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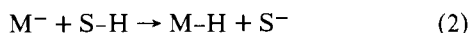
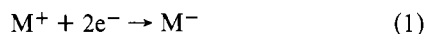
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Electrochemical Generation of $[\text{Rh}(\text{diphos})_2]^0$ and Its Role in an Electrocatalytic Reduction of Cyclohexyl Halides

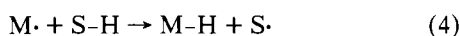
Sir:

The role of odd-electron complexes in the chemistry of oxidative addition reactions, radical-chain processes, and the activation of C-H bonds is a subject of current interest.¹ An important factor in this last category is the selectivity of the activation process, which is related to the "energy content" of the $\text{M}\cdot$ species. Electrochemical methods for generating odd-electron complexes are appealing because no additional reagents are needed, the reduction potential provides a measure of $\text{M}\cdot$ reactivity, and the subsequent chemical reactions of $\text{M}\cdot$ generation can be monitored by both chemical and electrochemical techniques. In this report we describe the electrochemical formation of the d^9 Rh(0) species $[\text{Rh}(\text{diphos})_2]^0$ (diphos = 1,2-bis(diphenylphosphino)ethane) and some of its chemical reactions.

Our results contrast with the previous report² of Pilloni, Vecchi, and Martelli on the electrochemistry of $[\text{Rh}(\text{diphos})_2]\text{Cl}$ and its Ir analogue. These authors reported that the electrochemical reduction of these d^8 complexes proceeded by an EC mechanism involving a single $2e^-$ reduction to give an anionic intermediate which was quenched by proton abstraction from solvent to give the metal hydrides,



Ginsberg et al.³ reexamined the electrochemistry of $[\text{Ir}(\text{diphos})_2]^+$ and established by cyclic voltammetry and constant potential coulometry experiments that the hydride forms via an ECE mechanism



in which $1e^-$ transfer occurs to generate an Ir(0) species, followed by H-atom abstraction and reduction of the solvent radical. The rhodium complex, $[\text{Rh}(\text{diphos})_2]\text{Cl}$, reduces at

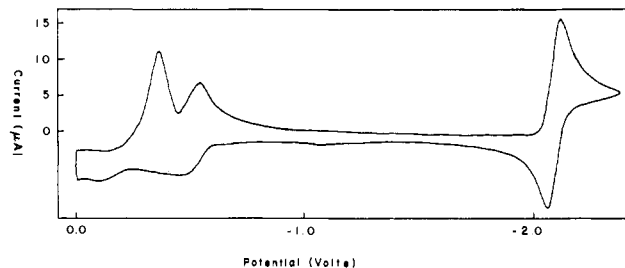


Figure 1. Cyclic voltammogram of 1×10^{-3} M $[\text{Rh}(\text{diphos})_2]\text{Cl}$ in 0.1 M $(n\text{-Bu}_4\text{N})\text{ClO}_4$ in CH_3CN at a scan rate of 100 mV/s on HMDE vs. a 0.1 M Ag/AgNO_3 reference.

Table I. Cyclic Voltammetry Data for the Reduction of $[\text{Rh}(\text{diphos})_2]\text{Cl}$

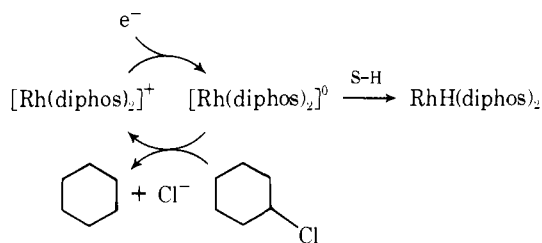
scan rate, mV s ⁻¹	$E_p^{\text{red},a}$ V	ΔE_p , mV	$\Delta E_p^{\text{cor},b}$ mV	$i_p^{\text{red}}/i_p^{\text{ox}}$
200	-2.16	72.5	65.3	1.00
150	-2.16	68.9	65.7	1.00
100	-2.16	66.0	66.0	1.05
90	-2.16	65.3	65.3	1.09
80	-2.16	63.8	63.8	1.10
70	-2.16	61.7	61.7	1.12
60	-2.15	58.1	58.1	1.09
50	-2.15	55.8	55.8	1.17
40	-2.15	54.4	54.4	1.18
30	-2.15	50.8	50.8	1.21
20	-2.14	47.2	47.2	1.22
10	-2.14	43.5	43.5	1.27

^a Scans were made on a HMDE in CH_3CN containing 0.1 M $(n\text{-Bu}_4\text{N})\text{ClO}_4$. Voltage are vs. a 0.1 M Ag/AgNO_3 reference at 23 °C.
^b $\Delta E_p^{\text{corr}} = (\Delta E_p^{\text{Rh}}/\Delta E_p^{\text{Fe}}) \times 65.3$.

approximately the same potential as its iridium analogue, yet shows reversible cyclic voltammetric behavior under similar conditions. It was thus of interest to determine whether electrochemically generated $[\text{Rh}(\text{diphos})_2]^0$ could be both a reactive and also selective reagent.

Cyclic voltammetry of $[\text{Rh}(\text{diphos})_2]\text{Cl}$ on a hanging mercury drop electrode (HMDE) in acetonitrile exhibits a reversible redox couple centered about -2.12 V at a scan rate of 100 mV s^{-1} , corresponding to the reduction of the complex, Figure 1.^{4,5} The redox couple centered about -2.12 V displays a variance in peak potential separation, ΔE_p , with scan rate, Table I. In order to compensate for the ohmic contribution to ΔE_p in acetonitrile and to demonstrate the behavior of a purely reversible one-electron system under identical conditions, the $\text{Fe}(\text{II})/\text{Fe}(\text{I})$ redox couple of $[\text{Fe}(\text{bpy})_3]^{2+/1+}$ (bpy = 2,2'-bipyridine) was used.⁶ At scan rates of 100 mV s^{-1} , or slower, the reversible one-electron couple for $[\text{Fe}(\text{bpy})_3]^{2+/1+}$ exhibits a peak separation of 65.3 mV. At fast scan rates, from 200 mV s^{-1} to $\sim 90 \text{ mV s}^{-1}$, $[\text{Rh}(\text{diphos})_2]\text{Cl}$ mimics the behavior of $[\text{Fe}(\text{bpy})_3]^{2+}$. At slower scan rates, the behavior of the Rh system begins to depart from the one-electron transfer model, $\Delta E_p = 65.3 \text{ mV}$, and shows increasingly smaller values of ΔE_p . This decrease in ΔE_p is the expected behavior for an ECE reduction such as eq 3-5 when the chemical reaction (eq 4) becomes kinetically significant and the second one-electron transfer is anodic to the first.⁷ Concomitant with the decrease in ΔE_p below 65.3 mV is an increase in the ratio of the reduction peak current to the oxidation peak current, $i_p^{\text{red}}/i_p^{\text{ox}}$. The system also agrees with the Nicholson and Shain diagnostic criterion⁷ for an ECE reduction such as eq 3-5. That is, an increase in $i_p^{\text{red}}/v^{1/2}$, where v is the scan rate, is observed as the scan rate decreases. Similar cyclic voltammetric results were obtained for the reduction of $[\text{Rh}(\text{diphos})_2]\text{Cl}$ in dimethyl sulfoxide, dimethylacetamide, and benzonitrile. These cyclic voltammetric results suggest that eq 3-5 are also valid for the mechanism of the reduction of $[\text{Rh}(\text{diphos})_2]\text{Cl}$.

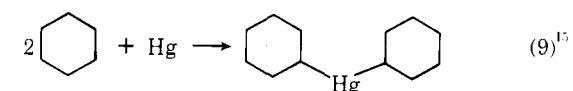
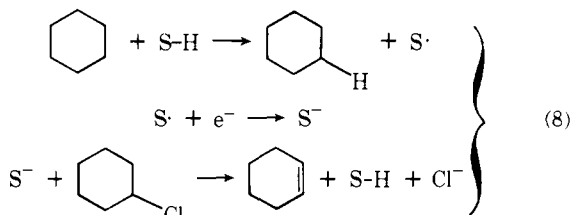
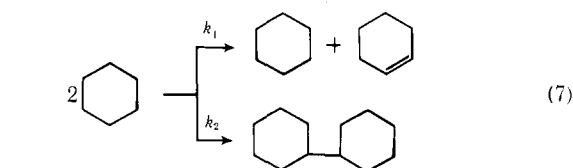
Scheme I



Constant potential coulometry of the reduction of $[\text{Rh}(\text{diphos})_2]\text{Cl}$ in all the aforementioned solvents yielded an “ n ” value of 2.0 ± 0.1 equiv of electrons passed per mole of $[\text{Rh}(\text{diphos})_2]\text{Cl}$.⁸ In all cases, the transition metal product was isolated as the hydride, $\text{RhH}(\text{diphos})_2$, and identified by comparison of its infrared spectrum with that of an authentic sample⁹ prepared by NaBH_4 reduction of $[\text{Rh}(\text{diphos})_2]\text{Cl}$. The isolated yields of $\text{RhH}(\text{diphos})_2$ are $\sim 90\%$. When the electrolysis was performed in CH_3CN in the presence of low concentrations of D_2O , 1 mol % or less, the isolated product was $\text{RhH}(\text{diphos})_2$.¹⁰ These experiments are consistent with what Ginsberg et al. observed for the reduction of $[\text{Ir}(\text{diphos})_2]\text{Cl}$ in CH_3CN with trace amounts of D_2O . However, at higher concentrations of D_2O in CH_3CN , electrolysis gives mixtures of $\text{Rh}(\text{H})$ and $\text{Rh}(\text{D})$ as the isolated products.¹¹

These cyclic voltammetry and constant potential coulometry experiments provide evidence for the formation of a reactive $\text{Rh}(0)$ species which can be quenched by solvent. Therefore, we sought to intercept the $\text{Rh}(0)$ species, $[\text{Rh}(\text{diphos})_2]^0$, with other reagents. When cyclohexylchloride is added to the $[\text{Rh}(\text{diphos})_2]^+$ electrolysis solution, the “ n ” value for the coulometric reduction in all solvents studied is greater than 2. Cyclic voltammetry of the solution after electrolysis shows that Cl^- is produced. This electrocatalytic reduction of cyclohexyl chloride is envisioned in Scheme I.

The cyclohexyl radicals generated in this manner have several possible channels for product formation. These are exemplified in eq 7-9 and were observed in the different sys-



tems shown in Table II. The organic products were identified by GC-MS after a bulb-to-bulb distillation of the electrolysis solution. The dialkylmercury compounds were crystallized out of the concentrated electrolysis solution and identified by mass spectrometry. When benzonitrile is the solvent, $\sim 40\%$ of the cyclohexyl radicals followed eq 7 and yielded a 1:1 ratio of cyclohexane and bicyclohexyl.¹⁶ The ratio, k_1/k_2 , has previously been determined to be about unity.¹⁷ This ratio and the formation of the other radical termination products gives further credence to the radical nature of the propagating species, $[\text{Rh}(\text{diphos})_2]^0$. The ability to increase the electro-

Table II. Electrocatalytic Reduction of Cyclohexyl Halides via $[\text{Rh}(\text{diphos})_2]\text{Cl}$

solvent	electrode	% X ^a	X	n ^b	product pathway
benzonitrile	Hg	33	Cl	4.1	7, 9
acetonitrile	Hg	50	Cl	3.4	9
acetonitrile	graphite	33	Cl	4.5	8
acetonitrile	Hg	10	Cl	2.0	
acetonitrile	Hg	10	Br	5.2	8, 9
acetonitrile	Hg	10	I	23	7, 8, 8 ^c
dimethylacetamide	Pt	10	Cl	3.7	8
dimethyl sulfoxide	Pt	33	Cl	16.0	d

^a This is the percentage by volume of cyclohexyl halide in the solvent. ^b The coulometric n value is based on the equivalents of $[\text{Rh}(\text{diphos})_2]^+$ present. ^c Pathway 7 accounted for 1.5% of the cyclohexyl radical formed. The electrolysis was stopped at this point owing to excessive solvent evaporation. ^d The products could not be properly characterized.

catalytic chain length and establish a reactive preference of $[\text{Rh}(\text{diphos})_2]^0$ for cyclohexyl halide vs. the solvent is indicated in the electrolyses containing cyclohexyl bromide and cyclohexyl iodide. As shown in Table II, the chain length of the system increases in the order cyclohexyl chloride < bromide < iodide. This is to be expected, since the order of the reduction potentials is $[\text{Rh}(\text{diphos})_2]\text{Cl} < \text{cyclohexyl iodide} < \text{cyclohexyl bromide} < \text{cyclohexyl chloride}$.

We have thus established by both electrochemical and chemical techniques that the reduction of $[\text{Rh}(\text{diphos})_2]\text{Cl}$ occurs via a one-electron transfer step to yield a reactive $\text{Rh}(0)$ complex. This transient intermediate is capable of abstracting a hydrogen atom from a variety of solvents. The complex may also be used in the electrocatalytic reduction of cyclohexyl halides. The reduction of cyclohexyl chloride can not be carried out directly in any of the solvent systems used in this paper. This exemplifies the utility of this Rh^+/Rh^0 electrocatalytic system. The high reactivity of the generated $\text{Rh}(0)$ complex and the reversibility of the Rh^+/Rh^0 couple makes this an interesting system for further study of substrate activation, in particular C-H bonds.

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- Reduction peaks are observed at -0.41 and -0.63 V and an oxidation peak appears at -0.53 V. These reduction and oxidation peaks coincide with those observed in the cyclic voltammogram of *n*-tetrabutylammonium chloride in CH_3CN on a HMDE and are assigned to Cl^- . In confirmation of this, the region between 0.00 and -0.70 V of the cyclic voltammogram of $[\text{Rh}(\text{diphos})_2]\text{Cl}$ is devoid of reduction and oxidation peaks if Pt or glassy carbon working electrodes are used, or if $[\text{Rh}(\text{diphos})_2]\text{ClO}_4$ is the reducible species.
- The iridium complex exhibits irreversible cyclic voltammetry, $i_p^{\text{red}}/i_p^{\text{ox}} > 1$, at this scan rate, as was reported in ref 3 and verified by our work. This is in contrast to that initially reported in ref 2.
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- When dry CD_3CN is used as solvent containing 0.1 M (*n*-Bu₄N) ClO_4 , only $\text{Rh}(\text{diphos})_2$ is isolated. This rules out reaction with the electrolyte as a major source of hydrogen atom.
- At high concentrations of D_2O accompanied by the high potential necessary to reduce $[\text{Rh}(\text{diphos})_2]\text{Cl}$, the reactive deuterium is probably found on the

surface of the electrode as one approaches the overpotential for the reduction of D₂O. This hypothesis is born out by the following observations. The competition favoring reaction of [Rh(diphos)₂]⁰ with D₂O vs. CH₃CN is more pronounced on a Pt electrode than a Hg electrode. The lower overpotential of water on Pt vs. Hg is well established.¹² The age of the HMDE in "wet" acetonitrile solutions greatly influences the reversibility, *i*_p^{red}/*i*_p^{ox}, of the Rh⁺/Rh⁰ couple.¹³

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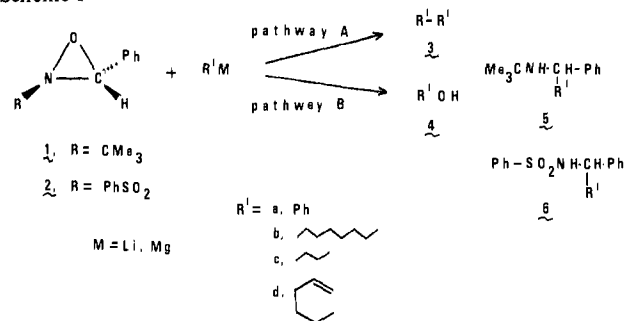
Coupling and Hydroxylation of Lithium and Grignard Reagents by Oxaziridines

Sir:

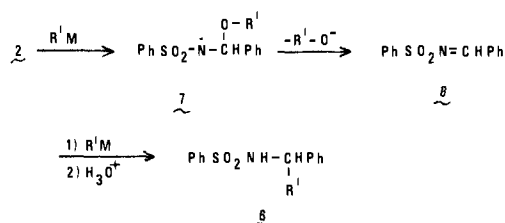
Oxaziridines represent a unique class of three-membered heterocyclic compounds which undergo novel thermal and photochemical transformations.^{1,2} At present, the chemistry of these compounds is not well understood. Despite the fact that oxaziridines have been known for nearly 25 years,³ there appears to have been no study of the reactions of this class of compounds with organometallic reagents. By contrast, the reactions of oxiranes, aziridines, and thiranes with these reagents have been extensively explored and constitute synthetically useful transformations. Oxiranes give ring-opened products resulting from attack of the lithium and Grignard reagent at the carbon atom adjacent to the oxygen.⁴ The situation for aziridines is somewhat more complicated, but similar ring-opened products have been described.⁵ Thiranes, on the other hand, are attacked at sulfur by organolithium compounds to afford the thiol and alkene stereospecifically.^{6,7} Grignard reagents react with thiranes in a manner similar to Grignard reagents with oxiranes and aziridines.⁸

In this context we report that lithium and Grignard reagents (R'M) react in an unprecedented manner with oxaziridines to afford coupling (pathway A) and hydroxylation (pathway B) products (Scheme I). Thus, addition of (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**1**)⁹ to a threefold excess of phenyl or *n*-octylmagnesium bromide¹⁰ in ether at 0 °C, afforded after 15 h biphenyl and hexadecane as the principal organic products

Scheme I



Scheme II



following hydrolysis with 5% hydrochloric acid (Table I, entries 1 and 2).¹¹ With *n*-butyllithium **1** gave *n*-octane and adduct **5c** (Table I, entry 4), but with phenyllithium **1** gave phenol and **5a** in good yield (Table I, entry 3).¹²

In contrast to oxaziridine **1**, (*E*)-2-benzenesulfonyl-3-phenyloxaziridine (**2**)^{1,13} reacts almost exclusively by pathway B with lithium and Grignard reagents (R'M) to afford phenol and alcohols (Table I, entries 5–8). Products were identified by comparison with authentic samples of the reaction products and were isolated by preparative TLC (silica gel).

A mechanism which explains the hydroxylation of R'M by oxaziridine **2** is outlined in Scheme II. In Scheme II we propose that the organometallic reagent (R'M) attacks the oxaziridine oxygen atom to afford intermediate or transition state **7** which collapses to *N*-benzylidenebenzenesulfonamide (**8**) and the hydroxylated product. A similar attack by sulfur on the oxaziridine oxygen atom has been proposed for the selective oxidation of sulfides and disulfides to sulfoxides and thioisulfates by **2**.¹⁴ Under the reaction conditions good yields of **6** were obtained when **8** was treated with R'M.

The hydroxylation of organolithium compounds by nitrobenzene¹⁵ and dialkyl peroxides¹⁶ and Grignard reagents by molecular oxygen¹⁷ and *tert*-butyl hydrogen peroxide¹⁸ is reported to occur with varying degrees of success. Hydroxylation of Grignard reagents by oxygen reportedly involves a radical-chain mechanism,¹⁹ while an S_N2 mechanism has been proposed for the formation of ethers from lithium reagents and

Table I. Products of the Reaction of Lithium and Grignard Reagents with Oxaziridines

entry	oxaziridine	temp, °C ^a	organometallic reagent (R'M)	products (% yield) ^b		
				R'OH ^c	R'R' ^c	adduct ^d
1	1	0	PhMgBr		3a (92–97)	
2	1	0	MgBr		3b (85–90)	ref 11
3	1	–78	PhLi	4a (70–75)		5a (95)
4	1	–78	Li		3c (82–87)	5c (73) + <i>e</i>
5	2	0	PhMgBr	4a (50–58)		6a (87–90) ^f
6	2	0	MgBr	4b (88–92)		6b (63–67)
7	2	–78	PhLi	4a (92–96)		6a (72) ^f
8	2	–78	Li	4c (51–61)	3c (15)	6b (65)

^a Temperature at which the oxaziridine was added to the organometallic reagent. ^b Products were analyzed by gas chromatography on a 6-ft 6% OV-17 on 60/80 mesh Chromosorb W (regular) column or on a 12-ft 20% Carbowax 20M on 45/60 Chromosorb W (regular) column by comparison of peak areas with standard solutions of the reaction products. Analyses were performed at least twice. Yields are corrected for blank solutions of these compounds in the organometallic reagents. ^c Yields were based on the original concentration of the oxaziridine. ^d Isolated yields. ^e A 15% yield of *N*-*tert*-butylbenzamide was also isolated. ^f H. Stetter and D. Theisen, *Chem. Ber.*, **102**, 1641 (1969).