

Sensitivity and Error Propagation Factors for Three-Parameter Ellipsometry

Hyeran Ihm, Gyusung Chung*, Woon-ki Paik, and Duckhwan Lee

Department of Chemistry Sogang University, Seoul 121-742 Korea

*Department of Chemistry Keonyang University, Nonsan 320-800 Korea

Received August 3, 1994

The sensitivity factors and the error propagation factors are defined for the three-parameter ellipsometry (TPE). The sensitivity factor is useful for understanding the nature of the TPE measurements in connection with determination of the optical properties and the thickness of a film. On the other hand, the error propagation factors provide a quantitative tool for predicting the optimum condition for TPE experiments. Their usefulness is demonstrated for the passive film formed on nickel in aqueous solution.

Introduction

The polarization of the light is changed upon reflection at an interface. Ellipsometry is an experimental technique to get information on surface or surface film from the change of polarization state of the light reflected at the interface.^{1,2} Ellipsometry is a non-destructive and sensitive technique which can be easily used for *in-situ* measurements. It has been applied to various studies in many different fields such as electrochemistry, polymer science, physics, and biology.

A three-layer model, consisted of a transparent ambient medium (medium 1), film (medium 2), and substrate (medium 3), as shown in Figure 1, is often employed for describing ellipsometry. The ambient medium is usually transparent, thus $\kappa_2=0$, in most ellipsometry experiments. The conventional ellipsometric measurements, Ψ and Δ , are given as functions of the optical properties of the three layers as well as the wavelength and the incident angle of the light,

$$\Psi = F(n_2, \kappa_2, \tau_2; n_1, n_3, \kappa_3, \lambda, \phi_1) \quad (1)$$

$$\Delta = G(n_2, \kappa_2, \tau_2; n_1, n_3, \kappa_3, \lambda, \phi_1) \quad (2)$$

The explicit expressions for Ψ and Δ can be found elsewhere.¹⁻⁴ In the conventional ellipsometry, two measurements, Ψ and Δ , are used to determine three properties of the film, n_2 , κ_2 and τ_2 . Thus the conventional ellipsometry is inherently an underdefined problem. There have been many attempts to resolve this difficulty of the conventional ellipsometry,⁵⁻⁸ such as changing substrates, thickness, and/or wavelength of incident light. The three-parameter ellipsometry (TPE)^{3,4} suggested by Paik and Bockris in 1971 is one of such attempts, in which the reflectance, R , is used as the necessary auxiliary measurement.

$$R = H(n_2, \kappa_2, \tau_2; n_1, n_3, \kappa_3, \lambda, \phi_1) \quad (3)$$

The TPE has been successfully applied for various problems including the study of passive films formed on metal surfaces⁹⁻¹³ and conducting polymer films.^{14,15} The TPE is especially useful for studying passive film formed on metal surface since the substrate and the ambient medium are fixed. A numerical technique such as Newton-Rapson method^{16,17} must be employed to invert Eqs. (1), (2), and (3) to find n_2 , κ_2 , and τ_2 from the TPE measurements of Ψ , Δ , and R .

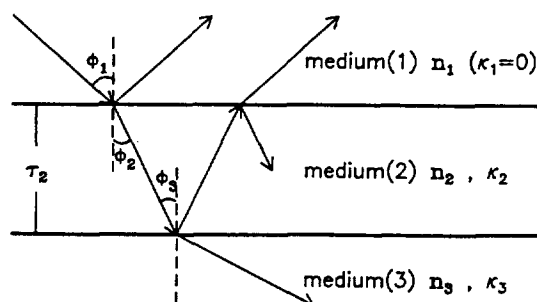


Figure 1. Reflection and transmission of light in three-layer model.

In order to achieve better understanding of the TPE, the relations between the TPE measurements, Ψ , Δ , and R , and the film properties, n_2 , κ_2 , and τ_2 , need to be analyzed in detail. For example, one needs to know how the film properties affect the TPE measurements and how the errors contained in the TPE measurements are propagated to the film properties determined from them. Such informations are useful not only for understanding the nature of the TPE measurements but also for determining the optimum experimental condition for TPE experiments. In our previous study¹⁸, the sensitivities of the TPE measurements with respect to the film properties and of the film properties with respect to the TPE measurements varying with the incident angle were analyzed in a qualitative manner.

In this work, a statistical approach is used to analyze the nature of the TPE in a more quantitative fashion. The sensitivity factors (SF's) and the error propagation factors (EPF's) are defined by linearizing the complicated relations in Eqs. (1), (2), and (3). The SF's indicate how the TPE measurements are affected by the variations of the film properties. On the other hand, the EPF's show how random errors included in the TPE measurements are reflected in the resulting film properties determined by the TPE. The optimum experimental condition for the TPE can be determined by analyzing these informations. Under the optimum experimental condition, the TPE measurements must be sensitive enough to the film properties and at the same time the random errors should propagate to the minimal extent to the

film properties.

Sensitivity and Error Propagation Analysis

The nature of the three TPE measurements, $M_i = (\Psi, \Delta, R)$, need to be studied for comprehensive understanding of the TPE. For example, it is important to know how the TPE measurements depend upon each of the three independent film properties, $F_j = (n_2, \kappa_2, \tau_2)$. In our previous study¹⁸, the forward sensitivity coefficients (FSC's), $(\partial M_i / \partial F_j)$, were used for qualitative understanding. In this work, the sensitivity is analyzed in a more quantitative manner by employing the widths of the TPE measurement distributions.

Suppose that each of the film properties, F_j , has normal distributions around the average values, \bar{F}_j , with a width σ_{F_j} , which is not too large. This is of course a hypothetical situation because any film of interest would have well-defined properties. Nevertheless, this hypothetical case is useful for providing the information on how sensitive the TPE measurements are to the film properties as will be demonstrated below.

Now, the variance of a TPE measurement, M_i , can be defined as following,

$$\sigma_{M_i}^2 = \left(\frac{\partial M_i}{\partial n_2} \right)^2 \sigma_{n_2}^2 + \left(\frac{\partial M_i}{\partial \kappa_2} \right)^2 \sigma_{\kappa_2}^2 + \left(\frac{\partial M_i}{\partial \tau_2} \right)^2 \sigma_{\tau_2}^2 \quad (4)$$

For Eq. (4), it is assumed that the three film properties, F_j , are independent with others so that the covariances between the F_j 's vanish. It is also assumed that the TPE measurements are approximately linear to the variations of the film properties. The linear approximation breaks down of course if distributions of the film properties are too broad. The partial derivatives defined around the average values of the film properties in Eq. (4) can be found in analytical forms. Now the square-root of the covariance, σ_{M_i} , can be defined as the sensitivity factor (SF) of M_i with respect to the overall variations of the film properties. For example, a large value of σ_{M_i} would indicate that the M_i is sensitive to the variations of the film properties. However, unlike the previous FSC's, the sensitivity factor defined from Eq. (4) can represent the collective effect of variations of the film properties on a TPE measurement.

On the other hand, any experimental measurements would have uncertainties to some extent. The experimental uncertainties of the TPE measurements would affect the film properties determined from them. The extents of the uncertainties in the film properties arising from the random errors in the TPE measurements can be represented by the following error propagation factor (EPF), σ_{F_i} :

$$\sigma_{F_i}^2 = \left(\frac{\partial F_i}{\partial \Psi} \right)^2 \sigma_{\Psi}^2 + \left(\frac{\partial F_i}{\partial \Delta} \right)^2 \sigma_{\Delta}^2 + \left(\frac{\partial F_i}{\partial R} \right)^2 \sigma_{R}^2 \quad (5)$$

Eq. (5) holds again if the variances of the experimental measurements are not too large. Unlike the partial derivatives in Eq. (4), the ones in Eq. (5), calculated at the average values of the experimental measurements, are not given in the analytical forms. Instead, they must be obtained from

$$\left(\frac{\partial F_i}{\partial M_j} \right) = \frac{\text{Co}(i, j)}{J} \quad (6)$$

where J is the Jacobian given by

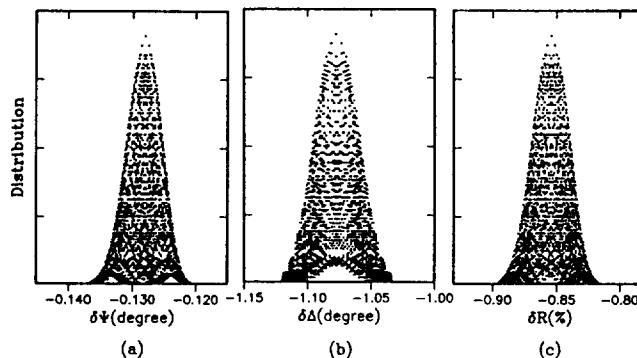


Figure 2. The expected distribution of ellipsometric measurements, ((a) $\delta\Psi$, (b) $\delta\Delta$, (c) δR) for a passive film on nickel for $\sigma_{n_2} = 1.0\%$, $\sigma_{\kappa_2} = 1.0\%$, $\sigma_{\tau_2} = 1.0\%$ of the determined values of the film and $\phi_1 = 55^\circ$. (The blank space inside the envelope is due to the limited number of data points for plotting.)

$$J = \begin{vmatrix} \left(\frac{\partial \Psi}{\partial n_2} \right) & \left(\frac{\partial \Psi}{\partial \kappa_2} \right) & \left(\frac{\partial \Psi}{\partial \tau_2} \right) \\ \left(\frac{\partial \Delta}{\partial n_2} \right) & \left(\frac{\partial \Delta}{\partial \kappa_2} \right) & \left(\frac{\partial \Delta}{\partial \tau_2} \right) \\ \left(\frac{\partial R}{\partial n_2} \right) & \left(\frac{\partial R}{\partial \kappa_2} \right) & \left(\frac{\partial R}{\partial \tau_2} \right) \end{vmatrix} \quad (7)$$

and $\text{Co}(i, j)$ is the cofactor for the (i, j) -th element of the above Jacobian.

Like the SF's, the EPF's represent the collective effect of the random errors of the experimental measurements on the film properties. A large value of a EPF would mean that the experimental errors become serious in determining the film property.

Once the characteristics of the SF's and the EPF's are understood, it is now possible to determine the optimum experimental condition such as the optimum angle of incidence.

Results and Discussion

For the purpose of analysis, a passive film on nickel formed in aqueous solution ($n_1 = 1.336$, $n_2 = 1.9614$, $\kappa_2 = 0.3831$, $\tau_2 = 11.63 \text{ \AA}$, $n_3 = 1.99$, $\kappa_2 = 3.44$) is chosen. The wavelength of the incident light is 6328 \AA .¹²

Sensitivity Factors. In this Section, the sensitivity factor defined from Eq. (4) is used to analyze the nature of the TPE measurements, (Ψ, Δ, R) . The film properties, (n_2, κ_2, τ_2) , are assumed to have normal distributions around their values determined from the experimental measurements. It is emphasized that the distributions of the film properties are arbitrarily assumed to see the sensitivity of the TPE measurements. Figure 2 shows typical calculated distributions of the TPE measurements. When the distributions of the film properties are narrow enough, the TPE measurements are also close to normal distributions as shown in Figure 2. However, the distributions become distorted for broader film properties indicating the break-down of the linear approximation. For such broad distributions, the analysis based on Eqs. (4) and (5) must be carefully undertaken.

The SF's for various hypothetical cases of the distributions of the film properties are given in Table 1 at two different

Table 1. Sensitivity factors for the passive film on nickel in aqueous solution.

Width ^a			55°			70°		
σ_{n_2}	σ_{κ_2}	σ_{τ_2}	σ_{Ψ}^b	σ_{Δ}^b	σ_R^c	σ_{Ψ}^b	σ_{Δ}^b	σ_R^c
1.0	0.0	0.0	0.00197	0.01480	0.01076	0.00573	0.01963	0.00280
0.0	1.0	0.0	0.00137	0.00081	0.00480	0.00171	0.00252	0.00447
0.0	0.0	1.0	0.00126	0.01072	0.00870	0.00048	0.01685	0.00233
1.0	1.0	0.0	0.00239	0.01482	0.01178	0.00598	0.01979	0.00527
1.0	0.0	1.0	0.00234	0.01827	0.01384	0.00575	0.02587	0.00364
0.0	1.0	1.0	0.00186	0.01075	0.00993	0.00177	0.01704	0.00504
1.0	1.0	1.0	0.00271	0.01829	0.01465	0.00600	0.02599	0.00576

^aThe widths are represented as the percentages of the determined values of the film. ^bin degree. ^cin percentage.

Table 2. Error propagation factors for the passive film on nickel in aqueous solution.

Width			55°			70°		
$\sigma_{\Psi}(\text{°})$	$\sigma_{\Delta}(\text{°})$	$\sigma_R(\%)$	$\sigma_{n_2}^a$	$\sigma_{\kappa_2}^a$	$\sigma_{\tau_2}^b$	$\sigma_{n_2}^a$	$\sigma_{\kappa_2}^a$	$\sigma_{\tau_2}^b$
0.01	0.00	0.00	0.05890	0.03446	0.4900	0.07003	0.01830	0.5668
0.00	0.01	0.00	0.00775	0.00797	0.1902	0.00615	0.00289	0.1246
0.00	0.00	0.01	0.01812	0.01032	0.1720	0.03019	0.01719	0.2866
0.01	0.01	0.00	0.05941	0.00868	0.5256	0.07030	0.01853	0.5804
0.01	0.00	0.01	0.06162	0.01088	0.5193	0.07626	0.02511	0.6351
0.00	0.01	0.01	0.01970	0.01303	0.2564	0.03081	0.01743	0.3125
0.01	0.01	0.01	0.06211	0.01348	0.5530	0.07651	0.02528	0.6472

^adimensionless. ^bin Å.

angles of incidence, 55° and 70°. The widths σ_{M_i} calculated by using Eq. (4) are in good agreement with the widths estimated from Figure 2 when the hypothetical distributions of the film properties are not too broad. The incident angle of 70° has been preferred in the conventional two-parameter ellipsometry, while 55° has been widely used for the TPE. The widths of the distributions of the film properties are given in percentages with respect to their true values. The calculated widths of the TPE measurements obtained from the figures such as the ones given in Figure 2 are expressed by the absolute values.

First of all, the reflectance is clearly more sensitive to the film properties at 55° than at 70°. This has been already predicted from the variation of the reflectance with respect to the incident angle.⁷ The other measurements, Δ and Ψ , do not show any evident preference as long as the incident angle is concerned. It appears thus that the choice of 55° is to achieve the better sensitivity of R especially at the expense of the sensitivity of Ψ . Secondly, it can be seen from Table 1 that all of the TPE measurements are the most sensitive to n_2 at 55° and 70° except R at 70°. R is the most sensitive to κ_2 at 70°. On the other hand Δ is the least sensitive to κ_2 . Furthermore, it can be seen from the Table 1 that the sensitivity factors are nearly additive when two or more of the film properties have distributions.

In Figure 3, the variations of the SF's with respect to the angle of incidence are depicted for the passive film on nickel. First of all, the SF's are strongly dependent upon the angle of incidence. Therefore, the judicious choice of the incident angle would be crucial for the success of the

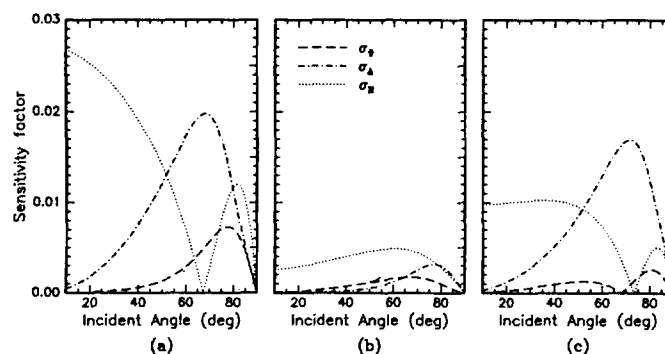


Figure 3. The incident angle dependences of sensitivity factors for a passive film on nickel when (a) $\sigma_{n_2}=1.0\%$, (b) $\sigma_{\kappa_2}=1.0\%$, (c) $\sigma_{\tau_2}=1.0\%$ of the determined values of the film.

TPE experiments. Again, the TPE measurements are more sensitive to n_2 and τ_2 than to κ_2 in general. It can be seen from Figure 3 that Ψ is the least sensitive measurement and that Δ is the most sensitive one in general. R is not sensitive to n_2 and τ_2 near at 70°.

This type of analysis clearly shows how each of the TPE measurements depends on the film properties. Through this analysis, one can obtain better understanding of the nature of TPE measurements. In order for a TPE experiment to be successful for determining thin film properties, the TPE measurements should be sensitive enough to discern films of different characteristics.

Error Propagation Factors. In this Section, the EPF's

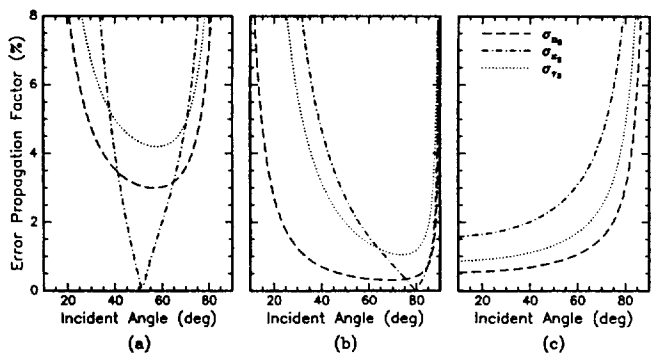


Figure 4. The error propagation factors, represented as the percentages of the determined values of the film, for a passive film on nickel when (a) $\sigma_\Psi=0.01^\circ$, (b) $\sigma_\Delta=0.01^\circ$, (c) $\sigma_R=0.01\%$.

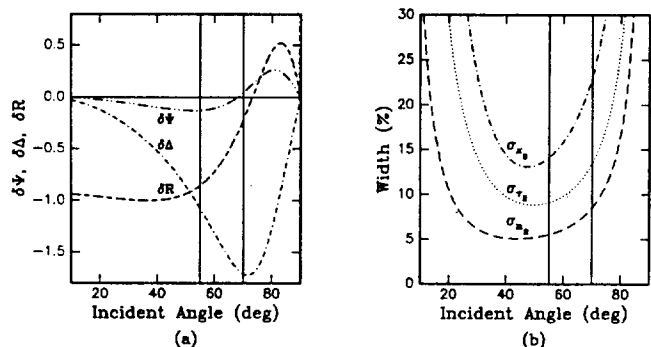


Figure 5. The incident angle dependences of (a) TPE measurements and (b) EPF's for a passive film on nickel.

defined from Eq. (5) are analyzed. Once again, the linear approximation used for Eq. (5) appears to be fairly good for small uncertainties in the TPE measurements.

Table 2 shows the EPF's for the passive film formed on nickel in aqueous solution. The EPF's for Ψ and Δ are expressed in the unit of degree and the EPF's for R are in percentage. A large value of an EPF implies that one must be more careful in the TPE experiment to determine a certain film property. Thus, it is clear from Table 2 that the incident angle of 55° is more preferable, especially for determining n_2 and τ_2 . However the EPF's do not seem to be additive unlike the SF's.

Figure 4 shows the incident angle dependencies of the EPF's. It is evident that low incident angle is more favorable when the measurements of Ψ and R are difficult. However high incident angle appears to be better when uncertainty is involved in Δ .

It is interesting to note that σ_{κ_2} becomes zero at certain incident angles, implying that the measurement of a certain TPE measurement does not affect the value of κ_2 determined. This is due to the fact that the crossing lines of the two of the Ψ , Δ , and R surfaces happen to be perpendicular to the κ_2 axis at these incident angles.

Optimum Experimental Condition. It is clear now that the analysis of the SF's and the EPF's can be used to determine the optimum condition for the TPE experiments. The TPE measurements must be sensitive enough to discern different films. At the same time, the uncertainties

in the TPE measurements must not affect too significantly the film properties determined. The TPE measurements are affected by many other factors in addition to the incident angle. For example, judicious choices of the wavelength of the incident light and the optical properties of the ambient medium and the substrate are also important for success of a TPE experiment.

As an example, Figure 5 shows the variation of the TPE measurements and the EPF's with respect to the incident angle for the passive film formed on nickel in aqueous solution. The incident angles of 55° and 70° are denoted by vertical solid lines. Although the magnitude of Δ is smaller at 55° , all of the EPF's are more favorable at 55° . In actual experiments, however, a change in Δ is large enough at almost any incident angle and the uncertainty in the measurement of R is often much larger than the uncertainty in Δ . Therefore, the relatively small change in Δ at 55° does not pose any serious difficulty.

Concluding Remarks

We have defined the sensitivity factors (SF's) for understanding the nature of the TPE measurements in connection with the film properties. The error propagation factors (EPF's) are also defined in a quantitative manner to represent the extent of the uncertainties in the film properties arising from experimental errors in the TPE measurements. Their usefulness is demonstrated by using the passive film formed on nickel in aqueous solution. Especially the EPF's can be used to determine the optimum condition for a TPE experiment.

Acknowledgment. The financial supports from the Ministry of Education, and the Korea Science and Engineering Foundation are greatly appreciated.

References

1. Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, 1977.
2. Gottesfeld, S. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989, Vol. 15.
3. Paik, W.; Bockris, J. O'M. *Surf. Sci.* **1971**, *28*, 61.
4. Paik, W. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E. Ed.; Plenum: New York, 1993, Vol. 25.
5. Reddy, A. K. N.; Genshaw, M. A.; Bockris, J. O'M. *J. Chem. Phys.* **1968**, *48*, 671.
6. Kruger, J.; Calbert, J. P. *J. Electrochem. Soc.* **1967**, *114*, 43.
7. Dell'Oca, C. J.; Young, L. *Surf. Sci.* **1969**, *16*, 331.
8. Johnson, J. A.; Bashara, N. M. *J. Opt. Soc. Am.* **1971**, *61*, 457.
9. Paik, W.; Szklarska-Smialowska, Z. *Surf. Sci.* **1980**, *96*, 401.
10. Gottesfeld, S.; Reichman, B. *Surf. Sci.* **1974**, *44*, 377.
11. Horkams, J.; Cahan, B. D.; Yeager, E. *Surf. Sci.* **1974**, *46*, 1.
12. Kang, Y.; Paik, W. *Surf. Sci.* **1987**, *182*, 257.
13. Paik, W.; Koh, S. *Bull. Korean Chem. Soc.* **1991**, *12*, 540.
14. Hammett, A.; Christensen, P. A.; Higgins, S. J. *Analyst*, **1994**, *119*, 735.

15. Hammett, A.; Hillman, A. R. *Ber. Bunsenges. Chem.* 1987, 91, 329.
16. Kuo, S. *Computer Applications of Numerical Method*; Addison-Wesley: Reading, 1971.
17. Cahan, B. D. *Surf. Sci.* 1976, 56, 354.
18. Chung, G.; Lee, D.; Paik, W. *Bull. Korean Chem. Soc.* 1991, 12, 477.
19. Eadie, W. T. et al. *Statistical Methods in Experimental Physics*; North-Holland: Amsterdam, 1971.
20. Meyer, S. L. *Data Analysis for Scientists and Engineers*; John Wiley: New York, 1975.

Synthesis and Characterization of 1,4-Diimine Complexes of 1,2,3,4,5-Pentamethylcyclopentadienylrhodium and iridium

Cheolki Paek, Jaejung Ko*, and Jae-Kook Uhm†

Department of Chemical Education, Korea National University of Education, Chungbuk 363-791, Korea

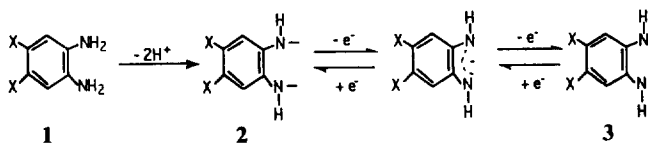
†Department of Chemistry, College of Natural Science, Keimyung University, Daegu 704-701, Korea

Received July 22, 1994

Monomeric rhodium and iridium diimine complexes $\text{Cp}^*\text{M}(\text{HNRNH})(\text{Cp}^*=1,2,3,4,5\text{-pentamethylcyclopentadienyl})$ ($\text{M}=\text{Ir}$; $\text{R}=\text{o-C}_6\text{H}_4$ (**1a**), 4,5-(CH_3)₂- C_6H_2 -1,2 (**1b**), 4,5-(Cl)₂- C_6H_2 -1,2 (**1c**), $\text{NCC}=\text{CCN}$ -1,2 (**1d**); $\text{M}=\text{Rh}$; $\text{R}=\text{NCC}=\text{CCN}$ -1,2 (**1e**)) have been synthesized from $[\text{Cp}^*\text{MCl}_2]_2$ and 2 equiv. of diamine in the presence of NEt_3 . The crystal structure of **1a** was determined by X-ray diffraction method: **1a** was crystallized in the monoclinic system, space group $P2_1/c$, with lattice constants $a=9.543$ (1) Å, $b=16.286$ (1) Å, $c=10.068$ (1) Å and $\beta=99.25$ (1), with $Z=4$. Least-squares refinement of the structure led to R factor of 0.049. The coordination sphere of rhodium and iridium can be described as a 2-legged piano-stool. All complexes are highly colored. Electrochemical studies show that **1d** and **1e** display quasi-reversible reduction and **1a-1c** display irreversible reductions, suggesting that the acceptor orbital might be localized on the diimine ring.

Introduction

Since the discovery of the square-planar $\text{M}\{\text{C}_5\text{H}_4(\text{NH})_2\}_2^{0,1+}$ systems¹ with $\text{M}=\text{Ni}$, Pd , Pt and Co in 1966, transition metal diimine complexes have been reported, including derivatives of Co^2 , Rh^3 , Fe^4 , Cr^5 , Mo^6 , W^7 and Ru^8 by the reactions carried out under basic conditions, using KOH , NR_3 or an excess of the diamine in order to deprotonate the ligand. The diimine ligand is coordinated in a chelate or bridging fashion. Transition-metal complexes of the diaminy-lato ligands have attracted interest because of their oxidation-reduction propensities. It has been suggested that the redox forms for the diamine ligand **1**, consist of the terminally reduced diamine dianion **2**, and the terminally oxidized neutral diimine **3**.



We⁹ recently described the reaction of tetraazenido dianion and $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M}=\text{Rh}$ or Ir) to give the transition-metal tetraazadiene complexes. The compounds give us a good model of nitrogen extrusion because of the weak bond strength of middle N-N. The fact stimulated us to explore the preparation of transition-metal diimine complexes, isoelectric with transition-metal tetraazadiene complexes. Herein we report-

ed the syntheses of transition-metal diimine complexes by the reaction of Rh and Ir complexes with the diamine ligands in the presence of NEt_3 .

Experimental Section

All manipulation of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer in CDCl_3 . Chemical shifts are given in parts per million relative to TMS for ^1H NMR spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Mass spectra were obtained on a high resolution VG70-VSEG spectrometer. Cyclic voltammetry was carried out with a Potentiostat-Galvanostat Model 273 at a glassy-carbon electrode with an Ag/AgCl couple as a reference and tetra-n-butyl ammonium perchlorate (TBAP) as an electrolyte in CH_3CN . Elemental analyses were carried out at the Basic Science Center. Reagent grade THF and toluene were distilled under argon from sodium-benzophenone ketyl. Pentane and hexane were distilled under argon from sodium. Methylene chloride was distilled under argon from P_2O_5 . $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2]_2$ ($\text{M}=\text{Rh}$, Ir)¹⁰ and $\text{o-C}_6\text{H}_4(\text{NHSiMe}_3)_2$ ¹¹ were prepared according to literature methods. $\text{MCl}_3 \cdot x\text{H}_2\text{O}$ ($\text{M}=\text{Rh}$, Ir) were purchased from Strem Chemical Inc.. 1,2,3,4,5-Pentamethylcyclopentadiene, $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, 4,5-dimethyl-1,2-phenylenediamine, 4,5-dichloro-1,2-phenylenediamine, and diaminomaleonitrile were