Studies on Electrochemical Properties of Lithium/Oxyhalide Cell: Electrocatalytic Effects on the Reduction of Thionyl Chloride

Woo-Seong Kim, Yong-Kook Choi*, and Ki-Hyung Chjo

Department of Chemistry, Chonnam National University Kwangju, 500-757

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Catalytic effects of various cobalt phenylporphyrin compounds on the reduction of thionyl chloride at glassy carbon electrode have been evaluated by determining kinetic parameters with cyclic voltammetric techniques. The concentration of catalysts and the electrode immersion time have been found to affect the catalyst performance strongly, leading to a conclusion that the compounds are first adsorbed at the electrode surface and act as catalysts. Significant improvements in cell performance have been noted in terms of both exchange rate constants of up to 3 times and current densities of up to 150% at glassy carbon electrode.

Introduction

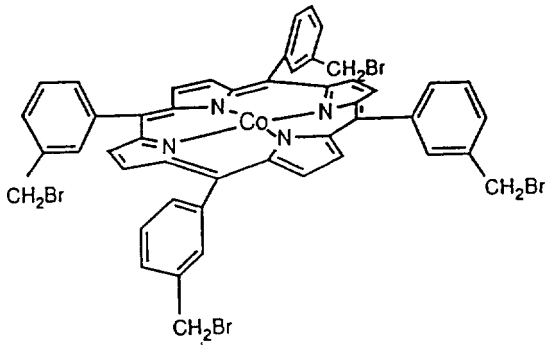
The electrochemical reduction of thionyl chloride has been studied extensively due to its importance in high energy density primary batteries based on the Li-$SOCl_2$ chemistry[1-18]. While Li-$SOCl_2$ batteries can have very high energy density and good power density characteristics, a reasonable performance of these batteries originates from the fact that neat thionyl chloride is used as a catholyte. The electrode kinetics of the cathode discharge reaction is rather poor due to the formation of passive LiCl films at the cathode as a result of the reaction,

$$2SOCl_2 + 4e^- \rightarrow SO_2 + 4Cl^- + S \quad (1)$$

On the other hand, the passive film formed on the lithium anode protects it from undergoing spontaneous reactions with thionyl chloride by forming a *solid/electrolyte interface (SEI)*; it is also the source of the voltage delay owing to its overly passive nature. It is why many investigators tried to get around the problem of too high passivity without destroying its capability to form the *SEI*. One approach to enhance the cell performance can be the addition of catalyst molecules, which makes the rate of electron transfer faster. It has been shown by several investigators[19-24] that adding a small amount of metal phthalocyanines improves cell performance by changing both thermodynamic and kinetic parameters for the thionyl chloride reduction. The improvement is achieved by shifting the reduction potential of thionyl chloride toward more positive direction enhancing reduction currents for the thionyl chloride with these additives. The former provides larger cell voltages. In this report, we describe the effect of several cobalt phenylporphyrin compounds on the reduction of thionyl chloride by evaluating electrokinetic parameters involved. To our knowledge, this is the first effort to evaluate the effect of these catalyst molecules quantitatively.

Experiment

Single compartment cells, in which a platinum or glassy carbon working, a molybdenum wire counter, and a lithium wire reference electrodes are housed, were used for this study. Glassy carbon and platinum electrode have 0.071 and 0.0225 cm^2 of geometric area, respectively. Lithium chloride (Aldrich, 99.995%, ultra dry), aluminum chloride (Aldrich, 99.99%, ultra dry) were used to make up 1.50 M $LiAlCl_4$ solution in thionyl chloride (Aldrich, 99.9%). Cofacial *bis*-cobalt 5, 10, 15, 20,-tetraphenylporphyrins (Co-TPP) as shown in scheme 1 and 2 were prepared according to established method[25]. All solutions were prepared in a glove box under Ar gas atmosphere. A Princeton Applied Research (PAR) 273 potentiostat/galvanostat was used for recording cyclic voltammograms, which was interfaced with 386 DX microcomputer through an IEEE-488 bus.



Co(II) - TPP
Co(II)-5,10,15,20-tetrakis-((α-bromo-m-tosyl)porphyrine)

Scheme 1.

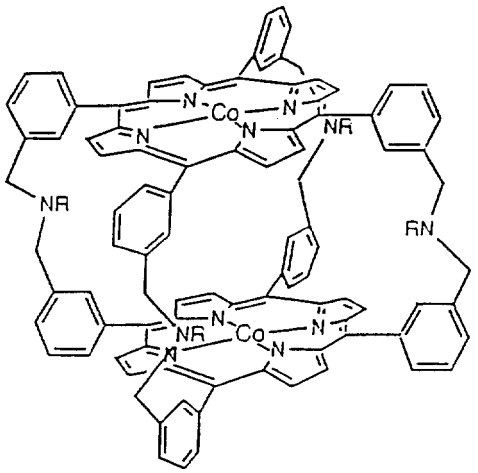
Results and Discussion

Catalytic activities of metal phthalocyanines have been demonstrated in a number of previous studies[19-24]. Doddapaneni [24] reported two voltammetric peaks for the reduction of thionyl chloride with phthalocyanine molecule, followed by two steps fast electron transfer to the adduct. Two consecutive electron transfer reactions were described as

$$M\text{-}Pc \cdot SOCl_2 + e^- \rightarrow M\text{-}Pc \cdot SOCl^{\cdot} + Cl^- \quad (2)$$

$$M\text{-}Pc \cdot SOCl^{\cdot} + e^- \rightarrow M\text{-}Pc + 1/2S + 1/2SO_2 + Cl^- \quad (3)$$

which explain two voltammetric peaks observed. Here M is a metal ion.



Co(II)$_2$-1 TPP R = $-SO_2-$(2-pyridine)

Co(II)$_2$-tetrakis[m,m-methylene((α-pyridinesulfonyl)imino)-methylene]-strati-bis(5,10,15,20-tetraphenylporphyrine)

Co(II)$_2$-2 TPP R = $-SO_2-$(1-methyl-2-pyridinium)

Co(II)$_2$-tetrakis[m,m-methylene((formamido)imino)methylene]-strati-bis)5,10,15,20-tetraphenylporphyrine)

Scheme 2.

More recently, however, Bernstein and Lever[26] described the reaction as a typical catalytic (EC′) reaction after running an extensive number of experiments in 1,2-dichlorobenzene. Thus, two cyclic voltammetric (CV) peaks observed during the catalytic reduction of thionyl chloride should represent those of reducing Co(III)-Pc to Co(II)-Pc first and then to Co(I)-Pc. The overall catalytic cycle is

$$\begin{aligned} &\text{Co(III)-Pc} + 2e^- \rightarrow \text{Co(I)-Pc} \qquad \text{(at the electrode)} \\ &\text{Co(I)-Pc} + SOCl_2 \rightarrow \text{Co(III)-Pc} + 1/2S + 1/2SO_2 \qquad \text{(in the bulk)} \end{aligned} \tag{4}$$

These investigators have shown convincingly that $SOCl_2$ oxidizes Co(I)-Pc through a two-electrons transfer reaction. Bernstein and Lever's conclusion suggests that there are both thermodynamic and kinetic requirements for electrocatalysts: the reduction potential of the $SOCl_2$ must be more positive than the oxidation potential of metal phthalocyanines and also that the electron transfer kinetics must be more favorable at these compounds than thionyl chloride. The thermodynamic requirement depends on the electron affinity of the central metal ion of a catalyst molecule, the latter would be met easily by considering that most metal phthalocyanines are known to undergo reversible reaction due to their favorable molecular geometries[26].

Cyclic voltammograms (CV) recorded for the reduction of neat thionyl chloride at platinum electrode in the absense (a) and presence (b) of Co-TPP (0.62 mM) are shown in Figure 1. A large current peak at 2.9 V *vs.* Li, which is absent in the original CV for the reduction of thionyl chloride (Figure 1(a)), shows up at a potential more negative than the

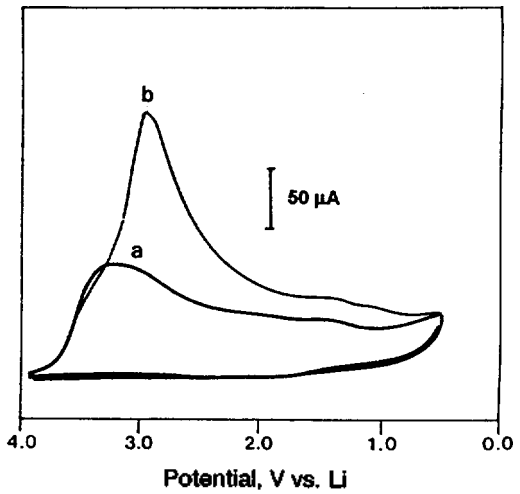


Figure 1. Cyclic voltammograms recorded at the Pt electrode for the reduction of $SOCl_2$ solution containing: a) 0 and b) 0.62 mM Co-TPP. Scan rate was 50 mV/s.

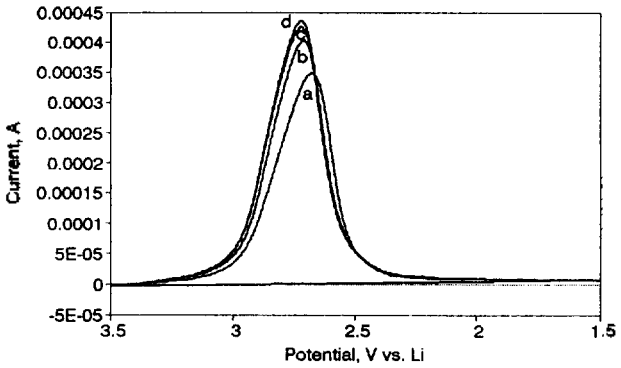


Figure 2. Voltammograms recorded at the glassy carbon electrode for the reduction of $SOCl_2$ solution containing: a) 0, b) 0.35, c) 0.45, and d) 0.62 mM Co(II)-TPP. Scan rate was 50 mV/s.

thionyl chloride reduction (see Figure 1(b)). This is perhaps because the Pt electrode is already a good electrocatalyst for the thionyl chloride reduction. Thus, an excessive overvoltage for the reduction of thionyl chloride is not required. For this reason, the CV peak for the reduction of thionyl chloride appears at more negative potential than that of Co-TPP. The CV peak observed in the presence of Co-TPP is perhaps the result of the reduction of Co(III)-TPP to Co(II)-TPP or Co(I)-TPP, which again reduces $SOCl_2$ through a catalytic (EC′) mechanism[27]. While the presence of Co-TPP enhances the $SOCl_2$ reduction current, it does not affect its reduction potential significantly at Pt electrode. This was the case for all cofacial cobalt tetraphenylporphyrine that we studied here. Therefore, we did not pursue further efforts to study on the effects of electrocatalysts at Pt electrode. Moreover platinum electrode is not used in real Li/$SOCl_2$ cells.

The CV shapes are also shown to be a function of the catalyst concentration in thionyl chloride solution. Figure 2 shows CVs recorded in a thionyl chloride solution containing (a) 0.00 (b) 0.35 (c) 0.45 and (d) 0.62 mM Co(II)-TPP. As shown in this figure, shapes of voltammograms are affected

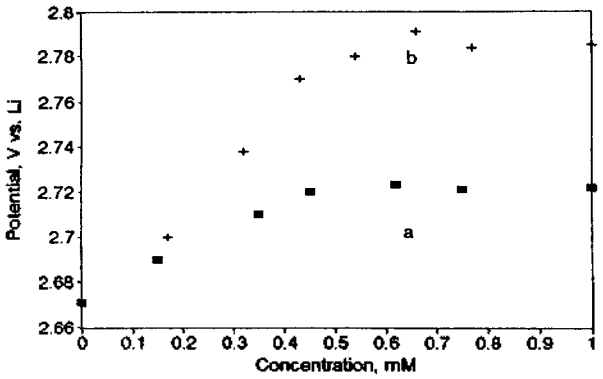


Figure 3. Plots the peak potential vs. the concentration of Co (II)-TPP catalyst for the reduction of $SOCl_2$ at glassy carbon electrode. a) Co(II)-TPP and b) $Co(II)_2$-1 TPP.

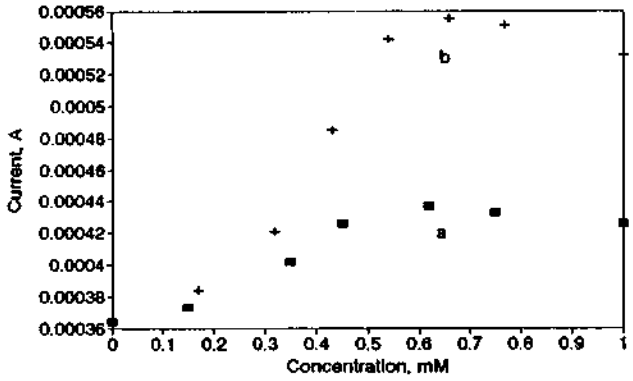


Figure 4. Plots the peak current vs. the concentration of Co(II)-TPP catalyst for the reduction of $SOCl_2$ at glassy carbon electrode. a) Co(II)-TPP and b) $Co(II)_2$-1 TPP.

strongly by the concentration of catalysts. This is true for all Co(II)-TPP and $Co(II)_2$-TPP studied, although the extent of effects is different.

The magnitude of the reduction current appears to be a strong function of catalyst concentration in thionyl chloride solution containing catalyst molecules. This indicates that the first step for the catalytic activity of these compounds must be the adsorption of catalyst molecules on the electrode surface, followed by its own reduction at the electrode, which in turn reduces thionyl chloride[22].

In Figure 3 and 4, peak currents and peak potentials are plotted as a function of the catalyst concentration for Co-TPP at glassy carbon electrode. There is an optimum concentration for each Co-TPP. Figure 5 shows voltammograms of catalytic effect in thionyl chloride solution containing Co-TPP at glassy carbon electrode. The catalytic effects are clearly seen as shown by the shift of the reduction potential for thionyl chloride toward positive direction and an increase in peak current. Peak currents and potentials observed for the reduction of thionyl chloride in the presence of several catalyst molecules are summarized in Table 1. As can be seen in Table 1, the peak currents increased and the peak potentials shifted to positive for most catalysts. In general, however, these compounds show good catalytic activities at glassy carbon electrode. These results in overlap

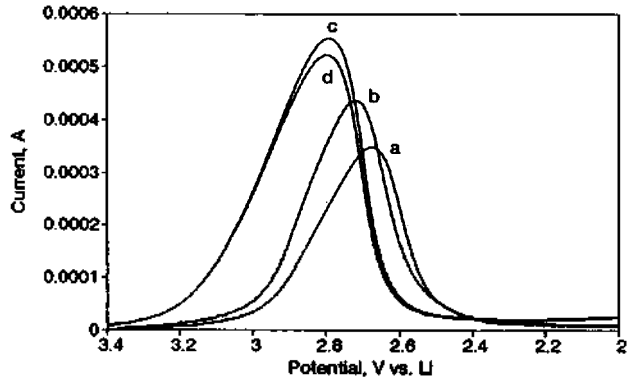


Figure 5. Voltammograms recorded at the glassy carbon electrode for the reduction of $SOCl_2$ solution containing: a) bare, b) Co(II), c) $Co(II)_2$-1 and d) $Co(II)_2$-2 TPP. Scan rate was 50 mV/s.

Table 1. CV Peak Currents and Peak Potentials Observed in the Presence of Various Catalysts

Catalysts	Concentration (mM)	Peak potential (V *vs.* Li)	Peak current (A/cm^2)
Bare	–	2.671	0.00513
Co(II)	0.62	2.723	0.00615
$Co(II)_2$-1	0.65	2.791	0.00782
$Co(II)_2$-2	0.65	2.798	0.00734

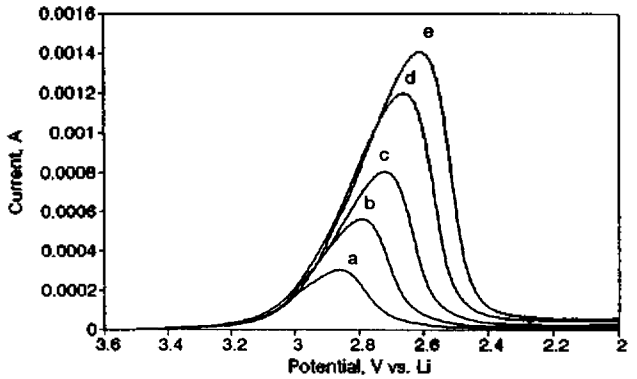


Figure 6. Scan rate dependency of the voltammograms recorded at glassy carbon electrode for the reduction of $SOCl_2$ solution containing 0.65 mM $Co(II)_2$-1 TPP. Scan rate were a) 20, b) 50, c) 100, d) 200, and e) 300 mV/s.

of two electrochemical processes of thionyl chloride reduction, which make the system, appear more catalytic for the reaction.

By the reason stated above, cyclic voltammmetric experiments only at an "optimum" catalyst concentration were conducted to evaluate kinetic parameters after waiting for some time until voltammograms develop to a well defined shape. Voltammograms are taken after the electrode is immersed in a freshly prepared catalyst soultion. The data were reasonably reproducible although some scattered points were observed, depending on the status of electrode surface. Figure

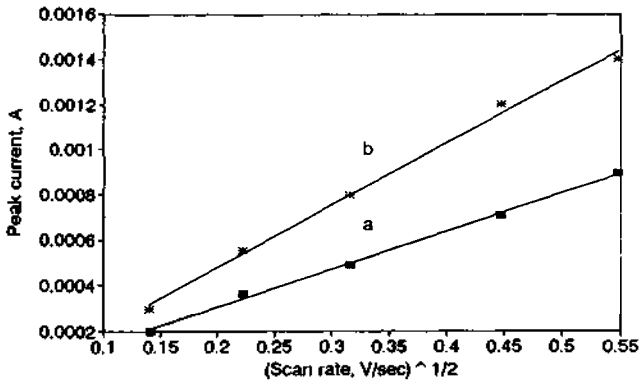


Figure 7. Plots of i_p *vs.* $v^{1/2}$ for bare glassy carbon electrode (a) and $SOCl_2$ solution containing 0.65 mM $Co(II)_2$-1 TPP catalyst (b).

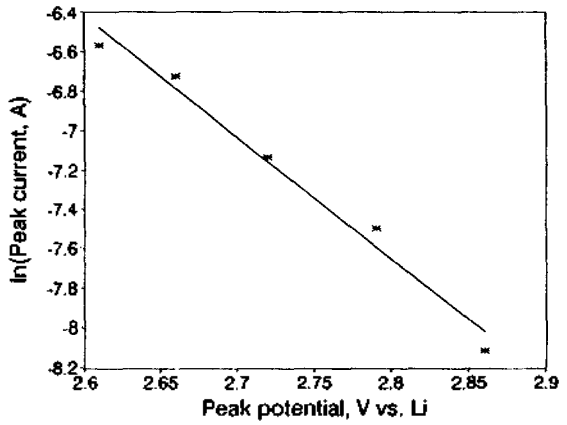


Figure 8. Plots of ln (i_p) *vs.* E_p for $SOCl_2$ solution containing 0.65 mM $Co(II)_2$-1 TPP catalyst.

6 shows a series of cyclic voltammograms recorded at various scan rates in thionyl chloride solution containing $Co(II)_2$-1 TPP. Figure 7 shows a plot of peak current *vs.* $v^{1/2}$ (v: scan rate) from voltammetric results obtained at glassy carbon electrode under "optimum" conditions. This plot shows good linear relationship. The peak current from CV in irreversible case is given as[28].

$$i_p=(2.99\times10^5)n(\alpha n_a)^{1/2}AC_o^*D_o^{1/2}v^{1/2} \quad (5)$$

where n is the number of electrons transferred, α the transfer coefficient, n_a the apparent number of electrons involved in the rate determining step. A electrode area in cm^2, C_o^* the bulk concentration of an electroactive compound in mole/cm^3, and D_o the diffusion coefficient of the electroactive compound or other charge carrier in cm^2/s. Examination of Eq. (5) reveals that the plot of i_p *vs.* $v^{1/2}$ allows one to obtain the diffusion coefficient, provided α and n_a are known. From the relationship between i_p with E_p[28]

$$i_p=0.227nFAC_o^*k^o\exp[-\{(\alpha n_aF)/(RT)\}(E_p-E^{o'})] \quad (6)$$

where k^o is the exchange rate constant in cm/s and $E^{o'}$ is the standard electrode potential in volt. A plot of ln (i_p) *vs.* E_p should yield a straight line with a slope, $\alpha n_aF/RT$, and an intercept, $\ln(0.227nFAC_o^*k^o)$, from which αn_a and k^o values can be calculated, respectively. In this calculation, the thermodynamic $E^{o'}$ value of 3.734 V *vs.* Li is used as it is obtained from Eq. (1) using free energies of formation for reactants and productants. The ln (i_p) *vs.* E_p plots are shown in Figure 8 for the reduction of $SOCl_2$ at glassy carbon electrode in the presence of various catalysts. Now, the αn_a value obtained from this equation can be used to evaluate the diffusion coefficient according to Eq. (5). Kinetic parameters calculated from these plots in "optimum" catalyst concentrations are listed in Table 2 for glassy carbon electrode. As can be seen Table 2, diffusion coefficients are determined to be in the order of 10^{-9} cm^2/s and exchange rate constant are estimated to be in the order of 10^{-8}-10^{-7} cm/s at catalyst supported glassy carbon electrode. Enhancements in current densities of about 150% are noted for the glassy carbon electrode. These results are in accordance with previous cell test results reported by Doddapaneni[19-22,24]. Most of the enhancement originates from improvements in apparent diffusion coefficients and exchange rate constants in thionyl chloride solution containing catalysts.

Table 2. Kinetic Parameters for Catalysts Coated Electrode

Catalysts	Concentration (mM)	αn_a	k^o (cm/s)	D_o (cm^2/s)
Bare	–	0.18	6.82×10^{-8}	1.31×10^{-10}
Co(II)	0.62	0.22	8.19×10^{-8}	1.34×10^{-9}
$Co(II)_2$-1	0.65	0.23	2.20×10^{-7}	3.35×10^{-9}
$Co(II)_2$-2	0.65	0.21	1.98×10^{-7}	2.42×10^{-9}

Conclusion

It is clear that some Co(II)-TPP and $Co(II)_2$-TPP show sizable catalytic activities for the reduction of thionyl chloride. From our results, we conclude that:

1. The catalyst molecules are probably adsorbed on the electrode surface first;
2. The possible adsorbed molecules would be reduced on the electrode surface which in turn reduces thionyl chloride resulting in a generation of oxidized catalyst molecules and thus completes the catalytic cycle;
3. There is an optimum concentration for each catalyst compound;
4. Relative catalyic effects are larger in thionyl chloride solution containing $Co(II)_2$-TPP compared to Co(II)-TPP;
5. Enhancements in current densities of up to 150% at the glassy carbon electrodes are noted.

If the catalytic effects result from purely catalytic EC' reaction through a homogeneous electron transfer reaction as was concluded by Bernstein and Lever[26], higher catalytic effects should always have been observed in a solution containing higher catalyst layer on the electrode surface shuttles electron transfer between the electrode and the solution. Thus, this should have to be checked do with adsorption isotherms of each catalyst on the electrode surface. We hope to illuminate this question employing *in-situ* techniques such as spectroelectrochemical measurements.

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Synthesis and Characterization of 1-Transition Metal Complex Substituted-2,3,4,5-Tetraphenyl-1-Silacyclopentadienyl Complexes and Generation of Transition Metal Complex-Substituted Silylene

Cheolki Paek, Jaejung Ko*, Youngkun Kong†, Chang Hwan Kim‡, and Myong Euy Lee‡

Department of Chemical Education, Korea National University of Education, Chungbuk 363-791
†Department of Chemistry, Kyunggi University, Suwon 440-270
‡Department of Chemistry, Yonsei University, Seoul 120-749
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New silicon-monosubstituted (η^4-2,3,4,5-tetraphenyl-1-silacyclopentadiene)transition metal complexes are described. (7-Alkyl-7-silanorbornadienyl)MLn(Alkyl=Methyl : MLn=$CpRu(CO)_2$: Alkyl=Methyl : MLn=CpNi(CO) : Alkyl=Ethyl : MLn=CpNi(CO) complexes were prepared from the corresponding silole-transition metal complexes with dimethyl acetylenedicarboxylate. Cycloaddition products were obtained with 2,3-dimethyl-1,3-butadiene, 2,3-butanedione, and 1,4-benzoquinone through the ruthenium-substituted silylene. We have determined the crystal structure of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium by using graphite monochromated Mo-Ka radiation. The compound was crystallized in the monoclinic space group $P2_1/c$ with $a=9.838(1)$, $b=15.972(3)$, $c=18.327(3)$ Å, and $\beta=94.28(1)°$. The ruthenium moiety $CpRu(CO)_2$ on silicon is in an axial position.

Introduction

Transition metal complexes of nonfunctional siloles have been well documented,[1] and the silole functions as an η^4-ligand in all complexes reported thus far.[2] Transition-metal complexes of siloles [$Ph_4C_4Si(R)MLn$] draw our attention because they are presumed to function as a silylene precursor or as precursors for the generation or detection of an