Organometallic Electrochemistry. X. Organomagnesium Reagents

Theodore Psarras and Raymond E. Dessy[1]

Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia, and the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio. *Received May 23, 1966*

Abstract: The polarographic behavior of organomagnesium species in $CH_3OCH_2CH_2OCH_3$ has been studied and the nature of the oxidative and reductive processes at a Hg electrode elucidated. Bisorganomagnesium species oxidize ($n = 2$) to R_2Hg and Mg^{2+} and reduce ($n = 1$), when R is a stable carbanion precursor, to $R:^-$ and RMg, the latter being unstable, decomposing to $R\cdot$ and Mg. Grignard reagents show two reductive waves (total $n = 1$), the first corresponding to the reduction of $MgBr_2$ ($n = 2$), the second to the one-electron reduction of RMgBr. The data support a Schlenk equilibrium of $R_2Mg + MgX_2 \rightleftarrows 2RMgX$ with $K \cong 4$. The fate of the subvalent RMg produced by RMgX reduction is decomposition to $R\cdot$ and Mg.

The electrochemical reduction of organometallic derivatives of groups IIb, IV, V, and the transition series has been reported,[2-4] and eight fates for the reduced assembly, $RmQ\cdot^-$, found (eq 1). The present

$$\begin{array}{l} \mathrm{RmQ} \xrightarrow{\mathrm{e}} \mathrm{RmQ}\cdot^- \\ (\mathrm{CH_3OCH_2{-}})_2 \\ \mathrm{Bu_4NClO_4}\ (0.1\ M) \end{array} \longrightarrow \left\{ \begin{array}{l} 1.\ \ \text{stable} \\ 2.\ \ -\mathrm{Q}^- + Rm \\ \quad \text{a. RmH} \\ \quad \text{b. RmmR} \\ \quad \text{c. } \mathrm{R_2m + m} \\ \quad \text{d. } \mathrm{R_2Hg + m}\ \text{(Hg electrode)} \\ \quad \text{e. stable} \\ 3.\ \ +\mathrm{e} \longrightarrow \mathrm{Rm}:^- + \mathrm{Q}^- \\ \quad \text{a. stable} \\ \quad \text{b. } \mathrm{R}:^- + \mathrm{m} \end{array} \right. \tag{1}$$

paper presents data on the oxidative and reductive processes associated with typical organomagnesium species at Hg and Pt microelectrodes. The fate of the subvalent RMg produced in these species adds a new possibility to the above list: $Rm \rightarrow R\cdot + m$. In addition, the study provides information concerned with the position of the Schlenk equilibrium

$$\mathrm{R_2Mg + MgX_2} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{2RMgX} \tag{2}$$

in this basic, polar environment.

Experimental Section

The equipment and techniques are as previously described.[2-4] The Grignard reagents were prepared in dimethoxyethane and standardized by acid-base titration.[2b] Bisorganomagnesium compounds were prepared *via* dioxane precipitation of ethereal solutions, followed by filtration and solvent replacement, or by R_2Hg-Mg exchange reactions.[2b] They were standardized by acid-base titration. Magnesium bromide was prepared *via* reaction of magnesium with $BrCH_2CH_2Br$ in ether, as suggested by Professor E. Becker.

All manipulations were done in an inert atmosphere box equipped with a purge train of BTS Catalyst (BASF), P_2O_5, and 5X molecular sieve. P_2O_5 trays were used internally. Argon (99.999%) was used as the atmosphere. Meticulous care was needed to obtain meaningful results.

Results and Discussion

The electrochemistry of Grignard reagents has been studied previously only under conditions involving nondiffusion control of the electrode process, thus invoking excessive concentration polarization and mass transport of substrate and lack of separation of parameters associated with the cathodic and anodic processes. In these pioneering studies Evans[5] reported the decomposition potentials, E_d, of Grignard reagents in ether at concentrations near 0.5 M, employing two Pt macroelectrodes immersed in solution. Application of increasing potential differences between the electrodes led to i–E plots from which the toe of the curve was extrapolated to zero current to obtain E_d. The contribution to this voltage from the *cathodic* and *anodic* processes could not be ascertained. Product analysis indicated the following: (1) Mg was deposited at the cathode; (2) radicals, $R\cdot$, appeared at the anode and suffered a decomposition dependent upon the structure of R (at noninert electrodes, *e.g.*, Al, it was suggested that new organometallics were produced); (3) all concentration losses occurred in the cathode, the anode showing gains in all solute constituents (R, Mg, X) even after loss of an equivalent of R by electrolysis. The electrochemical steps proposed were

$$\begin{array}{ll} \text{anode} & \left\{ \begin{array}{l} \mathrm{R_2MgX^-} \xrightarrow{-\mathrm{e}} \mathrm{R\cdot + RMgX} \\ \mathrm{R_3Mg^-} \xrightarrow{-\mathrm{e}} \mathrm{R\cdot + R_2Mg} \\ \mathrm{RMgX_2^-} \xrightarrow{-\mathrm{e}} \mathrm{R\cdot + MgX_2} \end{array} \right. \\ \text{cathode} & \quad \mathrm{2MgX^+} \xrightarrow{\mathrm{2e}} \mathrm{2MgX} \longrightarrow \mathrm{Mg + MgX_2} \end{array} \tag{3}$$

Obviously, it would be of interest to investigate, separately, the cathodic and anodic processes involved in the electrolysis of a Grignard reagent. Hopefully, the study might, by means of a direct physical method, yield information concerning (a) the identity, or nonidentity, of mixtures of R_2Mg with $MgBr_2$ (synthetic Grignard reagent) and the product of the reaction of $RBr + Mg \rightarrow$ "RMgBr" (natural Grignard reagent) and (b) position of the Schlenk equilibrium in this basic, polar environment: $R_2Mg + MgBr_2 \leftrightarrows 2RMgBr$.

This last area has been of intense interest during the past few years, after the extremely elegant and imagina-

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[1] To whom requests for reprints should be sent: Department o Chemistry, Virginia Polytechnic Institute, Blacksburg, Va.

[2] R. E. Dessy, W. Kitching, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 453 (1966); (b) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *ibid.*, **88**, 460 (1966).

[3] R. E. Dessy, T. Chivers, and W. Kitching, *ibid.*, **88**, 467 (1966).

[4] (a) R. E. Dessy, F. E. Stary, R. B. King, and M. Woldrup, *ibid.*, **88**, 471 (1966); (b) R. E. Dessy, R. B. King, and M. Woldrup, *ibid.*, **88**, 5112 (1966).

[5] *Cf.* W. Evans, *ibid.*, **64**, 2865 (1942), and preceding papers in this series.

Table I

$$\underset{10^{-3}\,M}{\text{R-mg}} \xrightarrow[\text{Bu}_4\text{NClO}_4,\ 0.1\ M]{(\text{CH}_3\text{OCH}_2\text{-})_2\ \pm\ \text{e},\ \text{Hg}}$$

	$-E_{1/2}$ (n)[a]			
	R_2Mg		R_2Mg + MgX_2	"RMgX"
R	Redn	Oxidn[b]	Redn	Redn
CH_3	. . .	1.2	2.49, . . .	2.49, . . . (1)
C_2H_5	. . .	1.2(−2)	2.43, 2.66	2.44, 2.70 (1)
i-C_3H_7	. . .	1.2	2.46, 2.74	2.44, 2.75 (1)
i-C_4H_9	. . .	1.2	2.50, 2.78	2.46, 2.75
C_6H_5	. . .	1.2(−2)	2.50, 2.83	2.46, 2.80 (1)
$C_6H_5CH_2$	2.74 (1)	1.2		
$CH_2{=}CHCH_2$	2.65 (1)	1.2		
C_5H_5	2.50 (1)	1.2		
Br	2.47 (2)	0.6(−2)		
ClO_4	2.30 (2)	. . .		

[a] *Vs.* 10^{-3} *M* $AgClO_4|Ag$ reference; 2×10^{-3} *M* in substrate.
[b] All oxidative waves had pronounced maxima making establishment of the nature and value of $E_{1/2}$ difficult.

tive experiments of Ashby reopened the question of the constitution of the Grignard reagent.[6a,7] At present, although some puzzling dichotomies still exist, there appears to be sound evidence for the existence of RMgBr species in both basic ethers, such as THF, and in diethyl ether environments for simple R groups. The identity of natural and synthetic Grignard reagents has been claimed by application of conductometric,[6b] dielectric,[6b] and thermal measurements,[6e] in addition to nmr spectroscopic studies.[6d] On the other hand, their nonidentity has been claimed on the basis of colligative property data[6f] and X-ray studies on isolated crystals.[6g] It has been suggested that perhaps the two routes *can* lead to the same species but may not always do so, especially in diethyl ether solutions.[6a,b]

Attempts at probing the value of *K* in the Schlenk equilibrium in THF,[6c] using an apparent c–mg stretch in the infrared absorption spectrum, suggested a statistical value of 4 for simple alkyl groups. Attempts at probing the value in ether solutions, employing colligative property data or triethylamine quenching, suggested much higher values.[6a,e]

The data presented in this paper are in agreement with the existence in glyme solvents (with 0.1 *M* Bu_4NClO_4) of a Schlenk equilibrium with $K = 4$ for simple alkyl Grignards and the identity in this solvent system of the natural and synthetic Grignard. In the process of developing this argument, some knowledge about the cathodic and anodic processes involved in Grignard electrolyses can be derived.

For the present study an inert atmosphere box, equipped with an effective recycle train, was altered to allow passage of shielded cables leading to (1) a Metrohm Polarecord (polarographic unit) equipped with a Sargent IR compensator or (2) an operational manifold adapted for three-electrode potentiostatic electrolysis. The box itself contained an H cell with medium frit. Three electrodes could be employed as test electrodes: (1) a dropping mercury electrode (dme), (2) a Hg pool, and (3) a rotating Pt electrode (rpe). The Hg pool was used for controlled-potential electrolysis. A Hg counter electrode was employed; the reference electrode was a 10^{-3} *M* $AgClO_4|Ag$ assembly.

Table I shows $E_{1/2}$ values for the various organomagnesium species studied at millimolar concentrations at a dme. The steps for $MgBr_2$, $(C_6H_5CH_2)_2Mg$, "C_6H_5MgBr," $(C_6H_5)_2Mg$ + $MgBr_2$, "*i*-PrMgBr," and "EtMgBr" were irreversible, diffusion-controlled processes, ascertained from i_d *vs.* $h_{1/2}$ and/or i_d *vs.* *c* plots. The precision of reductive $E_{1/2}$ values is ±40 mv, that of *n*, determined by controlled-potential electrolysis, is ±0.1. The maxima in the oxidative waves make these $E_{1/2}$ values very uncertain, and they should be used only qualitatively.

Bisorganomagnesium Species

Reduction. As indicated, reduction of MgBr species in solution is a two-electron process. $Mg(ClO_4)_2$, dissolved in the supporting electrolyte solution, undergoes a two-electron reduction at more anodic potentials (−2.3 *vs* −2.47 v) indicating that the species discharging in $MgBr_2$ solutions *is not* Mg^{2+}. Triangular voltammetry at a rpe in both cases reveals the deposition of Mg at the reductive step suggesting

$$MgBr_2 \xrightarrow[-2.47\ v]{2e} Mg + 2Br^- \tag{4}$$

Dialkymagnesium species do not reduce at potentials anodic to supporting electrolyte discharge. However, R_2Mg species containing R groups capable of yielding fairly stable carbanions[2b] (parent hydrocarbon pK_a's < 44) reduce *via* a *one-electron* process as evidenced from controlled-potential reduction at −3.0 v ($n = 1$) and a comparison of i_d^{oxidn}/i_d^{redn} for these species, which is 2.

This is true for dibenzyl, diallyl, and dicyclopentadienylmagnesium. Triangular voltammetry at a rpe in the first case reveals the deposition of Mg upon reduction, suggesting

$$R_2Mg \xrightarrow{1e} R:^- + RMg \longrightarrow Mg + R\cdot \longrightarrow \begin{array}{l}\text{abstraction}\\ \text{coupling}\\ \text{disproportionation}\end{array} \tag{5}$$

The radical postulated *does not* alkylate the Hg electrode, $2R\cdot \rightarrow 2RHg \rightarrow R_2Hg + Hg$. $(C_6H_5CH_2)_2Hg$ shows a reductive step $-E_{1/2} = 2.7$ v, $n = 2$. If $(C_6H_5CH_2)_2Hg$ was formed on reduction of $(C_6H_5CH_2)_2Mg$ the *n* value should be 1.5.

Oxidation. Exhaustive controlled-potential oxidation at −0.4 v of $MgBr_2$ ($n = 2$) gives $Mg(ClO_4)_2$ and $HgBr_2$ as evidenced by reductive polarographic steps at −1.2 and −2.47 v in the final solution. The wave for Mg(II) occurs at −2.47, not −2.3 v as expected for $Mg(ClO_4)_2$, because of the presence at the electrode of bromide ion from discharge of $HgBr_2$. Test polarograms of $HgBr_2$–$Mg(ClO_4)_2$ support this.

Diphenylmagnesium ($n = -2$) gives, upon exhaustive controlled-potential oxidation, diphenylmercury and $Mg(ClO_4)_2$ as indicated by the polarographic evidence of the former ($-E_{1/2} = 3.34$, $n = -2$) and the latter ($-E_{1/2} = 2.30$, $n = -2$) in the final solution. The

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(6) Pertinent references in this area are: (a) E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964); **87**, 2509 (1965); (b) R. E. Dessy, R. M. Salinger, and S. I. E. Green, *Tetrahedron Letters*, **21**, 1369 (1964); (c) R. M. Salinger and H. S. Mosher, *J. Am. Chem. Soc.*, **86**, 1782 (1964); (d) H. Roos and W. Zeil, *Ber. Bunsenges. Physik. Chem.*, **67**, 28 (1963); (e) M. B. Smith and W. E. Becker, *Tetrahedron Letters*, **43**, 3843 (1965); (f) A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **83**, 1096 (1964); (g) A. D. Vreugdenhil, Second International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1965.

(7) A current review of this troublesome area may be found in R. E. Dessy and W. Kitching *Advan. Organometal. Chem.*, **4**, 280 (1966).

processes involved are

$$\mathrm{MgBr_2} \xrightarrow[\mathrm{Hg}]{-2\mathrm{e}} \mathrm{HgBr_2} + \mathrm{Mg^{2+}} \tag{6}$$

$$\mathrm{R_2Mg} \xrightarrow[\mathrm{Hg}]{-2\mathrm{e}} \mathrm{HgR_2} + \mathrm{Mg^{2+}} \tag{7}$$

In a similar manner the dialkylmagnesium species show $n = -2$ upon oxidation at -1.0 v. $\mathrm{Mg(ClO_4)_2}$ is formed, but the $\mathrm{R_2Hg}$ species probably formed are not seen polarographically since they would discharge beyond supporting electrolyte.[2b]

Grignard Reagents

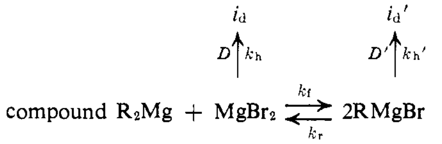
Reduction. When "natural" Grignard reagents ($\mathrm{RX + Mg \rightarrow}$ "RMgX") and "synthetic" Grignards ($\mathrm{R_2Mg + MgX_2}$) are compared polarograpically, *no difference* is observed. Except for $\mathrm{R = CH_3}$, all show *two* well-defined steps. The first step in each case is within experimental error of that for $\mathrm{MgBr_2}$ (±40 mv). Under exhaustive controlled-potential electrolysis conditions in which amplifier control is maintained throughout the experiment, reduction yields at the *first or second wave* $n = 1 \pm 0.1$.

It is tempting to attempt to describe the two waves occurring in Grignard reagents to the sequence

$$\mathrm{RMgX} \xrightarrow{\mathrm{e}} \mathrm{X^-} + \mathrm{RMg} \xrightarrow{\mathrm{e}} \mathrm{R{:}^-} + \mathrm{Mg}$$

However, the observed n value precludes this, and the insensitivity of $E_{1/2}$ to R supports this exclusion. It would appear that in the alkyl and phenyl series, where $\mathrm{R_2Mg}$ species do not reduce, a new species is present. A development based on RMgX seems best, although more complex schemes could undoubtedly be proposed.

The discussion which follows will end by having all of the available data consistent with a Schlenk equilibrium and capable of excluding many simple alternatives. The system described by eq 8 is capable of giving two well-defined polarographic waves only if k_r is finite[8] and well below the diffusion-controlled limit, say $10^6\ M^{-1}\ \mathrm{sec}^{-1}$. The electrochemical reduction of the proposed system

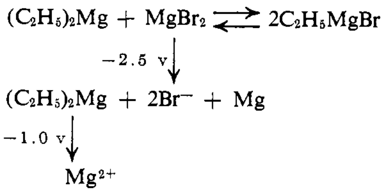


$$\begin{tikzcd} & i_\mathrm{d} & & i_\mathrm{d}' \\ \text{compound } \mathrm{R_2Mg} + & \mathrm{MgBr_2} \arrow[u, "D"', "k_\mathrm{h}"] \arrow[rr, shift left, "k_\mathrm{f}"] & & \mathrm{2RMgBr} \arrow[u, "D'"', "k_\mathrm{h}'"] \arrow[ll, shift left, "k_\mathrm{r}"] \end{tikzcd} \tag{8}$$

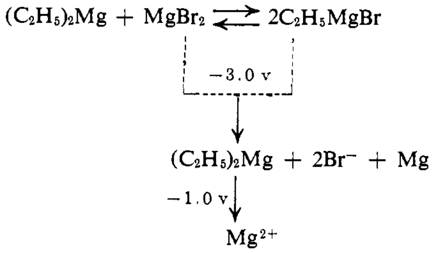
$-E_{1/2}$	no wave	2.47 v	2.74 ± 0.1 v
n	..	2	(1)

under controlled-potential conditions, using RMgBr concentration units, will appear to have $n = 1$ at the first wave only if k_r is of moderate rate, say $10\ M^{-1}\ \mathrm{sec}^{-1}$. Essentially one is electrolyzing $\mathrm{MgBr_2}$.

Controlled-potential electrolysis at the top of the second wave shows $n = 1$ also. It can clearly be demonstrated that this n is not due to the discharge of $\mathrm{MgBr_2}$ alone, with continual equilibrium shift. If "$\mathrm{C_2H_5MgBr}$" is control-potential *reduced* at the *first wave* and then *oxidized* (after changing the Hg macroelectrode) at -1.0 v [$\mathrm{(C_2H_5)_2Mg}$ being oxidized], a wave due to $\mathrm{Mg(ClO_4)_2}$ appears (eq 9a). If this is compared to that produced by *reduction* at the *second* wave followed by a similar *oxidation* (eq 9b), the ratio of diffusion currents (9a)/(9b) is 1.7/1. This simultaneously suggests the $\mathrm{C_2H_5MgBr}$ is discharging, it is present in relatively large amounts, and it reduces by a one-electron process. The reasoning is as follows. In process 9a, due to the shift in equilibrium as reduction proceeds, the final solution contains all of the original ethyl groups as $\mathrm{(C_2H_5)_2Mg}$, a compound which has been shown to oxidize to $\mathrm{Mg^{2+}}$. In (9b), as $\mathrm{C_2H_5MgBr}$ discharges also, a reductive route which subverts a large amount of the alkyl moiety is present. Thus on reoxidation less $\mathrm{Mg^{2+}}$ is seen, suggesting



$$\begin{tikzcd} \mathrm{(C_2H_5)_2Mg} + \mathrm{MgBr_2} \arrow[d, "-2.5\ \mathrm{v}"'] \arrow[r, shift left] & \mathrm{2C_2H_5MgBr} \arrow[l, shift left] \\ \mathrm{(C_2H_5)_2Mg} + \mathrm{2Br^-} + \mathrm{Mg} \arrow[d, "-1.0\ \mathrm{v}"'] & \\ \mathrm{Mg^{2+}} & \end{tikzcd} \tag{9a}$$



$$\begin{tikzcd} \mathrm{(C_2H_5)_2Mg} + \mathrm{MgBr_2} \arrow[d, dashed, "-3.0\ \mathrm{v}"] \arrow[r, shift left] & \mathrm{2C_2H_5MgBr} \arrow[l, shift left] \arrow[ld, dashed] \\ \mathrm{(C_2H_5)_2Mg} + \mathrm{2Br^-} + \mathrm{Mg} + ? \arrow[d, "-1.0\ \mathrm{v}"'] & \\ \mathrm{Mg^{2+}} & \end{tikzcd} \tag{9b}$$

$$\mathrm{RmgBr} \xrightarrow{1\mathrm{e}} \mathrm{Br^-} + \mathrm{RMg} \longrightarrow \mathrm{Mg} + \mathrm{R}\cdot \longrightarrow \begin{array}{l} \text{abstraction} \\ \text{coupling} \\ \text{disproportionation} \end{array} \tag{10}$$

If n for this step were 2, the observed n value at the second wave could not be 1. No $\mathrm{(C_5H_5)_2Hg}$ or $\mathrm{C_6H_5HgBr}$ was observed when phenyl Grignard was reduced at -2.8 v, precluding a sequence $\mathrm{C_6H_5Mg \rightarrow C_6H_5Hg \rightarrow (C_6H_5)_2Hg}$.

The large contribution of RMgBr is consistent with the observed i_d heights for the first and second reduction waves exhibited by the Grignard reagents. At the top of the second wave, where the calculated rate values for electron transfer, fk_h, are high, so that of the two parameters governing the rate of charge transfer, it is the diffusion coefficients of the species, D, which is important, the ratio of $i_\mathrm{d}/i_\mathrm{d}'$ would measure K_eq. This ratio is near 1, suggesting $K = 4$ (refer to eq 8 for definition of symbols).

Although the data above are mutually consistent a more direct proof of the Schlenk equilibrium's existence would be desirable. If the proposal is correct, according to LeChatelier's principle, addition of either $\mathrm{R_2Mg}$ or $\mathrm{MgBr_2}$ to the Grignard system should affect the ratio of $i_\mathrm{d}/i_\mathrm{d}'$ and the magnitude of i_d relative to standardization polarograms. Thus, for isopropylmagnesium bromide, the addition of $\mathrm{MgBr_2}$ does increase the height of the second wave, i_d', although it necessarily increases i_d simultaneously. More clearly, the addition of diisopropylmagnesium, which is not electroactive, causes an increase in the second wave, i_d', at the expense of the first wave, i_d, such that the total diffusion-limited current at the top of the second wave, $i_\mathrm{d}^\mathrm{total}$, is constant within ±4%, over a ratio of $\mathrm{R_2Mg/RMgBr}$ from 0 to 3. Figure 1 shows the values.

Similar behavior is observed with ethyl or phenyl Grignards, both natural and synthetic. The con-

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[8] An excellent discussion of this area may be found in E. F. Caldin, "Fast Reactions in Solution," John Wiley and Sons, Inc., New York, N. Y., 1964.

stancy of i_d^{total} suggests that D for the two discharging species is very similar, and since Vreugdenhil[6f] reports $MgBr_2$ to be almost completely monomeric in ether at such low concentrations, the form of the Schlenk equilibrium used for the calculations seems warranted. Calculations of K from the above data using i_d values and $MgBr_2$ working curves gives for R: i-C_3H_7, 3.3 ± 0.3; C_6H_5, 6.1 ± 0.3; C_2H_5, 2.2 ± 0.3. It is the authors' opinion that the figures are more precise than accurate. Problems posed by accurate measurements of diffusion currents in systems where drop characteristics are affected greatly by small amounts of surface active agents, where the rates of k_f and k_r are only bracketed and may vary from R to R′, and where the effects of the inhomogeneous potential field near the drop surface are unknown, make it seem wise to conclude that the method merely indicates that in highly polar, basic media simple Grignard reagents exhibit an equilibrium with approximately a statistical distribution of groups about Mg. It is unfortunate that an extrapolation of this method to solutions lacking a supporting electrolyte are, of course, impossible. It would provide the long-needed physical probe. However, the unsurprising conclusion from a comparison of the data of Mosher,[6c] Ashby,[6a] and Smith and Becker[6e] with the present data is that K is very solvent dependent.

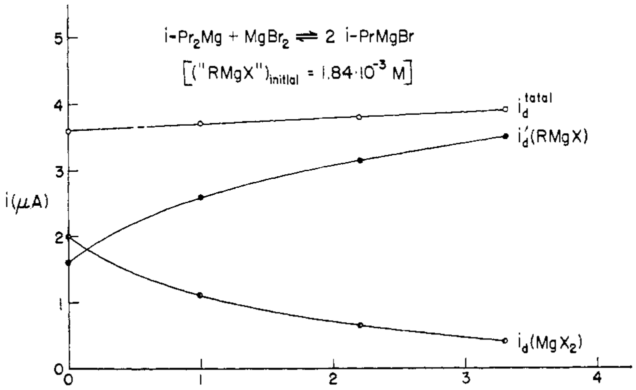

Figure 1.

A comparison of the present work with Evans' data indicates that the only major conflict is on the nature of the process at the cathode where he suggested $2MgX^+ \rightarrow 2MgX \rightarrow MgX_2 + Mg$. The loss of alkyl moiety in the experiments described by eq 10a and b precludes this.[5] It seems highly likely that actually his conditions (two-electrode cell, several hundred volts potential) led to $RMg + e \rightarrow R{:}^- + Mg$ processes, which could be followed by alkylation, $R{:}^- + RMgX \rightarrow R_2Mg + X{:}^-$. A comparison of the potentials for the RHgX, RMgX series seems to support such a concept which places the reduction of the postulated RMg to $R{:}^-$ beyond −3.7 v,[2] the limit set by the present supporting electrolyte, which was, of course, absent in Evans' work.

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Oxyplatination and Oxypalladation Reactions of Diolefins[1]

John K. Stille and Richard A. Morgan[2]

Contribution from the Department of Chemistry, University of Iowa,
Iowa City, Iowa 52240. *Received May 19, 1966*

Abstract: The structures of the methoxy platinum(II) and palladium(II) complexes formed from the reaction of the corresponding diolefin complexes with methanol and base have been determined. Oxyplatination of *endo*-dicyclopentadiene, dipentene, 1,5-cyclooctadiene, and norbornadiene and oxypalladation of *endo*-dicyclopentadiene and norbornadiene were investigated. Structural assignment was made by reduction of the complexes to known or independently synthesized ethers and by nmr studies on the complexes. Several reactions of the methoxy complexes were studied.

Some unusual complexes of platinum(II) and palladium(II) have been reported from the reaction of alcohols with the corresponding diolefin complex.[3] The products were assigned the general dimeric structure involving chloride bridges and both a metal–carbon σ bond and a π-coordinate bond from the remaining olefin ligand to the metal.[3] Alkyl platinum(II) and palladium(II) complexes are generally stable only when some other ligand is present which affords large crystal field splitting.[4] The olefins which form these products have the geometry necessary to accomplish this stabilization.

The first preparation of this type of complex was realized from the reaction of dicyclopentadiene with potassium chloroplatinite in aqueous alcohol,[5] al-

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[1] A portion of this work appears in a preliminary communication: J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Am. Chem. Soc.*, **87**, 3282 (1965).

[2] Abstracted in part from the Ph.D. thesis of R. A. Morgan, University of Iowa, Iowa City, Iowa, June 1966.

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[5] K. A. Hoffman and J. V. Narbutt, *Ber.*, **41**, 1625 (1908).