The Halogen Effect in Oxidative Addition of Trimethylsilyl and Trimethyltin Halides to Platinum(II): Synthesis and Characterization of Silylplatinum(IV) Complexes

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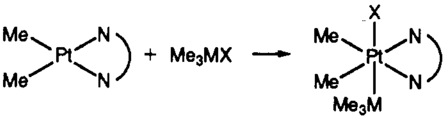
Summary: The reactions of group IV halo trimethyl compounds with electron-rich Pt(II) complexes give facile oxidative addition of the M–X bond (M = Si, X = Br, I; M = Sn, X = Cl, Br, I). Equilibrium studies when M = Sn show that there is a pronounced thermodynamic favorability of the reactions with heavier halides, and it is this effect which makes isolation of silylplatinum(IV) complexes possible. The crystal structure of [PtIMe$_2$(SiMe$_3$)(2,2′-bipyridyl)] has been determined and shows an exceptionally long Pt–I bond arising from the strong trans influence of the trimethylsilyl group.

The platinum-catalyzed hydrosilation of alkenes is generally proposed to proceed *via* a silylplatinum(IV) intermediate. Ebsworth and co-workers have reported spectroscopic evidence for such species formed by the addition of Si–H bonds to the Pt(II), but the complexes were not isolable.[1] We report the synthesis and isolation of a series of silyl- and stannyl-ligated Pt(IV) species as well as the structure of [PtIMe$_2$(SiMe$_3$)(bpy)] (bpy = 2,2′-bipyridyl), which was determined by X-ray diffraction.

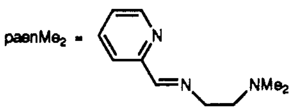
A number of new stannylplatinum(IV) species (**1b**–**l**) have been synthesized by oxidative addition following the method of Kuyper, who first reported the oxidative addition of Me$_n$SnCl$_{4-n}$ (n = 1–4) to the complex [PtMe$_2$(N–N)] with N–N = bpy.[2] We have extended this work to include oxidative-addition products of Me$_3$SnX (X = Cl, Br, I) to [PtMe$_2$(N–N)] (Scheme 1) with a range of diimine ligands (N–N). All new compounds were obtained in high yields and were characterized by NMR,[3] IR, and elemental analysis. The compounds Me$_n$SiCl$_{4-n}$ (n = 1–3) do not oxidatively add to [PtMe$_2$(N–N)], in accord with the observations of Kuyper, who attempted R$_3$SiCl (R = Me, Pt) addition.[4]

Scheme 1[a]



1a–l, **2a–h**

[a] Legend: **1a**, M = Sn, N–N = bpy, X = Cl; **1b**, M = Sn, N–N = bpy-*t*-Bu$_2$, X = Cl; **1c**, M = Sn, N–N = py-*n*-Pr, X = Cl; **1d**, M = Sn, N–N = paenMe$_2$, X = Cl; **1e**, M = Sn, N–N = bpy, X = Br; **1f**, M = Sn, N–N = bpy-*t*-Bu$_2$, X = Br; **1g**, M = Sn, N–N = py-*n*-Pr, X = Br; **1h**, M = Sn, N–N = paenMe$_2$, X = Br; **1i**, M = Sn, N–N = bpy, X = I; **1j**, M = Sn, N–N = bpy-*t*-Bu$_2$, X = I; **1k**, M = Sn, N–N = py-*n*-Pr, X = I; **1l**, M = Sn, N–N = paenMe$_2$, X = I; **2a**, M = Si, N–N = bpy, X = Br; **2b**, M = Si, N–N = bpy-*t*-Bu$_2$, X = Br; **2c**, M = Si, N–N = py-*n*-Pr, X = Br; **2d**, M = Si, N–N = paenMe$_2$, X = Br; **2e**, M = Si, N–N = bpy, X = I; **2f**, M = Si, N–N = bpy-*t*-Bu$_2$, X = I; **2g**, M = Si, N–N = pyr-*n*-Pr, X = I; **2h**, M = Si, N–N = paenMe$_2$, X = I. Abbreviations: bpy = 2,2′-bipyridyl; bpy-*t*-Bu$_2$ = 4,4′-di-*tert*-butyl-2,2′-bipyridyl.



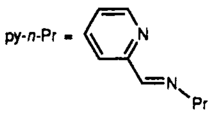


Table 1. K_{eq} (L mol^{-1}) for Oxidative Addition of Me$_3$Sn–X to Me$_2$Pt(N–N) at 25 °C

	Me$_3$SnCl	Me$_3$SnBr	Me$_3$SnI
Me$_2$Pt(paenMe$_2$)	80.3 ± 0.4	150.3 ± 0.8	37800 ± 600
Me$_2$Pt(py-*n*-Pr)	123.5 ± 0.6	190 ± 10	14100 ± 300
Me$_2$Pt(bpy)	114.9 ± 0.5	231 ± 7	34300 ± 400
Me$_2$Pt(bpy-*t*-Bu$_2$)	46.5 ± 0.2	145.0 ± 0.7	40800 ± 500

Table 2. Enthalpy Change With Halide Change (kJ mol^{-1})[7]

	$\Delta H°_{Cl} - \Delta H°_{Br}$	$\Delta H°_{Cl} - \Delta H°_{I}$	$\Delta H°_{Br} - \Delta H°_{I}$
Me$_2$Pt(paenMe$_2$)	1.5 ± 0.1	15.2 ± 0.2	13.7 ± 0.2
Me$_2$Pt(py-*n*-Pr)	1.1 ± 0.1	11.7 ± 0.2	10.7 ± 0.2
Me$_2$Pt(bpy)	1.7 ± 0.1	14.1 ± 0.2	12.4 ± 0.2
Me$_2$Pt(bpy-*t*-Bu$_2$)	2.8 ± 0.1	16.8 ± 0.2	14.0 ± 0.2
calcd	4.5	15.0	10.5

The ease and reversibility of the oxidative addition of Me$_3$SnX (X = Cl, Br, I) to [PtMe$_2$(N–N)] offers an opportunity to determine the equilibrium constants for these reactions. Equilibrium constants were determined by UV–visible spectroscopy,[5] using the intense metal–ligand charge-transfer band of each Pt(II) species to monitor its concentration. Table 1 shows the equilibrium constants obtained from Scatchard plots[6] and clearly indicates the halogen effect, with a small to moderate increase in the equilibrium constant on going from chloride to bromide and a large increase on going from bromide to iodide. These data have been used to calculate the change in enthalpy for the oxidative addition, corresponding to a change in halide (Table 2).[7] We see a small enthalpy change (1.1–2.8 kJ mol^{-1}) on going from chloride to bromide and a considerably larger change (11.7–16.8 kJ mol^{-1}) on going from bromide to iodide. Also shown are the

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(1) (a) Bentham, J. E.; Ebsworth, E. A. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 145. (b) Bentham, J. E.; Cradock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587. (c) Anderson, D. W. W.; Ebsworth, E. A. V.; MacDougall, J. K.; Rankin, D. W. H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2259.

(2) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171.

(3) For example, for **1i** in CD$_2$Cl$_2$: δ(^{1}H) −0.248 [s, br, $^2J_{SnH}$(av) = 48.3 Hz, Me–Sn], 1.49 [s, $^2J_{PtH}$ = 61.9 Hz, Me–Pt], 7.5–9.1 [pyridinyl protons].

(4) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 77.

(5) Solutions of (1–3) × 10^{-4} M PtMe$_2$(N–N) in dry toluene were titrated with 0.1, 0.08, and 0.002 M dry toluene solutions of Me$_3$SnCl, Me$_3$SnBr, and Me$_3$SnI, respectively, at 25 °C under anhydrous conditions. The λ_{max} (nm) and ϵ (L mol^{-1} cm^{-1}) values for the Pt(II) compounds are as follows: 513, 3311(11), PtMe$_2$(bpy); 505.5, 3899(9), PtMe$_2$(bpy-*t*-Bu$_2$); 546, 3469(14), PtMe$_2$(py-*n*-Pr); 542, 3431(10), PtMe$_2$(paenMe$_2$).

(6) Harris, D. C. *Quantitative Chemical Analysis*, 2nd ed.; Freeman: New York, 1987; pp 517–519.

(7) The assumption has been made that changes in $T\Delta S$ between reactions are small and hence $\Delta H°_1 - \Delta H°_2 = \Delta G°_1 - \Delta G°_2$. Attempts to determine the equilibrium constants as a function of temperature, and so to test this assumption, are in progress.

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Table 3. Bond Dissociation Energies (kJ mol^{-1})

Me_3Sn–Cl	356^a	Me_3Si–Cl	472 ± 8^b	(Pt–Cl) – (Pt–Br)	33.5^c
Me_3Sn–Br	318^a	Me_3Si–Br	402 ± 8^b	(Pt–Cl) – (Pt–I)	82 ± 10^d
Me_3Sn–I	259^a	Me_3Si–I	321 ± 8^b	(Pt–Br) – (Pt–I)	48.5^e

[a] Neumann, W. P. *Pure Appl. Chem.* **1970**, *23*, 433. [b] Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Toronto, 1989; p 385. [c] Borkovskii, N. B.; Kovrilov, A. B.; Lipnitskii, I. V.; Umreiko, D. S. *Koord. Khim.* **1982**, *8*, 523. [d] Mortimer, C. T.; Wilkinson, M. P.; Puddephatt, R. J. *J. Organomet. Chem.* **1979**, *165*, 269. [d] Derived from (Pt–Cl) – (Pt–Br) and (Pt–Cl) – (Pt–I) values.

calculated values[8] obtained from the bond energy data in Table 3, which agree well with our findings, though the accuracy of the literature bond energy data is uncertain. The observations can be rationalized in terms of the addition of an M–X bond of a harder metal center (Si or Sn) to a softer metal center (Pt) becoming more favorable for a softer and therefore larger halogen; they represent the first quantitative data on the thermodynamics of the halogen effect in oxidative addition. Similar calculations for Me_3SiX oxidative addition yield $\Delta H°_{Cl} - \Delta H°_{Br} = 37$ kJ mol^{-1}, $\Delta H°_{Cl} - \Delta H°_{I} = 69$ kJ mol^{-1}, and $\Delta H°_{Br} - \Delta H°_{I} = 33$ kJ mol^{-1}. This indicates larger energy differences than with Me_3SnX oxidative addition, as well as similar enthalpy differences for $\Delta H°_{Cl} - \Delta H°_{Br}$ and $\Delta H°_{Br} - \Delta H°_{I}$, suggesting that Si–I or Si–Br oxidative addition to Pt(II) might occur despite the fact that Si–Cl addition does not.

Capitalizing on the halogen effect, we have successfully synthesized the oxidative-addition products of Me_3SiX (X = Br, I) with [Me_2Pt(N–N)] (Scheme 1) to give the first examples of silicon–halide bond oxidative addition to Pt(II) (**2a–h**) and one of the few examples of its addition to a transition metal.[9] Yields in these reactions range from 50 to 93%. The silylplatinum(IV) species have been characterized by NMR,[10] IR, and elemental analysis. UV-visible studies of these compounds were not possible due to side reactions occurring at low concentrations.

X-ray-quality crystals of **2e** were grown by solvent diffusion of pentane into methylene chloride at −30 °C under a nitrogen atmosphere. The crystal structure[11] (Figure 1) shows a *trans* configuration for the trimethylsilyl and iodide ligands. The trimethylsilyl group is known to have one of the strongest *trans* influences of any ligand,[12] and this manifests itself in the extremely long Pt–I bond length of 2.962(2) Å. This is by far the longest single Pt–I bond reported,[13] the structure of [$PtIMe_3${(PPh_2)CH(PPh_2)CH_2NHCH_2Ph}], where iodide is *trans* to a methyl group, having the next longest at 2.853(6) Å.[14] The Pt–Si bond length of 2.313(6) Å is average in comparison to those in the reported silylplatinum(II) structures.[15]

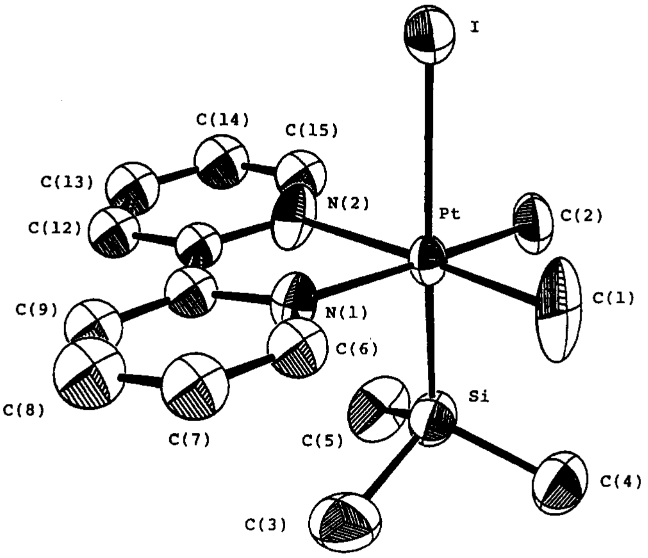

Figure 1. ORTEP diagram of **2e** showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: Pt–C(1), 2.096(18); Pt–C(2), 2.120(16); Pt–N(1), 2.186(12); Pt–N(2), 2.156(13); Pt–I, 2.962(2); Pt–Si, 2.313(6); I–Pt–Si, 177.0(2); I–Pt–C(1), 93.5(5); I–Pt–C(2), 91.1(6); I–Pt–N(1), 88.2(4); I–Pt–N(2), 88.4(4); Si–Pt–C(1), 83.5(5); Si–Pt–C(2), 88.8(6); Si–Pt–N(1), 92.1(4); Si–Pt–N(2), 94.6(4); C(1)–Pt–C(2), 90.0(7); N(1)–Pt–N(2), 77.8(5).

In conclusion, the halogen effect on oxidative addition has been clearly demonstrated for Sn–X additions to platinum(II), and its value is shown by the synthesis of uniquely stable silylplatinum(IV) complexes, which are of interest as models for catalytic intermediates in hydrosilation. It should find more general application.

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Supplementary Material Available: Details of the X-ray structure determination for [$PtIMe_2(SiMe_3)$(bpy)], including tables of crystal data and experimental details, bond distances and angles, positional and thermal parameters, least-squares planes and dihedral angles, and torsion angles (8 pages). Ordering information is given on any current masthead page.

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(8) We have made the approximation that $\Delta H°_{ox.\ add.} = D°(Sn{-}X) - [D°(Sn{-}Pt) + D°(Pt{-}X)]$.

(9) Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* **1990**, 2107 and references therein.

(10) For example, for **2e** in CD_2Cl_2: $\delta(^1H)$ −0.322 [s, $^2J_{SiH} = 6.23$ Hz, $^3J_{PtH} = -19.0$ Hz, Me–Si], 1.46 [s, $^2J_{PtH} = 64.3$ Hz, Me–Pt], 7.5–9.1 [pyridinyl protons].

(11) Crystal data for $C_{15}H_{23}N_2ISiPt$: fw 581.4; monoclinic, space group $P2_1/n$; $a = 14.371(2)$ Å, $b = 9.371(2)$ Å, $c = 13.865(2)$ Å, $\beta = 90.99(1)°$; $V = 1867(1)$ Å^3; $Z = 4$; calculated density 2.08(2) g cm^{-3}; 18 °C; graphite-monochromated Mo Kα radiation; ω-scan technique for $24.1 \leq 2\theta \leq 31.6°$; octants measured $\pm h,k,l$; total reflections 3975; $R = 0.048$, $R_w = 0.046$; goodness of fit 3.66 for 131 variables and 2272 reflections with $I \geq 2.5\sigma(I)$. All calculations were carried out by using a SUN 3/80 workstation running a version of NRCVAX. NRCVAX: Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. C. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(12) (a) Chatt, J.; Eaborn, C.; Ibekwe, S. *Chem. Commun.* **1966**, 700. (b) Yamashita, H.; Hayashi, T.; Kobayashi, T.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417 and references therein.

(13) Based on a search of Pt–I-bonded species done on the Cambridge Structural Database containing structures to Oct 1992. Bond lengths were obtained using the GSTAT program.

(14) Hassan, F. S. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 3011.

(15) For examples, see: Hitchcock, P. B. *Acta Crystallogr.* **1976**, *B32*, 2014 and ref 11b therein.