cis*-**12** was possible by adding 4 equiv of *n*-BuLi to a solution of *cis*-**12** in THF at 0 °C (Scheme 7).[32] The bisstannane product **20** was purified by column chromatography.

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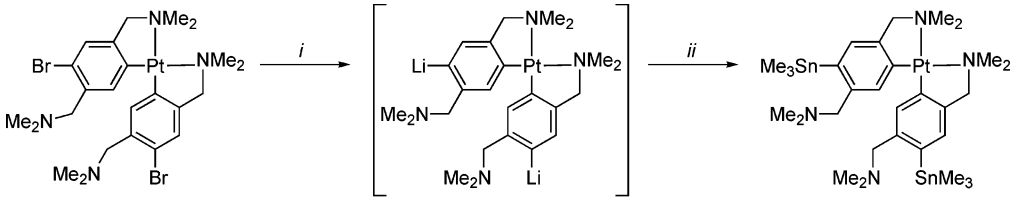
Scheme 7. Lithiation and Transmetalation Reaction with *cis*-12[a]



cis-**12** **20**

[a] (*i*) *n*-BuLi, THF, 0 °C, 15 min; (*ii*) [$SnBrMe_3$], THF, 0 °C → RT, 1 h.

Selective double lithiation of *cis*-**10** at the bromide position could not be achieved. Using either *n*-BuLi or *t*-BuLi in THF at low temperatures (< −80 °C, 15 min to 1 h) did not result in the required lithiation. Each time, unchanged *cis*-**10** was recovered after the lithiation reaction and it could even be reused after purification. At higher temperatures in THF (> −30 °C, 5 min to 1 h), mixtures of products were obtained from the reaction of *cis*-**10** with *n*-BuLi and subsequent quenching with [$SnBrMe_3$]. Next to some nonreacted *cis*-**10**, some transmetalated complexes and significant amounts of *n*-butyl-functionalized complexes were obtained. As each complex can react at the 4- and 4′-bromide positions, a variety of products can be expected to form, for example, [Pt(C,N-4-{$SnMe_3$})(C,N-4-{*n*-Bu})], [Pt(C,N-4-{$SnMe_3$})$_2$], [Pt(C,N-4-Br)(C,N-4-{*n*-Bu})], etc. Separation of these complexes was not possible. The ratios of these products were dependent on the applied reaction conditions; higher temperatures or longer reaction times resulted in higher conversions to transmetalated and *n*-butyl-functionalized complexes. The *n*-butyl-functionalized complexes are formed in a cross-coupling reaction of the lithiated complex and in situ generated 1-bromobutane.[30a] Activation of the bromide position of *cis*-**10** was also attempted by reaction with [*i*-PrMgCl] according to recently reported procedures by Knochel et al.[33] Surprisingly, upon using 8 equiv of [*i*-PrMgCl] in THF at temperatures from 0 to 40 °C (3 h), no reaction was observed.

The fact that full lithiation of *cis*-**10** appeared to be impossible is in contrast to the results obtained with *cis*-**12** and the previously reported terdentate *N,C,N*-chelating aminoaryl Pt^{II} complexes [PtX{C_6H_2I-4-(CH_2NMe_2)$_2$-2,6}] (X = Br, I). The latter complexes smoothly lithiated at the iodo position *para* to the platinum center, by reaction with 2 equiv of *t*-BuLi in THF at −100 °C.[3,26] The potentially chelating amino groups in *cis*-**12** stabilize the formed lithium species, which prevents further reaction with the *n*-bromobutane present in the reaction mixture.

C−C Coupling and Palladation Reactions. The presence of the halide functionalities should, next to lithiation, also enable the attachment of new groups via metal-catalyzed C−C coupling reactions. To test this possibility, a Suzuki−Miyaura coupling reaction between *cis*-**10** and a boronic acid was performed. For this reaction, a *para*-functionalized SCS-pincer ligand was used, because of its usefulness for further metalation reactions. The SCS-pincer ligand (SCS = [C_6H_3(CH_2SR)$_2$-2,6]−, R = Ph, Bu, etc.) is well known to easily undergo cyclopalladation. Moreover, its cationic palladium complexes have a versatile coordination chemistry with Lewis bases.[34] The *cis*-[Pt(C,N)$_2$] complexes functionalized with SCS-Pd pincers could therefore be used as multimetallic building blocks in coordination chemistry for the construction of supramolecular assemblies.

The reagent for the C−C coupling reaction, the pinacol-protected boronic acid of the SCS-pincer, was prepared starting from 3,5-bis(bromomethyl)bromobenzene (**21**, Scheme 8). Nucleophilic displacement of the benzylic bromides in **21**, employing *t*-BuSNa in ethanolic solution, yielded **22** in high yield.[34a] Compound **22** was reacted in a one-pot synthesis with 2 equiv of *t*-BuLi in Et_2O at −78 °C and $B(OMe)_3$, and pinacol to form **23**. This compound is well soluble in organic solvents and contrary to most boronic acids ($RB(OH)_2$) insoluble in water. The pinacol-protected boronic acid **23** was reacted with *cis*-**10** under Suzuki coupling reaction conditions at 70 °C, without affecting the C−Pt bonds in the complex. The reaction was complete within 3 h. It is noteworthy that no decomposition of *cis*-**10** was observed and that conversion to the *cis*-complex **24** was quantitative. Purification by column chromatography afforded **24** in moderate yield as an air- and moisture-stable, white solid.

The commonly applied method for cyclopalladation of SCS-pincer ligands is by reaction with [Pd(NCMe)$_4$]-(BF_4)$_2$.[34] Indeed, complex **24** could be cyclopalladated twice by reaction with [Pd(NCMe)$_4$](BF_4)$_2$ in the presence of NEt_3, following the method reported by Swager and co-workers.[35] The in situ formed dicationic bisacetonitrile complex, which contains two noncoordinating $[BF_4]^-$ counteranions, was reacted with NaCl to form the neutral *cis*-complex **25**. This air- and moisture-stable complex was purified by slow distillation of Et_2O to a saturated solution of **25** in CH_2Cl_2.

Full conversion to the bis-SCS-functionalized complex **24** and its cyclopalladated derivative **25** was confirmed by MALDI-TOF mass analysis. The positive MALDI-TOF spectrum of **24** showed a signal corresponding to $[M + H]^+$ (*m/z* = 1024.9), while the spectrum of **25** showed a signal corresponding to $[M - Cl]^+$ (*m/z* = 1270.7).

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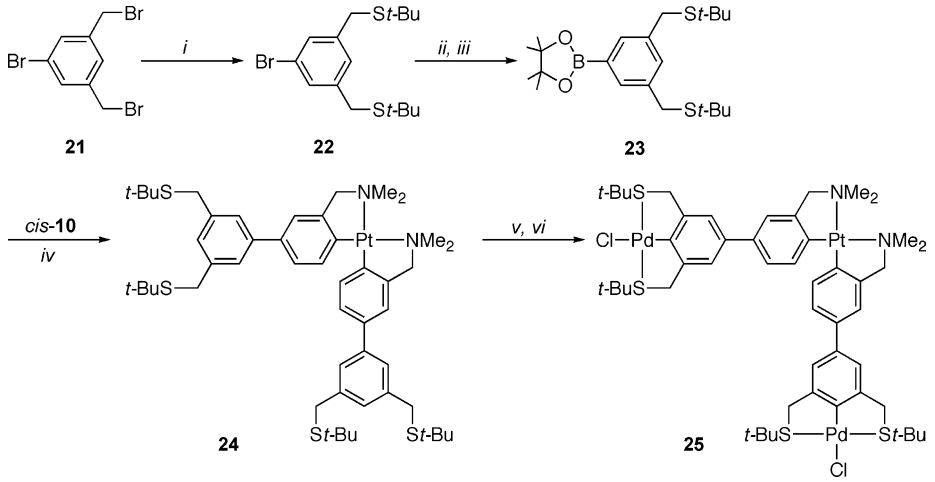
Scheme 8. Synthesis of SCS-Functionalized Corner Complexes 24 and 25 via Suzuki–Miyaura Coupling[a]



[a] (*i*) *t*-BuSNa, EtOH, Δ*T*; (*ii*) 2 equiv *t*-BuLi, Et_2O, −78 °C, 10 min, $B(OMe)_3$, −78 °C → RT, 16 h; (*iii*) pinacol, HOAc, 1 h; (*iv*) thf/dme/H_2O (1:1:1), [$PdCl_2$(dppf)], Na_2CO_3, 70 °C, 3 h; (*v*) 2 equiv [$Pd(NCMe)_4$](BF_4)$_2$, NEt_3, MeCN, Δ*T*, 2 h; (*vi*) NaCl (aq), 1 h.

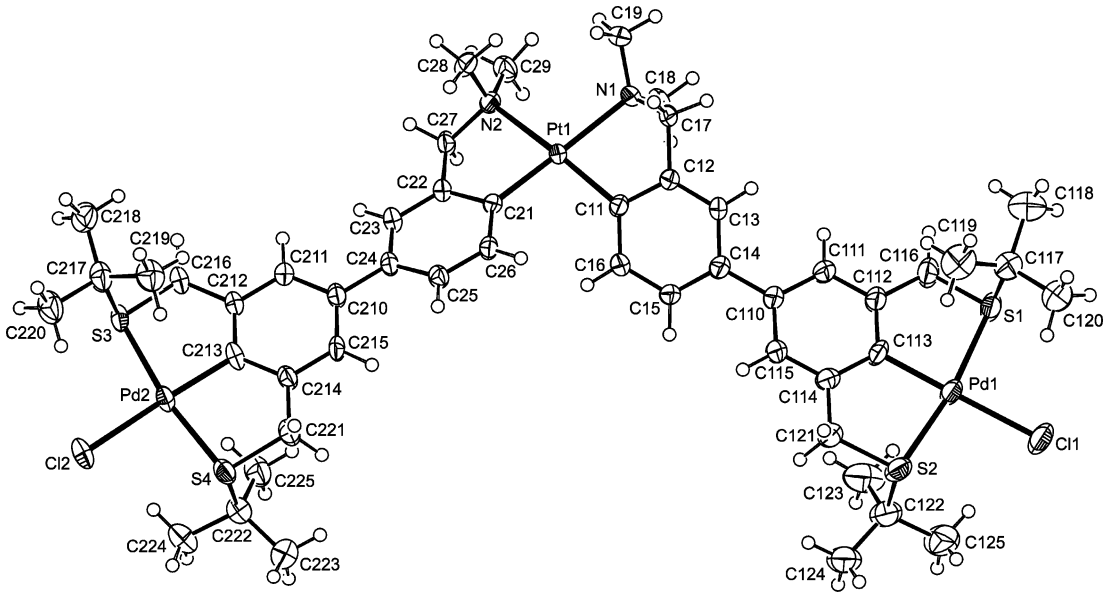


Figure 5. Displacement ellipsoid plot (50% probability level) of the molecular structure of **25**·*x*CH_2Cl_2, with the adopted labeling scheme. Solvent molecules have been omitted for clarity.

Table 6. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 25·*x*CH_2Cl_2

Pt(1)−C(11), Pt(1)−C(21)	1.999(4), 1.985(4)	Pt(1)−N(1), Pt(1)−N(2)	2.218(3), 2.208(3)
Pd(1)−Cl(1), Pd(2)−Cl(2)	2.4064(12), 2.4213(11)	Pd(1)−C(113), Pd(2)−C(213)	1.979(4), 1.976(4)
Pd(1)−S(1), Pd(1)−S(2)	2.3071(14), 2.3076(13)	Pd(2)−S(3), Pd(2)−S(4)	2.3181(12), 2.2959(13)
N(1)−Pt(1)−C(11)	80.54(15)	N(2)−Pt(1)−C(21)	80.38(15)
C(11)−Pt(1)−C(21)	98.31(17)	N(1)−Pt(1)−N(2)	101.50(13)
Cl(1)−Pd(1)−C(113), Cl(2)−Pd(2)−C(213)	178.58(15), 175.83(13)	S(1)−Pd(1)−S(2), S(3)−Pd(2)−S(4)	170.91(5), 169.63(4)
S(1)−Pd(1)−C(113), S(2)−Pd(1)−C(113)	85.48(14), 85.48(14)	S(3)−Pd(2)−C(213), S(4)−Pd(2)−C(213)	85.25(14), 84.80(14)
Pd(1)−S(1)−C(117), Pd(1)−S(2)−C(122)	109.9(2), 109.53(19)	Pd(2)−S(3)−C(217), Pd(2)−S(4)−C(222)	107.26(18), 107.07(17)
C(21)−Pt(1)−C(11)−C(16), C(11)−Pt(1)−C(21)−C(26)	31.8(4), 25.3(4)	N(1)−Pt(1)−C(11)−C(12), N(2)−Pt(1)−C(21)−C(22)	14.3(3), 13.5(3)
S(1)−Pd(1)−C(113)−C(112), S(2)−Pd(1)−C(113)−C(114)	9.9(5), 6.0(4)	S(3)−Pd(2)−C(213)−C(212), S(4)−Pd(2)−C(213)−C(214)	−8.6(4), −11.7(4)
C(15)−C(14)−C(110)−C(115)	−34.8(8)	C(25)−C(24)−C(210)−C(215)	−18.9(7)

Structural aspects of 24 and 25. Solid-State Structure of 25. Single crystals of **25**·*x*CH_2Cl_2 were obtained by cooling a solution of **25** in CH_2Cl_2/Et_2O (10:1) at −30 °C. A plot of its molecular structure is depicted in Figure 5, while Table 6 shows a selection of bond lengths, bond angles, and torsion angles. In the crystal two diastereoisomers (*SS*,*SS* and *RR*,*RR*) are present (Figure 6). The molecular structure of **25**·*x*CH_2Cl_2 reveals a platinum(II) center that is ligated by two bidentate *C*,*N*-bonded amino aryl ligands in a *cis*-fashion. Each aryl group is substituted at the *para*-position with a diorganosulfide aryl moiety, which is

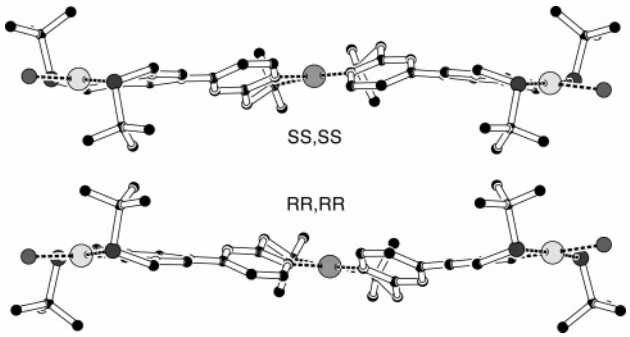


Figure 6. PLUTON plot of the two diastereoisomers of **25**·$x$$CH_2Cl_2$.

cyclopalladated at the position between the CH_2S(*t*-Bu) groups. This affords square-planar Pd^{II} centers with a ligand environment that comprises a tridentate SCS coordination by the organic moiety and a chloride *trans* to the metal-bonded aromatic carbon atom. The Pt−C and Pt−N bonds fall in the range observed for *cis*-**12** and *cis*-**14**, and the angles and torsion angles of the organoplatinum moiety fall in the range observed for *cis*-**12**. Figure 6 clearly shows that the structure is nearly flat. The palladium atoms adopt slightly distorted square-planar geometries with angles and distances that are similar to related *tert*-butylsulfido SCS-Pd^{II} complexes.[36] The four butyl groups are oriented *anti* with respect to the square planes, in axial positions, with Pd−S−C(*t*-Bu) angles of 107.07(17)−109.9(2)°, similar to reported SCS(*t*-Bu)-Pd^{II} complexes (107.5(4)−113.5(9)°).[36] The torsion angles between the C,N-aryl and SCS-aryl rings of −34.8(8)° and −18.9(7)° (C(15)−C(14)−C(110)−C(115) and C(25)−C(24)−C(210)−C(215), respectively) fall in the range normally observed for biphenyl compounds.

Structure in Solution. The ^1H NMR spectra of complexes **24** and **25** in $CDCl_3$ showed the same signals for the dimethylbenzyl amino groups as *cis*-**10**. The singlet signals of the CH_2S and S(*t*-Bu) groups of **25** are shifted downfield with respect to the free ligand **24**, $\Delta\delta$(H) = 0.41 and 0.24 ppm for CH_2S and S(*t*-Bu), respectively. The resonance of the diastereotopic CH_2S protons of **25** is somewhat broadened due to fluxional behavior. This behavior is attributed to the pyramidal inversion of the sulfur atoms and/or to the inversion of the ring puckering, leading to a multiplicity of isomers with axial and/or equatorial positions for each SBu group in a single molecule.[37] These two combined processes give rise to a dynamic equilibrium between two conformational isomers that make the benzylic protons nonequivalent. At lower temperatures (down to −60 °C) no significant changes were observed for **24**. For complex **25**, the coupling of the two diastereotopic CH_2S protons resulted in splitting of the signal into two AB patterns, 3.76/4.65 ($^2J_{H-H}$ = 17 Hz) and 4.05/4.37 ($^2J_{H-H}$ = 16 Hz) ppm at low temperatures (down to −60 °C). This points to the presence of two isomers; that is, the *t*-Bu groups are in axial or equatorial positions with respect to the palladium coordination plane.[37] The coalescence of the CH_2S signals occurred at −10 °C. The singlet signal resonance of the *tert*-butyl groups of **25** splits in two singlet signals with a coalescence point of −30 °C. Although large differences for the SCS-pincer units of **25** were observed at low temperatures, no significant changes were observed for the dimethylbenzyl amino groups. Lowering the temperature to −60 °C did not result in decoalescence of the singlet peaks of the benzylic protons of **24** and **25**, as was also observed for the parent complex *cis*-**10**.

Conclusions

We have synthesized a series of new homoleptic *C,N-ortho*-chelated aminoaryl platinum(II) complexes as *cis*- and *trans*-isomers in one- or two-step reactions. The *cis*/*trans* ratio is dependent on the functionalities on the aryl ring, such as halide, methyl, naphthyl, and (dimethylamino)methyl groups. Sterically demanding groups at the *ortho*-position favor the formation of *cis*-complexes, which in that case contain a planar-chiral metal center. The *trans*-complexes could be irreversibly isomerized to the thermodynamically more stable *cis*-isomers. The complexes could be further functionalized by (1) ligand displacement, (2) lithiation of the halide groups, followed by a transmetalation reaction with [$SnClMe_3$], and (3) C−C Suzuki−Miyaura coupling reactions, affecting neither the conformation nor the nature of the complexes. By the latter method a bis-SCS-pincer functionalized complex was prepared, which could be cyclopalladated twice in an additional reaction. This yielded an unusual neutral mixed trinuclear bis-palladium/platinum corner complex, which has potential applications in the synthesis of larger (self-assembled) molecular architectures. Addition of other functionalities is of course also possible via either lithiation or C−C coupling reactions. The halide-functionalized complexes are thus excellent precursors for the synthesis of various organometallic complexes as, for example, molecular squares.[38]

Experimental Section

General Comments. 4-Bromo-2-bromomethyl-1-iodobenzene (**2**),[10] 5-bromo-1-bromomethyl-2-iodo-3-methylbenzene (**3**),[10] 1,4-dibromo-2,5-bis(bromomethyl)benzene (**4**),[10] 1-bromo-2-dimethylaminomethylnaphthalene (**9**),[11] and 3,5-bis(bromomethyl)bromobenzene (**21**)[10] were synthesized according to literature procedures. All solvents and other reagents were obtained from commercial sources and were used without further purification unless stated otherwise. Reactions involving organolithium and -magnesium derivatives were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Et_2O and THF were distilled from Na/benzophenone prior to use. The ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra were recorded at 300, 75.5, 81, and 64.3 MHz, respectively, at 25 °C. Chemical shifts are reported in ppm. ^{195}Pt NMR spectra were referenced to external K_2PtCl_4 (δ = −1630). MALDI-TOF mass spectra were acquired using a Applied Biosystems Voyager System 6347, with dithranol as matrix. Elemental analyses were obtained from Kolbe, Mikroanalytisches Laboratorium (Mülheim a.d. Ruhr, Germany).

Crystal Structure Determinations. X-ray intensities were measured on a Nonius KappaCCD diffractometer with

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Table 7. Crystallographic Details[a]

	cis-**12**·Et_2O	*cis*-**14**·xC_6H_6	**19**	**25**·xCH_2Cl_2
formula	$C_{24}H_{36}Br_2N_4Pt·C_4H_{10}O$	$C_{26}H_{28}N_2Pt$ + disordered solvent	$C_{45}H_{48}Br_2N_2P_2Pt$	$C_{50}H_{70}Cl_2N_2Pd_2PtS_4·2CH_2Cl_2$ + disordered solvent
fw	809.60	563.59 [*]	1033.70	1475.96 [*]
cryst size [mm^3]	0.48 × 0.12 × 0.12	0.21 × 0.21 × 0.21	0.42 × 0.18 × 0.06	0.42 × 0.09 × 0.06
cryst color	colorless	yellow	colorless	yellow
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2/c$ (no. 13)	$P\bar{1}$ (no. 2)
a [Å]	11.2540(1)	9.9208(1)	10.0910(10)	11.0727(1)
b [Å]	13.4683(1)	11.6735(1)	9.3702(7)	17.2827(2)
c [Å]	20.6529(2)	21.8509(2)	23.476(3)	18.1957(2)
α [deg]	90	90	90	86.1892(7)
β [deg]	100.3196(4)	99.9722(5)	111.232(7)	79.8100(8)
γ [deg]	90	90	90	82.8972(4)
V [$Å^3$]	3079.77(5)	2492.33(4)	2069.1(4)	3397.27(6)
Z	4	4	2	2
D_{calc} [g/cm^3]	1.746	1.502 [*]	1.659	1.443 [*]
μ [mm^{-1}]	7.177	5.642 [*]	5.433	2.967 [*]
abs corr	analytical	analytical	analytical	multiscan
abs corr range	0.21−0.56	0.33−0.48	0.32−0.70	0.66−0.84
measd/unique reflns	35 139/7012	37 241/5674	30 763/4772	65 488/15 545
params/restraints	333/37	266/0	239/0	620/0
R1/wR2 [$I>2\sigma(I)$]	0.0304/0.0684	0.0208/0.0451	0.0322/0.0881	0.0391/0.1047
R1/wR2 [all reflns]	0.0364/0.0705	0.0297/0.0474	0.0339/0.0891	0.0489/0.1104
S	1.133	1.049	1.095	1.072

[a] Derived parameters do not contain the contribution of the disordered solvent.

rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K. The structures were solved with automated Patterson methods[39] (*cis*-**12**·Et_2O, *cis*-**14**·xC_6H_6, **25**·xCH_2Cl_2) or direct methods[40] (**19**) and refined with SHELXL-97[41] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. Structure calculations and checking for higher symmetry were performed with the PLATON package.[42]

The crystals of *cis*-**14**·xC_6H_6 contain large voids (374.6 $Å^3$/unit cell) filled with severely disordered benzene solvent molecules. Their contribution to the structure factors was secured by back Fourier transformation with the SQUEEZE procedure of PLATON,[42] resulting in 94 electrons/unit cell.

The crystals of **19** appeared to be nonmerohedrally twinned with a 2-fold rotation about hkl = (001) as twin operation. The HKLF5 twin refinement[43] resulted in a twin fraction of 0.3666(11).

The crystals of **25**·xCH_2Cl_2 contain ordered CH_2Cl_2 molecules and additionally large voids (678.4 $Å^3$/unit cell) filled with severely disordered CH_2Cl_2 solvent molecules. The contribution of the latter to the structure factors was secured by back Fourier transformation with the SQUEEZE procedure of PLATON,[42] resulting in 178 electrons/unit cell.

Further details about the crystal structure determinations are given in Table 7.

4-Bromo-2-(dimethylamino)methyl-1-iodobenzene (5). To a solution of **2** (17.1 g, 45.5 mmol) was added dimethylamine (60 mL, 865 mmol, 19 equiv) in Et_2O (250 mL) at room temperature. After 2 h the salts were removed by filtration and the reaction mixture was concentrated in vacuo. The resulting oil was purified by flash distillation, yielding 13.4 g of **5** (39.3 mmol, 86%). ^1H NMR ($CDCl_3$): δ 2.29 (s, 6H, NCH_3), 3.40 (s, 2H, CH_2N), 7.07 (d, 1H, $^3J_{H-H}$ = 10 Hz, ArH-5), 7.55 (s, 1H, ArH-3), 7.64 (d, 1H, $^3J_{H-H}$ = 10 Hz, ArH-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.8 (NCH_3), 67.8 (CH_2N), 98.4 (ArC-1), 122.9 (ArC-4), 131.9, 133.3, 140.8, 143.6 (ArC-2). Anal. Calcd for $C_9H_{11}NBrI$: C, 31.79; H, 3.26; N, 4.12. Found: C, 31.97; H, 3.32; N, 4.20.

5-Bromo-1-(dimethylamino)methyl-2-iodo-3-methylbenzene (6). Compound **3** (1.36 g, 3.49 mmol) was dissolved in Et_2O (40 mL) and treated with dimethylamine (4 mL, 56 mmol, 16 equiv) at room temperature. After 2 h the salts were removed by filtration and the reaction mixture was concentrated in vacuo. The resulting oil was purified by protonating with excess of HCl (4 M), extraction with water, addition of excess NaOH, and extraction with Et_2O. Yield of **6**: 0.62 g (1.75 mmol, 50%). ^1H NMR ($CDCl_3$): δ 2.30 (s, 6H, NCH_3), 2.44 (s, 3H, $ArCH_3$), 3.44 (s, 2H, CH_2N), 7.28 (s, 1H, ArH-5), 7.36 (s, 1H, ArH-3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.4 ($ArCH_3$), 45.7 (NCH_3), 68.7 (CH_2N), 105.7 (ArC-4), 122.2 (ArC-1), 130.1, 131.0, 153.8, 144.1. Anal. Calcd for $C_{10}H_{13}NBrI$: C, 33.93; H, 3.70; N, 3.96. Found: C, 34.02; H, 3.82; N, 3.80.

1,4-Dibromo-2,5-bis{(dimethylamino)methyl}benzene (7). To a solution of **4** (5.6 g, 13.2 mmol) in Et_2O (130 mL) was added dimethylamine (15 mL, 216 mmol, 16 equiv) at room temperature. The suspension was stirred for 2 h, after which the salts were removed by filtration. The reaction mixture was washed with brine (40 mL, 2×). Evaporating the solvent in vacuo yielded 4.0 g of **7** as a white solid (11.4 mmol, 87%). ^1H NMR ($CDCl_3$): δ 2.31 (s, 12H, NCH_3), 3.49 (s, 4H, CH_2N), 7.64 (s, 2H, ArH-3,6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.7 (NCH_3), 62.7 (CH_2N), 123.5 (ArC-1,4), 134.6 (ArC-3,6), 138.7 (ArC-2,5). Anal. Calcd for $C_{12}H_{18}N_2Br_2$: C, 41.17; H, 5.18; N, 8.00. Found: C, 41.08; H, 5.03; N, 7.88.

1,4-Diiodo-2,5-bis{(dimethylamino)methyl}benzene (8). Compound **7** (1.9 g, 5.5 mmol) was dissolved in Et_2O (40 mL), and to this solution was added *n*-BuLi (7.8 mL, 1.6 M in hexane, 12.5 mmol, 2.3 equiv) at −78 °C. The reaction mixture was stirred for 15 min at this temperature, after which the suspension was allowed to reach room temperature and stirred for 45 min. The reaction mixture was quenched with a solution of 1,2-diiodoethane (3.2 g, 11.5 mmol, 2.1 equiv) in Et_2O (30 mL) and stirred for 15 min. The mixture was acidified with a 2 M solution of HCl (20 mL), and the aqueous layer was separated from the organic layer and washed with Et_2O (40 mL). The aqueous layer was made basic with KOH pellets until the amino compound precipitated from solution. Extracting

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with Et_2O and removal of the solvent yielded 2.14 g of **8** as an off-white powder (4.8 mmol, 88%). ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 12H, NCH_3), 3.42 (s, 4H, CH_2N), 7.86 (s, 2H, ArH-3,6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 45.6 (NCH_3), 67.1 (CH_2N), 100.3 (ArC-1,4), 140.5 (ArC-3,6), 141.9 (ArC-2,5). Anal. Calcd for $C_{12}H_{18}N_2I_2$: C, 32.46; H, 4.09; N, 6.31. Found: C, 32.58; H, 4.15; N, 6.39.

***cis*-[Pt(C_6H_3Br-4{CH_2NMe_2}-2)$_2$] (*cis*-10) and *trans*-[Pt(C_6H_3Br-4{CH_2NMe_2}-2)$_2$] (*trans*-10).** To a solution of **5** (1.4 g, 4.12 mmol) in Et_2O (30 mL) was added *n*-BuLi (4.16 mmol, 1.6 M in hexane, 2.6 mL, 1 equiv) at −78 °C. The reaction mixture was stirred for 5 min, after which a suspension of *trans*-[$PtCl_2(SMe_2)_2$] (0.80 g, 2.06 mmol, 0.5 equiv) in Et_2O (10 mL) was added. The off-white suspension was allowed to warm to room temperature and stirred for 2 h. The precipitate was isolated by centrifugation, dissolved in CH_2Cl_2, and filtered over Celite. The solvent was removed in vacuo. The remaining white solid (ratio *cis*/*trans* = 85:15) was washed with THF (10 mL) and precipitated from refluxing THF to give 0.56 g (0.90 mmol, 44%) of the *cis*-complex *cis*-**10** as a white solid. The THF mother liquor was evaporated in vacuo to yield a mixture of *trans*-**10** and *cis*-**10** as a white solid (*cis*/*trans* = 25:75). *cis*-**10**: ^{1}H NMR ($CDCl_3$): δ 2.80 (s, $^3J_{Pt-H}$ = 11 Hz, 12H, NCH_3), 3.85 (s, $^3J_{Pt-H}$ = 18 Hz, 4H, CH_2N), 7.11 (d, $^3J_{H-H}$ unresolved, 2H, ArH-5), 7.12 (s, 2H, ArH-3), 7.25 (d, $^3J_{H-H}$ = 12 Hz $^3J_{Pt-H}$ = 18 Hz, 2H, ArH-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.3 (NCH_3), 73.1 ($^2J_{Pt-C}$ = 55 Hz, CH_2N), 116.5 (ArC-4), 124.3 ($^3J_{Pt-C}$ = 45 Hz, ArC-3), 128.9 ($^3J_{Pt-C}$ = 91 Hz, ArC-5), 137.4 ($^1J_{Pt-C}$= 1182 Hz, C_{ipso}), 140.2 ($^2J_{Pt-C}$ = 116 Hz, ArC-6), 149.6 (ArC-2). ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ −3387.9. Anal. Calcd for $C_{18}H_{22}N_2PtBr_2$: C, 34.80; H, 3.57; N, 4.51. Found: C, 34.71; H, 3.61; N, 4.50. *trans*-**10**: ^{1}H NMR ($CDCl_3$): δ 3.02 (s, $^3J_{Pt-H}$ = 43 Hz, 12H, NCH_3), 3.96 (s, $^3J_{Pt-H}$ = 40 Hz, 4H, CH_2N), 7.22 (d, $^3J_{H-H}$ = 8 Hz, 2H, ArH-5), 7.28 (s, 2H, ArH-3), 7.37 (d, $^3J_{H-H}$ = 8 Hz, $^3J_{Pt-H}$ unresolved, 2H, ArH-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 53.8 (NCH_3), 79.5 (CH_2N), 116.4 (ArC-4), 124.0 ($^3J_{Pt-C}$ = 45 Hz, ArC-6), 128.0 ($^3J_{Pt-C}$ = 37 Hz, ArC-3,5), 136.5 ($^3J_{Pt-C}$ = 43 Hz, ArC-3,5), 151.5 (ArC-2), 167.6 (ArC_{ipso}). ^{195}Pt-{^{1}H} NMR ($CDCl_3$): δ −2871.5.

***cis*-[Pt(C_6H_3{CH_2NMe_2}-2-Br-4-Me-6)$_2$] (11).** To a solution of **6** (0.62 g, 1.75 mmol) in Et_2O (15 mL) at −78 °C was added *n*-BuLi (1.6 M in hexane, 1.1 mL, 1.76 mmol, 1 equiv). The resulting yellow suspension was stirred for 10 min at this temperature, after which neat *trans*-[$PtCl_2(SMe_2)_2$] (0.32 g, 0.81 mmol, 0.46 equiv) was added. The reaction mixture was warmed to room temperature and stirred for 3 h. The solvent was removed in vacuo. The mixture was dissolved in CH_2Cl_2 and filtered over Celite. After removal of the solvent by evaporation, the solid was washed with Et_2O (5 mL) and pentane (5 mL, 2×), yielding 0.4 g of the *cis*-isomer of **11** as an off-white solid (0.62 mmol, 77%). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 6H, $ArCH_3$), 2.37 (s, $^3J_{Pt-H}$ = 18 Hz, 6H, NCH_3), 2.94 (s, $^3J_{Pt-H}$ = 12 Hz, 6H, NCH_3), 3.28/4.48 (AX, $^2J_{H-H}$ = 12 Hz, $^3J_{Pt-H}$ unresolved, 4H, CH_2N), 6.87 (s, $^4J_{Pt-H}$ = 24 Hz, 2H, ArH-3), 6.92 (s, 2H, ArH-5). ^{13}C{^{1}H} NMR (C_6D_6): δ 26.5 ($^3J_{Pt-C}$ = 81 Hz, $ArCH_3$), 47.8 (NCH_3), 50.8 (NCH_3), 73.9 ($^2J_{Pt-C}$ = 57 Hz, CH_2N), 115.7 (ArC-4), 122.0 ($^3J_{Pt-C}$ = 42 Hz, ArC-3), 128.8 ($^3J_{Pt-C}$ = 65 Hz, ArC-5), 138.9 ($^1J_{Pt-C}$ = 1215 Hz, ArC_{ipso}), 148.0 (ArC-6), 148.7 (ArC-2). ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ −3470.3. Anal. Calcd for $C_{20}H_{26}N_2PtBr_2$: C, 36.99; H, 4.04; N, 4.31. Found: C, 36.91; H, 3.94; N, 4.25.

***cis*-[Pt(C_6H_2Br-4-{CH_2NMe_2}$_2$-2,5)$_2$] (*cis*-12) and *trans*-[Pt(C_6H_2Br-4{CH_2NMe_2}$_2$-2,5)$_2$] (*trans*-12).** To a suspension of **7** (0.39 g, 1.12 mmol) in Et_2O (20 mL) was added *n*-BuLi (1.12 mmol, 1.6 M in hexane, 0.7 mL, 1 equiv) at −78 °C. The green suspension was stirred for 15 min at this temperature, after which *trans*-[$PtCl_2(SMe_2)_2$] (0.22 g, 0.56 mmol, 0.5 equiv) in Et_2O (10 mL) was added. The reaction mixture was stirred for 15 min at −78 °C, warmed to room temperature (30 min), and stirred for an additional 3 h. All solvents were then evaporated, and the yellow solid was dissolved in CH_2Cl_2 and filtered over Celite. Evaporation of the solvent in vacuo and washing the solid with Et_2O (5 mL) and pentane (5 mL, 2×) yielded 0.20 g (0.27 mmol, 48%) of **12** as a mixture of the *cis*-(*cis*-**12**) and *trans*-isomers (*trans*-**12**). Ratio *cis*/*trans* = 60:40. The *cis*-complex was isolated by precipitation from a CH_2Cl_2/Et_2O mixture. Crystals of the *cis*-complex (colorless needles) were obtained by slow distillation of Et_2O in a saturated solution of *cis*-**12** in CH_2Cl_2/EtOH (90:10) for 2 days at room temperature. *cis*-**12**: ^{1}H NMR (C_6D_6): δ 1.98 (s, $^3J_{Pt-H}$ = 19 Hz, 12H, CH_2NCH_3-2), 2.23 (s, 12H, CH_2NCH_3-5), 3.20 (s, $^3J_{Pt-H}$ = 13 Hz, 4H, CH_2NCH_3-2), 3.64 (s, 4H, CH_2NCH_3-5), 7.28 (s, $^4J_{Pt-H}$ = 16 Hz, 2H, ArH-3), 7.90 (s, $^3J_{Pt-H}$ = 64 Hz, 2H, ArH-6). ^{13}C{^{1}H} NMR (C_6D_6): δ 45.5 (CH_2NCH_3-2), 49.2 (CH_2NCH_3-5) 64.0 (CH_2NCH_3-2), 72.4 (CH_2NCH_3-5), 119.5 (ArC-4), 125.4 (ArC-3), 135.5 (ArC-5), 139.5 (ArC_{ipso}), 142.2 (ArC-6), 148.5 (ArC-2). ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ −3384.6. Anal. Calcd for $C_{24}H_{36}N_4Br_2Pt$: C, 39.19; H, 4.93; N, 7.62. Found: C, 39.25; H, 4.93; N, 7.51. *trans*-**12**: ^{1}H NMR (C_6D_6): δ 2.29 (s, 12H, CH_2NCH_3-5), 2.59 (s, $^3J_{Pt-H}$ = 44 Hz, 12H, CH_2NCH_3-2), 3.33 (s, $^3J_{Pt-H}$ = 40 Hz, 4H, CH_2NCH_3-2), 3.76 (s, 4H, CH_2NCH_3-5), 7.37 (s, $^4J_{Pt-H}$ = 28 Hz, 2H, ArH-3), 7.85 (s, $^3J_{Pt-H}$ = 25 Hz, 2H, ArH-6). ^{13}C{^{1}H} NMR (C_6D_6): δ 45.7 (CH_2NCH_3-2), 53.2 (CH_2NCH_3-5) 64.2 (CH_2NCH_3-2), 78.9 (CH_2NCH_3-5), 119.2 (ArC-4), 125.2 (ArC-3), 134.3 (ArC-5), 137.9 (ArC-6), 150.5 (ArC-2), 168.8 (ArC_{ipso}). ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ −2865.4.

***cis*-[Pt(C_6H_2I-4{CH_2NMe_2}$_2$-2,5)$_2$] (*cis*-13) and *trans*-[Pt(C_6H_2I-4{CH_2NMe_2}$_2$-2,5)$_2$] (*trans*-13).** The synthesis of *cis*-**13** and *trans*-**13** is similar to the synthesis of *cis*-**12** and *trans*-**12**, but starts from **8** (0.5 g, 1.1 mmol) in Et_2O (30 mL) with *n*-BuLi (0.7 mL, 1.6 M in hexane, 1.1 mmol, 1 equiv) and *trans*-[$PtCl_2(SMe_2)_2$] (0.22 g, 0.6 mmol, 0.5 equiv). The reaction mixture was concentrated in vacuo, dissolved in CH_2Cl_2, and filtered over Celite. After removal of the solvent in vacuo and washing with hexane (5 mL), an off-white powder was obtained. The *cis*/*trans* ratio was 47:53. Yield of **13**: 0.43 g (0.5 mmol, 46%). *cis*-**13**: ^{1}H NMR (C_6D_6): δ 1.96 (s, $^3J_{Pt-H}$ = 10 Hz, 12H, CH_2NCH_3-2), 2.22 (s, 12H, CH_2NCH_3-5), 3.18 (s, $^3J_{Pt-H}$ = 17 Hz, 4H, CH_2NCH_3-2), 3.55 (s, 4H, CH_2NCH_3-5), 7.57 (s, 2H, ArH-3), 7.84 (s, $^3J_{Pt-H}$ = 63 Hz, 2H, ArH-6). ^{13}C-{^{1}H} NMR (C_6D_6): δ 45.6 (CH_2NCH_3-2), 49.4 (CH_2NCH_3-5) 68.4 (CH_2NCH_3-2), 72.3 (CH_2NCH_3-5), 94.6 (ArC-4), 132.1 (ArC-3), 138.6 (ArC-5), 140.9 (ArC_{ipso}), 142.2 (ArC-6), 149.3 (ArC-2). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −3390.7. Anal. Calcd for $C_{24}H_{36}N_4I_2Pt$: C, 34.75; H, 4.37; N, 6.75. Found: C, 34.63; H, 4.31; N, 6.79. *trans*-**13**: ^{1}H NMR (C_6D_6): δ 2.28 (s, 12H, CH_2NCH_3-5), 2.58 (s, $^3J_{Pt-H}$ = 45 Hz, 12H, CH_2NCH_3-2), 3.31 (s, $^3J_{Pt-H}$ = 40 Hz, 4H, CH_2NCH_3-2), 3.67 (s, 4H, CH_2NCH_3-5), 7.64 (s, 2H, ArH-3), 7.79 (s, $^3J_{Pt-H}$ = 25 Hz, 2H, ArH-6). ^{13}C-{^{1}H} NMR (C_6D_6): δ 45.7 (CH_2NCH_3-2), 53.2 (CH_2NCH_3-5) 68.9 (CH_2NCH_3-2), 78.5 (CH_2NCH_3-5), 94.3 (ArC-4), 131.8 (ArC-3), 137.1 (ArC-5), 137.7 (ArC-6), 151.1 (ArC-2), 169.9 (ArC_{ipso}). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −2880.1.

***cis*-[Pt($C_{10}H_6${CH_2NMe_2}-2)$_2$] (*cis*-14) and *trans*-[Pt($C_{10}H_6${CH_2NMe_2}-2)$_2$] (*trans*-14).** To a solution of **9** (0.27 g, 1.02 mmol) in Et_2O (40 mL) was added *n*-BuLi (1.6 M in hexane, 0.64 mL, 1.02 mmol, 1.0 equiv) at −78 °C. After 30 min at this temperature, *trans*-[$PtCl_2(SMe_2)_2$] (180 mg, 0.46 mmol, 0.45 equiv) was added. The mixture was stirred for 15 min at −78 °C and slowly warmed to room temperature. The reaction was complete after 2 h. The solvents were evaporated in vacuo. The remaining solid was dissolved in CH_2Cl_2 and filtered over Celite. Subsequent evaporation of the solvent and washing the remaining yellow solid with pentane (5 mL, 3×) yielded **14** as a mixture of *cis*- and *trans*-isomers. Ratio *cis*/*trans* = 85:15. Yield of **14**: 0.21 g (0.38 mmol, 82%). The *cis*-isomer was obtained pure by crystallization from a saturated solution of **14** in benzene/pentane (9:1). *cis*-**14**: ^{1}H NMR (C_6D_6): δ 1.93 (s, $^3J_{Pt-H}$ unresolved, 6H, NCH_3), 2.20 (s, $^3J_{Pt-H}$ unresolved, 6H, NCH_3), 3.08/4.46 (AX, $^2J_{H-H}$ = 12 Hz, $^3J_{Pt-H}$ unresolved, 4H, CH_2N), 6.69 (t, $^3J_{H-H}$ = 8 Hz, 2H, NaphH-7), 6.97 (t, $^3J_{H-H}$ = 8 Hz, 2H, NaphH-6), 7.26 (d, $^3J_{H-H}$ = 8 Hz,

2H, NaphH), 7.66 (d, $^3J_{H-H}$ = 8 Hz, 4H, NaphH), 8.20 (d, $^3J_{H-H}$ = 8 Hz, 2H, NaphH-8). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 47.5 and 50.1 (NCH_3), 75.0 ($^2J_{Pt-C}$ = 60 Hz, CH_2N), 121.1 ($^3J_{Pt-C}$ = 47 Hz), 123.4, 123.7, 124.8, 129.3, 133.3 ($^3J_{Pt-C}$ = 54 Hz), 135.4 ($^3J_{Pt-C}$ = 92 Hz), 141.6, 142.9, 143.9 ($^1J_{Pt-C}$ = 1133 Hz, C_{ipso}). $^{195}Pt\{^1H\}$ NMR (C_6D_6): δ −3439.9. Anal. Calcd for $C_{26}H_{28}N_2Pt$: C, 55.41; H, 5.01; N, 4.97. Found: C, 55.28; H, 4.96; N, 4.89. *trans*-**14**: ^1H NMR (C_6D_6,): δ 2.44 (s, 6H, NCH_3), 2.47 (s, 6H, NCH_3), 3.03/4.69 (AX, $^2J_{H-H}$ = 13 Hz, 4H, CH_2N), 7.43 (t, $^3J_{H-H}$ = 6 Hz, 2H, NaphH), 7.74 (d, $^3J_{H-H}$ = 8 Hz, 2H, NaphH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 51.5 (NCH_3), 56.0 (NCH_3), 80.5 (CH_2N), 121.1 ($^3J_{Pt-C}$ = 47 Hz), 123.5, 123.6, 124.5, 132.2, 133.9, 141.2, 144.6, 174.4 (C_{ipso}). One aromatic signal remained unresolved due to overlap with solvent signals. $^{195}Pt\{^1H\}$ NMR (C_6D_6): δ −2826.6.

General Procedure for Isomerization Reactions. A mixture of the *cis*- and *trans*-isomers of **10**, **12**, **13**, or **14** (0.6 mmol) was dissolved in toluene (40 mL) and refluxed for several hours. The conversion of *trans*-**12** and *trans*-**13** was complete within 3−5 h, whereas the conversion of *trans*-**10** and *trans*-**14** was only complete in 16 h (determined by ^1H NMR spectroscopy). After full isomerization the reaction mixtures were allowed to cool to room temperature, after which the solvent was removed in vacuo. The solid residues were washed with Et_2O (5 mL, 2×). Yield of *cis*-**10**: 83%, *cis*-**12**: 53%, *cis*-**13**: 77%, *cis*-**14**: 79%.

***trans*-[PtCl(C_6H_3Br-4-{CH_2NMe_2}-2)(SEt_2)] (17).** The synthesis of **17** is similar to the synthesis of **10**, starting from **5** (1.28 g, 3.8 mmol) in Et_2O (40 mL) with *n*-BuLi (2.3 mL, 1.6 M in hexane, 3.7 mmol, 0.98 equiv) and [$PtCl_2(SEt_2)_2$] (1.62 g, 3.63 mmol, 0.97 equiv). The reaction mixture was concentrated in vacuo, dissolved in CH_2Cl_2, and filtered over Celite. After removal of the solvent in vacuo and washing with pentane (5 mL, 3×), **17** was obtained as an off-white powder, with 5% of *cis*-**10** as impurity. The complexes were separated by column chromatography over silica (CH_2Cl_2/pentane = 90:10, R_f(**17**) = 0.57, R_f(*cis*-**10**) = 0.73). Yield of **17**: 1.47 g (2.75 mmol, 76%). ^1H NMR ($CDCl_3$): δ 1.38 (m, 6H, SCH_2CH_3), 2.86 (m, 2H, SCH_2CH_3), 2.98 (s, $^3J_{Pt-H}$ = 34.8 Hz, 6H, NCH_3), 3.27 (m, 2H, SCH_2CH_3), 3.90 (s, $^3J_{Pt-H}$ = 41.7 Hz, 2H, CH_2N), 7.09 (d, $^2J_{H-H}$ = 8 Hz, 1H, ArH-5), 7.16 (s, 1H, ArH-3), 7.26 (d, $^2J_{H-H}$ = 8 Hz, $^3J_{Pt-H}$ = 60 Hz 1H, ArH-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.3 (SCH_2CH_3), 31.9 (SCH_2CH_3), 52.4 (NCH_3), 74.5 ($^2J_{Pt-C}$ = 51 Hz, CH_2N), 117.3 (ArC-4), 124.6 ($^3J_{Pt-C}$ = 37 Hz, ArC-3), 128.3 ($^3J_{Pt-C}$ = 62 Hz, ArC-5), 133.3 ($^1J_{Pt-C}$ = 1077 Hz, ArC_{ipso}), 133.5 ($^2J_{Pt-C}$ = 68 Hz, ArC-6), 149.6 (ArC-2). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −3699.8. Anal. Calcd for $C_{13}H_{21}BrClNPtS$: C, 29.25; H, 3.97; N, 2.62. Found: C, 29.23; H, 3.89; N, 2.49.

Reaction of 17 with 16 to Yield 10. To a solution of **5** (0.25 g, 0.74 mmol) in Et_2O (20 mL) was added *n*-BuLi (1.6 M in hexane, 0.45 mL, 0.72 mmol, 1.0 equiv) at −78 °C. After 5 min, solid **17** (0.36 g, 0.67 mmol, 0.9 equiv) was added and the mixture was allowed to warm to room temperature and stirred for 3 h. After standard workup, 0.25 g of **10** (0.40 mmol, 60%) was obtained in a *cis*/*trans* ratio of 80:20, after analysis by NMR spectroscopy.

[PtI_2(C_6H_3Br-4-{CH_2NMe_2}-2)$_2$] (18). Complex *cis*-**10** (33 mg, 0.054 mmol) was dissolved in CH_2Cl_2 (1 mL). To this I_2 (4.0 mL, 0.014 M in toluene, 0.056 mmol, 1.0 equiv) was added dropwise. A dark red-orange precipitate was formed immediately. After 1 h stirring, the precipitate was isolated, washed with Et_2O (5 mL, 2×), and dried in vacuo. Yield of **18**: 45 mg (0.051 mmol, 94%). ^1H NMR ($CDCl_3$): δ 2.78 (s, $^3J_{Pt-H}$ = 10 Hz, 12H, NCH_3), 4.04 (s, $^3J_{Pt-H}$ = 11 Hz, 4H, CH_2N), 7.07−7.23 (m, 6H, ArH). Anal. Calcd for $C_{18}H_{22}Br_2I_2N_2Pt$: C, 24.71; H, 2.53; N, 3.20. Found: C, 24.86; H, 2.47; N, 3.12.

***cis*-[Pt(η^1-C_6H_3Br-4-{CH_2NMe_2}-2)$_2$(η^2-dppp)] (19).** To a solution of *cis*-**10** (63.6 mg, 102 μmol) in CH_2Cl_2 (6 mL) was added dppp (42.2 mg, 102 μmol, 1.0 equiv) at room temperature. The solution was stirred for 4 h at room temperature, after which the solvent was evaporated. The white product was purified by precipitation from a CH_2Cl_2/pentane mixture. Yield of **19**: 64.1 mg (62 μmol, 61%). Crystals (colorless needles) were obtained by cooling a saturated solution of **19** in CH_2Cl_2 at 4 °C. ^1H NMR ($CDCl_3$): δ 2.00 (m, 2H, $P(CH_2)_3P$) 2.08 (s, 12H, NCH_3), 2.41 (m, 2H, $P(CH_2)_3P$), 2.56 (m, 2H, $P(CH_2)_3P$), 2.73/3.88 (AX, $^2J_{H-H}$ = 14 Hz, 4H, CH_2N), 6.58 (d, $^3J_{H-H}$ = 6 Hz, 2H, ArH), 6.86 (m, 4H, PPh), 6.99 (s, 2H, ArH-3), 7.12 (m, 6H, PPh), 7.28 (m, 2H, ArH), 7.44 (m, 6H, PPh), 7.86 (m, 4H, PPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.3, 31.8, and 22.8 ($P(CH_2)_3P$), 45.9 (NCH_3), 65.7 ($^3J_{Pt-H}$ = 70 Hz, CH_2N), 116.7 (ArC-4), 127.2 ($^3J_{Pt-C}$ = 66 Hz, ArC-3), 127.9, 128.6, 129.2 ($^3J_{Pt-C}$ = 49 Hz, ArC-5), 129.7, 130.8 131.8, 134.0, 139.5 ($^2J_{Pt-C}$ = 32 Hz, ArC-6), 147.0 (ArC-2), 155.7 (dd, $^2J_{P-C}$ = 98 Hz (*trans*), $^2J_{P-C}$ = 15 Hz (*cis*), C_{ipso}). ^{31}P NMR ($CDCl_3$): δ −4.46 ($^1J_{Pt-P}$ = 1723 Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −4479.4 (d, $^1J_{Pt-P}$ = 1744 Hz). Anal. Calcd for $C_{45}H_{48}N_2P_2Br_2Pt$: C, 52.29; H, 4.68; N, 2.71. Found: C, 52.34; H, 4.61; N, 2.67.

***cis*-[Pt{C_6H_2($SnMe_3$)-4-(CH_2NMe_2)$_2$-2,5}$_2$] (20).** A solution of *cis*-**12** (67 mg, 0.09 mmol) in THF (15 mL) was cooled to −35 °C, after which *n*-BuLi (0.36 mmol, 0.53 M in hexane, 0.7 mL, 4.0 equiv) was added. After 15 min at this temperature, the reaction mixture was quenched with [$SnBrMe_3$] (0.4 mmol, 0.50 M in THF, 0.8 mL, 4.4 equiv). The mixture was stirred for 1 h at room temperature and extracted with a CH_2Cl_2/brine mixture. A white solid was obtained after evaporation of the solvents, which was purified using column chromatography over silica (CH_2Cl_2/NEt_3 = 97:3). Yield of **20**: 53 mg (0.06 mmol, 67%). ^1H NMR (C_6D_6): δ 0.45 (s, $^2J_{Sn-H}$ = 53 Hz, 18H, $SnCH_3$), 2.06 (s, $^2J_{Sn-H}$ unresolved, 12H, CH_2NCH_3-5), 2.13 (s, 12H, CH_2NCH_3-2), 3.44 (s, $^2J_{Sn-H}$ = unresolved, 4H, CH_2NCH_3-5), 3.51 (s, 4H, CH_2NCH_3-2), 7.53 (s, $^3J_{Sn-H}$ = 56 Hz, 2H, ArH-3), 7.82 (s, $^3J_{Pt-H}$ = 20 Hz, $^4J_{Sn-H}$ = 62 Hz, 2H, ArH-6). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −7.2 ($^1J_{Sn-C}$ = 338 and 353 Hz, $SnCH_3$), 45.3 (CH_2NCH_3-2), 49.5 (CH_2NCH_3-5), 67.0 (CH_2NCH_3-2), 73.6 (CH_2NCH_3-5), 129.5, 133.7, 140.5, 142.3, 142.8, 146.9. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −3412.1. Anal. Calcd for $C_{30}H_{54}N_4PtSn_2$: C, 39.89; H, 6.03; N, 6.20. Found: C, 39.83; H, 5.95; N, 6.16.

3,5-Bis(*tert*-butylsulfidomethyl)bromobenzene (22). Sodium (1.14 g, 49.6 mmol) was dissolved in EtOH (150 mL), and *t*-BuSH (5.5 mL, 48.8 mmol, 0.98 equiv) was added. This mixture was heated to reflux for 30 min, after which **21** (8.35 g, 24.35 mmol, 0.50 equiv) was added. The reaction was heated to reflux for 16 h. The white suspension was concentrated, extracted with pentane, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. Yield of **22** as an off-white solid: 7.79 g (21.6 mmol, 89%). ^1H NMR ($CDCl_3$): δ 1.33 (s, 18H, CCH_3), 3.68 (s, 4H, CH_2S), 7.25 (s, 1H, ArH-4), 7.35 (s, 2H, ArH-2,6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.0 (CCH_3), 32.9 (CH_2S), 43.2 (CCH_3), 122.4 (ArC-1), 128.4 (ArC-4), 130.5 (ArC-2,6), 141.1 (ArC-3,5). Anal. Calcd for $C_{16}H_{25}BrS_2$: C, 53.17; H, 6.97; S, 17.74. Found: C, 53.25; H, 6.89; S, 17.65.

3,5-Bis(*tert*-butylsulfidomethyl)pinacolboranebenzene (23). To a solution of **22** (4.16 g, 11.5 mmol) in Et_2O (100 mL) was added *t*-BuLi (16 mL, 24 mmol, 2.1 equiv, 1.5 M in hexane) at −78 °C. The reaction mixture was stirred at this temperature for 20 min, after which $B(OMe)_3$ (2.0 mL, 17.5 mmol, 1.5 equiv) was added dropwise. The mixture was slowly warmed to room temperature overnight. Pinacol (1.43 g, 12.1 mmol, 1.1 equiv) was added, followed by HOAc (0.7 mL, 12.1 mmol, 1.1 equiv) after 10 min. The reaction mixture was stirred for 1 h and filtered, and the solvents were evaporated in vacuo. The product was washed with MeOH (10 mL, 2×) and evaporated to dryness, after which **23** was obtained as a white solid. Yield: 3.31 g (8.1 mmol, 70%). ^1H NMR ($CDCl_3$): δ 1.33 (s, 12H, $OCCH_3$), 1.35 (s, 18H, $SCCH_3$), 3.74 (s, 4H, CH_2S), 7.46 (s, 1H, ArH-4), 7.62 (s, 2H, ArH-2,6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.0 ($OCCH_3$), 31.0 ($SCCH_3$), 33.3 (CH_2S), 43.0 ($SCCH_3$), 83.9 ($OCCH_3$), 132.8, 134.0, 138.0. Anal. Calcd for

$C_{22}H_{37}BO_2S_2$: C, 64.69; H, 9.13; S, 15.70. Found: C, 64.70; H, 8.92; S, 15.51.

***cis*-[Pt(dmba-4-SCS{*t*-Bu})$_2$] (24).** Complex *cis*-**10** (280 mg, 0.45 mmol), **23** (391 mg, 0.96 mmol, 2.1 equiv), [$PdCl_2$-dppf] (21 mg, 0.029 mmol, 6%), and Na_2CO_3 (266 mg, 2.51 mmol, 5.6 equiv) were introduced in a Schlenk flask, which was evacuated for 30 min. To this, a degassed mixture of DME (10 mL), THF (10 mL), and H_2O (10 mL) was added. The reaction mixture was stirred at 70 °C until the reaction was complete (±3 h). The reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (50 mL), dried over $MgSO_4$, and evaporated to dryness. The product was purified by column chromatography (basic alumina, CH_2Cl_2, $R_f = 1.0$) and subsequently washed with hexane and Et_2O (5 mL, 3×). Complex **24** was isolated as a white solid. Yield: 0.36 g (0.35 mmol, 78%). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 36H, CCH_3), 2.84 (s, 12H, NCH_3), 3.80 (s, 8H, CH_2S), 3.95 (s, 4H, CH_2N), 7.25 (m, 6H, ArH), 7.46 (s, 4H, ArH-8,12), 7.55 (d, $^3J_{H-H}$ = 9 Hz, 2H, ArH-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.1 (C*C*H_3), 33.6 (CH_2S), 43.0 (*C*CH_3), 50.3 (NCH_3), 73.8 (CH_2N), 120.0, 124.7, 125.9, 127.6, 134.8, 138.6, 139.0, 139.2 (C_{ipso}), 142.6, 148.0. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ −3385.8. Anal. Calcd for $C_{50}H_{72}N_2S_4Pt$: C, 58.62; H, 7.08; N, 2.73; S, 12.52. Found: C, 58.47; H, 7.19; N, 2.78; S, 12.46.

***cis*-[Pt(dmba-4-{PdCl(SCS{*t*-Bu})})$_2$] (25).** To a solution of **24** (145 mg, 0.14 mmol) in degassed MeCN (30 mL) was added $[Pd(NCMe)_4](BF_4)_2$ (125 mg, 0.28 mmol, 2.0 equiv). After 10 min NEt_3 (39 μL, 0.28 mmol, 2.0 equiv) was added. The reaction mixture was heated at reflux for 2 h, cooled to room temperature, and filtered over Celite. The mixture was diluted with CH_2Cl_2 (50 mL) and stirred with brine (20 mL) for 1 h. The organic layer was collected, dried over $MgSO_4$, and evaporated to dryness. A concentrated solution of the remaining solid in CH_2Cl_2 was prepared. Slow distillation of Et_2O into this mixture afforded pure **25** as light yellow crystals or a powder. Crystals suitable for X-ray structure determination were obatined by cooling a saturated solution of **25** in a mixture of CH_2Cl_2/Et_2O (10:1) at −30 °C. Yield: 102 mg (0.078mmol, 56%). ^{1}H NMR ($CDCl_3$): δ 1.61 (s, 36H, $CCH_3)_3$), 2.84 (s, 12H, NCH_3), 3.94 (s, 4H, CH_2N), 4.21 (s, 8H, CH_2S), 7.18 (m, 8H, ArH), 7.52 (d, $^3J_{H-H}$ = 7 Hz, 2H, ArH-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.8 (C*C*H_3), 42.8 (*C*CH_3), 50.3 (NCH_3), 52.1 (CH_2S), 73.8 (CH_2N), 119.6, 119.7, 124.2, 134.5, 138.6, 139.2 (C_{ipso}, Pt), 148.3, 150.3, 157.1 (C_{ipso}, Pd). ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ −3381.4. Anal. Calcd for $C_{50}H_{70}N_2S_4Cl_2PtPd_2$: C, 45.98; H, 5.40; N, 2.14; S, 9.82. Found: C, 46.08; H, 3.84; N, 2.03; S, 9.74.

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Supporting Information Available: CIF files for the X-ray structural data of complexes *cis*-**12**·Et_2O, *cis*-**14**·*x*C_6H_6, **19**, and **25**·*x*CH_2Cl_2. This material is free of charge via the Internet at http://pubs.acs.org.

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