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Skeletal rearrangements of arylborane complexes mediated by redox reactions: thermal and photochemical oxidation by metal ions ^{*,**}

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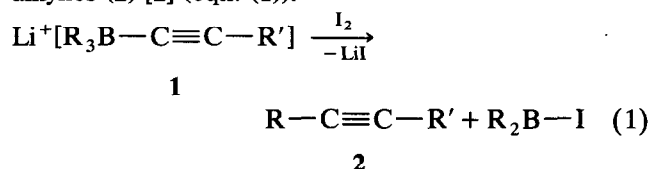
Abstract

A variety of metal salts have been found to undergo reduction by thermal and photochemical interaction with tetraarylborate salts and with neutral alkyl- and aryl-borane complexes. In the cases of Cu^{2+} , Cu^+ , Ni^{2+} , Co^{2+} , Pd^{2+} , Pt^{2+} , Ag^+ , Zn^{2+} , Hg^{2+} , Sn^{2+} , Pb^{2+} and Rh^{3+} salts, such photochemical reductions with NaBPh_4 led to the deposition of the free metal, while a number of binary mixtures of metal salts led to the codeposition of both metals, sometimes as true alloys, under such photoreductions. In the course of these reductions the arylborate reductants underwent oxidative coupling of the aryl groups to form biaryls in a strictly intra-ionic (for BAr_4^-) or intramolecular (Ar_3B) manner respectively. Individual studies of the photochemistry of the tetraarylborate anion itself, of cuprous tetraphenylborate and of the triphenylborane-pyridine complex have adduced evidence for a gamut of reactive intermediates capable of serving as the photoreductant for metal ions, such as triarylborane radical anions, diarylborate(I) anions or arylborenes, 7-borabicycloheptadiene anions or neutral complexes and finally arylborohydride anions or arylboron hydrides. The role of these intermediates both in the photoinduced skeletal rearrangements of arylboranes and in the concomitant reduction of metal ions is discussed in critical detail.

Key words: Boron; Aryl; Oxidation; Copper; Nickel; Zinc

1. Introduction

The oxidation of tetraorganylborate salts by various procedures can induce skeletal rearrangements in the anion that lead to coupling of the organyl substituents [1]. Treatment of lithium trialkyl(alkynyl)borates (1) with iodine, for example, has been developed as an excellent route to homo- and hetero-disubstituted alkynes (2) [2] (eqn. (1)):



Such oxidative couplings of tetraarylborates have

been induced not only by halogens [1,3], but also by reducible metal ions [1,3–5], electron acceptors [1], electrochemical oxidation [6] and photochemical redox reactions [7–16]. In those cases where hetero-aryl-substituted borate salts $\text{M}^+[\text{Ar}_n\text{Ar}'_{4-n}]\text{B}^-$ have been examined, the biaryls formed have been consistent with the view that coupling occurs only at the initial carbon-boron bonds and ensues in a strictly intra-ionic manner [1,5,6]. A recently discovered variant of this reaction, namely the photochemically induced metal-ion coupling of biaryls in tetraarylborates is of unusual practical value in that it provides an avenue for the photodeposition of metals or their alloys onto a suitable surface [17]. For the specific case of copper salts, the method has proved applicable for the preparation of printed circuits for the electronics industry [18].

In the light of the potential importance of such tetraarylborates as commercial reducing agents for metal ions, we have undertaken a detailed study of both the thermal and the photochemical reduction of copper salts by such arylborates. Furthermore, we have examined the scope of these photoreductions for other individual metal salts or mixtures of metal salts. In addition, we have sought to determine the origin of the

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* Part 15 of Bora-aromatic systems. Previous part: J.J. Eisch, T. Dluzniewski and M. Behrooz, *Heteroatom Chem.*, 4 (1993) 235, as well as Part 26 of Rearrangements of organometallic compounds. Previous part: J.J. Eisch, C.A. Kovacs and P. Chobe, *J. Org. Chem.*, 54 (1989) 1275.

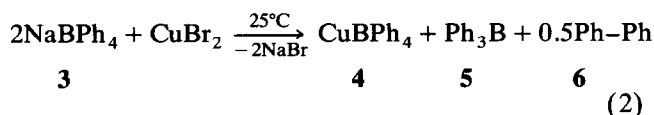
** Dedicated to Professor Heinrich Nöth of the Ludwig Maximilian University of Munich, Germany, on the occasion of his 65th birthday.

reducing power exhibited by irradiated tetraarylborate salts themselves. Finally, we have surveyed the feasibility of substituting neutral triorganylboranes R_3B or their Lewis complexes $R_3B:D$ for the arylborates in such photoreductions of metal ions. The present study has thereby uncovered some unusual features both in the mechanistic pathways and in the reactive intermediates involved in these thermal and photochemical redox processes.

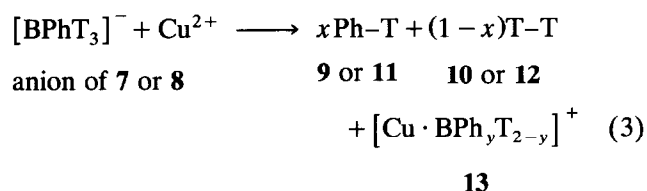
2. Results

2.1. Thermal reduction of cupric ion by the tetraarylborate anion

Wittig and Raff [19] first reported that the thermal reaction of $CuBr_2$ and $LiBPh_4$ in ether required several weeks to produce $CuBPh_4$ (4). In the present work, sodium tetraphenylborate (3) in 1,2-dimethoxyethane (DME) was found to produce almost quantitative yields of 4, triphenylborane (5) and biphenyl (6) within hours at 25°C, according to eqn. (2):

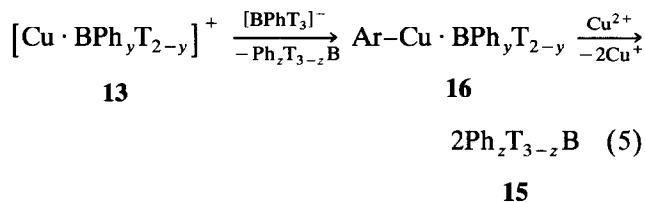
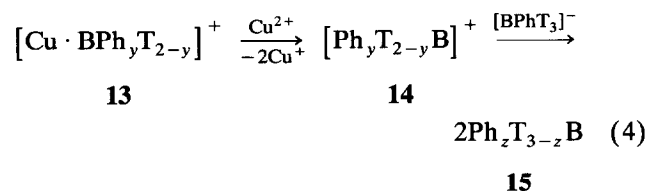


The observed biaryl coupling of both sodium phenyl(tri-*m*-tolyl)borate (7) and sodium phenyl(tri-*p*-tolyl)borate (8) in this reaction with $CuBr_2$ was most informative; only *m*-methylbiphenyl (9) and *m,m'*-bitolyl (10), in a 1.0:2.1 ratio, were formed from 7 and only *p*-methylbiphenyl (11) and *p,p'*-bitolyl (12), in a 1.0:2.5 ratio, were formed from 8. The failure to detect even traces of biphenyl (6) signifies that the biaryls arose from a single tetraarylborate anion (eqn (3)):



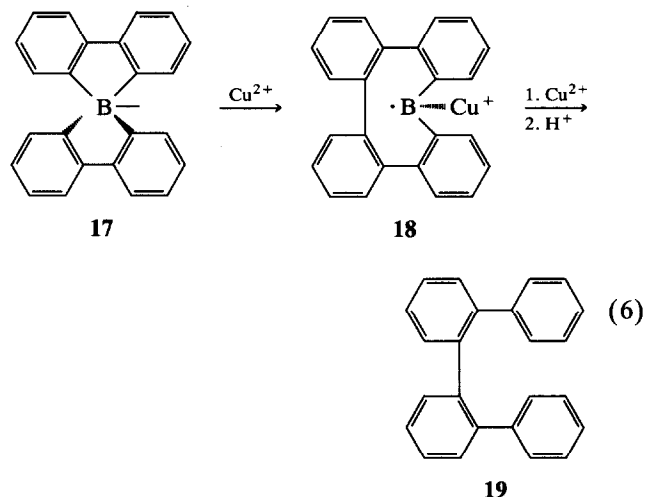
(T = *m*- or *p*-tolyl)

This finding implies the intermediacy of 13, formally a cuprous complex of the diarylboranyl radical, which could then be rapidly converted into triarylboranes via a number of pathways (e.g., eqns. (4) and (5)):



Whether the triarylboranes 15 arise from the electrophilic attack of 14 on 7 or 8 (eqn. (4)) or from the oxidation of 16 and subsequent reductive elimination will be considered in a future report.

However, highly pertinent to the mechanism of such reductions is the observation that sodium bis(2,2'-biphenylene)borate (17) undergoes oxidation with cupric ion, as it does with ceric ion [1], to yield *o,o'*-quaterphenyl (19) upon protodeboronative work-up. This indicates that intraionic biaryl coupling can occur to yield 18, the cuprous complex analog of 13, despite the stereorrigidity of the starting structure 17 (eqn. (6)):



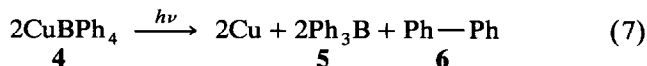
From this observation of successful C-C bond formation within anion 17, it is therefore unlikely that an aryl-bridged transition state (cf. structure 28) could be involved in the conversion of 17 to 18. Such an aryl-bridged configuration would be exceeding strained in forming from *spiro* 17 [1].

Sodium tetraarylborates have been shown to exert a similar thermal reducing action on other metal ions, such as ceric [4,6], ferric [5], nickel(II), cobalt(II), palladium(II) and titanium(IV) [17]. In the last case, reduction halts at the titanium(III) state [20].

2.2. Photoreduction of copper ions by arylborane complexes

The irradiation of these metal salts led to photoreduction to metal most efficiently when wavelengths below 300 nm were employed and maximally between 200 and 260 nm. The course of reaction with copper(I)

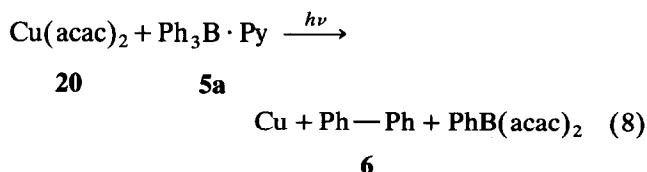
tetraphenylborate (4) and its tetrakis(triethylphosphite) complex (4a) was parallel to that shown in the thermal reduction of CuBr_2 (eqn. (2)); copper metal was efficiently produced* and triphenylborane (5) and biphenyl (6), in a 2:1 ratio, were the only discernible products (eqn. (7)):



From irradiation of the mixed sodium tetraarylborate salts 7 and 8 themselves, it was also shown that the biaryls generated again arose from a single tetraarylborate anion and thus the coupling was intra-anionic (*cf. infra*).

The irradiation of the triethyl-phosphite complex 4a, in tetrahydrofuran (THF) or in 1,2-dimethoxyethane (DME), led to the development of a blood-red color in the photolysate solution but after prolonged irradiation little (DME) or no (THF) copper metal had deposited.

In evaluating the photoreducing action of neutral triorganylboranes on copper salts, no attempt was made to study any thermal reduction separately. However, no color change was noted upon admixing copper(II) acetylacetonate (20) with either Ph_3B (5) or ${}^n\text{Bu}_3\text{B}$ (21) and so we conclude that any thermal reduction is relatively slow. On the other hand, irradiation of such mixtures led to the efficient deposition of copper metal. The reaction products from the reduction of 20 by the pyridine complex of Ph_3B (5a) were examined in detail and are given in eqn. (8):



It is noteworthy that the photoreduction of 20 by 5a is significantly slower than by 5 (the former, 60% in 12 h; the latter, 99% in 8 h).

An attempt to photoreduce 20 by trimesitylborane (21) was unsuccessful and the 1:1 adduct of 21 with sodium gave only thermal reduction to the cuprous salt.

2.3. Photoreduction of metal salts

Metal salts, such as those of Cu^{2+} , Ni^{2+} , Co^{2+} , Pd^{2+} , Pt^{2+} , Ag^+ , Zn^{2+} , Hg^{2+} , Sn^{2+} , Pb^{2+} and Rh^{3+} ,

* Copper metal deposition in a given photoreaction led to the formation of 60–95% of the theoretical amount, depending upon how effectively the copper film forming on the tube wall blocked the entrance of light. Re-irradiation of such photolysate solutions in a clean tube led to essentially quantitative deposition of copper metal.

TABLE 1. Photoreduction of metal salts by sodium tetraphenylborate (3)

No.	Metal salt	Time of irradiation at 254 nm (h)	Metal deposited (%)
1	CuBr_2	8	75
2	CuI	1	100
3	$\text{Cu}(\text{acac})_2$	18	80
4	NiBr_2	8	80
5	$\text{Ni}(\text{acac})_2$	8	90
6	ZnBr_2	4	99
7	ZnI_2	2	100
8	$\text{Zn}(\text{acac})_2$	4	80
9	SnCl_2	8	80

underwent facile photoreduction with sodium tetraphenylborate in DME, either individually (Table 1) or as binary mixtures (Table 2). The anion appears to have a considerable effect on the rate of such photoreductions, with iodide being clearly superior to, and acetylacetonate somewhat better than, bromide.

Examination of some of the metal films obtained from the photoreduction of binary salt mixtures by electron spectroscopy for chemical analysis (ESCA) has revealed that such films can be formed as true alloys. To achieve uniform alloy films by these techniques would seem to require a careful study of salt ratio, concentration and intensity of irradiation.

TABLE 2. Photodeposition of metals from solutions of mixed metal salts by sodium tetraphenylborate (3)

No.	Metal-salt mixtures	Molar ratio	Time of irradiation at 254 nm (h)	Atomic ratio of metals in photodeposition product
1	CuBr_2	1	10	Cu, 49
	NiBr_2	1		Ni, 48
2	CuBr_2	1	18	Cu, 48
	$\text{Ni}(\text{acac})_2$	1		Ni, 40
3	CuBr_2	1	10	Cu, 24
	NiBr_2	3		Ni, 73
4	CuBr_2	1	14	Cu, 49
	SnCl_2	1		Sn, 49
5	CuBr_2	1	10	Cu, 48
	CoCl_2	1		Co, 47
6	CuBr_2	3	8	Cu, 74
	ZnI_2	1		Zn, 24
7	$\text{Cu}(\text{acac})_2$	3	18	Cu, 100
	$\text{Zn}(\text{acac})_2$	7		Zn, 0

2.4. Photochemical redox reactions of sodium tetraarylborates

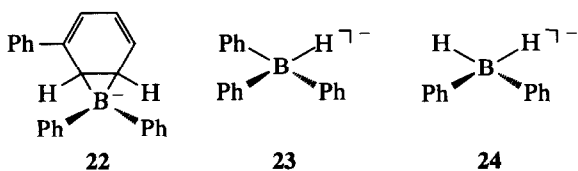
2.4.1. Spectral monitoring

Irradiation of the 15-crown-5-ether complex of sodium tetraphenylborate (**3**) in diethyl ether solution for 8 h led to the deposition of a red solid. This solid displayed a broad (45 G) electron spin resonance (ESR) signal that had no hyperfine structure. Exposed to air the red solid turned colorless and the ^1H nuclear magnetic resonance (NMR) spectrum of the colorless product showed only the presence of biphenyl (**6**) and the crown ether complex of **3**.

Irradiation of a solid sample of **3** for 20 min in the cavity of an ESR spectrometer at -110°C led to the development of a broad (45 G) unresolved signal, centered at 3275 G. After irradiation for 5 h the signal intensified and developed some shoulders indicative of more than one component. Warming the sample to -10°C caused the spectrum to change significantly to one having a breadth of 100 G and about four uneven absorptions. This signal persisted after 24 h at 25°C . The persisting spectrum was remarkably similar in its major splittings (attributable to the quartet splittings of ^{11}B nuclei having $I = \frac{3}{2}$) to that of the trimesitylborane radical anion in the solid state [21] and hence we conclude that the present signal arises from the triphenylborane radical anion [22a].

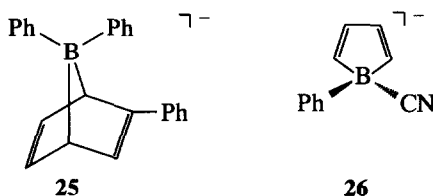
The evanescent spectral contribution, which was stable only below -110°C , might have arisen from a biphenyl radical ion, either cation or anion. Since the irradiation of **3** is known to produce biphenyl, such biphenyl could be photoionized to the cation radical or its could acquire an electron from a donor such as **3** to yield its anion radical. In support of this latter possibility is the observed photo-induced transfer of electrons from aromatic radical anions or dianions to neutral aromatic hydrocarbons [22b].

A sample of **3** in DME was irradiated and examined periodically by ^{11}B NMR spectroscopy. The first new signal formed was at -26.5 ppm and can be assigned to the bicyclic borate **22** [15]; further irradiation led to doublet and triplet signals, at -8.0 ppm and -15.1 ppm respectively, which can be attributed to the $\text{Ar}_3\text{B}-\text{H}^-$ (**23**) [23] and Ar_2BH_2^- (**24**) anions [24], where Ar is most likely phenyl:



The significant singlet at -16.7 ppm that increases in intensity upon irradiation appears to be due to the

bicyclic isomer of **22**, namely **25**. The basis for this assignment is the observation that organoborates situated in a C_4B -unsaturated ring display their ^{11}B signal between -8.0 and -17.0 ppm and specifically **26** absorbs at -15.3 ppm [25]:

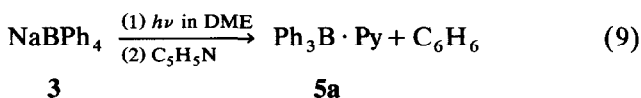


The only other signal unaccounted for develops and then decays at 5.9 ppm; its possible origin will be considered later.

2.4.2. Reaction products

Previous and present studies of the photolysis products of **3** have shown that, upon work-up with *O*-deuterioacetic acid, varying proportions of H_2 , HD, D_2 , biphenyl and *m*- and *p*-terphenyl are formed [13,14]. The latter hydrocarbons contained moderate amounts of monodeuteriated isomers.

Irradiations of sodium phenyl (tri-*m*-tolyl)borate (**7**) and sodium phenyl (tri-*p*-tolyl)borate (**8**) individually in DME gave only the corresponding methylbiphenyl and bitolyl as coupling products, **7** giving a 1.1:1.0 ratio of **9** and **10**, and **8** giving a 1.0:2.7 ratio of **11** and **12**. Since no biphenyl (**6**) was found, the photocoupling to produce the biaryls occurs strictly intra-ionically. The photoconversion of these tetraarylborates, to biaryls in the absence of promoters, is under 50%, regardless of the duration of the irradiation. A significant competing reaction, which also consumes the starting borate, is the loss of an aryl group and the formation of Ar_3B . Thus, if the photolysate solution of **3** is treated with dry pyridine before hydrolytic work-up, **5a** can be isolated (eqn. (9)):

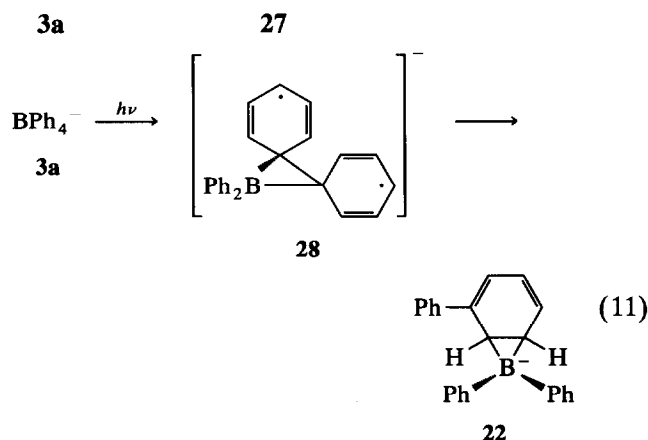
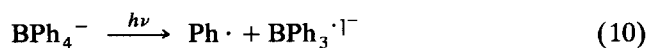


3. Discussion

The chief questions posed by these findings are as follows: what is the origin of the reducing power of irradiated arylborane complexes and what are the prevailing mechanisms for these photoreductions of metal ions? In attempting to answer these questions, we should consider, in particular (1) the detailed study of the irradiation of sodium tetraarylborates and (2) the closely related situation, the irradiation of copper(I) tetraphenylborate.

3.1. Reducing action of tetraarylborates

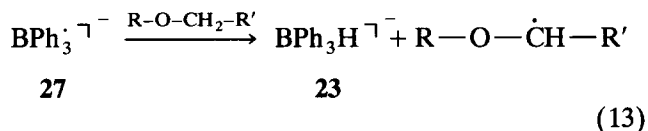
In this and previous studies it has been shown that irradiation of NaBPh_4 in ethers produces borohydrides [13–15]. The generation of these well-known reducing agents would readily explain why metal ions are reduced to metals by the photolysis of arylborates, but the question persists as to whether the actual reducing agent toward metal ions might not be some precursor of the borohydrides. In the present work we have found that irradiation of the BPh_4^- anion (**3a**) does initially produce the triphenylborane radical anion (**27**) and presumably the phenyl radical as shown in the first of the following equations; previously it had been shown that **3a** can also photoisomerize to **22**, most probably via bridging intermediate **28** (eqn. (11)) [15]:



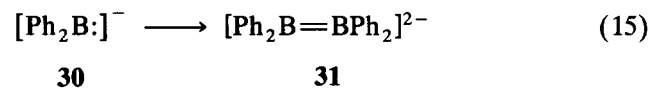
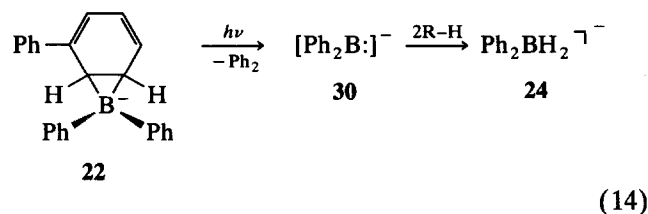
The necessity of such bridging for the photoisomerization is clear from two findings: (1) the photocoupling to yield biaryls is strictly intraionic; (2) the spiroborate **17**, where such a bridging intermediate could form only with great strain [1], does not undergo such photocoupling to yield an *o,o'*-quaterphenyl precursor.

Now there is ample evidence that persistent radical anion **27*** and intermediate **22** are themselves strong reducing agents, capable of reducing metal ions. Trimesitylborane radical anion (**29**) was shown in this study to reduce cupric ion to metal and others have used **29** to reduce C=C and C–Br bonds [27]. Addition of cupric ions to solutions containing **22** also leads to copper reduction. Furthermore, it is most probable that **27** is the precursor both to Ph_3B (**5**) and to the BPh_3H^- anion (**23**). By donating its electron for C–O bond cleavage of the ether solvent, ** **27** would be

converted into **5** (eqn. (12)) and, by photo-assisted H-atom abstraction, **23** would be formed (eqn. (13)):

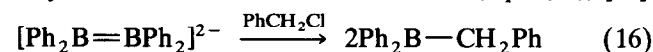


Monitoring of the photolysis of **3** over time has now shown that biphenyl (largely undeuterated from THF solutions upon work-up with DOAc) and $[\text{Ph}_2\text{B}]^-$ anion (**24**) are ultimately formed. These products could be considered to have arisen from photo-elimination of the diphenylborate(I) anion (**30**) from **22** and the abstraction of hydrogen atoms by **30** from the solvent (eqn. (14)):



If it were an intermediate, **30** might well have a linear Ph–B–Ph bonding and exist in the triplet state, as is the case with the isoelectronic diphenylcarbene [29]. If **30** could dimerize (**31**) (eqn. (15)), such an intermediate might persist in solution as a singlet, since the 1,1,2-trimesityl-2-phenyl-substituted analog of **31** has recently been synthesized and found to be stable as its lithium salt, $[\text{Li}(\text{OEt}_2)]_2^{2+} [\text{Mes}_2\text{B}=\text{B}(\text{Mes})\text{Ph}]^{2-}$ (**32**) [30]. We therefore scrutinized the ^{11}B NMR spectrum of the photolysate solution of **3** and could observe a singlet at 5.9 ppm that we could not assign to the known boron-containing products. The ^{11}B signal of **32** occurs at 24.7 ppm and that of $[\text{R}_2\text{C}=\text{BR}_2']^-$ systems between –2.42 and 40 ppm; such chemical shifts can vary by 5–10 ppm pending upon the specific cation and solvent. Thus the signal at 5.9 ppm might indicate the presence of **31**.

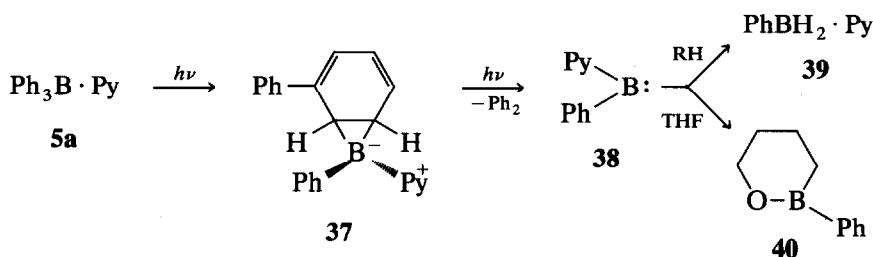
Chemical evidence consistent with the persisting presence of **30** or **31** in solution is the formation of benzyl(diphenyl)borane when benzyl chloride is added to the photolyzed solution of **3** (eqn. (16)) and the evolution of substantial portions of D_2 when the photolyzed solution is treated with DOAc (eqn. (17)) [14]:



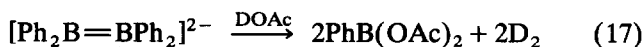
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* In the absence of light and oxygen, **27** with Na^+ or K^+ gegeions is stable in solution for weeks at 25°C [26].

** Radical anions can cleave ethers by SET processes. Heating $2\text{Li}^+ \text{Ph}_2^{2-}$ in THF leads to the formation of 1-butanol [28].



Scheme 1.

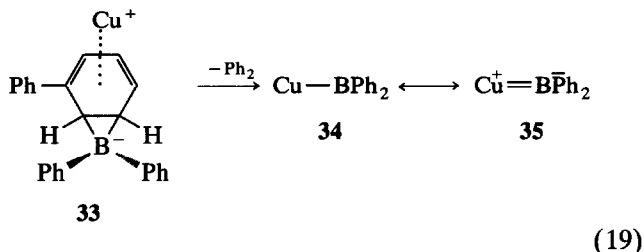
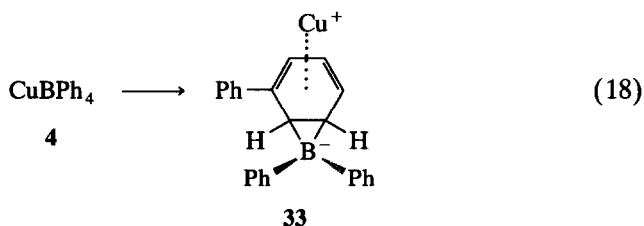


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In conclusion, a variety of reducing agents capable of producing metals from metal ions are generated by the photolysis of **3**, namely $[\text{BPh}_3]^-$ (**27**), bicycloborate (**22**), $[\text{Ph}_2\text{B}]_n^{n-}$ (**30** and **31**), BPh_3H^- (**23**) and $\text{BPh}_2\text{H}_2^{2-}$ (**24**). However, to the best of our knowledge, **27**, **22** and possibly **30** are formed directly by primary photoprocesses and thus are the most likely reductants toward metal salts.

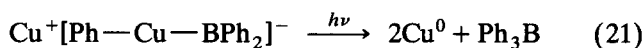
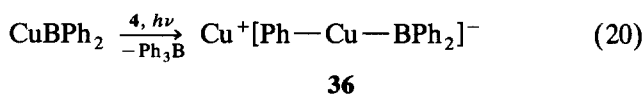
3.1.1. The irradiation of copper(I) tetraphenylborate (4)

That neither copper(I) nor copper(II) ions play a primary role in these photoreductions is evident from the photo-inertness of ether solutions of CuX and $\text{Cu}(\text{acac})_2$ to prolonged irradiation at 254 nm. Accordingly, copper(I) tetraphenylborate (**4**) most likely first undergoes a photoisomerization to **33** (eqn. (18))*, which might thereupon undergo an elimination of CuBPh_2 (**34**):



* That the cuprous ion forms a π complex with the 1,3-cyclohexadienyl unit in **33** and with a phenyl group in **4** itself is made most probable by the X-ray crystal structure of $\text{Rh}[\text{P}(\text{OMe})_3]_2\text{BPh}_4$, in which the rhodium ion is so bonded [31]. The slowness with which $\text{Cu}[\text{P}(\text{OEt})_3]_4\text{BPh}_4$ underwent photoreduction may be due to the absence of $\text{Cu}^+ \cdots \text{PhBPh}_3$ coordination.

Such a cuprous diphenylboride might owe its relative stability to its carbene-complex-like character (**35**), where copper provides $d_\pi-p_\pi$ electron donation to the boron $2p_z$ orbital. ** Thereupon, **34** might undergo phenylation to form cuprate **36** (eqn. (20)) and reductive elimination to yield the following products (eqn. (21)):



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3.1.2. Reducing action of triorganylboranes

Although the photoreductants generated from arylborates are now well understood, what occurs in the photoreductions of R_3B is not. Simple irradiation of Ph_3B (**5**) in dry ether leads to little or no reaction [7]; the addition of water or alcohols gives modest yields of biphenyl or dihydrobiphenyls [8]. Apparently, oxyborates formed photochemically, $[\text{ROBPh}_3]^-$, undergo the aforementioned photoisomerization (eqn. (11)). By contrast, we have observed that $\text{Ph}_3\text{B} \cdot \text{Py}$ (**5a**) in THF undergoes photolysis to produce, upon treatment with HOAc, biphenyl (**6**), terphenyls and hydrogen gas. Furthermore, some of the THF is found to be cleaved to 1-butanol. The similarity in products to those resulting from photolyzing **3** itself naturally suggests a similar mechanism (Scheme 1). The suggested borenene **38** would be expected to abstract H atoms to yield **39** and insert into THF to produce **40**. The latter reaction has been observed for other photogenerated borenenes [33].

Therefore the reducing action of uncomplexed Ph_3B toward metal salts undoubtedly required coordination of the metal salt's anion with **5** to form $\text{A}-\text{BPh}_3^-$ anions and the photoisomerization to intermediates analogous to **22** and **33** for reduction. This mechanism is not applicable, of course, for metal ion reductions by

** In a similar manner, cuprous salts are suggested to stabilize carbenes in copper(I)-catalyzed cyclopropanations with diazoalkanes [32].

$n\text{Bu}_3\text{B}$. Apparently, some kind of alkylative or hydride transfer reduction is operative in this situation.

4. Experimental details

4.1. Starting materials

4.1.1. Sodium tetraphenylborate (3)

The commercial product (Aldrich; purity, 99 + %) was recrystallized from purified 1,2-dimethoxyethane at -78°C to yield **3** solvated with 1 mol of DME. Heating to 125°C yielded unsolvated **3**.

4.1.2. Triphenylborane (5) and triphenylborane-pyridine complex (5a)

This arylborane (**5**) was synthesized by a known procedure and then recrystallized from pure anhydrous diethyl ether, all operations being conducted under a dry oxygen-free nitrogen atmosphere (melting point (m.p.), $146\text{--}147^\circ\text{C}$) [34]. Its adduct with pyridine (**5a**) was formed in ethyl ether solution and recrystallized from warm pyridine-ether solution (m.p., $238\text{--}240^\circ\text{C}$).

4.1.3. Sodium bis(2,2'-biphenylene)borate (17)

This salt was prepared as its tris(1,2-dimethoxyethane) solvate by a known procedure [35].

4.1.4. Sodium (a) and potassium (b) salts of the phenyl(tri-*m*-tolyl)borate (7) and phenyl(tri-*p*-tolyl)borate (8) anions

Tri-*m*-tolylborane and tri-*p*-tolylborane were prepared by known procedures [34] in a manner analogous to that employed for triphenylborane. Treatment of each arylborane with 1.1 equivalents of phenyllithium and conversion to the corresponding ammonium phenyl(tritolyl)borate by a known procedure [34] gave a borate complex from which either the sodium or potassium salts could be generated [35].

4.1.5. Sodium phenyl(tri-*m*-tolyl)borate (7)

This is a colorless solid. Anal. Found: C, 84.25; H, 6.97. $\text{BC}_{27}\text{H}_{26}\text{Na}$ calc.: C, 84.39; H, 6.82%. ^1H NMR ($\text{DMSO-}d_6$): 2.14 (s, 9H), 6.68 (m, 5h), 6.9 (d, 2H), 7.0–7.2 (br. m, 10) ppm.

4.1.6. Sodium phenyl(tri-*p*-tolyl)borate (8)

This is a colorless solid. Anal. Found: C, 84.45; H, 7.03. $\text{BC}_{27}\text{H}_{26}\text{Na}$ calc.: C, 84.39; H, 6.82%. ^1H NMR ($\text{DMSO-}d_6$): 2.17 (s, 9H), 6.68 (s, 2H), 6.82 (s, 5H), 6.9–7.2 (br. m, 10H) ppm.

4.1.7. Metal salts

The cupric bromide, nickel bromide, zinc iodide and stannous chloride were purchased as anhydrous

reagents of 99% or greater purity. They were employed as such and were transferred under anhydrous conditions. The anhydrous cupric and nickel acetylacetonates were purified by recrystallization of commercial samples from toluene.

4.1.8. Preparation of copper(I) tetraphenylborate (4) and its triethyl phosphite complex (4a)

This salt was prepared for the first time by the interaction of LiBPh_4 with a suspension of CuBr_2 in ether over the course of several weeks [19]. The following procedure proved more expeditious.

To a solution of 6.85 g (20.0 mmol) of NaBPh_4 in 100 ml of purified DME were added portionwise 2.25 g (10.0 mmol) of CuBr_2 (previously pulverized and dried at $50\text{--}70^\circ\text{C}$ *in vacuo*). The reaction mixture turned yellow as it was stirred for 48 h at 25°C , whereupon the DME was removed *in vacuo*. The solid residue was extracted, under nitrogen, first with three 25 ml portions of dry deoxygenated hexanes and then with three 25 ml portions of dry deoxygenated diethyl ether. The combined organic extracts were treated with 5 ml of anhydrous pyridine and the colorless precipitate of the triphenylborane-pyridine complex (3.05 g (95%)) was collected, recrystallized and identified by its melting point and IR spectrum. Evaporation of the filtrate from these organic extracts yielded 0.74 g (96%) of biphenyl. Further extraction of the reaction residue by three 50 ml portions of anhydrous THF and evaporation of these extracts under nitrogen yielded 3.26 g (85%) of copper(I) tetraphenylborate as a sky-blue amorphous solid.

A solution of 1.91 g (5.0 mmol) of CuBPh_4 in 30 ml of THF was treated with 3.45 ml (20 mmol) of triethyl phosphite at 20°C . The reaction solution was stirred for 2 h at 20°C , diluted with 30 ml of hexanes, concentrated *in vacuo* and cooled to 0°C to precipitate the colorless crystalline complex almost quantitatively. The known $\text{Cu}(\text{P}(\text{OEt})_3)_4\text{BPh}_4$ [36] was recrystallized from a 95% ethanol-chloroform mixture (8:2, v/v). ^1H NMR (CDCl_3): 1.5 (t, 36H), 3.95 (br. m, 24H), 6.85 (t, 4H), 7.05 (t, 8H), 7.45 (br. m, 8H).

4.2. Inert reaction media

All preparations and reactions involving air- and moisture-sensitive organometallic intermediates were conducted under an atmosphere of dry oxygen-free nitrogen with adherence to published procedures [37]. Solvents of reagent grade were used in all reactions. Specifically, peroxides were removed from DME and THF by passing such solvents through a column of neutral alumina under nitrogen. The eluted solvents were then allowed to reflux over LiAlH_4 for 5 h and

then distilled under an atmosphere of dry nitrogen just before use.

4.3. Instrumentation

All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded either on a Perkin-Elmer model 457 or model 238B grating spectrophotometer and the samples were prepared in solution, as KBr pellets or as mineral oil mulls. The proton (^1H NMR) spectra were measured with a Varian model EM 360 spectrometer and with a Bruker 300-MHz instrument equipped with an Aspect 3000 computer. The values are reported on the δ scale in parts per million with reference to internal tetramethylsilane, followed by the relative proton intensities. Mass spectra were determined either with an MS/902 CIS 2 instrument coupled with a V6 Datasystem 2040 computerized recorder, with a Varian MAT model CH5 spectrometer or with a Hewlett-Packard model 5993 GC/Ms apparatus equipped with capillary GC columns (OV-101). Vapor-phase chromatographic analysis (GC) and isolations were carried out on an F&M model 720 chromatograph equipped with a $6\text{ ft} \times 0.125$ in column of 10% SE-30 silicone gum rubber on Chromosorb P or with a Hewlett-Packard gas model 588A chromatograph equipped with GC columns packed with OV-101. Liquid chromatographic analyses were performed with a Perkin-Elmer model 400 HPLC apparatus, equipped with silica columns ($10\ \mu\text{m}$) coated with LCI-100. Irradiations were conducted in quartz vessels for the organic solutions of sodium tetraphenylborate, under anhydrous conditions where both solvent and reaction vessel were maintained under an atmosphere of dry nitrogen, by means of a Rayonet model 100 photochemical reactor. The reactor was provided with a cylindrical array of lamps emitting 254 nm irradiation and the cylindrical cavity of the lamp bank had a diameter of 24 cm.

4.4. Analytical procedures for photochemically deposited metals

4.4.1. Quantitative determination of pure metals

The metal deposited on the wall of the quartz phototube as well as any metal powder lying free at the bottom of the tube were carefully separated, under an argon atmosphere, from the photolysis solution and washed, in turn, with deoxygenated acetone and with water. After drying *in vacuo* the pre-weighed quartz tube was then weighed with its metal contents and the amount of metal formed thus determined.

The amount of metal formed, especially when smaller amounts were involved, could also be deter-

mined by dissolving the washed metal residues described above into 35% aqueous HNO_3 and conducting a complexometric titration on the resulting solution, such as with ethylenediaminetetraacetic acid (EDTA) for copper or nickel [38].

4.4.2. Quantitative determination of copper in the presence of other metals

The codeposition of copper and another metal occurring upon the photolysis of copper salt-metal salt systems required a different analytical procedure from the foregoing. In this situation the total amount of metal deposited was determined by weighing the separated and washed metal residues and the metals then dissolved by digesting for 30 min with 35% aqueous HNO_3 . The solution was then analyzed specifically for copper by the gravimetric method employing benzoin- α -oxime. This method is particularly suitable for the quantitative determination of copper in the presence of other metals, especially zinc [39].

4.4.3. ESCA Examination of some metal mixtures

Some of the binary metal mixtures were examined by ESCA measurements in an attempt to distinguish true alloy formation during the photodeposition from separate deposition of the two metal crystals.

4.5. Photoreduction

4.5.1. Copper(I) tetraphenylborate (4)

Under argon a 1.91 g sample of **4** (5 mmol) in 50 ml of THF was irradiated in a quartz phototube placed in a Rayonet model 100 photoreactor for 8 h at 254 nm. The tube became thickly coated with metallic copper and the photolysate solution had turned red. (Decanting this solution into a fresh phototube and continuing the irradiation led to the further deposition of copper metal.) By an EDTA titration the amount of copper deposited in the first irradiation was shown to be 76%. Examination of the concentrated photolysate solution by ^1H NMR spectroscopy showed the presence of biphenyl and triphenylborane (in about a 1:2 ratio) as the only discernible byproducts. The copper deposited on the phototube was confirmed to be Cu^0 by the high electrical conductivity it exhibited.

4.5.2. Tetrakis(triethylphosphite)copper(I) tetraphenylborate (4a)

This complex showed a greater resistance to photoreduction than **4** did. Although irradiation of a 2 mmol sample in 50 ml of DME gave a shiny copper coating in 4 h, this film was thin and redissolved upon standing. Furthermore, a similar sample dissolved in 50 ml of THF turned red after 18 h but there was no copper metal deposited.

4.5.3. Individual metal salts

A variety of metal salts were reduced to metals by the combined thermal and photochemical reducing action of the tetraphenylborate anion (**3**). Typically, a 5.0 mmol sample of the metal salt was combined with NaBPh₄ (5.0 mmol of **3** for univalent metals such as Cu⁺; 10.0 mmol of **3** for divalent metals such as Cu²⁺, Ni²⁺, Zn²⁺ and Sn²⁺) in 50 ml of purified DME and the solution irradiated under argon in the aforementioned photoreactor at 254 nm. Typical results are presented in Table 1. The nature of the anion can have a marked effect on the rate of the photoreduction. It is thus far clear that iodides reduce more rapidly than bromides or acetylacetonates (*cf.* Table 1, Nos. 1 and 2, and Nos. 6 and 7). In fact, adding small amounts of diiodine to CuBr₂ accelerates its photoreduction markedly. There are also indications that acetylacetonates photoreduce more efficiently than bromides, as will be seen in the photoreduction of cupric ion by Ph₃B · Py (**5a**) (*cf. infra*).

4.5.4. Binary mixtures of metal salts

Experiments were carried out in an attempt to deposit alloys by the simultaneous thermal and photochemical reduction of mixtures of metal salts by the tetraphenylborate anion. For divalent salts of Cu, Ni, Co, Zn and Sn, typically 2 mmol mixtures of two metal salts (4.0 mmol of both metals) were combined with 8.0 mmol of NaBPh₄ in 80 ml of DME and the resulting solution irradiated in the quartz phototube. The total amount of the metal deposited and its content of copper were determined by the procedures described above. The binary salt mixtures so reduced, the yields of metal and their proportions are given in Table 2. For Table 2, No. 6, the copper-zinc powder was examined by ESCA; more than 60% of the sample consisted of a Zn-Cu alloy and the balance of the particles were Zn and Cu metals.

4.5.5. Copper(II) acetylacetonate by triphenylborane-pyridine complex (**5a**)

A suspension of 1.28 g (4.0 mmol) of the cupric salt in 60 ml of THF was admixed with 0.51 g (2.0 mmol) of **5a** and the irradiation at 254 nm for 12 h. The deposited copper metal was 60% of that available. Analysis of the photolysate solution by thin layer chromatography and ¹H NMR spectroscopy confirmed the presence of unreacted **5a**, biphenyl and phenyl boron diacetylacetonate. The latter was separated from **5a** and biphenyl by removing the volatiles from this solution *in vacuo* and then extracting the residue with hexanes to remove the biphenyl and with CDCl₃ to form a solution of PhB(acac)₂. ¹H NMR (CDCl₃): 2.2 (s, 12H), 5.6 (s, 2H), 7.5 (t, 2H), 7.6 (t, 1H), 8.25 (d, 2H) ppm.

It is noteworthy that the attempted photoreduction of CuBr₂ by **5a** under the foregoing conditions failed to deposit any copper metal.

4.5.6. Copper(II) acetylacetonate by triphenylborane (**5**)

A similar irradiation of 0.512 g (2 mmol) of the copper salt and 1.0 g (4.1 mmol) of **5** in 60 ml of THF for 8 h led to the deposition of 99% of the available copper, as determined by the EDTA titration. Again, the photolysate solution contained biphenyl, PhB(acac)₂ and about 50% of unreacted **5**.

4.5.7. Copper(II) acetylacetonate by tri-*n*-butylborane

Irradiation of an initially blue solution of 1.30 (5.0 mmol) of the copper salt and 10 mmol of ⁿBu₃B in 60 ml of THF for 12 h led to the deposition of 80% of the available copper metal. The organic by products were not investigated.

4.5.8. Copper(II) acetylacetonate by trimesitylborane (**21**) or by the sodium-trimesitylborane adduct

Irradiation of 0.512 g (2 mmol) of the copper salt and 1.85 g (5 mmol) of **21** in 60 ml of THF for 18 h gave no reduction, no copper deposition and complete recovery of **21**.

Treatment of **21** with an excess of sodium metal in THF led to the generation of the blue sodium adduct [25]. Then one equivalent of CuBr₂ in THF was added and the blue solution immediately became pale green, signaling reduction to cuprous acetylacetonate. Subsequent irradiation for 18 h gave no deposition of copper metal.

4.6. Thermal reductions

4.6.1. Sodium phenyl(tri-*m*-tolylborate) (**7**) and copper(II) bromide

The interaction of 3.84 g (10 mmol) of **7** and 1.12 g (5 mmol) of CuBr₂ in 50 ml of purified DME was conducted for 24 h at 20°C. Under nitrogen, the reaction mixture was freed of solvent *in vacuo* and the residue extracted with four 25 ml portions of dry deoxygenated hexanes. The combined hexane extracts were treated with 5 ml of dry pyridine and the precipitated triarylborane-pyridine complexes filtered off. Analysis of the filtrate by gas chromatography revealed the presence of *m,m'*-bitolyl and *m*-methylbiphenyl in a 2.1 : 1.0 ratio and the absence of any trace of biphenyl.

4.6.2. Sodium phenyl(tri-*p*-tolylborate) (**8**) and copper(II) bromide

Similarly, the interaction of **8** and CuBr₂ led only to the formation of *p,p'*-bitolyl and *p*-methylbiphenyl in a 2.5 : 1.0 ratio.

4.6.3. Sodium bis(2,2'-biphenylene)borate (17) and copper(II) bromide

Similarly, the interaction of 17 and CuBr₂ led to the formation of *o,o'*-quaterphenyl (19) and biphenyl (6). The protodeboronation of the reaction mixture with glacial acetic acid had to be conducted at reflux for 20 h for efficient conversion to these hydrocarbons.

4.7. Photochemical redox reactions

4.7.1. Sodium tetraphenylborate (3)

Irradiation of 1.0 g (2.92 mmol) of 3 in 50 ml of THF for 24 h gave a deep-red solution, which turned colorless when treated with 98% *O*-deuterioacetic acid and evolved 37% of a gas, which was essentially pure HD. The reaction mixture was concentrated under nitrogen by distillation to a clear pale-yellow solution. This solution was heated at reflux for 16 h and then diluted with water. The mixture was extracted with 4–15 ml portions of ether, the combined ether extracts washed with 10% aqueous NaOH and with water, and the resulting solution dried over solid MgSO₄. After solvent removal the residue was analyzed by quantitative gas chromatography using bibenzyl and *o*-terphenyl as standards. In this manner it was shown that the yield of biphenyl was 37% and that of *p*-terphenyl was 7%. By sublimation of this residue and recrystallization from methanol, pure samples of biphenyl and *p*-terphenyl were isolated. The mother liquor was shown by GC to contain *m*-terphenyl and unknowns. By preparative GC a pure sample of *m*-terphenyl was isolated. The biphenyl was shown to be about 5% monodeuterated.

4.7.2. Sodium phenyl(*tri-m-tolyl*)borate (7)

A similar irradiation of 2.50 mmol of 7 in 50 ml of THF gave a 34% conversion to the biaryls, *m,m'*-bitolyl and *m*-methylbiphenyl, in a 1.0:1.1 ratio. Again, hydrogen gas was evolved when the photolysate solution was treated with glacial acetic acid.

4.7.3. Sodium phenyl(*tri-p-tolyl*)borate (8)

A similar irradiation of this isomeric borate led to a 40% conversion only to the biaryls, *p,p'*-bitolyl and *p*-methylbiphenyl, in a 2.7:1.0 ratio.

4.7.4. ¹¹B NMR spectral monitoring of the photochemical reaction of sodium tetraphenylborate (3) over time [40*]

A sample of 126 mg of 3 in 2.5 ml of DME was placed in a quartz tube (10 mm outside diameter) under argon and irradiated in the photoreactor. Periodic examination by ¹¹B NMR spectroscopy revealed the following.

(1) After 75 min a new singlet appeared at –26.5

ppm, which was about 20% the intensity of the singlet of 3 at –6.2 ppm.

(2) After 20 h the peak at –26.5 ppm was 275% the intensity of the peak at –6.2 ppm and new absorptions had developed (ppm, multiplicity, *J*(¹¹B–H), % of peak at 6.2 ppm): –16.7, s, 0, 20; –15.1, t, 77, 40; –8.0, d, 80, 190 and 5.9, s, 0, 30. The doublet and triplet could be decoupled into singlets; under the singlet at –26.5 ppm there might have been a partially obscured quadruplet.

(3) After 88 h the peak at –6.2 ppm had disappeared, the singlets at 5.9, –26.5 and –16.7 ppm and the doublet at –8.0 ppm were low in intensity and the only prominent signal was the triplet at –15.1 ppm (ten to 12 times the intensity of any other signal).

4.7.5. ESR Spectral monitoring of the photochemical reactions of sodium tetraphenylborate (3)

Irradiated samples of 3, either in ether solutions as a 1:1 complex with 15-crown-5-ether or in the solid state, were examined by ESR spectroscopy using an X-band Varian model V-4000 ESR spectrometer.

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