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

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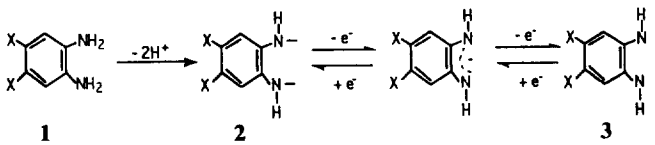
Monomeric rhodium and iridium diimine complexes Cp*M(HNRNH)(Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl : (M = Ir ; R = o-C_6H_4 (**1a**), 4,5-$(CH_3)_2$-C_6H_2-1,2 (**1b**), 4,5-$(Cl)_2$-C_6H_2-1,2 (**1c**), NCC=CCN-1,2 (**1d**) : M=Rh ; R=NCC=CCN-1,2 (**1e**)) have been synthesized from $[Cp^*MCl_2]_2$ 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 β=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 $M\{C_6H_4(NH)_2\}_2^{0,1+}$ systems [1] with M=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 diaminylato ligands have attracted interest because of their oxidation-reduction propensites. 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**.



1 **2** **3**

We[9] recently described the reaction of tetraazenido dianion and $[Cp^*MCl_2]_2$(M=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 reported 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. $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$(M = Rh, Ir)[10] and o-$C_6H_4(NHSiMe_3)_2$[11] were prepared according to literature methods. $MCl_3 \cdot xH_2O$ (M=Rh, Ir) were purchased from Strem Chemical Inc.. 1,2,3,4,5-Pentamethylcyclopentadiene, o-$C_6H_4(NH_2)_2$, 4,5-dimethyl-1,2-phenylendiamine, 4,5-dichloro-1,2-phenylenediamine, and diaminomaleonitrile were

purchased from Aldrich.

Preparation of Cp*Ir{$C_6H_4(NH)_2$-1,2} 1a. (a) To a stirred toluene solution (25 m*l*) of $[Cp^*IrCl_2]_2$ (0.26 g, 0.33 m mol; Cp*=1,2,3,4,5-pentamethylcyclopentadienyl) was added phenylenediamine (0.044 g, 0.66 m mol) and NEt_3 (0.2 m*l*). The solution was refluxed for 50 hr. The solvent was stripped off and the product was extracted with hexane (30 m*l*). The reddish-violet crystals were obtained by reducing the volume to *ca.* 10 m*l* and leaving the solution at −20 ℃. The yield was 82%. mp. 172 ℃. IR (on KBr pellet; cm^{-1}) 3308 (m) 3004 (w), 2966 (w), 2882 (m), 1472 (br), 1368 (m), 1344 (w), 1307 (s), 1220 (w), 1136 (m), 1102 (w), 1022 (m), 1012 (m), 894 (w), 728 (s), 692 (s), 632 (br); mass spectrum, m/e (relative intensity) 434 (M^+, 84). Anal. Calcd. for $C_{16}H_{21}IrN_2$: C, 44.30; H, 4.80. Found: C, 44.94; H, 4.62.

(b) To a stirred toluene solution (25 m*l*) of $[Cp^*IrCl_2]_2$ (0.20 g, 0.25 m mol) was added $C_6H_4(NHSiMe_3)_2$-1,2 (0.15 g, 0.6 m mol) and NEt_3 (0.1 m*l*). The solution was refluxed for 48 hr. The solvent was stripped off and the product was extracted by hexane (20 m*l*). The volume was reduced to *ca.* 10 m*l*. The reddish-violet crystals were obtained by leaving the solution in a refrigerator at −20 ℃. The yield was 74%.

Preparation of Cp*Ir{4,5-$(CH_3)_2$-$C_6H_2(NH)_2$-1,2} 1b. The same procedure was taken as described in the preparation of **1a**. The yield was 68%. mp. 178 ℃. IR (on KBr pellet; cm^{-1}) 3396 (m), 3008 (w), 2983 (w), 1468 (s), 1442 (w), 1422 (w), 1392 (m), 1364 (m), 1287 (s), 1222 (w), 1204 (m), 1184 (w), 1154 (w), 1084 (w), 942 (m), 844 (m), 704 (s), 632 (s).; mass spectrum, m/e (relative intensity) 461 (M^+, 24). Anal. Calcd. for $C_{18}H_{25}IrN_2$: C, 41.60; H, 5.40. Found: C, 41.96; H, 5.87.

Preparation of Cp*Ir{4,5-Cl_2-$C_6H_2(NH)_2$-1,2} 1c. The same procedure was taken as described in the preparation of **1a** except that the product was extracted by toluene (10 m*l*) and the reddish-violet crystals were obtained by leaving the solution in a refrigerator at 0 ℃. The yield was 92%. mp. 183 ℃. IR (on KBr pellet; cm^{-1}) 3365 (m), 3004 (w), 2914 (w), 1480 (s), 1382 (w), 1357 (w), 1311 (s), 1221 (m), 1163 (w), 1107 (w), 1084 (w), 1031 (m), 951 (m), 839 (m), 732 (w), 702 (s), 632 (br, s); mass spectrum, m/e (relative intensity) 502 (M^+, 44). Anal. Calcd. for $C_{17}Cl_2H_{19}IrN_2$: C, 40.60; H, 3.80 Found: C, 41.06; H, 3.98.

Preparation of Cp*Ir{NC(NH)C=C(NH)CN-1,2} 1d. The same procedure was taken as described in the preparation of **1a** except that the product was extracted by CH_2Cl_2 (10 m*l*) and the reddish-violet crystals were obtained by layering hexane (15 m*l*) to the solution and leaving the solution at −20 ℃. The yield was 84%. mp. 169 ℃. IR (on KBr pellet; cm^{-1}) 3296 (s), 2176 (s), 1372 (m), 1273 (m), 1248 (m), 1146 (w), 1042 (m), 732 (m), 692 (w), 664 (w); mass spectrum, m/e (relative intensity) 433 (M^+, 36). Anal. Calcd. for $C_{14}H_{17}IRN_4$: C, 38.80; H, 3.90. Found: C, 38.87; H, 3.71.

Preparation of Cp*Rh{NC(NH)C=C(NH)CN-1,2} 1e. The same procedure was taken as described in the preparation of **1d**. The yield was 74%. mp. 166 ℃. IR (on KBr pellet; cm^{-1}) 3326 (s), 2182 (s), 1376 (m), 1277 (m), 1254 (m), 1212 (w), 1146 (w), 1044 (m), 742 (m), 690 (w), 664 (w). Anal. Calcd. for $C_{14}H_{17}N_4Rh$: C, 48.80; H, 4.90. Found: C, 48.18; H, 4.52.

X-ray structure determination of 1a. The crystal of **1a** was grown from hexane at −20 ℃. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation and using the scan technique. Details on crystal data and intensity data are given in Table 1. A total of 3429 reflections were measured over the range $4<2\theta<53°$. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. Of the reflections measured a total of 1692 unique reflections with $I>3\sigma(I)$ were used during subsequent structure refinement. The structure was solved by standard heavy atom Patterson techniques followed by weighted Fourier syntheses. Refinement was by full-matrix least squares techniques based on F and converged with unweighted and weighted agreement factors of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.049$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o^2|)]^{1/2}=0.061$. Non-hydrogen atoms were refined anistropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined.

Table 1. Crystallographic Data for $(C_5Me_5)Ir\{C_6H_4(NH)_2$-1,2}

Empirica formular	$Ir_1N_2C_{16}H_{21}$
F_w	433.58
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
Cell parameters	
a (Å)	9.543 (1)
b (Å)	16.286 (1)
c (Å)	10.068 (1)
β (deg)	99.25 (1)
V (Å^3)	1544 (3)
D_{cacd} (g/cm^3)	1.86
μ (Mo-Kα)	86.0
Transmission factor	42.30-99.45%
Scan Type	ω-2θ
Scan width (ω) (deg)	0.74+0.52 tan(θ)
$2\theta_{max}$ (deg)	52.64
No. of reflections measured	3429
No. of reflection observed ($I>3\sigma(I)$)	1692
F (000)	832
No. of varables	172
Discrepancy indices	
R^a	0.049
R_w^b	0.061
Goodness of fit indicator^c	1.71
Maximum shift in final cycle	less than 0.01

$^aR=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bR_w=[(\Sigma w(F_o-F_o)^2/\Sigma w(F_o^2)]^{1/2}$. where $w=4F_o^2/\Sigma^2(F_o^2)$. Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where N_o=number of observations and N_v=number of variables.

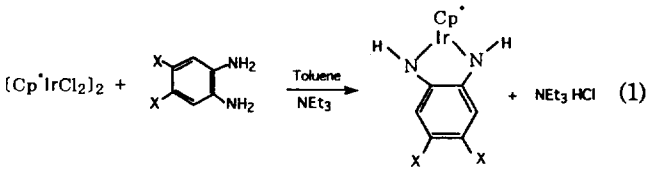
Result dand Discussion

The 1,4-diimine iridium complexes have been prepared according to Eq. 1.

Table 2. ^{1}H NMR and IR data for Complexes **1a-1e**

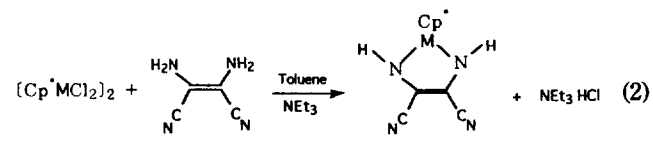
Complex	δ ($CDCl_3$), ppm				IR	
no.	Cp*	aromatic H[a]	NH	others	νNH, cm^{-1}	νCN, cm^{-1}
1a	2.06	7.22 (d, *J* 5.8, 2H)[b]	8.23		3308	
		6.98 (d, *J* 5.8, 2H)				
1b	1.99	6.83 (s, 2H)	8.18	1.14 (s, 6H, CH_3)	3396	
1c	2.07	7.26 (s, 2H)[b]	8.28		3365	
1d	2.05		8.22		3296	2176
1e	1.96		8.03		3326	2182

[a] *J* values in hertz. [b] Signal obscured by solvent peak.



1a X = H
1b X = Me
1c X = Cl

The reactions of iridium dimer with diamines in the presence of NEt_3 under the reflux condition gave reddish-violet solutions. The (1,2,3,4,5-pentamethylcyclopentadienyl)iridium diimine complexes were isolated as air-stable reddish-violet crystals in 68-92% yield. Bergman and coworkers[12] recently reported the similar complex with **1a** by the reaction of (η^6-p-Cymene)OsN-t-Bu with phenylenediamine. Maitlis and coworkers[3] also reported the complex $(C_5Me_5)Rh\{C_6H_4(NH)_2$-1, 2} by the reaction of rhodium dimer with phenylenediamine. They did not give any spectroscopic data and experimental details. However, the reaction of rhodium dimer with *o*-$C_6H_4(NH_2)_2$ under the same condition did not occur. The structure of compounds **1a-1c** were deduced from their ^{1}H NMR, IR, and mass spectra. The compound **1a** exhibits NH resonance at δ 8.23, as indicated in the Table 2. The value is quite similar to that of $CymOs[C_6H_4(NH)_2$-1,2]^{12} appeared at δ 8.68 and that of $Ni[C_6H_4(NH)_2$-1,2]^{13} appeared at δ 8.80. In the solid state, the infrared spectra of complexes **1a-1c** show sharp N-H stretch band in the 3300-3400 cm^{-1} region. Infrared stretching absorption characteristic of diimine ligand was observed at 3308 cm^{-1} for **1a**. The value is comparable to that of $Ru\{C_6H_4(NH)_2$-1,2}$(PPh_3)_3$[8] appeared at 3360 cm^{-1} and those of bis(cyclopentadienyliron)arene complexes with amine bridges[14] appeared at 3500 and 3400 cm^{-1}. The mass spectrum of **1a** showed the molecular ion peak. The photochemical excitation (λ>260 nm) of **1a** in the presence of unsaturated organic compound such as fumaronitrile was essentially inert. It may be attributable to the strong bond of Ir-N-C-C-N. The reaction of rhodium and iridium dimer with diaminomaleonitrile in the presence of NEt_3 under the reflux condition gave a reddish-violet solution according to Eq. 2.



1d M = Ir
1e M = Rh

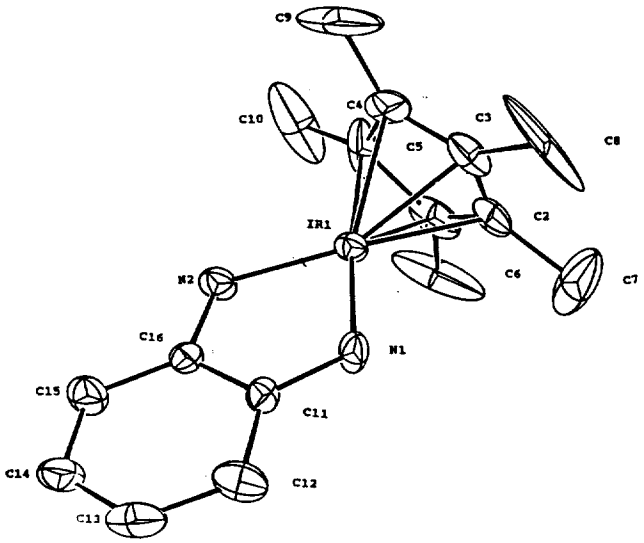


Figure 1. ORTEP plot of the complex **1a**.

The ^{1}H NMR spectrum of **1d** contained one signal of relative area 15 at δ 2.05, assigned to Cp* together with a singlet of relative area 2 at δ 8.22, assigned to NH protons. Infrared stretching absorption of ν(NH) was observed at 3296 cm^{-1} for **1d**. The rhodium compound **1e** is synthesized and characterized similarly.

Crystal Structure of 1a. The monomeric nature of **1a** was confirmed by an X-ray diffraction study performed on a red single crystal obtained from a hexane solution cooled to −20 ℃. The structure and atom labelling of **1a** are shown in Figure 1 and Figure 2. Selected interatomic distances and bond angles are listed in Table 3. Positional parameters and their estimated standard deviations are listed in Table 4. The coordination sphere of the iridium ion can be described as a 2-legged piano-stool with the η^5-pentamethylcyclopentadienyl ligand occupying three coordinate site and the bidentate diimine ligand coordinated through the 1,4-nitrogen atoms. The metallocycle is essentially planar with the average displacement of an atom from the least-squares plane of the ring 0.075 Å (See Figure 2); η^5-pentamethylcyclopentadienyl ring is almost orthogonal to the basal plane N(1)C(11) C(16)N(2)(88.2°). The average Ir-N distance of 1.97 (1) Å is short enough to consider some multiple-bond character[15]. The distance is quite similar to that of Mo-N in $[\{Mo(NO)L(I)\}_2\{C_6H_4(NH)_2$-1,2}](1.96 Å)[6] and that of W-N in $\{WCl_3[C_6H_4(NH)$-1, (NH_2)-2]$\}_2[\mu$-1,2-$(N)_2C_6H_4]$(1.92 Å)[7]. The distance is

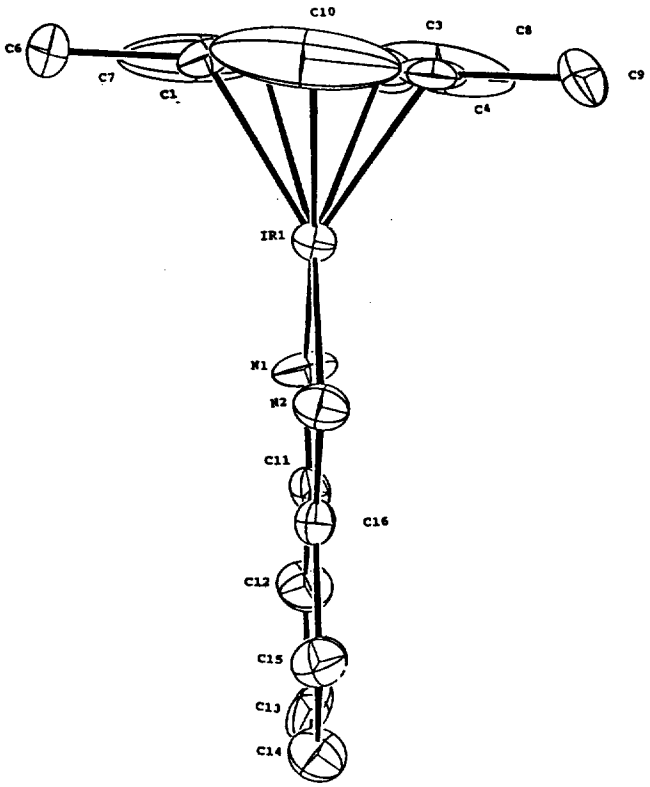


Figure 2. View perpendicular to the N(2)-C(16)-C(11)-N(1) plane.

Table 4. Positional Parameters and Their Estimated Standard Deviations

Atom	*x*	*y*	*z*	*B* (A2)
IR1	0.23981(7)	0.09464(4)	0.20324(6)	3.82(1)
N1	0.187(2)	0.0629(8)	0.379(1)	5.6(3)
N2	0.082(1)	0.1696(9)	0.215(1)	4.8(3)
C1	0.281(2)	0.027(1)	0.028(2)	8.8(5)
C2	0.374(2)	0.002(1)	0.137(2)	8.5(5)
C3	0.452(2)	0.061(1)	0.190(2)	6.7(6)
C4	0.417(2)	0.133(1)	0.119(2)	8.6(5)
C5	0.301(2)	0.116(1)	0.009(2)	10.2(5)
C6	0.166(3)	−0.024(2)	−0.063(3)	21.3(8)
C7	0.384(4)	−0.086(2)	0.190(4)	26(1)
C8	0.569(3)	0.035(3)	0.315(3)	24(2)
C9	0.491(3)	0.214(2)	0.150(3)	22.7(9)
C10	0.234(3)	0.168(3)	−0.096(2)	22(1)
C11	0.080(2)	0.106(1)	0.418(2)	4.0(3)
C12	0.022(2)	0.095(1)	0.541(2)	6.8(5)
C13	−0.090(2)	0.144(1)	0.567(2)	8.7(5)
C14	−0.152(2)	0.203(1)	0.474(2)	6.3(5)
C15	−0.101(2)	0.215(1)	0.354(2)	6.0(5)
C16	0.015(2)	0.165(1)	0.326(2)	4.2(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1, 1)+b2*B(2, 2)+c2*B (3, 3)+ab (cos gamma)*B (1, 2)+ac (cos beta)*B (1, 3)+bc (cos alpha)*B (2, 3)]

Table 3. Selcted Bond Lengths and Angles in **1a**

Distances (Å)			
Ir(1)-N(1)	1.98(1)	C(2)-C(3)	1.27(4)
Ir(1)-N(2)	1.96(1)	C(2)-C(7)	1.52(4)
Ir(1)-C(1)	2.16(2)	C(3)-C(4)	1.39(4)
Ir(1)-C(2)	2.15(2)	C(3)-C(8)	1.60(3)
Ir(1)-C(3)	2.13(2)	C(4)-C(5)	1.45(4)
Ir(1)-C(4)	2.10(2)	C(4)-C(9)	1.50(4)
Ir(1)-C(5)	2.16(2)	C(5)-C(10)	1.42(4)
N(1)-N(2)	2.49(2)	C(11)-C(12)	1.44(2)
N(1)-C(11)	1.36(2)	C(11)-C(16)	1.40(2)
N(2)-(16)	1.38(2)	C(13)-C(14)	1.40(4)
C(1)-C(2)	1.36(4)	C(12)-C(13)	1.40(4)
C(1)-C(6)	1.56(4)	C(14)-C(15)	1.39(2)
		C(15)-C(16)	1.43(2)
Angle (deg)			
N(1)-Ir(1)-N(2)	78.5(6)	N(1)-C(11)-C(12)	126(2)
N(1)-Ir(1)-C(1)	134(1)	N(1)-C(11)-C(16)	116(1)
N(2)-Ir(1)-C(1)	127(1)	C(12)-C(11)-C(16)	118(2)
C(1)-Ir(1)-C(3)	61(1)	C(11)-C(12)-C(13)	118(2)
Ir(1)-N(1)-C(11)	116(1)	C(13)-C(14)-C(15)	120(2)
Ir(1)-N(2)-C(16)	118(1)	C(14)-C(15)-C(16)	119(2)
C(1)-C(2)-C(3)	112(3)	N(2)-C(16)-C(11)	111(2)
C(2)-C(3)-C(4)	110(3)	N(2)-C(16)-C(15)	127(2)
C(3)-C(4)-C(5)	109(2)	C(11)-C(16)-C(15)	122(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

longer than that of Co-N in $[Co(C_6H_4(NH)_2\text{-}1,2)_2]_2$(1.84 Å)[16]. The N-C distances, 1.36 (2) and 1.38 (2) Å, found for $[Ni\{C_6H_4(NH)_2\text{-}1,2\}_2]$ for which a bond order 1.5 is assigned[13], are shorter than the N-C single bonds in arylamine and related derivatives. The value is very close to that of $[\{Mo(NO)L(1)\}_2\{C_6H_4(NH)_2\text{-}1,2,\}]$ (1.38 Å) and that of $\{WCl_3[C_6H_4(NH)\text{-}1,(NH_2)\text{-}2]\}_2[\mu\text{-}1,2\text{-}(N)_2C_6H_4]$ (1.36 Å). The short N-C bonds are consistent with a multiple bond character but not with the expected bond pattern for the C_6 diamide ring, suggesting an important electron delocalization in the iridium diimine system. Therefore, the reason why the complex **1a** in the presence of unsaturated organic compound is inert under the photochemical excitation may be explained by the short N-C bonds. The N(1)-Ir(1)-N(2) angle, 78.5 (6)°, is comparable to equivalent bond angles in compounds where the ligand is likely to be in a dianionic form[17].

Electronic Absorption Spectra. The iridium complex **1a** (see Table 4) shows two energy maxima at 254 and 424 nm, which are assigned to a combination of a metallacycle $\pi\rightarrow\pi^*$ transition and a $d\rightarrow\pi^*$ transition. These assignments resemble those proposed for $CpCo(1,4\text{-}H_2N_4)$[18]. The extinction coeffiients (32000, 23000 $M^{-1}cm^{-1}$) of **1a** suggest that these transitions are of ligand or charge transfer origin. A lower energy transition in **1a** may be interpreted by a shift of this bond to higher energy on going to more electronegative substituents when X is an electron-releasing substituent the excited state B is stabilized and its energy is decreased.

Electrochemistry. Complex **1a** displays a quasi reversible reduction in the cyclic voltamogram at a potential of −0.74 V *vs* an Ag/AgCl. The cyclic voltamograms of **1a** and

Table 5. Electronic Absorption spectra of Complexes **1a-1e**

Complex	Solvent	λ_{max}, nm	ε, $M^{-1}cm^{-1}$
1a	CH_2Cl_2	254	32000
		424	23000
1b	CH_2Cl_2	252	23000
		430	22000
1c	CH_2Cl_2	250	31000
		420	24500
1d	CH_2Cl_2	246	42000
		410	5900
1e	CH_2Cl_2	248	38000
		416	5200

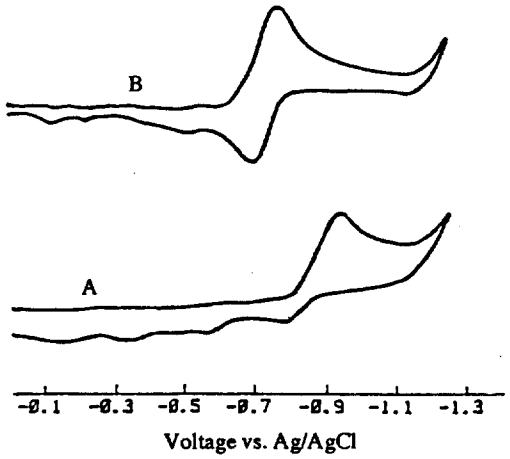
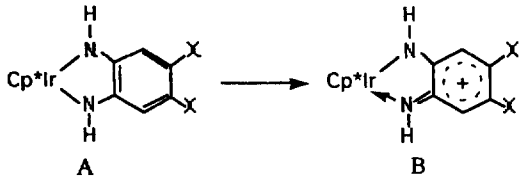


Figure 3. (A) Cyclic voltammogram of **1a** in 0.1 M (n-Bu_4N)(ClO_4)-DMF electrolyte solution. (B) Cyclic voltammogram of **1d** in 0.1 M (n-Bu_4N)(ClO_4)-DMF electrolyte solution.



1d is shown in Figure 3. The reason that **1d** displays a quasi reversible reduction may be interpreted by the fact that the acceptor orbital is easily delocalized on the diaminomaleonitrile ring. However, the cyclic voltamogram of **1a** showed that the complex was reduced at −0.92 V. It may be attributable to the difficulty of a delocalization in the matallacycle.

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Supplementary Material Available. Tables of fractional coordinates and isotopic temperature factors for the hydrogen atoms, additional bond lengths and angles, and anisotropic temperature factors for **1a** (24 pages). Supplementary materials are available from one of the authors (J. Ko) upon request.

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