Formation of C–X Bonds Through Stable Low-Electron Count Cationic Pt(IV) Alkyl Complexes Stabilized by N-Heterocyclic Carbenes.

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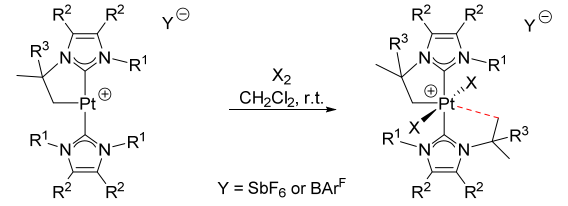
Supporting Information Placeholder

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 nucleophilic addition of pyridine, bromide or iodide to form new carbon-heteroatom bonds. 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.[1] The first example of a crystallographically characterized low electron count $\mathrm{Pt^{II}}$ complex was reported more than two decades ago,[2] and in recent years the number of authenticated species has increased considerably.[1a,3] However, five-coordinate, 16-electron Pt(IV) compounds have been surprisingly elusive until rather recently.[4] In most cases these complexes are neutral species stabilized by nitrogen-containing ligands together with methyl, silyl or hydrido ligands,[1d] with only a recent example reported by Rourke in which the platinum atom is surrounded by a cyclometalated phenylpyridine and three chloride ligands.[5] 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.[1b,d-6] We have very recently reported that during oxidation of a T-shaped Pt(II) alkyl complex with bromine a transient five coordinate Pt(IV) species, $\mathrm{[Pt(Br)_2(IPr')(IPr)][BAr^F]}$ (where IPr denotes the carbene ligand 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene and IPr' the cyclometalated IPr ligand), was identified on the basis of NMR spectroscopy.[7] 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 $\mathrm{[Pt(I)_2(IPr')(IPr)][BAr^F]}$ 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 $\mathrm{Br_2}$ or $\mathrm{I_2}$ to dichloromethane solutions of the cyclometalated T-shaped Pt(II) complexes **1** and **2** containing $\mathrm{I^tBu}$ and $\mathrm{I^iPr_2Me_2}$ ligands ($\mathrm{I^tBu}$ = 1,3-di-*tert*-butylimidazol-2-ylidene; ($\mathrm{I^iPr_2Me_2}$ = 4,5-dimethyl-1,3-di-*iso*-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.[5,8] Significantly, the Pt–$\mathrm{CH_2}$ moiety resonates in the ^{1}H 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 ^{1}H-^{195}Pt coupling constant falls in the range of 80-95 Hz, that is, notably smaller than that observed in **1** (120 Hz) and **2** (102 Hz). Similar conclusions can be drawn from the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (see ESI). Interestingly, one of the *tert*-butyl groups of the non-cyclometalated $\mathrm{I^tBu}$ ligand in derivatives **3** exhibits satellites due to coupling to ^{195}Pt (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*-butyl groups appear in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR at 35.2 ppm ($J_{\mathrm{C,Pt}}$ = 24 Hz) and 33.9 ppm ($J_{\mathrm{C,Pt}}$ = 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).

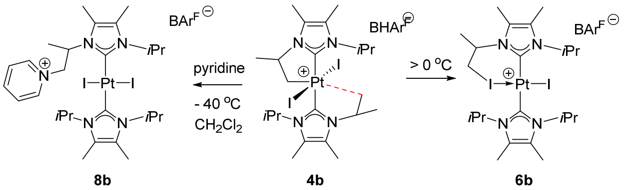
Scheme 1. Synthesis of Pt(IV) complexes **3a,b** and **4a,b**.



$\mathrm{R^1 = {}^tBu, R^2 = H, R^3 = Me}$ (**1**)
$\mathrm{R^1 = {}^iPr, R^2 = Me, R^3 = H}$ (**2**)
$\mathrm{R^1 = {}^tBu, R^2 = H, R^3 = Me, X = Br}$ (**3a**), I (**3b**)
$\mathrm{R^1 = {}^iPr, R^2 = Me, R^3 = H, X = Br}$ (**4a**), I (**4b**)

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.[7]

Scheme 2. Reactivity of complex **4b**.



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**[9] 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 *tert*-butyl groups of the non-cyclometalated I^{t}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.[10] As a consequence of this agostic interaction the I^{t}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–CH_2 bond distance of 2.228(11) Å is considerably long in comparison to that found in related Pt(II) systems (2.09 Å).[7]

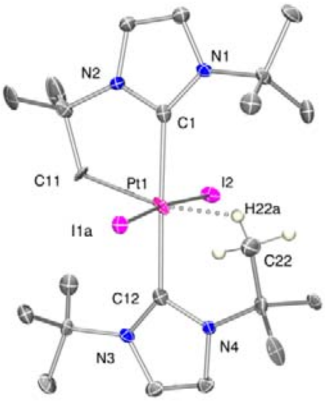
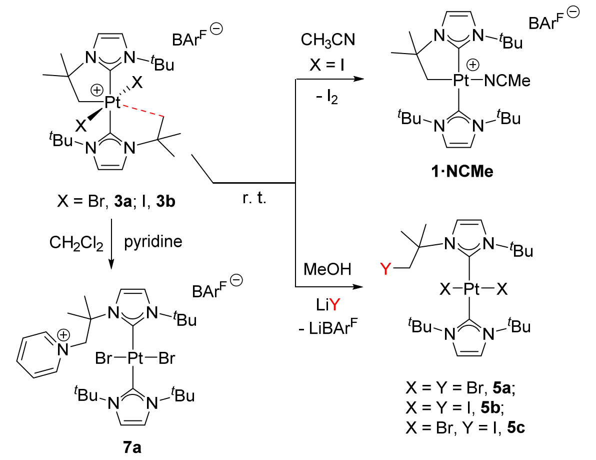


Figure 1. ORTEP drawing of the molecular structure of complex **3b**. Ellipsoids are set at 50% probability; SbF_6^- anion and hydrogen atoms, except those involved in the agostic interaction, are omitted for clarity.

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(I^{t}Bu')(I^{t}Bu)(NCMe)][BAr^F], **1·NCMe** (Scheme 3), through reductive elimination of iodine, whereas, the brominated derivate **3a** undergoes partial C–Br reductive coupling at r.t. 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 I_2.

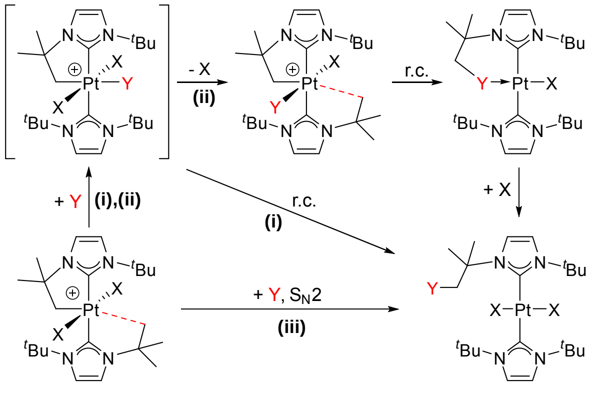
Scheme 3. Reactivity of complexes **3a**,**b**.



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).[11] 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.[1d] 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[7] and others.[12] 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 coordinatively 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.



X = Br, **3a**; I, **3b**

reductive coupling and (iii) direct nucleophilic attack to the electrophilic CH$_2$–Pt carbon atom.[13] Direct reductive coupling processes (pathway (i)) from 18-eletron Pt(IV) species are very rare.[14] 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 I^{t}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 I^{t}Bu. In support to all of this, coordinating solvents such as acetonitrile or THF do not bind to the metal center.

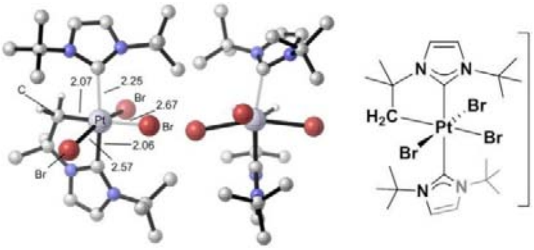


Figure 2. Left and middle figures: optimized geometry of the hexacoordinated intermediate resulting from bromide coordination to **3a**. The middle figure shows a view along the *C*H$_2$-Pt axis.

Finally, pathway (iii) involving nucleophilic addition to the carbon atom of the Pt–CH$_2$ fragment has been postulated in several occasions in platinum,[15] palladium,[16] rhodium[17] and gold[18] chemistry in high oxidation sates. Indeed, it is well known that Pt(IV)–C$_{sp3}$ 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 carbocation-like behaviour.[1c] 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–CH$_2$ carbon in the Pt(IV) species. This is further supported by QTAIM analysis[19] of the laplacian of the electron density of **3**, in which ‘holes’ in the valence shell charge concentrations near the Pt–CH$_2$ 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**.

	q(Pt)	***q***(CH2)	Δ***q***(Pt–CH2)
1	0.097	-0.005	0.102
3a	-0.140	0.151	0.291
3b	-0.307	0.130	0.437

This mechanism would explain why addition of lithium bromine to complex **3a** accelerates its transformation into **5a**,[20] 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. S$_N$2-like nucleophilic attack of pyridine or bromide to the Pt-*C*H$_2$ 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 *C*H$_2$-halide reductive coupling in **3a** is ca. 29 kcal·mol^{-1}. The resulting Pt(II) intermediate (6$_C$) can then undergo nucleophilic attack of pyridine or bromide to the *C*H$_2$-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-*C*H$_2$ in the formation of **5a** and **7a**.

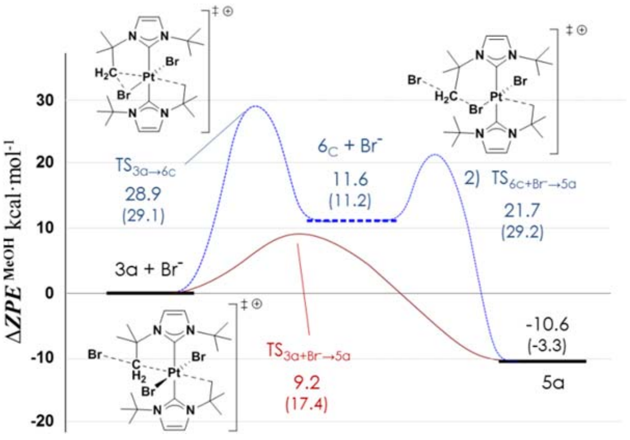


Figure 3. Zero point-corrected energy profiles in methanol for the formation of **5a** from **3a** and bromide. Free energy data are also shown in parentheses.

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–CH$_2$ 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. ^{1}H and ^{13}C{^{1}H} 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.

ACKNOWLEDGMENT

Financial support from the Junta de Andalucía (FQM-2126) and Spanish MICINN (CTQ2013-45011, FEDER support) is acknowledged. O. R.-W. and M. R.-M. thank the Spanish MICINN and the CSIC for a research grants. The use of Computational facilities of the supercomputing Center of Galicia (CESGA) is also acknowledged. J.L.-S thanks the MICINN and the European Social Fund for a "Ramón y Cajal" contract.

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(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.

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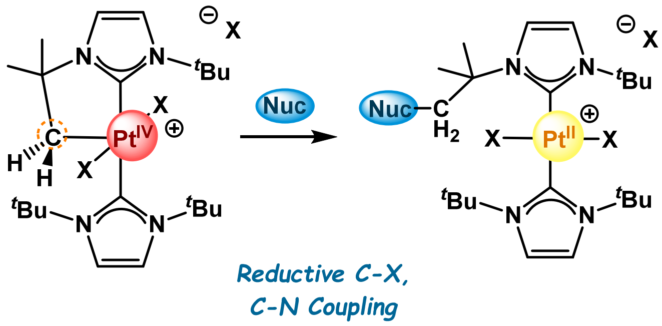
(20) In the absence of LiBr **3a** rearrange only partially into derivatives **5a** where the halide source has its very likely origin in the decomposition products of **3a** (thus explaining the observed low yield).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X
X
⊖ X
tBu
tBu
tBu
Reductive C-X,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