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Reductive Elimination of Ethane from Five-Coordinate Platinum(IV) Alkyl Complexes

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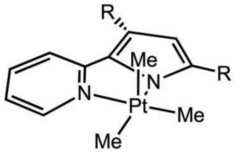
Five-coordinate platinum(IV) alkyl complexes bearing sterically nondemanding pyridylpyrrolide ligands, (LX)$PtMe_3$ [LX = 3,5-di-*tert*-butyl-2-(2-pyridyl)pyrrolide (**3a**) and 3,5-diphenyl-2-(2-pyridyl)pyrrolide (**3b**)] have been prepared. An X-ray structure of **3a** establishes that it is a five-coordinate Pt^{IV} complex with a square-pyramidal geometry. Thermolysis of **3a** or **3b** in C_6D_6 with ethylene results in reductive elimination of ethane (C_2H_6) and methane (CH_4 and CH_3D) and the formation of cyclometalated platinum(II) ethylene complexes **4a** or **4b**, respectively. Results of kinetic investigations of the reaction of **3b** are consistent with a mechanism of direct C–C reductive elimination from the five-coordinate Pt^{IV} compound. Thermolysis of **3a** in C_6D_6 with no ethylene present forms a novel dinuclear complex (**5**-d_6).

Coordinatively and electronically unsaturated species are often proposed as key intermediates in transition-metal-catalyzed reactions.[1] Five-coordinate d^6 and three-coordinate d^8 late-transition-metal species have received significant recent attention in this regard.[2] Because of their inherent reactivity, the isolation, characterization, and studies of such unsaturated complexes can be challenging. Although proposed for over 30 years as intermediates in reductive elimination and oxidative addition reactions to form and cleave C−H, C−C, and C−X bonds at Pt^{IV} and Pt^{II} centers, respectively,[2c,3] the first isolable examples of five-coordinate Pt^{IV} compounds were only reported in 2001: a series of trimethyl complexes with nacnac ligands, $[\{(o\text{-}R^1_2\text{-}p\text{-}R^2C_6H_2)NC(R^3)\}_2CH]PtMe_3$ (R^{1-3} = various combinations of H, Me, ^{t}Bu, and ^{i}Pr),[4] and silyl hydride complexes with a protonated trispyrazole borate ligand, $[\kappa^2\text{-}((Hpz')BHpz'_2)\text{-}Pt(H)_2SiR^4]^+$ (pz′ = 3,5-dimethylpyrazole; R^4 = Et_3, Ph_3, and Ph_2H).[5] More recently, the five-coordinate Pt^{IV} complex (AnIm)$PtMe_3$ (AnIm = $[o\text{-}C_6H_4\{N(C_6H_3{}^iPr_2)\}(CH{=}NC_6H_3{}^iPr_2)]^-$) has been crystallographically characterized.[6] A five-coordinate structure has also been proposed for a (dimethylsilyl)platinum(IV) pydridylindolide complex.[7]



3a (R= ^{t}Bu)
3b (R= Ph)

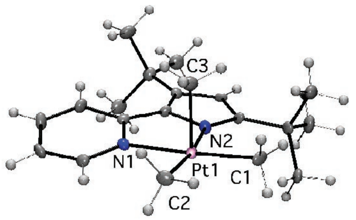


Figure 1. POV-Ray thermal ellipsoid diagram of **3a** (R = ^{t}Bu) with a 50% probability. Selected bond lengths (Å) and angles (deg): C1−Pt1, 2.068(5); C2−Pt1, 2.046(5); C3−Pt1, 2.038(5); N1−Pt1, 2.123(4); N2−Pt1, 2.189(4); C1−Pt1−C3, 86.47(19); N2−Pt1−C1, 104.91(18); N1−Pt1−N2, 77.40(15).

Notably, each of the known five-coordinate Pt^{IV} complexes contains an anionic bidentate ligand bearing N donor atoms. Similarly, in this contribution, 3,5-disubstituted 2-(2-pyridyl)-pyrrolide ligands are used to stabilize unsaturated Pt^{IV}. Mechanistic studies of the reductive elimination of ethane from these new five-coordinate platinum(IV) trimethyl compounds have been carried out, and the results are consistent with C−C coupling occurring directly from the five-coordinate complexes. Previous studies of alkyl C−C reductive elimination from six-coordinate Pt^{IV} have consistently found support for mechanisms involving preliminary ligand loss to generate steady-state concentrations of five-coordinate intermediates from which C−C coupling occurs.[3] By starting with a five-coordinate Pt^{IV} system, as in the work described here, a rate constant corresponding directly to the C−C bond-forming reductive elimination step can be measured.

The reaction of 3,5-di-*tert*-butyl-2-(2-pyridyl)pyrrole [DtBPP-H (**1a**)] or 3,5-diphenyl-2-(2-pyridyl)pyrrole [DPPP-

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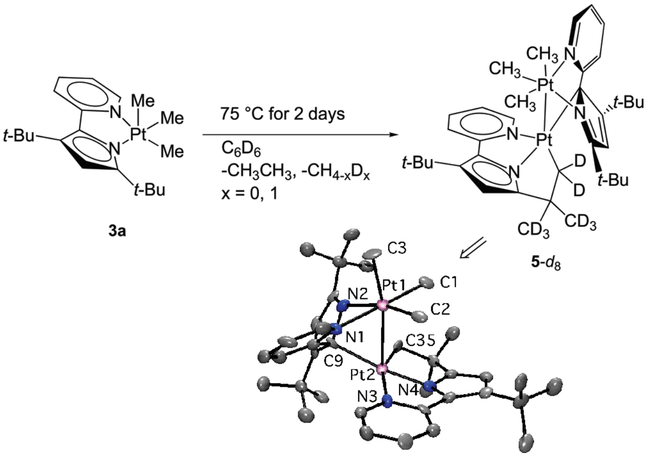


Figure 2. Formation of **5**-d_8 and POV-Ray diagram at a 50% probability. The H atoms and 1.5 equiv of benzene have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Pt2, 2.7688(6); Pt1−C1, 2.052(9); Pt1−C2 2.003(8); Pt1−C3, 2.067(8); Pt2−C35, 2.061(9); Pt2−C9, 2.124(9); N1−Pt1−N2, 75.2(3); C9−Pt2−Pt1, 67.3(2).

H (**1b**)][8] with KH in tetrahydrofuran affords the green salt DtBPP-K (**2a**) or DPPP-K (**2b**). The reaction of **2a** or **2b** with $[PtMe_3OTf]_4$ (OTf = trifluoromethylsulfonate) in toluene generates the orange five-coordinate complexes (LX)$PtMe_3$ [LX = DtBPP (**3a**) and DPPP (**3b**); Figure 1].[9]

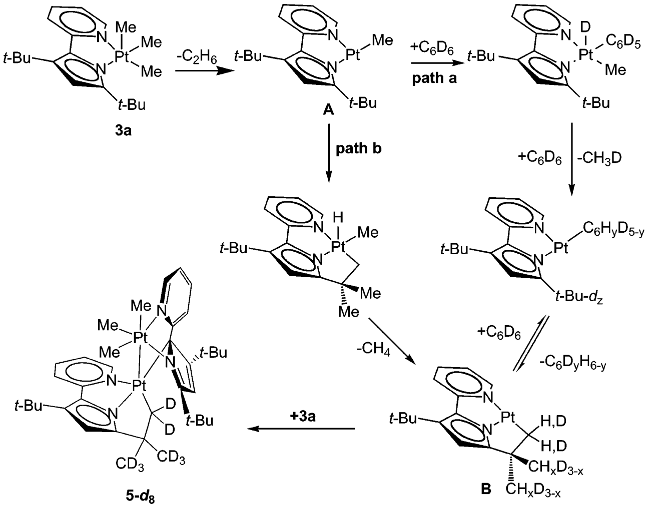
An X-ray structure of complex **3a** shows a square-pyramidal geometry (Figure 1). The ^{t}Bu groups do not provide intramolecular protection of the open site, and there is no evidence of intermolecular interactions.[9] Thus, steric protection of the open site is not required for the stability of unsaturated five-coordinate Pt^{IV} complexes.

In contrast to the square-pyramidal structure observed in the solid state, ^{1}H NMR spectra of **3a** and **3b** in C_6D_6 at 298 K show a single Pt−Me signal indicating that in solution the three inequivalent Me groups in each complex are averaged on the NMR time scale. Such high fluxionality in solution is typical for five-coordinate d^6 complexes.[4c,10]

Complexes **3a** and **3b** are thermally stable at room temperature. However, when **3a** was heated in C_6D_6 at 75 °C, ethane and methane (CH_4 and CH_3D) were formed along with one major Pt product (**5**-d_8, 57% by ^{1}H NMR). The X-ray structure of **5**-d_8, a dinuclear compound, is shown in Figure 2. Formal electron counting implies two Pt^{III} centers. Consistent with this assignment, the J_{Pt-H} values (77, 72, and 75.5 Hz) of the Pt-bound Me groups would be unusually high for Pt^{IV}.[11] Thermolysis of **3b** also produced ethane and methane (CH_4 and CH_3D), but no stable Pt product could be identified.

A different way to view the oxidation states in dinuclear complex **5**-d_8 would be as the interaction of a three-coordinate cyclometalated Pt^{II} species with a molecule of the Pt^{IV} starting complex **3a**. While the Pt^{III} dimer senario is more consistent with the spectral data, the Pt^{II}/Pt^{IV} view suggests a mechanism to generate **5**-d_8 (Scheme 1). Direct reductive elimination of two Me groups from the five-coordinate **3a** would lead to the three-coordinate Pt^{II} intermediate **A**.[12] Intermediate **A** could undergo oxidative addition of the C_6D_6 solvent (path a) or cyclometalation (path b) followed by reductive elimination of methane. The observation of both CH_3D and CH_4 (1:1.4) indicates that arene intermolecular and alkyl intramolecular C−H bond activation are competitive. The complete deuteration of the cyclometalated ^{t}Bu group would require reversibility of the cyclometalation and solvent activation. The formation of dinuclear **5**-d_8 would then result from trapping of the unsaturated Pt^{II} deuterated cyclometalated species **B** with a molecule of the five-coordinate **3a** starting compound. If this mechanistic scheme is viable, it should be possible to trap the Pt^{II} cyclometalated species **B** with an exogenous ligand.

Scheme 1



Indeed, the thermolysis of **3a** and **3b** at 85−100 °C in C_6D_6 in the presence of ethylene as a trapping ligand results in C−C reductive elimination to form ethane and methane (CH_4 and CH_3D) along with the cyclometalated platinum(II) ethylene complexes **4a** and **4b** (Scheme 2). For reactions run in C_6D_6, multiple deuterium incorporation into the cyclometalated ^{t}Bu group of **4a** was observed, but no deuterium was incorporated into **4b**. Yields of 68% for **4a** and 88−93% for **4b** were determined by ^{1}H NMR spectroscopy.[9]

The conversion of **3b** to **4b** at 98 °C in C_6D_6 was studied under pseudo-first-order conditions with excess ethylene (130−720 mM, 9−60 equiv). Clean first-order kinetic behavior was observed for the disappearance of Pt^{IV} in all kinetic experiments.[9] Surprisingly, as shown in Figure 3, ethylene was found to inhibit the rate of the reaction. However, the effect is quite small; an increase in $[C_2H_4]$ by 5.5 times reduced k_{obs} by only 28%.[9]

The unforeseen mild inhibition of reductive elimination by ethylene could be explained if ethylene coordinates to the open site of **3b** and prevents reductive elimination.

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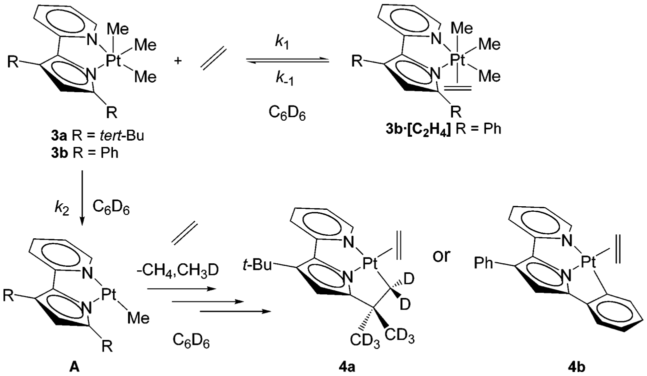
(12) Such unsaturated Pt^{II} species may be stabilized by solvent coordination or an agostic interaction.

Scheme 2



Olefins are not expected to bind strongly to Pt^{IV} because the back-bonding capacity of these high-valent centers should be quite small. Indeed, alkene coordination to Pt^{IV} has been reported but is rare.[13] Support for the proposal of ethylene coordination to **3b** is found in ^1H NMR spectra of **3b**; the Pt−Me signal shifts upfield with increasing ethylene concentration and decreasing temperature. More convincing is the ^1H NMR spectrum at 204 K of a toluene-d_8 solution of complex **3b** in the presence of ethylene; three inequivalent Pt−Me signals and a signal for coordinated ethylene (δ 4.31) are consistent with a platinum(IV) ethylene complex **3b·**[C_2H_4] (Figure S4 in the Supporting Information).

The evidence of ethylene binding to Pt^{IV} and the slight inhibition of the rate of reductive elimination are consistent with the mechanism in Scheme 2, wherein an equilibrium between **3b** and **3b·**[C_2H_4] exists but reductive elimination occurs only from five-coordinate **3b**.[14] The rate expression for the mechanism shown in Scheme 2 is $d[Pt^{IV}]/dt = k_{obs}[Pt^{IV}]$, where $k_{obs} = k_2/(K_{eq}[C_2H_4] + 1)$.[9] Values of $k_2 = 6.3(4) \times 10^{-4}\ s^{-1}$ and $K_{eq} = k_1/k_{-1} = 0.6(2)\ M^{-1}$ can be calculated from the plot of $1/k_{obs}$ vs [C_2H_4] shown in Figure 3.[15] The small K_{eq} for ethylene coordination to **3b** is consistent with the weak back-bonding expected for Pt^{IV}, but the ethylene binding is significant enough to inhibit the reductive elimination of ethane. Most important in this analysis is that because the reductive elimination occurs directly from **3b**, the k_2 value corresponds to the actual C−C bond-formation step. Previous measurements of the rate constants for C−C reductive elimination from six-coordinate Pt^{IV} have included contributions from the preequilibrium ligand loss step.[3]

Thus, the proposed reaction sequence that takes place upon thermolyses of **3a** or **3b** to form **4a** or **4b**, respectively, in the presence of ethylene or to form **5** from **3a** in the absence of ethylene can be related as detailed in Schemes 1 and 2. Following reductive elimination of ethane from **3a** or **3b**, the three-coordinate Pt^{II} intermediate **A** activates the C−H(D) bonds of the solvent or the ligand competitively, leading to the production of both CH_3D and CH_4 (1:1.3 from **3a** and 1:3.8 from **3b**). That deuterium from the solvent is incorporated into the ^{t}Bu group of **4a** but not the Ph group of **4b** indicates that the cyclometalation step is reversible for **4a** but not for **4b**. The higher proportion of CH_4 from **3b** versus **3a** is consistent with faster activation of an aryl versus an alkyl C−H bond, albeit steric constraints in the intramolecular reaction may also be important.[6] In the presence of ethylene, the three-coordinate cyclometalated Pt^{II} species[12] is trapped to produce **4a** or **4b**. In the absence of ethylene, the five-coordinate Pt^{IV} complex **3a** itself serves as the trap to form the dinuclear species **5**-d_8. Notably, scrambling of deuterium from C_6D_6 into an isolated sample of complex **5** is not observed after 1 day at 70 °C. Thus, the H/D scrambling into the cyclometalated ^{t}Bu group occurs prior to the formation of **5**-d_8.

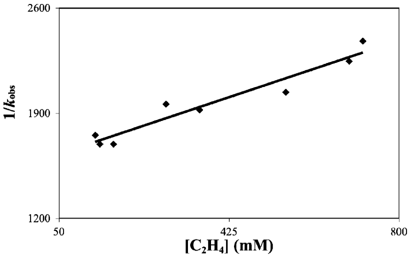


Figure 3. Plot of $1/k_{obs}$ vs [C_2H_4] (mM) for the thermolysis of **3b** at 98 °C. Ethylene concentrations were evaluated at room temperature.[15]

In summary, the bidentate anionic (pyridyl)pyrrole ligands have been used to prepare new five-coordinate platinum(IV) alkyl complexes. X-ray characterization shows that the square-pyramidal geometry is preferred even in the absence of steric considerations. Kinetic investigations indicate that C−C coupling occurs directly from the five-coordinate Pt^{IV} complex. Without the preliminary ligand loss as found in the previous mechanistic studies of C−C reductive elimination from six-coordinate Pt^{IV},[3] kinetic information relating to the C−C coupling step was accessible and a rate constant for this elementary step was obtained. The three-coordinate Pt^{II} products of reductive elimination in this system undergo intra- and intermolecular C−H bond activation and then are trapped by added ethylene or by Pt^{IV} starting material in the absence of added trapping agent. We are continuing our investigations of these and related unsaturated model species to probe the intimate mechanism of the C−C and C−H coupling and cleavage steps in reductive elimination/oxidative addition at Pt^{IV}/Pt^{II}.

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Supporting Information Available: Synthetic procedures and spectral characterization of Pt compounds, experimental details of kinetic experiments, and X-ray crystallographic data files for **3a** and **5**-d_8. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The possibility that reductive elimination of ethane follows after dissociation of one end of the bidentate N−N ligand cannot be ruled out. However, the energy of such an unsaturated intermediate (four-coordinate Pt^{IV}) is likely to be very high.

(15) Ethylene concentrations at 100 °C can be estimated, but the values for k_2 [$6.5(4) \times 10^{-4}\ s^{-1}$] and K_{eq} [$1.4(3)\ M^{-1}$] do not differ significantly from those calculated using [C_2H_4] determined by NMR integration at 25 °C.