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T-Shaped Platinum(II) Complexes Stabilised by Bulky N-Heterocyclic Carbene Ligands

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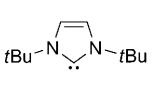
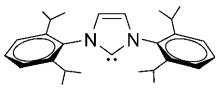
Coordinatively unsaturated transition-metal complexes have been invoked very often as intermediates in catalytic and stoichiometric reactions.[1] With regard to Pt^{II} chemistry, three-coordinated T-shaped complexes have been postulated in hydrocarbon C–H bond activation reactions,[2] particularly in the Shilov system for the functionalization of methane.[3] Such species are also believed to participate in thermal decomposition of dialkyls,[4] insertion reactions of unsaturated organic molecules into Pt–H bonds,[5] β-elimination processes[6] and ethylene dimerization.[7] Isolation of formally three-coordinated T-shaped Pt^{II} species has proved difficult, but it has been achieved in some instances with the use of bulky trialkyl phosphane ligands.[8] In all cases, agostic interactions are involved in the stabilization of these unusual species. Interestingly, Braunschweig and co-workers have isolated a 14-electron Pt^{II} complex that contains a boryl ligand in which agostic interactions seem to be almost negligible due to the strong *trans* influence exerted by this ligand.[9] More recently, Markó et al. have prepared an unprecedented Y-shaped Pt^{II} derivative stabilized by a bulky N-heterocyclic carbene (NHC).[10] NHCs have been successfully employed for the stabilization of electron-deficient transition-metal complexes,[11] but to date no reports have appeared regarding the characterization of T-shaped Pt^{II} complexes of these ligands. Herein, we report our initial findings on this subject, which include the synthesis and X-ray characterization of several 14-electron Pt^{II} derivatives stabilized by agostic interactions.

To synthesize the desired three-coordinated platinum(II) derivatives, we targeted complexes of general formula $[PtMeX(NHC)_2]$ (X = Cl, I) as starting materials, taking into consideration that the analogous $[PtMeX(PR_3)_2]$ species have been utilized for the isolation of coordinatively unsaturated $[PtMe(PR_3)_2]^+$ complexes.[8d,9] However, treatment of I*t*Bu (I*t*Bu = 1,3-di-*tert*-butylimidazol-2-ylidene) or IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with precursor [PtMeCl(cod)] gave a mixture of several products of unknown composition.



I*t*Bu



IPr

We then turned our attention to the Pt^{IV} precursor $[PtMe_3I]_4$ (**1**). It is known that **1** reacts with mono- and bidentate phosphanes to give the corresponding *trans*-$[PtMe_3I(PR_3)_2]$ or *cis*-$[PtMe_3I(P\text{-}P)]$ (P-P = bidentate phosphane ligand) derivatives, which upon heating release either ethane or methyl iodide to form $[PtMeI(PR_3)_2]$ or $[PtMe_2(PR_3)_2]$ complexes, respectively.[12] In accordance with very recent observations by Steinborn et al.[13] published during the course of our work, we have observed that treatment of $[PtMe_3I]_4$ with the very bulky I*t*Bu ligand (2:1 molar ratio of NHC to Pt^{IV}) at room temperature for 24 h gives $[PtMeI(I\textit{t}Bu)_2]$ (**2**; Scheme 1). However, we have also isolated minor amounts (≈10% by NMR spectroscopy) of $[PtMe(I\textit{t}Bu)(I\textit{t}Bu')]$ (**3**), which contains a monometalated I*t*Bu ligand (represented as I*t*Bu′). Both compounds can be separated by means of their different solubilities in pentane.

Spectroscopic data for complexes **2** and **3** support the structures shown in Scheme 1. ^1H and $^{13}C\{^1H\}$ NMR spectra

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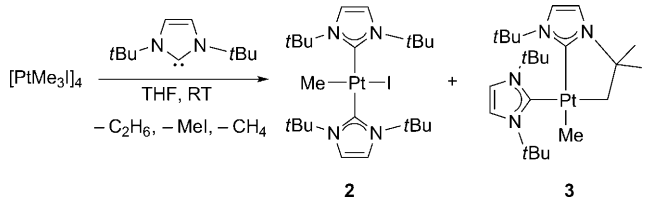


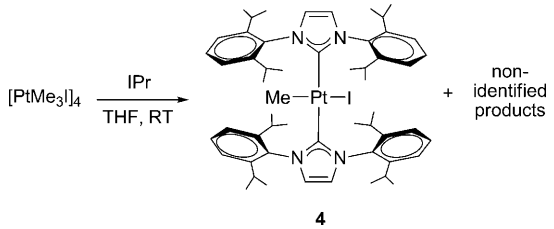
Scheme 1. Reaction of carbene I*t*Bu with complex $[PtMe_3I]_4$ to give complexes **2** and **3**.

for **2** show that the two NHC ligands are equivalent, consistent with their *trans* arrangement. A signal at $\delta = 0.39$ ppm ($^2J(H,Pt) = 89$ Hz), which integrates to give three protons, reveals that there is only one methyl group directly attached to the metal centre, the coordination sphere of which is completed with the iodide ligand. The structure has been confirmed by an X-ray diffraction study (see the Supporting Information).

In contrast, ^1H and $^{13}C\{^1H\}$ NMR data for complex **3** reveal that one of the two carbene fragments has undergone cyclometalation of one of the *tert*-butyl fragments (see the Supporting Information). Pt–CH_2 and Pt–CH_3 linkages give rise to signals at $\delta = 2.44$ (64 Hz) and 0.79 ppm (71 Hz), respectively. The values of ^2J(H,Pt) are in accord with the strong *trans* influence exerted by NHC ligands.[14] The *cis* distribution of the carbene moieties has been established by means of NOESY experiments.

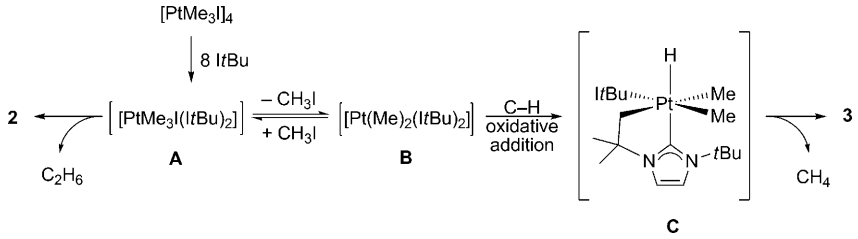
NHC ligand IPr behaves similarly to I*t*Bu in the reaction with **1**. Addition of IPr to complex **1** (2:1 molar ratio of IPr to Pt^{IV}) in THF leads to the formation of complex **4** (Scheme 2) as the major reaction product. Some non-identified products are also formed. Similarly to **2**, the NMR spectra of **4** show a highly symmetric pattern in accord with a *trans* arrangement of the IPr ligands.

A possible mechanism for the generation of compounds **2** and **3** (and thus extendable to **4**) is depicted in Scheme 3. It



Scheme 2. Reaction of carbene IPr with complex $[PtMe_3I]_4$ to give complex **4** and some non-identified products.

is likely that **2** and **3** share an unstable intermediate,[13] $[PtMe_3I(ItBu)_2]$ (**A**), that may evolve through two competitive reaction pathways, namely, reductive elimination of ethane or methyl iodide.[12] It has been established that C–I bond formation is kinetically preferred for $[PtMe_3I(dppe)]$, whereas C–C coupling products are thermodynamically favoured.[12b,c] In our system, ethane elimination from **A** would give complex **2**, whereas formation of **3** is proposed to require reversible reductive elimination of CH_3I to form **B**, followed by stepwise C–H oxidative addition to give **C** and then irreversible methane elimination. Conversion of **B** into **3** as described in Scheme 3 has been supported in recent work by the groups of Nolan and Goldberg.[15,16]

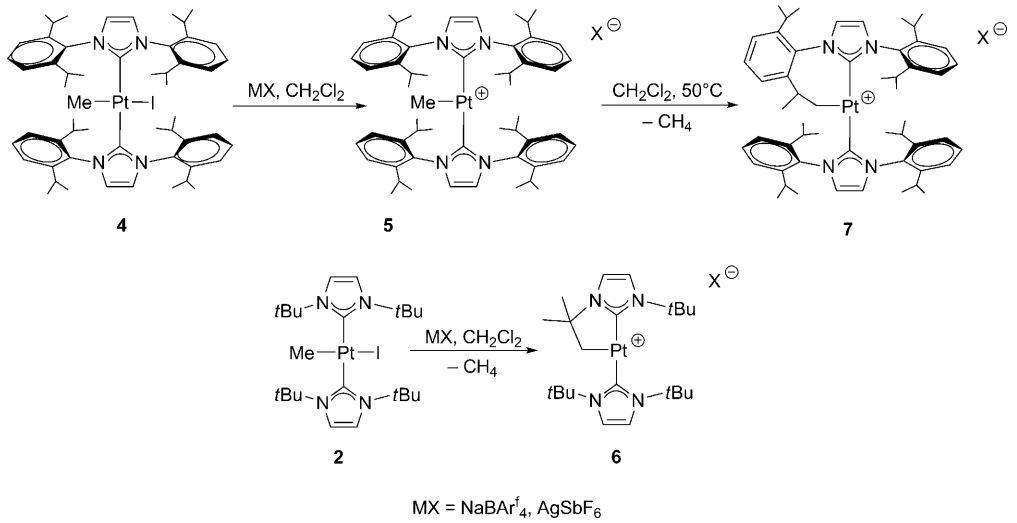


Scheme 3. Possible reaction mechanism for the formation of compounds **2** and **3**.

We have employed complexes **2** and **4** as precursors for 14-electron T-shaped platinum(II) derivatives. Thus, clean reactions ensue if solutions of **2** or **4** in dichloromethane are treated with $NaBAr^f_4$ or $AgSbF_6$ (Ar^f = (3,5-trifluoromethyl)phenyl) at room temperature (Scheme 4). Under these conditions, IPr compound **4** converts into cationic methyl derivative **5**, whereas I*t*Bu derivative **2** gives cyclometalated complex **6** as a result of C–H activation of a *t*Bu substituent and subsequent elimination of CH_4 (detected by ^1H NMR spectroscopy). The putative Pt–Me precursor of **6**, with a structure similar to **5**, was not detected even at low temperature (–70 °C), whereas isolable cationic Pt–Me complex **5** undergoes cyclometalation upon mild heating to afford **7**, that is, the IPr analogue of **5** (Scheme 4).

Complexes **6** and **7** are stable at room temperature in solution and in the solid state, and can be handled in air without noticeable decomposition. Cyclometalated IPr complexes are very rare; we are only aware of a recent iridium derivative.[17]

Some interesting features are readily discerned in the NMR spectra of complexes **5**–**7**. Thus, the Pt–CH_2 group in **6** gives rise to a ^1H resonance at $\delta = 3.44$ ppm that exhibits a large, two-bond, J(Pt,H) value of 120 Hz. The corresponding $^{13}C\{^1H\}$ signal is detected at $\delta = 18.3$ ppm and also presents a large coupling constant with the ^{195}Pt nucleus (975 Hz). Moreover, the non-metalated *t*Bu group of this I*t*Bu′ ligand features a small J(C,Pt) value of 25 Hz. These data are independent of the counterion, and can be taken as indicative of



Scheme 4. Synthesis of T-shaped platinum(II) complexes **5**–**7**.

a T-shaped structure stabilised by a δ agostic interaction (**D** in Figure 1). Similar data have been found by Baratta and co-workers in somewhat related platinum(II) compounds.[8d] With respect to derivative **5** only one set of ^{1}H and $^{13}C\{^{1}H\}$

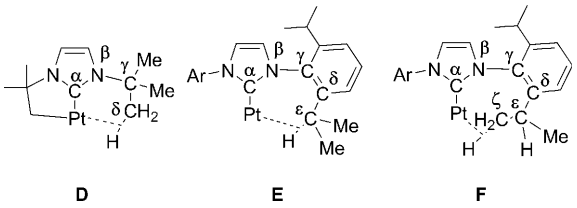


Figure 1. The different possible agostic interactions in derivatives **5**–**7**.

signals can be found for the two IPr ligands. In the $^{13}C\{^{1}H\}$ NMR spectrum, the Pt–Me group resonates at $\delta = -21.9$ ppm and shows a J(C,Pt) coupling constant of about 780 Hz. This is once more in agreement with this group being *trans* to a weakly coordinating ligand, that is, with the existence of a remote ε or ζ agostic interaction (Figure 1, structures **E** or **F**, respectively).

IPr-metalated compound **7** exhibits a complex ^{1}H NMR spectrum in which two different IPr units can be unmistakably distinguished. Multiplets at $\delta = 2.86$ and 1.98 ppm (Pt–CH_2) and at $\delta = 1.77$ ppm (Pt-CH_2-C*H*) appear for the metalated arm, but partial overlapping with the resonances due to the CH and CH_3 protons of the IPr ligands preclude assessment of the values of the J(H,Pt) couplings characteristic of the Pt–CH_2 unit. Nevertheless, the corresponding J-(C,Pt) coupling constant of 860 Hz points, once again, to the Pt–CH_2 bond being *trans* with respect to a weakly bound ligand. With the aim of detecting a possible agostic interaction (**F** in Figure 1) low-temperature (down to −80 °C) ^{1}H and $^{13}C\{^{1}H\}$ NMR studies were undertaken. No definite conclusions can be drawn from these studies.

Fortunately, crystals of **7**·SbF_6 suitable for X-ray diffraction study were obtained (Figure 2). As expected, the molecule contains two carbene ligands in a *trans* arrangement (C1-Pt1-C16 angle 179.52(8)°) together with a Pt–CH_2 moiety of the metalated IPr′ ligand. The fourth coordination site is occupied by a ζ agostic interaction (structure **F** in Figure 1) with one of the methyl groups of the non-metalated IPr ligand. The latter show Pt1–C50B and Pt1–H50E separations of 2.8760(1) and 2.017(6) Å, respectively, with a Pt-H50E-C50B angle of 145°. These values fall in the

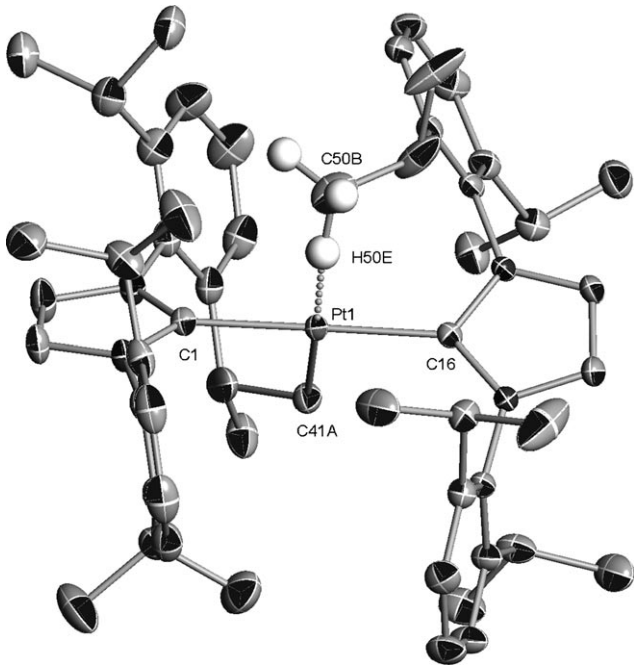


Figure 2. ORTEP representation of complex **7**·SbF_6 (ellipses drawn at the 30% probability level; the SbF_6^- anion and most of the H atoms have been omitted for clarity).

middle, lower and upper limits of known agostic interactions.[18]

In summary, bulky NHC ligands trigger reductive elimination of ethane or methyl iodide from Pt^{IV} precursor $[PtMe_3I]_4$,with concurrent formation of the Pt^{II} derivatives *trans*-$[PtMeI(NHC)_2]$ or *cis*-[PtMe(NHC)(NHC′)] (NHC′ = metalated NHC ligand). The former opens access to formally 14-electron, T-shaped platinum(II) species $[PtMe(IPr)_2]^+$ (**5**), $[Pt(I\mathit{t}Bu)(I\mathit{t}Bu')]^+$ (**6**) and [Pt(IPr)(IPr′)] (**7**), which are probably stabilized by remote δ- to ζ-agostic interactions. It is likely that the bulkiness of I*t*Bu in comparison with IPr prevents observation of a Pt–Me derivative analogous to **5** for the former ligand.

Acknowledgements

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Keywords: agostic interactions · C–H activation · nitrogen heterocycles · platinum · T-shaped complexes

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