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# Anionic d$^8$ Alkyl Hydrides – Selective Formation and Reactivity of Anionic *cis*-Pt$^{II}$ Methyl Hydride

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The pincer-type complexes [(PCN)PtR] {R = H, **2**; Me, **4**; PCN = $C_6H_4[CH_2P(tBu)_2](CH_2)_2N(CH_3)_2$} react with MeLi or $Et_3BHNa$, to give anionic *cis*-Pt(Me)H complexes [(PCN*)-Pt(H)(Me)]$^-$Li$^+$ (Me *trans* to P; PCN* denotes the PCN ligand in which the amine arm is not coordinated) and [(PCN*)-Pt(Me)(H)]$^-$Na$^+$ (H *trans* to P). Only the isomer in which the incoming nucleophile is situated *trans* to the phosphane ligand is formed. These first d$^8$ anionic alkyl hydride complexes were fully characterized spectroscopically. The hemilabile PCN ligand allows for reversible de-coordination of the amine arm, thereby providing a desirable balance of stability vs. reactivity. Theoretical calculations on model systems indicate a concerted mechanism in which the nucleophilic attack and the amine dissociation occur concurrently. The (unobserved) methane reductive elimination from the stable anionic methyl hydride complex [(PCN*)Pt(Me)(H)]$^-$Li$^+$ (**3**) is thermodynamically and kinetically unfavorable, as indicated by DFT. This complex reacts with electrophiles, such as water and methyl iodide, to yield exclusively methane and the corresponding organometallic product (either **2** or **4**). This reactivity was also further examined by DFT.

## Introduction

Selective activation and functionalization of simple alkanes is an important challenge,[1] and systems that help understand the mechanisms involved in such processes are a subject of much interest (for recent reviews, see[2]). Hydrido(alkyl)metal complexes are key intermediates in alkane functionalization, but examples of isolated complexes of this type with group 10 metals are not common, and limited mainly to the d$^6$ complexes (for examples of Pt$^{IV}$ alkyl hydrides, see ref.[3]). We are aware of only one example of a stable Pt$^{II}$ alkyl hydride complex.[4]

As the simplest alkane, methane has attracted much attention,[5] especially subsequent to its Pt-promoted selective functionalization reported by Shilov and co-workers in the 1970s[6] and later reports on Pt-catalyzed methane oxidation by other groups.[5e,5p,5q] As Pt$^{II}$ methyl hydrides may be intermediates in new approaches to methane functionalization, the generation and reactivity of such complexes is of interest.

Anionic transition metal complexes are important due to their potential as nucleophiles[7] and their involvement in catalytic processes.[8] However, the majority of such complexes have π-acceptor ligands that stabilize the complex by diminishing the high electron density on the metal center. This, however, reduces the nucleophilicity of such species.[9] In previous studies, we found that hemilabile, pincer-type PCN ligands {PCN = $C_6H_4[CH_2P(tBu)_2][(CH_2)_2N(CH_3)_2]$; for recent reviews on pincer ligands, see[10]} are useful in addressing the stability vs. reactivity issue of anionic complexes.[11] Due to the hemilability[12] of the σ-donating amine "arm," PCN-based complexes, and their PNN analogues that we have also studied,[13] can accommodate various electronic and steric environments[13a,13e,14] resulting in a broad range of reactivity.

Herein we report on the electron-rich complex [(PCN*)-PtMeH]$^-$Li$^+$ (where PCN* denotes the ligand in which the amine "arm" is not coordinated to the metal center) that smoothly reacts with electrophiles. This complex is, to the best of our knowledge, the first example of an isolated anionic d$^8$ alkyl hydride complex. The complex was fully characterized and aspects of the mechanisms of its selective formation and reactivity were studied, both experimentally and computationally.

## Results and Discussion

### Formation of Anionic [(PCN*)Pt(Me)(H)]$^-$ Complexes by Nucleophilic Attack

As we have previously described, the reaction of [(PCN)-PtCl] (**1**) with one equivalent of $Et_3BHNa$ results in the

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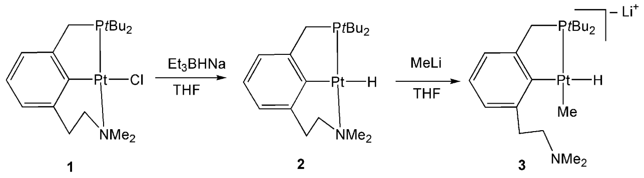
neutral hydride complex **2** (Scheme 1).[11] Upon addition of one equivalent of MeLi to a THF solution of complex **2**, the $^{31}P\{^1H\}$ NMR spectrum immediately reveals the formation of the new complex **3** (Scheme 1). To the best of our knowledge, complex **3** represents an unprecedented example of an anionic $d^8$ alkyl hydride complex.

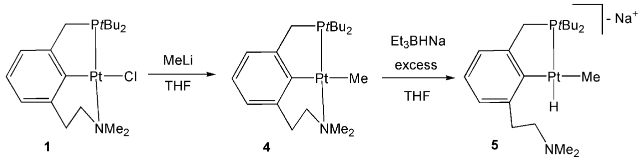


Scheme 1.

The structure of complex **3** was unambiguously confirmed by multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a signal at $\delta = 93.16$ ppm with Pt satellites ($J_{Pt,P} = 2317$ Hz). The relatively small Pt–P coupling (cf. $J_{Pt,P} \approx 4000$ Hz for the neutral system **1** and **2**) is indicative of the coordination of a strong σ-donor *trans* to phosphorus.[15] The coordinated methyl group is observed in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra at $\delta = 0.79$ ppm (dd, $J_{P\text{-}H} = 5.5$, $J_{H,H} = 1.5$, $J_{Pt\text{-}H} = 58$ Hz) and –15.15 ppm (d, $J_{P,C} = 101$, $J_{Pt\text{-}C} = 572$ Hz), respectively. The hydride appears in the $^1H$ NMR spectrum at –6.17 ppm as a doublet ($J_{P\text{-}H} = 12$, $J_{Pt\text{-}H} = 732$ Hz) with a small P–H coupling constant, which indicates that the hydride is situated *cis* to phosphorus (for comparison, see the P–H *trans* coupling hereinafter); in principle the hydride should be a double quartet, from coupling with the three methyl hydrogen atoms, but this coupling is not observed. In the $^{13}C\{^1H\}$ NMR spectrum, the *ipso* carbon appears at $\delta = 168.68$ ppm as a doublet ($J_{P,C} = 25$ Hz). The methyl groups of $NMe_2$ exhibit a single resonance without any Pt satellites in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra, clearly indicating that the amine "arm" of the PCN ligand is not coordinated to the metal center.[11]

It is interesting to note that the isomer of $[(PCN^*)PtHMe]^-Li^+$ with H *trans* to P is not obtained in this reaction. Thus, MeLi attack leads to a single product in which the nucleophile is situated *trans* to phosphorus.

In order to examine the selectivity of the attacking nucleophile, the complimentary reaction in which [(PCN)PtMe] (**4**) was treated with a hydride source was performed. Complex **4** was obtained by reaction of **1** with MeLi.[11] Interestingly, when an excess of $Et_3BHNa$ was added to a THF solution of **4**, only complex **5** was formed (Scheme 2). While complex **5** was stable in solution, it was unstable during work-up, making its isolation problematic, and it was thus characterized in solution. As in the case of **3**, the $^{31}P\{^1H\}$ NMR of **5** exhibits a downfield-shifted single resonance at $\delta = 74.03$ ppm with a small Pt–P coupling ($J_{Pt,P} = 2445$ Hz). The hydride appears in the $^1H$ NMR spectrum at –3.26 ppm as a doublet with $J_{P\text{-}H} = 167$ Hz (with platinum satellites of $J_{Pt\text{-}H} = 1061$ Hz). Such a large coupling unambiguously indicates *trans* coordination of the hydride and phosphane ligands. Again, selective nucleophilic attack takes place with the nucleophile always situated *trans* to the phosphane ligand.

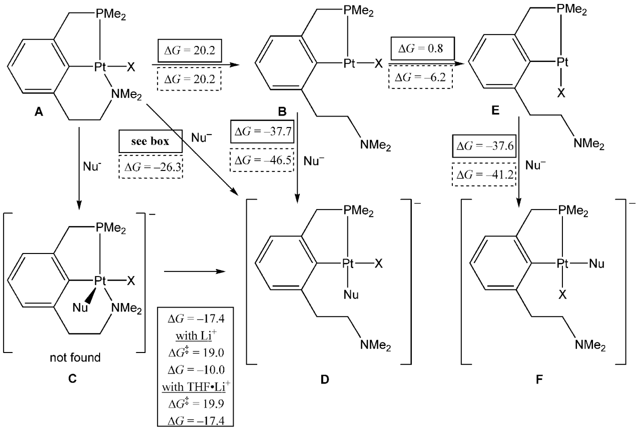


Scheme 2.

## DFT Calculations

In order to get a better understanding of the mechanism by which these nucleophilic attacks proceed, the system was studied using density functional theory. All theoretical energies herein, unless stated otherwise, are Gibbs free energies in solution (i.e., THF) at the PCM(THF)-M06/aug-SDB-cc-pVDZ//M06/SDD level of theory. The M06 exchange-correlation functional[16] was chosen as it has been shown to be superior in the study of transition metal complexes[16–17] (see Computational Details section for full details).

Three potential routes were considered (Scheme 3). The first route involves initial de-coordination of the amine arm, forming a T-shaped 14-electron complex, followed by attack of the nucleophile. The second route involves initial attack of the nucleophile, forming a five-coordinate, 18-electron complex, with subsequent de-coordination of the amine arm. The third route is a concerted mechanism wherein amine de-coordination and attack of the nucleophile occur simultaneously. Each pathway was considered using a model system where the *tert*-butyl substituents on the phosphanes were replaced by methyl groups.



Scheme 3. Reaction of the platinum complexes with nucleophiles. Reaction energies and barrier heights (in kcal/mol) are shown in solid boxes for X = Me and dotted boxes for X = H.

The first pathway, initial de-coordination with subsequent nucleophilic attack, requires the formation of a 14-electron complex (**B**). Such complexes tend to be high in energy. In addition, the isomer with the X *trans* to the phosphane (**E**), rather than to the phenyl ring (**B**), is likely to be more stable, as the phenyl ring is a stronger σ-donor than the phosphane (i.e., phenyl has a larger *trans* influence) and thus would prefer to be *trans* to the vacant site. Thus, this would likely lead to the isomer opposite to that observed experimentally (i.e., **F**). In fact, the reaction is strongly endergonic in both cases ($\Delta G_{298}$ = 20.2 kcal/mol in both the cases of X = Me and X = H). While in the case of X = Me, the two isomers **B** and **E** are practically isergonic (**E** is less stable by $\Delta G_{298}$ = 0.8 kcal/mol), in the case of X = H, complex **E** is more stable by $\Delta G_{298}$ = –6.2 kcal/mol. Therefore, in this case, the attack of MeLi would result in **F** and not **D** (i.e., the reaction of **2** + MeLi − see Scheme 1 − would result in **5** instead of the observed **3**).

The second route, initial nucleophilic attack followed by amine de-coordination, involves an 18-electron, $d^8$ species. Such species tend to be unstable due to repulsion between the vacant, high-energy $d_{z^2}$ orbital and the incoming ligand.[18] (It should be noted, however, that such species have been observed in the case of strongly elerctron-withdrawing ligands, such as *tris*-pyrrolylphosphane.[18]) In fact, all attempts to find the geometry of such a species using DFT failed and all attempts resulted in **D** rather than **C**.

The third pathway, concerted nucleophilic attack and amine de-coordination, does not suffer from these problems. Moreover, the concerted nature prevents isomerization and the formation of **F**. Overall, this reaction is exergonic by $\Delta G_{298}$ = –26.3 and –17.4 kcal/mol, respectively, for X = H and Me. In the former case, a transition state for the attack of MeLi was found (Figure 1). In the transition state, the amine arm has moved away from the Pt centre and the Me group is moving from the Li atom to the Pt centre in a manner reminiscent of an $S_E2$ attack of the metal centre on MeLi. This transition state results in a reaction barrier of $\Delta G^{\ddagger}_{298}$ = 19.0 kcal/mol, which is not unreasonable for a sluggish room temperature reaction. In the product, the lithium atom is situated between the platinum and amine centers. Overall, this reaction is exergonic by $\Delta G_{298}$ = –10.0 kcal/mol. If one includes an explicit THF molecule stabilizing the anion, then the barrier is slightly higher ($\Delta G^{\ddagger}_{298}$ = 19.9 kcal/mol) but the reaction is significantly more exothermic ($\Delta G_{298}$ = –17.4 kcal/mol). In the product, the lithium cation is surrounded by the platinum center, amine group and THF (Figure 2).

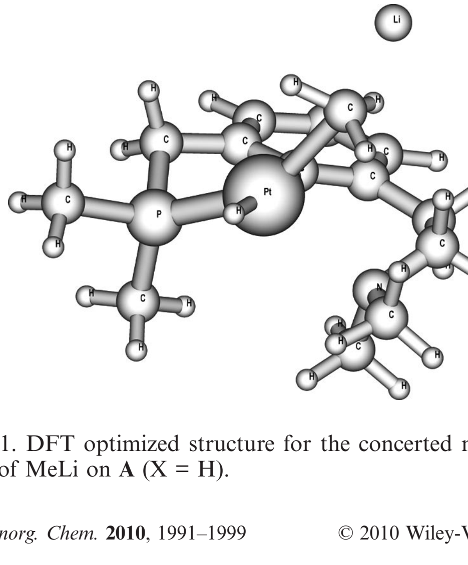


Figure 1. DFT optimized structure for the concerted nucleophilic attack of MeLi on **A** (X = H).

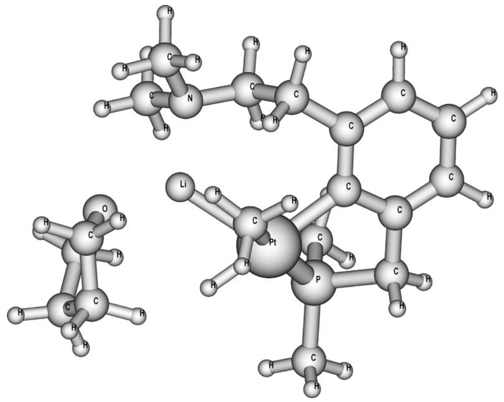


Figure 2. DFT optimized structure of **D**·Li$^+$·THF (X = H). Selected distances: N–Li: 2.042 Å; O–Li: 1.934 Å; Pt–Li: 2.470 Å.

Conceivably, the methyl-hydride complexes could have been formed by the oxidative addition of methane to the putative anionic Pt$^0$ complex [(PCN)Pt]$^-$. As the activation of methane is an important challenge, the reverse reaction, the reductive elimination of methane from **3**, was examined.

From the model system **3***, a transition state for methane reductive elimination was found (Figure 3). This leads to a barrier of $\Delta G^{\ddagger}_{298}$ = 28.4 kcal/mol. The reaction to give the anionic Pt$^0$ complex [(PCN)Pt]$^-$ is endergonic by $\Delta G_{298}$ = 20.1 kcal/mol. Thus, the reverse reaction would be very fast ($\Delta G^{\ddagger}_{298}$ = 8.3 kcal/mol) and [(PCN)Pt]$^-$ is expected to be very reactive, inter alia, towards C–H activation of various substrates, including the solvent. A 16 e$^-$ anionic Pt$^0$ complex that rapidly activates C–F bonds was recently reported by us.[19]

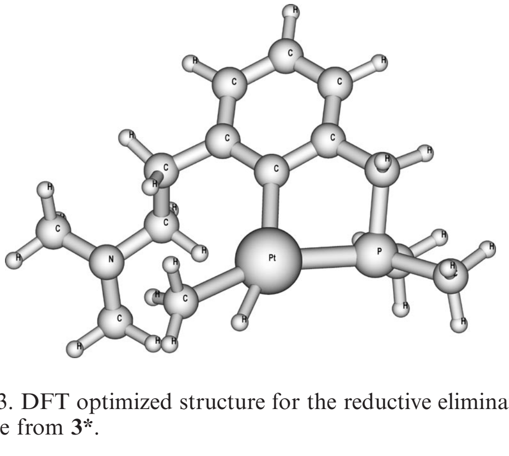
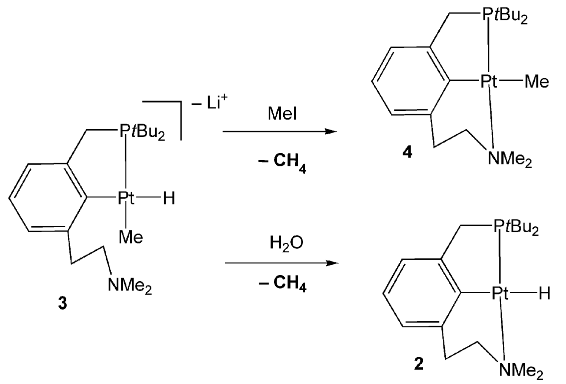


Figure 3. DFT optimized structure for the reductive elimination of methane from **3***.

### Reactions of Anionic [(PCN*)Pt(Me)(H)]$^-$Li$^+$ with Electrophiles

The chemistry of complex **3** is further enriched by the nucleophilic character of the coordinated methyl and hydride ligands. Upon reaction with electrophiles, complex **3** behaves as an R$^-$ donor (R = H, Me) with regeneration of the initial closed pincer framework (Scheme 4). For example, reaction of **3** with MeI immediately leads to formation of the neutral methyl complex **4** as observed by $^{31}P\{^1H\}$ NMR spectroscopy. Likewise, the reaction of **3** with $H_2O$ results in the immediate formation of the hydride complex **2**. In both cases, methane is selectively formed (detected by GC/MS) as the sole organic product. Neither ethane (in the first reaction) nor $H_2$ (in the second reaction) were observed, nor any other organometallic products.



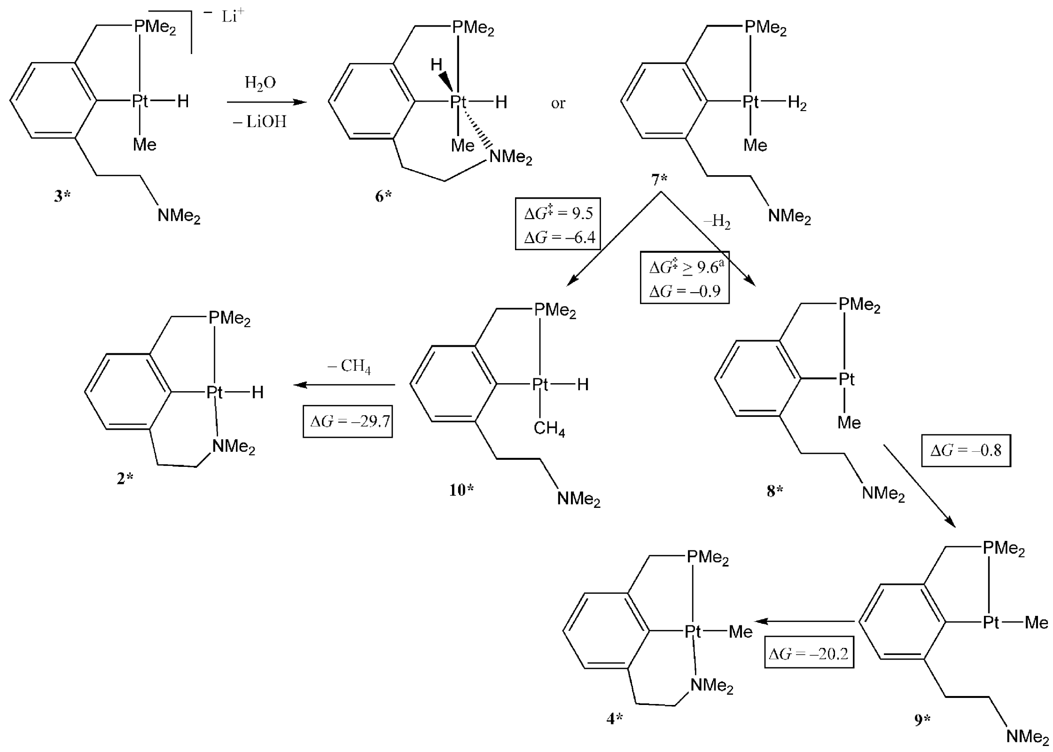
Scheme 4.

Mechanistically, these reactions may occur either via a direct attack of the electrophile on the methyl or hydride groups, or through oxidative addition of the electrophile to the Pt center followed by reductive elimination of the organic product. In our previous work, we demonstrated, using labeling experiments, that the reaction of [(PCN*)-Pt(Me)$_2$]$^-$Li$^+$ with MeI occurs via the second (oxidative addition) pathway.[11]

## DFT Calculations

The reactions of the anion **3** with water and methyl iodide to give methane, the corresponding lithium salt (LiOH or LiI) and, respectively, **2** and **4**, were examined by DFT. Again, a model system with methyl substituents on the phosphane was used. Model complexes are differentiated from their experimental counterparts by appending an asterisk (*) to the complex numbers.

*Reaction with Water.* The addition of water to **3*** results in three similar complexes (Scheme 5). One option is the formation of the *fac* dihydride complex, *fac*-[(PCN)-Pt(Me)(H)$_2$] (**6***); the more common, at least with pincer complexes, *mer* complex is impossible since the Me ligand already occupies the site *trans* to the phosphane. With typical pincer ligands, *fac* complexes are not considered due to the rigidity of the ligand, yet this PCN ligand has a two-methylene amine arm that affords greater flexibility. (While one could in principle consider an isomerisation process to obtain the *mer* complex, as shall soon be seen this is an unnecessary complication.) The other two complexes are non-classical $\eta^2$-dihydrogen complexes, [(PCN*)Pt(Me)($\eta^2$-H$_2$)] (**7a*** and **7b***), which differ in the orientation of the H$_2$ axis with respect to the plane of the PCN aromatic ring. The difference in energy between **7a*** and **7b*** ($\Delta G_{298}$ = 0.2 kcal/mol) and the very small barrier connecting them



Scheme 5. Reaction of **3*** with water. Reaction energies and barrier heights (in kcal/mol) are shown (lower estimate[a] of barrier height, see text).

($\Delta G^{\ddagger}_{298} < 1$ kcal/mol) indicate a very rapid equilibrium. Relative to **7***, complex **6*** is less stable by $\Delta G_{298}$ = 3.5 kcal/mol. The barrier for H–H activation [i.e., **TS(7*-6*)**], which includes dissociation of the amine arm, is $\Delta G^{\ddagger}_{298}$ = 8.2 kcal/mol. A transition state for the formation of **7*** by the protonation of the hydride ligand by water was found, resulting in a barrier of $\Delta G^{\ddagger}_{298}$ = 18.5 kcal/mol. Due to the formation of a salt (i.e., LiOH), it is not possible to accurately give a reaction energy for this step, although it is known to be exothermic. It is not possible to rule out a direct protonation of the metal center, which would result in **6***, and regardless, this has no significant bearing on the conclusions since **6*** can easily be converted to **7*** via a low barrier. However, a direct attack on the coordinate methyl ligand can be ruled out; a transition state for this direct attack was found and leads to a barrier of $\Delta G^{\ddagger}_{298}$ = 33.7 kcal/mol. The loss of $H_2$ from **7***, resulting in the T-shaped complex [(PCN*)PtMe] (**8***, with the vacant site *trans* to the PCN ring) is slightly exergonic with $\Delta G_{298}$ = –0.9 kcal/mol. Isomerisation to the second T-shaped complex **9*** ($\Delta G_{298}$ = –1.7 kcal/mol relative to **7***) and coordination of the amine arm ($\Delta G_{298}$ = –21.9 kcal/mol relative to **7***) results in [(PCN)PtMe] (**4***).

A transition state for the dissociation of $H_2$ was problematic to find. The reaction **3*** → **8*** is practically isergonic. The reaction profile along the Pt–H reaction coordinate shows that dissociation of the $\eta^2$-$H_2$ ligand requires $\Delta E$ = 11.0 kcal/mol (gas phase, M06/aug-SDB-cc-pVDZ level of theory). Since the reaction is exergonic, there should be a transition state along this reaction coordinate. Part of the urgency in obtaining a transition state is that formation of dihydrogen is not observed. A relaxed reaction profile (optimized at the M06/SDD level of theory) led to a dissociation energy of $\Delta G_{298}$ = 13.3 kcal/mol (in solution at the M06/aug-SDB-cc-pVDZ//M06/SDD level of theory). If the profile is relaxed as a transition state, then, before the calculation terminated, a barrier of $\Delta G^{\ddagger}_{298}$ = 8.6 kcal/mol was obtained; at the end of the run, the energy was leveling out but still slowly rising. A transition state optimization did yield a structure that might be the desired transition state, which would lead to a barrier of $\Delta G^{\ddagger}_{298}$ = 9.6 kcal/mol. While its imaginary frequency does seem to correspond to $H_2$-dissociation, its connectivity could not be confirmed by IRC calculations. Regardless, this is a reasonable estimate of the lower limit for the reaction barrier.

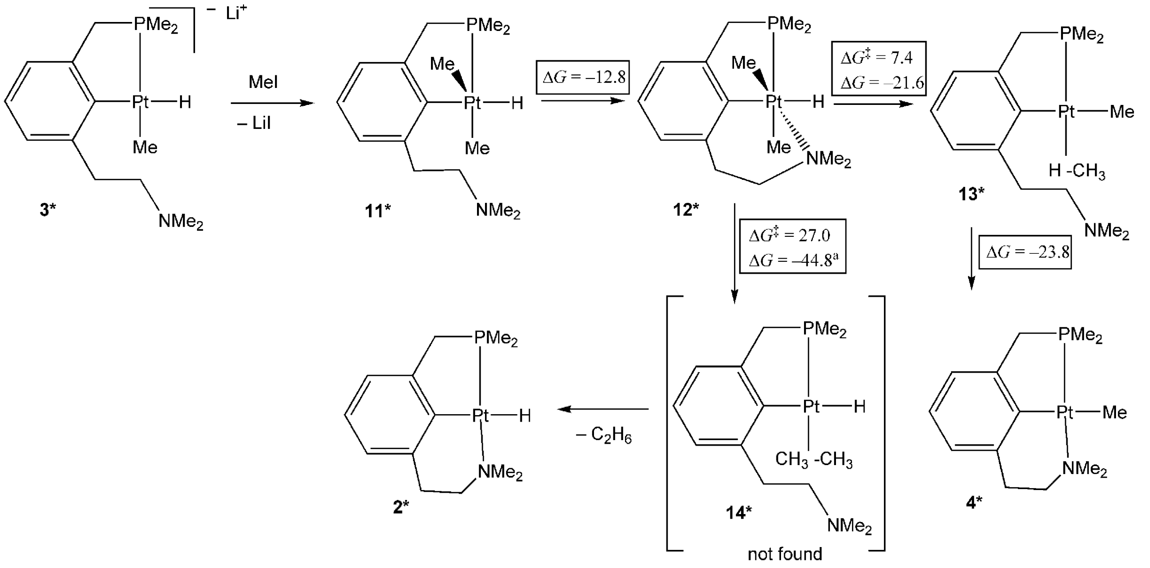
Two transition states for the formation of methane via C–H coupling were located, one from the *fac* complex **6*** (involving the hydride *trans* to the amine arm) and one from the non-classical dihydrogen complex **7***. In the latter, the reaction involves the transfer of a hydrogen atom from the dihydrogen complex in **7a***, in which the $H_2$ fragment axis is in plane with the PCN ligand, to the methyl group. (In fact, a third transition state was also found involving coupling in **6*** of the second hydride *trans* to the PCN phenyl ring, but this was considerably higher in energy since it involves concurrent dissociation of the phosphane ligand rather than the amine, and was thus not considered further.) These two transition states lead to barriers of $\Delta G^{\ddagger}_{298}$ = 16.4 and 9.5 kcal/mol, respectively. Thus, the reaction likely proceeds via the non-classical dihydrogen complex **7***, although the other barrier is still reasonable under these reaction conditions, except for the fact that it would be higher than the lower estimate for the barrier for $H_2$ loss. The initial product is a σ-methane complex, [(PCN*)Pt(H)(σ-$CH_4$)] (**10***) with an energy of $\Delta G_{298}$ = –6.4 kcal/mol relative to **7***. Loss of the weakly bound methane ligand, isomerisation of the resulting T-shaped complex and coordination of the amine arm lead to the final product, [(PCN)-PtH] (**2***), which has a relative energy (to **7***) of $\Delta G_{298}$ = –36.1 kcal/mol.

Estimates for the reaction barriers for methane and hydrogen formation were found. While both estimates are of similar height, the formation of methane from **7*** is much more exergonic ($\Delta\Delta G_{298}$ = 14.2 kcal/mol). Since the M–$CH_3$ bond is weaker than M–H bond for late metals,[15] it is preferable thermodynamically to eliminate methane over $H_2$.[20,21]

*Reaction with Methyl Iodide*. The initial product of the reaction of **3*** with MeI, in addition to LiI, is [(PCN*)-Pt(Me)$_2$(H)] (**11***) (Scheme 6). As in the previous case, the amine arm in this complex can close to give the *fac* complex *fac*-[(PCN)Pt(Me)$_2$(H)] (**12***); again the *mer* isomer is neither immediately accessible, since the site *trans* to the phosphane is occupied, nor required. In contrast to the previous situation, complex **12*** is considerably more stable ($\Delta G_{298}$ = –12.8 kcal/mol) than **11***. From complex **12***, there are three potential coupling reactions that can occur: two C–H coupling processes, each involving a different methyl group (one which involves Pt–P dissociation, is thus higher in energy, and thus not considered further), and one C–C coupling of the two methyl ligands. Transition states for the coupling reactions from **11*** could not be located, which is not significant since **12*** is considerably more stable.

The transition state for C–H coupling [**TS(12*-13*)**] results in a barrier of $\Delta G^{\ddagger}_{298}$ = 7.4 kcal/mol. The σ-methane complex **13***, the analogue of **10*** above, was located, although here the methane ligand is farther from the metal center. The formation of **13*** is exergonic by $\Delta G_{298}$ = –21.6 kcal/mol. Loss of methane and closure of the amine arm leads to the final product **4***. Overall, the formation of **4*** from **12*** is exergonic by $\Delta G_{298}$ = –45.4 kcal/mol.

The transition state for C–C coupling [**TS(12*-14*)**] results in a reaction barrier of $\Delta G^{\ddagger}_{298}$ = 27.0 kcal/mol. A σ-ethane complex **14*** could not be found, neither a C–H nor a C–C agostic complex. Overall, the formation of ethane and complex **2*** is exergonic by $\Delta G_{298}$ = –44.8 kcal/mol. Although both coupling processes are similarly exergonic, the significantly higher barrier for C–C coupling precludes its occurrence. Part of the reason is the greater steric interactions between the hydrogen atoms in the two methyl groups in the transition state. A second part is the poorer orbital overlap in the C–C coupling. This coupling requires the overlap of two carbon 2*p* orbitals, which are very directional, whereas C–H coupling involves coupling with the omnidirectional hydrogen 1*s* orbital.



Scheme 6. Reaction of **3*** with MeI. Reaction energies and barrier heights (in kcal/mol) are shown ([a] reaction energy is for the conversion of **12*** to **2***, since **14*** could not be found, see text).

## Conclusions

Reaction of the complexes [(PCN)PtR] (R = H, Me) with the nucleophiles MeLi and $Et_3BHNa$ yields single, anionic products with the incoming nucleophile (methyl or hydride, respectively) always situated *trans* to the phosphane. To the best of our knowledge, these are the first anionic $d^8$ alkyl hydride complexes. Theoretical calculations on model systems show that the reaction proceeds via a concerted mechanism in which the nucleophilic attack and the amine "arm" dissociation occur concurrently. Reductive elimination from the product $[(PCN)PtRR']^-$ complexes was considered in light of the importance of methane activation. This process was found to be thermodynamically and kinetically unfavorable and was not observed experimentally. The anionic $Pt^0$ complex $[(PCN)Pt]^-$, if it can be generated by alternative pathways, is expected to be very reactive in C–H oxidative addition.

The complex $[(PCN^*)Pt(Me)(H)]^-Li^+$ (**3**) readily reacts with electrophiles, like water and methyl iodide, to exclusively give methane and the corresponding organometallic product (either **2** or **4**). DFT calculations show that the reaction with water likely involves a $\eta^2$-$H_2$ intermediate, in which the $H_2$ ligand axis is in plane with the PCN ligand, followed by the direct transfer of a hydrogen atom from it to the methyl group, forming a coordinated methane intermediate.

## Experimental Section

**General Procedures:** All experiments with metal complexes and phosphane ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with an MO 40-2 inert gas purifier, or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated 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. Complexes **1**[11] and **2**[11] and the precursor $[Pt(COD)(CH_3)Cl]$[22] were prepared according to literature procedures. NMR spectra were recorded at 400 ($^1H$), 100 ($^{13}C$), 162 ($^{31}P$) and 155 ($^7Li$) MHz using a Bruker AMX-400 NMR spectrometer and at 500 ($^1H$), 126 ($^{13}C$) and 202 ($^{31}P$) MHz using a Bruker DPX 500 spectrometer. All spectra were recorded at 23 °C unless specified otherwise. $^1H$ NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. $^1H$ NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvent ($\delta$ = 3.58 ppm, tetrahydrofuran). In $^{13}C\{^1H\}$ NMR measurements the signals of $[D_8]THF$ ($\delta$ = 67.4 ppm.) was 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). 5-mm screw-cap NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR spectroscopic data are as follows: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet.

**Formation of $[(PCN^*)Pt(Me)(H)]^-Li^+$ (3):** To a THF solution (1.5 mL) of [(PCN)Pt(H)] (**2**, 30 mg, 0.06 mmol) cooled to –30 °C, was added 40 µL (0.065 mmol) of MeLi (1.6 M solution in diethyl ether). The $^{31}P\{^1H\}$ NMR spectrum immediately revealed quantitative formation of complex **3**. The non-deuterated solvents were evaporated and complex **3** was dissolved in $[D_8]THF$. Complex **3** is stable for about a month at –37 °C and for a couple of days at room temperature upon which it is converted into the monohydride complex **2**, probably by reaction with traces of water. Since conversion of **3** to **2** takes place at room temperature, complex **3** was characterized at –30 °C.

$^{31}P\{^1H\}$ NMR ($[D_8]THF$): $\delta$ = 93.16 ($J_{Pt\text{-}P}$ = 2317 Hz) ppm. $^1H$ NMR ($[D_8]THF$): $\delta$ = 6.70 (dt, $J_{H,H}$ = 7, $J_{P\text{-}H}$ = 1 Hz, 1 H, Ar), 6.56 (d, $J_{H,H}$ = 7 Hz, 1 H, Ar), 6.14 (d, $J_{H,H}$ = 7 Hz, 1 H, Ar), 3.26 (m, 2 H,$CH_2$-$CH_2$-N), 2.80 (m, 4 H, Ar-$CH_2$-P and $CH_2$-$CH_2$-N), 2.67 [s, 6 H, $N(CH_3)_2$], 1.65 [d, $J_{P\text{-}H}$ = 11 Hz, 18 H, $P(tBu)_2$], 0.79

(dd, $J_{Pt-H}$ = 58, $J_{P-H}$ = 5.5, $J_{H,H}$ = 1.5 Hz, 3 H, Pt-$CH_3$), –6.17 (d, $J_{Pt-H}$ = 732, $J_{P-H}$ = 12 Hz, 1 H, Pt-H) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]-THF): $\delta$ = 168.68 (d, $J_{P,C}$ = 25 Hz, *ipso*), 145.61 (s, $J_{Pt-C}$ = 38 Hz, Ar), 121.92 (s, Ar), 117.85 (d, $J_{P-C}$ = 14 Hz, Ar), 110.35 (s, Ar), 105.86 (d, $J_{P,C}$ = 19 Hz, Ar), 63.85 (s, $CH_2$-$CH_2$-N), 62.61 (s, $CH_2$-$CH_2$-N), 43.88 [s, N-$(CH_3)_2$], 43.08 {d, $J_{P-C}$ = 30 Hz, P[C-$(CH_3)_3]_2$}, 34.22 (s, $J_{Pt-C}$ = 38.5 Hz, Ar-$CH_2$-P), 27.97 {d, $J_{P-C}$ = 5 Hz, P-[C$(CH_3)_3]_2$}, –15.15 (d, $J_{P-C}$ = 101, $J_{Pt-C}$ = 572 Hz) ppm. $^7$Li NMR ([D$_8$]THF): $\delta$ = 0.20 ppm (bs).

**Formation of [(PCN*)Pt(H)(Me)]$^-$Na$^+$ (5):** To a [D$_8$]THF solution (1.5 mL) of [(PCN)Pt(Me)] (**4**, 30 mg, 0.06 mmol) was added an excess of $Et_3BHNa$ (120 µL, 0.12 mmol, 1 M solution in toluene). The $^{31}P\{^1H\}$ NMR spectrum immediately revealed formation of complex **5** as the only reaction product (80% by $^{31}$P NMR, while 20% is the initial complex **4**).

Because of its instability, **5** was not isolated and was characterized in the crude solution, with the main goal of identifying the signal of the coordinated hydride ligand (it was difficult to identify additional signals due to a presence of $Et_3BHNa$ excess and traces of initial complex **4**). Formation of complex **5** as the only product and the unambiguous *trans* coordination of the hydride ligand ($J_{P-H}$ = 167 Hz, cf. $J_{P-H}$ = 11 Hz in **3**) demonstrate that selective nucleophilic attack occurred.

Selected NMR Spectroscopic Data for Complex **5**. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): $\delta$ = 74.03 ($J_{Pt,P}$ = 2445 Hz) ppm. $^1$H NMR ([D$_8$]THF): $\delta$ = 1.83 [d, $J_{P-H}$ = 12 Hz, 18 H, P($t$Bu)$_2$], –3.26 (d, $J_{P-H}$ = 167, $J_{Pt-H}$ = 1061 Hz, 1 H, Pt–H) ppm.

*Note:* High excess (about 10-fold) of $Et_3BHNa$ causes almost quantitative formation of **5**; however, in this case the $^1$H NMR spectrum is very crowded with signals.

**Reaction of [(PCN*)Pt(Me)(H)]$^-$Li$^+$(3) with Water:** Upon injection of excess $H_2O$ (6 µL, 0.330 mmol) to a THF solution (0.7 mL) of **3** (20 mg, 0.033 mmol) in a 5-mm screw-cap NMR tube equipped with a septum, formation of the neutral monohydride complex **2** was immediately observed 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 $CH_4$ (*Mw* = 16 g/mol).

**Reaction of [(PCN*)Pt(Me)(H)]$^-$Li$^+$(3) with Iodomethane:** To a THF solution (0.7 mL) of **3** (20 mg, 0.033 mmol) in a 5 mm screw-cap NMR tube equipped with a septum was injected MeI (5 µL, 0.074 mmol). Formation of the neutral monomethyl complex **4** was immediately observed by $^{31}P\{^1H\}$ NMR spectroscopy. A 10 µL sample of the gas phase from the screw-cap NMR tube was analyzed by GC/MS revealing formation of $CH_4$ (*Mw* = 16 g/mol).

**Computational Details:** All calculations were carried out using Gaussian 03 Revision E.01[23] to which the MNGFM patch[24] was applied; this patch from the University of Minnesota adds the M06 (vide infra) family of DFT exchange-correlation functionals to the commercial version. The M06 functional,[16] was used. This is a *meta*-hybrid functional containing 27% HF exchange, which was shown to have superior performance in the study of transition metal reactions.[16–17]

With this functional, two basis set-RECP (relativistic effective core potential) combinations were used. The first, denoted SDD, is the combination of the Huzinaga-Dunning double-ζ basis set[25] on lighter elements with the Stuttgart-Dresden basis set-RECP combination[26] on transition metals. The second, denoted aug-SDB-cc-pVDZ, combines the Dunning aug-cc-pVDZ basis set[27] on the main group elements and the Stuttgart-Dresden basis set-RECP[26] on the transition metals with an added *f*-type polarization exponent taken as the geometric average of the two *f*-exponents given in the appendix of ref.[28] and the set of diffuse *sdpf* functions taken from ref.[29] Geometry optimizations were carried out using the former basis set while the energetics of the reaction were calculated at these geometries with the latter basis set.

The accuracy of the DFT method was improved by adding an empirical dispersion correction as recommended by Grimme.[30] This is a correction that is added to the final energy and is a function of the geometry of the final, optimized geometry. Briefly, the dispersion energy is equal to the equation below,[30]

$$E_{disp} = -s_6 \sum_{i}^{N_{at}-1} \sum_{j}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}\left(R_{ij}\right)$$

$$f_{dmp}\left(R_{ij}\right) = \left(1+\exp\left(-d\left(\frac{R_{ij}}{R_r}-1\right)\right)\right)^{-1}$$

$$C_6^{ij} = \sqrt{C_6^i C_6^j}$$

where $R_r$ is the sum of van der Waal radii ($r_{vdW}$) of the two atoms in question and $C_6{}^i$ is an empirical constant; these values for H-Xe have been determined by Grimme.[31] The $s_6$ is an empirical scaling factor unique for each DFT functional. For M06, it has been determined to be 0.25.[32]

The $r_{vdW}$ and $C_6{}^i$ values are missing for the third-row transition metals (i.e., the entire sixth row of the periodic table). These values for the first and second row transition metals were determined by Grimme by averaging the values for the Groups 2 and 13 elements of the same row.[31] Thus, the $r_{vdW}$ and $C_6{}^i$ parameters for the third row transition metals were determined by averaging the parameters for Ba and Tl; the lanthanides were assigned parameters in the same manner. The parameters for these two elements, as well as the rest of the sixth row of the periodic table were determined by a geometric extrapolation of the parameters for the preceding two rows.

Bulk solvent effects were approximated by single point energy calculations using a polarizable continuum model (PCM),[33] specifically the integral equation formalism model (IEF-PCM)[33a,33b,34] with tetrahydrofuran (THF) as the solvent as in the experiments. In the PCM model, the United Atom Topological Model was used with the atomic radii from the UFF force field with explicit spheres on the hydrogen atoms.

Geometries were optimized using the default pruned (75,302) grid, while the "ultrafine" [i.e., a pruned (99,590)] grid was used for energy and solvation calculations, especially essential for calculations with the M06-family of functionals.[35]

The connectivity of the transition states were confirmed by performing intrinsic reaction coordinate (IRC) calculations.[36]

**Supporting Information** (see also the footnote on the first page of this article): Multinuclear NMR spectroscopic data of complexes **3** and **5** and Cartesian coordinates of all DFT structures.

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