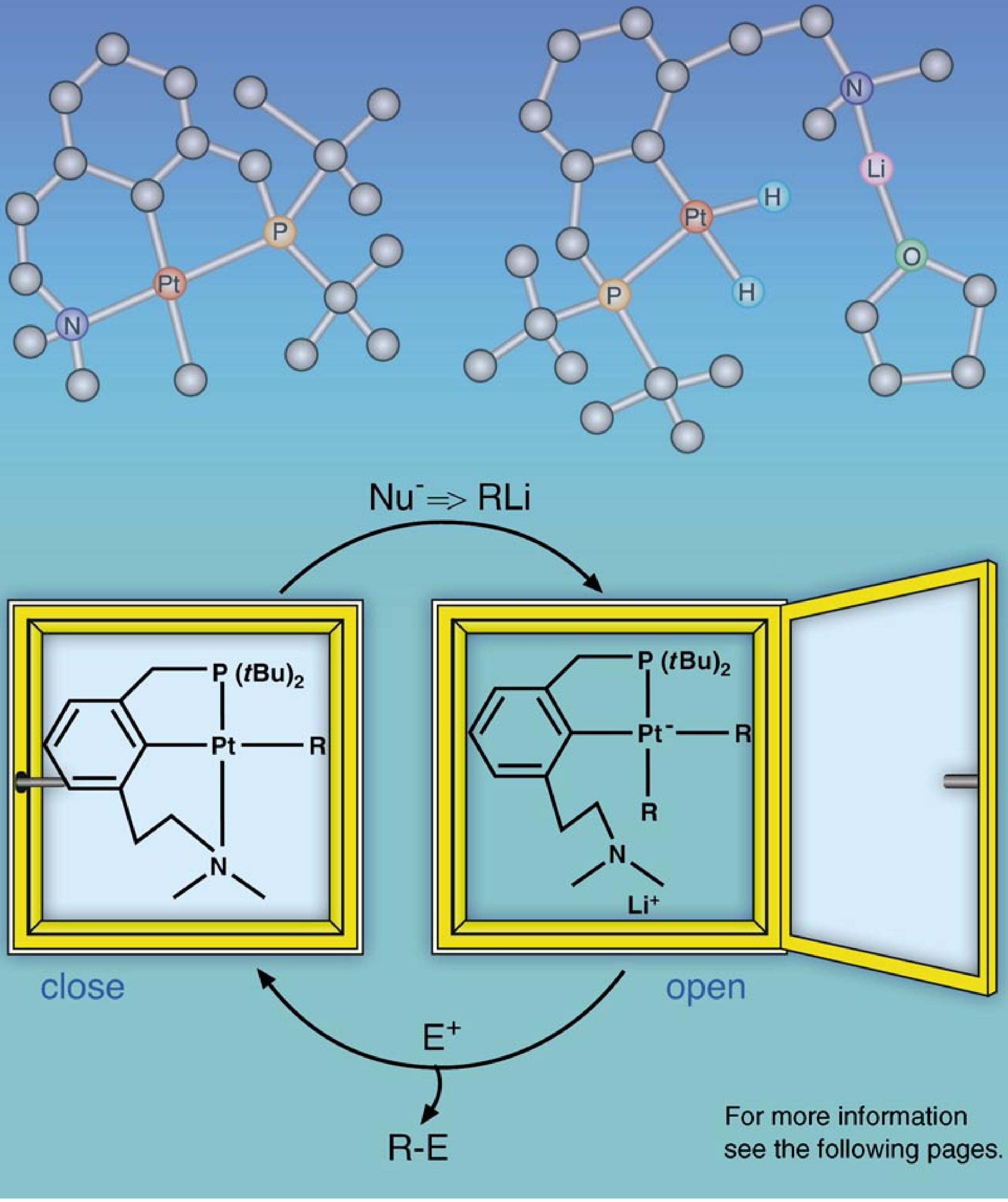
Nucleophilic De-coordination and Electrophilic Regeneration of "Hemilabile" Pincer-type Complexes



For more information see the following pages.

DOI: 10.1002/chem.200400514

Nucleophilic De-coordination and Electrophilic Regeneration of "Hemilabile" Pincer-Type Complexes: Formation of Anionic Dialkyl, Diaryl, and Dihydride Pt^{II} Complexes Bearing No Stabilizing π-Acceptors

Elena Poverenov,[a] Mark Gandelman,[a] Linda J. W. Shimon,[b] Haim Rozenberg,[b] Yehoshoa Ben-David,[a] and David Milstein*[a]

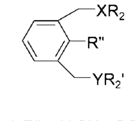
Abstract: Novel anionic dialkyl, diaryl, and dihydride platinum(II) complexes based on the new "long-arm" hemilabile PCN-type ligand $C_6H_4[CH_2P(tBu)_2](CH_2)_2N(CH_3)_2$ with the general formula $Li^+[Pt(PCN)(R)_2]^-$ (R = Me (**4**), Ph (**6**) and H (**9**)) were prepared by reaction of [Pt(PCN)(R)] complexes (obtained from the corresponding chlorides) with an equivalent of RLi, as a result of the opening of the chelate ring. Alkylating agents based on other metals produce less stable products. These anionic d^8 complexes are thermally stable although they bear no stabilizing π acceptors. They were characterized by ^1H, $^{31}P\{^1H\}$, ^{13}C, and ^7Li NMR spectroscopy; complex **9** was also characterized by single crystal X-ray crystallography, showing that the Li^+ ion is coordinated to the nitrogen atom of the open amine arm and to the hydride ligand (*trans* to the P atom) of a neighboring molecule (H–Li = 2.15 Å), resulting in a dimeric structure. Complexes **4** and **9** exhibit high nucleophilic reactivity, upon which the pincer complex is regenerated. Reaction of **4** with water, methyl iodide, and iodobenzene resulted in the neutral complex $[Pt(PCN)(CH_3)]$ (**3**) and methane, ethane, or toluene, respectively. Labeling studies indicate that the reaction proceeds by direct electrophilic attack on the metal center, rather than attack on the alkyl ligand. The anionic dihydride complex **9** reacted with water and methyl iodide to yield [Pt(PCN)(H)] (**8**) and H_2 or methane, respectively.

Keywords: hemilabile complexes · hydrides · N,P ligands · pincer ligands · platinum

Introduction

Anionic transition-metal complexes can exhibit remarkable nucleophilic behavior toward organometalic complexes and organic molecules. Their reactivity as alkylating reagents with various electrophiles[1,2] and as reducing hydride donors with polar molecules[3–6] is a subject of current interest. Usually, π-acceptor ligands, such as carbonyls[6,8] and olefins,[9] and electron-withdrawing phosphines[10] or halide ligands[11] are required in order to stabilize the high electron density on the metal center; this reduces the nucleophilic character of such species. Examples of anionic transition metal complexes that do not contain such π-acceptor ligands are rare[2,4,5,7] and their synthesis is a considerable challenge.

Complexes of PCP and NCN pincer-type ligands (**A**) have attracted much recent attention.[12] They have been very useful in various areas, including bond activation, catalysis, and the stabilization of unstable, elusive compounds.[12–15] The hardness of the chelating N donor in NCN-type ligands versus softness of P donor in PCP systems results in very different behavior of the corresponding NCN- and PCP-based complexes. While each of these systems has its unique chemistry, it is conceivable that a mixed PCN-type system could benefit from advantages of both ligands.[16] The different electron-donor properties of the phosphine and amine ligands and the more labile coordination of the amine arm in

A 

R, R' = alkyl,aryl. R'' = H,CH_3, OCH_3, OH.
X=Y=N (NCN), X=Y=P (PCP), X=P; Y=N (PCN).

---

[a] E. Poverenov, M. Gandelman, Y. Ben-David, Prof. Dr. D. Milstein
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, 76100 (Israel)
Fax: (+972) 893-44-142
E-mail: david.milstein@weizmann.ac.il

[b] Dr. L. J. W. Shimon, Dr. H. Rozenberg
Unit of Chemical Research Support
The Weizmann Institute of Science
Rehovot, 76100 (Israel)

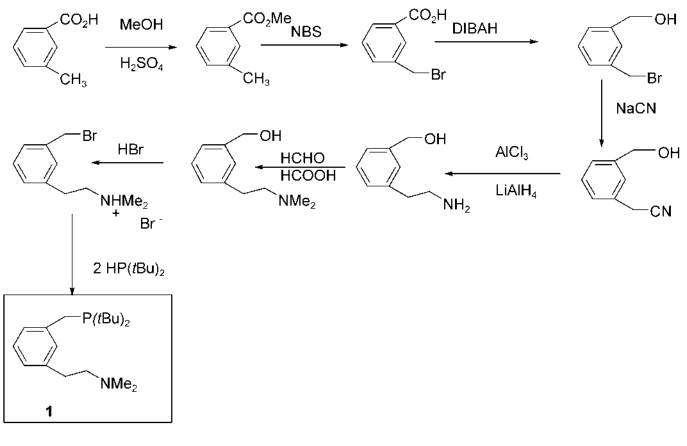
DOI: 10.1002/chem.200400514

comparison to the phosphine[17] open up additional reactivity patterns. The hemilabile[18] coordination of a PCN ligand could make the system adaptable to electronic, coordinative, and steric requirements in different steps of a catalytic cycle or of a stoichiometric reaction, enabling a desirable balance between stability and reactivity. Here we report on a new "long-arm" PCN system, which enables the synthesis of novel, anionic dialkyl and diphenyl complexes of Pt^{II} that do not bear stabilizing π-accepting ligands. In addition, an unprecedented anionic d^8 dihydride complex was synthesized and was spectroscopically and crystallographically characterized. Key features of the formation of these complexes are the chelate ring-opening of the PCN system and a significant counterion effect. These anionic complexes show high nucleophilic reactivity towards various electrophiles, upon which the pincer complex framework is regenerated.

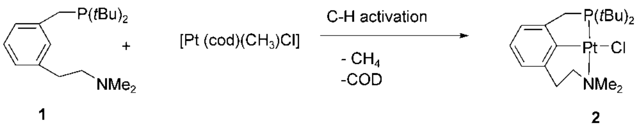
Results and Discussion

Synthesis of a "long-arm" PCN-type ligand: The new PCN ligand **1** bearing two methylene groups in the amine arm was prepared in order to enhance the labile coordination effect. It was synthesized from 3-(bromomethyl)benzyl alcohol, which was obtained by esterification, bromination, and reduction of 3-(methyl)benzoic acid according to a literature procedure.[19] The resulting 3-(bromomethyl)benzyl alcohol was treated with a slight excess of sodium or potassium cyanide to give 3-(cyanomethyl)benzyl alcohol, which was reduced with $LiAlH_4$ to yield 3-(aminoethyl)benzyl alcohol. This alcohol was methylated to give 3-(dimethylaminoethyl)benzyl alcohol, which upon reaction with an aqueous solution of HBr at room temperature yielded the HBr salt of 3-(dimethylaminoethyl)benzyl bromide. Treatment of this salt with 2.4 equivalents of tBu$_2$PH yielded the pure ligand **1** (Scheme 1).

Synthesis and characterization of a "long-arm" PCN-based platinum chloride complex: The PCN-based platinum chloride complex **2** was obtained as a result of C–H activation and methane liberation reactions (Scheme 2). When a solution of ligand **1** in THF was added to $[Pt(cod)(CH_3)(Cl)]$ (cod = cyclooctadiene), quantitative formation of **2** was observed after 30 min of heating at 100 °C.



Scheme 1.



Scheme 2.

The $^{31}P\{^1H\}$ NMR of **2** shows a singlet at 64.20 ppm with Pt satellites (J(Pt,P) = 4001 Hz). In the ^1H NMR spectrum, the NMe_2 group gives rise to singlets at 2.83 ppm (J(Pt,H) = 9 Hz) and 2.82 ppm (J(Pt,H) = 8 Hz) with Pt satellites. In the $^{13}C\{^1H\}$ NMR the ipso carbon atom exhibits a doublet at 149.80 ppm (J(P,C) = 11 Hz), and the methyl groups of NMe_2 appear as a singlets at 49.29 and 49.27 ppm. The fact that the two methyl groups of the dimethylamine unit have different chemical shifts indicates coordination of the amine to the metal center; this results in the lack of a plane of symmetry between the methyl groups. Colorless plates of **2** suitable for a single-crystal X-ray analysis were obtained by recrystallization of **2** from a benzene/pentane two-phase mixture. The platinum atom is located in the center of a square-planar structure in which the chloride is located *trans* to the aromatic ring, and the amine arm is coordinated to the metal center (Figure 1). The majority of known pincer-type complexes have two symmetric (five-membered) rings, providing the system with relative rigidity and stability, since five-membered organometalic rings are generally the most stable.[1a] The PCN-based complex **2** has a less stable, six-membered ring, formed by the amine arm, and hence labile coordination of the amine ligand is expected. Compatible with this expectation, the Pt–N bond length (2.188 Å) of complex **2** is relatively long in comparison with the usual Pt–N bond length (2.08 Å) in symmetric NCN systems.[20,21,22] On the other hand, the Pt–P bond length of

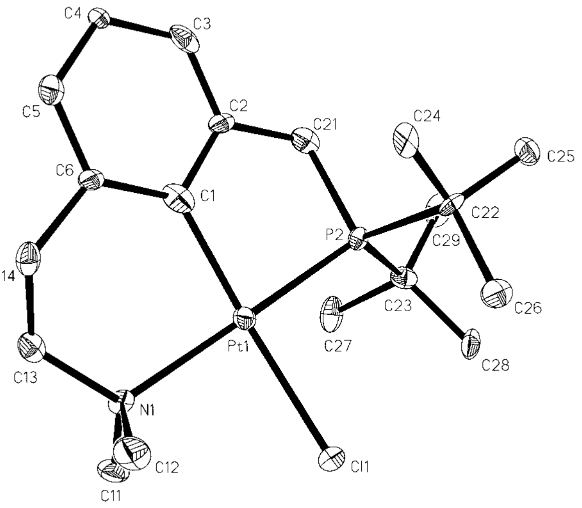


Figure 1. An ORTEP view of a molecule of complex **2**. Hydrogen atoms are omitted for clarity.

complex **2** (2.226 Å), which constitutes part of a five-membered ring, is similar to other reported Pt–P bond lengths of PCP complexes (2.25 Å).[23,24] Additional bond lengths and angles of **2** are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for complex **2**.

Pt1–C1	2.021(10)	C1-Pt1-N1	94.4(3)
Pt1–N1	2.188(7)	C1-Pt1-P2	84.9(3)
Pt1–P2	2.226(2)	C1-Pt1-Cl1	174.9(2)
Pt1–Cl1	2.419(2)	N1-Pt1-P2	175.2(2)
N1–C11	1.481(12)	N1-Pt1-Cl1	87.3(2)
N1–C12	1.486(11)	P2-Pt1-Cl1	93.89(8)
P2–C21	1.809(10)	C11-N1-C12	108.1(7)
P2–C23	1.864(9)	C11-N1-Pt1	109.6(6)

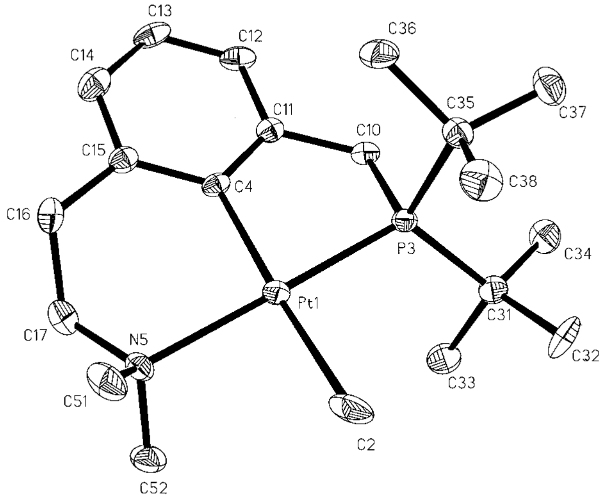
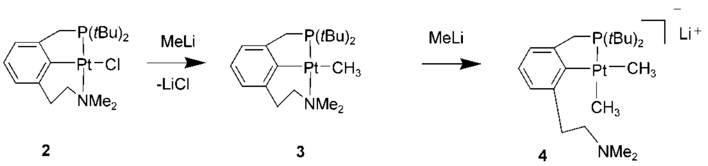


Figure 2. An ORTEP view of a molecule of complex **3**. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complex **3**.

Pt1–C1	1.971(5)	C1-Pt1-N1	82.84(19)
Pt1–N1	2.192(4)	C1-Pt1-P2	83.58(15)
Pt1–P2	2.217(13)	C1-Pt1-Cl3	174.36(14)
Pt1–Cl3	2.408(13)	N1-Pt1-P2	166.25(12)
N1–C14	1.500(7)	N1-Pt1-Cl3	93.22(12)
N1–C12	1.500(7)	P2-Pt1-Cl3	100.48(5)
P2–C21	1.849(5)	C14-N1-C12	108.3(4)
P2–C23	1.870(5)	C14-N1-Pt1	109.9(3)



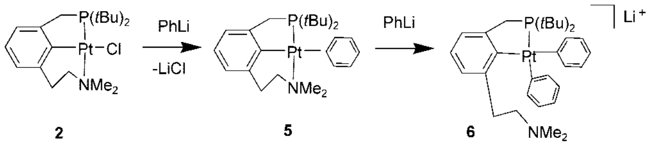
Scheme 3.

Formation of anionic dialkyl and diaryl complexes: As mentioned in the introduction, formation of stable anionic complexes usually requires the presence of strong π-acceptor ligands in order to stabilize the electron density on the metal center. However, such ligands decrease the nucleophilic features of the anionic complexes. The hemilabile coordination of the σ-donating amine arm of the new PCN ligand turned out to be useful in addressing this stability versus reactivity problem. Upon reaction of complex **2** with one equivalent of methyllithium, the neutral monomethyl Pt^{II} complex **3** was formed and was fully characterized by NMR spectroscopy (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of **3** exhibits a singlet with Pt satellites at 61.19 ppm (J(Pt,P) = 4228 Hz). In ^{1}H NMR spectrum the coordinated methyl group gives rise to a doublet with satellites at 0.57 ppm (J(P,H) = 1 Hz, J(Pt,H) = 41 Hz) and the two methyl groups on the amine arm give rise to two signals with Pt satellites at 2.37 (s, J(Pt,H) = 20.4 Hz) and 2.27 ppm (s, J(Pt,H) = 22 Hz). In ^{13}C{^{1}H} NMR spectrum, the Pt–**C**H$_3$ carbon appears at −1.65 ppm (d, J(P,C) = 8 Hz, J(Pt,C) = 508 Hz) and the carbon atoms of NMe$_2$ appear at 48.74 and 48.71 ppm.

Complex **3** was recrystallized from a benzene/pentane two-phase mixture at room temperature to give colorless crystals appropriate for a single-crystal X-ray analysis. The platinum atom is located in the center of a square-planar structure, in which the methyl group is *trans* to the aromatic ring, and the amine arm is coordinated to the metal center (Figure 2). Selected bond lengths and angles are given in Table 2.

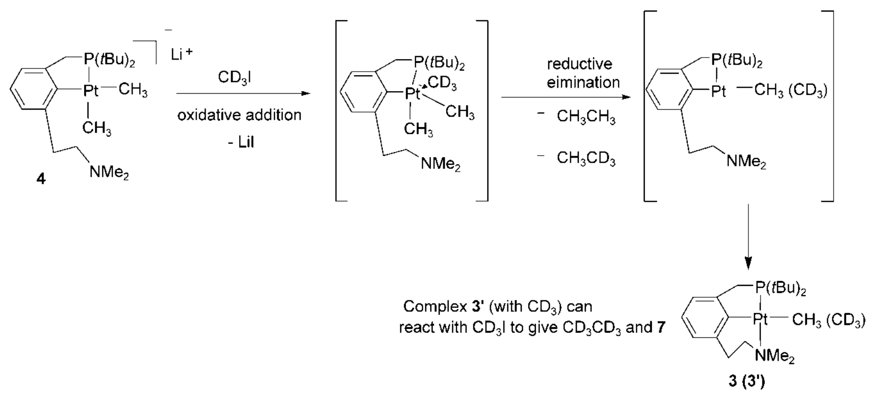
Remarkably, when a second equivalent of MeLi was added, the anionic dimethyl complex **4** was formed (Scheme 3). The ^{31}P{^{1}H} NMR spectrum shows a single resonance at 73.75 ppm with Pt–P satellites (J(Pt,P) = 2200 Hz). The relatively small Pt–P coupling (as compared with the typical coupling of this system of about 4000 Hz) points to coordination of a strong sigma donor *trans* to phosphorous.[1a] Two sets of coordinated methyl groups were observed at 0.37 (d, J(Pt,H) = 67 Hz, J(P,H) = 7 Hz) and 0.06 ppm (d, J(Pt,H) = 51 Hz, J(P,H) = 4 Hz) in the ^{1}H NMR spectrum, and at 5.11 (d, J(P,C) = 20 Hz, J(Pt,C) = 669 Hz) and −7.82 ppm (d, J(P,C) = 5 Hz, J(Pt,C) = 477 Hz) in ^{13}C {^{1}H} NMR spectrum. According to the ^{1}H and ^{13}C{^{1}H} NMR data, the amine arm of the PCN ligand is not coordinated to the metal center, since the methyl groups of NMe$_2$ exhibit a single resonance without Pt satellites. It is likely that Li^{+} is coordinated to the nitrogen atom of the opened amine arm, contributing to the stability of the anionic complex. The ^{7}Li NMR spectrum of complex **4** exhibits a broad singlet at 0.35 ppm, while the free Li^{+} ion from LiCl gives a narrow peak at 0 ppm. Crystallographic evidence for Li coordination were obtained for the analogous dihydride complex (vide infra).

The same mode of reactivity was observed with other organolithium compounds. Thus, reaction of **2** with a stoichiometric amount of phenyllithium led to formation of the monophenyl Pt^{II} complex **5**. This complex exhibits a single resonance at 59.86 ppm (J(Pt,P) = 4145 Hz) in the ^{31}P{^{1}H} NMR spectrum, and in ^{13}C {^{1}H} NMR spectrum the ipso signal due to the coordinated phenyl ring appears at 169.45 ppm, while the ipso signal of the PCN system of **5** appears at 164.31 ppm. Addition of two or more equivalents of PhLi to **2** gave the anionic diphenyl Pt^{II} complex **6** (Scheme 4). Similarly to **4**, the $^{31}P\{^1H\}$ NMR spectrum of **6** exhibits a downfield-shifted single resonance at 72.94 ppm with a small Pt–P coupling (J(Pt,P) = 1764 Hz) and the two methyl groups of NMe$_2$ give rise to one peak in the $^{13}C\{^1H\}$ and ^1H NMR spectra with no coupling to Pt. In the $^{13}C\{^1H\}$ spectrum two ipso signals at 174.44 (d, J(P,C) = 120 Hz) and 168.69 ppm (d, J(P,C) = 21 Hz) were found, confirming the coordination of two phenyl groups to the Pt center. The ipso signal of the PCN system of **6** appears at 157.03 ppm (J(Pt,C) = 620 Hz).



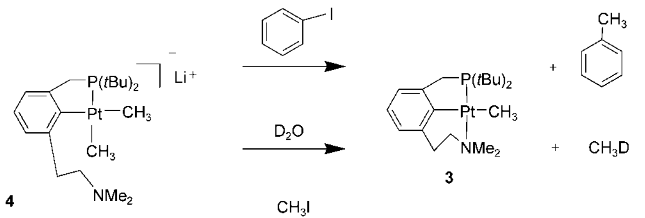
Scheme 4.

Thus, the "long-arm" PCN-based neutral alkyl and aryl complexes show remarkable reactivity towards nucleophilic attack, resulting in chelate-ring opening and formation of novel, stable anionic complexes. This reactivity pattern was not observed before with PCP, NCN, or other pincer-type systems. In fact, with the electron-rich [Pt(NCN)(X)] (X = halide) complexes, even nucleophilic substitution of halide by RLi to give stable *neutral* [Pt(NCN)(R)] complexes takes place only with an electron-withdrawing R group (R = aryl, acetylide), while with alkyllithium reagents [Pt(NCN)(alkyl)] products were unstable and could not be isolated.[22] In this context, the labile features of the amine arm of the PCN ligand not only allow coordination of a second nucleophile due to facile generation of a vacant site, but also de-coordination of the amine ligand decreases the electron density on the metal center, encouraging the nucleophilic attack.



Scheme 6.

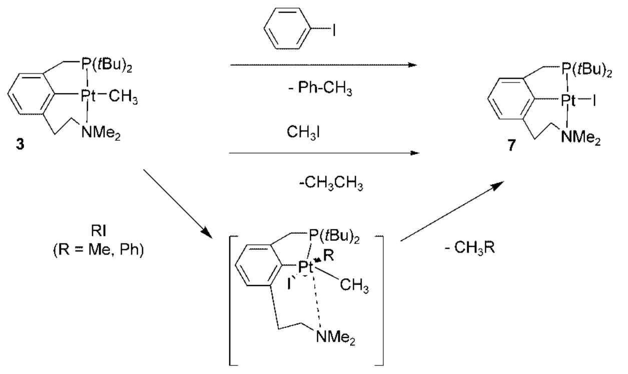
Reactivity of the anionic dialkyl complexes: The nucleophilic behavior of the anionic dimethyl complex **4** was explored, revealing that it is highly reactive with different electrophiles, regenerating the pincer complex framework (Scheme 5). For example, reaction of **4** with MeI led to formation of the monomethyl neutral complex **3**, which was detected by $^{31}P\{^1H\}$ NMR spectroscopy immediately after addition of the electrophile. Formation of ethane was detected by GC/MS and a yellow precipitate of LiI was formed. Likewise, reaction of **4** with D_2O led to immediate formation of complex **3** and CH_3D, which was detected by GC/MS. Significantly, complex **4** is capable of reaction even with weak electrophiles. For example, upon reaction with an excess of iodobenzene or bromobenzene, complex **3** and toluene were formed, the latter being detected by GC. This reaction was slower than the reactions with MeI or water and quantitative formation of **3** was observed only after 24 h.



Scheme 5.

Mechanistically, these reactions may proceed through direct attack of the electrophile on the alkyl group or through oxidative addition of the electrophile to the Pt center, followed by reductive elimination of the organic product (Scheme 6). Addressing this interesting issue, complex **4** was treated with CD_3I, and the product ethane was checked by GC/MS, revealing that CH_3CH_3/CD_3CH_3/CD_3CD_3 were formed in a ratio of 59:14:8. Formation of CH_3CH_3 and CD_3CD_3 suggests that the oxidative addition scenario is probably involved, since direct nucleophilic attack is expected to lead only to the mixed CH_3CD_3 (Scheme 6).

Interestingly, the neutral monomethyl complex is also capable of acting as a methyl donor. Reaction of complex **3** with methyl iodide and iodobenzene yielded complex **7** and ethane or toluene, respectively. However, these reactions were slower than the corresponding reactions of the dimethyl complex **4** and formation of complex **7** was complete only after 24 h (MeI) or 48 h (PhI) at room temperature. The mechanism of these reactions may involve oxidative addition to form a Pt^{IV} intermediate, followed by reductive elimination (Scheme 7).

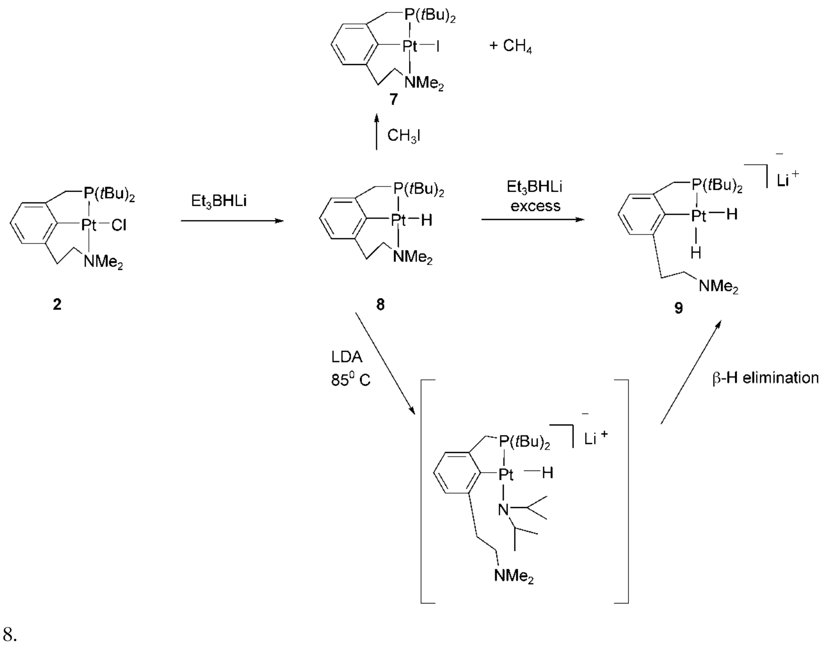


Scheme 7.

Formation and reactivity of an anionic dihydride complex: Anionic late-transition-metal hydrides that have no strong π-acceptor ligands are a very interesting rare class of complexes. Mono- and dihydride d^6 anionic complexes, such as $[\{Mo(\eta\text{-}C_5H_5)_2(H)Li\}_4]$,[4] and $K^+[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$[5] have been prepared and demonstrated remarkable hydridic chemistry. Anionic d^8 hydride complexes in the absence of π-accepting ligands are expected to have a very high electron density on the metal center. This is, perhaps, one of the reasons why, to the best of our knowledge, no synthesis and characterization of d^8 anionic hydride complexes have been reported. Using the hemilabile aptitude of the amine arm, we succeed in the preparation of an anionic d^8 platinum dihydride complex through direct nucleophilic attack on the metal center. Upon reaction of complex **2** with one equivalent of $LiEt_3BH$ the expected monohydride complex **8** was formed (Scheme 8). This complex was fully characterized by multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits a single resonance at 82.06 ppm with $J(Pt,P) = 4014$ Hz; in ^1H NMR spectrum the hydride gives rise to a doublet at −2.55 ppm with $J(P,H) = 27$ Hz and $J(Pt,H) = 136$ Hz. As observed with the monomethyl complex **3**, complex **8** reacted with methyl iodide to yield complex **7** and an equivalent amount of methane (Scheme 8). However, in this case, conversion of the monohydride to the iodide complex was relatively rapid, probably due to both electronic and steric reasons, which makes **8** more reactive than the methyl complex **3** in oxidative addition reactions.

Remarkably, when excess of Et_3BHLi was added to **8**, the anionic dihydride complex **9** was formed (Scheme 8). Complex **9** exhibits a singlet at 91.69 ppm with a relatively small Pt–P coupling ($J(Pt,P) = 2295$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. In ^1H NMR spectrum, the hydride *trans* to the phosphorous atom appears as a double doublet at −3.00 ppm with $J(Pt,H) = 1035$ Hz, $J(P,H) = 152$ Hz, and $J(H,H) = 8$ Hz, while the second hydride (*cis* to the phosphorous atom) exhibits a triplet at −7.07 ppm with $J(Pt,H) = 700$ Hz, $J(P,H) = 8$ Hz, and $J(H,H) = 8$ Hz. Similarly to the anionic complexes described above, the methyl groups of the NMe_2 moiety show one peak in ^1H and $^{13}C\{^1H\}$ NMR spectra at 2.12 and 46.31 ppm, respectively; this indicates de-coordination of the amine arm from the platinum center.

Crystals of the dihydride complex, suitable for a single-crystal X-ray analysis, were obtained by evaporation of the THF solvent from a highly concentrated solution of **9** (Figure 3, top). The Pt atom is located in the center of a distorted square-planar structure, and the two hydride ligands occupy *trans* and *cis* positions to the phosphorous atom. As indicated by the spectroscopic data in solution, the amine arm has opened, allowing coordination of a second hydride to the metal center. Significantly, the Li^+ ion is coordinated to the nitrogen atom and to a THF molecule. In addition, the high electron density on the metal center and on the hydride ligands is stabilized by a Li^+ ion from a neighboring molecule (Figure 3, middle and bottom). A short distance between the hydride *trans* to the phosphorous atom and the neighboring Li ion (H–Li = 2.15 Å) is observed. Taking into consideration the ionic radii of Li^+ (0.68 Å) and H^- (1.54 Å), such a distance is short enough to represent a bond and it is likely that these interactions lead to formation of the dimeric structure. In addition, a weak stabilizing interaction between the Pt atom and the neighboring Li ion (Pt–Li = 2.68 Å) was found (the anionic radius of Pt^{2+} is 0.80 Å, therefore this distance is too long to be considered a real bond). The Li–Li′ distance found in **9** of 3.13 Å is relatively long compared with known organolithium dimers.[25] The fact that **9** crystallized as a dimer is in agreement with the general tendency of organolithium compounds to form oligom-



Scheme 8.

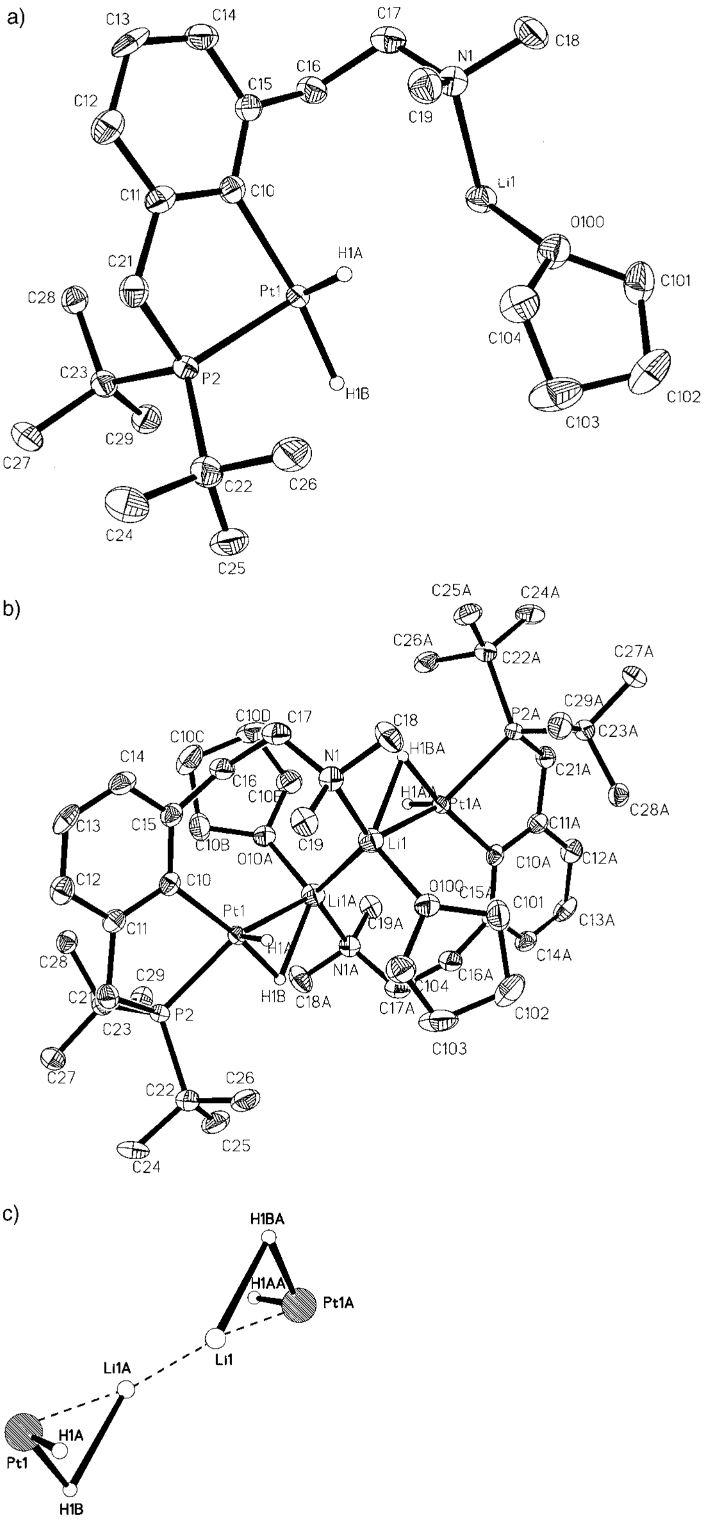


Figure 3. Top: An ORTEP view of a molecule of complex **9**. Middle: An ORTEP view of a dimeric molecule of complex **9**. Hydrogen atoms, except for hydrides, are omitted for clarity. Bottom: A view of the Li-Pt-H dimeric core of complex **9**.

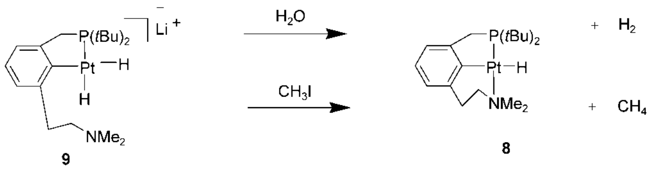
ers. It is usually attributed to the high ionicity of lithium bonds and hence large energies of association.[25,26] Additional bond lengths and angles are given in Table 3.

Table 3. Selected bond lengths and angles of complex **9**.

Pt1–C10	2.10(5)	C10-Pt1-P2	84.1(14)
Pt1–Li1	2.68(8)	C10-Pt1-Li1	131.1(2)
Pt1–P2	2.25(13)	P2-Pt1-Li1A	131.9(18)
Pt1–H1A	1.33(15)	C10-Pt1-H1A	78.0(6)
Pt1–H1B	1.66(4)	P2-Pt1-H1A	105.0(6)
N1–Li1	2.10(9)	Li1A-Pt1-H1A	113.0(6)
0100–Li1	1.97(10)	C10-Pt1-H1B	173.1(13)
Li1–Li1A	3.13(16)	Li1A-Pt1-H1B	53.4(14
Li1–H1B	2.153	H1A-Pt1-H1B	106.0(6)

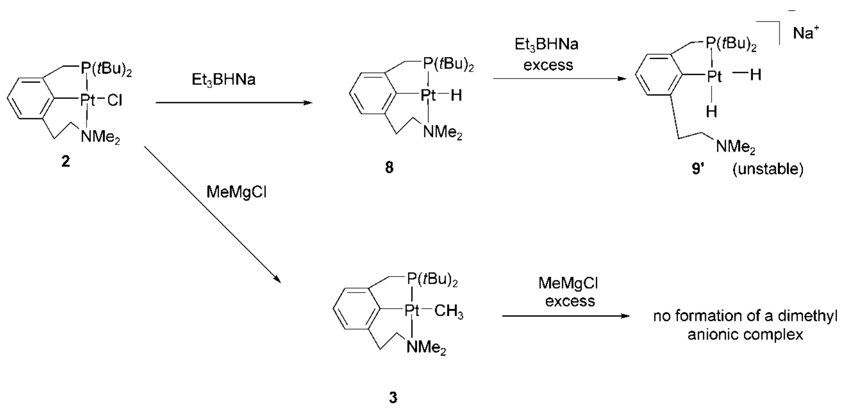
Interestingly, complex **9** can be alternatively prepared by reaction of **8** with one equivalent of lithium diisopropyl amide (LDA) at 85 °C for 5 h (Scheme 8). We believe that complex **8** undergoes nucleophilic attack (surprisingly LDA reacts as a nucleophile and not as a base), which leads to opening of the amine arm and coordination of diisopropyl amide to get an unobserved anionic intermediate; this in turn undergoes β-H elimination to form the dihydride complex **9** (Scheme 8).

Similar to the anionic dialkyl and diaryl complexes, complex **9** is highly reactive with electrophiles (Scheme 9). For example, it reacted readily with water and methyl iodide at room temperature, resulting in immediate formation of the monohydride complex **8** and H_2 or methane, respectively.



Scheme 9.

It is important to note the considerable effect of the counterion on these anionic systems. As shown by the X-ray structure of complex **9**, the Li cation coordinates to the nitrogen atom of the open amine arm and interacts with the hydride ligands. In addition, the strong coordination of Li^+ is reflected in the high stability of the anionic complexes reported here toward TMEDA or [12]crown-4, which possess high affinity for lithium ions. All our attempts to extract Li^+ from the anionic complexes were unsuccessful. Also, we found that the nature of counterion is very important. For example, use of $Na[Et_3BH]$ (instead of $Li[Et_3BH]$) in reaction with complex **2** resulted in a more difficult, slow formation of an unstable complex **9′**, whereas when MeLi was replaced by MeMgCl only formation of the monomethyl complex **3** and no formation of an anionic dimethyl complex was observed (Scheme 10). This significant cation effect is very likely a result of its ability to coordinate to the nitrogen atom, thus facilitating the nucleophilic attack and stabilizing the product. Li^+ coordination to the amine arm is more favorable than that of the other cations studied here.



Scheme 10.

Conclusion

Novel anionic dialkyl, diaryl, and dihydride platinum(II) complexes that do not bear π acid ligands were obtained by reaction of the new "long-arm" hemilabile [Pt(PCN)(R)] complexes with an equivalent of RLi. Formation of these very electron-rich d^8 complexes is based on the opening of the six-membered chelate ring of the amine arm; this provides the required coordination site and reduces the electron density at the metal prior to nucleophilic attack. This is an unprecedented demonstration of pincer complex hemilability upon nucleophilic attack. The thermal stablity of these complexes is surprising, since they do not contain strong π acceptors that can stabilize the anionic metal center. The stability of the complexes is counterion dependent, the Li^+ ion providing the highest stabilization. An X-ray crystallographic study of the anionic dihydride **9** shows that the Li^+ ion is coordinated to the nitrogen atom of the open amine arm and to the hydride ligand (*trans* to P) of a neighboring molecule, resulting in a dimeric structure. The anionic complexes exhibit high nucleophilic reactivity, upon which the pincer ligand framework is regenerated. Labelling studies indicate that the reaction proceeds through direct electrophilic attack on the metal center, rather than attack on the alkyl ligand. Current studies are exploring synthetic and mechanistic aspects of the reactivity of these complexes and the possible extension of the pincer hemilability approach as a synthetic tool in the preparation of highly nucleophilic, anionic complexes of other late transition metals without π-accepting ligands

Experimental Section

General procedures: All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or by using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The precursor $[Pt(cod)(CH_3)(Cl)]$ was prepared according to a literature procedure.[27] ^1H, ^{13}C, ^{31}P, and ^7Li NMR spectra were recorded at 400, 100, 162, and 155 MHz, respectively, by using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 23 °C. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.15 ppm, benzene; 7.24 ppm, chloroform; 3.58 ppm, tetrahydrofuran). In $^{13}C\{^1H\}$ NMR measurements the signals of C_6D_6 (128.0 ppm), $CDCl_3$ (77.0 ppm), and $[D_8]THF$ (67.4 ppm) were used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85 % solution of phosphoric acid in D_2O. In ^7Li NMR measurements LiCl was used as a standard (LiCl in THF = 0 ppm). Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. GC analysis was performed with a HP6890 chromatograph equipped with a FID detector using capillary columns Supelcowax 10 (30 m × 0.2 mm × 0.2 μm) and HP5 (30 m × 0.32 mm × 0.25 μm) and a stainless steel packed column 10 % Carbowax 20M +80/100 Supersupport 6′ × 1/8″. The retention time of the products was referenced to mesitylene.

Synthesis of the PCN ligand 1: The starting material for preparation of ligand **1**, was 3-(bromomethyl)benzyl alcohol, which was obtained by esterification, bromination, and reduction of 3-(methyl)benzoic acid according to a literature procedure.[19]

1) Preparation of 3-(hydroxymethyl)benzyl cyanide: 3-(Bromomethyl)-benzyl alcohol (46.0 g, 0.23 mol) was dissolved in absolute MeOH (310 mL) and a solution of KCN (18.3 g, 0.28 mol) in H_2O (100 mL) was added. The mixture was refluxed for 5 h and then concentrated to a low volume under vacuum. The mixture was transferred to an extraction funnel and extracted with ethyl acetate (3 × 250 mL). The organic layer was separated, dried over Na_2SO_4, and filtered, and the solvent was evaporated under vacuum. The resulting crude oil was distilled under vacuum (b.p. 140 °–150 °C at 0.8 mmHg), yielding 3-(hydroxymethyl)benzyl cyanide (21.20 g; 63 % yield). ^1H NMR ($CDCl_3$): $\delta = 7.15$–7.35 (4H; Ar), 4.61 (s, 2H; $\mathbf{CH_2}$–OH), 3.69 (s, 2H; $\mathbf{CH_2}$–CN), 2.85 ppm (brs, 1H; CH_2–**OH**); $^{13}C\{^1H\}$ NMR ($CDCl_3$)**:** $\delta = 142.08$(s, Ar), 130.07 (s, Ar), 129.22 (s, Ar), 126.93 (s, Ar), 126.27 (s, Ar), 126.43 (s, Ar), 117.97 (s, CH_2–**CN**), 64.39 (s, $\mathbf{CH_2}$–CN), 23.43 ppm (s, $\mathbf{C}H_2$–0H) (assignment of $^{13}C\{^1H\}$ NMR was confirmed by ^{13}C DEPT); IR (film)**:** $\tilde{\nu} = 2252\ cm^{-1}$ (CN).

2) Preparation of 3-(aminoethyl)benzyl alcohol: $AlCl_3$ (19.7 g) dissolved in dry THF (250 mL) was added to a solution of $LiAlH_4$ in THF (1 M, 148 mL). After 5 min of stirring at room temperature, a solution of of 3-(hydroxymethyl)benzyl cyanide (20.8 g, 0.14 mol) in of dry diethyl ether (300 mL) was added. The resulting mixture was stirred at room temperature for 20 h, followed by addition of H_2O (100 mL) and H_2SO_4 (6 N, 200 mL). The acidic mixture was extracted with diethyl ether (3 × 300 mL) and the aqueous layer was treated with KOH to pH 11. H_2O (850 mL) was added, and the solution was saturated with NaCl and extracted with ethyl acetate (4 × 200 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to yield 3-(aminoethyl)benzyl alcohol (16.2 g, 76 % yield), which was clean enough to be used in the next step without further purification. ^1H NMR (C_6D_6): $\delta = 6.98$–7.24 (4H; Ar), 4.65 (s, 2H; $\mathbf{CH_2}$OH), 2.72 (t, 2H; CH_2–$\mathbf{CH_2}$–NH_2), 2.55 ppm (t, 2H; $\mathbf{CH_2}$–CH_2–NH_2).

3) Preparation of 3-(dimethylaminoethyl)benzyl alcohol: Formic acid (7.5 g) was slowly added to 3-(aminoethyl)benzyl alcohol (7.5 g, 0.5 mol) cooled in an ice-water bath, avoiding a violent reaction; this was followed by the addition of formaldehyde (37 % solution, 9.5 mL). The flask was equipped with a reflux condenser, and the mixture was stirred at 80 °C for 24 h, while heavy bubbling was observed in the beginning of heating. The reaction was cooled and HCl (6 N, 50 mL) was added, followed by extraction with diethyl ether (3×75 mL). NaOH (50% aqueous solution) was added to the aqueous phase to give pH 11; then the mixture was saturated with NaCl, followed by extraction with ethyl acetate (3×300 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude mixture was distilled under vacuum (b.p. 123°C at 0.5 mmHg) yielding pure 3-(dimethylaminoethyl)benzyl alcohol as a viscous oil in 80% yield. ^{1}H NMR ($CDCl_3$): $\delta=7.02$–7.28 (4H; Ar), 4.58 (s, 2H; $\mathbf{CH_2}$–OH), 3.45 (brs, 1H; CH_2–**OH**), 2.71(t, 2H; CH_2–$\mathbf{CH_2}$–N), 2.45 (t, $\mathbf{CH_2}$–CH_2–N), 2.19 ppm (s, 6H; N($\mathbf{CH_3}$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=141.61$ (s, Ar), 140.24 (s, Ar), 128.44 (s, Ar), 127.59 (s, Ar), 127.14 (s, Ar), 124.65 (s, Ar), 64.77 (s, $\mathbf{C}H_2$–OH), 61.22 (s, CH_2–$\mathbf{C}H_2$–NH_2), 45.11 (s, N($\mathbf{C}H_3$)$_2$), 33.82 ppm (s, $\mathbf{C}H_2$–CH_2–NH_2) (assignment of ^{13}C{^{1}H} NMR was confirmed by ^{13}C DEPT).

4) Preparation of HBr salt of 3-(dimethylaminoethyl)benzyl bromide: In a round-bottomed 500 mL flask 3-(dimethylaminoethyl)benzyl alcohol (10.1 g, 0.056 mol) was dissolved in absolute MeOH (90 mL), followed by addition of an aqueous solution of HBr (48%, 90 mL). The mixture was stirred at room temperature for 24 h, followed by solvent removal under high vacuum. The obtained crude solid was re-crystalized from an MeOH/diethyl ether mixture, and the collected snow white solid was dried under high vacuum, yielding the HBr salt of 3-(dimethylaminoethyl)benzyl bromide (16.4 g, 90% yield). ^{1}H NMR (CD_3OD): $\delta=7.27$–7.43 (4H; Ar), 4.58 (s, 2H; $\mathbf{CH_2}$–Br), 3.43 (m, 2H; CH_2–$\mathbf{CH_2}$–N), 3.10 (m, $\mathbf{CH_2}$–CH_2–N), 2.97 ppm (s, 6H; N($\mathbf{CH_3}$)$_2$); ^{13}C{^{1}H} NMR (CD_3OD): $\delta=140.47$ (s, Ar), 137.94 (s, Ar), 130.64 (s, Ar), 130.41 (s, Ar), 129.86 (s, Ar), 129.16 (s, Ar), 59.57 (s, CH_2–$\mathbf{C}H_2$–NH_2), 43.64 (s, N($\mathbf{C}H_3$)$_2$), 33.72 (s, $\mathbf{C}H_2$–CH_2–NH_2), 31.55 ppm (s, $\mathbf{C}H_2$–Br), (assignment of ^{13}C{^{1}H} NMR was confirmed by ^{13}C DEPT).

*5) Preparation of ligand **1***: The HBr salt of 3-(dimethylaminoethyl)benzyl bromide (8.3 g, 0.026 mol) was dissolved in dry MeOH (45 mL) in a glass pressure vessel in a dry box. A solution of di-*tert*-butyl phosphine (9.0 g, 0.062 mol) in dry MeOH (15 mL) was added, causing the slightly orange solution to become colorless. The mixture was stirred at 45°C for 48 h outside the box in the sealed tube, cooled to room temperature and then re-introduced into the dry box. Triethylamine (18 mL) was added and the solution was stirred for 30 min. The solvents were removed under vacuum, resulting in a mixture of a white solid and viscous oil. The mixture was treated with diethyl ether and filtered, followed by washing with a copious amount of diethyl ether. The combined diethyl ether fractions were dried under vacuum to give a viscous oil. ^{31}P{^{1}H} and ^{1}H NMR spectra of the crude product showed very little impurities. The oil was purified by chromatography in the dry box through a short silica column with hexane/THF (1:1) as an eluent, yielding a pure product (7.40 g, 94% yield). ^{31}P{^{1}H NMR (C_6D_6): $\delta=32.12$ ppm (s); ^{1}H NMR (C_6D_6): $\delta=7.38$ (s,1H; Ar), 7.31 (d, J(H,H)=7 Hz, 1H; Ar), 7.16 (t, J(H,H)=7 Hz, 1H; Ar), 6.97 (d, J(H,H)=7 Hz, 1H; Ar), 2.77 (d, J(P,H)=6 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.73 (m, 2H; Ar–$\mathbf{CH_2}$–CH_2–N), 2.48 (m, 2H; Ar–CH_2–$\mathbf{CH_2}$–N), 2.11 (s, 6H; N($\mathbf{CH_3}$)$_2$), 1.08 ppm (d, J(P,H)=21 Hz, 18H; P(C($\mathbf{CH_3}$)$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): $\delta=142.08$ (d, J(P,C)=10 Hz, Ar), 141.20 (s, Ar), 130.73 (s, Ar), 130.65 (s, Ar), 126.37 (s, Ar), 126.35 (s, Ar), 62.12 (s, Ar–CH_2–$\mathbf{C}H_2$–N), 45.67 (s, N–($\mathbf{C}H_3$)$_2$), 35.05 (s, Ar–$\mathbf{C}H_2$–CH_2–N), 31.97 (d, J(P,C)=24 Hz, P–$\mathbf{C}$–(CH_3)$_3$), 30.07 (d, J(P,C)=14 Hz, P–C–($\mathbf{C}H_3$)$_3$, 29.23 ppm (d, J(P,C)=25 Hz, Ar–$\mathbf{C}H_2$–P) (assignment of ^{13}C{^{1}H} NMR was confirmed by ^{13}C DEPT).

Reaction of ligand 1 with [Pt(cod)(CH$_3$)(Cl)]—formation of [Pt(PCN)(Cl)] (2): A solution of the PCN ligand **1** (30 mg, 0.097 mmol) in THF (2.5 mL) was added to a solution of [Pt(cod)(CH_3)(Cl)] (cod=cyclooctadiene; 34.6 mg, 0.097 mmol) in THF (2.5 mL). The mixture was stirred at 100°C for 30 min, resulting in a colorless solution. ^{31}P{^{1}H} NMR spectroscopy revealed the formation of **2**. The solvent was evaporated and the resulting white solid was washed with pentane and dissolved in benzene. The benzene was evaporated, yielding **2** (45.3 mg, 0.084 mmol) as white crystals (87% yield). Colorless crystals of **2** suitable for single-crystal X-ray diffraction were obtained from a benzene/pentane two-phase mixture at room temperature. ^{31}P{^{1}H NMR ($CDCl_3$): $\delta=64.20$ ppm (s, J(P,Pt)=4001 Hz); ^{1}H NMR ($CDCl_3$): $\delta=6.92$ (d, J(H,H)=7 Hz, 1H; Ar), 6.77 (dt, J(H,H)=7 Hz, J(P,H)=2 Hz, 1H; Ar), 6.59 (d, J(H,H)=7 Hz, 1H; Ar), 2.84 (d, J(P,H)=11 Hz, J(Pt,H)=21 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.83 (s, J(Pt,H)=9 Hz, 3H; N–$\mathbf{CH_3}$), 2.82 (s, J(Pt,H)=8 Hz, 3H; N–$\mathbf{CH_3}$), 2.65 (m, 2H; CH_2–$\mathbf{CH_2}$–N), 2.56 (m, 2H; $\mathbf{CH_2}$–CH_2–N), 1.25 ppm (d, J(P,H)=16 Hz, 18H; P–***t*Bu**); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=149.80$ (d, J(P,C)=11 Hz, ipso), 142.23 (d, J(P,C)=1 Hz, Ar), 137.69 (d, J(P,C)=1 Hz, Ar), 124.71 (s, Ar), 123.71 (s, Ar), 121.41 (d, J(P,C)=17 Hz, Ar), 63.77 (d, J(P,C)=1 Hz, CH_2–$\mathbf{C}H_2$–N), 63.75 (d, J(P,C)=1 Hz, CH_2–CH_2–N), 49.29 (s, N–$\mathbf{C}H_3$), 49.27 (s, N–$\mathbf{C}H_3$), 34.65 (d, J(P,C)=27 Hz, Ar–CH_2–P), 34.44 (d, J(P,C)=34 Hz, P–$\mathbf{C}$–(CH_3)$_3$), 29.21 ppm (d, J(P,C)=3 Hz, J(Pt,C)=19 Hz, P–C–($\mathbf{C}H_3$)$_3$) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT); elemental analysis calcd (%) for $C_{19}H_{33}NPClPt$: C 43.12, H 7.42; found: C 42.98, H 7.41.

Reaction of [Pt(PCN)(Cl)] (2) with MeLi—formation of [Pt(PCN)(CH$_3$)] (3): A solution of [Pt(PCN)(Cl)] (20 mg, 0.037 mmol) in THF (1 mL) was cooled to −40°C and a solution of MeLi in diethyl ether (1.57 M, 23 μL, 0.037 mmol), also cooled to −40°C was added. ^{31}P{^{1}H} NMR spectroscopy revealed the formation of complex **3**. The solvent was evaporated, and the resulting white solid was washed with pentane and dissolved in benzene. After benzene evaporation, complex **3** (18 mg 0.035 mmol) was obtained as a white solid (95% yield). Colorless crystals of **3** suitable for single-crystal X-ray diffraction were obtained from a benzene/pentane two-phase mixture at room temperature. ^{31}P{^{1}H} NMR (C_6D_6): $\delta=61.19$ ppm (s, J(Pt,P)=4228 Hz); ^{1}H NMR (C_6D_6): $\delta=7.32$ (d, J(H,H)=7 Hz, 1H; Ar), 7.22 (dt, J(H,H)=7 Hz, J(P,H)=2 Hz, 1H; Ar), 7.00 (d, J(H,H)=7 Hz, 1H; Ar), 2.01 (d, J(P,H)=10 Hz, J(Pt,H)=36 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.57 (m, 2H; CH_2–$\mathbf{CH_2}$–N), 2.38 (s, J(Pt,H)=20.4 Hz, 3H; N–$\mathbf{CH_3}$), 2.37 (s, J(Pt,H)=22 Hz, 3H; N–$\mathbf{CH_3}$), 2.27 (m, 2H; $\mathbf{CH_2}$–CH_2–N), 1.22 (d, J(P,H)=12.8 Hz, 18H; P–***t*Bu**), 0.57 ppm (d, J(P,H)=1 Hz, J(Pt,H)=41 Hz, 3H; Pt–$\mathbf{CH_3}$); ^{13}C{^{1}H} NMR (C_6D_6): $\delta=149.78$ (d, J(P,C)=5 Hz, ipso), 143.54 (s, Ar), 124.41 (s, Ar), 122.86 (s, Ar), 121.09 (s, Ar), 120.93 (s, Ar), 65.73 (s, Ar–CH_2–$\mathbf{C}H_2$–N), 65.71 (s, Ar–$\mathbf{C}H_2$–CH_2–N), 48.74 (s, N–$\mathbf{C}H_3$), 48.71 (s, N–$\mathbf{C}H_3$), 38.59 (d, J(P,C)=16 Hz, Ar–$\mathbf{C}H_2$–P), 34.41 (d, J(P,C)=27 Hz, P–$\mathbf{C}$–(CH_3)$_3$), 29.58 (d, J(P,C)=3 Hz, J(Pt,C)=26 Hz, P–C–($\mathbf{C}H_3$)$_3$), −1.65 ppm (d, J(P,C)=8 Hz, J(Pt,C)=508 Hz, Pt–$\mathbf{C}H_3$) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT); elemental analysis calcd (%) for $C_{20}H_{36}NPPt$: C 46.51, H 6.98; found: C 46.60, H 7.05.

Reaction of [Pt(PCN)(Cl)] (2) with MeLi—formation of Li$^+$ [Pt(PCN)(CH$_3$)$_2$]$^-$ (4): A solution of MeLi in diethyl ether (1.57 M, 47 μL, 0.074 mmol) was added to a solution of complex **2** (20 mg, 0.037 mmol) in THF (1 mL). A yellow solution formed and ^{31}P{^{1}H} NMR spectroscopy revealed formation of a new complex. The solvent was evaporated and the resulting yellow solid was dissolved in pentane. The pentane was evaporated in vacuo, yielding a quantitative (by NMR spectroscopy) amount of complex **4**. In addition, **4** can be readily prepared by reaction of the neutral monomethyl complex **3** with one equivalent of MeLi. Complex **4** is stable for about a month at −37°C and for a couple of days at room temperature, upon which it is converted to the monomethyl complex **3**, probably by reaction with trace water. ^{31}P{^{1}H} NMR ([D$_8$]THF): $\delta=73.75$ ppm (J(Pt,P)=2220 Hz); ^{1}H NMR ([D$_8$]THF): $\delta=6.79$ (d, J(H,H)=6 Hz, 1H; Ar), 6.77(d, J(H,H)=6 Hz, 1H; Ar), 6.53 (d, J(H,H)=6 Hz, 1H; Ar), 3.06 (m, 2H;CH_2–$\mathbf{CH_2}$–N), 2.99 (d, J(P,H)=9 Hz, J(Pt,H)=27 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.55 (m, 2H;$\mathbf{CH_2}$–CH_2–N), 2.17 (s, 6H; N($\mathbf{CH_3}$)$_2$), 1.17 (d, J(P,H)=10 Hz,18H; P(***t*Bu**)$_2$), 0.37 (d, J(Pt,H)=67 Hz, J(P,H)=7 Hz, 3H; Pt–$\mathbf{CH_3}$), 0.06 ppm (d, J(Pt,H)=51 Hz, J(P,H)=4 Hz, 3H; Pt–$\mathbf{CH_3}$); ^{13}C NMR ([D$_8$]THF): $\delta=177.75$ (s, J(Pt,C)=692 Hz, ipso), 152.26 (d, J(P,C)=15 Hz, Ar), 149.49 (d, J(P,C)=3 Hz, Ar), 125.01 (s, J(Pt,C)=32 Hz, Ar), 120.55 (s, Ar), 119.86 (d, J(P,C)=13 Hz, Ar), 66.29 (s, $\mathbf{C}H_2$–CH_2–N), 64.16 (s, CH_2–$\mathbf{C}H_2$–N), 46.14 (s, N–(CH_3)$_2$), 40.90 (d, J(P,C)=21 Hz, P($\mathbf{C}$(CH_3)$_3$)$_2$), 34.32 (d, J(P,C)=7 Hz, J(Pt,C)=28 Hz, Ar–$\mathbf{C}H_2$–P), 30.24 (d, J(P,C)=5 Hz, P-(C($\mathbf{C}H_3$)$_3$)$_2$), 5.11 (d, J(P,C)=20 Hz, J(Pt,C)=669, Pt–$\mathbf{C}H_3$), −7.82 ppm (d, J(P,C)=5 Hz, J(Pt,C)=477 Hz); ^{7}Li NMR ([D$_8$]THF): $\delta=0.35$ ppm (brs).

Reaction of [Pt(PCN)(Cl)] (2) with PhLi—formation of [Pt(PCN)(C$_6$H$_5$)] (5): A solution of PhLi in pentane (1.4 M, 26 μL, 0.037 mmol) was added to a solution of complex **2** (20 mg, 0.037 mmol) in THF (1 mL). The solution turned brown-yellow and according to ^{31}P{^{1}H} NMR spectrum, complex **5** was immediately formed at room temperature. The solvent was evaporated and the resulting solid was washed with pentane and dissolved in benzene. After removing of the solvent under vacuum, the phenyl complex **5** (24 mg, 0.037 mmol) formed as a white-yellow solid (97% yield). ^{31}P {^{1}H} NMR (C_6D_6): $\delta=59.86$ ppm (s, J(Pt,P)=4145 Hz); ^{1}H NMR (C_6D_6): $\delta=3.55$ (d, J(P,H)=9 Hz, J(Pt,H)=39 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 3.04 (m, 2H; CH_2–$\mathbf{CH_2}$–N), 2.67 (m, 2H; $\mathbf{CH_2}$–

CH_2–N), 2.62 (s, *J*(Pt,H) = 28 Hz, 3H; N–$\mathbf{CH_3}$), 2.61 (s, *J*(Pt,H) = 27 Hz, 3H; N–$\mathbf{CH_3}$), 1.51 ppm (d, *J*(P,H) = 13 Hz, 18H; P-*t*Bu); the aromatic region was crowded due to the coordinated phenyl group and the aromatic ring of the PCN ligand; $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 169.45 (d, *J*(P,C) = 2 Hz, ipso of coordinated phenyl), 164.31 (d, *J*(P,C) = 1.5 Hz, ipso of ligand), 150.20 (d, *J*(P,C) = 3 Hz, Ar), 144.59 (s, Ar), 143.43 (s, Ar),143.44 (s, Ar), 127.08 (s, Ar), 124.53 (s, *J*(Pt,C) = 60 Hz, Ar), 123.76 (s, Ar), 122.51 (s, Ar), 121.41 (s, Ar), 121.26 (s, Ar), 65.58 (s, CH_2–$\mathbf{CH_2}$–N), 65.56 (s, $\mathbf{C}H_2$–CH_2–N), 50.03 (s, N–$\mathbf{C}H_3$), 50.00 (s, N–$\mathbf{C}H_3$), 38.44 (d, *J*(P,C) = 24 Hz, Ar–$\mathbf{C}H_2$–P), 35.10 (d, *J*(P,C) = 27 Hz, P–C–(CH_3)$_3$), 30.04 ppm (d, *J*(P,C) = 4 Hz, *J*(Pt,C) = 19 Hz, P–C–($\mathbf{C}H_3$)$_3$). elemental analysis calcd (%) for $C_{25}H_{38}PtPN$: C 51.90, H 6.57; found: C 51.78, H 6.48.

Reaction of [Pt(PCN)(Cl)] (2) with PhLi—formation of Li^+ $[Pt(PCN)(C_6H_5)_2]^-$ (6): A solution of PhLi in pentane (1.4 M, 79 µL, 0.104 mmol) was added to a solution of complex **2** (20 mg, 0.037 mmol) in THF (1 mL). After 3 h at room temperature a new complex was formed according to $^{31}P\{^1H\}$ NMR spectroscopy. The solvent was evaporated and the orange solid was washed with pentane and dissolved in benzene. After evaporation of the benzene solvent under vacuum, quantitative formation (by NMR spectroscopy) of **6** was observed. Complex **6** can be alternatively prepared by reaction of the neutral mono-phenyl complex **5** with one equivalent of PhLi. Complex **6** is stable for a couple of months at −37° C and for a week at room temperature. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 72.94 ppm (*J*(Pt,P) = 1764 Hz); ^1H NMR ([D$_8$]THF): δ = 3.75 (d, *J*(P,H) = 7 Hz, *J*(Pt,H) = 19 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.39 (m, 2H; CH_2–$\mathbf{CH_2}$–N), 2.02 (m, 2H; $\mathbf{CH_2}$–CH_2–N), 1.95 (s, 6H; N($\mathbf{CH_3}$)$_2$), 1.08 ppm (d, *J*(P,H) = 11 Hz, 18H; P(*t*Bu)$_2$); the aromatic region of the spectrum was very crowed due to two coordinated phenyls and the aromatic ring of the PCN ligand; $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 174.44 (d, *J*(P,C) = 120 Hz, ipso of phenyl, coordinated *trans* to P), 168.69 (d, *J*(P,C) = 21 Hz, ipso of phenyl, *cis* to P), 168.68 (d, *J*(P,C) = 20 Hz, ipso of coordinated ligand), 157.03 (s), 149.59 (s), 143.73 (s), 142.04 (s, *J*(Pt,C) = 25 Hz), 140.42 (s, *J*(Pt,C) = 48 Hz), 129.63 (s), 128.99 (s), 128.02 (s), 127.66 (s), 125.61 (s, *J*(Pt,C) = 23 Hz), 125.02 (d, *J*(P,C) = 6 Hz), 124.93 (s), 123.95 (s),122.77 (s), 118.55 (d, *J*(P,C) = 101 Hz) (these last 15 signals arise from the coordinated phenyl groups and to the aromatic ring of ligand), 64.46 (s, CH_2–$\mathbf{C}H_2$–N), 59.64 (s,$\mathbf{C}H_2$–CH_2–N), 46.24 (s, N–($\mathbf{C}H_3$)$_2$), 45.61 (d, *J*(P,C) = 24 Hz, Ar–$\mathbf{C}H_2$–P), 38.20 (d, *J*(P,C) = 10 Hz, P($\mathbf{C}$(CH_3)$_3$)$_2$), 30.84 ppm (d, *J*(P,C) = 4 Hz, P-(C($\mathbf{C}H_3$)$_3$)$_2$); ^7Li NMR ([D$_8$]THF): δ = −0.21 ppm (br s).

Reaction of [Pt(PCN)(CH$_3$)] (3) with MeI and iodobenzene—formation of [Pt(PCN)(I)] (7): A slight excess of iodomethane (4 µL, 0.062 mmol) was added to a solution of **3** (15 mg, 0.029 mmol) in THF (1 mL). After two days at room temperature $^{31}P\{^1H\}$ NMR spectroscopy revealed the quantitative formation of a new complex. GC analysis revealed formation of ethane. After evaporation of the THF, the resulting white solid was washed with pentane and dissolved in benzene, which was evaporated to give the clean complex **7**. The same mode of reaction was observed when **3** was reacted with a slight excess of iodobenzene (0.091 mmol, 19 µL).

Reaction of [Pt(PCN)(H)] (8) with MeI—formation of [Pt(PCN)(I)] (7): A slight excess of MeI (4 µL, 0.062) was added to a solution of **8** (15 mg, 0.030 mmol) in THF (1 mL). After 30 min formation of complex **7** was revealed by $^{31}P\{^1H\}$ NMR spectroscopy. The THF was evaporated, and **7** was washed by pentane and dissolved in benzene. After evaporation of benzene solvent, clean complex **7** was obtained. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 62.76 ppm (*J*(Pt,P) = 3928 Hz); ^1H NMR (C_6D_6): δ = 7.08 (dd, *J*(H,H) = 7 Hz, *J*(P,H) = 2 Hz, 1H; Ar), 7.04 (d, *J*(H,H) = 7 Hz, 1H; Ar), 6.77 (d, *J*(H,H) = 7 Hz 1H; Ar), 2.83 (s, *J*(Pt,H) = 34 Hz, 3H; N($\mathbf{CH_3}$)), 2.82 (s, *J*(Pt,H) = 34 Hz, 3H; N($\mathbf{CH_3}$)), 2.67 (d, *J*(P,H) = 2 Hz, *J*(Pt,H) = 30 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.39 (m, 2H;CH_2–$\mathbf{CH_2}$–N), 2.01 (m, 2H;$\mathbf{CH_2}$–CH_2–N), 1.31 ppm (d, *J*(P,H) = 14 Hz, 18H; P(***t*****Bu**)$_2$); ^{13}C NMR (C_6D_6): δ = 149.20 (d, *J*(P,C) = 10 Hz, ipso), 146.05 (s, Ar),143.71 (s, Ar), 142.57 (d, *J*(P,C) = 1 Hz, Ar), 124.42 (s, Ar), 121.33 (d, *J*(P,C) = 16 Hz, Ar), 64.53 (s, CH_2–$\mathbf{C}H_2$–N), 64.50 (s, $\mathbf{C}H_2$–CH_2–N), 52.31 (s, N–($\mathbf{C}H_3$)$_2$), 52.29 (s,N–($\mathbf{C}H_3$)$_2$), 36.74 (d, *J*(P,C) = 32 Hz, P($\mathbf{C}$(CH_3)$_3$)$_2$), 35.35 (d, *J*(P,C) = 26 Hz, Ar–$\mathbf{C}H_2$–P), 30.01 ppm (d, *J*(P,C) = 3 Hz, P–(C($\mathbf{C}H_3$)$_3$)$_2$).

Reaction of [Pt(PCN)(Cl)] (1) with $Na^+[Et_3BH]^-$—formation of [Pt(PCN)(H)] (8): A solution of Na[Et$_3$BH] in THF (1 M, 38 µL, 0.037 mmol) was added to a solution of complex **2** (20 mg, 0.037 mmol) in THF (1 mL). Upon addition of the hydride reagent the solution turned yellow, and after 24 h $^{31}P\{^1H\}$ NMR spectroscopy revealed formation of complex **8** (reaction with one equivalent of a solution of Li[Et$_3$BH] in THF (1 M, 38 µL 0.037 mmol) led to immediate formation of this complex). The solvent was evaporated and the resulting yellow-white solid was dissolved in pentane. After pentane evaporation pure **8** (17 mg, 0.034 mmol) was obtained (92 % yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 82.06 ppm (*J*(Pt,P) = 4014 Hz); ^1H NMR (C_6D_6): δ = 7.36 (d, *J*(H,H) = 10 Hz 1H; Ar), 7. 24 (dt, *J*(H,H) = 10 Hz, *J*(P,H) = 1 Hz,1H; Ar), 7.04 (d, *J*(H,H) = 10 Hz 1H; Ar), 3.00 (d, *J*(P,H) = 15.2 Hz, *J*(Pt,H) = 50 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.78 (s, *J*(Pt,H) = 47 Hz, 3H; N($\mathbf{CH_3}$)), 2.77 (s, *J*(Pt,H) = 49 Hz, 3H; N($\mathbf{CH_3}$)), 2.65 (m, 2H;CH_2–$\mathbf{CH_2}$–N), 2.27 (m, 2H;$\mathbf{CH_2}$–CH_2–N), 1.27 (d, *J*(P,H) = 21 Hz, 18H; P(***t*****Bu**)$_2$), −2.55 ppm (d, *J*(P,H) = 27 Hz, *J*(Pt,H) = 136.5 Hz, 1H; Pt–H); ^{13}C NMR (C_6D_6): δ = 173.01 (d, *J*(P,C) = 2 Hz, *J*(Pt,C) = 653 Hz, ipso), 151.63 (d, *J*(P,C) = 11 Hz, *J*(Pt,C) = 94 Hz, Ar), 142.68 (s, Ar), 124.34 (s, *J*(Pt,C) = 20 Hz, Ar), 123.51 (d, *J*(P,C) = 1 Hz Ar), 121.54 (d, *J*(P,C) = 16 Hz, *J*(Pt,C) = 48 Hz, Ar), 63.83 (s, CH_2–$\mathbf{C}H_2$–N), 63.82 (s, $\mathbf{C}H_2$–CH_2–N), 54.95 (s, N–($\mathbf{C}H_3$)$_2$), 54.93 (s, N–($\mathbf{C}H_3$)$_2$), 36.51 (d, *J*(P,C) = 33 Hz, *J*(Pt,C) = 105 Hz, P($\mathbf{C}$(CH_3)$_3$)$_2$), 33.65 (d, *J*(P,C) = 30 Hz, *J*(Pt,C) = 87 Hz, Ar–$\mathbf{C}H_2$–P), 29.61 ppm (d, *J*(P,C) = 3 Hz, *J*(Pt,C) = 26 Hz, P–(C($\mathbf{C}H_3$)$_3$)$_2$); IR (film): $\tilde{\nu}$ = 1863 cm^{-1} (Pt–H). elemental analysis calcd (%) for $C_{19}H_{44}PtPN$: C 45.42, H 6.77; found: C 45.29, H 6.72.

Reaction of [Pt(PCN)(Cl)] (2) with $Li^+[Et_3BH]^-$ or reaction of [Pt(PCN)(H)] (8) with LDA—formation of $Li^+[Pt(PCN)(H)_2]^-$ THF (9):

1) A solution of super hydride Li[Et$_3$BH] in THF (1 M, 190 µL, 0.200 mmol) was added to a solution of complex **2** (20 mg, 0.037 mmol) in THF (1 mL). The solution became brown, and after 3 h $^{31}P\{^1H\}$ NMR spectroscopy revealed formation of complex **9**. The solvent was evaporated, and the brown solid was washed with pentane and extracted with benzene. Evaporation of the solvent gave complex **9** in quantitative yield (by NMR spectroscopy). It was very sensitive to adventitious moisture, converting to the neutral complex **8.**

2) A solution of LDA in THF/heptane/ethylbenzene (2 M, 80 µL 0.162 mmol) was added to a solution of the monohydride complex **8** (80 mg, 0.162 mmol) in THF (1 mL). The resulting solution was heated for 5 h at 85 °C and $^{31}P\{^1H\}$ NMR spectroscopy revealed formation of complex **9** (quantitative yield by NMR spectroscopy). The concentrated THF solution of **9** was gently evaporated, causing precipitation of colorless crystals, suitable for a single-crystal X-ray analysis. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 91.69 ppm (*J*(Pt,P) = 2295 Hz); ^1H NMR ([D$_8$]THF): δ = 6.91 (d, *J*(H,H) = 7 Hz, 1H; Ar), 6.70 (d, *J*(H,H) = 7 Hz, 1H; Ar), 6.60 (dt, *J*(H,H) = 7 Hz, *J*(P,H) = 1 Hz ,1H; Ar), 3.21 (m, 2H; $\mathbf{CH_2}$–CH_2–N), 3.04 (d, *J*(P,H) = 2 Hz, *J*(Pt,H) = 31 Hz, 2H; Ar–$\mathbf{CH_2}$–P), 2.47 (m, 2H; CH_2–$\mathbf{CH_2}$–N), 2.12 (s, 6H; N($\mathbf{CH_3}$)$_2$), 1.20 (d, *J*(P,H) = 12 Hz, 18H; P(***t*****Bu**)$_2$), −3.00 (dd, *J*(Pt,H) = 1035 Hz, *J*(P,H) = 152 Hz, *J*(H,H) = 8 Hz, 1H; Pt–**H**), −7.07 ppm (t, *J*(Pt,H) = 700 Hz, *J*(P,H) = 8 Hz, *J*(H,H) = 8 Hz, 1H; Pt–**H**); $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 154.71 (d, *J*(P,C) = 14 Hz, ipso), 149.00 (s, *J*(Pt,C) = 37 Hz, Ar), 126.32 (s, Ar), 123.18 (s, *J*(Pt,C) = 26 Hz, Ar), 122.29 (s, Ar), 120.22 (d, *J*(P,C) = 16 Hz, Ar), 64.61 (s, $\mathbf{C}H_2$–CH_2–N), 64.57 (s, CH_2–$\mathbf{C}H_2$–N), 46.31 (s, N–($\mathbf{C}H_3$)$_2$), 33.90 (d, *J*(P,C) = 22 Hz, Ar–$\mathbf{C}H_2$–P), 30.50 (d, *J*(P,C) = 16 Hz, P($\mathbf{C}$(CH_3)$_3$)$_2$), 30.05 ppm (d, *J*(P,C) = 5 Hz, P–(C($\mathbf{C}H_3$)$_3$)$_2$); ^7Li NMR ([D$_8$]THF): δ = 0.53 ppm (br s); IR (film): $\tilde{\nu}$ = 1610 (Pt–H, *cis* to P), 1456 cm^{-1} (Pt–H, *trans* to P; H interacts with Li^+ from the a neighboring molecule).

X-ray structure determination and refinement of complexes 2, 3, and 9: The crystals were mounted in a nylon loop and flash frozen in a cold nitrogen stream (120 K) on a Nonius Kappa CCD diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71071 Å). Accurate unit cell dimensions were obtained from 20° of data. The data were processed with the Denzo-Scalepack package. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97). Idealized hydrogen atoms were placed and refined in the riding mode. Crystal data are given in Table 4. CCDC-239558 (**2**), CCDC-239557 (**3**), and CCDC-239559 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Table 4. Experimental crystallographic data for complexes **2**, **3**, and **9**.

	2	**3**	**9**
color, shape	colorless, plates	colorless, prism	colorless, plate
formula	$C_{19}H_{33}ClPNPt$	$C_{20}H_{36}NPPt$	$C_{23}H_{43}NPPt$
F_w	536.97	516.56	580.57
crystal system	monoclinic	rhombohedral	monoclinic
space group	$P2_1/c$ (no. 14)	$R\bar{3}$ (no. 148)	$P2_1/n$ (no. 14)
a [Å]	16.431(3)	24.224(3)	9.680(2)
b [Å]	7.487(2)	24.224(3)	12.483(3)
c [Å]	17.060(3)	17.900(4)	20.667(4)
α [°]	90	90	90
β [°]	108.35(1)	90	97.05(3)
γ [°]	90	120	90
ρ_{calcd} [g cm^{-3}]	1.791	1.697	1.562
μ (MoKα) [mm^{-1}]	7.259	7.021	5.759
crystal size [mm]	0.1 × 0.05 × 0.0	0.1 × 0.1 × 0.1	0.1 × 0.05 × 0.1
total reflections	16431	24580	24580
unique reflections	2676	5649	5890
R_{int}	0.136	0.067	0.057
parameters/restraints	216/0	217/0	264/0
$R1/wR2$	0.0461/0.0541	0.038/0.050	0.0336/0.0530
residual density [e Å^3]	2.056	1.611	2.164

Reactions with electrophiles

Reaction of $Li^+[Pt(PCN)(CH_3)_2]^-$ (4) with water: Upon injection of excess D_2O (6 µL, 0.333 mmol) into a solution of **4** (20 mg, 0.033 mmol) in THF (0.7 mL) in a 5 mm screw cap NMR tube equipped with a septum, formation of the neutral monomethyl complex **3** was immediately revealed by $^{31}P\{^1H\}$ NMR spectroscopy. GC/MS analysis of a 10 µL sample of the gas phase from the screw cap tube revealed formation of CH_3D (M_w = 17 g mol^{-1}). D_2O was used instead of H_2O, since detection of CH_3D is easier than that of CH_4 (CH_4 is ambiguous in GC/MS detection, since the MS peak at 16 could also stem from O_2).

Reaction of $Li^+[Pt(PCN)(CH_3)_2]^-$ (4) with iodomethane: A slight excess of MeI (5 µL, 0.074 mmol) was injected into a solution of **4** (20 mg, 0.033 mmol) in THF (0.7 mL) in a 5 mm screw cap NMR tube equipped with a septum. Formation of the neutral monomethyl complex **3** was immediately revealed by $^{31}P\{^1H\}$ NMR spectroscopy, while after 48 h complex **3** was completely converted to **7**. A sample of 10 µL of the gas phase from the screw cap NMR tube was analyzed by GC/MS revealing formation of C_2H_6 (M_w = 30 g mol^{-1}). In order to learn about the mechanism of ethane formation CD_3I (4.5 µL, 0.074 mmol) was used under the same conditions; this resulted in a mixture of CH_3CH_3, CH_3CD_3, and CD_3CD_3 in the ratio of 59:14:8 as observed by GC/MS.

Reaction of $Li^+[Pt(PCN)(CH_3)_2]^-$ (4) with iodobenzene: Excess iodobenzene (41 µL, 0.372 mmol) was added to a solution of **4** (20 mg, 0.033 mmol) in THF (0.8 mL). Conversion of **4** to **3** was followed by $^{31}P\{^1H\}$ NMR spectroscopy and after 24 h no more **4** was observed. The main product was the monomethyl complex **3**, which started conversion to the iodide complex **7**. The organic product of the reaction, toluene, was detected by GC (0.018 mmol, yield 55 %), using mesitylene as an internal standard.

Reaction of $Li^+[Pt(PCN)(H)_2]^-$ (9) with water: Excess H_2O (12 µL, 0.67 mmol) was injected into a solution of **9** (40 mg, 0.068 mmol) in THF (0.7 mL) in a 5 mm screw cap NMR tube equipped with a septum; this resulted in immediate formation of the neutral monohydride complex **8** as revealed by $^{31}P\{^1H\}$ NMR spectroscopy. Since, it is difficult to detect unambiguously formation of H_2 by using NMR or GC methods, trapping of hydrogen gas was performed by using the complex $[Ir(PNP)(coe)]^+$ PF_6^- (PNP = $C_5NH_3(CH_2P(t\text{Bu})_2)_2$, coe = cyclooctene). This complex reacts with hydrogen gas to yield an iridium dihydride cationic complex.[28] 1 mL of the gas phase from the screw cap NMR tube was injected into a screw cap NMR tube containing a the complex $[Ir(PNP)(COE)]^+$ PF_6^- and after 12 h formation of the dihydride complex was revealed by $^{31}P\{^1H\}$ (singlet at 65.03 ppm) and ^1H NMR spectroscopy (hydride signal at −23.75 ppm).

Reaction of $Li^+[Pt(PCN)(H)_2]^-$ (9) with iodomethane: A slight excess of CD_3I (4.5 µL, 0.074 mmol) was injected into a solution of **9** (20 mg, 0.034 mmol) in THF (0.7 mL) in a 5 mm screw cap NMR tube with a septum. Formation of the neutral monohydride complex **8** was immediately revealed by $^{31}P\{^1H\}$ NMR spectroscopy, which was completely converted to **7** after 30 min. GC/MS analysis on 10 µL of the gas phase from the screw cap NMR tube revealed formation of CHD_3 (M_w = 19 g mol^{-1}). CD_3I was used instead of CH_3I in order to get unambiguous evidence of methane formation using GC/MS.

Acknowledgements

This work was supported by the Israel Science Foundation, by the Minerva Foundation, Munich (Germany) and by the Helen and Martin Kimmel Center for Molecular Design. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry.

---

[1] a) R. H. Crabtree, *The Organometalic Chemistry of the Transition Metals*, Wiley, New York, **1994**; b) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Application of Organotransition Metal Chemistry*, Univerity Science Books: Mill Valley, CA, **1987**; c) M. J. Kraus, R. G. Bergman, *J. Am. Chem. Soc.* **1985**, *107*, 2972.

[2] a) G. W. Rice, R. S. Tobias, *J. Am. Chem. Soc.* **1977**, *99*, 2141; b) H. Nakazawa, F. Ozawa, A. Yamamoto, *Organometallic*s **1983**, *2*, 241; c) M. P. Garcia, L. A. Oro, F. J. Lahoz, *Angew. Chem.* **1988**, *100*, 1766; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1700; d) J. J. Brunet, G. Commenges, D. Neibecker, L. Rosenberg, *J. Organomet. Chem.* **1996**, *522*, 117; e) D. G. Gusev, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **1998**, *120*, 13138.

[3] a) A. Dedieu, *Transition Metal Hydrides*, VCH, Weinheim, **1991**, p. 361.

[4] a) F. W. S. Benfield, R. A. Fonder, M. L. H. Green, G. A. Moser, K. Prout, *J. Chem. Soc. Chem. Commun.* **1973**, 759; b) B. R. Francis, M. L. H. Green, L. Tuyet, G. A. Moser, *J. Chem. Soc. Dalton Trans.* **1976**, 1339.

[5] a) G. P. Pez, R. A. Grey, J. Corsi, *J. Am. Chem. Soc.* **1981**, *103*, 7528; b) R. A. Grey, G. P. Pez, A. Wallo, *J. Am. Chem. Soc.* **1981**, *103*, 7536; c) R. A. Grey, G. P. Pez, A. Wallo, *J. Am. Chem. Soc.* **1980**, *102*, 5949.

[6] P. L. Gaus, S. C. Kao, K. Youngdahl, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1985**, *107*, 2428.

[7] a) J. W. Bruno, J. C. Huffman, M. A. Green, K. G. Caulton, *J. Am. Chem. Soc.* **1984**, *106*, 8310; b) A. A. Del Paggio, R. A. Andersen, E. L. Muetterties, *Organometallics* **1987**, *6*, 1260.

[8] a) J. E. Ellis, R. A. Faltynek, *J. Am. Chem. Soc.* **1977**, *99*, 1801; b) J. E. Ellis, C. P. Parnell, G. P. Hagen, *J. Am. Chem. Soc.* **1978**, *100*, 3605.

[9] H. B. Chin, R. Bau, *J. Am. Chem. Soc.* **1976**, *98*, 2434.

[10] a) M. A. Bennet, J. D. Patmore, *Inorg. Chem.* **1971**, *10*, 2387; b) E. L. Muetteries, F. J. Hirsekorn, *J. Am. Chem. Soc.* **1974**, *96*, 7920.

[11] C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314.

[12] Reviews: a) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759; c) J. T. Singleton, *Tetrahedron* **2003**, *59*, 1837; d) A. Vigalok, D. Milstein, *Acc. Chem. Res.* **2001**, *34*, 798.

[13] Recent papers from our group: a) D. Milstein, *Pure Appl. Chem.* **2003**, *75*, 2003; b) R. Cohen, B. Rybtchinski, M. Gandelman, H. Rozenberg, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 6532; c) R. Cohen, B. Rybtchinski, M. Gandelman, L. J. W. Shimon, J. M. L. Martin, D. Milstein, *Angew. Chem.* **2003**, *115*, 1993; *Angew. Chem. Int. Ed.* **2003**, *42*, 1949; d) A. Vigalok, B. Rybtchinski, Y. Gozin, T. S. Koblenz, Y. Ben-david, H. Rozenberg, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 15692.

[14] a) C. J. Moulton, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1976**, 1020; b) C. Crocker, D. Empsall, R. J. Errington, E. M. Hyde, W. S. McDonald, R. Markham, M. C. Norton, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1982**, 1829.

[15] a) J. A. M. van Beek, G. van Koten, W. J. J. Smeets, A. L. Spek, *J. Am. Chem. Soc.* **1986**, *108*, 5010; b) M. Albrecht, P. Dani, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2000**, *122*, 11822; c) M. Q. Slagt, H. P. Dijkstra, A. McDonald, R. J. M. L. Gebbink, M. Lutz, D. D. Ellis, A. M. Mills, A. L. Spek, G. van Koten, *Organometallics* **2003**, *22*, 27; d) H. P. Dijkstra, N. Ronde, G. P. M. van Klink, D. Vogt, G. van Koten, *Adv. Synth. Catal.* **2003**, *345*, 364.

[16] a) M. Gandelman, A. Vigalok, L. J. W. Shimon, D. Milstein, *Organometallics* **1997**, *16*, 3981; b) M. Gandelman, A. Vigalok, L. Konstantinovsky, D. Milstein, *J. Am. Chem. Soc.* **2000**, *122*, 9848; c) M. Gandelman, L. J. W. Shimon, D. Milstein, *Chem. Eur. J.* **2003**, *9*, 4295; d) M. Gandelman, D. Milstein, *Chem. Commun.* **2000**, 1603; e) M. Gandelman, L. Konstantinovski, H. Rozenberg, D. Milstein, *Chem. Eur. J.* **2003**, *9*, 2595.

[17] Review on nitrogen donors in organometallic chemistry: A. Togni, L. Venanzi, *Angew. Chem.* **1994**, *106*, 517; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497.

[18] For reviews on hemilabile ligands, see: a) A. Bader, E. Linder, *Coord. Chem. Rev.* **1991**, *108*, 27; b) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233; c) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702; *Angew. Chem. Int. Ed.* **2001**, *40*, 681; d) A. D. Burrows, *Sci. Prog.* **2002**, *85*, 199; e) review on P,N-type ligands: P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *195*, 499.

[19] P. J. O'Hanlon, N. H. Rogers, *Eur. Pat .Appl.* **1982**, AN 406065.

[20] F. Maassarani, M. F. Davidson, I. C. M. Wehman-Ooyevaar, D. M. Grove, M. A. van Koten, W. J. J. Smeets, A. L Spek, G. van Koten, *Inorg. Chim. Acta* **1995**, 327.

[21] M. Q. Slagt, R. J. M. Klein Gebbink, M. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **2002**, 2591.

[22] J. Terheijden, G. van Koten, F. Muller, D. M. Grove, K. Vrieza, E. Nielsen, C. H. Stam, *J. Organomet. Chem.* **1986**, *315*, 401.

[23] R. P. Hughes, A. Williamson, C. D. Incarvito, A. L. Rheingold, *Organometallics* **2001**, *20*, 4741.

[24] J. M. Longmire, X. Zhang, *Organometallics* **1998**, *17*, 4374.

[25] a) Review on X-ray structures of organolithium compounds: W. N. Setzer, P. von R. Scheyer, *Adv. Organomet. Chem.* **1985**, *24*, 353; b) M. M. Andrianarison, A. G. Avent, M. C. Ellerby, I. B. Gorrell, P. B. Hitchcock, J. D. Smith, D. R. Stanley, *J. Chem. Soc. Dalton Trans.* **1998**, 249; c) R. Boulatov, B. Du, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **1999**, *38*, 4554.

[26] R. Goikhman, M. Aizenberg, H.-B. Kraatz, D. Milstein, *J. Am. Chem. Soc.* **1995**, *117*, 5865.

[27] H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411.

[28] E. Ben-Ari, M. Gandelman, H. Rozenberg, L. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 4714.

Received: May 24, 2004