Transcyclometalation Processes with Late Transition Metals: C_{aryl}−H Bond Activation via Noncovalent C−H···Interactions

Martin Albrecht,[†] Paulo Dani,[†] Martin Lutz,[‡] Anthony L. Spek,[‡,§] and Gerard van Koten*[,†]

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

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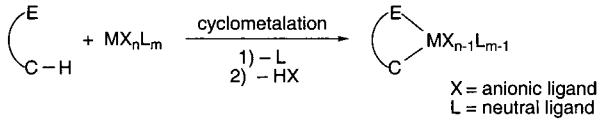
Abstract: The bis(*ortho*-)chelated platinum complex [PtCl(NCN)], **1** (NCN = $[C_6H_3(CH_2NMe_2)_2$-2,6$]^-$), has been used as a novel metal precursor for C−H bond activation and subsequent cyclometalation of the potentially terdentate coordinating pincer ligand PCHP (PCP = $[C_6H_3(CH_2PPh_2)_2$-2,6$]^-$). Depending on the reaction temperature various intermediates, each with unique structural features, could be isolated and identified during the formation of the final, bis(*ortho*-)cyclometalated product [PtCl(PCP)], **2**. These results provide valuable insight into the intimate steps of this reaction for which we like to introduce the term *transcyclometalation process* (see note). *At room temperature*, a sparingly soluble dimetallic complex is formed, which comprises a η^1-monodentate *C*-bound NCN ligand and a bridging, *P,P* η^2-ϵ^2-coordinating PCHP ligand. Solution spectroscopy and X-ray analysis of this platinum dimer established a C−H bond which is interacting by intramolecular noncovalent H···Cl hydrogen bonding with the Pt−Cl motif. As a further intermediate, the formation of a *trans*-bis(phenyl) complex [Pt(η^3-PCP)(η^1-HNCN)]Cl, **5**, has been identified, which is characterized by a bis(*ortho*-)cyclometalated PCP ligand which is η^3-*P,C,P′* coordinated to the platinum center as well as an η^1-monodentate *C*-bound NCN ligand. The equivalent HCl, which is formally released during the formation of **5**, is intramolecularly trapped by one of the basic amine groups, as is apparent from the identification of precursors of **5**, i.e., compounds in which either one (**[3]Cl**) or two (**[4]X$_2$**) of the NMe_2 groups have become protonated (see Scheme 5). Remarkably, the proton in **[4]X$_2$** is not only bound to the nitrogen lone pair but also interacts with the filled d_{z^2} orbital of the nucleophilic platinum(II) center, thus disclosing complex **5** as an organometallic proton sponge that is able to sequester protons due to *Pt,N*-bidentate chelating properties. Prolonged exposure of the reaction mixture at 80 °C or performing the reaction at 110 °C afforded the transcyclometalated complex **2** and 1 equiv of the diaminoarene NCHN as the two ultimate products.

Introduction

The selective activation of (unstrained) C−H bonds is a significant key step in the synthesis of both commodity and fine chemicals, as this offers a general method for the introduction of new functional groups.[1] Since its discovery, cyclometalation involving (transition) metals (Scheme 1) has been widely applied and represents an elegant methodology for the creation of a metal-to-carbon bond under relatively mild conditions in terms of temperature and/or pressure.[2]

In particular, the (site-selective) functionalization of aromatic rings has attracted much attention.[3] Various electron-donating heteroatoms (E) have been successfully used in the (late) transition metal-mediated activation of C−H bonds of potentially *E,C*-bidentate and "pincer"-type[4] *E,C,E′*-terdentate coordinating ligand precursors (E, E′ = P, N, etc; C = aryl or alkyl).[2,4,5] However, detailed mechanistic aspects of the intimate C−H bond activation and cleavage steps are elusive, despite the numerous studies devoted to cyclometalation processes.[6] A primary conclusion common to most of these investigations concerns the initial step, which comprises the substitution of a weakly bound (frequently neutral) ligand L on the metal precursor M by a stronger donor E (Scheme 1). Subsequent ligand dissociation and formation of a coordinatively unsaturated and electron deficient metal center has been proposed to create

Scheme 1



* Corresponding author. Fax: +31-30-2523615. Phone: +31-30-2533120. E-mail: g.vankoten@chem.uu.nl.

[†] Debye Institute, Department of Metal-Mediated Synthesis.

[‡] Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry.

[§] Corresponding author pertaining crystallographic data. E-mail: a.l.spek@chem.uu.nl.

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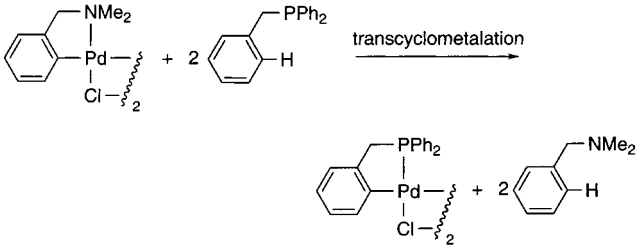
the reactive intermediate for cyclometalation,[2d] which then probably reacts along a reaction pathway that includes formation of an arenium-type intermediate.[7,8]

Complexes containing pincer-type ligands are especially attractive for such investigations, because these polydentate ligands can (i) stabilize intermediates during a reaction, which allows their proper identification,[9] and (ii) retard the reaction which may provide insight into kinetic and thus mechanistic aspects of the cyclometalation process.[10] Recently, cyclometalated Ru(II) complexes, i.e. [RuCl(NCN)(PPh_3)] (NCN is the abbreviation of the monoanionic terdentate ligand [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$), have been successfully used as metal precursors for cycloruthenation of another PCHP ligand (PCHP is the *meta*-bis(phosphino)arene ligand [$C_6H_4(CH_2PPh_2)_2$-1,3], which represents the precursor of the monoanionic terdentate PCP ligand [$C_6H_3(CH_2PPh_2)_2$-1,3]$^-$).[11] The outcome of this reaction is surprising, since this formal exchange of cyclometalated ligands at the metal center is rarely observed and has predominantly been reported to occur in palladium(II) complexes (Scheme 2).[12] In analogy to transesterification reactions (eq 1), we like to introduce the term *transcyclometalation reaction* to describe the overall process of this reaction (eq 2).[13,14]

Scheme 2



$$R''-COOR + R'OH \rightleftarrows R''-COOR' + ROH \quad (1)$$

$$M(C,E) + (CH,E') \rightleftarrows M(C,E') + (CH,E) \quad (2)$$

Here, we report on our recent studies using the bis(*ortho*-)chelated complex [PtCl(NCN)] as a substrate for the transcycloplatination reaction with *meta*-bis(phosphino)arene ligands PCHP. Several interesting intermediates on the way to the bis(*ortho*-)chelated product [PtCl(PCP)] have been isolated and fully characterized, in particular some containing unprecedented noncovalent C−H···Cl−Pt interactions.

Results

Heating of a toluene solution containing equimolar amounts of the *meta*-diphosphinoarene ligand $C_6H_4(CH_2PPh_2)_2$-1,3 (abbreviated as PCHP) and the cyclometalated complex [PtCl(NCN)], **1**, to 110 °C leads to a rapid formation of a white precipitate. When heating was continued for several days, most of the solid dissolved again. Analysis of the products obtained after workup (see Experimental Section) revealed the clean formation of the transcyclometalated complex [PtCl(PCP)], **2**, in high yields, as is demonstrated unambiguously by the pertinent spectroscopic data (Scheme 3).[15] The second product of this reaction which is formed in equivalent amounts was identified as the noncoordinated *meta*-bis(amino)arene NCHN.

Neutral and Protonated Pt(PCP)(NCN) Complexes. Detailed examination of the products formed in the reaction which was carried out in benzene at reflux temperature, i.e. at 80 °C, provided insight in the nature of the intermediates preceding the formation of the final products **2** and NCHN. Similar to the reaction at 110 °C, the immediate formation of a precipitate is observed. When the temperature is kept at 80 °C, this solid did not dissolve even after prolonged reaction time (3 days). Isolation of this solid and purification under neutral conditions gave a single product, which according to NMR spectroscopic analyses appeared to be a complex of the type [Pt(η^3-PCP)(η^1-HNCN)]. This complex, **[3]Cl**, contains two mutually trans-*C*-

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(13) In analogy to transamination and transesterification, a transcyclometalation process involves the interconversion of one cylometalated ligand metal complex M(C,E) into another M(C,E′) with the concomitant consumption and formation of the corresponding arene ligands (CH,E′) and (CH,E), respectively (see Schemes 2 and 3). The driving force in this reaction is the difference in heteroatom−metal bond strength which is highest for the P−M bond in the case of the late transition metals Pd^{II}, Pt^{II}, or Ru^{II}.

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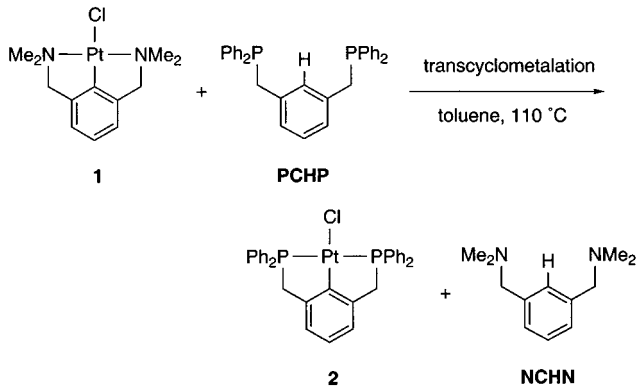
Scheme 3



bonded monoanionic NCN and PCP ligands. In **[3]Cl**, both *ortho*-phosphorus donors are also coordinated to the platinum center whereas the amines are both noncoordinating while one is in addition protonated (see Scheme 4).

The ^{31}P NMR spectrum shows a singlet at 31.2 ppm (Table 1), which is typical for symmetrically bis(*ortho*-)chelate bonded PCP-type ligands.[14,16] The presence of coupling signals due to ^{195}Pt (natural abundance 34%; $^1J_{PPt} = 2970$ Hz) unambiguously demonstrates coordination of the phosphine donors to the metal center. Moreover, also the (PCP) benzylic proton resonances show coupling with ^{195}Pt ($\delta_H = 4.15$, $^3J_{HPt} = 28.3$ Hz; Table 2). Mutual trans configuration of the aryl units is suggested by the chemical shift of the two *ipso*-carbons (located at $\delta_C = 160.1$ and 169.0 ppm, respectively; see Table 3).

The singlet due to the NCH_3 protons is considerably upfield shifted (from 3.07 ppm in **1** to 1.69 ppm in **[3]Cl**), which strongly points to the absence of metal-coordinated amine/ammonium groups in **[3]Cl** (cf. δ_H for NCH_3 amounts to 2.21 in free NCHN), as does the lack of satellites due to $^3J_{HPt}$ coupling. Most interestingly, the equivalent HCl, which was liberated during the cyclometalation process, has been found to be present in **[3]Cl** even after thorough drying in vacuo (see correct elemental analyses). This indicates that, in solution, **[3]Cl** contains a η^1-C-bonded NCN ligand, which formally possesses one dimethylammonium and one dimethylamine substituent, i.e., a complex [Pt(η^3-PCP)(η^1-NHCN)]Cl. On the basis of the narrow line width of the NCH_3 signal at 1.69 ppm of **[3]Cl**, a fast acid/base equilibrium is assumed comprising (probably) intermolecular exchange of the acidic proton of a dimethylammonium center to a dimethylamine substituent. This most likely Cl^--mediated proton migration process can be slowed by cooling, as is shown by a severe broadening of the characteristic NCH_3 resonance ($w_{1/2} = 23$ Hz) at 178 K ($C_2F_4Br_2$ solution). However, complete decoalescence of the signal is not observed even at these low temperatures, which points to a very fast exchange rate, as is indeed expected for proton transfer in amine/ammonium systems.

Addition of pentane to a solution of **[3]Cl** in CH_2Cl_2 induced disproportionation of **[3]Cl** to the bis-protonated complex [Pt(η^3-PCP)(η^1-NHCNH)]Cl_2, **[4]Cl$_2$**, and neutral [Pt(η^3-PCP)(η^1-NCN)], **5** (Scheme 5). Fractional precipitation gave first the bis-protonated complex **[4]Cl$_2$** and subsequently neutral **5**. Both compounds were isolated as colorless solids.

The ^{1}H NMR data of the complex **[4]Cl$_2$** in $CDCl_3$ shows some significant differences compared to those of **[3]Cl**. First, a downfield shift of the NCH_3 (0.2 ppm) and the $ArCH_2N$ (0.3 ppm) proton resonances is noted. Second, a broad signal at 11.8 ppm in the spectrum of **[4]Cl$_2$** was observed which integrated for two protons and which disappeared completely after addition of a few drops of D_2O to this solution. Furthermore, characteristic cross-peaks were observed in a ^{1}H−^{1}H COSY NMR spectrum of **[4]Cl$_2$** (but not in the corresponding spectrum of **[3]Cl**) between the resonance at 11.8 ppm and those attributed to the $ArCH_2N$ and the NCH_3 protons. These findings provide evidence for the presence of two symmetry-related and heteroatom-stabilized H−N (ammonia) moieties in **[4]Cl$_2$**.[17,18] The ^{1}H NMR spectra of solutions of **[4]Cl$_2$** in $CDCl_3$ at different temperatures pointed to a significant temperature dependence of the resonances of the protons in the CH_2NHMe_2 substituents. The broad signal due to the ammonia N−H proton at $\delta_H = 11.8$ ppm varies between 11.88 ppm (328 K) and 11.17 ppm (213 K). Similar but less pronounced chemical shift differences were observed for the benzylic $ArCH_2N$ protons ($\Delta\delta = 0.11$ ppm) and for the NCH_3 groupings ($\Delta\delta = 0.08$ ppm) in the same temperature range.

Exchange of the (noncoordinating) anions in **[4]Cl$_2$** from Cl^- to BF_4^-, i.e., the formation of **[4](BF$_4$)$_2$**, did not significantly change the spectroscopic properties. An exception is the disappearance of the signal in the ^{1}H NMR spectrum at 11.8 ppm (assigned to N−H) and the presence of a new very broad resonance at 5.8 ppm ($w_{1/2}$ ca. 150 Hz). This highfield shift presumably is a consequence of the different hydrogen acceptor capacity of the BF_4^- anion with respect to Cl^-. Upon cooling, the δ_H values shift to higher field ($\Delta\delta = 0.6$ ppm) as described for this proton in **[4]Cl$_2$**, concomitant with a significant narrowing ($w_{1/2}$ = ca. 35 Hz at 213 K).

Whereas **[3]Cl** and **[4]Cl$_2$** could not be crystallized, suitable single crystals for an X-ray structure determination were obtained for **[4](BF$_4$)$_2$** (from a CH_2Cl_2 solution). Most evidently, a crystallographic rotation axis (C_2) is present, which is defined by the C_{ipso} and C_{para} nuclei of both the PCP and the NCN ligand and the platinum center. This relates the two nitrogen and the two phosphorus donors, respectively, by symmetry and forces the metal in the PCP and NCN aryl planes, respectively (Figure 1). Notably, the η^1-coordinating NCN aryl ring does not adopt a perpendicular orientation (vide infra) but is rotated by 76.2(2)° with respect to the metal coordination plane and to the terdentate coordinating PCP ligand (for relevant bond lengths and angles, see Table 4). Refinement of the obtained data set converged best by using a disordered model for the position of the $NHMe_2^+$ moieties. In one conformation (50% population) the nitrogen center points toward the platinum center (Figure 2a). This orientation fixes the ammonium proton between the nitrogen and the platinum. Intramolecular chelation of nitrogen and platinum is indicated by short N−H···Pt distances (2.82 Å for H···Pt and 3.535(10) Å for N···Pt; angle N−H···Pt 134°). Hence, this conformation of **[4](BF$_4$)$_2$** shows a hydrogen-bonding motif which involves a nucleophilic platinum(II) center as acceptor site and represents another example of an organometallic proton sponge.[17,19] The alternative conformation (50% population) is characterized by the position of the ammonium entities pointing away from the metal center, toward the unsubstituted part of the NCN aryl ring (Figure 2b). The nitrogen-bound protons interact with the BF_4 anions, thus

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Scheme 4

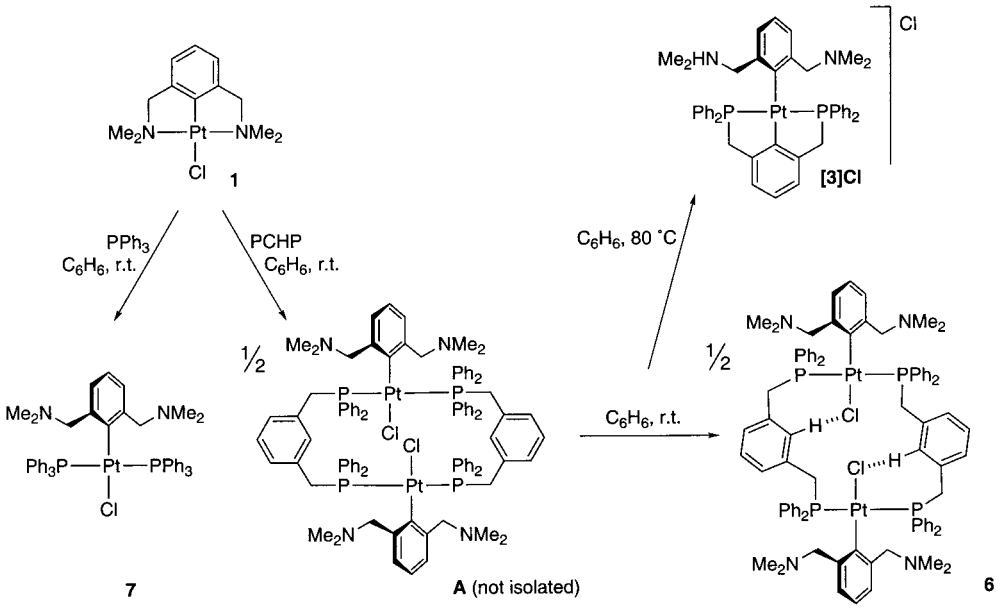


Table 1. Selected ^{31}P NMR Data[a]

complex	δ_P ($^1J_{PPt}$)
PCHP[b]	−9.9
A[b]	17.6 (3005)
2[c]	33.1 (2970)
[3]Cl	31.7 (2983)
[4]Cl$_2$	32.0 (2866)
5	31.6 (3050)
6	10.5 (3041),[d] 18.2 (3069)[d]
7	20.5 (3092)

[a] From $CDCl_3$ solution, unless stated otherwise; δ in ppm and J in Hz. [b] From C_6D_6. [c] From ref 15. [d] $^2J_{PP}$ = 429 Hz.

Table 2. Selected ^{1}H NMR Data[a]

complex	ArCH$_2$P ($^3J_{HPt}$)	ArCH$_2$N	NCH$_3$	C$_{aryl}$–H
PCHP	3.41			7.51−7.36, 7.09−6.88
1		4.02	3.07	6.99, 6.80
A[b]	3.85 (br)	3.62	2.10	7.69, 7.3−6.6
2[c]	3.90 (25.6)			7.96−7.06
[3]Cl	4.15 (28.3)	3.37	1.69	7.3−7.1
[4]Cl$_2$	4.22 (27.6)	3.73	1.94	11.8, 7.79−7.06
5	4.14 (28.3)	3.05	1.56	7.15−7.03
6	4.75−3.51	5.41−1.88[d]	1.87, 1.37	9.93, 8.25−5.74
7		3.49	1.77	7.69−7.1, 6.80, 6.67

[a] From $CDCl_3$ solution, unless stated otherwise; δ in ppm and J in Hz. [b] From C_6D_6. [c] From ref 15. [d] Eight AB doublets centered at δ_H 5.41, 4.76, 4.57, 3.84, 3.78, 3.51, 2.32, and 1.88.

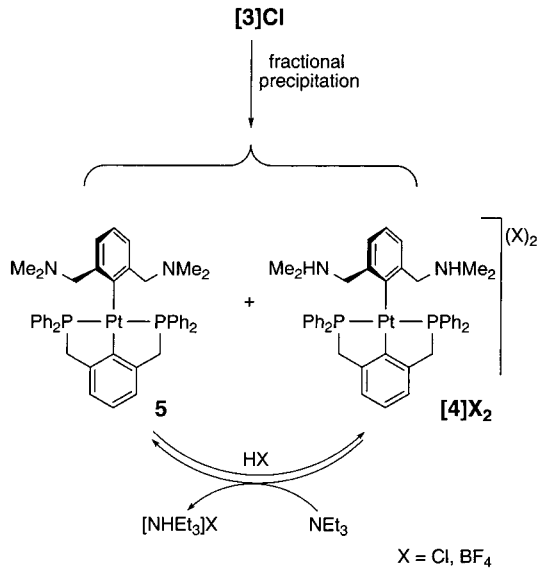
Table 3. Selected ^{13}C NMR Data[a]

complex	ArCH$_2$P ($^2J_{CPt}$)	ArCH$_2$N	NCH$_3$	C−Pt
PCHP	35.9			130.5
1		77.1	53.7	144.5
[3]Cl	46.5	66.7	43.8	169.0, 160.1
[4]Cl$_2$	46.1	65.5	42.7	167.6, 161.0
5	47.0	68.3	45.6	171.1, 158.6
6	35.5, 34.0	68.5, 66.0	45.3	141.3
7		68.2	45.1	139.6

[a] From $CDCl_3$ solution; δ in ppm and J in Hz.

forming N−H···F hydrogen bonding motifs. Instead of the NHMe$_2$ groups (as found in the first conformation), benzylic protons occupy the virtual z axis of the square plane defined by the metal-bound ligands and are located 2.67 Å from the metal center (distance Pt···H$_{benzyl}$).[20] Both conformations of the **[4](BF$_4$)$_2$** molecular geometry in the solid state are in concert with earlier conclusions made for the positioning of the ammonium NH and the benzylic CH$_2$N protons in the coordination sphere of the platinum center of **[3]Cl** and **[4]X$_2$** in solution (X = Cl, BF$_4$). From the X-ray diffraction experiment, however, an identical result is obtained, when the single molecule comprises both structural motifs, i.e., hydrogen bonding of one ammonium substituent to the platinum center and the other having a N−H···F-mediated cation−anion hydrogen bonding (Figure 2c). This requires a reduced crystallographic symmetry of the molecule and a random distribution of relative orientation of the nitrogen substituents. Theoretical considerations support such a confirmation, since the filled d_{z^2} orbital of neutral platinum(II) complexes, which is pivotal for this type of

Scheme 5



(20) (a) Albinati, A.; Arz, C.; Pregosin, P. S. *J. Organomet. Chem.* **1988**, *356*, 367. (b) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812. (c) Brookhart, M.; Green, M. H. L.; Wong, L. L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1988; Vol. 36, p 1.

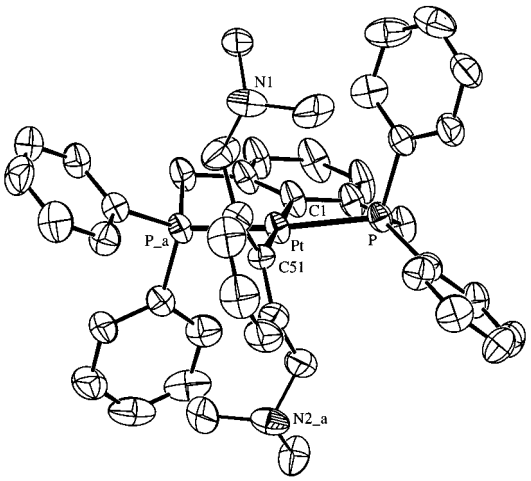


Figure 1. Perspective view (50% probability) of **[4](BF$_4$)$_2$** showing the adopted numbering scheme. Only one of the two disordered positions for the CH_2NMe_2 groups is shown (50% occupancy each). All hydrogen atoms and the BF_4^- anions have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complexes **[4](BF$_4$)$_2$**, **[6]·4C$_6$H$_6$**, and **[7]·1/6C$_6$H$_{14}$**[a]

	[4](BF$_4$)$_2$	**[6]·C$_6$H$_6$**	**[7]·1/6C$_6$H$_{14}$**
		Bond Lengths	
Pt− C51	2.096(12)	2.034(3)	2.043(4)
Pt−P	2.2753(12)	2.3036(6)−2.3165(6)	2.3124(10)−2.3159(10)
Pt−L	2.083(12)	2.4392(6)	2.4084(10)
		Bond Angles	
P−Pt−P	161.26(6)	177.57(2)	176.12(3)
L−Pt−C51	180	176.48(7)	178.29(13)
P−Pt−L	80.63(3)	87.45(2)−91.38(2)	89.05(3)−89.10(4)
P−Pt−C51	99.37(3)	89.30(7)−92.00(7)	90.39(14)−91.36(14)
	Dihedral Angle between the Pt Coordination Plane and the NCN Aryl Plane		
	76.2(2)	89.9(1)	85.5(2)

[a] L = Cl ([**b**] and [**7**]), C1 ([**4**]).

interactions, functions rather as a 2e donor (monofunctional Lewis base) than as a 4e donor (bifunctional Lewis base, Figure 2a).[21]

Neutral Pt(PCP)(NCN) Complex 5. The second product obtained by fractional precipitation of a solution of **[3]Cl** is identical to the product which is isolated after treatment of **[3]Cl** or **[4]Cl$_2$** with an excess of base (e.g., NEt_3) and has been characterized as complex **5** (Scheme 5). Due to its neutral character, **5** is much better soluble in organic solvents than the ionic complexes **[3]Cl** or **[4]X$_2$**. When the spectroscopic properties of **5** are compared to those of the corresponding ionic complexes, the absence of acidic protons is an obvious difference. In addition, the singlets due to the NCH_3 and $ArCH_2N$ protons are shifted to higher field and are located at 1.56 and 3.05 ppm, respectively. Only small shift differences of the benzylic $ArCH_2P$ signals (δ_H = 4.14, $^3J_{HPt}$ = 28.3 Hz) and the phosphorus signal (δ_P = 31.6, $^1J_{PPt}$ = 3052 Hz) are observed.

Various attempts to crystallize **5** resulted invariably in the formation of thin needles which had a low diffractive response. Hence, the obtained crystal data set is of a quality which is too low for the detailed discussion of structural aspects (bond lengths and angles). Preliminary studies suggest, however, a molecular connectivity pattern as anticipated from investigations on the

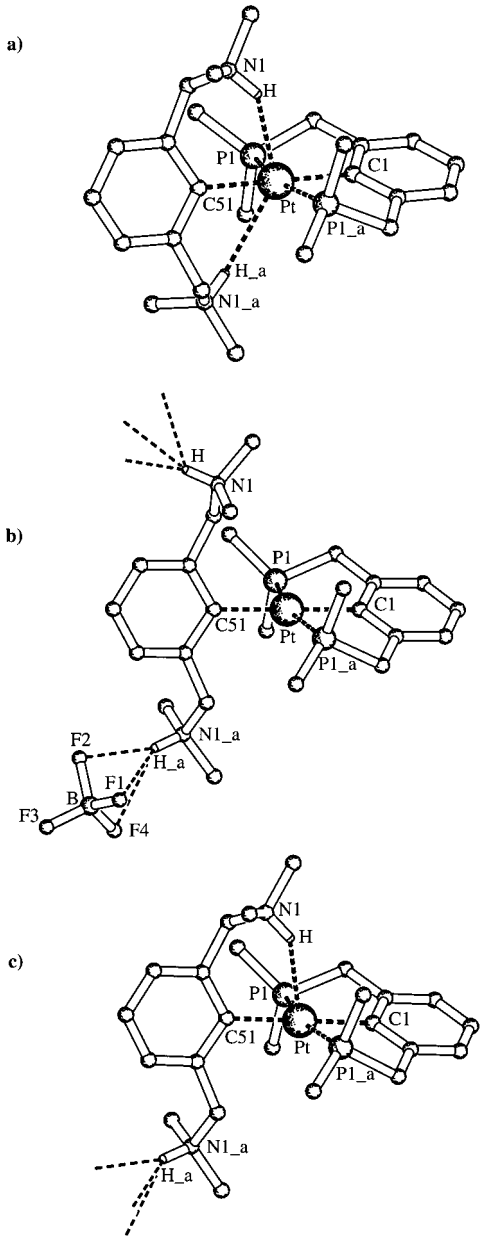


Figure 2. Molecular structures of complex **[4](BF$_4$)$_2$**, showing the two disordered models (occupancy factor 0.5 each). The carbon-bound hydrogen atoms and also the phenyl substituents on phosphorus (except C_{ipso}) have been omitted in the representations: (a) The $NHMe_2$ groups are bent toward the metal center, giving rise to intramolecular N−H···Pt bonding. (b) The NMe_2 groups are directed away from the platinum nucleus toward the BF_4 anion, resulting in N−H···F hydrogen-bonded anion−cation pairs. (c) Superposition of the two structures shows intramolecular N−H···Pt hydrogen bonding and also cation−anion interactions in the same molecule.

structure of **5** in solution. This comprises a platinum nucleus as the center of a (distorted) square plane defined by the two phosphorus nuclei and the two *ipso*-carbons from the PCP ligand and the NCN ligand, respectively. Furthermore, the aryl plane of the monodentate binding NCN pincer ligand seems to be orientated perpendicular to the central aryl ring of the PCP ligand. Such a conformation has been found in other complexes containing two aryl units in mutual trans position and can be justified by considering both stereochemical (vide supra) and electronic arguments (orbital situation at the metal center and at the aryl units).[22]

(21) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, P. A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484.

The neutral complex **5** contains tertiary amines and in the presence of an acid HX therefore rapidly interconverts to the dicationic complex **[4]X$_2$**. For example, the addition of HBF_4 to **5** results in the quantitative formation of **[4](BF$_4$)$_2$**. However, in the presence of a large excess of acid, e.g., HCl, **[4]X$_2$** undergoes Pt−C bond cleavage, resulting in the formation of the transmetalated product PtCl(PCP) with concomitant elimination of the *meta*-bis(ammonio)arene $[C_6H_4\{CH_2NHMe_2\}_2\text{-}1,3]^{2+}$ as a water-soluble dichloride salt.

Intermediates Preceding the Formation of Pt(PCP)(NCN), 5. When the reaction of PCHP with PtCl(NCN) is carried out in C_6H_6 at *room temperature* (instead of 80 °C), a white powder is formed, which has been identified as the dimetallic complex **6** (Scheme 4). This dimeric Pt_2 species is hardly soluble in $CHCl_3$ and insoluble in C_6H_6. Its complicated ^{31}P NMR spectrum ($CDCl_3$ solution) has been analyzed by simulations, which point to the presence of two chemically inequivalent, mutually trans-positioned ^{31}P atoms (see Supporting Information). The calculated positions of the resonance signals and of the corresponding coupling constants ($\delta_{PA} = 10.5$, $\delta_{PB} = 18.2$ ppm; $^2J_{PAPB} = 429$ Hz, $^1J_{PAPt} = 3041$ Hz, $^1J_{PBPt} = 3069$ Hz) fit the measured data excellently. From the ^{1}H NMR spectra, further evidence is gained for a low symmetry of this complex. For example, eight different (partially overlapping) benzylic ^{1}H signals have been found between 5.4 and 1.9 ppm. From ^{1}H−^{1}H COSY measurements they were all identified as parts of AB doublets, some of them displaying $^2J_{HP}$-type interactions to phosphorus. Another indication for a highly dissymmetric complex is the two different signals due to the NCH_3 protons, located in a 1:1 ratio at 1.87 and 1.37 ppm, respectively. These chemical shift values and the absence of any coupling resonances with the ^{195}Pt nucleus are characteristic for two different noncoordinated amines. All of the observed proton resonances are rather broad and suggest a dynamic behavior of the molecule. Remarkably, one sharp singlet is found at 9.93 ppm, which displays only a weak cross-peak in the ^{1}H−^{1}H COSY spectrum, related to a $^4J_{HH}$ coupling with the aromatic protons of the central phenyl unit of the PCHP ligand. Hence, this resonance has been attributed to the C1-bound proton PC*H*P. Unambiguous evidence for the assignment of this signal has been provided by an experiment using PCDP, a modified PCHP ligand precursor containing a deuterium substituent on carbon C1. When PtCl(NCN), **1,** is treated with equimolar amounts of PCDP, again a white precipitate, **6**-D, is formed. Its ^{1}H and ^{31}P NMR spectra are fully identical with those of **6** except for the absence of the signal at 9.93 ppm in **6**-D.

When compared to the line width of the other signals of **6**, the remarkably sharp signal due to the PC*H*P protons is pointing to a reduced dynamic behavior in this part of the molecule. Together with the extraordinary large downfield shift of this aromatic proton (more than 1.2 ppm downfield from the other aryl-bound protons in **6**), an additional stabilization by weak interactions can be deduced, e.g., owing to hydrogen bonding of the C1-bound proton to a heteroatom. Detailed elucidation of the structure of **6** in the solid state has been achieved by a single-crystal X-ray structure determination.

Neutral [PtCl(NCN)(PCHP)] Complex 6. The molecular structure of **6** in the crystal is depicted in Figure 3 and shows a bimetallic 16-membered macrocycle comprising two PCHP ligands bridging between two square-planar coordinated platinum(II) centers. An inversion center relates, e.g., the two platinum centers to each other (C_i symmetry). Each of the platinum centers is bound to a chloride as well as to a η^1-*C*-bonded NCN ligand (through C51), while both nitrogen atoms of the amino substituents are not coordinated (Table 4). The structure clearly demonstrates the reduced symmetry of the NCN and PCP ligands in the solid state, which parallels the dissymmetry observed for **6** in solution (cf. the ^{1}H NMR pattern revealing eight different benzylic protons and two inequivalent NCH_3 groups). These observations strongly suggest that the structure of **6** in the solid state is retained in solution. Perhaps the most intriguing aspect of the molecular structure is the particularly short distance found between the C1-bound proton and chloride (H1···Cl = 2.66(3) Å; angle C1−H1···Cl is 153(2)°), suggesting intramolecular noncovalent C−H···Cl hydrogen bonding (Figure 3).[23] Additional short contacts of particular relevance in view of a subsequent cyclometalation reaction have been found around the metal center; i.e., the distances Pt···C1 (3.568(3) Å) and Pt···H1 (2.88(3) Å) are both slightly shorter than the sum of the corresponding van der Waals radii. These structural features are in good agreement with earlier reported data on related palladium complexes.[24]

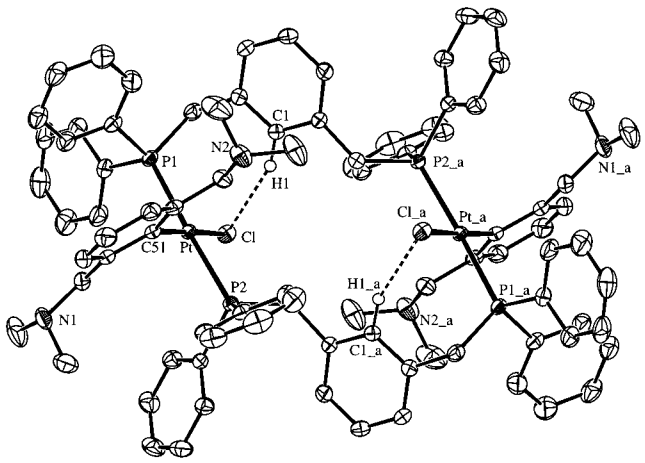


Figure 3. Perspective view (50% probability) of **[6]·4C$_6$H$_6$** showing the adopted numbering scheme. Hydrogen atoms except H1, and the included solvent molecules have been omitted for clarity. Note the short intramolecular contacts in the macrocycle of **6** (Pt···C1 3.568(3) Å; Pt···H1 2.88(3) Å) and the hydrogen-bonding motif (Cl···H1 2.66(3) Å; Cl···C1 3.554(3) Å; C1−H1···Cl 153(2)°).

Monitoring of the Transcyclometalation Process. The formation of the dimetallic complex **6** has been followed by ^{1}H and ^{31}P NMR spectroscopy. Upon mixing of the metal precursor PtCl(NCN), **1**, and the phosphine PCHP in C_6D_6 at room temperature, the signal due to free PCHP ($\delta_P = -9.9$) disappears instantaneously (^{31}P NMR). Instead, a new singlet is observed at 17.6 ppm, which originates from two equivalent phosphines that are trans-bound to a platinum center ($^1J_{PPt} = 3005$ Hz; vide infra complex **7**). Consequently, formation of a dimeric species **A** immediately after mixing of the reactants is assumed (see Scheme 4). This is corroborated by the high-field shift of the signals due to $ArCH_2N$ and NCH_3 in the ^{1}H NMR spectrum, which is diagnostic for noncoordinating amine ligands.[9a] Complex **A** slowly reacts in solution, as is unambiguously demonstrated by ^{31}P NMR spectroscopy; the signal at 17.6 ppm gradually disappears and concomitantly a new set of signals appears, which corresponds to that of **6**. These changes are linear in time and suggest therefore (pseudo-) zero-order

(22) Terheijden, J.; van Koten, G.; Muller, F.; Grove, D. M.; Vrieze, K.; Nielsen, E.; Stam, H. C. *J. Organomet. Chem.* **1986**, *315*, 401.

(23) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(24) Khare, G. P.; Little, R. G.; Veal, J. T.; Doedens, R. J. *Inorg. Chem.* **1975**, *14*, 2475.

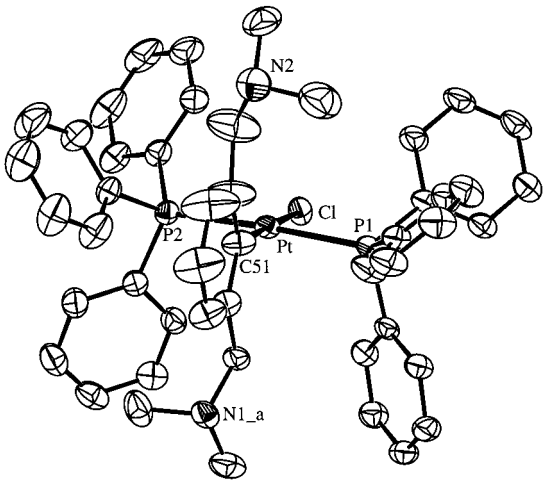


Figure 4. Displacement ellipsoid plot representation (50% probability) of **[7]·1/6C_6H_{14}** showing the adopted numbering scheme. Only one of the two positions for the NCH_3 group is shown (50% occupancy). All hydrogen atoms and the solvent residue have been omitted.

reaction kinetics for the rate-determining step of this probably intramolecular process.

Following the formation of **6** by ^{1}H NMR spectroscopy confirms these conclusions. Immediately after mixing of **1** and PCHP, a signal pattern is observed which is fully consistent with the presence of **A** only. Within the subsequent 0.5 h, all these resonances broaden significantly, and eventually, gradual appearance of broad resonances due to **6** (and likewise concomitant disappearance of those assigned to **A**) is noted. These new signals remain broad with exception of the signal at 9.93 ppm, assigned to the C1-bound proton PC*H*P (vide supra).

The formation of **A** and hence fast replacement of the amine ligands by phosphorus donors has been studied in a separate experiment. Mixing of **1** with 2 mol equiv of PPh_3 under identical conditions as applied for the preparation of **6** affords a single product **7**, containing the two phosphine ligands mutually trans positioned and an η^1-*C*-bonded NCN ligand (Scheme 4). As expected, the spectroscopic properties of **7** are very closely related to the data earlier obtained for [PtBr(η^1-NCN)(PPh_3)$_2$][9a] and show also high similarities to those of **A** (see Tables 1 and 2).

In contrast to **A**, its mononuclear analogue **7** is inherently stable in the solid state and in solution, which allowed detailed analyses (Tables 1−3) by a single-crystal X-ray structure determination. The molecular structure shows a square-planar platinum(II) complex which possesses two PPh_3 ligands in mutually trans configuration and a monodentate *C*-bonded NCN ligand (Figure 4). As a result, the Pt−C51 bond is stretched from 1.907(5) in **1** to 2.043(4) Å in **7**. In contrast, the Pt−Cl bond is hardly affected (Table 4). In addition, the NCN aryl plane in **7** is oriented perpendicular to the coordination plane of the platinum(II) center, which contrasts to the almost coplanar situation in **1** (vide supra).

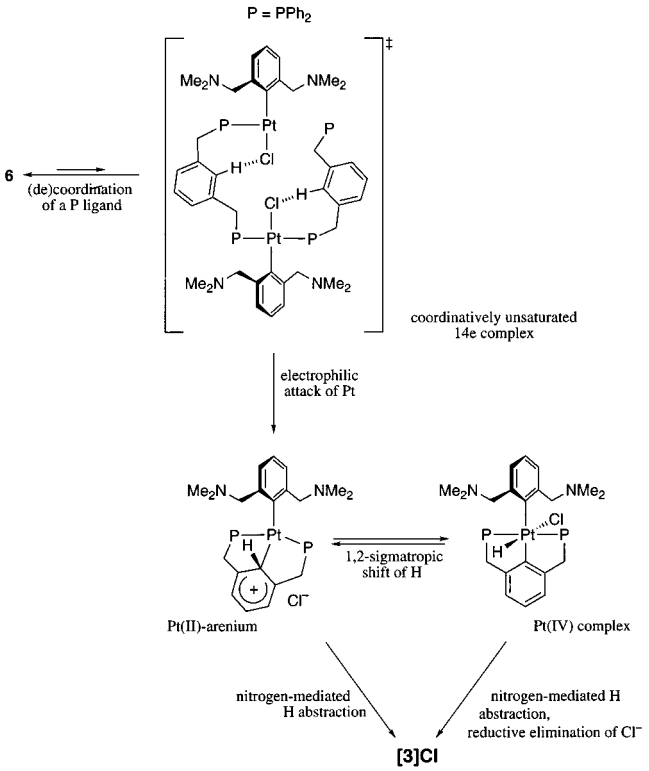
Discussion

The present transcyclometalation reaction has no precedent in that various intermediate stages in the process could be isolated and identified. Moreover, a sequence of intermediates could be established comprising the rapid formation of **A** and its conversion to dimeric **6** at room temperature, formation of the monoprotonated bisaryl product and its redistribution to the neutral bisarylplatinum and the bis-protonated derivatives (cf. **5** and **[4]X_2**) below 80 °C, and finally the formation of the transcyclometalated product **2** and the corresponding arene NCHN at 110 °C after prolonged heating. This transcycloplatination process of the PCHP ligand precursor is occurring with high stereoselectivity as only one C−H bond, *ortho*, *ortho* orientated to the phosphorus-containing substituents, is activated.[5a−f] It must be noted that the transcyclometalated product **2** has been obtained quantitatively from the bis(*ortho*-)cyclometalated compound **1**. The latter PtX(NCN) complex is known to have an exceptional stability and a high resistance toward various reagents as HCl.[25] In this context, the formation of **2** from PtCl(NCN) **1** is remarkable and represents the first detailed example of a transcyclometalation reaction in organoplatinum(II) chemistry.[12,14d−e] From this study it is obvious that the transcyclometalation reaction is a multistep process. In the next sections, the importance of the various unique structural features of the various intermediates will be discussed.

Ligand Substitution and C−H Bond Activation. Previous reports have shown that substitution of a (relatively) weakly coordinated ligand by an incoming stronger bonding ligand initiates the cyclometalation reaction.[2] Accordingly, addition of PCHP to the cyclometalated platinum precursor **1** is expected to result in replacement of the hard amine ligands by phosphine ligands, which are known to be much softer σ donors;[26] cf. the formation of [PtBr(η^1-NCN)(PPh_3)$_2$][9a] from [PtBr(NCN)] and PPh_3 as well as the formation of **7** in the present study. Clearly, in these complexes, bis(*ortho*-)chelation of the NCN ligand does not compensate for the stronger bonding of platinum(II) to phosphorus ligands.[27] A similar reactivity has been observed between the platinum precursor **1** and PCHP, affording dimeric **A** as the initially detectable product, in which the PCHP ligand bridges between two platinum centers. Coordination of the two phosphorus donor atoms of the PCHP ligand to the same platinum nucleus, i.e., an η^2-*P*,*P*-bonding mode as found in [(PCP)Ru(PCHP)](OTf)[11] apparently is not favored.[28] Complex **A** (symmetry D_{2h}) is thermodynamically unstable and spontaneously rearranges to the conformational isomer **6**, which displays a lower symmetry (C_i). The bimetallic complex **6** is unprecedented, and its formation from **A** demonstrates the extra stabilization brought about by formation of the C−H···Cl bonding. Most importantly, the noncovalent hydrogen bonding interactions (C_{aryl}-H···Cl) have been established both in the solid state (X-ray) and in solution (NMR, IR). Computational studies have suggested that noncovalent hydrogen bonds play a significant role in C−H bond activation.[29] The dimeric complex **6** seems to illustrate this view, since it displays an extraordinary high degree of steric and electronic preorganization for cyclometalation, mainly imposed by the hydrogen-bonding motif. First, the metal center is located in close proximity to H1 and, more importantly, also to C1. Second, the C_{aryl}–H bond is considerably weakened by the interaction of the proton with the metal-bound chloride and may be envisaged as an "activated" bond. Third, the electrophilicity of the platinum center is significantly increased (reduced σ donation of the chloride to the metal center due to competitive electron release into the noncovalent C_{aryl}-H···Cl hydrogen bond). In contrast, the arene system (predominantly C1) possesses an enhanced electron

(25) Albrecht, M.; van Koten, G. *Adv. Mater*. **1999**, *11*, 171.
(26) (a) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79. (b) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339.
(27) In the corresponding Ni(II) complexes, chelation of the NCN ligand vs phosphine coordination is strongly dependent on the nature of the amines; see: van Beek, J. A. M.; van Koten, G.; Ramp, M. J.; Coenjaarts, N. C.; Grove, D. M.; Goubitz, K.; Zoutberg, M. C.; Stam, C. H.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 3059.
(28) Shaw, B. L. *Adv. Chem. Ser.* **1982**, *196*, 101.
(29) Mohr, M.; Zipse, H. *Chem. Eur. J.* **1999**, *5*, 3046.

Scheme 6



density, imposed by the stronger polarization of the C1−H1 bond (vide NMR data). Therefore, this is a predestinated system for electrophilic substitution reactions (cf. activated arene moiety, electrophilic platinum(II) nucleus as E^+).

Cyclometalation Process. In view of this intramolecular preorganization in **6** in the solid state as well as in solution, it is no surprise that cyclometalation of **6** (in hot C_6H_6) indeed occurs, yielding complex **[3]Cl**. Due to the poor solubility properties of **6**, no (spectroscopic) evidence could be obtained whether **6** represents a true kinetic *intermediate*[30] in the cyclometalation process of the PCHP ligand or a *resting state* (i.e., a thermodynamic "sink", thus involving regeneration of the higher symmetrical complex **A** as essential step for successful C−H activation). Moreover, it is possible that either prior Pt−P bond dissociation occurs leading to a 14e arylmetal chloride species with a monodentate coordinated PCHP ligand[2d,12] or a monometallic η^2-E,E-coordinating intermediate is formed which precedes the cyclometalation step.[31] It is interesting to note, however, that similar dinuclear complexes containing the PC(Me)P ligand (type **A** coordination) do not form subsequently type **6** complexes with intramolecular hydrogen bonds and also do not undergo any cyclometalation reaction.[32]

Considering the various aspects outlined above, the following mechanism for the cyclometalation of the PCHP ligand in **6** is proposed (Scheme 6): eventual dissociation of a Pt−P bond in **6** affords the reactive intermediate, a strongly electron-deficient coordinatively unsaturated 14e metal center.[3c,33] Recoordination of the phosphorus ligand is expected to quench the reaction successfully, which might provide another reason for the long reaction time required for the formation of **[3]Cl** (vide supra). In the forward process, the arene moiety of the PCHP ligand may supply additional electron density to the deficient metal center. This is inducing an electrophilic aromatic substitution process by the platinum center and formation of an arenium intermediate.[7,34] As evidenced in related platinum arenium chemistry,[10a] a subsequent reversible 1,2-sigmatropic migration of the proton H1 from C1 to the metal center leads to a platinum(IV) product. Such platinum(IV)−hydride complexes have been shown to be reasonably stable when a strong base is coordinated trans to the metal-bound hydride.[17,21,35] In the present system, this is achieved by intramolecular attack of the noncoordinating tertiary amines of the NCN ligand. Alternatively, the amine substituents assist in stabilizing the hydrogen by acting as a base and hence by formation of a N−H···Pt bonding motif. This weakens the H···Pt interaction and eventually affords a cationic ammonium entity, concomitant with the reduction of the metal center to platinum(II). Formally, this corresponds to an intramolecular, nitrogen-mediated reductive elimination of HCl from a platinum(IV) complex, affording **[3]Cl**. This sequence implies that, during the cyclometalation process, Pt−Cl bond cleavage in the metal precursor is preferred over Pt−C_{aryl} bond fission under the applied conditions (C_6H_6, 80 °C), and hence, HCl is (formally) released as a byproduct (Scheme 4). Obviously, the intramolecular stabilization of the platinum(IV) intermediate prevents further migration of the hydrogen by a second 1,2-sigmatropic shift onto the NCN ligand. A second pathway, which is sterically rather unfavored, would involve direct nitrogen-assisted proton abstraction from the arenium complex, without passing through an oxidation−reduction cycle of the platinum center (Scheme 6).

Formation of [Pt(PCP)(NCN)], **5**, could point to an associative mechanism involving an octahedral platinum(IV) center comprising a metal-bound chloride and a hydride ion.[17] However, as follows from the present results, some other intermediates are preceding the formation of **5**, of which $[Pt(PCP)(NCNH)]^+$, $\mathbf{[3]}^+$, is an important one. This clearly corresponds to a kinetic product as a change of the solvent leads to irreversible formation of neutral [Pt(PCP)(NCN)], **5**, and dicationic $[Pt(PCP)(NHCNH)]^{2+}$, $\mathbf{[4]}^{2+}$.

Notably, treatment of **5** with a large excess of an acid HX results initially in the ionic complex $\mathbf{[4]X_2}$. Subsequently, cleavage of the nonstabilized Pt−C bond is promoted and corresponds to the formal completion of the transcyclometalation reaction forming the product [PtX(PCP)], **2** (X = e.g. Cl) and the arene NCHN. This last stage probably involves an oxidative addition−reductive elimination sequence with intermediate formation of a platinum(IV)−hydride complex [Pt(X)(H)(PCP)(NCN)] as indicated in Scheme 6.[3c,17c]

Finally it should be noted that the transcyclometalation reaction presented here takes place under neutral conditions and without auxiliaries. Previously used catalysts (e.g. by using HOAc or $HOAc^F$ as a solvent)[12] may be disadvantageous for such TCM reactions, as a proper choice of the solvent system

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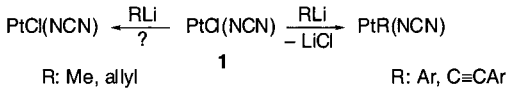
greatly stabilizes the transition state(s) and/or lowers the activation energy for its formation. Addition of an acid as catalyst implies, however, that H^+ is facilitating e.g. the M−N bond cleavage by protonation of the dissociated (free) nitrogen ligand.

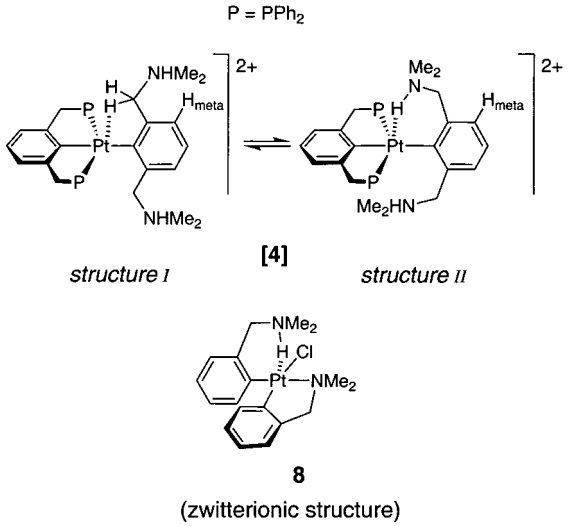
Another cyclometalation mechanism involving heteroatom induced proton abstraction in **6** *before* electrophilic aromatic substitution may be discarded, since addition of weak bases (intramolecularly present as $R-NMe_2$ entities) or strong bases (NaOH, K_2CO_3) to **6** did not accelerate the formation of **[3]Cl**. Similarly, the reaction of the cationic platinum solvato complex $[Pt(NCN)(H_2O)](BF_4)$ with PCHP did not cause any product containing a cyclometalated PCP ligand.[36] These findings are consistent with the proposed mechanism (Scheme 6) and emphasize the crucial influence of the electronic properties of the metal center and of the presence of a platinum−halogen bond. The high significance of the trans C−M−X arrangement in similar square-planar complexes is well-documented.[9,37] This is further underlined by the fact that addition of $AgBF_4$ to **6** only affords the solvato complex $[Pt(NCN)(H_2O)](BF_4)$. Its formation is probably preceded by cleavage of the H···Cl hydrogen bonded assembly due to silver-mediated chloride abstraction. This reduces the preorganization for cyclometalation as found in dimer **6** and, more importantly, probably increases the electrophilic character of the metal center to such an extent that the crucial P−Pt bond cleavage and formation of the unsaturated 14e intermediate is fully inhibited.

This cycloplatination reaction provides a mild access to platinum(II) complexes containing two C−Pt σ-bonds. Commonly, cyclometalation is used for the introduction of the first M−C σ-bond. Cases where this route can be applied for the preparation of a second M−C σ-bond are rare.[14e,38] Noteworthy, alternative routes for the preparation of stable compounds of the type [PtR(NCN)] (R = aryl, alkyl, alkyne) containing two M−C bonds exist, e.g., by reacting **1** with RLi. However, little is known about this reaction. For example, it has been shown that for R = tolyl or phenylacetyl, a second M−C bond is formed with concomitant elimination of LiCl.[22] In contrast, alkyllithium reagents (R = allyl, Me) result in the formation of **1** only instead of the alkylated products (eq 3). In the case of [Pt(NCN)(C≡CR)], it has been shown that the reaction with CuCl affords [PtCl(NCN)] and Cu(C≡CR).[39] A similar preference for the cleavage of the Pt−C bond trans to carbon C1 by LiCl could be responsible for the observed result.



Transcycloplatination vs Transcycloruthenation of PCHP Ligands. When a ruthenium(II) complex analogous to **1**, [RuCl(NCN)(PPh_3)], is used as the metal precursor for the cyclometalation of PCHP, elimination of NCHN is observed; i.e., this transcyclometalation process does not involve Ru−Cl bond cleavage and concomitant HCl formation but rather Ru−C_{aryl} bond cleavage (cf. Scheme 6).[10] Ultimately, both reactions produce the transcyclometalated products but apparently via different routes; i.e., the transcycloplatination of **1** proceeds via Pt−Cl bond cleavage and formation of the bisarylplatinum species, whereas transcycloruthenation apparently occurs via H transfer. Note that both transcyclometalations have to proceed from the neutral species. This identifies the $[Pt(NCN)]^+$ and the $[RuCl(PPh_3)]^+$ units as isolobal monocationic ML^+ synthons. The selectivity in cleaving either the M−Cl or the M−C bond, viz. elimination of either first HCl or NCHN directly, probably originates from the different nature of the relevant (metal-centered) frontier orbitals in the corresponding ruthenium or platinum arenium intermediates during the cyclometalation process (Scheme 6). In a d^8 metal center (platinum(II) complexes), electron density perpendicular to the platinum coordination plane (viz. a d_{z^2}-type orbital) can participate in stabilizing a proton by chelation.[40]

Scheme 7



Organometallic Proton Sponges. Various similar *trans*-bis(aryl)platinum(II) complexes are known that contain aminoaryl type ligands.[22] Characteristic to these complexes is a hindered rotation around the Pt−C σ-bond of the η^1-bonded aryl ligand and the approximately perpendicular position of the nonchelating aryl ligands with respect to the metal coordination plane. For complexes **3**−**5**, a similar conformational situation has been found, which is particularly emphasized due to the presence of two sterically bulky ortho-substituents on the η^1-coordinating aryl unit (see Pt−C(51)). Hence, two limiting isomeric structures for the positioning of the ammonium groups and the source of the heteroatom stabilization of the acidic protons in the dicationic complex **[4]Cl_2** exist: either the nitrogen nuclei are directed toward the metal center (structure I, Scheme 7) or they

(36) Equimolar amounts of PCHP and $[Pt(NCN)(H_2O)](BF_4)$ were stirred in THF at reflux for several hours. As indicated by the diagnostic ^{31}P NMR spectrum ($\delta_P = 41$), the obtained product contains a coordinated phosphine trans to the metal-bound carbon of the terdentate-bonded NCN ligand; for similar reactivities, see: Maassarani, F.; Davidson, M. F.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, M. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1995**, *235*, 327.

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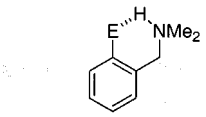
(40) Hence, a 3c−4e Pt···H···N bond is formed,[17] which promotes the (reversible) 1,2-sigmatropic migration of the hydrogen onto the metal center. In contrast, stabilization of a metal-bound hydrogen in the hypothetical *z*-axis of the corresponding ruthenium(II) complex is much less pronounced (d^6 configuration, d_{z^2} orbital empty). Hence, the equilibrium between a cationic ruthenium(IV) complex and an arenium (either a NCN- or PCP-arenium system) is shifted onto the arenium side. In both arenium structures, the M−$C_{arenium}$ bond is weakened. Whereas Ru−C bond fission is hampered in the PCP ligand due to chelation of the phosphines, this bond is relatively labile in the NCN-arenium moiety (η^1-*C*-bonded). Consequently, Ru−C bond breaking of the NCN-arenium ligand results in the formation of [RuCl(PCP)(PPh_3)] and elimination of NCHN. The different reactivities of the platinum(II) and ruthenium(II) metal precursors therefore indirectly support the mechanism as proposed in Scheme 6.



E = NMe_2; protonated 'proton sponge'
E = Pt(PCP); **[3]X** or **[4](X)$_2$**

Figure 5. Structural similarities between organic and organometallic proton sponges.

are oriented away from platinum (structure II). Structure I represents an organometallic analogue of the organic "proton sponge",[41] with one amine nitrogen substituted by an electron-rich platinum center (Figure 5). This *N,Pt*-system displays an excellent donor motif for selective proton scavenging via 3c−4e N−H···Pt(II) interactions and hence a rare example of an organometallic proton sponge.[17,42] Strongly related zwitterionic platinum(II) complexes, viz. *cis*-[PtX(C∼N)(C∼NH)] (X = Cl, Br; C∼N = $C_6H_4\{CH_2NMe_2\}$-2), **8** (Scheme 7), have been reported, which contain unprecedented N−H···Pt hydrogen bonds.[17] In these structures, a diagnostic ^{1}H NMR signal of the interlocked N−*H*···Pt(II) proton appeared between 13 and 16 ppm, which showed ^{195}Pt coupling resonances.[43] The size of these coupling constants correlates directly with the structural position of the proton between nitrogen and platinum; i.e., the larger the coupling constant the smaller the Pt···H distance and the longer the N−H bond. In analogous platinum(IV) complexes containing a metal-bound hydride rather than a metal-stabilized proton, a signal at ca. −20 ppm is observed.[21] When these data are compared with the observed values of **[4]Cl$_2$** (δ_H = 11.8 ppm, no $^1J_{HPt}$ resolved), Pt···H interactions in solution may be deduced for **[4]Cl$_2$**, which are relatively weak. This is further corroborated by the ^{1}H−^{1}H NOESY spectrum, which clearly revealed cross-peaks stemming from nuclear Overhouser effects (nOe's) between the spins of the H_{meta} protons of the monodentate zwitterionic NHCNH ligand (Scheme 7) and *both* the NCH_3 groupings and the benzylic $ArCH_2N$ protons. Similarly, the characteristic IR data of **[4]Cl$_2$** show a broad vibration band observed at 2480 cm^{-1} (assigned to the asymmetric stretching mode ν_{as} of the N−H bond), which is higher than the strongly interlocked N−H stretch vibration in the organometallic N−H···Pt proton sponge **8** (2340 cm^{-1})[17] but considerably lower than the expected ν_{as} of N−H bonds in free ammonium compounds (2700 cm^{-1}).[44] A rather weak interaction between the platinum(II) center and the nitrogen-bound proton is also supported by solid-state analyses, which indicate disordered CH_2NHMe_2 units in the single crystals of **[4](BF$_4$)$_2$**.

The N−H···Pt hydrogen bond motif directly reflects the proton sequestering capacity of the *organometallic* proton sponges **[4]X$_2$** and **8** and their corresponding deprotonated precursors. The difference in strength is best understood by considering the situation at the platinum center: in the case of **8**, a zwitterionic structure is present which comprises an ammonium unit and a platinate, whose anionic charge increases the donating nature of filled d_{z2}-type orbitals significantly. In the dicationic complex **[4]X$_2$**, however, the metal center is neutral, which reduces its donating properties and therefore weakens the chelation strength. Another important aspect for the effectiveness of (organometallic) proton sponges is the steric constrain of the skeleton connecting the two donor atoms. Due to the aryl backbone in **[4]X$_2$** and **8**, the nitrogen donor is held rigidly in a place above the platinum coordination plane, which forces the proton to be located also in close proximity to a mutual d_{z2} orbital of the metal center. This deshielding effect is confirmed by the chemical shift values of the interlocked proton, which is at lower field when the N−H···Pt skeleton is more rigid.

Conclusion

Transcyclometalation, i.e., the substitution of one cyclometalated ligand by another, has been used as a versatile methodology which provides a novel access to metal-to-carbon bonds. This concept has been applied for the substitution of a bis(*ortho*-)cyclometalated NCN ligand on a platinum center by a terdentate bonding PCP-type pincer ligand under neutral conditions.

An essential prerequisite for successful transcyclometalation in the present case is the difference in bond strength of the platinum−heteroatom bond, which has to be stronger in the product than in the reactant (viz. Pt−P stronger than Pt−N bond). A reaction trajectory is favored that is similar to that of electrophilic aromatic substitutions. Hence, transcyclometalation is proposed to be initiated by weak C−H···Cl−M hydrogen bonds, which induce a remarkable substrate−reactant preorganization and presumably promote the transient arenium formation.

Another intriguing intermediate that has been detected during the transcyclometalation of **1** is the organometallic complex **5**, which displays typical characteristics of organic proton sponges. This is a consequence of the fixed proximity of the electron-rich platinum(II) center to the lone pairs of the noncoordinating nitrogen nuclei. Hence, this *Pt,N* chelating unit is capable of sequestering an equimolar amount of protons, leading to the formation of mono- or bis-protonated organoplatinum complexes, e.g. **[4](BF$_4$)$_2$**.

Finally it is important to note that at the present state of our studies it is clear that the reaction profile outlined in this report displays only *one of probably several different reaction mechanisms* of the transcyclometalation process (cf. [PtCl(NCN)] vs [RuCl(PPh)(NCN)]). However, it is very well possible that a limited, well-defined set of routes exists. Which mechanism is operative is strongly dependent on the nature (hardness, acidity) of the metal center and the ligands. Moreover, a proper choice of auxiliaries, such as catalytic or stoichiometric amounts of AcOH, may either accelerate or inhibit transcyclometalation. Reinvestigation of previously reported, though not as such recognized, transcyclometalations could be a fruitful approach to obtain valuable information about various pathways for conversion of an aromatic C−H bond into the corresponding aryl−metal bond.

Experimental Section

General Comments. All reactions involving free phosphines were performed under an atmosphere of N_2 using standard Schlenk techniques. Pentane, toluene, and C_6H_6 were distilled from Na−benzophenone, and CH_2Cl_2 was distilled from CaH_2. Starting materials were obtained commercially (PPh_3) or prepared according to published procedures (PCHP,[15] [PtCl(NCN)][9b]). Elemental analyses were obtained from Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). Incorporated solvent molecules were identified by NMR spectroscopy.

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Table 5. Crystallographic Data for Complexes **[4](BF$_4$)$_2$**, **[6]·4C$_6$H$_6$**, and **[7]·1/6C$_6$H$_{14}$**

	[4](BF$_4$)$_2$	**[6]·C$_6$H$_6$**	**[7]·1/6C$_6$H$_{14}$**
empirical formula	$C_{44}H_{48}N_2P_2Pt\cdot 2BF_4$	$C_{88}H_{94}Cl_2N_4P_4Pt_2\cdot 4C_6H_6$	$C_{48}H_{49}ClN_2P_2Pt\cdot 1/6C_6H_{14}$
fw	1035.49	2105.06	960.74
cryst system	monoclinic	monoclinic	triclinic
space group	*C*2 (No. 5)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cryst size/mm	0.15 × 0.15 × 0.08	0.25 × 0.25 × 0.13	0.36 × 0.33 × 0.21
cryst color	colorless	colorless	colorless
unit cell dimens			
a/Å	12.8866(3)	13.0416(2)	11.5811(3)
b/Å	15.9008(3)	15.5605(3)	12.4431(3)
c/Å	12.1765(3)	24.1866(5)	17.6349(5)
α/deg	90	90	70.7122(10)
β/deg	121.535(1)	92.638(1)	84.1765(11)
γ/deg	90	90	69.4615(13)
V/Å^3	2126.58(8)	4903.08(16)	2245.87(10)
Z	2	2	2
D_{calc}/g cm^{-3}	1.617	1.426	1.421
μ/mm^{-1} (Mo Kα)	3.444	3.020	3.289
abs corr	PLATON (DELABS)	PLATON (MULABS)	PLATON (MULABS)
transm range	0.24−0.70	0.61−0.68	0.34−0.43
(sin θ/λ)$_{max}$/Å^{-1}	0.61	0.65	0.65
reflcns measd, unique obsd	18 789, 3974, 3972	91 192, 11 238, 9612	43 828, 10 268, 9219
R_{int}	0.073	0.067	0.061
params, restraints	296, 95	567, 0	517, 39
R_1[a] (obsd/all reflcns)	0.0278/0.0278	0.0261/0.0362	0.0351/0.0408
wR_2[b] (obsd/all reflcns)	0.0703/0.0703	0.0551/0.0585	0.1017/0.1050
S	1.04	1.04	1.07
resid density/e Å^{-3}	−0.67 < 0.76	−1.24 < 1.08	−1.99 < 2.11

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

All NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C), and 121 MHz (^{31}P), respectively, in $CDCl_3$ solution (25 °C), unless stated otherwise. Internal $SiMe_4$ (^{1}H and ^{13}C) and external H_3PO_4 (^{31}P) were used as references ($\delta = 0.00$ ppm, *J* in Hz; see Tables 1−3). Infrared measurements were performed on a Perkin-Elmer FT-IR spectrometer using $CHCl_3$ as solvent.

[PtCl(PCP)], 2. A solution of PCHP (90 mg, 190 μmol) and PtCl(NCN) (80 mg, 190 μmol) in toluene (10 mL) was heated to reflux temperature for 3 days. The formed precipitate was filtered off, and all volatiles of the filtrate were evaporated in vacuo. The white residue (131 mg, 98%) was recrystallized from CH_2Cl_2 (2 mL), which was carefully layered with pentane (10 mL). This yielded colorless crystals of **2**. The spectroscopic properties of **2** are in full agreement with the reported data.[15]

[Pt(PCP)(η^1-*C*-C$_6$H$_3${CH$_2$NMe$_2$}-2-{CH$_2$NHMe$_2$}-6)]Cl, [3]Cl. A solution of PCHP (110.8 mg, 234 μmol) and PtCl(NCN) (100.2 mg, 238 μmol) in C_6H_6 (10 mL) was refluxed for 3 days. The white precipitate, which had gradually formed, was collected, washed with cold C_6H_6 (2 × 1 mL), and dried in vacuo to afford **[3]Cl**, quantitatively. Anal. Found (calcd for **[3]Cl**·1.5C_6H_6): C, 63.00 (62.81); H, 5.68 (5.57); N, 2.67 (2.76).

[Pt(PCP)(η^1-*C*-C$_6$H$_3${CH$_2$NHMe$_2$}$_2$-2,6)]Cl$_2$, [4]Cl$_2$. To a solution of **[3]Cl** (98.8 mg, 0.11 mmol) in CH_2Cl_2 (1 mL) was added pentane (4 mL). The formed precipitate was collected and dried in vacuo, which gave **[4]Cl$_2$** as a white microcrystalline solid (40.2 mg; 39%). Anal. Found (calcd **[4]Cl$_2$**·1.5CH_2Cl_2): C, 51.85 (51.55); H, 4.95 (4.85); N, 2.42 (2.63).

[Pt(PCP)(η^1-*C*-C$_6$H$_3${CH$_2$NHMe$_2$}$_2$-2,6)](BF$_4$)$_2$, [4](BF$_4$)$_2$. Method A. A solution of **5** (172 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) was treated with HBF_4 (0.10 mL, 0.6 mmol; 54% in Et_2O). After being stirred for 1 h, the solution was layered with Et_2O, which yielded pure **[4](BF$_4$)$_2$** as colorless crystals (98.5 mg; 95%).

Method B. A solution of **[4]Cl$_2$** (129 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was treated with $AgBF_4$ (58.4 mg, 0.30 mmol) in the absence of light. After 0.5 h, the suspension was filtered through Celite and the filtrate concentrated to 1 mL. This solution was layered with pentane, which gave colorless crystals of **[4](BF$_4$)$_2$** (133 mg, 86%). Anal. Found (calcd **[4](BF$_4$)$_2$**·1.25CH_2Cl_2): C, 47.29 (47.60); H, 4.86 (4.46); N, 2.49 (2.45).

[Pt(PCP)(η^1-*C*-C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6H)], 5. Method A. To a solution of **[3]Cl** (98.8 mg, 0.11 mmol) in CH_2Cl_2 (1 mL) was added pentane (4 mL). The formed precipitate was removed, and the solute was treated with additional pentane (4 mL). This afforded **5** as a second precipitate, which was collected and dried in vacuo (45.2 mg; 44%).

Method B. An excess of NEt_3 (1 mL, 14 mmol) was added to a solution of **[3]Cl** (67.1 mg, 75 μmol) in CH_2Cl_2 (4 mL). After the solution was stirred for 0.5 h, water was added (3 mL) and the two phases were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL), and the combined organic phases were dried over $MgSO_4$ and subsequently evaporated to dryness, thus affording 59.3 mg (92%) of **5**. Crystal needles for X-ray structure determination were grown by diffusion of hexane into a solution of **5** in CH_2Cl_2. Anal. Found (calcd): C, 61.28 (61.46); H, 5.31 (5.39); N, 3.34 (3.26).

[PtCl(η^1-*C*-C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)(PCHP)]$_2$, 6. A solution of PCHP (52.5 mg, 111 μmol) and PtCl(NCN) (48.0 mg, 114 μmol) in C_6H_6 (4 mL) was stirred for 4 h. The white precipitate, which formed gradually, was collected, washed with cold C_6H_6 (2 × 1 mL), and precipitated from CH_2Cl_2/C_6H_6. Drying in vacuo afford 88.3 mg (89%) of pure **6**. Crystals which were suitable for X-ray structure determination were obtained by slow evaporation of the (saturated) C_6H_6 layer of the reaction mixture. Anal. Found (calcd): C, 58.94 (58.96); H, 5.21 (5.29); N, 3.06 (3.13); P, 6.87 (6.91).

[PtCl(η^1-*C*-C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)(PPh$_3$)$_2$], 7. Addition of PPh_3 (80.3 mg, 306 mmol) to a solution of PtCl(NCN) (64.4 mg, 153 μmol) in C_6H_6 (5 mL) afforded, after stirring for 2 h and removal of all volatiles, the crude title product. Purification was achieved by repeated crystallization of **7** from CH_2Cl_2/Et_2O. Yield: 118.8 mg (82%). Crystals suitable for X-ray structure determination were grown by recrystallization from CH_2Cl_2/hexane (gas diffusion). Anal. Found (calcd): C, 60.72 (60.92); H, 5.31 (5.22); N, 2.84 (2.96); P, 6.73 (6.55).

X-ray Structure Determination of Complexes [4](BF$_4$)$_2$ and 5−7. Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo Kα, $\lambda = 0.710\,73$ Å) at a temperature of 150 K. Crystal data and details on data collection and refinement for all complexes are summarized in Table 5. The structures were solved with Patterson methods (DIRDIF-97[45]) and refined with the program SHELXL-97[46] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, and hydrogen atoms were refined as rigid groups. In structure **[6]**·4C_6H_6, the hydrogen

atom H1 was refined freely with an isotropic displacement parameter. In structure **[7]**·$1/6C_6H_{14}$, the hexane molecule was refined with isotropic displacement parameters and a ratio of 1/6 with respect to the Pt complex. The benzylamino groups at N1 of **[4](BF$_4$)$_2$** and **[7]**·$1/6C_6H_{14}$ were refined with disorder models. All calculations, graphical illustrations, and checking for higher symmetry were performed with the PLATON[47] package.

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Supporting Information Available: A figure showing the measured and simulated ^{31}P NMR spectrum of **6** as well as tables of additional crystallographic and refinement parameters, anisotropic thermal parameters, and complete nearest-neighbor distances and angles of the complexes **[4](BF$_4$)$_2$**, **6**, and **7** (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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