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Characterization of a Paramagnetic, Mononuclear Pt(III)−Alkyl Complex Intermediate in Carbon−Halogen Bond Coupling Reactions

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Ⓢ *Supporting Information*

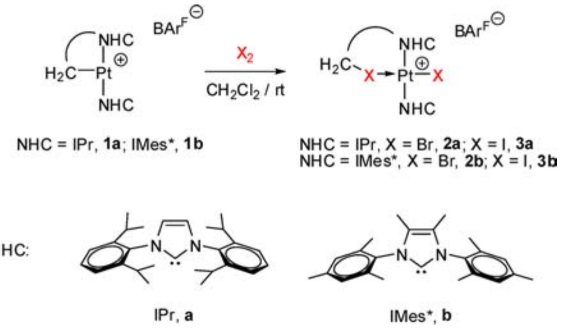
ABSTRACT: Addition of Br_2 or I_2 to 14-electron, cationic Pt(II)-alkyl complexes led to the formation of the corresponding carbon−halogen Pt(II) coupling products. Low temperature experiments with Br_2 allowed us to isolate and characterize crystallographically a very unusual mononuclear, paramagnetic Pt(III)-alkyl intermediate with a seesaw structure that can be further oxidized to a transient Pt(IV) species before reductive carbon−halogen coupling reaction takes place.

Oxidation of platinum(II) alkyl complexes is of central importance in the catalytic and/or stoichiometric functionalization of C−H bonds of hydrocarbons.[1] This is particularly true for the oxidation of methane to chloroform and methanol in the Shilov chemistry, for which several reports point to the participation of Pt(IV) complexes as key intermediates in the formation of the functionalized (oxidized) methane.[2] However, in a few occasions, it has been suggested that oxidation reactions (either chemical or electrochemical) of platinum(II) alkyls lead to the formation of transient paramagnetic Pt(III) species that with no exception are either very unstable toward disproportionation to Pt(II) and Pt(IV) or easily oxidized to Pt(IV), making it impossible to ascertain their nature.[3] For example, Labinger, Bercaw, and Goldberg reported that, during oxidation of dimethylplatinum(II) complexes $[Pt(CH_3)_2(L\text{-}L)]$ (L-L = bpy, phen, tmeda) by O_2, formation of blue solutions containing mixed-valence oligoplatinum paramagnetic species of similar nature than the so-called platinum blues[4] were detected before final oxidation to Pt(IV) compounds occurred.[3d] Similarly, Tilset found that electrochemical oxidation of bis(imine) dimethylplatinun(II) $[Pt(CH_3)_2(N{-}N)]$ complexes afford Pt(II) and Pt(IV) compounds formed through a formal disproportionation of short-lived Pt(III) species.[3c] Although dialkyl Pt(III) complexes appear to be very unstable,[5] Bercaw and Labinger have hinted that monomethyl-Pt(III) derivatives might have longer half-lives.[2a] Nevertheless, no reports on stable Pt(III)-monoalkyl complexes have been published. Herein, we describe the synthesis and X-ray characterization of the first mononuclear Pt(III)-alkyl complex that, in addition, is an intermediate in carbon−halogen coupling reactions during oxidation reactions of Pt(II)-alkyl compounds with bromine.[6]

We[7a,b] and others[8] have recently reported that N-heterocyclic carbene ligands (NHCs) promote rapid reductive elimination of ethane when reacted with the Pt(IV) tetramer $[PtMe_3I]_4$, leading to the formation of the thermodynamically favored Pt(II) complexes *trans*-$[PtMeI(NHC)_2]$. These latter complexes were used as precursors for the synthesis of coordinatively unsaturated, 14-electron Pt(II) species $[PtMe(NHC)_2]^+$ and $[Pt(NHC')(NHC)]^+$ (where NHC′ stands for the cyclometalated NHC ligand).[7] Encouraged by the fact that the bulkiness of the NHC ligands destabilizes to some extent the formation of Pt(IV) complexes, we launched a research program aimed at investigating the reactivity of coordinatively unsaturated Pt(II) complexes toward halogens (Br_2 and I_2), having in mind that although a remarkable outburst of $C(sp^2)$−X (X = F, Cl, Br, I) bond forming reactions through C−H bond activation processes have appeared in recent years,[9] construction of $C(sp^3)$−X bonds is still rare.[10]

Addition of X_2 (X = Br, I) to dichloromethane solutions of the electron deficient cyclometalated complexes $[Pt(NHC')(NHC)][BAr^F]$ (NHC = IPr, **1a**; IMes*, **1b**; BAr^F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), at rt, lead to the clean formation of complexes **2a−b** and **3a−b** (see Scheme 1) that have been identified as Pt(II) complexes on the basis of

Scheme 1



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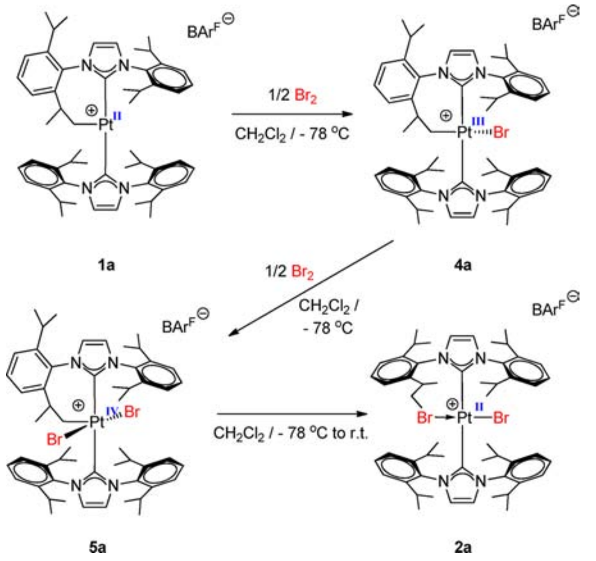
NMR spectroscopy and X-ray crystallography (*vide infra*). Evidently, the new products arise from a formal carbon–halogen bond coupling reaction of the metalated CH_2 fragment with the incoming X (halogen) source. The identity of the CH_2–X (X = Br, I) moiety has been clearly established on the basis of ^1H and $^{13}C\{^1H\}$ NMR spectra for which signals at 3.16–4.71 and 16.6–52.1 ppm, respectively, have been assigned. Coordination of the X atom of the CH_2–X fragment to the metal center is supported by the observation, in the ^1H NMR, of satellites due to coupling of the CH_2X to ^{195}Pt (see Supporting Information (SI)). Their structures were further borne out by X-ray crystallographic studies on complexes **2a** and **3b** (see SI).

With the aim of observing any possible intermediates during addition of X_2 to complex **1a**, the reactions were carried out at low temperature (−78 °C) in an NMR tube. No intermediates were detected when I_2 was used as a reagent. However, it was found that reaction of complex **1a** with 1 equiv of Br_2 at −78 °C formed a new complex that has been tentatively identified as the coordinatively unsaturated Pt(IV) compound **5a** (Scheme 2) on the basis of NMR data. This complex exhibits ^1H NMR chemical shifts for the Pt–CH_2 fragment of 4.77 (d) and 3.77 (dd) ppm, with coupling constants to ^{195}Pt of 77 and 81 Hz, respectively. These chemical shifts are significantly downfield shifted (*ca*. 1.5 ppm) with respect to complex **1a**, in agreement with an increase in the oxidation state at the metal.[11] **5a** was thermally unstable toward formation of **2a** at temperatures above −15 °C.

Scheme 2



Very intriguingly, when Br_2 was added very slowly to solutions of **1a** at low temperature, an initial color change to deep-blue preceded before fading, upon addition of all bromine, to the characteristic yellow colored solutions of **2a**. Being aware of the formation of paramagnetic Pt(III) intermediates during oxidation reactions of some Pt(II) complexes, we decided to investigate the nature of the contents of the blue solutions formed at the initial stages of the reaction. It proved that addition of just 0.5 equiv of Br_2 to **1a**, in dichloromethane at −78 °C, generates persistent blue solutions that remained unaltered for at least a few days at temperatures below −20 °C, but decomposed completely in solution (CH_2Cl_2) after 3 h at rt. Low-temperature (−40 °C) ^1H NMR allowed us to identify two different compounds, a minor one (*ca*. 10%) showing well-resolved ^1H NMR signals that were assigned to the Pt(IV) complex **5a**, and another major species showing very broad resonances spanning from −7 to 16 ppm (see SI). As discussed below, this latter complex has been identified as the paramagnetic, mononuclear Pt(III) complex **4a** (Scheme 2). It was possible to separate the two complexes by slow-diffusion crystallization at low temperatures. Thus, deep-blue crystals of complex **4a** were obtained and analyzed by different spectroscopic and analytic techniques. The solution magnetic moment of **4a** (μ_{eff} = 1.75 μ_B), measured by Evan's method,[12] fits well for one-electron paramagnetic species, with a d^7 configuration. ^1H and $^{13}C\{^1H\}$ NMR spectra proved not to be informative about the nature of the blue complex **4a**, due to line broadening of all the signals (together with the loss of proton–proton splittings) and the unsymmetrical character of the NHC ligands. Nonetheless, its structure was ascertained by X-ray crystallographic studies (Figure 1). Complex **4a** is a mononuclear species,[13] featuring a unique seesaw, tetracoordinate geometry around the platinum center. The C54–Pt1–Br1 angle of 149.50(9)° is quite deviated from linearity, and the bond distance C54–Pt1 (2.051(3) Å) has a value slightly shorter than that found on its Pt(II) precursor, **1a** (*ca*. 2.095 Å).[7b] Additionally, the Pt1–Br1 bond distance is similar to those found in platinum(II) complexes in *trans* to ligands with moderate *trans* influence. The C–C and C–N bond distances in the imidazolyl ring exhibit metric parameters almost identical to that of its precursor whereas the Pt–C1 and Pt–C28 bond distances are almost indistinguishable, within experimental error, to those found in complex **2a**. All these data are in line with the very few crystallographically characterized third-row metal-centered radical complexes containing NHC ligands.[14]

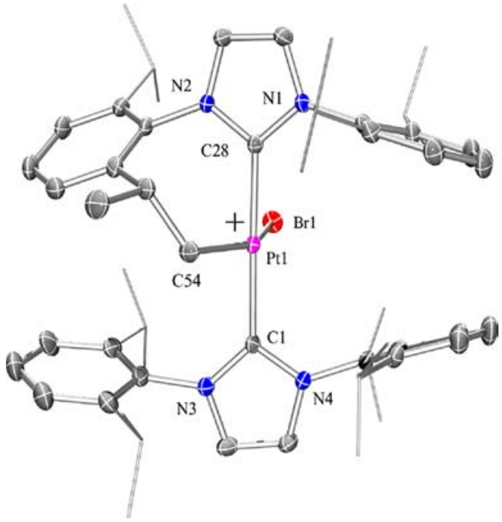


Figure 1. Molecular structure of cationic Pt(III) complex **4a**. BAr^F anion has been omitted and the size of *iso*-propyl groups has been diminished for clarity.

To gain further insight into the electronic properties of this unusual complex, DFT calculations were performed using the BHHLYP functional.[15,16] Optimization of complex **4a** gives the expected seesaw structure with a C–Pt–Br angle of 143.2°. The Pt atom accounts for 59% of the Mulliken spin density population whereas Br and C (cyclometalated) atoms perform 28% and 11% respectively. The NHC moiety does not show a relevant amount of spin density. These values agree with the shape of the single occupied molecular orbital (SOMO, Figure 2).

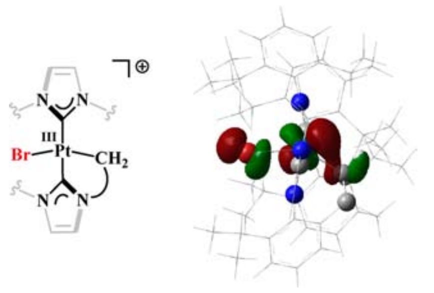


Figure 2. Calculated SOMO of complex **4a** (isovalue of 0.05).

Experimental reports on mononuclear Pt(III) complexes[13b,c] confirm square planar geometries. Theoretical studies suggest that d^7-complexes can appear as tetrahedral or square planar structures,[17] but for heavy metals the latter one is usually preferred in low-spin configurations.[18] In order to assess the origin of the adoption of a seesaw structure instead of a square planar one, and particularly to discriminate between electronic and steric effects, we have performed calculations in a simplified system **4a′** in which the phenyl NHC wings have been replaced by methyls (Figure 3). Full-optimized calculation of **4a′** gives a seesaw structure with a Br−Pt−C angle (148.3°) very close to that of the actual complex. Therefore, steric hindrance is not responsible for the distorted geometry and electronic effects should be decisive. The existence of a bonding interaction between the alkyl ligand and the metal in the SOMO of the seesaw structure was identified as being responsible for the structural preference. This interaction decreases when the Br−Pt−C angle increases and vanishes at the square planar geometry (see SI).[19]

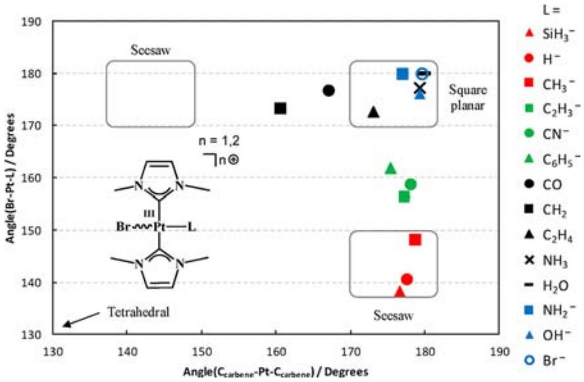


Figure 3. Distribution of calculated Pt(III) complexes according to the $C_{carbene}$−Pt−$C_{carbene}$ and the Br−Pt−L angles.

The precedent result pointed out that the nature of the ligand in *trans* position to bromide could have an important effect in deciding the seesaw or square planar geometry of the complex. Based on this idea, we generated a set of hypothetical complexes substituting the σ-donor methyl group by other anionic ligands (L) with different electron-donating effects (Figure 3). For the set of optimized complexes the $C_{carbene}$−Pt−$C_{carbene}$ (X axis) and Br−Pt−L (Y axis) angles are plotted in Figure 3.[20] According to the graph, the Br−Pt−L angle is decreased following the ligand trend $Br^- \approx OH^- \approx NH_2^- < C_6H_5^- \approx CN^- \approx C_2H_3^- < CH_3^- < H^- \approx SiH_3^-$. Therefore the higher the σ-donating character is, the higher the deformation from a square planar geometry that is observed, enhancing the seesaw one. For instance, the OH^- ligand (blue triangle) induces a square planar geometry with $\alpha = 176.1°$ whereas the SiH_3^- ligand (red triangle) forces a seesaw structure with $\alpha = 138.4°$. In addition, several neutral ligands were also tested (labeled in black). Some of them, those which exhibit strong back-donation character, mainly affect the $C_{carbene}$−Pt−$C_{carbene}$ angle, but its influence is less disturbing. On the whole, these d^7-Pt(III) complexes present a soft potential for L^1−Pt−L^2 bending, leading to structures spanning a wide range of Br−Pt−L angles, depending on the electronic nature of the ligands. In particular, anionic ligands with strong σ-donor ability strongly distort the square planar structure.

As stated above, the Pt(III) complex **4a** decomposes in solution at rt. The ^1H NMR spectrum revealed that a disproportionation process to the Pt(II) complex **1a** and the Pt(IV) **5a** (that subsequently rearranges into **2a**) is taking place, together with some decomposition leading to platinum species of unknown composition and the free carbene ligand in its protonated form (*ca.* 10%). These two latter species were not observed in the reaction of **1a** with 1 equiv of Br_2.

With the aim of assessing the thermodynamic feasibility of the sequence of reactions depicted in Scheme 2 as well as comparing bromine and iodine behaviors, the relative energies in dichloromethane (DCM) of the reactants, intermediates and products of the halogen addition process were computed. The relative energies are gathered in Table 1, where **6a** and **7a** stand for the iodo-analogues of **4a** and **5a**, respectively. In order to calculate the relative energies in a proper way, preserving the reaction stoichiometry, an extra molecule of reactant **1a** has been included. The different behaviors of Br_2 and I_2 additions are apparent from the data in this table. The bromine intermediates (**4a** and **5a**) are much more stable with respect to the reactants than the corresponding iodine intermediates (**6a** and **7a**),[21,22] in agreement with the experimental observation of **4a** and **5a**. Overall bromine addition is much more exothermic than the iodine one.

Table 1. Relative Energies in DCM Solvent (kcal mol^{-1}) of the Species along X_2 Addition to 1a (X = Br, I)

complex	ΔE_{DCM}	complex	ΔE_{DCM}
1a + **1a** + Br_2	0.0	**1a** + **1a** + I_2	0.0
4a + **4a**	−9.5	**6a** + **6a**	+4.5
1a + **5a**	−16.3	**1a** + **7a**	+1.0
1a + **2a**	−30.6	**1a** + **3a**	−16.2

In summary, carbon−halogen bond coupling reactions occur during addition of Br_2 or I_2 to unsaturated 14-electron Pt(II) complexes. Reactions with Br_2 allowed us to isolate a mononuclear, paramagnetic Pt(III)-alkyl species which exhibits an unprecedented seesaw geometry. This complex is a rather stable intermediate that can be further oxidize to a Pt(IV)-alkyl dibromo derivative that is unstable toward reductive carbon−halogen coupling. Theoretical calculations on the formation and structure of the Pt(III) are consistent with experimental observations, showing the thermodynamic viability of such a radical with a high spin density at the Pt atom. Calculations also point out that electronic effects account for its seesaw structure, predicting such a geometry for Pt(III) $[PtBr(NHC)_2L]$ complexes when very strong σ-donating L ligands are *trans* to the bromine atom. Further studies are currently being pursued in order to obtain additional information on the stability and reactivity of these types of Pt(III) complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectroscopic data, crystallographic information (CIF) and computational details. 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 interest.

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