Properties of some Tetraphenylboronates of Transition Metal Complexes

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Summary
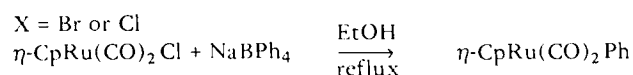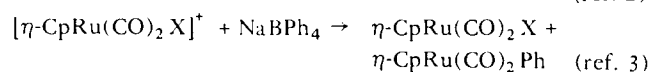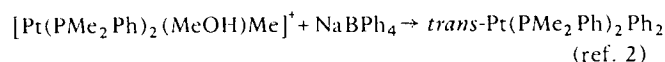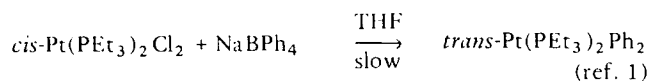
Solid tetraphenylboronates of some cations, *e.g.*
$[Fe(1,10 \text{ phen})_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, with $E°$ values ≥ -0.26 V
are unstable, either thermally or photochemically, or both.
Products of such redox reactions are identified. The contrasting situation with more reducing cations, *e.g.* $[Cr(en)_3]^{3+}$,
is described.

Introduction

The tetraphenylboronate(III) anion, $[BPh_4]^-$, is used
commonly as a counterion to precipitate complex metal
cations from aqueous solution as their insoluble tetraphenylboronates. In such aqueous applications, the anion is regarded as chemically fairly inert and possesses no redox
properties. Of course, in nonaqueous systems, particularly
involving organometallic compounds, tetraphenylboronate
may serve as a source of phenyl anions as in (1).

$$[BPh_4]^- + X^+ \rightarrow XPh + BPh_3 \qquad (1)$$
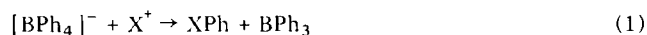
Presumably the other product is triphenylboron, though
this seems not actually to have been characterized in any
of the known examples of such reactivity:

$$cis\text{-}Pt(PEt_3)_2Cl_2 + NaBPh_4 \xrightarrow[\text{slow}]{THF} trans\text{-}Pt(PEt_3)_2Ph_2$$
$$(\text{ref. 1})$$

$$[Pt(PMe_2Ph)_2(MeOH)Me]^+ + NaBPh_4 \rightarrow trans\text{-}Pt(PMe_2Ph)_2Ph_2$$
$$(\text{ref. 2})$$

$$[\eta\text{-}CpRu(CO)_2X]^+ + NaBPh_4 \rightarrow \eta\text{-}CpRu(CO)_2X +$$
$$\eta\text{-}CpRu(CO)_2Ph \quad (\text{ref. 3})$$

$$X = Br \text{ or } Cl$$
$$\eta\text{-}CpRu(CO)_2Cl + NaBPh_4 \xrightarrow[\text{reflux}]{EtOH} \eta\text{-}CpRu(CO)_2Ph$$

The purpose of the present paper is to point out some anomalously high reactivities of the tetraphenylboronates of some
simple Werner cations.

A study[4] of the photochemical behaviour of aqueous
and alcoholic solutions of sodium tetraphenylboronate revealed that when light of wavelength 254 nm was used to
irradiate the solutions, biphenyl, together with some phenyl-cyclohexadienes and borinic acid derivatives, were formed.
Some years ago during a survey[5 a] of the solubilities of
tetraphenylboronates, prompted by the observation[5 b]

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that whereas *trans*-$[Co(en)_2Cl_2](BPh_4)$ was very insoluble in
water, its *cis*-isomeric salt was not, we prepared a number
of complex cobalt(III) and rhodium(III) tetraphenylboronates. In general[5 a] the rhodium salts were stable, whereas
those of cobalt(III) were not. For example, the solid tetraphenylboronate salt of the complex cation
cis-$[Co(trien)(H_2O)_2]^{3+}$ was unstable[5 c] in nitrogen and
over a period of a week decomposed to leave a brown solid
which contained phenol. Likewise[5 d] solid tetraphenylboronate salts of some Ru^{III} amines *e.g.*
$[Ru(en)_2(C_2O_4)](BPh_4)$ and *cis*-$[Ru(en)_2Cl_2](BPh_4)$ have
been reported to be photochemically unstable.

During this work on transition metal complexes, we have
often had cause to try to make tetraphenylboronates of cations and have noted their instability, usually as solids. We
collect much of this information here, report a study of the
thermal and photochemical reactions of some tetraphenylboronates, and comment on the underlying chemistry.

Results and Discussion

Details of the preparation and decompositions of a
number of tetraphenylboronates are given in the Experimental Section. Results are summarized in Table 1, and noteworthy features of the individual reactions are in the Experimental Section.

The solid tetraphenylboronates were all more reactive
than the corresponding chlorides, the tetraphenylboronate
salts reacting completely in a matter of a few weeks whereas the corresponding chloride salts were, at most, only slightly reacted under similar conditions. Further, the energy of
the radiation (*i.e.* visible light) necessary to cause reaction
of tetraphenylboronates is considerably less than that used
in previous solid state studies of other salts. Thus, although
the reaction[2] below is known[6] to occur, it is accomplished
only by using xenon flash tube radiation.

$$[Cr(en)_3]X_3 \xrightarrow{h\nu} cis\text{-}[Cr(en)_2X_2]X + en \qquad (2)$$

$$X = Cl, Br.$$
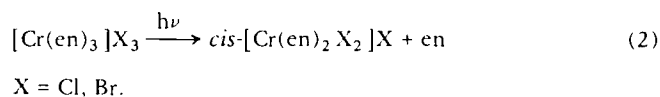
Similarly[7], the cobalt complexes $[Co(en)_3]X_3$, where
$X = F, Cl, Br, I$, underwent reaction when exposed to 254
nm radiation but not with radiation of 365 nm or of longer
wavelength. The large tetraphenylboronate anion apparently
is making these complex cations less stable in the solid state
than when smaller anions like halides are used as the gegenion.

The type of reaction these compounds undergo, *i.e.* redox
or substitution, can be seen to be determined by the $E°$
values for the one electron reduction of the complexes, *viz.*
Table 2.

Table 1. Decompositions of tetraphenylboronates

Starting Complex	Conditions	Complex product	Electronic spectral properties λ(nm)	Other products
[Cr(NH₃)₅Cl](BPh₄)₂	hv/4 weeks	[Cr(NH₃)₂(H₂O)₂(OH)Cl](BPh₄)	578, 420	NH₃ + BPh₃
[Cr(NH₃)₅Cl]Cl₂	hv/4 weeks	Little Change	–	NH₃ Small amount
[Cr(NH₃)₅Cl](BPh₄)₂	Dark	No reaction	–	–
[Cr(en)₃](BPh₄)₃	hv/4 weeks	cis-[Cr(en)₂(H₂O)(OH)](BPh₄)₂	520 in Me₂CO	BPh₃
[Cr(en)₃]Cl₃	hv/4 weeks	Little change	–	–
[Cr(en)₃](BPh₄)₃	Dark	No reaction	–	–
[Co(en)₃](BPh₄)₃	hv/4 weeks	[Co(en)₃](BPh₄)₂ "uncertain"	No distinct maxima	BPh₃ + PhPh
[Co(en)₃]Cl₃	hv/4 weeks	No reaction	–	–
[Co(en)₃](BPh₄)₃	Dark	No reaction	–	–
[Co(NH₃)₆](BPh₄)₃	hv/1 week	[Co(NH₃)(H₂O)₅](BPh₄)(OH) "uncertain"	No distinct maxima	BPh₃ + PhPh
[Co(NH₃)₆]Cl₃	hv/1 week	No reaction	–	–
[Co(NH₃)₆](BPh₄)₃	Dark	Possibly similar product to photochemical reaction.	No distinct maxima	BPh₃ + PhPh
[Fe(o-phen)₃]³⁺	Aqueous NaBPh₄	[Fe(o-phen)₃](BPh₄)₂	512 in Me₂CO	BPh₃ + PhPh

Table 2. Decompositions of tetraphenylboronates and reduction potentials

Couple		E°/v[8]	D[a]
[Fe(o-phen)₃]³⁺ + e⁻ ⇌	[Fe(o-phen)₃]²⁺	1.06[b]	R
[Co(NH₃)₆]³⁺ + e⁻ ⇌	[Co(NH₃)₆]²⁺	0.06	R
[Co(en)₃]³⁺ + e⁻ ⇌	[Co(en)₃]²⁺	-0.26	R
Cr³⁺ + e⁻ ⇌	Cr²⁺	-0.41	S
[Cr(NH₃)₆]³⁺ + e⁻ ⇌	[Cr(NH₃)₆]²⁺	-0.7	S

[a] This column describes the mode of decomposition: R, redox, S, substitution.

[b] This half cell, although it does not involve H⁺, shows a marked variation of potential with acidity: we commented recently on this [R. D. Gillard and P. A. Williams, *Transition Met. Chem. 2*, 109 (1977)]. However, in the present context, it suffices that the ferric form is a strong oxidant.

Thus, under the prevailing conditions, it was not possible to isolate [Fe(o-phen)₃](BPh₄)₃: an immediate reduction to the ferrous state occurred on adding the tetraphenylboronate to the [Fe(o-phen)₃]³⁺ ion. The cobalt complexes with their E° values at ca. 0.0 V are probably just on the borderline of stability for isolation as tetraphenylboronates*. Thus although both the hexammine and trisethylenediamine complexes were isolated, the ammonia complex proved to be unstable and could not be kept for longer than a few days without decomposition occurring, even in the dark. As expected, in their reactions as tetraphenylboronates, the cobalt(III) complexes undergo a redox process with formation of cobalt(II).

Chromium(III) on the other hand has a much more negative E° which means that the Cr^III is more thermodynamically stable than Cr^II, so that when reaction does occur, it is restricted to the M^III oxidation state, with the result that substitution or possibly isomerization rather than redox processes occur on irradiation. Photochemical studies[9] on a few other Cr^III compounds in the solid state have shown

no evidence for the presence of any oxidation state other than M^III during the reactions.

The fate of the tetraphenylboronate anion that is 'lost' in these reactions has been shown for the chromium compounds to involve formation of BPh₃. However, the fate of the fourth phenyl group has not been determined: nevertheless, the *absence of any biphenyl* amongst the products strongly suggests that the phenyl group abstracts a proton to form benzene.

Previous work[7] on the photochemical reaction of solid [Co(en)₃]X₃, where X = F, Cl, Br, I, using λ = 254 nm reported that the product was a 1:1 mixture of Co^II and Co^III.

The Co^III and Co^II were present allegedly as a binuclear complex in which the two cobalt atoms were linked by a polyamine, possibly triethylenetetramine, formed by condensation of the ethylenediamine. In contrast, no evidence for diethylenetriamine or triethylenetetramine was found amongst the products of the photochemical reaction of [Co(en)₃](Ph₄B)₃ nor were any Co^III species a product in the photochemical reaction of both the cobalt complexes. It thus seems that all the cobalt is reduced to Co^II in these reactions. Other work on the photochemical behaviour of Co^III complexes in the solid state such as [Co(NH₃)₅Cl]Cl[9, 10] [Co(phen)₂Ox]Cl, 4H₂O[9, 11], and K₃[Co(Ox)₃] · 3H₂O[9, 12] has shown that Co^II species, sometimes of unknown composition, have been the sole cobalt-containing products. Because the reactions of the cobalt complexes involve a redox process, the fate of the tetraphenylboronate anion differs from that in cases involving the Cr^III compounds. Biphenyl and triphenylboron are the main products of the reaction.

The thermal reaction of the [Fe(o-phen)₃]³⁺ ion with tetraphenylboronate is presumably an analogous redox process but although the iron-containing product has been shown to be [Fe(o-phen)₃]²⁺, the nature of the other species apart from biphenyl has not been determined. Because of the excess of chlorine in the system, these other species are likely to be a complicated mixture. It has also been shown[13] that ferriin, [Fe(o-phen)₃]³⁺, can be used as an oxidant to oxidize relatively simple organic molecules. Thus cyclohexan-

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* Although, of course, their salts with less easily oxidized anions are stable for years.

Table 3. Analyses of tetraphenylboronates

Complex	Formula	Found (Calcd.)%		
		C	H	N
[Co(en)$_3$]$_3$(BPh$_4$) · H$_2$O	C$_{78}$H$_{86}$B$_3$CoN$_6$O	77.6 (77.1)	7.5 (7.1)	7.0 (6.9)
[Cr(NH$_3$)$_5$Cl]$_2$(BPh$_4$) · 3 H$_2$O	C$_{48}$H$_{61}$B$_2$ClCrN$_5$O$_3$	67.1 (66.7)	7.1 (7.1)	8.1 (8.1)
[Cr(en)$_3$]$_3$(BPh$_4$) · 2 H$_2$O	C$_{78}$H$_{88}$B$_3$CrN$_6$O$_2$	76.2 (76.4)	7.3 (7.2)	6.5 (6.9)
trans-[Co(en)$_2$Cl$_2$](BPh$_4$)	C$_{28}$H$_{36}$BCl$_2$CoN$_4$	58.9 (59.1)	6.32 (6.4)	
trans-[Rh(py)$_4$Cl$_2$](BPh$_4$)	C$_{44}$H$_{40}$BCl$_2$N$_4$Rh	65.5 (65.3)	5.3 (4.9)	6.9 (6.9)

one was oxidized to 2-hydroxycyclohexanone, the first step in the mechanism being the abstraction of an electron by the ferriin from the cyclohexanone to form the radical 2-oxocyclohexyl.

Perhaps most interesting, from the point of view of generalization, is the correlation between rapid base hydrolysis [as in complexes of ruthenium(III), cobalt(III), and tris(phenanthroline)iron(III)] and redox instability of the tetraphenylboronates. A number of predictions may be made, including the instability of tetraphenylboronates of the oxidized states of platinum(IV), iridium(IV), and many complexes of cobalt(III).

Experimental

Preparation of the complexes

The chloride salts of the cobalt, chromium, and rhodium complexes were prepared by standard procedures. Conversion into the tetraphenylboronates was accomplished by double decomposition, adding a cold solution of the chloride of the complex cation to a slight excess of a cold aqueous solution of sodium tetraphenylboronate (B.D.H. Laboratory reagents: the commercial name is "sodium tetraphenylboron"), the precipitates were washed with ice cold H$_2$O and dried over P$_2$O$_5$. The analyses are summarized in Table 3.

[Co(NH$_3$)$_6$](BPh$_4$)$_3$ was made by a similar procedure but it was not possible to keep samples for more than a few days, even in the dark, without some reaction occurring. Because of this, no analysis of the complex was obtained.

Photochemical reactions

Preliminary experiments were carried out by placing the compound together with a few glass beads in a stoppered conical flask (25 cm^3) which was attached to a mechanical shaker. The flasks were then irradiated with an Osram 150 W photoflood bulb while being shaken so that a new surface was being exposed continuously to the irradiation. The weight losses accompanying irradiation were determined by irradiating a known weight of compound contained in a sintered glass funnel. At frequent intervals the solid was disturbed with a spatula so as to expose new solid to the light and occasionally the solid was washed with Et$_2$O and C$_6$H$_6$ and then sucked dry before reweighing.
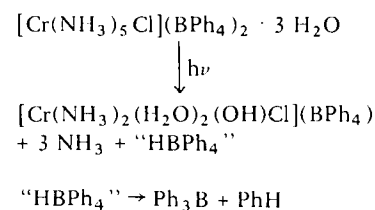
Chromatography was carried out using plastic sheets precoated with silica gel 60 F$_{254}$ and using isooctane as the solvent.

Irradiation of [Cr(NH$_3$)$_5$Cl](BPh$_4$)$_2$

Irradiation for several days of the pale purple [Cr(NH$_3$)$_5$Cl](BPh$_4$)$_2$ in a closed system resulted in darkening of the solid together with a bathochromic shift of the electronic spectral maxima. The electronic spectrum was measured using Me$_2$CO as solvent but after several days' irradiation all the solid no longer dissolved. Ammonia was detected. When the reaction was conducted on a sintered funnel open to the atmosphere and the solid was washed with C$_6$H$_6$ and Et$_2$O until no further weight loss occurred (ca. four weeks), the final blue grey solid was completely insoluble in H$_2$O or Me$_2$CO but the reflectance spectrum had maxima at 578 and 420 nm. The weight loss during this time indicated that the blue grey product had a molecular weight of ca. 525 and the i.r. spectrum showed the presence of Ph$_4$B$^-$, N—H and O—H, the main difference between the i.r. spectrum of product and factor being that the bands associated with N—H were much weaker in the product. Analysis of the product gave: C, 58.3; H, 6.2; N, 5.4; Cl, 6.3; B, 2.5, consistent with the formulation [Cr(NH$_3$)$_2$(H$_2$O)$_2$(OH)Cl](BPh$_4$) (M.W. = 493.5) calcd.: C, 58.4; H, 6.3; N, 5.7; Cl, 7.2; B, 2.2%. This formulation is supported by dissolving the product in warm 1 M perchloric acid. The resulting solution had absorption bands at 564 and 408 nm {cf. the known cation[14] [Cr(NH$_3$)$_2$(H$_2$O)$_3$Cl]$^{2+}$, has bands at 562 and 406 nm } .
i.e. [Cr(NH$_3$)$_2$(H$_2$O)$_2$(OH)Cl]$^+$ + H$^+$ → [Cr(NH$_3$)$_2$(H$_2$O)$_3$Cl]$^{2+}$.

The Et$_2$O and C$_6$H$_6$ washings resulting from the irradiation of [Cr(NH$_3$)$_5$Cl](BPh$_4$)$_2$ on a glass sinter were evaporated to dryness and t.l.c. of the resulting solid showed the absence of biphenyl. A mass spectrum of the solid however produced peaks at mass number 242 and 241 corresponding to ^{11}BPh$_3$ and ^{10}BPh$_3$.

The overall stoichiometry of the reaction can thus be written:

[Cr(NH$_3$)$_5$Cl](BPh$_4$)$_2$ · 3 H$_2$O

$\downarrow h\nu$

[Cr(NH$_3$)$_2$(H$_2$O)$_2$(OH)Cl](BPh$_4$)
+ 3 NH$_3$ + "HBPh$_4$"

"HBPh$_4$" → Ph$_3$B + PhH

The water involved in the reaction may be either atmospheric or water of crystallization. The fate of the other phenyl group is uncertain but it seems probable that it abstracts a proton from one of the water molecules to give benzene.

Samples of [Cr(NH$_3$)$_5$Cl](BPh$_4$)$_2$ left in the dark remained unreacted for several months. A sample of the chloride in a stoppered flask exposed to radiation for several

days showed no change in colour or in its electronic spectrum, but there were traces of ammonia in the flask. The photo-chemical reaction of the chloride salt is much slower than that of the corresponding tetraphenylboronate salt.

Irradiation of $[Cr(en)_3](BPh_4)_3 \cdot 2 H_2O$

Irradiation of solid $[Cr(en)_3](BPh_4)_3 \cdot 2 H_2O$ for a few hours produced a colour change from pale cream to pink. When the solid was irradiated for a much longer period and occasionally washed with Et_2O and C_6H_6 to constant weight (*ca.* 4 weeks), the product had a peak in the electron-ic spectrum (in Me_2CO) at 520 nm. The i.r. spectrum in-dicated the presence of Ph_4B, N–H and O–H. The weight loss during the irradiation suggested that the molecular weight of the product was *ca.* 852 and the analysis was con-sistent with the formulation of the product as $[Cr(en)_2(H_2O)(OH)](BPh_4)_2$ (M.W. = 845) calcd.: C, 73,8; H, 7.0; N, 6.6; B, 2.6. Found: C, 73.4; H, 7.3; N, 6.4; B, 2.5%.

The *cis*-geometry can be assigned to this product: in water the known $[cis\text{-}Cr(en)_2(H_2O)(OH)]^{2+}$ has[15] a maximum at 515 nm whereas the *trans*-isomer has λ max at 495 nm. The Et_2O and C_6H_6 washings from the $[Cr(en)_3](BPh_4)_3 \cdot 2 H_2O$ during the irradiation were evaporated to dryness and a t.l.c. of the resulting solid revealed a trace of biphenyl. A mass spectrum of the same solid gave peaks at mass numbers 241 and 242 due to $^{10}BPh_3$ and $^{11}BPh_3$. A peak at mass number 154 due to biphenyl was also observed but its in-tensity was less than 1% of that due to BPh_3. The stoichio-metry of the reaction can thus be written to a good approx-imation as:

$$[Cr(en)_3](BPh_4)_3 \cdot 2 H_2O$$
$$\downarrow h\nu$$
$$cis\text{-}[Cr(en)_2(H_2O)(OH)](BPh_4)_2 + en + BPh_3 + PhH$$
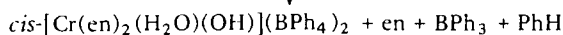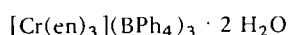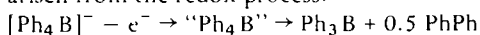
Here again the fate of the fourth phenyl group of the de-composed $[BPh_4]^-$ is uncertain but it seems likely that it abstracts a proton to form benzene. The water and hydrox-ide that are attached to the chromium in the product may be the original water of crystallization or atmospheric water.

Samples of $[Cr(en)_3](BPh_4)_3$ were stable in the dark in-definitely. Similarly, samples of $[Cr(en)_3]Cl_3$ showed no evidence of reaction in the dark: however, when samples were exposed to irradiation a colour change was observed but at a much slower rate than for the tetraphenylboronate

salt as indicated by only a small change in the electronic spectrum. Such 'photochromism' of hydrated solid halides of chelated amines of chromium(III) was remarked repeated-ly in the older literature.

The reaction of $[Co(en)_3](BPh_4)_3$ and of $[Co(NH_3)_6](BPh_4)_3$ with light, and of $[Co(NH_3)_6](BPh_4)_3$ in the dark

Both these compounds, when exposed to light for only a few hours, had changed noticeably, from pale yellow orange to light brown. When the photochemical reaction was fol-lowed to completion, *i.e.* in *ca.* four weeks for $[Co(en)_3](BPh_4)_3$ and *ca.* one week for $[Co(NH_3)_6](BPh_4)_3$, the spectra of the resultant brown solids dissolved in Me_2CO showed no distinct peaks (the brown solid resulting from the irradiation of the $[Co(NH_3)_6](BPh_4)_3$ did not all dis-solve in Me_2CO. However, when the brown solids were warmed with concentrated HCl some solid remained un-dissolved but the spectra of the solutions were typical of Co^{II}. The i.r. spectrum of the solid resulting from the irrad-iation of $[Co(en)_3](BPh_4)_3$ indicated the presence of $H_2NCH_2CH_2NH_2$ and of $[Ph_4B]^-$ whereas for the solid re-sulting from the irradiation of the $[Co(NH_3)_6](BPh_4)_3$ the i.r. spectrum, apart from indicating N–H and O–H, gave four strong bands in the $1500–1350 \text{ cm}^{-1}$ region. All the other substances containing BPh_4 have no more than two strong bands in this region, see Table 4. The presence of four strong bands is taken[3, 16] to indicate the presence of tetraphenylboronate coordinated to a metal ion through a π bond of a phenyl ring, although that seems inherently unlikely with cobalt(II) ions. The t.l.c. of solids obtained on evaporating to dryness the Et_2O and C_6H_6 washings of the two compounds during irradiation revealed the pre-sence of biphenyl. A mass spectrum of these same solids revealed biphenyl, BPh_3 and $[Ph_4B]^-$. These would have arisen from the redox process:
$$[Ph_4B]^- - e^- \rightarrow \text{``}Ph_4B\text{''} \rightarrow Ph_3B + 0.5 \, PhPh$$
Complementary with the oxidation of the $[Ph_4B]^-$ would be the reduction of Co^{III} to Co^{II}. The exact nature of the Co^{II} species formed is uncertain, but analyses of the pro-ducts together with the weight loss during irradiation suggest that the stoichiometry of the reactions follow:
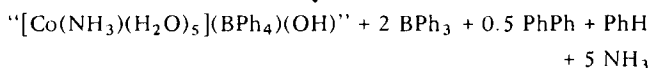
$$[Co(NH_3)_6](BPh_4)_3 + 6 \, H_2O$$
$$\downarrow h\nu$$
$$\text{``}[Co(NH_3)(H_2O)_5](BPh_4)(OH)\text{''} + 2 \, BPh_3 + 0.5 \, PhPh + PhH$$
$$+ 5 \, NH_3$$

Table 4. I.r. spectra of phenylborons ($1500–1350 \text{ cm}^{-1}$)

$NaBPh_4$[a]	1480s	1452vw	1425s	1390vw[b]
$[\text{cation}]^+(BPh_4)^-$[c]	*ca.* 1480s		*ca.* 1429s	
$[Rh(PPh_3)_2BPh_4]$[a, d]	1480s	1460s	1430s	1388s
$[Co(NH_3)(H_2O)_5](BPh_4)(OH)$[e]	1483s	1443s	1431s	1394s
BPh_3[f]	1492w		1430s	1350m
Ph_2BCl[g]	1493s		1435s	1375w
Ph_2BOCH_3[h]	1493m sh.	1460s	1439s	

a) Ref. 16; b) Assigned to in plane skeletal C–C stretching modes of phenyl ring.
c) Cation = $[Cr(NH_3)_5Cl]^{2+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, *trans*-$[Co(en)_2Cl]^+$, $[Fe(o\text{-}phen)_3]^{2+}$, *trans*-$[Rh(py)_4Cl_2]^+$. d) The two extra strong bands at 1460 and 1390 cm^{-1} are diagnostic of a coordinated $[BPh_4]^-$ *i.e.* coordinated via one π-bonded aromatic ring. See also ref. 3. e) Product of the reaction of $[Co(NH_3)_6](BPh_4)_3$ with light f) D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674, (1957). g) Chlorodiphenylborine, *Sadtler Standard Spectra*. h) Methyl diphenyl-borinate, *Sadtler Standard Spectra*.

M.W. (product) = 502; M.W. from exptl. wt loss = *ca.* 450 (Found: C, 56.4; H, 6.0; N. 2.6. Calcd.: C, 57.4; H, 6.8; N, 2.8%).

$$[Co(en)_3](BPh_4)_3 \cdot H_2O \rightarrow [Co(en)_3](BPh_4)_2 + Ph_3B + 0.5\ PhPh + H_2O$$
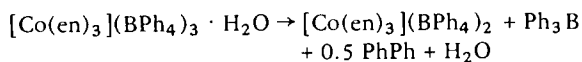
M.W. (product) = 877; M.W. from exptl. wt loss = *ca.* 900. (Found: C, 73.7; H, 6.8; N, 9.8. Calcd.: C, 73.9; H, 7.3; N, 9.6%).

$[Co(NH_3)_6](BPh_4)_3$ also underwent decomposition even in the dark and it was not possible to keep a sample of this compound for longer than a few days without some colour change occurring. This dark reaction was not investigated in detail but the i.r. spectrum of the product was similar to that of the solid product in the photochemical reaction. It was also possible to identify by t.l.c. and mass spectrometry, PhPh and BPh$_3$ among the products. The photochemical and dark reactions of $[Co(NH_3)_6](BPh_4)_3$ appear very similar.

Samples of $[Co(en)_3](BPh_4)_3$ were stable indefinitely in the dark and the chloride salts of the two cobalt complexes showed no colour change when irradiated for a similar time, i.e. several weeks.

Reaction of $[Fe(o\text{-}phen)_3]^{3+}$ *with aqueous NaBPh$_4$*

A solution of $[Fe(o\text{-}phen)_3]^{3+}$ was made by bubbling chlorine through a solution containing $FeSO_4 \cdot 7\ H_2O$ and *o*-phen in a 1 : 3 mole ratio; the solution was also 0.3 M in sulphuric acid. The initial red solution of $[Fe(o\text{-}phen)_3]^{2+}$ gradually turned blue as $[Fe(o\text{-}phen)_3]^{3+}$ was formed. On adding a slight excess of a neutral solution of NaBPh$_4$, an immediate red precipitate was formed which was collected, washed with water and dried. (Although NaBPh$_4$ is not stable in acid solution, the decomposition is not rapid and under our conditions, practically no decomposition of the NaBPh$_4$ occurred before precipitation). The dried red solid was then washed with Et$_2$O and the Et$_2$O washings were taken to dryness. A solution of the red solid in Me$_2$CO gave an electronic spectrum with a peak at 512 nm, characteristic of the $[Fe(o\text{-}phen)_3]^{2+}$ cation; analysis of the solid was consistent with this formulation:
(Found C, 79.6; H, 5.1; N, 5.8. Calcd. for $[Fe(o\text{-}phen)_3](BPh_4)_2 \cdot 2\ H_2O$: C, 79.4; H, 5.4; N, 6.6%).

The t.l.c. of the solid resulting from the Et$_2$O washings revealed the presence of PhPh (as major product) but several other unidentified spots were present on the plate. To a first approximation, the stoichiometry of the reaction can be written:

$$[Fe(o\text{-}phen)_3]^{3+} + 3[BPh_4]^- \rightarrow [Fe(o\text{-}phen)_3](BPh_4)_2 + Ph_4B$$

$$Ph_4B \xrightarrow{(?)} 0.5\ PhPh + BPh_3$$
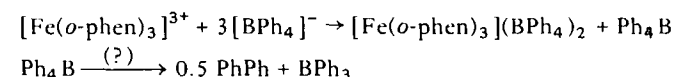
Irradiation of $[Co(NH_3)_5Cl](BPh_4)_2$, *trans-*$[Co(en)_2Cl_2](BPh_4)$ *and trans-*$[Rh(py)_4Cl_2](BPh_4)$

These reactions were not studied in detail but a colour change was observed after only a few days irradiation. The electronic spectra in Me$_2$CO solution of the products of the reactions did not have any characteristic maxima. Washing the irradiated solids with Et$_2$O and C$_6$H$_6$ and evaporating the solution to dryness produced solids which for the cobalt compounds was shown by t.l.c. to contain an appreciable amount of PhPh. In the case of the rhodium compound only a very little solid was obtained and this was also shown to contain a trace of PhPh. It thus seems very probable that the cobalt compounds are undergoing a redox reaction similar to that observed with the other cobalt complexes, whereas the reaction of the rhodium compound is not so clear.

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