Coordinative Unsaturation in Platinum(IV) Chemistry: From Proposed Reaction Intermediates to the First Structurally Characterized Complexes**

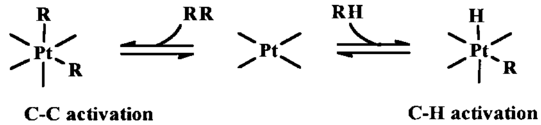
Richard J. Puddephatt*

Coordinatively unsaturated intermediates are recognized to be important in homogeneous catalysis and bond activation using transition metal complexes, as was most explicitly stated in Tolman's 16- and 18-electron rule.[1] However, direct proof of 16-electron platinum(IV) complexes has been difficult to come by and only recently have two papers been published that describe structural characterization of such compounds.[2, 3] Herein some of the history in highlighting the new breakthroughs is summarized.

Classical Werner-type platinum(IV) complexes, such as $[PtCl_6]^{2-}$ or $[PtCl_4(NH_3)_2]$ are invariably octahedral with 18-electron configurations, and they are inert towards ligand-substitution reactions. Ligand dissociation to give 16-electron intermediates must therefore be very difficult in these compounds and, to avoid this step, most substitution reactions occur by redox mechanisms. The reactions often involve catalysis, and overall substitution at platinum(IV) occurs by atom transfer or by substitution in transient platinum(II) or platinum(III) intermediates. These conclusions were drawn based on pioneering research on inorganic reaction mechanisms beginning in the 1950's, as summarized in the classic text by Basolo and Pearson.[4] There is naturally some controversy when such conventional wisdom is challenged.

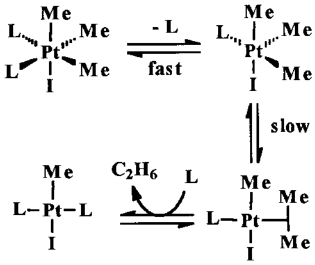
16-Electron Platinum(IV) Complexes as Reaction Intermediates

The study of alkyl and hydrido complexes of platinum(IV) was spurred on by the discovery of the activation of alkanes by platinum(II) complexes in 1969 by Shilov and co-workers, in which alkyl or alkyl(hydrido) complexes of platinum(IV) were suggested as key intermediates (Scheme 1).[5] The key reaction is the activation of C–H (or, in principle, C–C bonds, though this is possible only in very special cases, such as in strained cyclopropane derivatives) by concerted *cis* oxidative addition to platinum(II) centers of C–H (or C–C) bonds. However, the catalytic systems were then too complex to allow study of the individual steps.[5, 6]



Scheme 1. Activation of alkanes (R = alkyl) by platinum(II) species; C–H activation is much easier than C–C activation.

At that time alkylplatinum(IV) compounds were already known, and the reductive elimination to form platinum(II) compounds by C–C bond reductive elimination was established.[7] Since this is the microscopic reverse of the alkane activation step of Scheme 1, the mechanism of the reductive elimination was studied. The reductive elimination of ethane from *fac*-$[PtIMe_3L_2]$, L = tertiary phosphane ligand, was strongly retarded in the presence of free ligand L, and it was suggested that the reaction occurred by loss of a phosphane ligand to give a 16-electron intermediate $[PtIMe_3L]$ from which the key reductive-elimination step occurred through a C–C σ-bond complex transition state (Scheme 2).[8]



Scheme 2. Mechanism of C–C bond reductive elimination from platinum(IV) centers.

From Scheme 2 it can be deduced that the reductive elimination would be more difficult with ligands L that could not easily dissociate, and it was shown that these reactions are much more difficult with chelating diphosphane ligands.[8] On the other hand, if the reverse alkane activation is to be achieved, the alkane must displace L from the platinum(II) center in the first step and so at least one very labile ligand should be present. A T-shaped 14-electron platinum(II) complex would be ideal, and such unsaturated intermediates are

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[*] Prof. R. J. Puddephatt
Department of Chemistry
University of Western Ontario
London N6A 5B7 (Canada)
Fax: (+1) 519-661-3022
E-mail: pudd@uwo.ca

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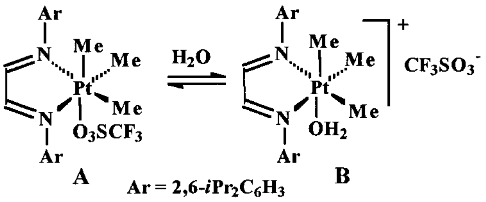
now also established as reaction intermediates.[9] Why are the Werner complexes and organometallic complexes different? The key factor is that strong σ-donor groups hydride or alkyl, and also related groups such as silyl or stannyl, have a very strong *trans*-influence[10] that weakens and polarizes the *trans* Pt–L bond and can lead to easy ligand dissociation with formation of short-lived 16-electron platinum(IV) or 14-electron platinum(II) complexes.

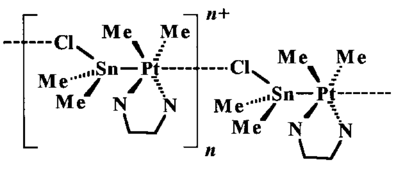
Subsequent mechanistic studies have confirmed that 16-electron platinum(IV) complexes are intermediates in most reductive-elimination reactions that lead to C–H[11] or C–C[12, 13] bond formation, as well as in the opposite C–H[5, 6, 14] or C–C[15] bond activation reactions by oxidative addition to platinum(II) centers. They have also been proposed as intermediates in α- or β-elimination reactions from alkylplatinum(IV) complexes,[16] in alkyl transfer reactions,[12] and in skeletal rearrangements of platina(IV)cyclobutane complexes.[17]

The recent discovery of the selective oxidation of methane to methyl bisulfate by SO_3, catalyzed by [$PtCl_2$(2,2′-bipyrimidine)] has stimulated renewed interest in the alkane-activation chemistry at platinum(II) centers,[18] and in the nature of the 16-electron platinum(IV) intermediates. Several theoretical studies have indicated that these intermediates should have square-pyramidal geometry,[19] but the challenge remained to isolate such compounds and to confirm their structures experimentally.

Synthesis of 16-Electron Platinum(IV) Complexes

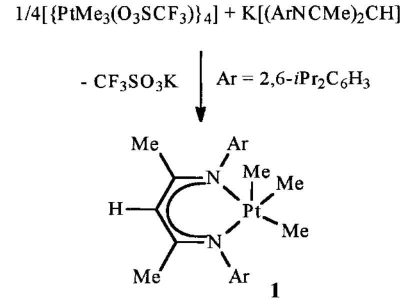
The first attempts to prepare 16-electron platinum(IV) complexes were inconclusive or unsuccessful. For example, reaction of complexes [$PtXMe_3L_2$], X = halide, with silver triflate or of [$PtMe_2L_2$] with methyl triflate gave complexes, **A** or **B**, with weakly bound triflate or water molecules in the sixth coordination site when L_2 = ArN=CHCH=NAr (Ar = 2,6-$i$$Pr_2C_6H_3$) or led to reductive elimination of ethane when $L_2 = Ph_2PCH_2CH_2PPh_2$.[12] The complexes **A** and **B** were in very rapid equilibrium, presumably because the 16-electron complex was very close in energy.[12] An attempt to use the very high *trans*-influence of the stannyl or silyl group to stabilize the 16-electron intermediate led to isolation of a complex [$PtMe_2(SnMe_2Cl)(bu_2bipy)$][$BF_4$] (**C**; bipy = 2,2′bipyridine), but in the solid state it formed weak intermolecular SnCl–Pt bonds at the potentially vacant site.[20] The complexes [$PtMe_2(MPPh_3)(bipy)$]$^+$, M = Ag or Au, were thought to be 16-electron complexes but could not be crystallized, but the perfluorophenyl complex [$Pt(C_6F_5)_3(SC_4H_8)(AgPPh_3)$] was structurally characterized.[20]





C, $\widehat{NN}$ = bu_2bpy

The final breakthrough occurred as the 16-electron platinum(IV) complexes [$PtMe_3\{(NArCMe)_2CH\}$] (**1**; Ar = 2,6-$i$$Pr_2C_6H_3$), and [$PtH_2(SiEt_3)(Tp')$]$^+$ (**2**; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate), were prepared (Scheme 3[2] and 4.[3]) and characterized both spectroscopically and by X-ray structure determinations.



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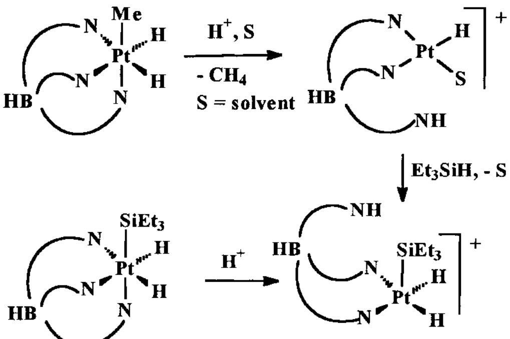
Scheme 3. A 16-electron trimethylplatinum(IV) complex.



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Scheme 4. Two routes to a cationic 16-electron silyldihydridoplatinum(IV) complex.

Complex **1** has square-pyramidal geometry and is highly fluxional in solution such that the axial and equatorial methyl groups appear to be equivalent in the NMR spectrum, even at low temperature.[2] Complex **1** is thermally stable in solution at room temperature but, on photolysis, it undergoes an unusual reaction in which a methyl group is transferred from platinum to the ligand to give a platinum(II) complex [$PtMe_2\{(NArCMe)_2CH\mathit{Me}\}$].[2]

The stereochemistry of complex **2** is not determined unequivocally from the X-ray structure determination since the hydride ligands were not directly located, but a combination of the X-ray data with spectroscopic and chemical data leave little doubt that it is correct.[3] Other potential structures, such as a hydrido(silane)platinum(II) formulation [$PtH(HSiEt_3)(Tp')$] are excluded by NMR and infrared (IR) spectroscopic data. While complex **1** has close to ideal square-pyramidal geometry, complex **2** is more distorted with angles N-Pt-Si = 120.2(1) and 126.8(1)° much greater than the ideal

90°.[3] Similar complexes with $SiPh_3$ or $SiHPh_2$ in place of the $SiEt_3$ group in **2** were also reported.[3]

What factors allowed these remarkable 16-electron complexes **1** and **2** to be isolated? Comparison of complex **1** with the six-coordinate complexes **A** and **B**, with ligands that have similar bulky substituents, suggests that the presence of the anionic ligand giving the neutral complex **1** is the determining factor in this case. Complex **2** is cationic but the charge is well-removed from the platinum center, and the very high *trans*-influence of the silyl group as well as the presence of the bulky Tp′ ligand should give extra stabilization. A whole new chemistry of the new 16-electron platinum(IV) complexes can now be expected, and the important role of these types of complexes in catalysis will be better defined by such studies.

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