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Bismuth–Halide Oxidative Addition and Bismuth–Carbon Reductive Elimination in Platinum Complexes Containing Chelating **Diphosphine Ligands**

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ABSTRACT: Reaction of BiX₃ (X = Cl, Br, I) with $[PtMe_2(P-P)]$, (1a, P-P = dppm; 1b, P-P = dppe), occurs easily to yield a mixture of platinum(II) complexes [PtMeX(P-P)], 2, and [PtX₂(P-P)], 3, and the binuclear complex [Pt₂Me₂(μ -X)(μ $dppm)_{2}$]X, 4. On the basis of ³¹P NMR and UV-vis spectroscopy, a mechanism is proposed in which the rate determining step is conversion of the yellowish Pt(II)-BiX₃ adduct BiI₃·[PtMe₂(dppm)], A, into the Pt(IV)-Bi(III) intermediate [PtMe₂(BiX₂)-X(P-P)], IM1. Density functional theory (DFT) studies suggest that intermediate IM1 may be formed in acetone solution which undergoes the Bi-C reductive elimination process before formation of complexes 2 and 3. The structures of intermediates IM1 were theoretically determined using DFT calculations. In dilute acetone solution, as monitored by UV-vis spectroscopy, the oxidative addition processes follow first order kinetics. The overall reaction is slower for heavier halide.

INTRODUCTION

Oxidative addition reaction of different polar and nonpolar reagents to transition metal complexes has been extensively investigated and is considered as a key step in many catalytically important chemical processes.¹ In particular, the related reactions involving Pt complexes with a wide variety of reagents have been studied in detail.² Oxidative addition of heavy metal compounds to transition metal complexes has also been investigated, and the addition of reagents including Sn-X, Hg-X, Te-X, and Ge-X bonds (X = halogen), to electron rich platinum(II) centers have been reported.³ Besides, Braunschweig and co-workers have recently reported the oxidative addition of the bismuth-chloride bond to a Pt(0)complex.⁴ As such, the BiCl₃ reagent acts as a Lewis-acid because of the relativistic contraction of the valence 6s Bi AO,⁵ and the nucleophilic Pt(0) center in the first place attacks the Bi–Cl σ^* -orbital.⁴

On the other hand, reductive elimination reactions are among the most fundamental organometallic processes. In contrast to many reports on reductive elimination of R-R, R-H, Ar–Ar, and C– X_{1}^{6} on the basis of our knowledge, no studies on reductive elimination of Bi-C bonds from Pt(IV) complexes have been reported, although organobismuth compounds are useful in organic synthesis because of mild Lewis acidity, low toxicity, air stability, low cost, and ease of handling.⁷

In continuation of our interest in the investigation of oxidative addition reactions of different types of reagents to organoplatinum complexes, 8 in the present work, we have studied the reactions of platinum(II) complexes [PtMe2(P-P)], 1, in which P-P = 1,1-bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe), with bismuth trihalides, BiX_3 (X = Cl, Br, I). This seems to be the first example of bismuth-halide oxidative addition to organoplatinum(II) complexes and bismuth-carbon reductive elimination from Pt(IV) complexes.

EXPERIMENTAL SECTION

The NMR spectra were recorded as CDCl₃ or acetone-d₆ solutions on a Bruker Avance DRX 500 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ¹H (500 MHz, TMS) and ³¹P (202 MHz, 85% H₃PO₄). All the chemical shifts and coupling constants are given in units of ppm and Hz, respectively. The absorption spectra and kinetic studies were measured using a Perkin-Elmer Lambda 25 UV-vis spectrometer with temperature control using an EYELA NCB-3100 constanttemperature bath. The complexes $[PtMe_2(dppm)]^9$ and

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Scheme 1



Figure 1. Reaction of complex [PtMe₂(dppm)], **1a**, with BiI₃ as monitored by variable-temperature ³¹P NMR spectroscopy in acetone-d₆; (a) Pure **1a** at $-28 \ ^{\circ}C$, (b) immediately after addition of BiI₃ at $-28 \ ^{\circ}C$, (c) 6 min after addition of BiI₃ at $-28 \ ^{\circ}C$, (d) 12 min after addition of BiI₃ at $-8 \ ^{\circ}C$, (e) 18 min after addition of BiI₃ at $16 \ ^{\circ}C$, (f) 25 min after addition of BiI₃ at $27 \ ^{\circ}C$, and (g) 1 h after addition of BiI₃ at $27 \ ^{\circ}C$. Peak assignments are shown; platinum satellites are observed and shown for all involved species.

 $[PtMe_2(dppe)]^{10}$ were prepared as reported. The Pt(II) compounds [PtMe(X)(P-P)] (PP = dppm⁹ or dppe¹¹), 2, $[Pt(X)_2(P-P)]$,¹² 3, and $[Pt_2Me_2(\mu-X)(\mu-dppm)_2]X$, 4,^{9b,13} were characterized by comparing their ¹H and ³¹P NMR spectra with those of the authentic samples. The byproducts of the reactions were BiMeX₂ and BiMe₂X which were identified from their reported ¹H NMR data.¹⁴

Reaction of [PtMe₂(dppm)] with BiCl₃. To a solution of [PtMe₂(dppm)] (50 mg, 0.08 mmol) in 20 mL of acetone was added BiCl₃ (25.9 mg, 0.08 mmol). The solution was stirred for 2 h. The solvent was removed, and the resulting residue was dried to form a white solid as a mixture of **3a** and **4a** (see Scheme 1). Selected NMR data for **3a** (30%, minor product) in CDCl₃: δ (³¹P) -64.0 [s, ¹J_{PtP} = 3070 Hz]; δ (¹H) 4.62 [br, 2H, CH₂P₂]. Selected NMR data for **4a** (70%, major product): δ (³¹P) 13.6 [s, ¹J_{PtP} = 3033 Hz]; δ (¹H) 0.50 [t, ³J_{PH} = 8.1 Hz, ²J_{PtH} = 88.0 Hz, 6H, Pt-Me], 4.15 [br, 2H, CH₂P₂].

The following reactions were done similarly by using the appropriate starting complexes 1a or 1b and BiX_3 (X = Cl, Br, I).

Reaction of [PtMe₂(dppm)] with BiBr₃. Selected NMR data for **3b** (50%) in CDCl₃: $\delta({}^{31}P) - 63.8$ [s, ${}^{1}J_{PtP} = 3030$ Hz]; $\delta({}^{1}H) 4.58$ [br, 2H, CH₂P₂]. Selected NMR data for **4b** (50%): $\delta({}^{31}P) 13.5$ [s, ${}^{1}J_{PtP} = 3024$ Hz]; $\delta({}^{1}H) 0.52$ [t, ${}^{3}J_{PH} = 7.0$ Hz, ${}^{2}J_{PtH} = 85.0$ Hz, 6H, Pt–Me], 4.21 [br, 2H, CH₂P₂].

Reaction of [PtMe₂(dppm)] with Bil₃. Selected NMR data for 3c in CDCl₃: $\delta({}^{31}\text{P}) - 71.1$ [s, ${}^{1}J_{\text{PtP}} = 2880 \text{ Hz}$]; $\delta({}^{1}\text{H}) 4.60$ [t, ${}^{2}J_{\text{PH}} = 22.0 \text{ Hz}$, ${}^{3}J_{\text{PtH}} = 34.1 \text{ Hz}$; 2H, CH₂P₂].

Reaction of [PtMe₂(dppe)] with BiCl₃. Selected NMR data for 2d in CDCl₃: $\delta({}^{31}\text{P})$ 44.0 [s, ${}^{1}J_{\text{PtP}}$ = 1725 Hz, P trans to Me], 43.1 [s, ${}^{1}J_{\text{PtP}}$ = 4264 Hz, P trans to Cl]; $\delta({}^{1}\text{H})$ 0.62 [dd, ${}^{3}J_{\text{P(trans)H}}$ = 8.1 Hz, ${}^{3}J_{\text{P(cis)H}}$ = 3.9 Hz, ${}^{2}J_{\text{PtH}}$ = 54.0 Hz, 3H, Pt-Me], 2.41 [br, 4H, PCH₂CH₂P].

Reaction of [PtMe₂(dppe)] with BiBr₃. Selected NMR data in CDCl₃, **2e** (70%): $\delta(^{31}P)$ 41.2 [s, $^{1}J_{PtP} = 1745$ Hz, P trans to Me], 36.2 [s, $^{1}J_{PtP} = 4241$ Hz, P trans to Br]; $\delta(^{1}H)$ 0.75 [dd, $^{3}J_{P(trans)H} = 8.2$ Hz, $^{3}J_{P(cis)H} = 4.1$ Hz, $^{2}J_{PtH} = 55.9$ Hz, 3H, Pt-Me], 2.33 [br, 4H, PCH₂CH₂P]; **3e** (30%): 44.8 [s, $^{1}J_{PtP} = 3560$ Hz].

Reaction of [PtMe₂(dppe)] with Bil₃. Selected NMR data in CDCl₃, **2f** (50%): δ ⁽³¹P) 45.2 [s, ¹J_{PtP} = 1725 Hz, P trans to Me], 45.9 [s, ¹J_{PtP} = 4072 Hz, P trans to I]; δ ⁽¹H) 0.80 [dd, ³J_{P(trans)H} = 7.0 Hz, ³J_{P(cis)H} = 3.1 Hz, ²J_{PtH} = 54.1 Hz, 3H, Pt-Me], 2.25 [br, 4H, PCH₂CH₂P]; **3f** (50%): 46.0 [s, ¹J_{PtP} = 3375 Hz].

Monitoring the Reaction of $[PtMe_2(dppm)]$ with Bil₃ by ³¹P NMR Spectroscopy. To a solution of $[PtMe_2(dppm)]$ (10 mg, 0.016 mmol) in acetone-d₆ (0.7 mL) in an NMR tube was added Bil₃ (9.7 mg, 0.016 mmol). The tube was then placed in the probe of the NMR

Scheme 2. Suggested Mechanism for the Reactions of Complexes 1 with BiX₃



RESULTS AND DISCUSSION

Reactions of Dimethylplatinum(II) Complexes with BiX₃. As is depicted in Scheme 1, reaction of the complexes $[PtMe_2(P-P)]$, **1**, with BiX₃ in 1:1 molar ratio gave a mixture of the monomeric complexes [PtMe(X)(P-P)], **2**, and $[Pt(X)_2(P-P)]$, **3**, and the binuclear complex $[Pt_2Me_2(\mu$ -



Figure 2. Changes in the UV–vis spectrum during the reaction of $[PtMe_2(dppm)]$ with BiI₃ (each 1.0×10^{-4} M) in acetone at 25 °C: (a) pure 1a; (b) pure BiI₃; (c) spectrum immediately after addition of BiI₃; successive spectra recorded at intervals of 30 s.



10

15

20

5

0.1

0.05

0

X)(μ -dppm)₂]X, 4. The products were characterized using ³¹P and ¹H NMR spectroscopy, details of which are described in the Experimental Section.

The reaction of chelating dppm complex **1a** with BiI₃ was monitored using variable-temperature ³¹P NMR spectroscopy, as shown in Figure 1. On the basis of the results obtained from the ³¹P NMR and UV-vis spectroscopies (see next section), a mechanism described in Scheme 2 is suggested to occur during the reaction progress. Note that complexes **1a**, **2c**, and **3c** were characterized by comparing their ¹H and ³¹P NMR spectra with those of the authentic samples and so their characteristic ³¹P NMR data were used to indicate the complexes. Thus, immediately after the addition of BiI₃ at -28 °C, a broad singlet signal at δ -40.3 (with ¹J_{PtP} = 1455 Hz) which is assigned to a Pt(II)→Bi(III) adduct BiI₃·[PtMe₂(dppm)], **A** (see Scheme 2), was observed.¹⁸ The formation of adduct **A** was further confirmed using UV-vis studies (see next section). Meanwhile, a Pt(II) species assigned as the complex [PtMeI-

Table 1. Rate Constants^{*a*} and Activation Parameters for Oxidative Addition of Bi–X Bonds to Complex 1a in Acetone Solvent

reagent	T/°C	$10^2 \ k/s^{-1}$	$\Delta H^{\ddagger}/kJ mol^{-1}$	$\Delta S^{\ddagger}/J \text{ K}^{-1} \text{ mol}^{-1}$
BiCl ₃	10	0.90	52.8 ± 4.3	-98 ± 14
	20	1.52		
	25	2.86		
	30	4.12		
	40	7.89		
BiBr ₃	10	0.51	55.7 ± 2.9	-99 ± 10
	20	1.00		
	25	1.53		
	30	2.56		
	40	5.19		
BiI_3	10	0.17	51.9 ± 3.9	-115 ± 13
	20	0.30		
	25	0.43		
	30	0.75		
	40	1.45		

^{*a*}Estimated errors in k values are $\pm 5\%$.



Figure 4. Eyring plots for the oxidative addition of complex 1a with (a) BiCl₃; (b) BiBr₃; (c) BiI₃ in acetone.



Figure 5. Absorbance–time curve for the reaction of $[PtMe_2(dppe)]$, **1b**, with BiBr₃, under 1:1 stoichiometric condition, in acetone at 25 °C. The monoexponential fit for the reaction is shown.

(dppm)], **2c**, was also detected with two doublet signals at δ –46.5 (with ¹*J*_{PtP} = 3702 Hz and ²*J*_{PP} = 45 Hz, due to P atom trans to I) and at δ –47.3 (having a significantly lower value of

 ${}^{1}J_{\text{PtP}} = 1279$ Hz, due to the P atom locating trans to Me with comparatively higher trans influence than I, 19 and ${}^{2}J_{\text{PP}} = 45$ Hz). As time passed and the temperature increased, the signal due to adduct **A** disappeared while those due to the complex **2c** grew and then later started to decrease, and meanwhile a comparatively weak singlet signal, at δ –69.8 with ${}^{1}J_{\text{PtP}} = 2866$ Hz, due to the monomeric complex [PtI₂(dppm)], **3c**, was also observed. As the reaction progressed, only complex **3c** obtained pure which was found by DFT to be more stable as compared to complex **2c** (see theory section). The 1 H NMR spectrum was recorded at the end of the reaction, and the observation of one singlet signal at δ 2.27 ppm confirmed the formation of BiMe₂I.

UV-visible Studies of the Reaction of [PtMe₂(dppm)], 1a, with BiX₃. The kinetics of the reaction of equimolar amounts of complex [PtMe2(dppm)], 1a, and bismuth trihalides in acetone solution were studied by using UV-vis spectroscopy. A series of spectra, recorded during the reaction of complex 1a with BiI₃, is shown in Figure 2. The complex 1ais colorless, and no MLCT band in the visible region was observed for this complex. Immediately after addition of Bil₃ to a solution of complex 1a under second-order 1:1 stoichiometric conditions, a new broad absorption band at 490 nm was observed. It is worthy to mention that when we performed the reaction in the presence of excess BiI_{3} , the reaction was too fast for any reasonable measurement. The absorption at 490 nm is ascribed to the 5d_{π} (Pt) \rightarrow (Bi–I σ^* -orbital) charge transfer band, which is suggested to be responsible for the yellowish color of the adduct A and is used to study the kinetics of the oxidative addition reaction. The assignment of this absorption to other complexes, shown in Scheme 2, is ruled out because the intermediates IM1 and IM2 containing Pt(IV) center are not expected to contain any charge transfer and complexes 1, 2, 3, and 4 are colorless. Notice that it has been reported that the complex $[PtCl(PCy_3)_{2}{BiCl_{2}}]$, having a Pt(II)-Bi(III) bond, has an orange color in tetrahydrofuran (THF) solution.⁴ Also formation of such adducts for Pt(II) complexes has been reported in the reaction of [PtMe₂(bipy)] with iodine.^{8e} On the basis of a fully optimized ground-state structure (see theory section), time-dependent TDF (TD-DFT) has been also used to predict the absorbance spectra of adduct A and intermediate IM1c. For adduct A, the TD-DFT calculation predicts one intense electronic transition at 477 nm in good agreement with the observed experimental data ($\lambda_{exp.}$ = 490 nm in acetone). The calculated electronic spectrum of complex IM1c shows one electronic transition at 384 nm. As is clear from TD-DFT calculation, the observed experimental wavelength at 490 nm is in good agreement with the calculated one for adduct A, giving more support for the assignment of yellowish color to adduct A.

From the ³¹P NMR and UV–vis observations, the formation of the adduct **A** was too fast for monitoring, but the conversion of the adduct **A** to form Pt(IV) intermediate **IM1c** could be studied by monitoring the decay of the absorption band of the adduct **A** at 490 nm. Typical plots of absorbance at $\lambda = 490$ nm versus time are shown in Figure 3. The disappearance of the adduct **A** to form the intermediate complex **IM1c** followed good first-order kinetics, as confirmed by fitting the data with the first order equation $A_t = (A_0 - A_\infty) \exp(-kt) + A_\infty$. The first order rate constants at different temperatures are given in Table 1. Activation parameters were then obtained in the usual way from the Eyring equation (Figure 4), and the data are collected in Table 1.



Table 2. Computed Reaction Enthalpies and Free Energies (Values in kcal mol⁻¹) for Each Step Reaction of BiX₃ (X = Cl, Br, I) with $[PtMe_2(P-P)]$, P-P =dppm, 1a; P-P =dppe,1b, in Acetone

	X = Cl $X = Br$		= Br	X = I					
reaction	ΔH	ΔG^{a}	ΔH	ΔG^{a}	ΔΗ	ΔG^{a}			
P-P = dppm									
$1a + BiX_3 \rightarrow IM1$	-22.5	-8.4	-20.9	-6.4	-17.9	-1.8			
$IM1 \rightarrow 2 + MeBiX_2$	-12.4	-26.7	-15.3	-29.6	-17.6	-32.8			
$2 \rightarrow (1/2) 4$	2.6	7.3	0.9	5.7	0.7	5.8			
2 + XBiMeX→IM2	10.9	24.8	12.2	26.3	13.3	28.1			
$IM2 \rightarrow 3 + Me_2BiX$	-18.9	-32.0	-20.2	-34.0	-22.0	-36.4			
P-P = dppe									
$1b + BiX_3 \rightarrow IM1$	-17.8	-5.4	-15.7	-3.4	-12.2	1.1			
$IM1 \rightarrow 2 + MeBiX_2$	-16.2	-30.4	-19.2	-33.7	-22.2	-37.3			
2 + XBiMeX→IM2	6.0	28.1	19.0	36.9	21.8	38.3			
$IM2 \rightarrow 3 + Me_2BiX$	-24.3	-36.4	-27.1	-45.3	-29.7	-45.5			
^{<i>a</i>} At 298.15 K and 1 atm.									



Figure 6. Free energy profiles for reaction of BiX₃ (X = Cl, Br, I) with [PtMe₂(dppm)] (left) and [PtMe₂(dppe)] (right) in acetone.

When the reaction of complex [PtMe₂(dppe)], **1b**, with BiBr₃ was performed in acetone at 25 °C, the oxidative addition process (see Figure 5) occurred at a slower rate, with k = 0.38 (±0.03) × 10⁻² s⁻¹, as compared with the value of k = 1.53 (±0.07) × 10⁻² s⁻¹ for the related reaction involving dppm complex [PtMe₂(dppm)], **1a**, at the same condition.

DFT Investigation of the Product Formation. The oxidation state +2 (d⁸) is undoubtedly the most common oxidation state for Pt metal. The stereochemistry of Pt(II) four coordinate complexes is square planar especially with strong field ligands such as methyl. The oxidative addition process is considered here with an emphasis on the differences between

Table 3. Energies (eV) and Main Compositions (%) of the Relevant Frontier Orbitals of Species Involved in the Reaction of Complex 1a with $BiCl_3$ (X = Cl, Br, I)

orbital HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO	E (eV) -5.137 -1.002 -8.720 -3.370 -8.117 -3.648 -7.534 -3.989 -6.056 -1.961 -5.789 -2.271	Pt 70 3 16 23 9	Bi 60 56 56 10 41 5	X ^a 100 40 100 44 100 44 52 9
HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO	$\begin{array}{r} -5.137 \\ -1.002 \\ -8.720 \\ -3.370 \\ -8.117 \\ -3.648 \\ -7.534 \\ -3.989 \\ -6.056 \\ -1.961 \\ -5.789 \\ -2.271 \end{array}$	70 3 16 23 9	60 56 56 10 41	100 40 100 44 100 44 52 9
UMO HOMO UMO HOMO UMO HOMO UMO HOMO UMO HOMO UMO HOMO	$-1.002 \\ -8.720 \\ -3.370 \\ -8.117 \\ -3.648 \\ -7.534 \\ -3.989 \\ -6.056 \\ -1.961 \\ -5.789 \\ -2.271$	3 16 23 9	60 56 56 10 41	100 40 100 44 100 44 52 9
HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO	-8.720 -3.370 -8.117 -3.648 -7.534 -3.989 -6.056 -1.961 -5.789 -2.271	16 23 9	60 56 10 41	100 40 100 44 100 44 52 9
UMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO HOMO HOMO	-3.370 -8.117 -3.648 -7.534 -3.989 -6.056 -1.961 -5.789 -2.271	16 23 9	60 56 10 41	40 100 44 100 44 52 9
10M0 JUM0 10M0 JUM0 10M0 JUM0 10M0 JUM0 10M0	-8.117 -3.648 -7.534 -3.989 -6.056 -1.961 -5.789 -2.271	16 23 9	56 56 10 41	100 44 100 44 52 9
UMO HOMO JUMO HOMO JUMO HOMO JUMO HOMO	-3.648 -7.534 -3.989 -6.056 -1.961 -5.789 -2.271	16 23 9	56 56 10 41	44 100 44 52 9
10M0 JUMO 10M0 JUM0 10M0 JUM0 10M0	-7.534 -3.989 -6.056 -1.961 -5.789 -2.271	16 23 9	56 10 41	100 44 52 9
JUMO HOMO JUMO HOMO JUMO HOMO	-3.989 -6.056 -1.961 -5.789 -2.271	16 23 9	56 10 41	44 52 9
HOMO JUMO HOMO JUMO HOMO	6.056 1.961 5.789 2.271	16 23 9	10 41	52 9
JUMO HOMO JUMO HOMO	-1.961 -5.789 -2.271	23 9	41	9
HOMO ,UMO HOMO	-5.789 -2.271	9	5	
JUMO IOMO	-2.271		3	70
IOMO		21	43	10
	-5.527	6	3	78
JUMO	-2.591	19	44	10
łomo	-5.447	25		41
JUMO	-1.237	3		1
łomo	-5.247	18		58
JUMO	-1.263	2		1
IOMO	-4.979	12		71
JUMO	-1.306	5		1
IOMO	-5.808	21	15	46
JUMO	-2.301	27	20	14
IOMO	-5.577	8	1	83
LUMO	-2.529	26	22	16
IOMO	-5.319	5	1	86
LUMO	-2.727	25	22	20
IOMO	-5.763	26		68
JUMO	-1.502	26		11
IOMO	-5.513	1		77
JUMO	-1.696	24		13
IOMO	-5.099	2		86
JUMO	-1.740	25		18
	UMO IOMO JUMO IOMO JUMO IOMO JUMO IOMO JUMO IOMO JUMO IOMO JUMO IOMO JUMO	UMO -1.237 IOMO -5.247 JUMO -1.263 HOMO -4.979 JUMO -1.306 HOMO -5.808 JUMO -2.301 HOMO -5.577 JUMO -2.529 HOMO -5.319 JUMO -2.727 HOMO -5.763 JUMO -1.502 HOMO -5.513 JUMO -1.696 HOMO -5.099 JUMO -1.740	JUMO -1.237 3 HOMO -5.247 18 JUMO -1.263 2 HOMO -4.979 12 JUMO -1.306 5 HOMO -5.808 21 JUMO -2.301 27 HOMO -5.577 8 JUMO -2.529 26 HOMO -5.319 5 JUMO -2.727 25 HOMO -5.763 26 JUMO -1.502 26 HOMO -5.513 1 JUMO -1.696 24 HOMO -5.099 2 JUMO -1.740 25	-1.237 3 $10MO$ -5.247 18 UMO -1.263 2 $10MO$ -4.979 12 UMO -1.306 5 $10MO$ -5.808 21 15 UMO -2.301 27 20 $10MO$ -2.301 27 20 $10MO$ -5.577 8 1 UMO -2.529 26 22 $10MO$ -5.519 5 1 UMO -2.727 25 22 $10MO$ -5.763 26 22 $10MO$ -5.513 1 1 UMO -1.696 24 1 $10MO$ -5.099 2 2 $10MO$ -1.696 24 1 $10MO$ -1.696 24 1 $10MO$ -1.740 25 1

the nature of the halides (Cl, Br, and I) in three bismuth(III) halides. The processes shown in Scheme 2 will be explored on the basis of DFT calculations.

In the related reaction profile in acetone solvent, shown in Scheme 3 (see Table 2 for calculated results), the metal center of $[PtMe_2(P-P)]$ attacks the bismuth atom of the oxidative addition reagent BiX₃ while the X atom leaves and the Pt(IV) complex, IM1, is formed. As such, the Pt-Me and Pt-Bi bond distances vary more substantially than any other bond lengths. For example as shown in Scheme 3, in the case of P-P = dppmand X = Cl, the Pt-C(Me) distance increases from 2.090 Å in complex 1a to 2.123 Å in intermediate IM1a, whereas the Pt-Bi distance decreases from far apart in reactant 1a and BiCl₃ to 2.693 Å in intermediate IM1a. In the intermediate IM1, one of the Bi-X bonds is completely broken while the Pt-Bi bond is formed. The resulting $d^{\tilde{6}}$ complex [PtX(BiX₂)Me₂(P-P)] (X = Cl, Br, I) adopts an octahedral conformation with the bismuth group BiX_2 and X being in the trans position. The Pt(IV)complexes $[PtX(BiX_2)Me_2(dppm)]$, IM1, easily undergo X₂Bi-Me reductive elimination to produce complexes 2. Then the Pt(II) center of complex 2 attacks to the bismuth atom of X-BiXMe under a second oxidative addition process to form the Pt(IV) intermediates IM2. The complex IM2 contains two Pt-X bonds, one trans to a P atom and another

trans to a BiMeX group with different bond lengths. For example, in complex **IM2a**, these Pt–Cl bond distances are 2.522 and 2.581 Å, respectively. During the oxidative addition of Cl–BiClMe bond to complex **2a**, the Pt–Me, Pt–P (trans to Me), Pt–P (trans to Cl), and Pt–Cl bond distances increase from 2.085, 2.430, 2.257, and 2.455 Å in complex **2a** to 2.098, 2.540, 2.318, and 2.522 Å in complex **IM2a**, respectively (see Scheme 3). The Pt–Bi distance decreases from far apart in reactant **2a** and Cl–BiClMe to 2.802 Å in intermediate **IM2a**. Finally, the Me–BiMeX reductive elimination from **IM2** occurs easily to form more stable complex **3**.

Free energy changes along these paths are given in Figure 6. We found that the first oxidative addition of BiX₃ to the Pt(II) complexes 1 to yield the complexes IM1 is exergonic for most of halides and span a range of 1.1 kcal mol⁻¹ to -8.4 kcal mol⁻¹ as shown in Table 2 and Figure 6. When P–P = dppm, the free energies of this process (1 + BiX₃ \rightarrow IM1) are slightly lower than the related free energies calculated for P–P = dppe which is due to presence of ring strain in 4-membered rings of dppm complexes. The second oxidative addition reactions (i.e., 2 + XBiMeX \rightarrow IM2) are endergonic for all halides and P–P. This suggests that the second oxidative addition, probably because of the presence of a halide ligand which reduces the electron

Scheme 4. Suggested Mechanism for Oxidative Addition of BiI₃ to Complex 1a and Bi-C Reductive Elimination Form Complex IM1c



Figure 7. Relative energies (kcal mol⁻¹) for product 2c, adduct A, intermediate **IM1c** and **B**, and transition states **TS1** and **TS2**, arising from the reaction of $1a + BiI_3$ (E = 0) in acetone solution.

density of Pt(II) center in complexes **2**. As shown in Table 3 (see next section), in [PtMe₂(dppm)] as an example, the highest occupied molecular orbital (HOMO) is localized on the platinum atom (70% Pt) with significant contribution of the d_{z^2} orbital, but in complex [PtMe(Cl)(dppm)], **2a**, the composition of the HOMO is 25% Pt + 41% X, showing a transmission of electron density from the Pt atom to the X atom.

While the free energy for both steps of oxidative addition $(1 + BiX_3 \rightarrow IM1 \text{ and } 2 + XBiMeX \rightarrow IM2)$ decreases in the order X = Cl > Br > I, both reductive elimination reactions $(IM1 \rightarrow 2 + MeBiX_2 \text{ and } IM2 \rightarrow 3 + Me_2BiX)$ are exergonic for all halides, and the trend for free energy of these reactions decreases in the order X = Cl < Br < I. For example when P-P = dppm, the free

energies for the reaction $1 + BiX_3 \rightarrow IM1$ are -8.4, -6.4, and -1.8 kcal mol⁻¹ for X = Cl, Br, and I, respectively. On the basis of HSAB (hard and soft acids and bases) principles, the Pt(IV) center is harder than the Pt(II) center, and the preference for halides toward the Pt(IV) center follows the order Cl > Br > I. Conversely, the free energies for the reductive elimination reactions $IM1\rightarrow 2 + MeBiX_2$ are -26.7, -29.6, and -32.8 kcal mol⁻¹ for X = Cl, Br, and I, respectively. This can also be explained on the basis of the HSAB principle, which suggests the preference for the halides as Cl < Br < I for the soft Pt(II) center of complexes 2.

The HSAB principle can also be used to explain the experimental product ratios in the reactions of BiX₃ with complexes **1**. The percentage of complexes **3**, compared to complexes **2**, increases according to Cl < Br < I. For example in the reaction **1a** with BiX₃, the percentage of complexes **3** is 30, 70, and 100% for X = Cl, Br, and I, respectively. The same was observed in the reaction of **1b** with BiX₃ as 0, 30, and 50% for X = Cl, Br, and I, respectively. The soft Pt(II) center is I > Br > Cl, so due to the greater tendency of I to bind the soft Pt(II) center, the ratio of complexes **3** with two X ligands will be increased as I > Br > Cl. The free energies for reductive elimination processes have large negative values (ranging from -26.7 to -36.4 kcal mol⁻¹ for P–P = dppm and from -5.4 to -45.5 kcal mol⁻¹ when P–P = dppe).

While the Pt(IV)-M complexes (M = Sn, Hg, Te, and Ge) can simply be prepared, 3b,d,e,i the related Pt(IV)-Bi(III) analogues are not stable and easily undergo Bi-C reductive elimination. To verify this, we calculated the reaction profiles and energies for the Bi-I oxidative addition to complex 1a and Bi-C reductive elimination from the intermediate complex IM1c in acetone solution (see Scheme 4 and Figure 7). The calculation indicates an easy reaction to give the adduct A, followed by a slower reaction to give **B** and **IM1c**. Note that, in the kinetic experiments, the loss of adduct A is measured so that the rates refer to formation of IM1c. The calculation of the energy of the transition state TS1 (+15.2 kcal mol⁻¹) is in reasonable agreement with the observed value of $\Delta H^{\ddagger} = 12.4$ kcal mol⁻¹. It is suggested that the reductive elimination from 5-coordinate d⁶ metal complexes occurs more easily than from the corresponding 6-coordinate complexes.²⁰ So, the Me-Bil₂ reductive elimination from the saturated d⁶ six-coordinate complex IM1c may occur via initial loss of iodide ligand. The BiMeI₂ reductive elimination from intermediate B proceeds through transition state TS2, (Scheme 4), in which the bonds between Pt and leaving groups (Me and BiI₂) are elongated and the Me-Pt-Bi bond angle is reduced. The free energy of activation for reductive elimination process is 6.4 kcal mol⁻¹. As BiMeI₂ dissociates, the Pt(II)-I bond is formed giving the complex 2c. Our calculations show that following oxidative addition, the Bi-C reductive elimination barrier is rather small suggesting that the Pt(IV)-Bi(III) complex is very prone to undergo the reductive elimination decreasing the possibility of identifying the Pt(IV) complexes from the experimental point of view which is consistent with the experimental observations. Figure 6 shows free energy profiles for reaction of BiX_3 (X = Cl, Br, I) with [PtMe₂(dppm)] (left) and [PtMe₂(dppe)] (right) in acetone.

Structural Investigation of Pt(IV)-Bi(III) Intermediates. Since dihalobismuth complexes of platinum(IV) are not known so far, we discuss here the structures of these Pt(IV)-BiX₂ (X = Cl, Br, I) intermediate complexes (IM1a-f). Upon going from X = Cl to X = I, the trend for the calculated Pt-Bi



Figure 8. (a) HOMO of $[PtMe_2(dppm)]$, (b) LUMO of BiCl₃, (c) interactions of Lewis acidic bismuth center of BiX₃ with electron-rich Pt(II) center of $[PtMe_2(dppm)]$ and (d) HOMO of $[PtCl(BiCl_2)Me_2(dppm)]$, IM1a.

bond distance in the complexes [PtX(BiX₂)Me₂(dppm)] increases as 2.693 Å (IM1a) < 2.719 Å (IM1b) < 2.752 Å (IM1c). The well-known trans influence of the halides (bound to M) follows the order $I^- > Br^- > Cl^-$; that is, the strength of the Pt–Bi bond decreases on going from X = Cl to X = I in the complexes $[PtX(BiX_2)Me_2(dppm)]$. This is in agreement with the bond orders calculated for Pt-Bi bonds in complexes 2 (0.712, 0.677, and 0.638 for X = Cl, Br, and I, respectively).The same behaviors have been observed for complexes $[Pt(X)_2(BiMeX)Me(dppm)]$, IM2a-c, and dppe complexes (IM1d-f and IM2d-f). The Pt-X optimized bond distances, 2.565, 2.721, and 2.916 Å, for X = Cl, Br, and I in IM1a, IM1b, and IM1c, respectively, are longer than that expected for the single Pt-X bond on the basis of covalent radii predictions (Pt-Cl = 2.28 Å, Pt-Br = 2.43 Å, Pt-I = 2.62 Å). The calculated bond orders of the optimized Pt-X bond distances in these complexes are 0.83 (X = Cl; IM1a), 0.79 (X = Br; IM1b), and 0.76 (X = I; IM1c). The optimized Bi-X bond distances, 2.525, 2.764, and 2.915 Å in complexes IM1a, IM1b, and IM1c, respectively, are slightly longer than that expected for the single Bi-X bond on the basis of covalent radii predictions (Bi-Cl = 2.51 Å, Bi-Br = 2.66 Å, Bi-I = 2.85 Å). The X-Pt-Bi bond angles in these complexes are almost linear. The geometry at bismuth is that of a distorted trigonal pyramid with the X-Bi-X and Pt-Bi-X bond angles in the range 95-106°.

Frontier Molecular Orbitals. Qualitative representations of the HOMO of [PtMe₂(dppm)] and lowest unoccupied molecular orbital (LUMO) of BiCl₃ are presented in Figure 8, and their composition and energy of the starting materials, intermediates, and products are reported in Table 3. The HOMO-LUMO gap of $[PtMe_2(dppm)]$ is equal to 4.135 eV. In $[PtMe_2(dppm)]$, platinum is formally d⁸ and as expected the HOMO is localized on the platinum atom with significant contribution of the d_{z^2} orbital. The value of the energy separations between the HOMO and LUMO of [PtX(BiX₂)- $Me_2(dppm)$, **IM1**, are equal to 4.095 (X = Cl), 3.518 (X = Br), and 2.936 (X = I) eV. The main contribution to the Pt–Bi in the Pt(IV) complexes, IM1, comes from the overlap of the d_{z^2} HOMO of the platinum complex with the LUMO of BiX₂ (which is σ^* orbital of Bi–X bond). So it is reasonable to view the oxidation process formally as the removal of electrons from the HOMO of the [PtMe₂(dppm)] complex into the LUMO of BiX₃.

CONCLUSION

The reaction of organoplatinum(II) complexes [PtMe₂(P–P)], P–P = dppm or dppe, with bismuth trihalides proceeds



through bismuth-halide oxidative addition and bismuthcarbon reductive elimination reactions to yield a mixture of the platinum(II) complexes [PtMeX(P-P)], 2, and [Pt-P] $(X)_2(P-P)$], 3 (X = Cl, Br, I). These reactions, which are the first examples of addition of bismuth trihalides to organoplatinum(II) complexes, were monitored using ³¹P NMR and UV-vis spectroscopy, and a mechanism shown in Scheme 2 is proposed for the reaction. As such, immediately after the addition of BiX₃ to the starting complex $[PtMe_2(P-$ P)], 1, the platinum(II) center, which is electron rich, orients its filled d_{z^2} orbital to the empty σ^* (Bi-X) orbital of BiX₃ to form a yellowish $Pt(II) \rightarrow Bi(III)$ adduct, **A**, with $\lambda = 490$ nm in acetone solvent. The rate of this step is too fast to measure, but the rate of conversion of the yellowish adduct A to the colorless Pt(IV)-Bi(III) intermediate IM1 was easily monitored by the decay of the absorption band of the $Pt(II) \rightarrow Bi(III)$ adduct (see Figure 2). Note that the addition occurs by loss of X from A, followed by attack by X opposite the BiX₂ group. The nature of halide has an effect on the rates of oxidative addition of BiX₃ to Pt(II) complexes; the process becomes slower as the halide becomes larger (see Table 1). This complies with the suggested mechanism in a way that when the d_{z^2} orbital of Pt(II) center donates its electron density into the empty $\sigma^*(Bi-Cl)$ orbital of BiCl₃, which is a stronger Lewis acid as compared with BiBr₃ and BiI₃, the Bi-Cl becomes weaker, as compared to Bi-Br and Bi-I, which makes transfer of Cl⁻ to the Pt center, to form

Table	4. Enthalpy	Changes for	r Reductiv	ve Elimination	of Some	C–Y Bonds	s from Pt(IV)	Complexes
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reaction	С-Ү	$\Delta H/\mathrm{kcal} \mathrm{mol}^{-1}$	ref.
$[PtMe_3I(dppe)] \rightarrow [PtMe_2(dppe)] + MeI$	C-I	14.4	6a
$[PtMe_{3}I(dppe)] \rightarrow [PtMeI(dppe)] + C_{2}H_{6}$	C-C	-25.1	6a
$[PtI(BiI_2)Me_2(dppm)] \rightarrow [PtIMe(dppm)] + BiI_2Me$	C-Bi	-17.6	this work
$[PtI(BiI_2)Me_2(dppe)] \rightarrow [PtIMe(dppe)] + BiI_2Me$	C-Bi	-22.2	this work

IM1, easier with a greater rate (see Scheme 5). The same line of reasoning goes with the other two halides BiBr₃ and BiI₃.

Consistent with this mechanism, the rate of conversion involving the starting dppm complex [PtMe₂(dppm)], **1a**, in reaction with BiBr₃ [$k = 1.53 (\pm 0.07) \times 10^{-2} \text{ s}^{-1}$] at 25 °C is nearly 3 times greater than that involving the starting dppe complex [PtMe₂(dppe)], **1b**, at the same condition [$k = 0.38 (\pm 0.03) \times 10^{-2} \text{ s}^{-1}$]. Here, according to DFT calculations, the Pt center of adduct **A** containing dppm is less positive and more electron rich, as compared to that containing dppe. This makes the Pt–Bi bond weaker in adduct **A** with a dppm ligand (with the greater rate of conversion) than that involving a dppe ligand (with the smaller rate of conversion).

A theoretical study is presented where the structure of all intermediates containing neutral bismuth complexes of platinum are investigated. It is shown that the oxidative addition of BiX₃ to the Pt(II) complex is exergonic for all bismuth halides. The operative mechanism is suggested to involve nucleophilic attack of platinum(II) center (occupied d_{z^2} orbital) on the bismuth atom of BiX₃ (σ^* orbital of Bi-X bond) to give the platinum(IV) intermediates, [PtX(BiX₂)- $Me_2(P-P)$], which undergo reductive elimination. The free energies for oxidative addition steps involved in the reactions decrease in the order X = Cl > Br > I and dppe > dppm, while it increases for the reductive elimination step as I < Br < Cl. The reductive elimination of X_2Bi-CH_3 from the Pt(IV)-Bi(III) complex is thermodynamically favored by heavier halides, largely because of a change in enthalpy. The enthalpy changes for reductive elimination of some C-Y (Y = C, Bi, and I) bonds from Pt(IV) complexes are shown in Table 4. The reductive elimination of C-C and C-Bi bonds are clearly favored over C–I, and enthalpy values decrease as C-I > C-Bi> C-C. DFT calculations show that the Pt(IV)-Bi(III)complexes are not stable and immediately would undergo Bi-C reductive elimination. Note that no Pt(IV)-Bi(III) octahedral complex has been reported so far.

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Notes

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