Radical-Forming Electron-Transfer Reactions Involving Main-Group Organometallics

Wolfgang Kaim

Institut für Anorganische Chemie, Niederurseler Hang, D-6000 Frankfurt am Main 50, West Germany

Received May 8, 1984 (Revised Manuscript Received March 20, 1985)

The notion that molecules react preferentially by electron pair mechanisms—supported by the quantum mechanical phenomenon of spin pairing—has pervaded the field of organic and organometallic chemistry for a long time. Textbooks illustrate that for reactions proceeding at ambient temperatures in solution and in the absence of intense irradiation, the process of intermediate bond breaking is mostly concerted or polar ("ionic"). Homolytic cleavage, on the other hand, is thought to be a mechanism typical of high temperature or photoinduced reactions.

In particular, the exchange of a *single* electron between closed-shell, diamagnetic molecules, so-called "single electron transfer",[1] has sometimes been viewed as a rather exotic phenomenon, occurring thermally only between electron-poor and electron-rich species. Since organometallics, including hydrides, are electron rich[2,3] and can be used as reductants, single electron transfer may occur with suitable acceptors according to theoretical models[4] such as the Marcus theory. In fact, persistent[5] radicals have been reported as products of several such reactions, starting with the pioneering work of Russell, Janzen, and Strom in 1964,[6,7] followed by that of House[8] and recently emphasized again by Ashby and co-workers in a series of communications.[9] The connection between the structure of the reactants, the proposed mechanism, and the nature and proper identity of these radical products has not always been established clearly, often due to the lack of good spectroscopic information.

It is the purpose of this Account to give a brief outline of the concept of single electron transfer (SET) and to explain the occurrence of long-lived radical complexes in reactions of common organometallics. The paramagnetic products can be identified by high-resolution electron spin resonance (ESR) and other powerful spectroscopies such as electron nuclear double resonance (ENDOR[10]). These spectroscopic studies make it possible to relate SET with the structure and coordination properties of the reactants.

Some "Disturbing" Reaction Products

During studies on the electronic structures of early main-group organometal complexes with unsaturated nitrogen ligands we became interested in the preparation of organomagnesium coordination compounds such as 1. Although the use of α-diimine ligands as color indicators in the analytical determination of "carbanionic" reagents[11] suggested the formation of
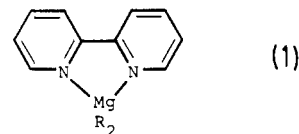
coordination compounds, workup of the reaction mixtures from, e.g., 2,2′-bipyridine and Grignard-type reagents, did not yield defined complexes. In fact, unsuccessful attempts to synthesize 1 had already been reported by Coates and Green,[12] who, in contrast, had obtained well-behaved zinc and beryllium analogues. In an effort to gain information on the kinds of products formed we tried to study these reaction mixtures by NMR. Unusually broad lines led us to perform the reactions in an ESR spectrometer, where well-resolved ESR spectra were recorded. Detailed analyses of the hyperfine structures did not suggest "free" anion radicals but provided evidence for some coordination (2) with electrophilic organomagnesium species;[13] later studies demonstrated that these radical complexes may also be generated via "conventional" pathways, viz.,

(1) Although there are some reservations concerning the usefulness of the prefix "single" in addition to the term "electron transfer", this now widely adapted acronym "SET" will be used throughout the article.

(2) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(3) For electrochemical oxidation potentials of "carbanions", cf.: (a) Jaun, B.; Schwarz, B.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. (b) Holm, T. *Acta Chem. Scand. Ser. B* **1983**, *B37*, 567.

(4) For a comprehensive review on the use of electron transfer theories in organic chemistry, cf.: Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79. Cf. also: *Acta Chem. Scand. Ser. B* **1984**, *B38*, 439.

(5) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

(6) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.

(7) For an even earlier report, cf.: Brown, H. W.; Jones, R. C. *J. Chem. Phys.* **1962**, *37*, 1571.

(8) House, H. O.; Chu, C. Y. *J. Org. Chem.* **1976**, *41*, 3083. House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.

(9) (a) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 7779; **1981**, *103*, 5623. (b) Ashby, E. C.; Goel, A. B.; DePriest, R. N.; Prasad, H. S. *J. Am. Chem. Soc.* **1981**, *103*, 973. (c) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 4783. (d) Ashby, E. C.; Goel, A. B. *J. Organomet. Chem.* **1981**, *221*, C15. (e) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1879. (f) Ashby, E. C.; Goel, A. B.; Park, W. S. *Ibid.* **1981**, *22*, 4209. (g) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1981**, *22*, 4355. (h) Goel, A. B.; Ashby, E. C. *J. Organomet. Chem.* **1981**, *214*, C1. (i) Ashby, E. C.; Goel, A. G. *J. Org. Chem.* **1981**, *46*, 3934. (k) Ashby, E. C.; Goel, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 4983. (l) Ashby, E. C.; Argyropoulos, J. N.; Meyer, G. R.; Goel, A. B. *Ibid.* **1982**, *104*, 6788. (m) Ashby, E. C.; Coleman III, D. T.; Gamasa, M. P. *Tetrahedron Lett.* **1983**, *24*, 851. (n) Ashby, E. C.; Park, W. S. *Ibid.* **1983**, *24*, 1667.

(10) Kurreck, H.; Kirste, B.; Lubitz, W. *Angew. Chem.* **1984**, *96*, 171; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 173.
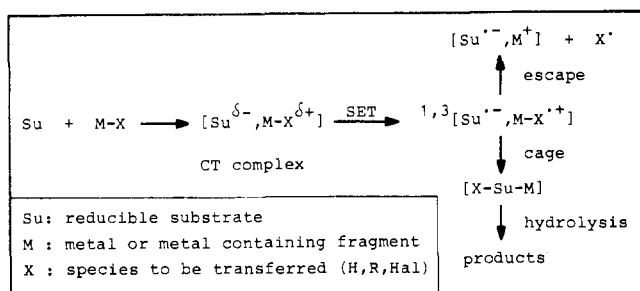
(11) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(12) Coates, G. E.; Green, S. I. E. *J. Chem. Soc.* **1962**, 3340.

(13) (a) Kaim, W. *Angew. Chem.* **1982**, *94*, 150; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 140; *Angew. Chem. Suppl.* **1982**, 289. (b) Kaim, W. *J. Organomet. Chem.* **1981**, *222*, C17. (c) Kaim, W. *J. Am. Chem. Soc.* **1982**, *104*, 3833.

Wolfgang Kaim studied chemistry in Konstanz and Frankfurt and received his Ph.D. in 1977, working with Hans Bock. After a postdoctoral year with F. A. Cotton at Texas A&M University, he returned to Frankfurt. He was appointed Privatdozent in 1982 and in the same year was awarded the Karl Winnacker Fellowship. His interests encompass electronic structures and electron-transfer reactivity of organic, organometallic, and inorganic compounds.

Scheme I

Su: reducible substrate
M : metal or metal containing fragment
X : species to be transferred (H,R,Hal)

NMR signals;[18] we found[17,19a] that the reaction solutions display well-resolved ESR spectra, indicating the formation of "triple ions" which had been obtained previously by Al-Baldawi and Gough in another "conventional" procedure (4).[20]

$$(4)$$

paramagnetic open-shell reductants such as alkali metals could be used to introduce the unpaired electron (2).
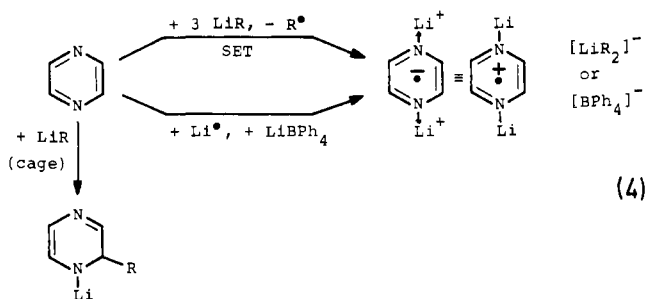

$$(2)$$
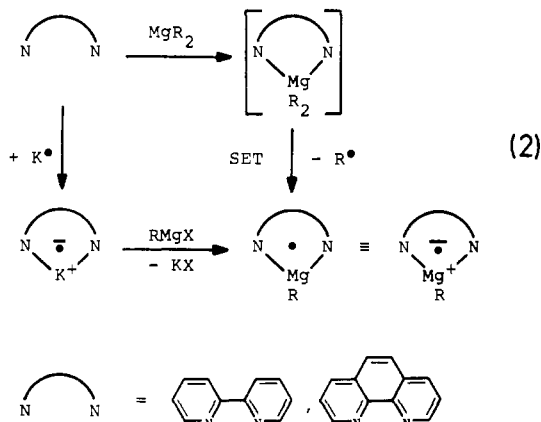
Similar attempts to prepare organoaluminum complexes of these unsaturated chelate ligands proved to be frustrating; although stable complexes (N͡N)·AlR$_3$ can be obtained, they often tend to decompose yielding colored products.[14] In particular, aluminum hydride reagents behaved much like the organomagensium species and, again, ESR analysis of such reaction mixtures revealed the presence of radical complexes.[15] This time identification of these species was aided by the strong interaction between the ^{27}Al nucleus ($I = {}^5/_2$; 100%) and the unpaired electron. Some of these radical complexes had been obtained previously by conventional procedures (3).[16]

$$(3)$$
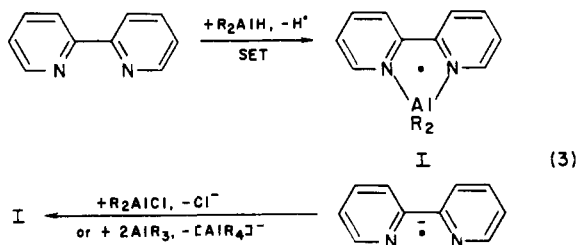
A third such case occurred during investigations with the small bridging ligand pyrazine (1,4-diazine):[17] The reaction of pyrazine with phenyllithium to the 1,2-dihydro adduct was reported to yield considerable amounts of tarry products and insufficiently resolved

The Electron-Transfer Mechanism

The explanation of "non-conventional" pathways in reactions 2–4 by thermal "single electron transfer" deserves comment. In the reaction of an electron-poor substrate Su with an organometallic (or hydridic) reductant M–X, consider the mechanistic sequence shown in Scheme I. Prior to full electron exchange, a donor–acceptor complex, Su–M–X, is formed in which electrons are transferred in excited states of the complex, giving rise to characteristic charge transfer bands in the absorption spectrum. The structural arrangement of the complex

$$Su \rightarrow M^+ \leftarrow X^-$$

involves a diamagnetic metal bridging two organic nucleophiles before electron transfer and resembles in many ways the transition state of an "inner-sphere" redox reaction of metal complexes. There a nucleophilic *ligand L* bridges two metal centers M and M′

$$M \leftarrow L \rightarrow M'$$
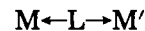
to bring about electron exchange between those two centers.[21] Many reactions between electron-poor substrates and electron-rich organometallics stop at this stage and require additional activation, e.g., irradiation into the charge-transfer band, for further transformation.[2]

Complete transfer of an electron can then generate in a solvent cage the radical anion of the substrate and the radical cation of the donor, the organometallic compound in Scheme I. Pairs of oppositely charged radical ions[22] are usually not persistent, however; their formation can be demonstrated by trapping experiments in matrices and by detection of their triplet ESR spectra.[23] Transient photogenerated pairs of radical ions may also be studied in solution by using the CID-

(14) Thiele, K. H.; Brüser, W. *Z. Anorg. Allg. Chem.* **1967**, *349*, 33; Lehmkuhl, H.; Kobs, H. D. *Liebigs Ann. Chem.* **1968**, *719*, 11.

(15) (a) Kaim, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 783. (b) Kaim, W. *J. Am. Chem. Soc.* **1984**, *106*, 1712. (c) Lubitz, W.; Kaim, W., unpublished results.

(16) Kaim, W. *J. Organomet. Chem.* **1980**, *201*, C5; **1981**, *215*, 325, 337.

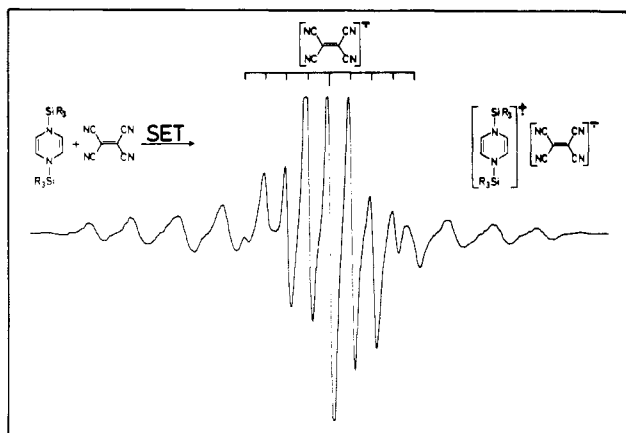(17) Kaim, W. *Angew. Chem.* **1983**, *95*, 201; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 171.

(18) van der Stoel, R. E.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 116.

(19) (a) Kaim, W. *Angew. Chem.* **1982**, *94*, 150; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 141; *Angew. Chem. Suppl.* **1982**, 298. (b) Kaim, W.; Lubitz, W. *Angew. Chem.* **1983**, *95*, 915; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 892; *Angew. Chem. Suppl.* **1983**, 1209.

(20) Al-Baldawi, S. A.; Gough, T. E. *Can. J. Chem.* **1970**, *48*, 2798.

(21) Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970.

(22) The term "radical ion pair" is confusing because it has been used in the sense of "radical ion-pair" (cf. ref 32) and "radical-ion pair" (cf. Figure 1). In order to avoid confusion, the term "radical complex" is recommended for the former species, this would also include "triple ions", irrespective of their overall charge (4).

(23) Emori, S.; Weir, D.; Wan, J. K. S. *Chem. Phys. Lett.* **1981**, *84*, 512.

Scheme II

arated pair of radical ions in Figure 1.[26]

After their generation, the pairs of radical ions may follow one of the radical pair alternatives (Scheme I), according to their spin state.[24] Rearrangement and recombination of electrons inside the solvent cage yield the diamagnetic cage products. Escape of a radical X· into the solution, where it may be scavenged by the solvent or dimerize, disproportionate, induce polymerization, or recombine to form "secondary" cage products, leaves behind a radical ion complex[22] in the doublet state, the escape product (Scheme I). Depending on the thermodynamics and kinetics of the reaction,[4] these escape products are formed in widely varying amounts,[29,30] the diamagnetic products being reductively alkylated, arylated, or hydrogenated substrates (4; Scheme II).[15] Since paramagnetic species are easily detected by ESR they used to be taken as evidence for an electron transfer reaction. Alternative mechanisms of radical formation in such reactions have been discussed recently,[4,39] invoking electron transfer from base-generated anions or dianions. The following examples illustrate the kinds of species produced and the conditions of their formation.
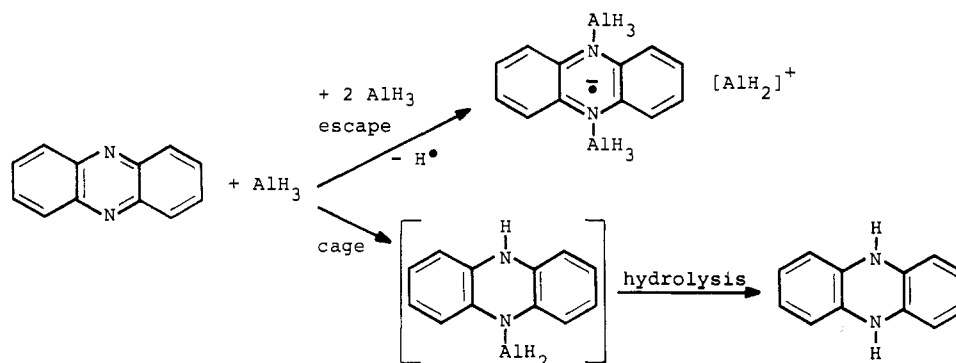
Figure 1. Single electron exchange is observed in the reaction of 1,4-bis(trialkylsilyl)-1,4-dihydropyrazines with TCNE, in agreement with their redox potentials.[26] A typical ESR spectrum in CH_2Cl_2 shows overlapping spectra of the individual radical ion components, indicating the presence of solvent-separated pairs of the two oppositely charged radical ions. Note the characteristic lack of inversion symmetry because of slightly different g values of the two paramagnetic species.

NP effect[24] or fast techniques such as picosecond laser spectroscopy.[25]

Only in very few instances (cf. Figure 1)[26] are *both* radicals persistent enough to be observed simultaneously as ion pairs under stationary conditions; in particular, simple organometallic radical cations are notoriously short-lived because of their tendency to cleave the metal–carbon bond.[2,27,28] It must be noted here that additional features in the ESR spectra of ketyls have recently led Ashby and co-workers to claim radical anion/radical cation pairs as long-lived intermediates in SET reductions with common organometallics such as Grignard reagents[9k] or AlH_3;[9a] however, the doublet character of the spectra reported rather points to the anion radical/organometal complexes described below. ESR spectra of radical cation/radical anion pairs should exhibit either triplet features[23] (strong spin interaction) or superposition of the spectra of the two individual paramagnetic constituents, as shown for a solvent-sep-

Nature of the Substrate

Common electron poor substrates for electron-transfer reactions with main-group organometallics are unsaturated hydrocarbons,[7,9b,20] heterocycles,[6,9c,13,15,19] nitro[6] and carbonyl compounds[6,8,9a,d,g–i,k,30] or imines.[29] When comparing the properties of the substrate in the neutral and in the reduced anionic state, it is important to remember that anion radicals are generally more nucleophilic than the neutral parent molecules, even if the additional electron resides mainly in the π-system and coordination takes place through heteroatom lone pairs in the π-nodal plane. Recent studies of already nucleophilic N-heterocycles have illustrated this enormous difference: The basicities of 2,2′-bipyridines and 1,10-phenanthrolines (cf. 2) increase by about 20 orders of magnitude upon one-electron reduction![31] Accordingly, it has long been known that such anion radicals tend to form tight ion pairs with alkali-metal cations.[32] More recently, the coordination chemistry of anion

(24) Lawler, R. G. *Acc. Chem. Res.* **1972**, *5*, 25. For typical applications cf.: Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 4303. Smith, D. W.; Pienta, N. J. *Tetrahedron Lett.* **1984**, *25*, 915.

(25) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535. Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277.

(26) Kaim, W. *Angew. Chem.* **1984**, *96*, 609; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 613.

(27) Walther, B. W.; Williams, F.; Lau, W.; Kochi, J. K. *Organometallics* **1983**, *2*, 688.

(28) For an exception cf.: Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9.

(29) van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem.* **1983**, *250*, 49.

(30) Razuvaev, G. A.; Abakumov, G. A.; Klimov, E. S.; Gladyshev, E. N.; Bayushkin, P. Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 1128 and papers cited therein.

(31) Krishnan, C. V.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1983**, *105*, 5617.

(32) Sharp, J. H.; Symons, M. C. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M. ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 177.

Table I.
Reduction Potentials E_{red} (V vs. SCE) of Coordination Complexes of Pyrazine (pz) with Some Electrophiles in DMF

compd	E_{red}	compd	E_{red}
pz	-2.06	pz[CpMn(CO)$_2$]$_2$	-1.36
pz(O)$_2$^{a}	-1.62	pz[Cr(CO)$_5$]$_2$	-1.05^c
pz(BEt$_3$)$_2$	-1.50	pz(Li$^+$)$_2$	-0.68^b
		pz(Et$^+$)$_2$	+0.35^b

^{a}Kubota, T.; Nishikida, K.; Miyazaki, H.; Iwatani, K.; Oishi, Y. *J. Am. Chem. Soc.* 1968, *90*, 5080. ^{b}Anodic peak potential (cyclic voltammetry). ^{c}Cathodic peak potential (irreversible process).

radicals has been extended to encompass other electrophiles such as electron-deficient main-group organometal species MR$_n$ or $^+$MR$_{n-1}$[16,30,33,34] and coordinatively unsaturated transition-metal fragments such as metal carbonyls[35,36] and cyclopentadienyls.[37]

Obviously, the redox process affects the coordination properties of the substrate to a great extent. Vice versa, the coordination of electron-transfer substrates with organometallic electrophiles can affect the redox potentials of the substrates, generally facilitating electron transfer. The effect of coordinated electrophiles on the reduction potential of the complex formed is shown in Table I, using 1,4-diazine (pyrazine, pz) as a substrate. This system provides a clear illustration of the effect because double coordination at the nitrogen centers exerts a particularly strong perturbation.[17]

The fact that coordination tends to lower the barrier to electron transfer is most obvious with substrates capable of forming chelate complexes, such as α-diketones, o-quinones, and α-diimines. Therefore, these compounds have been among the favorite systems for electron-transfer studies involving metal electrophiles,[13,15,29,30] as reactions **2** and **3** demonstrate. The reactivity exhibited in sequences such as in (2) or (3) explains why certain organometallic coordination complexes such as **1** or **5** have eluded preparation under
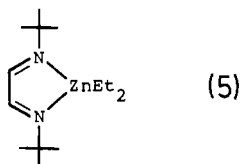
ordinary laboratory conditions;[12,29] chelate coordination lowers the barrier to the "reverse" inner-sphere electron transfer. The effect of chelate coordination may be rationalized as follows: A configuration such as in (6) with coordination number four at the metal center puts the electron-donating metal–carbon (or metal–hydrogen) σ-bonds in optimum position for hyperconjugative (σ/π) interaction with the π-system, triggering subsequent electron transfer. Such σ*/π*-interactions are evident from both ESR[15b] and ETS (electron trans-

(33) Stegmann, H. B.; Ulmschneider, K. B.; Scheffler, K. *J. Organomet. Chem.* 1975, *101*, 145. Stegmann, H. B.; Schrade, R.; Saur, H.; Schuler, P.; Scheffler, K. *Ibid.* 1981, *214*, 197.

(34) (a) Kaim, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1981, *36B*, 677, 1110. (b) Kaim, W. *Chem. Ber.* 1981, *114*, 3789. (c) Kaim, W. *J. Organomet. Chem.* 1983, *241*, 157.

(35) (a) Kaim, W. *Inorg. Chim. Acta* 1981, *53*, L151. (b) Kaim. W. *Chem. Ber.* 1982, *115*, 910. (c) Kaim, W. *J. Organomet. Chem.* 1984, *262*, 171; 1984, *264*, 317. (d) Kaim, W. *Inorg. Chem.* 1984, *23*, 504, 3365.

(36) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* 1979, *181*, 355. Creber, K. A. M.; Ho, T. I.; Depew, M. C.; Weir, D.; Wan, J. K. S. *Can. J. Chem.* 1982, *60*, 1504.

(37) Gross, R.; Kaim, W. *Angew. Chem.* 1984, *96*, 610; *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 614.
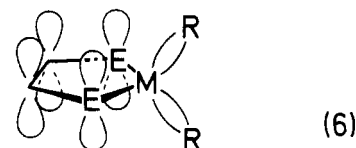
E : donor atom (N, O)
M : metal
R : H, alkyl, aryl, halogen

mission spectroscopy) studies[38] of organometallics.

The chelate arrangement facilitates not only electron transfer but may also determine the composition of the organometallic radical complex formed in the escape process. Thus, the chelating 2,2'-bipyridine forms a neutral 1:1 complex with AlH$_2$ on reduction with AlH$_3$ in THF whereas, under identical circumstances, the isomeric but bridging 4,4'-bipyridine forms a 1:2 complex anion radical with two AlH$_3$ molecules (7).[15b]
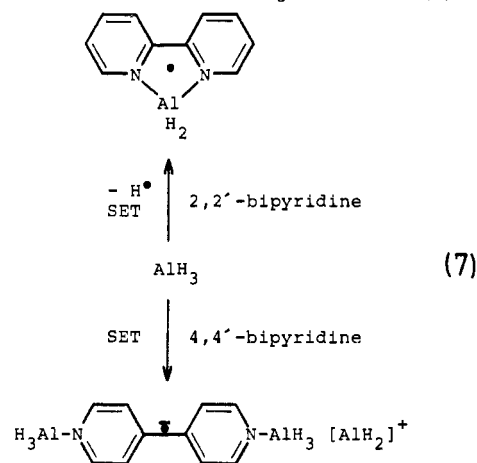
Incidently, the ESR studies of neutral radicals such as in (2) or (3) indicate clearly that they must be formulated as complexes of the ligand radical anion with a cationic metal fragment and not as low-valent metal derivatives.[13,15]

Nature of the Organometallic Reagent

In general, organometallic compounds and hydrides of electropositive metals can serve as electron-transfer agents toward electron-poor substrates.

Alkali Metals. It is not surprising that many reactions leading to radical products have been observed with alkali metal,[6] especially lithium reagents, including alkyls,[7,19a] aryls,[19a] dialkylamides,[39] diorganocuprates,[8] and complex hydrides.[9b,c,i,19] In most cases, the ensuing radicals were presumed to be Li$^+$/anion radical pairs, however, bifunctional compounds such as pyrazine (4) can also form "triple ions"[20] [Li$^+$, Su$^-$, Li$^+$] because of their increased basicity.[19] Table I illustrates that the coordination of two positively charged Li$^+$ ions lowers the reoxidation potential of the radical complex by more than 1 V!

Magnesium. Less reactive, but no less important for the synthetic chemist, are magnesium reagents such as diorganomagnesium compounds MgR$_2$ and, of course,

(38) Giordan, J. C.; Moore, J. H. *J. Am. Chem. Soc.* 1983, *105*, 6541. Giordan, J. C. *Ibid.* 1983, *105*, 6544.

(39) Newkome, G. R.; Hager, D. C. *J. Org. Chem.* 1982, *47*, 601. Scott, L. T.; Carlin, K. J.; Schultz, T. H. *Tetrahedron Lett.* 1978, 4637. A different mechanism for radical formation with lithium dialkylamides has been suggested recently: Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* 1984, *106*, 2450.

Grignard systems RMgX. For the latter, an additional complication for the coordination chemistry arises by the *Schlenk* equilibrium in coordinating solvents
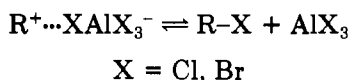
$$2RMgX \rightleftharpoons MgR_2 + MgX_2$$

which provides three magnesium species as potential electrophiles.[3b,40] Still, it has been noted by several workers that certain carbonyl compounds yield radical products on Grignard reduction;[9k,41] the nature of these radicals, especially the fate of the magnesium part, remained a matter of speculation. Avoiding the Schlenk equilibrium, our own studies have been focussing on the species MgR_2 which react in a homogenous fashion.[13] With the bifunctional N-heterocycle pyrazine as an electron-transfer "trap",[17] it is possible to demonstrate by ESR and ENDOR techniques what kinds of organomagnesium radical complexes (8) are formed in reduction processes (Figure 2).

(8)
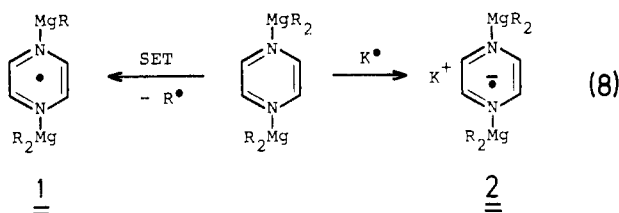
Zinc. Organozinc compounds, although less reactive than their magnesium analogues, have been shown to react at least in part by electron transfer with certain α-diimines.[29] Detailed mechanisms of the reaction have been given, taking into account all the products formed.

Aluminum. Organoaluminum reagents, including hydrides, constitute a very useful class of reductants. They may also serve to illustrate the relationship between coordination and electron-transfer from another point of view. In one respect, aluminum compounds AlX_3 have donating properties because they contain rather labile Al^+-X^- bonds. However, they are also acceptors which can act as strong electrophiles via their unoccupied metal p orbital.

The well-balanced combination of both properties allows a unique dichotomy of electron-transfer reactivity. Compounds such as $AlCl_3$ act as one-electron oxidants toward electron-rich systems[28,42] and as one-electron reductants toward electron-poor species,[43] depending on the substrate *and* on the reaction medium (9)! Evidence has been presented[42] that the one-electron oxidation (9) by $AlCl_3$ in CH_2Cl_2[28] may yield $ClCH_2CH_2Cl$ as coproduct. This would at least formally implicate electron transfer from the electron-rich substrate to the carbocationic system

$$R^+ \cdots XAlX_3^- \rightleftharpoons R-X + AlX_3$$
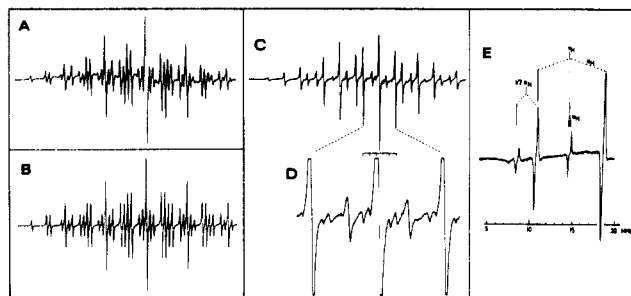
$$X = Cl, Br$$

Figure 2. ESR/ENDOR spectra of radicals formed in reductive processes in the system pyrazine/$MgPh_2$ (8). (A) ESR spectrum of complex 1 from the reaction of pyrazine and diphenylmagnesium in THF.[34a] (B) Computer simulation of spectrum A, exhibiting some anisotropic line broadening for A and nonequivalent ring protons due to the reduced symmetry of species 1. The ^{14}N coupling constants are apparently not affected by this unsymmetry. (C) ESR spectrum of complex 2 generated by potassium reduction in THF; this spectrum shows only one ring proton and one ^{14}N coupling constant. Expansion and amplification of the central part (D) reveals isotope coupling for *two* ^{25}Mg nuclei in natural abundance of 10%, according to the nuclear spin of $I = {}^5/_2$ one observes a partially resolved sextet. The ENDOR spectrum (E) of complex 2 finally reveals—besides the hyperfine features already detected by ESR—some very small proton coupling with the unpaired electron which must be assigned to the organic substituents at magnesium.

(9)
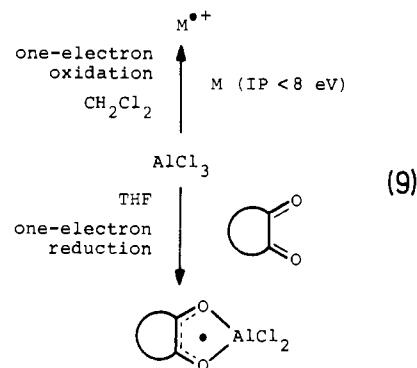
and subsequent dimerization of the R· radicals formed.[44] Such a reaction would be complementary to the process shown in Scheme I, i.e., involving SET from "carbocations" instead of "carbanions".

Although aluminum alkyls AlR_3 are not very potent reductants per se, they can undergo electron transfer with suitable substrates,[29,30] as shown in (10). Much more reactive, however, are species containing Al-H bonds such as AlH_3,[9a,15b] R_2AlH,[15a] $LiAlH_4$,[9b,c,19a] or $NaAlEt_2H_2$.[15c] The latter complex hydrides offer a more complicated pattern of possible reaction paths[45] because of the various dissociation equilibria in coordinating solvents;[46] recent results by Ashby and co-workers[47] have suggested that AlH_3 is the actual electron-transfer active species in etheral solutions of $LiAlH_4$. It is also important to realize that aluminum alkyls often contain small amounts of hydridic impurities due to preparation

(40) The shift of the Schlenk equilibrium on addition of an electron-transfer substrate has been observed recently: Poppitz, W.; Uhlig, E. *J. Organomet. Chem.* **1983**, *244*, C1. Cf. also: Cope, A. C. *J. Am. Chem. Soc.* **1938**, *60*, 2215.

(41) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545. Dagonneau, M. *Bull. Soc. Chim. Fr.* **1982**, II-269.

(42) Graalmann, O.; Hesse, M.; Klingebiel, U.; Clegg, W.; Haase, M.; Sheldrick, G. M. *Angew. Chem.* **1983**, *95*, 630; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 621.

(43) Abakumov, G. A.; Klimov, E. S. *Dokl. Akad. Nauk SSSR* **1972**, *202*, 827. Barker, P. E.; Hudson, A.; Jackson, R. A. *J. Organomet. Chem.* **1981**, *208*, C1.

(45) Boone, J. R.; Ashby, E. C. *Top. Stereochem.* **1979**, *11*, 53. Haubenstock, H. *Ibid.* **1983**, *14*, 231.

(46) Nöth, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 119.

(47) Ashby, E. C.; DePriest, R. N.; Pham, T. N. *Tetrahedron Lett.* **1983**, *24*, 2825.

(44) An alternative mechanism simply involves the dimerization of the radical anions AlX_3^- to $Al_2X_6^{2-}$, related species are well-known for the heavier homologues, e.g., gallium: Brown, K. L.; Hall, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1843.

3,5- or 3,6-
di^{t}butyl-o-benzoquinone
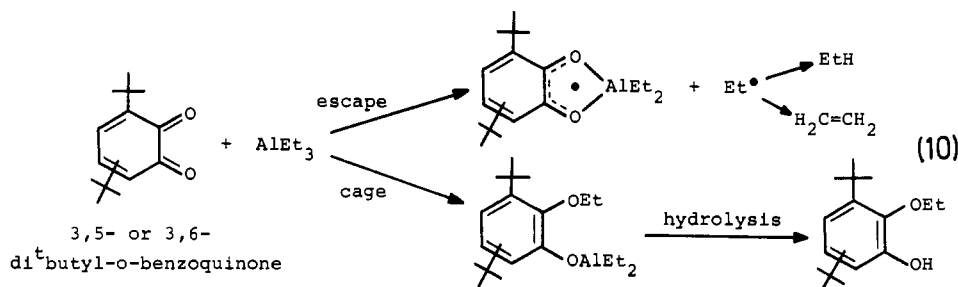
and purification procedures;[48a] such impurities may interfere with the electron-transfer reactivity of the aluminum trialkyls proper.

The identification by ESR of the radical species from electron-transfer reactions of aluminum compounds often involves the detection of the hyperfine coupling between the nucleus ^{27}Al (100%, $I = ^5/_2$) and the unpaired electron. This feature may complicate ESR spectra,[9a] on the other hand, thorough analysis by ESR[15,16] and ENDOR/TRIPLE spectroscopies[15c] helps to establish the identity of the radical complexes. There is a difficulty—not only restricted to aluminum species[34]—in determining whether the reduced substrate coordinates with neutral molecules such as AlR_3 or with cations $^+AlR_2$ from the dissociation equilibrium

$$2AlR_3 \rightleftharpoons {}^+AlR_2 + {}^-AlR_4$$

which exists in coordinating solvents.[48b] Only by studying the system with R = H could this matter be definitely resolved for various N-heterocycles (7).[15b] The fact that radical *anion* complexes are found in case of bridging substrates such as pyrazine again emphasizes the important role of coordination equilibria. With organolithium systems, including $LiAlH_4$ in THF, one obtains (solvated) radical cations (= triple ions, 4),[19a] while neutral unsymmetrical complexes are formed (cf. Figure 2) with diorganomagnesium reagents under the same circumstances (Scheme III).

Boron. Boron–carbon bonds are not very labile and organoboranes are not very electron transfer active unless a boron–hydrogen bond is present. In that case, particularly with the strongly reducing "Super Hydrides" and "Selectrides" MBR_3H (M = Li, Na, K),[49] electron transfer to unsaturated N-heterocycles has recently been observed.[21f] Extensive hyperfine coupling with the boron nuclei (^{10}B, 19%, $I = 3$; ^{11}B, 81%, $I = ^3/_2$) has made it necessary to use heteratom ENDOR techniques for full identification of the paramagnetic escape products. Again, coordination equilibria determine the nature of the radical complexes formed (11).[19b]

Main Group 14.[57] Most organometallic compounds out of this group are coordinatively saturated, and, except for hydrides such as R_nMH_{4-n} (M = Si, Ge, Sn),[50] they are not ordinarily considered to be common one-electron reductants. However, extensive literature ex-

Scheme III
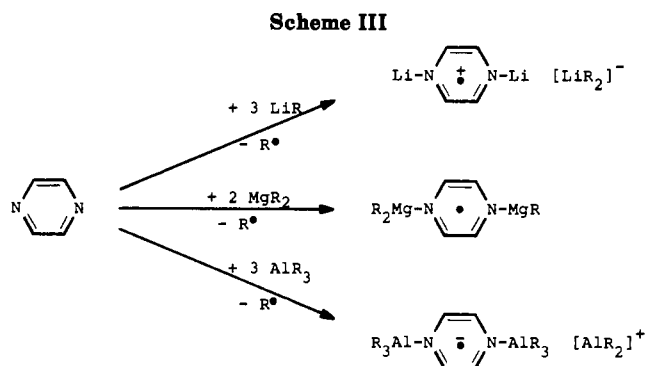
ists[2,50,51] on the charge-transfer complex formation and *photoinduced* electron-transfer reactivity of such hydridic species as well as of mono- and polynuclear organometal compounds of group 14[57] with acceptors such as α-dicarbonyls or tetracyanoethylene, TCNE. An interesting example, demonstrating again the instability of the primary pair of radical ions, is the photoinduced electron transfer between TCNE and n-Bu$_3$GeH in an acetonitrile/1,2-dichloropropane matrix at -175 °C, yielding H· (!) and the TCNE anion radical as paramagnetic products.[50]

If this inherent instability of organometallic radical cations is circumvented by incorporating them in a reduced π-system such as in 1,4-dihydropyrazines,[52]
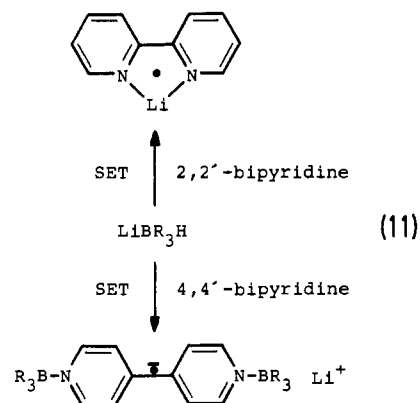
they can be observed as separate intermediates simultaneously with the reduced substrate (Figure 1).[26] Note that the organosilicon radical *cations* formed in this reaction are isoelectronic[53] with the organoaluminum radical *anions* obtained in other electron-transfer processes (cf. Scheme III), starting with the fully oxidized form of the pyrazine substrate (12). The

(49) Brown, H. C.; Kim, S. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 1.

(50) Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

(48) Lehmkuhl, H.; Ziegler, K. "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1970; Vol. XIII/4, (a) p 29; (b) p 274. Cf. also: Nöth, H.; Wiberg, E. *Fortschr. Chem. Forsch.* **1967**, *8*, 321.

(51) Mochida, K.; Kochi, J. K.; Chen, K. S.; Wan, J. K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2927. Cf. also: Sakurai, H.; Kira, M.; Uchida, T. *Ibid*, **1973**, *95*, 2826.

(52) Kaim, W. *J. Am. Chem. Soc.* **1983**, *105*, 707.

(53) Kaim, W. *Angew. Chem.* **1980**, *92*, 940; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 911.

(12)
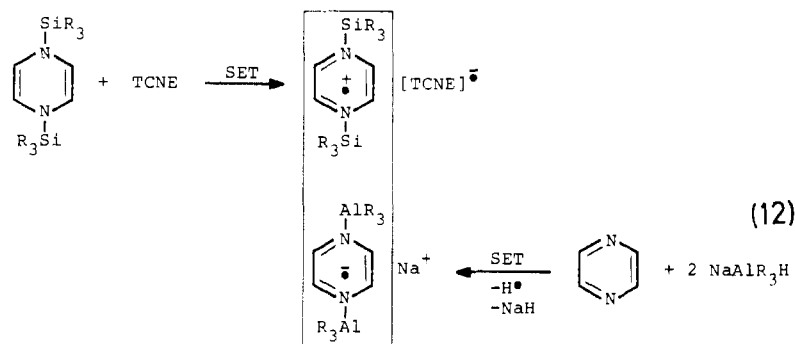
difference between both ESR-monitored electron-transfer experiments (12) is that the first reaction shows the intermediate radical anion/radical cation pair while in the second and more common situation only one persistent paramagnetic species from the escape process is observed.

Concluding Remarks

The preceding examples have focused on the radical complexes formed in thermal electron-transfer reactions of common main-group organometallic reductants. It is apparent that electron-transfer reactivity may be understood as an *intramolecular phenomenon of the precursor, the charge-transfer complex*.[2] According to this inner-sphere electron-transfer arrangement, coordinative aspects must play an important role. For the reductants described above, these aspects are of particular significance because most of them are coordinatively unsaturated or solvated. Although the coordinative aspects are most obvious when already nucleophilic substrates such as aromatic N-heterocycles or α-dicarbonyls are used, the basic principles outlined will also apply to other systems, including weak nucleophiles such as unsaturated hydrocarbons. Similar reactivity can be expected from so-called complex reducing agents (CRA)[54] and from the increasingly popular transition-metal reductants, e.g., titanium reagents;[55] in the latter case with the additional complication (and opportunity!) that the metal center is redox active, too.

The coordinative aspect can be significant because of the stereochemistry imposed,[45] and it has been shown (6) that chelate coordination tends to facilitate electron transfer. Another point to be emphasized is the complementarity of σ- coordination and π -redox function-

ality: Coordination lowers the redox potential, thereby facilitating electron transfer, while, on the other hand, charge transfer and electron transfer can increase the basicity of the substrate toward the organometallic fragments available.

Although the extent of electron-transfer reactivity and the significance of the radical products are still a matter of discussion[4] for the systems described, it is known on a qualitative level how steric and electronic effects affect the amount of paramagnetic species produced. As a general rule, the formation of paramagnetic escape vs. diamagnetic cage products is favored by steric hindrance of the reactands,[9a] unfavorable electronic structures (such as antiaromaticity[52]) of cage products,[13,15,19,26] polar solvents (large dielectric constant),[4,58] high temperatures, and especially, irradiation into the CT band of the precursor.[2,56]   In any case, before mechanistic studies can be successful, the nature of all the products, including the paramagnetic ones must be unambiguously established. Just as NMR has become a routine method for diamagnetic molecules and, through the CIDNP effect, a spectroscopic tool to investigate radical reaction mechanisms,[24] the use of ESR and ENDOR to characterize the long-lived radical products from electron-transfer reactions should become common practice.

(55) Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1. Weidmann, B.; Seebach, D. *Angew. Chem.* **1983**, *95*, 13; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31. McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.

(54) Caubère, P. *Angew. Chem.* **1983**, *95*, 597; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 599.

(56) Julliard, M.; Ehanon, M. *Chem. Rev.* **1983**, *83*, 425.

(57) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 and through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(58) Waack, R.; Doran, M. A. *J. Organomet. Chem.* **1965**, *3*, 94.