Transmetalation reactions with nitrogen-containing "pincer"-class ligands on platinum(II) centers

Martin Albrecht, Stuart L. James, Nora Veldman, Anthony L. Spek, and Gerard van Koten

Abstract: The transmetalation reaction of the aryllithium compound $[Li(NCN)]_2$ (NCN is the monoanionic "pincer" ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) with the cyclometalated arylplatinum complex [PtCl(NCN)] afforded the bisaryl platinum(II) complex $[Pt(NCN)_2]$ (**3**) containing one η^3-*N*,*C*,*N*-terdentate and the other η^1-*C*-monodentate-bonded pincer ligand. Spectroscopic analyses on **3** suggest that η^3 to η^1 interconversion of the ligand binding mode (or vice versa) is inhibited. Two independent X-ray structure determinations on crystals of **3** revealed the existence of a rare polymorph containing one and three crystallographically independent molecules, respectively, in the unit cell. A similar transmetalation reaction with lithium and platinum complexes containing heteroleptic $NCN^{RR'}$ ligands ($NCN^{RR'}$ is $[C_6H_3(CH_2NRR')\text{-}2,6]^-$ with R = R′ = Me or R = Me, R′ = Et) pointed to the formation of a heterodinuclear cationic bisaryl platinum lithium species as an intermediate of a preequilibrium to the final transmetalation products, involving, rapid transcyclometalation (TCM) reactions. These TCM reactions comprise the exchange of the monoanionic $NCN^{RR'}$ ligands between the platinum(II) and lithium centers. A consequence of the latter properties is that the strong Pt—N bonds in [PtX(NCN)] complexes are considerably weakened by the presence of Li^+ cations.

Key words: transmetalation, transcyclometalation (TCM), platinum, bisaryl complex, polymorphism.

Résumé : La réaction de transmétallation du composé aryllithium $[Li(NCN)]_2$ (NCN = ligand « en pince » monoanionique $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) avec le complexe d'arylplatine cyclométallé [PtCl(NCN)] conduit à la formation du complexe bisaryle de platine(II) $[Pt(NCN)_2]$ (**3**) qui contient un ligand η^3-*N*,*C*,*N*-terdentate et l'autre ligand en forme de pince lié de façon η^1-*C*-monodentate. Les analyses spectroscopiques de **3** suggèrent qu'il y a une inhibition à l'interconversion η^3 à η^1 (ou vice versa) du mode de fixation du ligand. Deux déterminations indépendantes de la structure des cristaux de **3** par diffraction des rayons X révèlent l'existence d'une polymorphie rare dans laquelle chacune des formes comprend respectivement une et trois molécules cristallographiquement indépendantes par maille. Une réaction de transmétallation semblable avec des complexes de lithium et de platine contenant les ligands hétéroleptiques $NCN^{RR'}$ ($NCN^{RR'}$ = $[C_6H_3(CH_2NRR')\text{-}2,6]^-$ avec R = R′ = Me ou R = Me, R′ = Et) suggère qu'il y a formation d'une espèce bisaryle de platine et de lithium hétérodinucléaire cationique comme intermédiaire d'un prééquilibre vers les produits finaux de transmétallation et qu'il implique des réactions rapides de transcyclométallation (TCM). Ces réactions de TCM incluent l'échange des ligands monoanioniques $NCN^{RR'}$ entre les centres de platine(II) et de lithium. En conséquence de ces propriétés, les fortes liaisons Pt—N présentes dans les complexes de [PtX(NCN)] sont de beaucoup affaiblies par la présence des cations Li^+.

Mots clés : transmétallation, transcyclométallation (TCM), platine, complexe bisaryle, polymorphie.

[Traduit par la Rédaction]

Introduction

The reversible formation of an intermediate metal-to-carbon bond is a crucial step in many catalytic cycles (1). In particular, making and breaking of C_{aryl}—M σ-bonds is of great significance, e.g., in C_{aryl}—C_R cross coupling reactions (Heck: R = alkene; Sonogashira: R = alkyne; Suzuki:

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Dedicated to Brian James on the occasion of his 65th birthday in admiration for his great contribution to homogeneous catalysis and our friendship.

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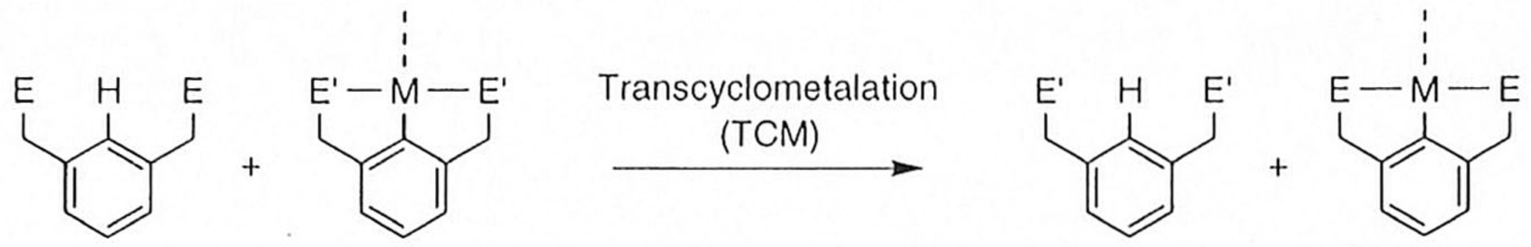
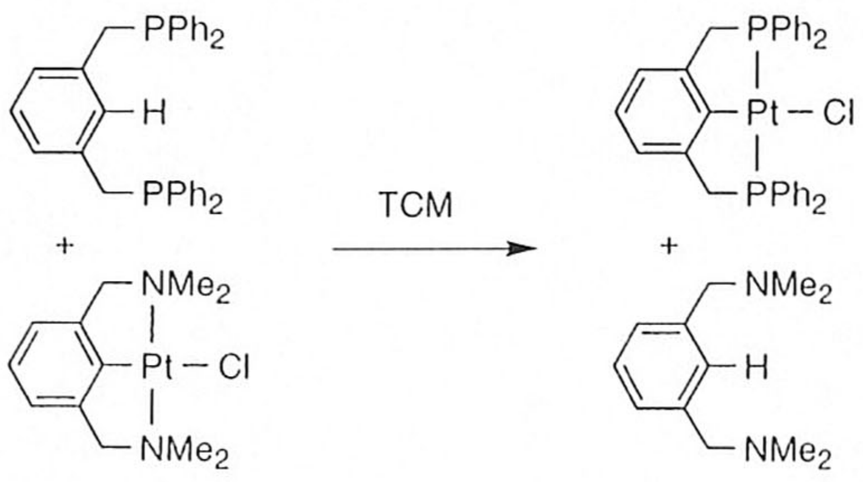
Scheme 1. General representation of TCM reactions with terdentate coordinating ligands; interconversion of one metallacycle into another.



Scheme 2. TCM reaction of [PtCl(NCN)] with PCHP to give [PtCl(PCP)] and NCHN (12*d*).



R = aryl) and in C_{aryl}—E bond activation processes (E = carbon or heteroatom) (for examples of cross coupling see ref. 2*a*; for examples of bond activation see ref. 2*b*). Intramolecular stabilization of this C—M bond by heteroatom coordination, i.e., formation of metallacycles, has been demonstrated to be an efficient methodology for stabilizing the metal-to-carbon bond. As a consequence, the rate of (catalytic) processes is often considerably reduced, which provides insight into mechanistic details and thus important information for efficient catalyst design (3, 4). Other applications of transition metal complexes containing C_{aryl} σ–bonding chelates include the engineering and processing of materials properties, e.g., for gas storage (5) and sensoring purposes (6).

Up to now, cyclometalated complexes containing C—M σ-bonds have been accessible predominantly via two different methods: (*i*) transmetalation of (main group) organometallics (C-Mg, C-Li, C-Sn) with a suitable metal precursors (7); or (*ii*) direct cyclometalation via C—E bond activation (E = e.g., C, Si, halide) (8). Recently, transcyclometalation (TCM) reactions have been introduced as a new methodology for the generation of cyclometalated transition-metal complexes. In close relation to (organic) transesterification reactions (9), TCM reactions consist of the substitution of one (monoanionic) cyclometalated ligand by another one (Scheme 1). In some cases, this has the advantage of being a cleaner reaction than direct cyclometalation. Previous examples, though at that time not recognized as TCM reactions, include a variety of ligand systems, which were predominantly activated with palladium complexes (10). More recently, the TCM reaction of a terdentate coordinated NCN-type pincer-ligand (11) by another bis(*ortho*)-chelating PCP pincer-ligand has been described to occur on a ruthenium(II) (i.e., M in Scheme 1 is $RuCl(PPh_3)$) and a platinum(II) (Scheme 2) metal center, respectively, (12). As a primary conclusion of these studies (12*a*), the higher bond strength of the M—P bond compared to the analogous M—N bond is anticipated to be the driving force. Indeed, the selective and quantitative replacement of the amines by phosphorus donors has been demonstrated to initiate the TCM process. In this report we present evidence that also cyclometalated aryllithium and platinum compounds can undergo TCM reactions. This leads even for η^3-coordinated NCN ligands to the formation of mixtures of cyclometalated compounds.

Results and discussion

Initial attempts to transcyclometalate aryl ligands of the type $NC(H)N^{RR'}$ ($NCN^{RR'}$ denotes the monoanionic bis(*ortho*)-substituted aryl ligand $[C_6H_3(CH_2NRR')_2\text{-}2,6]^-$) with either the neutral cyclometalated complex $[PtCl(NCN^{Me_2})]$ (**2**), or its cationic analogue $[Pt(NCN^{Me_2})(H_2O)](BF_4)$ (13) gave no detectable reaction. Obviously, the Pt—N bond in [PtCl(NCN)] cannot be displaced by an amino group of the $NCHN^{RR'}$ ligand, and consequently, a TCM process is prevented since in these reactions ligand substitution has been identified as an initial step. Hence, half an equivalent of the dimeric aryllithium species $[Li(NCN^{Me_2})]_2$ (**1-Li**) (14) was reacted with the arylplatinum(II) complex **2** in polar solvents and at elevated temperatures (THF, reflux temperature). This afforded the bisaryl platinum(II) complex $[Pt(\eta^3\text{–}NCN^{Me_2})(\eta^1\text{–}C\text{–}NCN^{Me_2})]$ (**3**) in 60% yield (Scheme 3). This complex contains two differently bonded pincer ligands, one monodentate η^1-*C* and the other terdentate η^3-*N,C,N* coordinating. This compound may be envisaged as an intermediate in the full substitution of one NCN ligand by another in the TCM reaction, cf. the isolation of $[Pt(\eta^3\text{–}P,C,P\text{–PCP})(\eta^1\text{–}C\text{–NCN})]$ in the TCM reaction of **1** with PCHP (Scheme 2). This is further underlined by the reactivity of **3** towards aq HCl, which results in rapid Pt—C bond cleavage of the η^1-coordinated ligand and formation of the starting materials **2** and **1** as the diprotonated chloride salt (Scheme 3). Remarkably, these conditions affect neither the Pt—N nor the Pt—C bonds of the η^3-*N,C,N* chelating ligand, and are a good indication for the excellent stability of the [Pt(NCN)] unit. This is also in concert with the fact that **2** does react with the bis-phosphinoarene PCHP but not with the bis-aminoarene NCHN.

Unambiguous confirmation of the connectivity pattern in **3** was accomplished by detailed X-ray structure analyses of single crystals, which were grown by slow evaporation of a saturated Et_2O solution.

Solid-state structure of 3

The molecular structure of **3**, measured at room temperature, is shown in Fig. 1 and reveals a platinum(II) center that is ligated by a terdentate, η^3-*N,C,N*-bound, and a mono-

Scheme 3. Synthesis of the homoleptic bisaryl platinum(II) complex **3** and its reactivity towards MeI.

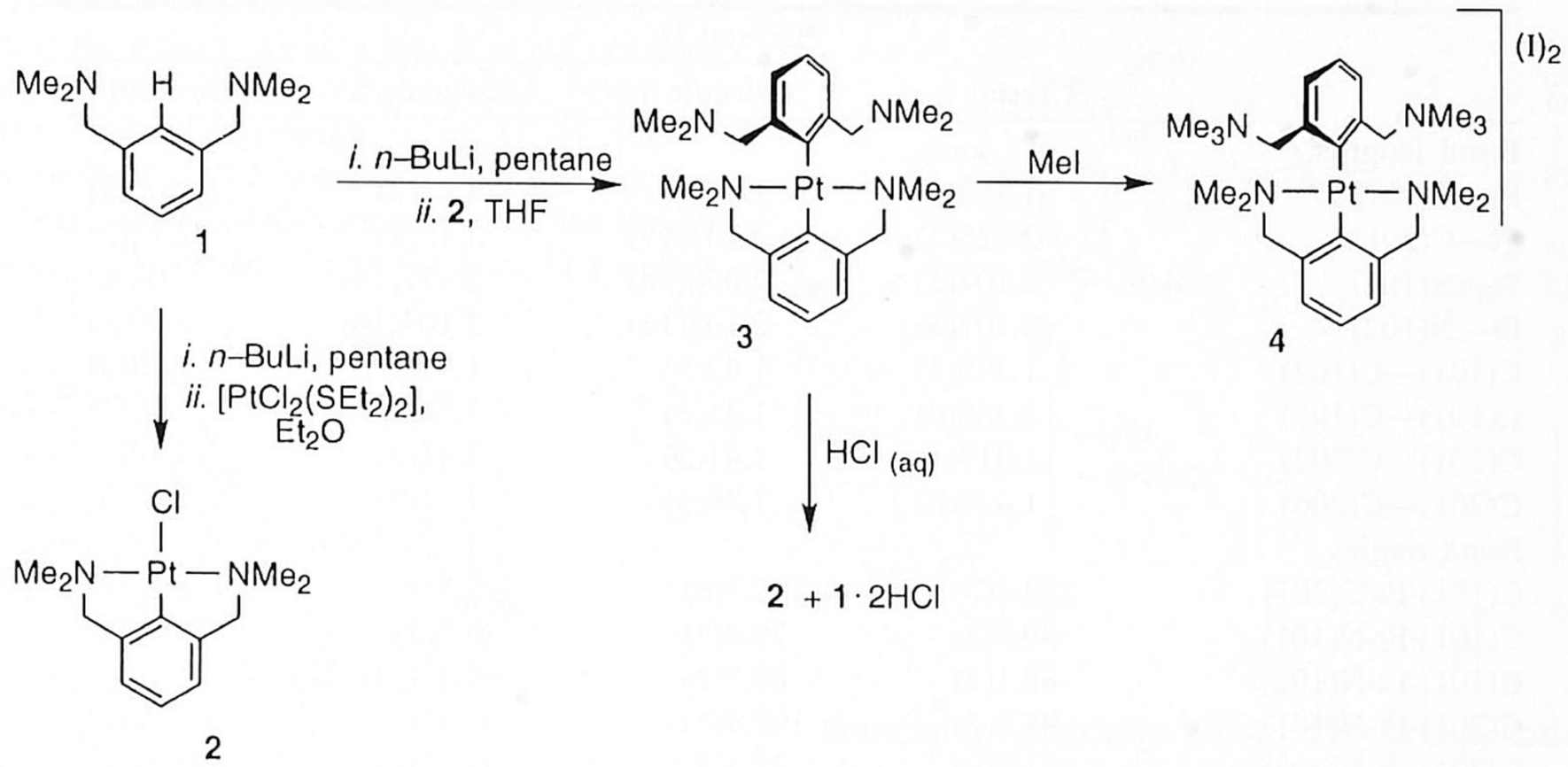
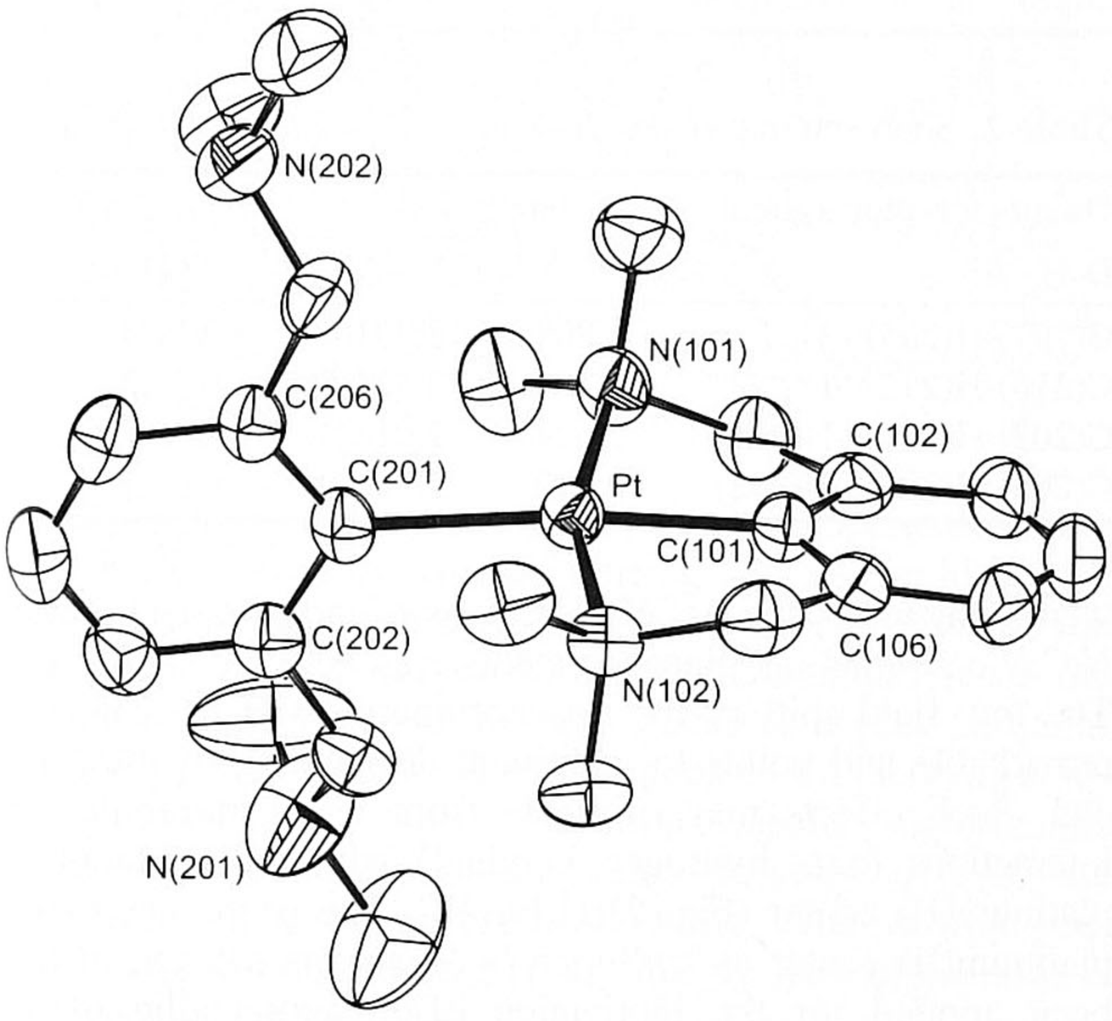


Fig. 1. Perspective view of the molecular structure of **3** (50% probability level, crystal **I**).



dentate, η^1-*C*-bound, NCN pincer ligand, resulting in a *trans* positioning of the two aryl groups across the metal square plane. The puckered five-membered chelate ring conformations, bond lengths, and bond angles of the [Pt(η^3-NCN^{Me_2})] moiety are normal for square planar platinum(II) complexes containing this ligand (Table 1) (13, 15). As a consequence of the different denticity of the ligands, the metal-to-carbon σ-bond of platinum to the monodentate bonded NCN ligand is considerably longer (Pt—C(201) 2.126(5) Å) than the one to the terdentate coordinating NCN ligand (Pt—C(101) 1.963(6) Å). Moreover, the aromatic ring of the η^1-*C*-bonded ligand system is considerably distorted (the internal angle at C_{ipso} is 114.3(5)° for the η^1-*C*-NCN, and 121.4(5)° for the η^3-*N*,*C*,*N*-bonded ligand), which is presumably a consequence of the steric crowding around the platinum nucleus. The noncoordinating tertiary amines are directed away from the metal center.

Two different structural motifs have been identified, for the orientation of the CH_2NMe_2 groups with respect to the arylplatinum unit. The first comprises short interatomic C-H···N contacts between the aryl protons H(201) and H(203) and the nitrogen atoms of the η^1-coordinated NCN ligand (C_{aryl}-H···N 2.627 and 2.679 Å, respectively; see Fig. 2 and Table 2). The second motif has the benzylic protons H(205) and H(212) of the η^1-coordinating pincer ligand positioned near the virtual *z* axis of the platinum center (Pt···H 2.803 and 2.704 Å, respectively). The filled d_z2 orbitals in such d^8 metal centers, particularly in bisaryl platinum(II) complexes, have been established to be important frontier orbitals. As a consequence, the observed C-H···Pt arrangement provides additional stabilization to this particular CH_2NMe_2 conformer (12*a*, 16).

Surprisingly, a second crystal structure determination, which was performed at 150 K, revealed a polymorph (17). While the overall connectivity was the same as established for the first X-ray analysis, distinctly different intramolecular orientations for the CH_2NMe_2 substituents were identified for the crystal structures. Representative sections of the two polymorphous crystal structures (**I** and **II**) are shown in Fig. 3. Form **I** (data collected at room temperature, Fig. 3*a*) contains one molecule per asymmetric unit, in which the two free amine arms are both positioned on the same side of the aryl ring to which they are connected, i.e., they have a *cisoid* arrangement. The asymmetric unit in the polymorph **II** (150 K), however, contains three independent molecules, two of which have the *cisoid* conformation as observed in **I**, while the third (molecule 3, Fig. 3*b*) has the free amine groups positioned on opposite sides of the aryl ring (*transoid*). It is noteworthy that no phase transition was observed on cooling of crystal **I** to 150 K.

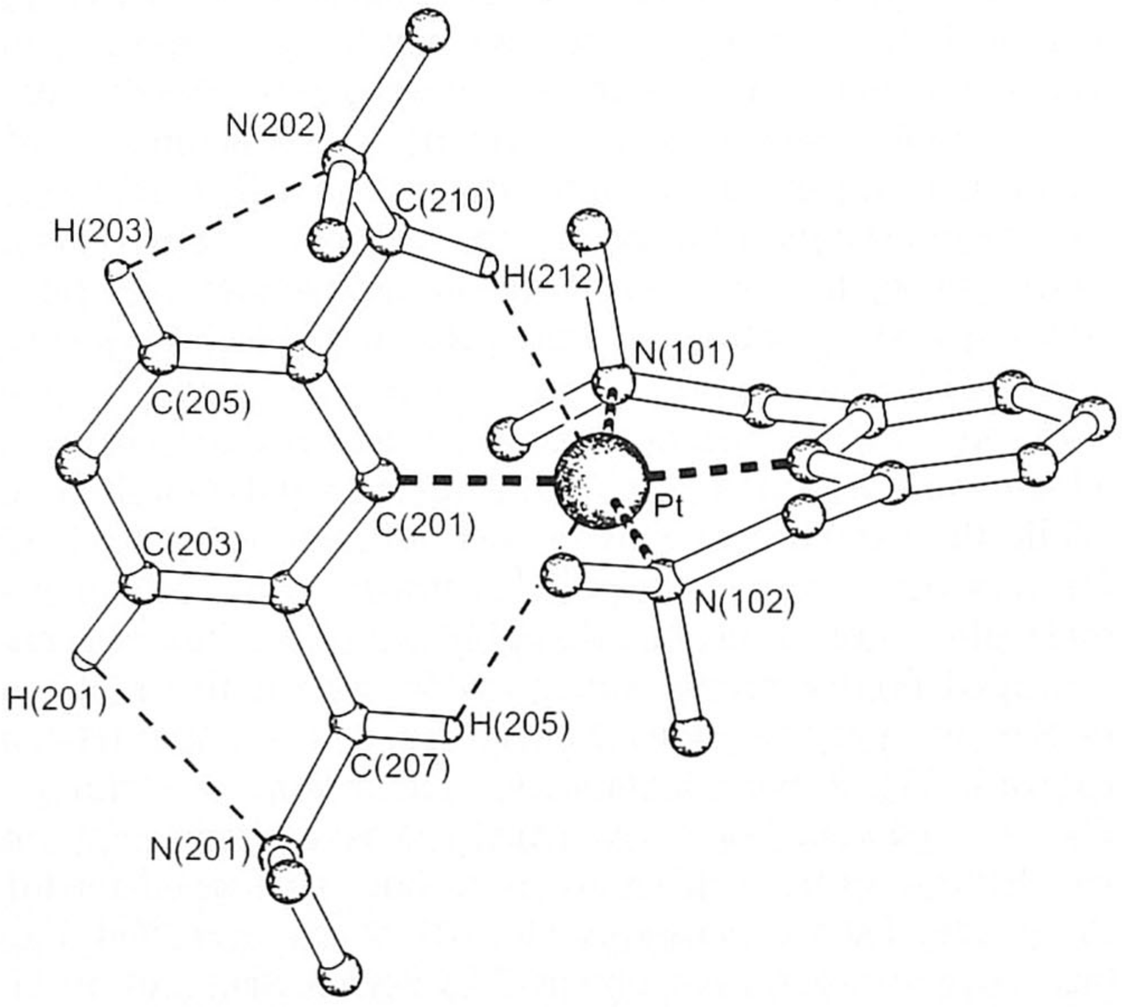
Structural aspects of 3 in solution

As a result of the ligand arrangement at the platinum center (viz. two metal-bound aryl units and two noncoordinating *tert*-amine moieties), complex **3** displays good solubility in apolar solvents (e.g., in Et_2O and pentane) which is unusual for related platinum-halide species such as **2** (13). In the ^1H NMR spectrum (C_6D_6 solution), two distinct signals for the

Table 1. Interatomic bond lengths (Å) and angles (deg) of **3**.

	Crystal **I**	Crystal **II**		
		Molecule 1	Molecule 2	Molecule 3
Bond lengths				
Pt—C(101)	1.963(6)	1.92(2)	1.95(2)	2.00(2)
Pt—C(201)	2.126(5)	2.131(19)	2.15(2)	2.12(2)
Pt—N(101)	2.104(5)	2.096(14)	2.117(14)	2.075(18)
Pt—N(102)	2.107(5)	2.102(16)	2.104(16)	2.090(17)
C(101)—C(102)	1.385(8)	1.42(3)	1.40(3)	1.34(3)
C(101)—C(106)	1.388(9)	1.41(3)	1.38(3)	1.39(3)
C(201)—C(202)	1.419(8)	1.41(3)	1.41(3)	1.40(2)
C(201)—C(206)	1.424(8)	1.39(3)	1.41(3)	1.40(3)
Bond angles				
C(101)-Pt-C(201)	174.1(2)	177.7(8)	177.6(7)	176.8(8)
C(101)-Pt-N(101)	80.9(2)	79.4(7)	80.9(7)	78.4(7)
C(101)-Pt-N(102)	80.1(2)	80.8(7)	80.2(7)	81.1(8)
C(201)-Pt-N(101)	97.8(2)	102.4(7)	101.4(7)	101.0(7)
C(201)-Pt-N(102)	101.3(2)	97.3(6)	97.5(7)	99.4(7)
N(101)-Pt-N(102)	160.9(2)	160.3(6)	161.1(6)	159.5(7)
C(102)-C(101)-C(106)	121.4(5)	123.5(19)	119.3(19)	125(2)
C(202)-C(201)-C(206)	114.3(5)	116.5(18)	116.4(18)	113.8(17)

Fig. 2. Short intramolecular contacts of the noncoordinating *ortho*-substituents from the η^1-coordinating pincer ligand.



NMe_2 groups are observed, which are located at 2.41 and 2.58 ppm, respectively. The resonance at 2.41 ppm is typical for noncoordinating amine methyl groups, but is shifted to higher frequency when compared to free ligand (δ_H (NMe_2) = 2.21 ppm in **1**). In contrast, the signal at 2.58 ppm displays a coupling pattern ($^3J_{HPt}$ = 42 Hz) which is diagnostic for nitrogen coordination to the metal center, even though these nuclei seem to be considerably shielded when compared to related groups, in **2** and analogues where the chloride in **2** is replaced by another halide or a *para*-tolyl ligand, cf. δ_H (NMe_2) = 2.95–3.18 (13*a*). Similar features are also observed for the resonances at 4.38 and 3.57 ppm, which, on the basis of either the absence or presence of ^{195}Pt coupling ($^3J_{HPt}$ = 47.0 Hz),

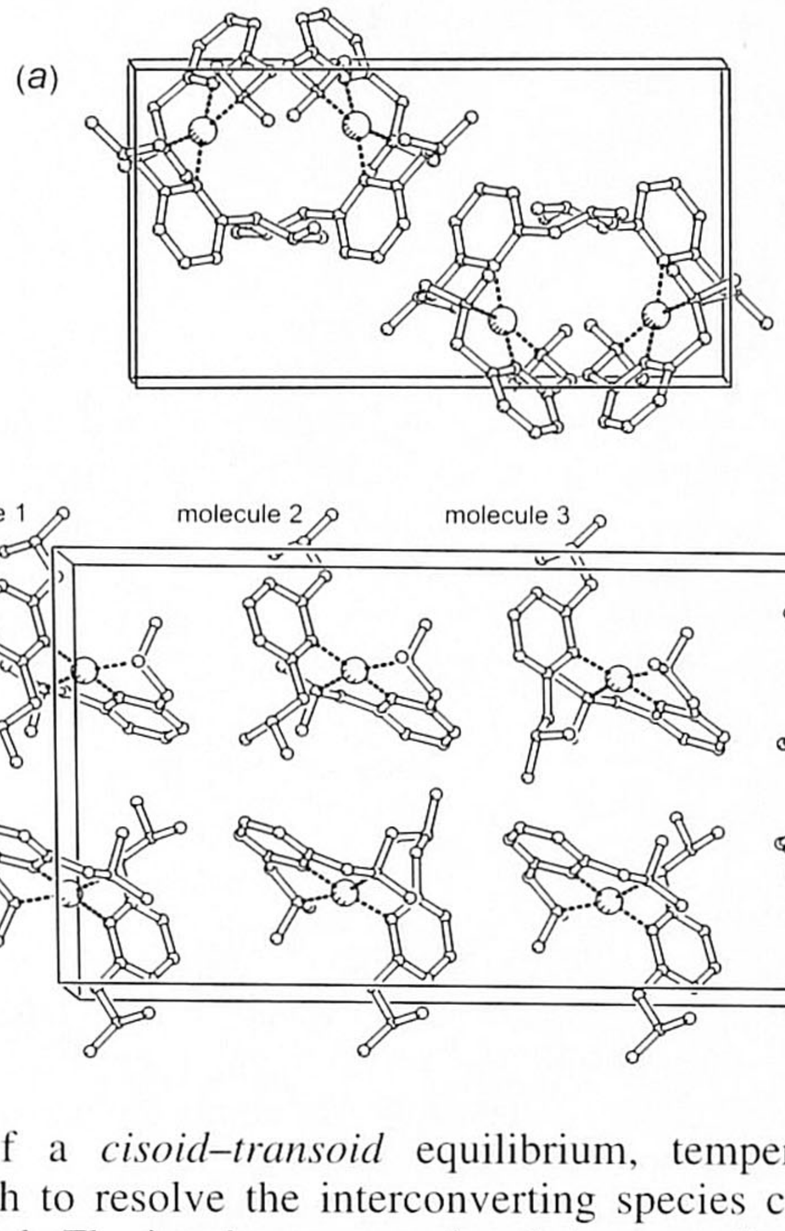
Table 2. Short intramolecular distances (Å) and angles (deg) in **3**.

Donor–acceptor system	Distances (Å)		Angles (deg)
D-H···A	H···A	D···A	D-H···A
C(207)-H(205)···Pt	2.803	3.391(6)	119.8
C(210)-H(212)···Pt	2.704	3.324(6)	122.2
C(203)-H(201)···N(201)	2.627	2.914(9)	98.5
C(205)-H(203)···N(202)	2.679	2.960(9)	98.3

were assigned to the $ArCH_2N$ protons of the η^1-*C* and the η^3-*N*,*C*,*N*-coordinating pincer systems, respectively, (12*a*, 13). The low field shift of the noncoordinating CH_2N protons is remarkable and points to additional deshielding of these nuclei. Such effects may originate from weak intramolecular interactions (e.g., hydrogen bonding) with the nucleophilic platinum(II) center (Fig. 2) (12*a*, 18). The properties of the platinum(II) center as hydrogen bond acceptor have recently been applied for the fabrication of organometallic proton sponges (12*a*, 19). Further confirmation of the structure of **3** was obtained from ^{13}C NMR spectroscopy. In particular, the two signals at 172.6 and 182.2 ppm are characteristic for Pt(NCN) type complexes containing an aryl anion in mutual *trans*-position to the metal-bound pincer-carbon N*C*N (13). As expected, two sets of benzylic carbons (at 68.4 and 80.8 ppm) and nitrogen-bound methyl carbons (at 45.9 and 54.7 ppm) were observed, which belong to the monodentate coordinating and to the chelating ligand, respectively. The symmetric structure in solution, indicated by ^{1}H and ^{13}C NMR spectra, is consistent with a purely *transoid* arrangement of the free arms, or fast exchange between *transoid* and *cisoid* forms on the NMR time scale.

Variable temperature NMR experiments were carried out to probe in particular whether dynamic processes could be feasible involving a fluxional switch between η^3- and η^1-bonding of each of the pincer ligands. At low temperature (–80°C, CD_2Cl_2) the signals due to the free amine arms broaden. Although this may be due to the onset of freezing

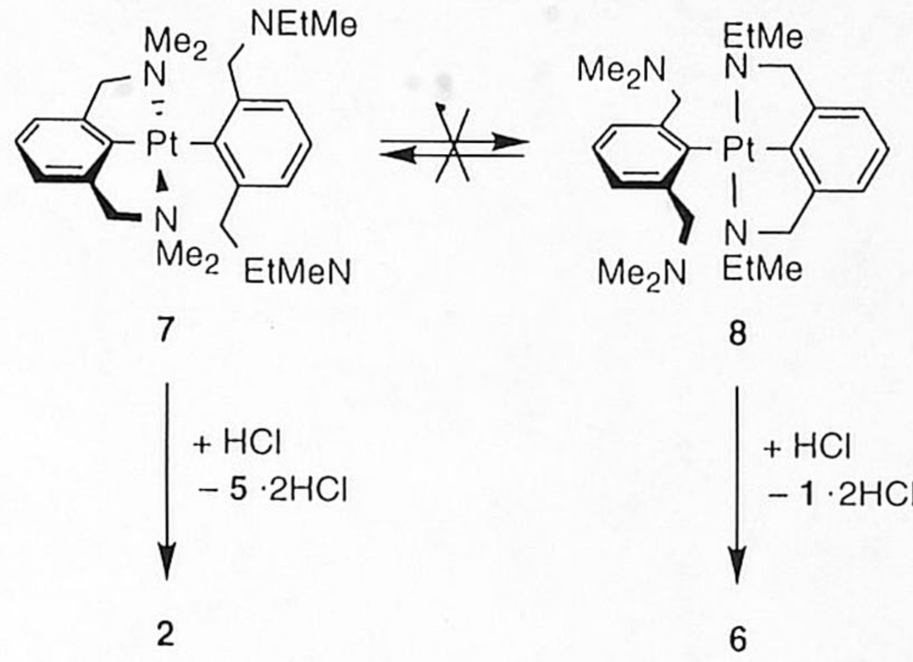
Fig. 3. Polymorphism in crystalline **3**: (*a*) crystal structure of crystal **I**, which is characterized by one single independent molecule of **3**. Note that the noncoordinating nitrogens are in *cisoid* configuration with respect to the bisecting aryl plane of the η^1-bound ligand; (*b*) the second polymorph, crystal **II**, contains three independent molecules of **3** in the unit cell. Molecule 1 and 2 display a similar *cisoid* confirmation as identified for crystal **I**, whereas molecule 3 contains the non-coordinating amines in a *transoid* position.



out of a *cisoid–transoid* equilibrium, temperatures low enough to resolve the interconverting species could not be attained. Fluxional processes involving coordination of the free amine groups with associated decoordination of the bonded amine groups could also occur at higher temperatures. However, neither ^{1}H NMR spectra in toluene-d_8 solution at 110°C nor spin saturation transfer experiments revealed any evidence for a dynamic behavior of **3** on the NMR time scale. These results show that even *intra*molecular substitution of coordinated amines by free amine sites is not occurring (vide infra).

The presence of noncoordinating tertiary amines in **3** was further established by derivatization with MeI, which gave the bis-ammonium salt [Pt(η^3-NCN^{Me_2})(η^1-NCN^{Me_3})](I)$_2$ (**4**) (Scheme 3). Interestingly, no arenium species was formed, as might be expected on basis of previous results related to the reaction of NCN platinum(II) aryl complexes with MeI (20). Two different explanations may rationalize these observations: Either the bulk of the noncoordinating CH_2NMe_2 groups of the η^1-monodentate bound pincer ligand efficiently reduce the accessibility of the platinum center or alternatively, oxidative addition of MeI may take place to form an intermediate platinum(IV) species (4*a*, 21), followed by irreversible trapping of the platinum-bound methyl group by the noncoordinated amine groups, and formation of a cationic

Scheme 4. Selective acid-mediated cleavage of the unsupported Pt—C bond.



ammonium structure as **4**. The accumulation of positive charges and (or) steric crowding in close proximity to the metal center apparently prevents the reaction of **4** with another equivalent of MeI. The methyl groups of the terdentate pincer ligand in **4** are chemically inequivalent (viz. two singlet resonances with ^{195}Pt couplings in the ^{1}H NMR spectrum at δ_H = 2.69 and 2.74, respectively). Also, the benzylic protons of the η^3-bonded ligand in **4** became diastereotopic as shown by the AB-type pattern with δ_A at 3.83 ppm and δ_B at 5.03 ppm, respectively. These observations suggest a reduced symmetry in **4**, which may be due to a frozen wagging of the methylene CH_2 groups of the five-membered metallacycles. In solution, puckering effects are usually fast and cannot be slowed down significantly by cooling (22). However, the steric constraints of the bulky ammonium groups on the η^1-bonded ligand may reduce the fluxionality of the metallacycles considerably. This is corroborated by the anticipated relative position of the aryl planes of the η^1-bonded and η^3-bonded pincer ligands, which are most likely significantly tilted from an ideal perpendicular orientation, cf. the solid-state structure of related bis-ammonium complexes (12*a*).

Bisaryl platinum(II) complexes containing heteroleptic pincer ligands

It must be noted that during the formation of **3**, a TCM type reaction could be operative, which is undetectable as it is degenerative in the products. To distinguish a transmetalation reaction, i.e., Li–Pt exchange on NCN, from an eventually competitive TCM type process, a chemical modification in one ligand framework was introduced. Ideally, such a modification should allow to distinguish between the different amine donors but not cause significantly different coordination properties. Therefore, the prochiral pincer ligand precursor NCHN^{EtMe} (**5**) containing one methyl and one ethyl group bound to each nitrogen donor, was used as a marker.[4] Lithiation and subsequent transmetalation of this ligand readily afforded the corresponding platinum complex [PtCl(NCN^{EtMe})] (**6**) (23).

[4] It has been shown previously that replacement of all methyl groups by ethyl substituents severely disturbes nitrogen coordination and reduces the accessibility of the metal center rigorously. As a consequence, the platinum center in complexes such as [PtX(NCN^{Et_2})] is not available anymore for, e.g., SO_2 (23) or I_2 (4*b*) coordination. Moreover, X-ray structure analyses revealed that the puckering of the metallacycle in, e.g., [PtI(NCN^{Et_2})] is considerably smaller than in the corresponding NCN^{Me_2} complexes (23).

Scheme 5. Heteroleptic bisaryl platinum(II) complex formation by using modified pincer ligands containing ethyl-labeled amino groups.

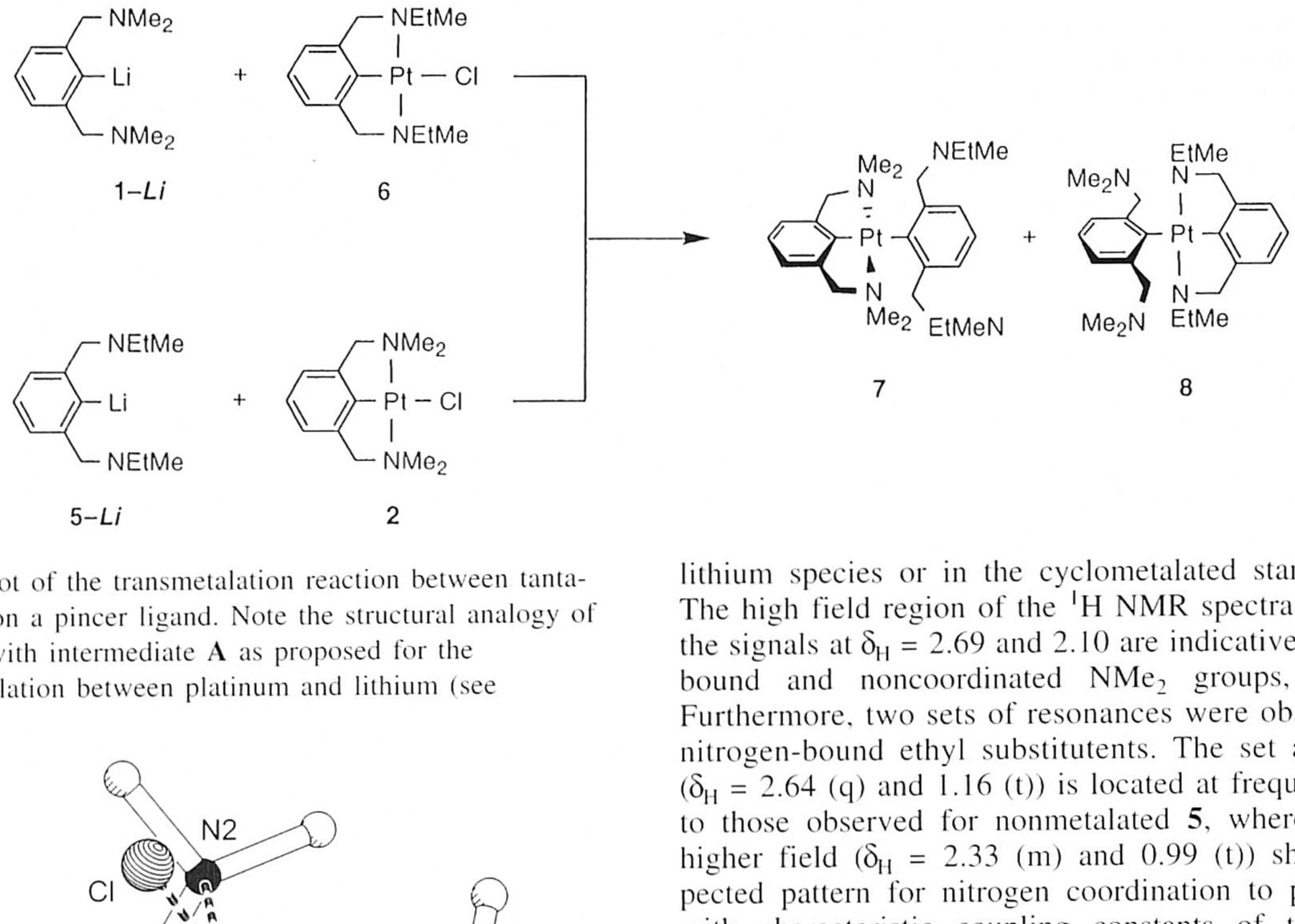
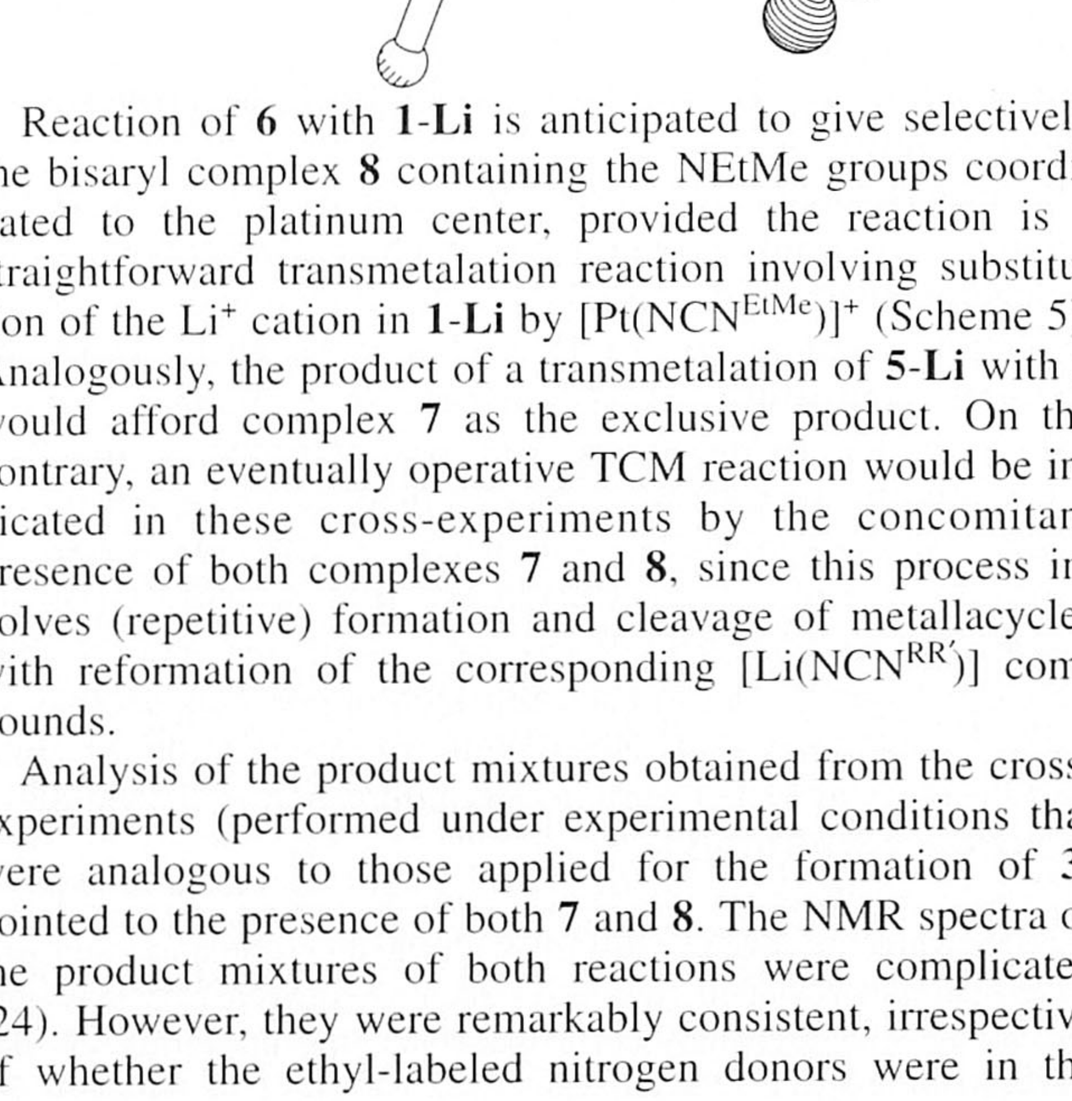


Fig. 4. Snapshot of the transmetalation reaction between tantalum and zinc on a pincer ligand. Note the structural analogy of this complex with intermediate **A** as proposed for the transcyclometalation between platinum and lithium (see Scheme 6).



Reaction of **6** with **1-Li** is anticipated to give selectively the bisaryl complex **8** containing the NEtMe groups coordinated to the platinum center, provided the reaction is a straightforward transmetalation reaction involving substitution of the Li^+ cation in **1-Li** by $[Pt(NCN^{EtMe})]^+$ (Scheme 5). Analogously, the product of a transmetalation of **5-Li** with **2** would afford complex **7** as the exclusive product. On the contrary, an eventually operative TCM reaction would be indicated in these cross-experiments by the concomitant presence of both complexes **7** and **8**, since this process involves (repetitive) formation and cleavage of metallacycles with reformation of the corresponding $[Li(NCN^{RR'})]$ compounds.

Analysis of the product mixtures obtained from the cross-experiments (performed under experimental conditions that were analogous to those applied for the formation of **3**) pointed to the presence of both **7** and **8**. The NMR spectra of the product mixtures of both reactions were complicated (24). However, they were remarkably consistent, irrespective of whether the ethyl-labeled nitrogen donors were in the lithium species or in the cyclometalated starting material. The high field region of the ^1H NMR spectra is diagnostic: the signals at $\delta_H = 2.69$ and 2.10 are indicative for platinum-bound and noncoordinated NMe_2 groups, respectively. Furthermore, two sets of resonances were observed for the nitrogen-bound ethyl substitutents. The set at lower field ($\delta_H = 2.64$ (q) and 1.16 (t)) is located at frequencies similar to those observed for nonmetalated **5**, whereas the set at higher field ($\delta_H = 2.33$ (m) and 0.99 (t)) showed the expected pattern for nitrogen coordination to platinum (24), with characteristic coupling constants of the methylene NCH_2 protons to the platinum center ($^3J_{HPt} = 78$ Hz). A product ratio between **7** and **8** of 3:5 was estimated based on the signals due to the NCH_2CH_3 methyl groups. Interestingly, this ratio is nearly constant and independent of the chosen starting materials, i.e., the cycloplatinated starting materials **2** or **6**. This implies an equilibrium situation which precedes the ultimate formation of the transmetalation products.

Product analyses using variable temperature ^1H NMR lead to similar results as obtained for **3**. In the measured temperature range (–80 to +100°C, toluene-d_8 solution), no significant line-broadening was observed. More importantly, the product ratio between **7** and **8** remained constant, implying a high kinetic barrier for the transition of **7** to **8** and vice versa (Scheme 4). These results exclude a potential equilibrium situation *after* the transmetalation sequence.

When the complexes **3**, or **7** and **8** were treated with an excess of aq HCl, rapid fission of the unsupported Pt—C bond was observed, thus giving the cyclometalated platinum chloride complexes **2** and **6**, respectively, along with the protonated pincer ligands **1**·2HCl and **5**·2HCl (Scheme 4). Since the non-chelating Pt—C bond is cleaved selectively (the Pt—C bond in complex **2** was stable towards HCl at 60°C for several hours), quantification of the product ratio between **2** and **6** provides an a posteriori method for the determination of the ratio between **7** and **8**.

Mechanistic consequences for TCM reactions with $[Li(NCN^{RR'})]$ complexes

Related transmetalation studies have emphasized the relevance of bimetallic intermediates comprising an aryl carbanion bridging to two (different) metal centers through *3c—2e* or *3c—4e* bonding (Fig. 4) (25). A similar

Scheme 6. Rapid and reversible TCM process in a preequilibrium of the transmetalation reaction. Note that structure **A** is the common intermediate of both the TCM and the transmetalation process.

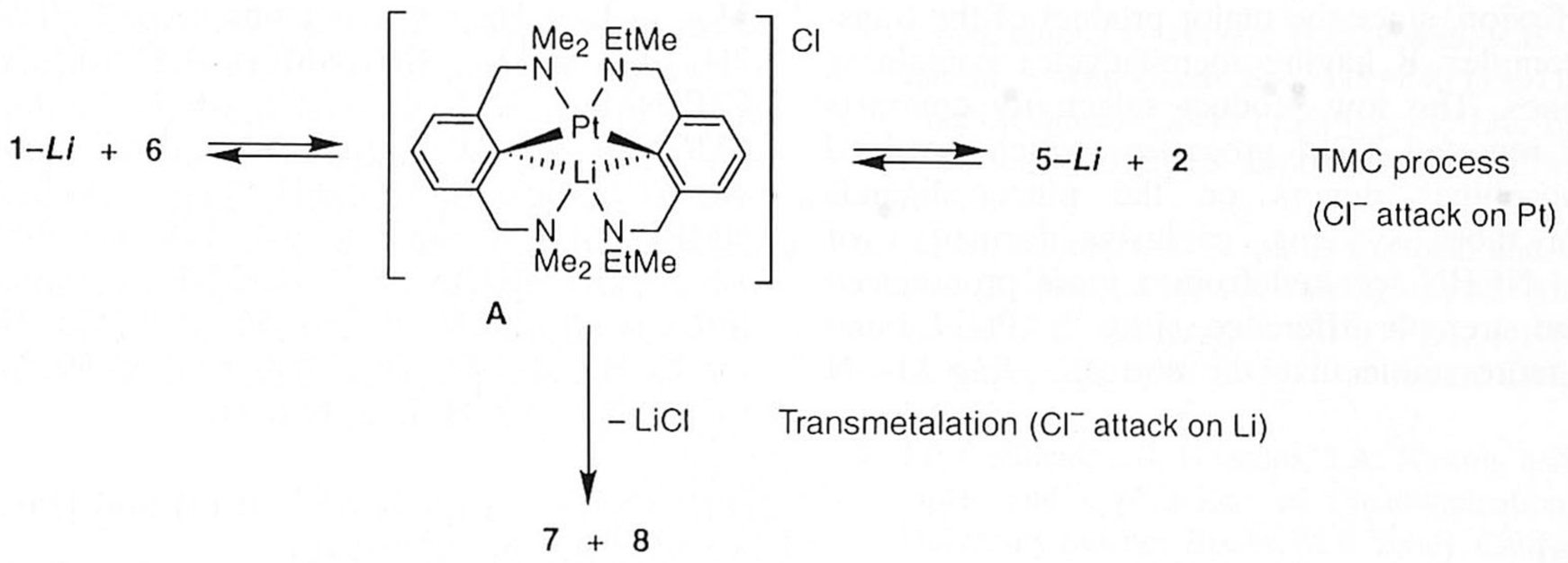


Table 3. Crystallographic data for both polymorphs of complex **3**.

	Crystal **I**	Crystal **II**
Empirical formula	$C_{24}H_{38}N_4Pt$	$C_{24}H_{38}N_4Pt$
Formula weight	577.67	577.67
T (K)	298	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Crystal size (mm)	0.50 × 0.50 × 0.50	0.38 × 0.38 × 0.15
Crystal color	Colorless	Colorless
Unit cell dimensions		
a (Å)	10.3234(7)	16.954(2)
b (Å)	19.1763(12)	27.422(2)
c (Å)	12.3632(8)	18.023(2)
β (deg)	93.271(5)	121.271(10)
V (Å^3)	2443.5(3)	7161.8(15)
Z	4	12
D_{calc} (g cm^{-3})	1.5703(2)	1.6073(3)
μ (mm^{-1}) (Mo Kα)	5.76	5.89
Abs. correction	PLATON (DELABS)	PLATON (DELABS)
Transmission range	0.386–1.000	0.585–1.000
(sin θ/λ) Max (Å^{-1})	0.65	0.65
Reflections collected, unique	8598, 5592	14374, 13561
R_{int}	0.0301	0.0581
Parameters, restraints	271, 0	538, 0
R_1,[a] wR_2,[b] S	0.0372, 0.0811, 1.027	0.0680, 0.1363, 1.017
w^{-1} [c]	$\sigma^2(F_o^2) + (0.0250P)^2 + 5.13P$	$\sigma^2(F_o^2) + (0.0170P)^2 + 100.31P$
Resid. density (e Å^{-3})	–0.79 < 1.18	–1.99 < 2.13

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for all I > 4σ(I).
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.
[c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

intermediate (A) is likely to be involved in the transmetalation of **1-Li** or **5-Li** by the cyclometalated platinum(II) complexes **6** and **2**, respectively, (Scheme 6). Due to the low stability of such complexes, it is expected that intermediate **A** equilibriates rapidly with the starting materials. Notably, it is not possible to deduce the precursors, i.e., **2** and **5-Li** or **6** and **1-Li**, from complex **A** and formation of either of these two sets of starting materials occurs on nucleophilic attack of Cl^- on the platinum center. This interconversion of **2** and **5-Li** to **6** and **1-Li** and vice versa corresponds to a transcyclometalation (TCM) reaction between the platinum and lithium centers. Alternative attack of the Cl^- nucleophile on the lithium center in intermediate **A** induces the formation of LiCl and the respective bisaryl platinum(II) product, which is probably an irreversible reaction sequence. Apparently, the equilibrium situation of the TCM reaction with complex **A** as an intermediate must be reached rapidly. This is an interesting further reaction trajectory for a TCM process and contrasts to earlier established reactions where one starting material was metal-free. The relatively low selectivity of this TCM reaction (Scheme 6) in terms of product distribution (nearly equal yields of **7** and **8**) is most likely a direct consequence of the only small differences in the bond strength of the platinum center to either N^{Me_2} or N^{EtMe} type amines. Similar arguments account for the Li—N^{Me_2} and Li—N^{EtMe} bond strengths. According to

spectroscopic analyses (NMR signal integration), there is a slight preference for initial Li—N^{EtMe} bond cleavage rather than Li—N^{Me_2} fission, since the major product of the transmetalation is complex **8** having metallacycles containing N^{EtMe} type amines. The low product selectivity contrasts with previously reported TCM processes, which involved amine and phosphines donors on the pincer ligands (Scheme 2). In those systems, exclusive formation of [PtCl(PCP)] and NCHN resulted from a more pronounced donor-metal bond strength difference, since the Pt—P bond is significantly more stable than the corresponding M—N bond.

Experimental

Reactions involving organolithium derivatives were carried out using standard Schlenk techniques under an inert atmosphere of dry, oxygen-free nitrogen. Hexane, Et_2O, and THF were distilled from Na–benzophenone, CH_2Cl_2 from CaH_2 prior to use. All ^1H and ^{13}C NMR spectra were recorded on a Bruker AC300 or a Varian Inova 300 spectrometer, operating at 300 and 75 MHz, respectively. Spectra were obtained at 25°C, unless stated otherwise, and are referenced to external TMS (δ = 0.00 ppm, J in Hz). Elemental analyses were obtained from Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany).

The ligand precursors $NC(H)N^{Me_2}$ (**1**), $NC(H)N^{EtMe}$ (**5**), and the platinum complexes [$PtCl(NCN^{Me_2})$] (**2**) and [$PtCl(NCN^{EtMe})$] (**6**), were prepared according to described procedures (13, 15, 23).

[Pt(η^3-NCN^{Me2})(η^1-NCN^{Me2})] (3)

To a pentane solution of **1** (0.25 g, 1.3 mmol in 4 mL) was added *n*-BuLi (1.5 M hexane solution, 0.87 mL, 1.3 mmol) at –80°C. The reaction mixture was allowed to warm to room temperature over 14 h. All volatiles were then removed in vacuo and the residue was redissolved in THF. To this solution was added the platinum complex **2** (0.50 g, 1.2 mmol) and the mixture was heated to reflux temperature for 4 h. After cooling to room temperature, the solvents were removed and the residue was extracted with Et_2O (3 × 20 mL). The combined ether layers were concentrated to 5 mL and pentane was overlayered, which caused slow crystallization of the product. Yield: 0.41 g (60%). ^1H NMR (C_6D_6) δ: 7.70 (d, 2H, $^3J_{HH}$ = 7.0, Ar*H*), 7.40 (t, 1H, $^3J_{HH}$ = 7.0, Ar*H*), 7.17 (t, 1H, $^3J_{HH}$ = 8.0, Ar*H*), 6.93 (d, 2H, $^3J_{HH}$ = 8.0, Ar*H*), 4.38 (s, 4H, CH_2N), 3.57 (s, $^3J_{HPt}$ = 47, 4H, CH_2NPt), 2.58 (s, $^3J_{HPt}$ = 42, 12H, $PtNCH_3$), 2.41 (s, 12H, NCH_3). ^{13}C NMR (C_6D_6) δ: 182.2 (C_{ipso}, $^1J_{HPt}$ not resolved), 172.6 (C_{ipso}, $^1J_{HPt}$ not resolved), 147.4, 145.1, 127.4, 122.7, 122.3, 119.0 (all Ar*C*), 80.8 (CH_2NPt), 68.4 (CH_2N), 54.7 ($PtNCH_3$), 45.9 (NCH_3). Anal. calcd. for $C_{24}H_{38}N_4Pt$ (587.66): C 49.90, H 6.63, N 9.70; found: C 50.07, H 6.90, N 9.59.

[Pt(η^3-NCN^{Me3})(η^1-NCN^{Me3})]$(I)_2$ (4)

To a stirred solution of **3** (0.50 g, 0.87 mmol) in CH_2Cl_2 (5 mL) was added a solution of MeI (0.28 g, 2.0 mmol) in CH_2Cl_2 (2 mL) and the mixture stirred for 3 h. The volatiles were removed to leave **4** as an off-white solid (0.72 g, 97%). Analytically pure **4** was obtained by recrystallization from H_2O–acetone. ^1H NMR (D_2O, 200 MHz) δ: 7.41 (d, 4H, $^3J_{HH}$ = 7.3, Ar*H*), 7.27 (t, 2H, $^3J_{HH}$ = 7.3, Ar*H*), 5.04 (d, 2H, $^3J_{HH}$ = 13.2 Hz, $^3J_{HPt}$ not observed, C*H*$HNMe_2$), 4.84 (d, 2H, $^3J_{HH}$ = 11.6, C*H*$HNMe_3$), 4.52 (d, 2H, $^3J_{HH}$ = 11.6, C*H*$HNMe_3$), 3.83 (d, 2H, $^3J_{HH}$ = 13.4, $^3J_{HPt}$ not observed, CH*H*NMe_2), 3.24 (s, 18H, NMe_3), 2.75 (s, 6H, $^3J_{HPt}$ = ca. 40, N*C*H_3Me), 2.73 (s, 6H, $^3J_{HPt}$ = 36.2, NMe*C*H_3). ^{13}C NMR (D_2O) δ: 175.8 (C_{ipso}), 149.2, 132.8, 130.5, 123.6, 123.5 (all Ar*C*), 78.9 (CH_2NPt), 74.9 (CH_2N), 56.1 ($PtNCH_3Me$), 52.9 (NMe_3), 51.7 ($PtNMeCH_3$). Anal. calcd. for $C_{26}H_{44}I_2N_4Pt{\cdot}H_2O$ (879.57): C 35.50, H 5.27, N 6.37; found: C 35.50, H 5.42, N 6.21.

[Pt(η^3-NCN^{Me2})(η^1-NCN^{EtMe})] (7) and [Pt(η^3-NCN^{EtMe})(η^1-NCN^{Me2})] (8)

These complexes have been prepared following a similar protocol as for **3**. The products were obtained as mixtures, which precipitated as off-white powders from pentane–Et_2O systems. All attempts to separate the products were unsuccessful.

Method A

From **1** (0.17 g, 0.89 mmol) in pentane (4 mL), *n*-BuLi (1.5 M in hexane, 0.60 mL, 0.9 mmol), and **6** (0.37 g, 0.82 mmol). Yield: 0.22 g (44%).

Method B

From **5** (0.26 g, 1.2 mmol) in pentane (6 mL), *n*-BuLi (1.5 M in hexane, 0.8 mL, 1.2 mmol), and **2** (0.46 g, 1.1 mmol). Yield: 0.35 mg (53%).

^1H NMR (C_6D_6) δ: 7.83 (d, $^3J_{HH}$ = 7.4, Ar*H*), 7.55 (s, Ar*H*), 7.43 (t, $^3J_{HH}$ = 7.4, Ar*H*), 7.31–7.19 (m, Ar*H*), 7.04 (t, $^3J_{HH}$ = 7.5, Ar*H*), 6.93 (d, $^3J_{HH}$ = 7.4, Ar*H*), 6.64 (d, $^3J_{HH}$ = 7.5, Ar*H*), 4.47 (s, CH_2N (**8**)), 3.57 (s, $^3J_{HPt}$ = 43.7, CH_2NPt (**7**)), 3.40 (s, CH_2N (**7**)), 3.29 (s, $^3J_{HPt}$ = 30.3, CH_2NPt (**8**)), 2.69 (s, $^3J_{HPt}$ = 38.0, $PtNCH_3$ (**8**)), 2.64 (q, $^3J_{HH}$ = 7.1, N*C*H_2CH_3 (**7**)), 2.58 (s, $^3J_{HPt}$ = 43.6, $PtNCH_3$ (**7**)), 2.41 (s, NCH_3 (**8**)), 2.33 (q, $^3J_{HH}$ = 7.1, $^3J_{HPt}$ = 78.0, $PtNCH_2CH_3$ (**8**)), 2.10 (s, NCH_3 (**7**)), 1.16 (t, $^3J_{HH}$ = 7.1, 2.25H, NCH_2CH_3 (**7**)), 0.99 (t, 3.75H, $^3J_{HH}$ = 7.1, $PtNCH_2CH_3$ (**8**)). ^{13}C NMR (C_6D_6) δ: 181.6 (C_{ipso}), 172.7 (C_{ipso}), 147.5, 145.1, 143.8, 140.2, 130.0, 127.4, 126.9, 122.9, 122.6, 122.5, 119.2, 119.0 (all Ar*C*), 80.9 ($^2J_{CPt}$ = 28.0, CH_2NPt (**8**)), 77.7 ($^2J_{CPt}$ = 65.0, CH_2NPt (**7**)), 66.8 (CH_2N (**7**)), 62.6 (CH_2N (**8**)), 54.8 ($^2J_{CPt}$ not resolved, $PtNCH_3$ (**8**)), 54.0 ($^2J_{CPt}$ = 15.3, $PtNCH_3$ (**7**)), 52.0 (NCH_2CH_3 (**7**)), 51.6 ($PtNCH_2CH_3$ (**8**)), 42.0 (NCH_3 (**7**)), 41.6 (NCH_3 (**8**)), 13.5 (NCH_2CH_3 (**7**)), 12.8 ($PtNCH_2CH_3$ (**8**)).

Reaction with HCl

A solution of the bisarylplatinum complex **3**, or **7** and **8** in CH_2Cl_2 was saturated with freshly prepared anhyd HCl. Stirring was maintained for 1 h and all volatiles removed in vacuo. Identification of the products (^1H NMR) was performed by comparison with authentic samples of **2** and **6**, respectively.

Structure determination and refinement of 3

Intensities were measured on an Enraf–Nonius CAD4-T diffractometer with rotating anode (Mo Kα, λ = 0.71073 Å). Crystal data and details on data collection and refinement

are collected in Table 3.[5] The structures were solved with Patterson methods (DIRDIF-92 (26)) and refined against F^2 of all reflections (SHELXL-93 (27)). Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Weights were optimized in the final refinement cycles. Neutral atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables of Crystallography*. All calculations, graphical illustrations, and checking for higher symmetry were performed with the PLATON package (28).

Conclusions

The use of labeled NCN pincer ligands suggested that the transmetalation of [Li(NCN)] with cyclometalated [PtCl(NCN)] precursors is preceded by a comparatively fast and reversible TCM process between lithiated and platinated metallacycles. Such a TCM reaction does not involve C—H bond activation and therefore follows a distinctly different reaction coordinate than previously analyzed TCM processes. Importantly, in this case the product distribution is most likely determined by steric preferences rather than metal-to-heteroatom bond strength arguments as established previously. A cationic heterodinuclear bisaryl platinum lithium species has been suggested as a key intermediate. Attack of chloride on the platinum center of this intermediate induces a TCM reaction, whereas attack on lithium completes the transmetalation trajectory with formation of the corresponding bisaryl platinum(II) complex and LiCl. Investigations towards the stabilization and characterization of the proposed intermediate of this novel TCM process are currently in progress.

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[5] Copies of material on deposit may be purchased from The Depository of Unpublished Data, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). Crystallographic data (excluding structure factors) for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as deposition no. CCDC-149 827 (crystal **I**) and CCDC-149 828 (crystal **II**). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336 033, e-mail: deposit@ccdc.cam.ac.uk).

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