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A Stable Five-Coordinate Platinum(IV) Alkyl Complex

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Coordinatively and electronically unsaturated species are short-lived intermediates in a large number of reactions involving late transition metal complexes.[1] These species containing an "open-site" in the metal coordination sphere are notoriously difficult to characterize, owing to their inherent reactivity.[2] In particular, five-coordinate Pt(IV) alkyl species have been consistently proposed as key intermediates in reductive elimination/oxidative addition reactions to form or break C−C, C−H, C−O, and C−I bonds at Pt(IV)/Pt(II), but such species have never been isolated or unambiguously characterized.[3,4] The intermediacy of these five-coordinate complexes in bondbreaking and -making reactions of model Pt complexes has significant implications for their involvement in platinum-catalyzed selective alkane functionalization reactions.[5] While it has been possible to calculate the geometry of five-coordinate Pt(IV) alkyl intermediates using quantum chemical methods,[6] attempts to generate such species experimentally have invariably led to the observation that weakly coordinating anions or solvent molecules bind to the metal such that the examination of the truly coordinatively unsaturated species was not possible.[7,8b] No experimental evidence to establish the geometry of the five-coordinate Pt(IV) alkyl complexes has been reported.[8] We report herein the first example of an isolable and crystallographically characterized five-coordinate Pt(IV) alkyl complex.

The five-coordinate Pt(IV) complex, (L)PtMe$_3$ (**1**), where L$^-$ is the anionic β-diimine ligand $[\{(o\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC}(\mathrm{CH}_3)\}_2\mathrm{CH}]^-$ has been synthesized and fully characterized.[9,10] Compound **1** was prepared in good yield (75%) from the potassium salt of the ligand[11] and tetrameric trimethyl platinum(IV) triflate[12] in dry pentane solution. X-ray quality crystals of (L)PtMe$_3$ were obtained by reducing the volume of the pentane solution in vacuo. An ORTEP diagram of **1** is shown in Figure 1, with selected structural parameters contained in the figure legend.

While coordination geometries ranging from square pyramidal to trigonal bipyramidal are available for a five-coordinate complex, the geometry about the platinum in **1** is clearly a square pyramid. The Pt atom deviates only 0.099(3) Å toward C2 from the perfect N1−N1′−C1−C1′ plane. Nothing is coordinating to the open site on the Pt atom. No solvent molecules are found in the crystal structure. The platinum center of the next molecule in the crystal lattice is 7.1 Å away. The closest approach of nonbonded groups to the open site are the isopropyl methine hydrogens at 3.0 Å. This is the same distance observed in the related Pt(II) complex **2** discussed below. In solution, no ^{195}Pt satellites are seen for the ^{1}H NMR signals of the isopropyl hydrogens. Thus, there is no indication of agostic interactions between the isopropyl moieties on the ligand and the metal. It is interesting that the methyl group *trans* to the open site shows only a slightly shorter Pt−C distance compared to methyl *trans* to nitrogen (2.038(7) versus 2.056(4) Å). A larger difference might have been expected based on *trans* influence arguments.[13,14]

The NMR spectral data[9] impressively demonstrate the high solution-phase fluxionality of this five-coordinate complex. The apparent symmetry of the molecule is greater in solution than in the solid-state structure. The isopropyl groups above and below the NCCCNPt plane are equivalent by NMR. The same is observed for the aromatic hydrogens, and this pseudo-C_{2v} sym-

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[†] UW Chemistry X-ray Facility.

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(2) Cases where suitable stabilizing ligand systems have been found involve mainly ruthenium, iridium, and rhodium, e.g.: (a) Gottschalk-Gaudig, T.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 5241. (b) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406. (c) Budzelaar, P. H. M.; de Gelder, R.; Gal, A. W. *Organometallics* **1998**, *17*, 4121.

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(8) (a) Structurally characterized bimetallic or multimetallic complexes that are *models* for five-coordinate alkylplatinum(IV) have been reported. These involve metal complex fragments which are isolobal to CH$_3^+$ coordinated to Pt(II). See for example: Arsenault, G. J.; Anderson, C. M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 2094. (b) A potentially five-coordinate Werner-type complex of platinum(IV), PtCl$_5^-$, has dichloromethane (which was disordered in the crystal structure) in the sixth coordination site. Cook, P. M.; Dahl, L. F.; Dickerhoof, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5511. (c) Five-coordinate silyl(dihydrido) Pt(IV) complexes have only recently been structurally characterized: Reinartz, S.; White, P.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425−6426.

(9) (L)PtMe$_3$ (**1**): ^{1}H NMR (750.1 MHz, pentane-d_{12}, 223 K) δ 7.12 (4 H, d, $^3J_{\mathrm{H-H}} = 7.5$ Hz, H$_m$), 7.04 (2 H, t, $^3J_{\mathrm{H-H}} = 7.5$ Hz, H$_p$), 4.99 (1 H, s, β-CH), 2.89 (4 H, septet, $^3J_{\mathrm{H-H}} = 6.8$ Hz, C***H***Me$_2$), 1.72 (6 H, s, α-Me), 1.16 (24 H, d, $J_{\mathrm{H-H}} = 7$ Hz, CH***Me***Me′, CHMe***Me′***, coincidently degenerate) 0.85 (9 H, s, $^2J_{\mathrm{Pt-H}} = 74$ Hz, Pt-Me). At 200 MHz (298 K, cyclohexane-d_{12}), the Pt-coupling to ligand hydrogens can be resolved: δ 4.98 (1 H, s, $J_{\mathrm{Pt-H}} = 4.4$ Hz, β-CH), 1.71 (6 H, s, $J_{\mathrm{Pt-H}} = 3.2$ Hz, α-Me). ^{13}C{^{1}H} NMR (188.6 MHz, pentane-d_{12}, 272 K) δ 159.1 ($J_{\mathrm{Pt-C}} = 12$ Hz, C$_\alpha$), 148.2 (C$_o$), 142.3 ($J_{\mathrm{Pt-C}} = 10$ Hz, C$_{ipso}$), 126.1 (C$_p$), 124.0 (C$_m$), 99.5 ($J_{\mathrm{Pt-C}} = 33$ Hz, C$_\beta$H), 29.5 (***C***HMe$_2$), 26.1 ($J_{\mathrm{Pt-C}} = 11$ Hz, α-Me), 25.15, (CH***Me***Me′), 25.00 (CHMe***Me′***), 1.66 ($J_{\mathrm{Pt-C}} = 682$ Hz, Pt-Me; ^{1}H coupled experiment: $J_{\mathrm{H-C}} = 135$ Hz). Anal. Calcd for $C_{32}H_{50}N_2Pt$: C, 58.43; H, 7.66; N, 4.26. Found C, 58.93; H 7.73; N, 4.23.

(10) (L)PtMe$_3$ (**1**): $C_{32}H_{50}N_2Pt$, MW = 657.83, clear orange cube; orthorhombic, space group = *Pnam*, $T = 130(2)$ K, $a = 14.1080(3)$ Å, $b = 9.8470(3)$ Å, $c = 21.7820(4)$ Å, $Z = 4$, $R_1 = 0.0348$, $wR_2 = 0.0892$. GOF (F^2) = 1.065

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(12) (a) Baldwin, J. C.; Kaska, W. C. *Inorg. Chem.* **1979**, *18*, 686. (b) Schlecht, S.; Magull, J.; Fenske, D.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1994.

(13) For a recent discussion of the *trans* influence in **six**-coordinate platinum(IV) trimethyl complexes, see: Fekl, U.; van Eldik, R.; Lovell, S.; Goldberg, K. *Organometallics* **2000**, *19*, 3535.

(14) In contrast, DFT calculations for (NH$_3$)$_2$PtMe$_3^+$ indicated a slightly longer Pt−C distance (Δ = 0.01 Å) *trans* vs *cis* to the open site.[6a]

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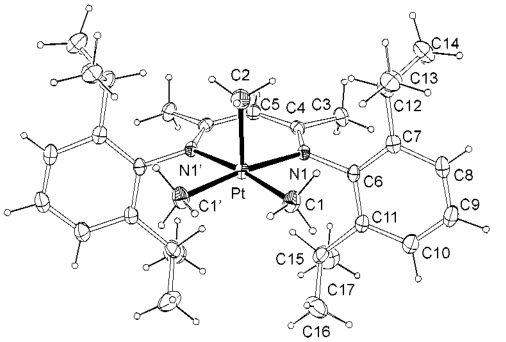

Figure 1. Thermal ellipsoid (30% probability) plot for **1**. Selected distances and angles (Å, deg): Pt−C1, 2.056(4); Pt−C2, 2.038(7); Pt−N1, 2.127(3); N1−Pt−N1′, 89.9(1); C1−Pt−C1′, 84.4(3); C2−Pt−C1, 89.6(2). There is a crystallographic mirror plane through atoms C2, C5, and Pt.

metry of the ligand L is observed from room temperature down to at least 223 K. A single, averaged signal is observed for the two basal and the single apical methyl groups, at δ 0.88 ($^2J_{Pt-H}$ = 74 Hz) in the ^{1}H NMR and δ 1.66 (J_{Pt-C} = 682 Hz, $^1J_{H-C}$ = 135 Hz) in the ^{13}C NMR. The spectra show sharp lines at all measured temperatures; no line-broadening or other indication for decoalescence of equatorial and apical methyl groups is observed.[15] The magnitude of the coupling constants to Pt is consistent with the assignment as platinum(IV).[16]

Since five-coordinate Pt(IV) alkyl complexes are highly labile intermediates in many reductive elimination reactions from Pt(IV) complexes,[3,4] the stability of **1** is of significant interest**.** Compound **1** was found to be stable in pentane or cyclohexane at ambient temperature for days, but only if protected from light. If exposed to ambient room light, a new compound (**2**) is formed within 2−3 days. The NMR spectrum of **2** shows a Pt−Me signal at δ 0.12 ($^2J_{Pt-H}$ = 88.5 Hz) which integrates to two methyl groups.[17] The large coupling to ^{195}Pt is consistent with a Pt(II) oxidation state.[16] A new methyl signal appears in the ligand part of the spectrum of **2** at δ 2.17, exhibiting a coupling constant ($^3J_{H-H}$) of 7 Hz to the central hydrogen of the ligand and integrates to three hydrogens. The isopropyl groups above and below the plane are nonequivalent. These data are consistent with a Pt(II) dimethyl product which results from the formal transfer of CH_3^+ from the Pt(IV) to the central anionic carbon of the ligand. Thus, **2** is an isomer of **1** containing four-coordinate platinum(II) and the methylated ligand L-Me.[18] The identity of (L-Me)$PtMe_2$ (**2**) was confirmed by a single-crystal X-ray structure determination of the product.[19] The conversion of **1** to **2** is depicted in Figure 2. Relevant structural parameters for **2** can be found in the legend of Figure 2.

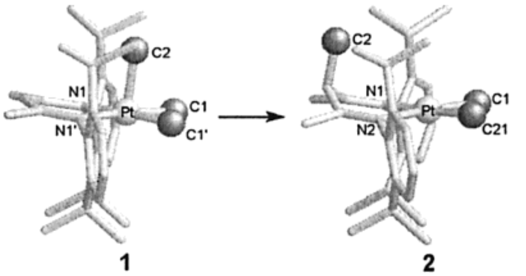

Figure 2. Methyl migration from five-coordinate platinum(IV) (**1**) to the central carbon of the coordinated chelate ligand (**2**). Both structures are from single-crystal X-ray determinations. Selected distances and angles (Å, deg) for **2**: Pt−C1, 2.041(7); Pt−C21, 2.027(9); Pt−N1, 2.141(5); Pt−N2, 2.137(6); C1−Pt−C21, 82.8(3); N1−Pt−N2, 88.0(2).

Transformation of **1** into **2** was not observed by thermal activation. Instead, heating a solution of **1** in cyclohexane at 90 °C in the dark led to decomposition to a variety of products, including platinum black, over the course of half a day. The expected product of C−C reductive elimination from **1**, ethane (60% yield), along with a small amount of methane (14%) were the only products observed in the ^{1}H NMR spectrum of the volatile portion of the reaction mixture.[20] Compound **2** is also unstable at this temperature but is not an intermediate in the major pathway for the thermal decomposition of **1** as ethane was not detected upon thermolysis of **2**.

In contrast, 100% conversion (^{1}H NMR) of **1** to **2** was observed within 10 min of irradiation of a sample of **1** at ambient temperature using a commercial Hg/Xe lamp. There is strong precedent that photolysis of methylplatinum(IV) compounds can lead to homolytic Pt−C bond cleavage.[21] Thus, a radical pathway may be involved in the transformation of **1** to **2**. Experiments to examine the mechanism of this unusual photochemical reaction as well as the thermal production of ethane from **1** are in progress. The syntheses of related five-coordinate Pt(IV) complexes and the reactivity of these species with two-electron donor ligands/nucleophiles are also under investigation.

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Supporting Information Available: Synthetic procedures for **1** and **2**, an ORTEP drawing for **2** (PDF); X-ray crystallographic data files for **1** and **2** (CIF). This information is available free of charge via the Internet at http://pubs.acs.org.

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[15] The ^{1}H chemical shifts show only a slight temperature dependence: On going from ambient *T* to 223 K: $\Delta\delta = -0.025$ ppm for Pt−Me.

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[17] (L-Me)$PtMe_2$ (**2**): ^{1}H NMR (500 MHz, cyclohexane-d_{12}, 298 K) δ 7.03−7.14 (6 H, m, H_m, $H_{m'}$, H_p), 3.75 (2 H, septet, $^3J_{H-H}$ = 7 Hz, C***H***Me$_2$), 3.39 (1 H, q, $^3J_{H-H}$ = 7 Hz, β-H), 3.03 (2 H, septet, $^3J_{H-H}$ = 7 Hz, C***H′***Me$_2$), 2.17 (3 H, d, $^3J_{H-H}$ = 7 Hz, β-CH_3), 1.46 (6 H, s, α-CH_3), 1.29 (12 H, d, $^3J_{H-H}$ = 7 Hz, CH(Me)***Me***, CH(Me)***Me′***), 1.10 (6 H, d, $^3J_{H-H}$ = 7 Hz, CH(Me)***Me″***), 1.09 (6 H, d, $^3J_{H-H}$ = 7 Hz, CH(Me)***Me‴***), 0.12 (6 H, s, $^2J_{Pt-H}$ = 88.5 Hz, Pt-Me).

[18] Complexes in which the similar ligand L−H coordinates to metals are known.[11]

[19] (L-Me)$PtMe_2$ (**2**): $C_{32}H_{50}N_2Pt$, MW = 657.83, orange-yellow block; monoclinic, space group = $P2_1$, T = 130(2) K, a = 9.0970(4) Å, b = 13.9530(6) Å, c = 12.7610(6) Å, β = 109.996(3)°, Z = 2, R_1 = 0.0366, wR_2 = 0.0816, GOF (F^2) = 1.091.

[20] Yields of ethane and methane (mol % relative to **1**) were calculated by integration of their ^{1}H NMR signals against that of an internal standard. These yields should be regarded as lower limits since only the gases in solution are detected.

[21] (a) Hackelberg, O.; Wojcicki, A. *Inorg. Chim. Acta* **1980**, *44*, L 63. (b) Hux, J. E.; Puddephatt, R. J. *J. Organomet. Chem.* **1992**, *437*, 251.