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Supporting Information Placeholder

ABSTRACT: Cationic five coordinate Pt(IV) alkyl complexes stabilized by bulky N-heterocyclic carbenes have been isolated and fully characterized. Related species have been postulated as key intermediates in carbon-heteroatom coupling reactions, and most particularly in Shilov-type chemistry. The alkyl groups exhibit a pronounced electrophilic character and can undergo nucleophile attack on pyridine, bromide or iodide. Nevertheless, direct reductive coupling to form C–X bonds can be operative in the absence of an external nucleophile source.

Coordinatively unsaturated platinum complexes in +2 or +4 oxidation states have been invoked as key intermediates in several stoichiometric and catalytic processes. The first example of a crystallographically characterized low electron count PtII complex was reported more than two decades ago, and in recent years the number of authenticated species has increased considerably. However, five-coordinate, 16-electron Pt(IV) compounds have been surprisingly elusive until recently. In most cases these complexes are neutral species stabilized by nitrogen-containing ligands together with methyl, silyl or hydrido ligands, with only a recent example reported by Rourke in which the platinum atom is surrounded by a cyclometalated phenylpyridine and three chloride ligands. Nevertheless, cationic electron deficient Pt(IV) derivatives bearing at the same time a halogen atom and alkyl group have not been isolated, in spite of being suggested as intermediates in Shilov-type chemistry for the formation of carbon-heteroatom bonds. We have recently reported that during oxidation of a T-shaped Pt(II) alkyl complex with bromine a transient five coordinate Pt(IV) species, [Pt(Br)2(IPr')(IPr)][BARF] (where IPr denotes the carbene ligand [iso-propylimidazol-2-ylidene]) was identified on the basis of NMR experiments. Interestingly, one of the tert-butyl groups of the non-cyclometalated IPr ligand, and IPr the cyclometalated IPr ligand, was identified on the basis of NMR spectroscopy. However, the high thermal instability of this complex toward reductive carbon-halogen coupling precluded the full characterization of this unusual species. Moreover, the analogous iodide derivative [Pt(1)(IPr')(IPr)][BARF] was found to be too unstable to be observed. Herein we wish to report the successful isolation of 16-electron Pt(IV) complexes, stabilized by agostic interactions, containing an alkyl group in a cis arrangement to a halogen atom, their characterization by X-ray diffraction studies and their reactivity towards pyridine, bromide and iodide.

Addition of Br2 or I2 to dichloromethane solutions of the cyclometalated T-shaped Pt(II) complexes 1 and 2 containing fBu and fIPrM2 ligands ([fBu] = 1,3-di-tert-butylimidazol-2-ylidene; ([fIPr]M2 = 4,5-dimethyl-1,3-di-propylimidazol-2-ylidene) gives rise to the formation of the cationic Pt(IV) species 3 and 4, respectively (Scheme 1). The NMR data of 3 and 4 are consistent with an increase in the oxidation state at the metal center. Significantly, the Pt–CH2 moiety resonates in the 1H NMR at considerably lower field (5.08-5.60 ppm) compared to the starting materials (3.22 ppm, 1; 2.84 and 1.92 ppm, 2). Additionally, the 1H-195Pt coupling constant falls in the range of 80-95 Hz, that is, notably smaller than that expected for a simple Pt(IV) complex (102 Hz). Similar conclusions can be drawn from the 13C(1H) NMR (see ESI). Interestingly, one of the tert-buty1 groups of the non-cyclometalated fBu ligand in derivatives 3 exhibits satellites due to coupling to 195Pt (8 and 25 Hz for 3a and 3b, respectively) indicating that an agostic interaction is established between the methyl groups and the platinum atom. These tert-buty1 groups appear in the 13C(1H) NMR at 35.2 ppm (J(C,H) = 24 Hz) and 33.9 ppm (J(C,H) = 25 Hz) for 3a and 3b, respectively. With regard to complexes 4 no definite conclusions could be drawn due to the more complex nature of the NMR data and their lower stability (see below).

The stability of Pt(IV) derivatives 3 and 4 is significantly different. Complexes 4 are only stable at temperatures below 0 °C, with 4a decomposing to several species of unknown composition and 4b rearranging into the Pt(II) derivative 6b (Scheme 2), arising from C–I reductive coupling in a similar way as previous findings with aryl-substituted NHCs.

Scheme 1. Synthesis of Pt(IV) complexes 3a,b and 4a,b.

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On the contrary, derivatives 3a,b are perfectly stable (even under air) in the solid state, but decompose in dichloromethane solutions at room temperature after several hours to a mixture of unknown compounds. This thermal stability allowed us to obtain crystals suitable for X-ray crystallographic studies for both 3a and 3b. Figure 1 shows the molecular structure of the cation of derivative 3b. As expected from the NMR data its structure consists of two NHC ligands, one of them still cyclometalated, and two iodine atoms in a trans arrangement. One of the two iodine atoms occupies two different positions in the molecule. The sixth coordination site is occupied by an agostic interaction with one of the C atoms of the trialkyl group. Interestingly, the Pt–CH₂ bond distance of 2.228(11) Å is considerably long in comparison to the agostic interaction the I–Bu ligand that is characterized by Pt···H and Pt···C bond distances of 1.954(3) Å and 2.67(1) Å, respectively, and a Pt···H–C angle of 129.1(7)° that lay in the expected range of agostic interactions. As a consequence of this agostic interaction the I–Bu ligand is tilted toward the vacant site (the angles defined by the Pt₁–C₁₂–N₄ and Pt₁–C₁₂–N₃ are 116.9(4)° and 137.8(4)°, respectively). Interestingly, the Pt–CH₃ bond distance of 2.228(11) Å is considerably long in comparison to that found in related Pt(II) systems (2.09 Å).

As mentioned above, complexes 3 are unstable in solution, but evolution products are highly dependent on the solvent. Thus, 3b transforms into to the Pt(II) complex [Pt(THF)₂]⁻. 1·NCMe (Scheme 3), through reductive elimination of iodine, whereas, the brominated derivative 3a undergoes partial C–Br reductive coupling at r.t.

**Scheme 3. Reactivity of complexes 3a,b.**

In the same solvent yielding compound 5a in less than ca. 25% spectroscopic yield after a week, among some other species of unknown composition. This latter process is faster (12 h) when methanol is used as solvent. When 3b is dissolved in methanol, degradation takes place as well, but small amounts of complex 5b precipitate out in the course of the reaction after a few hours. Importantly, if 3a is dissolved in methanol in the presence of an exogenous source of bromine (LiBr, 5 equiv) or other nucleophiles such as iodide (LiI, 1.2 eq), complexes 5a,c are formed quantitatively (by NMR) within minutes. However, although addition of LiI to a solution of 3b in methanol accelerates its transformation (45 min) slightly increasing the quantity of 5b formed (spectroscopically) some decomposition together with formation of complex 1 is still observed. Therefore, the reactivity of 3b is partially governed by reductive elimination of I₂.

In line with the results aforementioned, when 3a is treated with pyridine at r. t., or upon addition of pyridine to freshly prepared solutions of 4b at −40 °C, a fast reaction takes place leading to the Pt(II) complexes 7a and 8b (Schemes 2,3). Definite proof of the structure of complex 7a came from X-ray diffraction studies (Figure S27). This result contrast with the observed reactivity of neutral 5-coordinate Pt(IV) compounds for which two-electron donors bind the metal centre without observing any coupling with the alkyl group. Once again, addition of pyridine to 3b induced iodine reductive elimination with concomitant formation of pyridine adduct 1·py.

Several mechanisms can be identified to account for the formation of C–X bonds depending on the reaction conditions. First, direct reductive coupling from Pt(IV) intermediates are most likely to operate in the absence of external nucleophiles. This is actually the case for the conversion of derivative 4b into 6b (scheme 2) and related examples previously reported by us and others. Nevertheless, this situation change when nucleophiles such as pyridine, bromide or iodide are added to the reaction media. Under these conditions, three different scenarios are possible (Scheme 4): (i) coordination of the nucleophile to the metal center to form an 18-electron Pt(IV) species followed by cis/trans isomerization and direct reductive coupling; (ii) nucleophilic attack to the platinum atom to yield again a coordinately saturated 18-electron species, subsequent dissociation of one of the ligands leading back to 16-electron derivatives and direct

**Scheme 4. Possible mechanistic pathways for C–X bond forming reactions.**
reductive coupling and (iii) direct nucleophilic attack to the electrophilic CH₂–Pt carbon atom. Direct reductive coupling processes (pathway (i)) from 18-electron Pt(IV) species are very rare. DFT calculations (PBE0/SDD/6-311g** – see ESI) carried out in our system disfavor associative pathways (i) and (ii), since they indicate that coordination of a bromine atom to Pt in 3a is endothermic by ca. 23 kcal·mol⁻¹, which places the resulting intermediate above the energy barriers of route (iii), as will be discussed below. This may be due to the protective role exerted by the agostic-bonded tert-butyl group. Figure 2 shows the distorted coordination of the tert-Bu ligand upon bromine coordination to Pt in 3a. Moreover, attempts to model pyridine coordination to Pt in 3a resulted in unobserved extrusion of the non-cyclometalated tert-Bu. In support to all of this, coordinating solvents such as acetonitrile or THF do not bind to the metal center.

Finally, pathway (iii) involves nucleophilic addition to the carbon atom of the Pt–CH₂ fragment has been postulated in several occasions in platinum, palladium, rhodium, and gold chemistry in high oxidation states. Indeed, it is well known that Pt(IV)–C₃⁺ bonds have an umpolung reactivity compared to Pt(II)–C bonds, that is, whereas the latter are best described with a partial negative charge at the carbon atom, the former are expected to have a carboxylation-like behaviour. Our calculations show the umpolung effect caused by the oxidation state increase in Pt (Table 1), which hints at an electrophilic character of the Pt–CH₂ carbon in the Pt(IV) species. This is further supported by QTAIM analysis of the laplacian of the electron density of 3, in which ‘holes’ in the valence shell charge concentrations near the Pt–CH₂ carbon (See Figures S21 and S25) can be related to nucleophilic attack sites.

Table 1. Natural Charges (e⁻, based on NBO analysis) of 1 and 3.

<table>
<thead>
<tr>
<th></th>
<th>q(Pt)</th>
<th>q(CH₂)</th>
<th>∆q(Pt–CH₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.097</td>
<td>-0.005</td>
<td>0.102</td>
</tr>
<tr>
<td>3a</td>
<td>-0.140</td>
<td>0.151</td>
<td>0.291</td>
</tr>
<tr>
<td>3b</td>
<td>-0.307</td>
<td>0.130</td>
<td>0.437</td>
</tr>
</tbody>
</table>

This mechanism would explain why addition of lithium bromine to complex 3a accelerates its transformation into 5a, being in this case the only product of the reaction. Moreover, addition of pyridine or iodine to 3a leads almost exclusively to the C–N and C–I coupling products, with only traces of the C– Br derivative observed (less than 2 %) in the reaction of 3a and LiI, in spite of having an unfavorable statistical probability to form a C–I bond (two bromides present per 1.2 iodides). Likewise, whereas complex 4a undergoes reductive coupling in solution after a few hours in the absence of an external nucleophile to form 6b, in the presence of one equivalent of pyridine, rapid C–N bond formation leading to 8b is observed. This different behavior has also been addressed by DFT methods. S₂N₂-like nucleophilic attack of pyridine or bromide to the Pt–C₃⁺ has the lowest calculated barriers of all the pathways investigated: 13.6 and 9.2 kcal·mol⁻¹ (in dichloromethane and methanol) respectively; the energy return of these reactions being 24.1 and 10.6 kcal·mol⁻¹ (for the formation of 7a and 5a respectively). However, the energy barrier for CH₂-halide reductive coupling in 3a is ca. 29 kcal·mol⁻¹. The resulting Pt(II) intermediate (6c) can then undergo nucleophilic attack of pyridine or bromide to the CH₂-Br carbon with barriers in the range of 15 to 10 kcal·mol⁻¹ (Figures 3 and S24). Thus, while this process may be feasible and could indeed account for the formation of 6b in the absence of external nucleophiles, it is not competitive with external nucleophilic attack to Pt–CH₂ in the formation of 5a and 7a.

Figure 2. Left and middle figures: optimized geometry of the hexacoordinated intermediate resulting from bromide coordination to 3a. The middle figure shows a view along the CH₂-Pt axis.

Figure 3. Zero point-corrected energy profiles in methanol for the formation of 5a from 3a and bromide. Free energy data are also shown in parentheses.

To summarize, we have succeeded in the isolation of formally 16-electron Pt(IV) alkyl species stabilized by agostic interactions related to Shilov-type chemistry. The nature of the NHC ligand determines the stability of this unusual species. Although in some cases direct C–X reductive coupling is very likely occurring, when certain nucleophiles are present in solution C–X bond formation can take place through nucleophilic addition to the highly electrophilic carbon atom of the Pt–CH₂ fragment with considerably lower energetic barriers than those for the direct reductive coupling according to DFT calculations. Ongoing work is currently underway to obtain further mechanistic data and to span these studies to other nucleophiles.

ASSOCIATED CONTENT
Supporting Information
Experimental details for the synthesis and characterization of new compounds. 1H and 13C{1H} graphical NMR spectra of new complexes. XYZ file with Energies and Cartesian coordinates of all computed species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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REFERENCES


(9) Two independent molecules are present in the unit cell. One of them exhibits metrical parameters similar to those of derivative 3b (see ESI, Fig. S26), whereas the disorder on the tert-butyl groups on the other precluded a reliable determination of bond distances and angles.


(11) Nucleophilic substitution of the bromine atom in the CH2–Br moiety of complex 5a by pyridine does not occur according to an independent experiment between complex 5a and pyridine.


(13) Dissociative pathways via transient 14-electron dicatonic species such as [Pt(Br)(Bu)(Br)]2+ may be supported by the fact that the C–X forming reaction occurs faster in more polar solvents. Two facts argue against this possibility. First, formation of 5a is faster in the presence of added bromide and secondly, the dissociation energy of bromide from complex 3a in methanol requires more than 40 kcal mol–1 according to DFT calculations.


(20) In the absence of LiBr 3a rearrage only partially into derivatives 5a where the halide source has its very likely origin in the decomposition products of 3a (thus explaining the observed low yield).
Reductive C-X, C-N Coupling