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Electrochemical Generation of $[Rh(diphos)_2]^0$ 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 M· species. Electrochemical methods for generating odd-electron complexes are appealing because no additional reagents are needed, the reduction potential provides a measure of M· reactivity, and the subsequent chemical reactions of M· 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 $[Rh(diphos)_2]^0$ (diphos = 1,2-bis(diphenylphosphino)ethane) and some of its chemical reactions.

Our results contrast with the previous report[2] of Pilloni, Vecchi, and Martelli on the electrochemistry of $[Rh(diphos)_2]Cl$ 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,

$$M^+ + 2e^- \rightarrow M^- \qquad (1)$$

$$M^- + S\text{-}H \rightarrow M\text{-}H + S^- \qquad (2)$$

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

$$M^+ + e^- \rightarrow M\cdot \qquad (3)$$

$$M\cdot + S\text{-}H \rightarrow M\text{-}H + S\cdot \qquad (4)$$

$$S\cdot + e^- \rightarrow S^- \qquad (5)$$

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, $[Rh(diphos)_2]Cl$, reduces at 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 $[Rh(diphos)_2]^0$ could be both a reactive and also selective reagent.

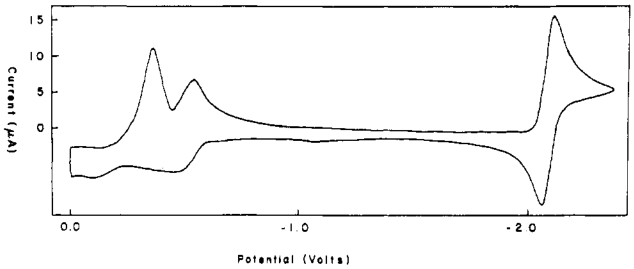

Figure 1. Cyclic voltammogram of 1×10^{-3} M $[Rh(diphos)_2]Cl$ in 0.1 M $(n\text{-}Bu_4N)ClO_4$ in CH_3CN at a scan rate of 100 mV/s on HMDE vs. a 0.1 M $Ag/AgNO_3$ reference.

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

scan rate, mV s^{-1}	$E_p^{red,a}$ V	ΔE_p, mV	$\Delta E_p^{cor,b}$ mV	i_p^{red}/i_p^{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 $(n\text{-}Bu_4N)ClO_4$. Voltage are vs. a 0.1 M $Ag/AgNO_3$ reference at 23 °C. [b] $\Delta E_p^{corr} = (\Delta E_p^{Rh}/\Delta E_p^{Fe}) \times 65.3$.

Cyclic voltammetry of $[Rh(diphos)_2]Cl$ 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 Fe(II)/Fe(I) redox couple of $[Fe(bpy)_3]^{2+/1+}$ (bpy = 2,2′-bipyridine) was used.[6] At scan rates of 100 mV s^{-1}, or slower, the reversible one-electron couple for $[Fe(bpy)_3]^{2+/1+}$ exhibits a peak separation of 65.3 mV. At fast scan rates, from 200 mV s^{-1} to ~90 mV s^{-1}, $[Rh(diphos)_2]Cl$ mimics the behavior of $[Fe(bpy)_3]^{2+}$. At slower scan rates, the behavior of the Rh system begins to depart from the one-electron transfer model, ΔE_p = 65.3 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^{red}/i_p^{ox}. The system also agrees with the Nicholson and Shain diagnostic criterion[7] for an ECE reduction such as eq 3–5. That is, an increase in $i_p^{red}/v^{1/2}$, where v is the scan rate, is observed as the scan rate decreases. Similar cyclic voltammetric results were obtained for the reduction of $[Rh(diphos)_2]Cl$ 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 $[Rh(diphos)_2]Cl$.

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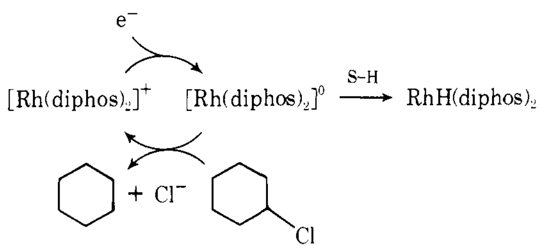
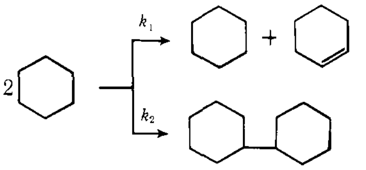
Scheme I

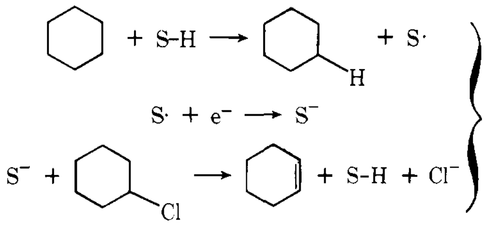


Constant potential coulometry of the reduction of [Rh(diphos)$_2$]Cl in all the aforementioned solvents yielded an "*n*" value of 2.0 ± 0.1 equiv of electrons passed per mole of [Rh(diphos)$_2$]Cl.[8] In all cases, the transition metal product was isolated as the hydride, RhH(diphos)$_2$, and identified by comparison of its infrared spectrum with that of an authentic sample[9] prepared by NaBH$_4$ reduction of [Rh(diphos)$_2$]Cl. The isolated yields of RhH(diphos)$_2$ are ~90%. When the electrolysis was performed in CH$_3$CN in the presence of low concentrations of D$_2$O, 1 mol % or less, the isolated product was RhH(diphos)$_2$.[10] These experiments are consistent with what Ginsberg et al. observed for the reduction of [Ir(diphos)$_2$]Cl in CH$_3$CN with trace amounts of D$_2$O. However, at higher concentrations of D$_2$O in CH$_3$CN, electrolysis gives mixtures of Rh(H) and Rh(D) as the isolated products.[11]

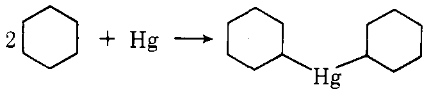
These cyclic voltammetry and constant potential coulometry experiments provide evidence for the formation of a reactive Rh(0) species which can be quenched by solvent. Therefore, we sought to intercept the Rh(0) species, [Rh(diphos)$_2$]^0, with other reagents. When cyclohexylchloride is added to the [Rh(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.



(7)



(8)



(9)[15]

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 systems 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, ~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, [Rh(diphos)$_2$]^0. The ability to increase the electrocatalytic chain length and establish a reactive preference of [Rh(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 [Rh(diphos)$_2$]Cl < cyclohexyl iodide < cyclohexyl bromide < cyclohexyl chloride.

Table II. Electrocatalytic Reduction of Cyclohexyl Halides via Rh(diphos)$_2$]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 [Rh(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.

We have thus established by both electrochemical and chemical techniques that the reduction of [Rh(diphos)$_2$]Cl occurs via a one-electron transfer step to yield a reactive 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 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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(2) G. Pilloni, E. Vecchi, and M. Martelli, *J. Electroanal. Chem.*, **45**, 483 (1973).

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(4) 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$_3$CN 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 [Rh(diphos)$_2$]Cl is devoid of reduction and oxidation peaks if Pt or glassy carbon working electrodes are used, or if [Rh(diphos)$_2$]ClO$_4$ is the reducible species.

(5) The iridium complex exhibits irreversible cyclic voltammetry, $i_p^{\mathrm{red}}/i_p^{\mathrm{ox}} >$ 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.

(6) N. Tanaka and Y. Sato, *Inorg. Nucl. Chem. Lett.*, **2**, 359 (1966).

(7) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965).

(8) The reductions in CH$_3$CN and C$_6$H$_5$CN were carried out on a Hg pool working electrode. The reductions in Me$_2$SO and DMA were performed on Pt.

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(10) When dry CD$_3$CN is used as solvent containing 0.1 M (*n*-Bu$_4$N)ClO$_4$, only RhD(diphos)$_2$ is isolated. This rules out reaction with the electrolyte as a major source of hydrogen atom.

(11) At high concentrations of D$_2$O accompanied by the high potential necessary to reduce [Rh(diphos)$_2$]Cl, the reactive deuterium is probably found on the

surface of the electrode as one approaches the overpotential for the reduction of D_2O. This hypothesis is born out by the following observations. The competition favoring reaction of $[Rh(diphos)_2]^0$ with D_2O vs. CH_3CN 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^+/Rh^0 couple.[13]

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(14) R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967).

(15) Dialkylmercury compounds are common products obtained upon the reduction of alkylhalides on a Hg electrode: G. M. McNamee, B. C. Willet, D. M. LaPerriere, and D. G. Peters, *J. Am. Chem. Soc.*, **99**, 1831 (1977).

(16) The equivalents of cyclohexyl radical produced was calculated from the current passed in excess of $n = 2$, which is obtained in the absence of cyclohexyl chloride.

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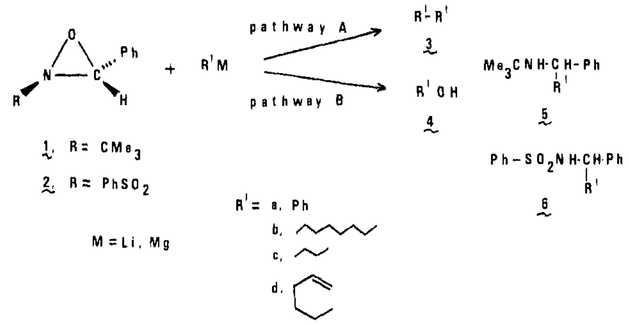
Coupling and Hydroxylation of Lithium and Grignard Reagents by Oxaziridines

Sir:

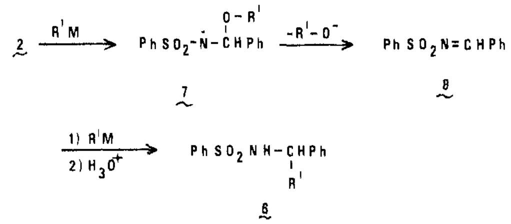
Oxaziridines represent a unique class of three-membered heterocyclic compounds which undergo novel thermal and photochemical transformations.[1,2] At present, the chemistry of these compounds is not well understood. Despite the fact that oxaziridines have been known for nearly 25 years,[3] there appears to have been no study of the reactions of this class of compounds with organometallic reagents. By contrast, the reactions of oxiranes, aziridines, and thiiranes 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] Thiiranes, on the other hand, are attacked at sulfur by organolithium compounds to afford the thiol and alkene stereospecifically.[6,7] Grignard reagents react with thiiranes 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 bromide[10] in ether at 0 °C, afforded after 15 h biphenyl and hexadecane as the principal organic products 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]

Scheme I



Scheme II

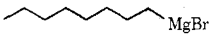
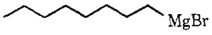
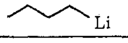


In contrast to oxaziridine **1**, (*E*)-2-benzenesulfonyl-3-phenyloxaziridine (**2**)[1,13] reacts almost exclusively by pathway B with lithium and Grignard reagents (R′M) to afford phenol and alcohols (Table I, entries 5–8). Products were identified by comparison with authentic samples of the reaction 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 thiolsulfinates 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 nitrobenzene[15] and dialkyl peroxides[16] and Grignard reagents by molecular oxygen[17] and *tert*-butyl hydrogen peroxide[18] 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			**3b** (85–90)	ref 11
3	**1**	−78	PhLi	**4a** (70–75)		**5a** (95)
4	**1**	−78			**3c** (82–87)	**5c** (73) + *e*
5	**2**	0	PhMgBr	**4a** (50–58)		**6a** (87–90)[f]
6	**2**	0		**4b** (88–92)		**6b** (63–67)
7	**2**	−78	PhLi	**4a** (92–96)		**6a** (72)[f]
8	**2**	−78		**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 oxazirdine. [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).

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