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High Quantum Yield Molecular Bromine Photoelimination from Mononuclear Platinum(IV) Complexes

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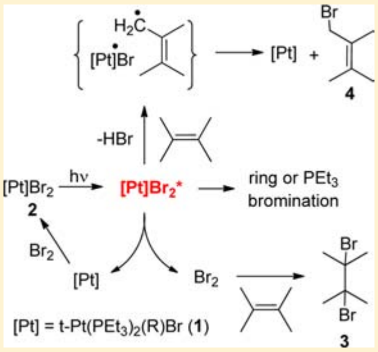
Supporting Information

ABSTRACT: Pt(IV) complexes *trans*-$Pt(PEt_3)_2(R)(Br)_3$ (R = Br, aryl and polycyclic aromatic fragments) photoeliminate molecular bromine with quantum yields as high as 82%. Photoelimination occurs both in the solid state and in solution. Calorimetry measurements and DFT calculations (PMe_3 analogs) indicate endothermic and endergonic photoeliminations with free energies from 2 to 22 kcal/mol of Br_2. Solution trapping experiments with high concentrations of 2,3-dimethyl-2-butene suggest a radical-like excited state precursor to bromine elimination.



INTRODUCTION

Efficient photochemical solar energy conversion to stored energy in chemical bonds is an important goal for global energy needs.[1] A promising process for the realization of this goal is the splitting of stable molecules into a reduced component (reductant) and an oxidized component (oxidant) that can then be recombined to release the stored energy.[2] Most often this concept is applied to water splitting into molecular hydrogen (reductant) and molecular oxygen (oxidant)[3−6] but may also be applied to the simpler and, in some ways, more advantageous[7] process of splitting hydrohalic acids into molecular hydrogen and molecular halogens (eq 1, X = a halogen).[5,8−11] A closely related alternative water splitting process, yielding molecular hydrogen and hydrogen peroxide (eq 1, X = OH), has also been proposed.[12]

$$2HX \xrightarrow{\text{light}} \underset{\text{reductant}}{H_2} + \underset{\text{oxidant}}{X_2} \qquad (1)$$

A potential key step in a transition metal catalyzed hydrohalic acid splitting process is the photoelimination of a halogen molecule from a dihalide complex (eq 2, X = a halide).

$$L_nMX_2 \xrightarrow{\text{light}} L_nM + X_2 \qquad (2)$$

Although there have been recent advances in this area,[10,11,13−16] halogen photoelimination from transition metal halide complexes (L_nMX_2) remains rare and poorly understood.

Herein, we report our studies on a family of mononuclear platinum(IV) bromo complexes that photoeliminate molecular bromine with quantum yields as high as 82%. Calorimetry and DFT calculations show that these are endergonic reactions that store between 2 and 22 kcal/mol. Bromine trapping experiments indicate that, in addition to reacting with the released bromine, more reactive traps also react directly with the excited state that precedes bromine elimination and the products indicate that this excited state has radical character.

RESULTS

Complex Synthesis and Characterization. Details may be found in the Experimental Section located in the Supporting Information. Platinum(IV) complexes *trans*-$Pt(PEt_3)_2(R)(Br)_3$ (**2**, Scheme 1) are easily prepared by Br_2 addition to the corresponding Pt(II) complexes, *trans*-$Pt(PEt)_2(R)(Br)$ (**1**). In the case of **1**(NPh), **1**(MeOPh) and **1**(Per), simultaneous ring bromination results in the isolation of **2**(BrNPh), **2**(BrMeOPh), and **2**(BrPer). Ring bromination subsequent to oxidative addition can also occur and **2**(BrNap) is formed when additional Br_2 is added to **2**(1-Nap).

^{31}P NMR spectra of **2** are diagnostic of the Pt center oxidation shown in Scheme 1 and the Pt(IV) complexes **2** all show singlets with satellites in the δ −8 to −10 region, shifts that are about 20 units negative of those for the corresponding Pt(II) precursors **1** (δ 12 to 13). Ring bromination generally leads to a small, but visible, shift decrease (<1 unit) from the corresponding unbrominated analog. $^{195}Pt-^{31}P$ coupling constants for **2** are in the rather tight range of 1600 to 1636 Hz and are reduced from those for **1** (2680 to 2770 Hz).

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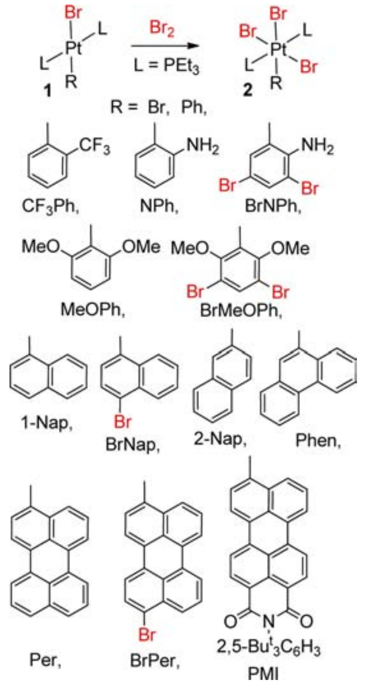
Scheme 1



UV–vis spectra of **2** (Supporting Information), with the exception of the BrPer and PMI derivatives, show broad and weak (ε_{max} < 5000 $M^{-1}cm^{-1}$) blue absorbance in the visible region tapering off from the UV and leading to light orange to light red compounds. The absorbance deeper into the UV region is stronger and, for the naphthalene and phenanthrene derivatives, vibronically coupled aromatic group $\pi-\pi^*$ bands are observed at about 300 nm. Dark brown **2**(BrPer) and dark purple **2**(PMI) show their vibronically coupled aromatic group $\pi-\pi^*$ bands in the visible region. The UV–vis spectra of the ring brominated derivatives are virtually indistinguishable from the spectra for the corresponding unbrominated analogues.

Photolysis. Many of the complexes **2** are light sensitive, even to ambient light. In the case of **2**(1-Nap), room light exposure of an orange toluene solution in an NMR tube results in the slow formation (days) of the naphthyl ring brominated Pt(II) complex **1**(BrNap) along with HBr (detected by reaction with 1,8-bis(dimethyamino)naphthalene) (Scheme 2). A 500 W halogen lamp or a medium pressure Hg lamp gives complete conversion in minutes. Mixtures of **1**(BrNap) and **1**(1-Nap) are also observed when toluene solutions of **2**(1-Nap) are irradiated in the presence of triphenylmethane or dihydroanthracene (Scheme 2 and Table 1). The amount of ring brominated **1**(BrNap) decreases from triphenylmethane to dihydroanthracene following the C–H bond strength (or the ease of bromination) of the organic molecule. Complex **2**(Phen) shows similar behavior but just toluene solutions give, in addition to ring brominated Pt(PEt)$_2$(10-bromo-9-phenanthryl)(Br) **1**(BrPhen), some (30%) unbrominated **1**(Phen) (Table 1). The solvent toluene is presumably trapping some of the bromine in this case.

Scheme 2

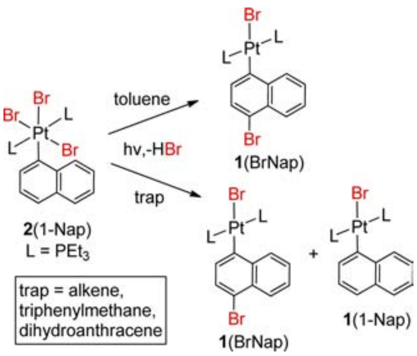
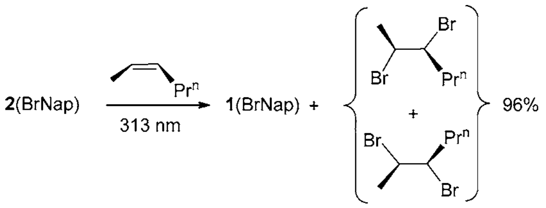


Table 1. Photolysis Product Yields for 2(1-Nap) and 2(1-Phen) in Toluene and with Added Bromine Traps

trap	1(1-Nap)	1(BrNap)	1(Phen)	1(BrPhen)[a]
no added trap	0%	100%	30%	70%
triphenylmethane (0.2 M)	44%	56%	85%	15%
dihydroanthracene (0.2 M)	62%	38%	91%	9%

[a] Pt(PEt)$_2$(10-bromo-9-phenanthryl)(Br).

With **2**(Br-Nap), the ring is already brominated and photolysis (313 nm) of this complex in the presence of *cis*-2-hexene yields **1**(BrNap) as the only Pt containing product. The *cis*-2-hexene is brominated in 96% yield (NMR) to the *anti*-addition product, a racemic mixture of (2R, 3S)- and (2S, 3R)-2,3-dibromohexane (eq 3). None of the *syn*-addition product (racemic mixture of (2R, 3R)- and (2S, 3S)-2,3-dibromohexane) is detected.[17] Under similar conditions, but in the absence of *cis*-2-hexene, **2**(BrNap) is only weakly photochemically active producing a small amount (8%) of **1**(BrNap) in the time it takes for complete conversion in the presence of *cis*-2-hexene (10 min). Continued irradiation gives further conversion and small amounts of additional phosphorus-containing products. The fate of the eliminated bromine is unknown but solvent may be involved. ^{1}H NMR spectroscopy after prolonged (1 h) irradiation also shows small amounts of 1,4-dibromonaphthalene.



(3)

Phenyl and 2-naphthyl derivatives **2**(Ph) and **2**(2-Nap) are nearly inactive even in the presence of a bromine trap. In the presence of 1-hexene only small amounts of **1**(Ph) or **1**(2-Nap) are produced on prolonged irradiation (hours). **2**(2-Nap) gives somewhat higher conversion and another Pt(II)-containing product that is probably ring brominated. Photoactivity is greatly increased by substitution at the 2-position of the phenyl ring. Thus, **2**(CF_3Ph) is very light sensitive and on irradiation at 313 nm in the presence of 1-hexene converts rapidly to **1**(CF_3Ph). Similarly, **2**(BrMeOPh) readily converts to **1**(BrMeOPh). Ring substituted **2**(BrNPh) is also photochemically active but much less so than **2**(CF_3Ph) and **2**(BrMeOPh). Photoinduced ring bromination is not observed for any of the phenyl derivatives.

To put the photoactivity of **2** on a more quantitative basis, quantum yields for photoreduction of selected **2** in the presence of 1-hexene were determined (Table 2). The yields

Table 2. Quantum Yields for Conversion of **2** to **1** in the Presence of 1-Hexene[a]

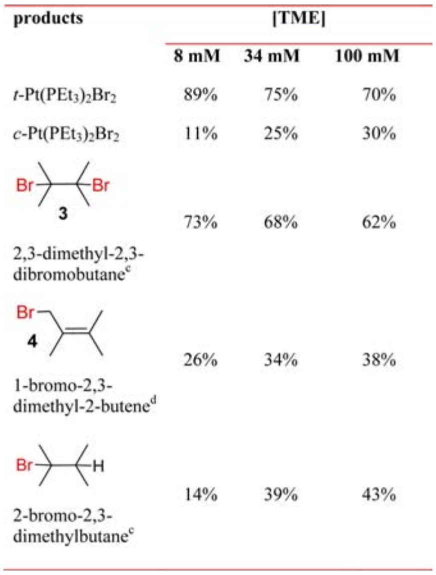
R	wavelength (nm)	quantum yield (%)
Br	313	59
Ph	313	<1
CF_3Ph	313	82
Br_2NPh	313	5
1-Nap	313	13
BrNap	313	19
2-Nap	313	<1
Phen	313	13, 15[b]
BrPer	440	48
PMI	470	4

[a] CH_2Cl_2 solvent, [1-hexene] = 0.13 M. [b] [1-hexene] = 1.0 M

bear out the qualitative results and show a remarkable 82% quantum yield for **2**(CF_3Ph). In addition, the strong $\pi-\pi^*$ transitions of **2**(BrPer) and **2**(PMI) allow the photolysis to be conducted in the visible (440 and 470 nm) rather than in the uv region as used for the other complexes.

To further probe the bromine photoelimination process, the electron rich trap 2,3-dimethyl-2-butene (TME) was used in the photolysis of **2**(Br) (Table 3). The Pt(II) product, $Pt(PEt_3)_2Br_2$ **1**(Br), is observed as cis and trans isomers with the trans isomer favored in $CDCl_3$. Several TME products are detected. The dibromoalkane, 2,3-dimethyl-2,3-dibromobutane (**3**), which is the exclusive product of Br_2 addition to TME, is the dominant product (73%), but its yield decreases with increasing TME concentration. Allylic bromination product, 1-bromo-2,3-dimethyl-2-butene (**4**), is the second most abundant and its yield increases with increasing TME concentration. The HBr addition product, 2-bromo-2,3-dimethylbutane, is also detected and presumably originates from the reaction of TME with HBr generated in the formation of the allylic bromination product **4**. In contrast to **2**(Br), photolysis of **2**(PMI) in the presence of TME gives exclusively the Br_2 addition product **3** over TME concentrations from 22 to 560 mM.

Table 3. Photolysis Product Yields[a] for *trans*-$Pt(PEt_3)_2Br_4$ (**2**(Br))[b] with 2,3-Dimethyl-2-butene (TME) Trap



products	[TME]		
	8 mM	34 mM	100 mM
t-$Pt(PEt_3)_2Br_2$	89%	75%	70%
c-$Pt(PEt_3)_2Br_2$	11%	25%	30%
3 2,3-dimethyl-2,3-dibromobutane[c]	73%	68%	62%
4 1-bromo-2,3-dimethyl-2-butene[d]	26%	34%	38%
2-bromo-2,3-dimethylbutane[c]	14%	39%	43%

[a] On the basis of **2**(Br). [b] [**2**(Br)] = 4 mM. [c] Ref 18. [d] Refs 19 and 20.

Nocera has shown that halogen photoelimination from metal halide complexes can occur from the solid state without a trap.[13] We find this is also possible for **2**. Vacuum photolysis of a solid film of **2**(BrNap) deposited on the inside walls of a quartz tube causes the orange-red solid to lighten and release Br_2, which was condensed onto a frozen solution of TME in $CDCl_3$. The mixture was thawed and ^1H NMR spectroscopy showed formation of the TME bromination product **3**. ^{31}P NMR analysis of the dissolved film remaining in the quartz tube showed partial conversion to **1**(BrNap). The degree of photoconversion of **2**(BrNap) to **1**(BrNap) is dependent on the film treatment. Much higher conversions are observed if the film was not exposed to a prolonged (h) dynamic vacuum (50 mtorr) suggesting that partial solvent retention promotes the photolysis. However, the factors involved have not been thoroughly investigated.

Thermal Reactions. Complex **2**(CF_3Ph) slowly reacts with 1-hexene at 25 °C in the dark to give **1**(CF_3Ph). This thermal reaction is first order in **2**(CF_3Ph) and zero order in 1-hexene over a 1-hexene concentration of 0.096 to 0.38 M with an average rate constant (k_{obs}) of $1.4(2) \times 10^{-3}$ s^{-1} or 2.0(2) d^{-1} (Supporting Information). All other **2** are thermally stable for days in the presence of 1-hexene at 25 °C, but show signs of reaction at temperatures ranging from 50 to 120 °C. In the case of **2**(1-Nap), ring bromination is observed with a ratio of **1**(BrNap) to **1**(1-Nap) of 10:7, approximately reversed from the ratio for the photochemical reaction under similar conditions. In the solid state, **2**(1-Nap) decomposes in the dark over a one-year period at room temperature to yield exclusively **1**(BrNap).

Calorimetry and DFT. The bromine reaction enthalpies for the three complexes, **1**(Ph), **1**(CF_3Ph) and **1**(BrNap) were determined by calorimetry in toluene (Table 4). Initial gas phase DFT calculation on **1′** (PMe_3 used in place of PEt_3) employing the B3LYP functional[21] gave a poor match to the experimental data. Solvent inclusion did not improve the results. The M06 functional[22] is reported to give better energy values for some transition metal systems and calculated values with this functional are in much better agreement with our experimental values. Free energies for the reactions were also calculated and are less negative than the enthalpies due to the unfavorable entropy change of going from two molecules to one. (Δ*G* is increased by about 3 kcal from the values in Table 4 when a simple correction factor[23,24] for the expected smaller entropy decrease in toluene, as compared to the gas phase, is applied.)

Table 4. Thermodynamic Values (kcal/mol) for the Bromination of **1** and **1′**

	Δ*H*			
R	exp[a]	B3LYP[b]	M06[b]	Δ*G* M06[b]
Ph	−38.3 ± 1.5	−20.7	−32.5	−21.8
Nap	−20.5 ± 1.5[c]	−10.6	−23.6	−10.5
CF_3Ph	−17.5 ± 2	−2.7	−16.3	−4.7
BrMeOPh			−16.8	−2.2
Br	−20.9 ± 1	−16.2	−27.4	−15.3
Per		−9.9	−22.4	−10.2

[a] Toluene solvent. [b] Gas phase for *trans*-$Pt(PMe_3)_2(R)(Br)$ **1′**. [c] R = BrNap.

Structures. The solid-state structures of **1**(CF_3Ph, NPh, MeOPh, BrMeOPh, 1-Nap, BrPhen, BrPer, PMI) and **2**(Br,

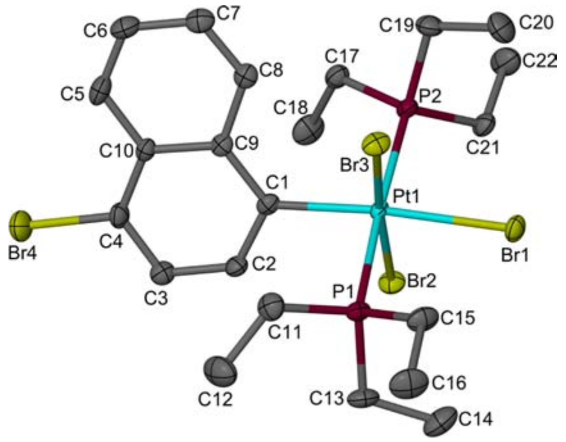


Figure 1. XSeed/POV-Ray drawing of **2**(BrNap). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.

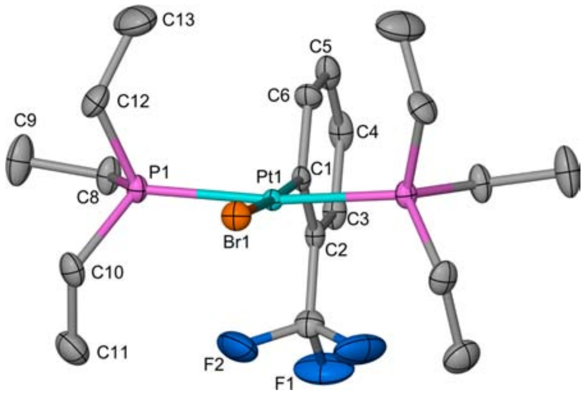


Figure 2. XSeed/POV-Ray drawing of **1**(CF_3Ph). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.

Table 5. Metrical Parameters Indicative of Steric Strain in 2 (R = BrNap, Phen, BrPer, BrMeOPh) and 2′(1-Nap)

atoms[a]	**2**(BrNap)	**2**(Phen)[b]	**2**(BrPer)	**2**(BrMeOPh)	**2′**(1-Nap)[c]
Pt1−C1	2.107(5)	2.109(7)	2.102(5)	2.104(2)	2.124
Pt1−C1−C4	172.8(4)	170(1)	173.2(3)	177.3(2)	173.4
Pt1−C1−C2	115.9(4)	115.7(2)	116.0(3)	121.9(2)	115.9
Pt1−C1−C9	127.4(4)	127.7(3)	127.4(3)	121.4(2)	126.2
C1−Pt1−P1	88.24(14)	90.3(6)	92.51(13)	93.72(6)	90.9
C1−Pt1−P2	94.93(14)	93.4(4)	95.47(14)	93.34(6)	95.9
C1−Pt1−Br2	89.38(14)	89.7(3)	90.04(13)	90.91(6)	90.0
C1−Pt1−Br3	95.10(14)	96(2)	93.89(13)	89.55(6)	94.3

[a] Numbering from **2**(BrNap). Corresponding atoms in other structures may have different numbers. [b] Average and standard deviation of the two independent molecules. [c] DFT (M06) structure of *trans*-$Pt(PMe_3)_2$(1-napthyl)$(Br)_3$ **2′**(1-Nap).

BrNPh, BrMeOPh, Phen, BrNap, BrPer) were determined by single crystal X-ray diffraction studies. Drawings of **2**(BrNap) and **1**(CF_3Ph) are given in Figures 1 and 2 while those for the other structures can be found in the Supporting Information. Remarkably, the structures of the organometallic complexes **2** (i.e., R ≠ Br) are the first reported for the PtL_2X_3R (L = a phosphine, X = a halogen) class and that of **2**(Br) is only the second reported member of the PtL_2X_4 (L = a phosphine, X = a halogen) class.[25] A notable feature of the organometallic derivatives is the steric crowding associated with the R group. In each case, the R groups contain either a hydrogen atom *peri* to the Pt atom (R = BrNap, Phen, BrPer) or a substituent at the 2-position or the 2- and 6-positions on a phenyl ring (R = BrNPh, BrMeOPh), which sterically interfere with the Br and PEt_3 ligands cis to the R group. To minimize the steric repulsion, the aromatic rings tilt at about 45° from the P−Pt−P axis such that the *peri*-hydrogen atom or the substituent(s) is situated between a cis Br atom and the adjacent PEt_3 ligand. Nonetheless, steric distortion of the structures is still apparent in the metrical parameters listed in Table 5. (Aryl ring disorder makes the data unreliable for **2**(BrNPh) and this structure is not included in the table.) The **2**(BrNap), **2**(Phen) and **2**(BrPer) structures are similar and only that of **2**(BrNap) will be discussed. The naphthalene ring system of **2**(BrNap) is visibly distorted (Figure 1). The Pt−C1--C4 angle, which would be expected to be close to linear in a strain-free complex, is compressed to 173°. Similarly, the bond angles around C1 show a larger than 120° angle on the side of the *peri*-hydrogen atom (Pt1−C1−C9 = 127.4°) and a smaller than 120° angle on the opposite side (Pt1−C1−C2 = 115.9°). The strain is also reflected in the angles around Pt, especially the ones involving the ligands *cis* to carbon atom C1. The angles on the side of the *peri*-hydrogen atom, C1−Pt−Br3 and C1−Pt−P2, are 95.1° and 94.9° respectively larger than the angles of 89.4° (C1−Pt−Br2) and 88.2° (C1−Pt−P1) on the opposite side, which are close to the expected 90°. In more colloquial terms, the bromine atom Br3 and the P2-PEt_3 ligand are bent away from the *peri*-hydrogen atom. These same distortions are observed in the DFT structures of the PMe_3 complexes **2′**. The DFT metrical parameters for *trans*-$Pt(PMe_3)_2$(1-napthyl)$(Br)_3$ **2′**(1-Nap) are included in Table 5 and compare well with those from the solid-state structure of **2**(BrNap), differing by 3% or less.

A similar bending away of the *cis*-ligands is observed in **2**(BrMeOPh), but with the MeO substituents on both sides of the phenyl ring the steric strain occurs with all four ligands cis to the aryl group C1 atom. In this case, the effect is focused on the two PEt_3 ligands (C1−Pt1−P1 = 93.7° and C1−Pt1−P2 = 93.3°) with the Br ligand angles within 1° of the expected 90°.

The structures of **2**(Br) and **1**(CF_3Ph, NPh, MeOPh, BrMeOPh, 1-Nap, BrPhen, BrPer, PMI) are more routine and generally do not require comment. One exception is that of **1**(CF_3Ph) shown in Figure 2. Like **2** (R = BrNap, Phen, BrMeOPh), this complex shows signs of steric strain. The phenyl ring CF_3 group lies between the two *trans*-PEt_3 ligands near the Pt center. The CF_3 group is rotated such that the Pt atom is nestled between two of the F atoms. Whereas this is favorable for steric interactions with the Pt center, it is less favorable for PEt_3 ligand interactions. As a result, the PEt_3 ligands bend away from the CF_3 group closing the expected P−Pt−P 180° angle to 171.95(4)°. Steric stress is also apparent in the angles around C1 which, like in the structures of **2**(BrNap, Phen, BrPer), are distorted and asymmetric: Pt1−C1−C4 = 174.0(3), Pt1−C1−C2 = 128.3(3), Pt1−C1−C6 = 116.2(3). Undoubtedly, strain is also present in **2**(CF_3Ph) giving distortions similar to that in **2**(BrNap, Phen, BrPer). The DFT structures of **2′**(CF_3Ph) and **2′**(BrNap, Phen, BrPer) show strain and match the distortions observed in the crystal structures.

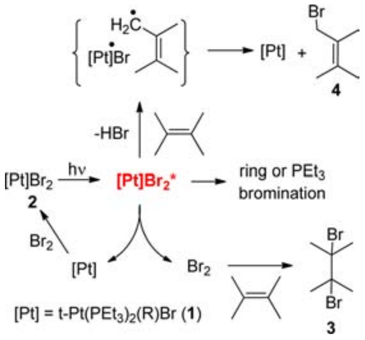
■ DISCUSSION

Photochemistry. Pt(IV) halide complexes $[PtX_6]^{2-}$ have long been known to be photochemically active.[26−46] For X = Br, the net aqueous photochemical reaction is aquation to give $[Pt(H_2O)Br_5]^{1-}$ and a bromine anion. The details of the photo process have been controversial with proposals of initial Br anion,[29,30] Br atom[27] and Br_2[28] elimination. Recent transient spectroscopic experiments combined with computational studies strongly support Br anion elimination.[45] However, under some conditions oxidation processes, involving an excited state Pt complex and oxidizable species, may be involved.[40,44]

Complexes **2** are related to $[PtBr_6]^{2-}$ by substitution of two bromine anions with two PEt_3 ligands and, except for R = Br, substitution of a third bromine anion with an R group. Yet, Br_2 elimination is indicated by our bromine trapping experiments with *cis*-2-hexene and TME described above. The high yield of the *cis*-2-hexene bromine *anti*-addition product with no allylic bromination is expected from the accepted bromonium ion mechanism of Br_2 addition to the double bond of alkenes[47,48] and this has been used previously as an indicator for Br_2 elimination.[14] Why is there this difference in the photochemistry of **2** and $[PtBr_6]^{2-}$? There are three notable differences in the two systems, one is the ligand-field strength, another is the charge, and finally there is the solvent. The insolubility of **2** in water eliminates the possibility of comparing their photochemistry in water. However, $[NBu_4]_2[PtBr_6]$ is soluble in dichloromethane (DCM) and we have examined its photochemistry in this solvent. $[PtBr_6]^{2-}$ is photoinactive in DCM, with or without the Br_2 trap TME. $[PtBr_6]^{2-}$ does, however, undergo photosubstitution of a bromide by added DMSO in DCM (experimental section). Thus, it appears that solvent is not a factor in the different photochemistry of **2** and $[PtBr_6]^{2-}$. This leaves charge and the ligand-field strength as possible factors. It can be argued that Br anion loss from neutral **2** is disfavored by charge separation. On the other hand, anion loss from $[PtBr_6]^{2-}$ should not be difficult as a positive charge is not formed from Br anion removal. The charge difference may then be an important factor in the different photochemical processes. The ligand-field strength is also expected to be important. The $[PtBr_6]^{2-}$ excited state from which Br anion loss occurs has been assigned to the lowest energy triplet, a metal-centered, ligand-field $^3T_{1g}$ state.[45] Close by are Br-to-Pt charge-transfer states.[49] The greater ligand-field strength in **2**, from replacement of the Br anions with PEt_3 and the R group (except **2**(Br)), destabilizes the T_{1g} state (ignoring the change in symmetry). A likely result is that the lowest energy triplet in **2** is a Br-to-Pt charge-transfer (LMCT) state with access to Br_2 elimination. DFT calculations on the lowest-energy triplet of **2**, to be reported later, indicate a CT excited state with Br radical character. Radical character would also be consistent with Co(III) halide system photochemistry, which show radical character in their analogous LMCT excited state.[50]

Whereas the trapping product (*anti*-addition product) with *cis*-2-hexene indicates Br_2 photoelimination from **2**, the products from the more reactive alkene, TME, are more diverse and, for **2**(Br), their yields depend on the TME concentration (Table 3). The major product is 2,3-dimethyl-2,3-dibromobutane (**3**), the same product obtained from Br_2 addition to TME, suggesting that this product is from trapping of released Br_2. The second product, 1-bromo-2,3-dimethyl-2-butene (**4**), is the expected product from a radical bromination and the yield of this product increases with TME concentration at the expense of Br_2 addition product **3**. Scheme 3 is consistent with these results. TME (but not *cis*-2-hexene) is proposed to react directly with the excited state of **2** and, consistent with a CT excited state with radical character, this gives the allylic radical bromination product **4**. This reaction must occur within the lifetime of the excited state. If not, decay of the excited state results in Br_2 elimination followed by Br_2 reaction with TME (or *cis*-2-hexene) to give **3**. At lower concentrations of TME, the probability of a TME molecule being in the vicinity of an excited state is less and greater amounts of Br_2 elimination occur giving more **3**. TME oxidation by electron transfer to the excited state is also possible. However, on the basis of the known oxidation chemistry of TME,[51,52] allylic **4** would not be expected from the TME radical cation.

Scheme 3

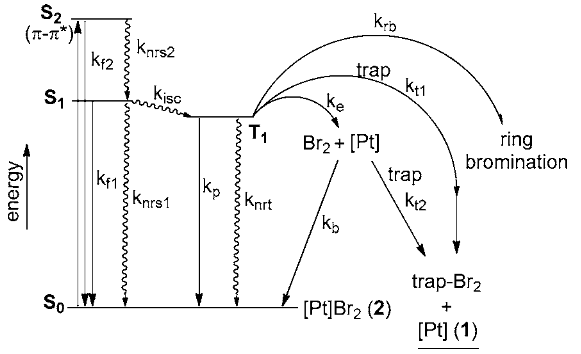


Interestingly, **2**(PMI) gives only the Br_2 addition product **3** at all concentrations of TME. This suggests that, in comparison to **2**(Br), either the excited state is less reactive to radical abstractions or Br_2 elimination is faster and the radical pathway is not competitive. A faster elimination rate might obtain from the expected steric crowding in the **2**(PMI) excited state (Structures above). However, the low lying PMI orbitals could delocalize radical character into the PMI unit, thereby reducing radical reactivity.

Also observed in the photochemistry is the ring bromination of **2**(1-Nap) and **2**(Phen). When does this occur? We observe ring bromination in the synthesis of **2**(BrNap), **2**(BrMeOPh) and **2**(BrPer), so it is possible that ring bromination occurs by reaction of eliminated Br_2 with remaining **2**. However, this would result in initially high ratios of ring brominated **1** to unbrominated **1** and the ratio would decrease as the concentration of **2** falls. This is not observed and, instead, the ratio remains relatively constant throughout the photolysis. Ring bromination could be an alternate excited state decay pathway (Scheme 3). This is consistent with the data in Table 1, which show that ring bromination is considerably reduced with strong radical traps that may react, at least partly, directly with the excited state.

The quantum yield variations of **2** (Table 2) are difficult to interpret. At first glance, there appears to be a reaction free energy dependence, as shown by comparison of **2**(Ph), **2**(1-Nap), and **2**(CF_3Ph), where the quantum yield varies inversely with the free energy of the elimination. However, attributing quantum yield variations to a single factor is simplistic. This is illustrated by the high quantum yield of **2**(Br), which has a relatively high Br_2 elimination free energy. To help in the discussion, a simplified Jablonski diagram is given in Scheme 4. Excitation into the strong π–π* band to the singlet excited state S_2 is shown but this is not necessary (and is impossible for **2**(Br), which has no π–π* transition) as the photoeliminations are still observed when irradiation is into the weak long-wavelength band(s) of **2**. This suggests that there is a lower energy singlet (S_1) through which the system transits. (Most likely, there are other singlet states between S_2 and S_1, but these are not shown.) S_1 is probably the LMCT excited state involving Br ligand lone pairs and a vacant σ* orbital on the Pt center as discussed above. Rapid intersystem crossing to the associated triplet state T_1 would follow. In complexes **2**, instead of Br anion dissociation character found for $[PtBr_6]^{2-}$, T_1 has more radical character and can be trapped with high concentrations of radical reactive species (k_{t1}) or can progress either to ring bromination (k_{rb}) or Br_2 elimination (k_e). $[Pt]Br_2$* in Scheme 3 can then be identified with T_1 in Scheme 4.

Scheme 4

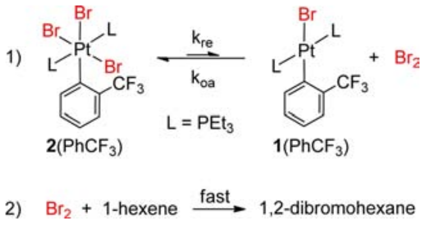


Coming back to the quantum yield for the reaction, from Scheme 4 it is the population and fate of T_1 that is central to the quantum yield. Population of T_1 will depend partly on the various decay pathways for the precursor excited states. One that is easily investigated is emission (k_{f1}, k_{f2}, k_p). Weak emission (Supporting Information) is observed from solutions of **2**(PMI) with excitation into the π-to-π* band. However, relatively concentrated solutions must be used and the emission spectrum can be attributed to low level impurities of highly emissive **1**(PMI) and BrPMI or PMI. Thus, radiative decay from S_2 (k_{f2}), at least for **2**(PMI), does not appear to be a significant decay pathway. Emission from S_1 and/or T_1 could still be present but below our observation limit (700 nm).

Initially, we thought that steric crowding was important in preventing bromine recombination (k_b). This idea was based primarily on the very low quantum yield of **2**(Ph) and **2**(2-Nap) as compared to **2**(1-Nap) and **2**(Phen) and on the observation that introducing a substituent at the phenyl ring 2-position "turned-on" the photochemical reaction in 2 (CF_3Ph) and **2**(BrNPh). Whereas this may be a factor, the high quantum yield of sterically unencumbered **2**(Br) clearly indicates other factors, probably related to population and decay of the excited states, are important. In addition, we have studied the bromination of **1**(CF_3Ph), one of the most sterically encumbered complexes, by low temperature NMR spectroscopy and find that, even at −30 °C, bromination of **1**(CF_3Ph) is too fast to observe. Aryl ring rotation in some organic molecules is known to be important in excited state deactivation and can be sterically blocked.[53,54] If phenyl ring rotation is a deactivation pathway in **2**(Ph), then the enhanced quantum yield of the substituted aryl complexes and the polycyclic complexes with a hydrogen atom peri to the Pt may be associated with restricted rotation about the Pt−C bond.

Thermochemistry. Steric strain in **2** is reflected in the thermochemistry of Br_2 addition to **1**. The steric strain revealed in the X-ray crystal structures of **2**(BrNap), **2**(Phen), and **2**(BrMeOPh) and in the DFT structures destabilizes six-coordinate **2** relative to four-coordinate **1**. In fact, we have previously shown that in *trans*-Pt(PEt_3)$_2$(9-anthracenyl)(Br) (**1**, R = 9-anthracenyl) the two anthracenyl *peri*-hydrogen atoms completely block the Pt center axial sites and eliminate access to the six-coordinate Pt(IV) complex Pt(PEt_3)$_2$(9-anthracenyl)(Br)$_3$ (**2**(9-anthracenyl)).[55] Steric destabilization is also evident in the thermal stability of **2**. Complex **2**(CF_3Ph), which both calorimetry and DFT calculations indicate is the least stable to thermal Br_2 elimination, decomposes, even in the solid state, to **1**(CF_3Ph). The solution kinetic data (above) indicate a first-order reaction in 2(CF_3Ph) and zero order in 1-hexene trap suggesting the mechanism in Scheme 5, where k_{re} ~ k_{obs} = 1.4(1) × 10^{-3} s^{-1}. In conjunction with the calculated free energy of ~5 kcal this indicates a k_{oa} of at least 10 s^{-1} M^{-1}, consistent with our inability to observe the bromination reaction by NMR spectroscopy.

Scheme 5



Electronic factors should also be important in the thermochemistry but are difficult to separate from steric factors in these congested complexes. The relatively unhindered **2**(Br) and **2**(Ph) that perhaps can be compared. The electron donating phenyl group of **2**(Ph) should stabilize the Pt(IV) state more than the Br ligand in **2**(Br) and this is supported by the more negative free energy of bromination of **1**(Ph) to **2**(Ph).

■ CONCLUSIONS

Platinum(IV) complexes *trans*-Pt(PEt_3)$_2$(R)(Br)$_3$ **2** photoeliminate molecular bromine with quantum yields as high as 82% and reaction free energies from 2 to 22 kcal/mol of Br_2. The photoelimination is independent of wavelength over the UV−vis region where the complexes absorb and the excitation wavelength can be shifted into the visible by introducing polycyclic aromatic chromophores as the R group. The excited state precursor to molecular bromine elimination can undergo radical reactions with good hydrogen atom donors and is probably Br-to-Pt charge transfer (LMCT) in character. Details of the Br_2 elimination mechanism are under investigation and will be reported in later publications. The change from the bromine anion elimination photochemistry of related $[PtBr_6]^{2-}$ is probably due to the increased ligand field and the high energy of ± charge separation in neutral **2**. Similar molecular elimination chemistry is possible with chloro and hydroxo complexes and is currently under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and experimental details, ^{1}H NMR spectra, crystal structure drawings, UV−vis spectra for **2**, emission spectra for **2**(PMI), dark reaction kinetics for **2**(CF_3Ph), calorimetry information and DFT data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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