August, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **54**, *2309—2312 (1981)* 2309

A Novel Cationic Optically Active Complex of Platinum(II) Containing 2-Methyl-2-butene and *o*-Benzenediamine. The Circular Dichroism Spectrum and Kinetics of Olefin Exchange

Shin'ya Miya, Kazuo Kashiwabara,[†] and Kazuo Saito*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

[†]*Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464*

(Received January 23, 1981)

An optically active cationic olefin complex, [PtCl(*o*-benzenediamine)((*S*)-2-methyl-2-butene)]$B(C_6H_5)_4$ was obtained for the first time as crystal stable in air at room temperature. It deteriorates slightly in solution, but is still stable enough to be characterized. Comparison of its CD spectrum with that of related complexes disclosed that the coordinating atoms at the *cis* sites to the olefin have a dominant influence upon the CD pattern in the region 20000—35000 cm^{-1}, as compared with those at the *trans* site. Substitution of *cis*-1,2-dichloroethylene for the coordinated (*S*)-2-methyl-2-butene (*S*-mbn) proceeds in accordance with the second order rate law; there is no contribution of the solvent path. The second order rate constant is smaller than that of *trans*-[$PtCl_2$(pyridine)(*S*-mbn)]. The steric effect of the *o*-benzenediamine at the transition state seems responsible for the small rate rather than the basicity of the ligand at the *trans* site to mbn.

Asymmetric coordination of prochiral olefins to square planar complexes gives several circular dichroism (CD) peaks in the region 20000—45000 cm^{-1}. The pattern is largely dependent on the absolute configuration of the coordinated olefin,[1] but also on the ligands including asymmetric nitrogen donor atoms.[2,3] Studies were carried out on stereoselectivity accompanied by the olefin exchange of platinum(II) complexes of the types [$PtCl_3$(olefin)]$^-$ and [PtCl((*S*)-amino carboxylate)(olefin)] both kinetically and thermodynamically in organic solvents.[4,5] However, all the known optically active platinum(II) olefin complexes are chargeless or negatively charged. Cationic platinum(II) complexes containing η^2-olefin are unstable.[6] Uguagliati *et al.* identified [PtCl(C_2H_4)(bpy)]$^+$ (bpy, bipyridine) as reaction intermediate. However, it liberates the ethylene almost instantaneously to give [$PtCl_2$(bpy)].[7] Theophanides and Kong[8] suggested the formation of solid complex [PtCl(C_2H_4)(en)]$^+$ (en, ethylenediamine), which was not characterized because it decomposed quickly to give *cis*-[$PtCl_2$(en)]. Recently Tiripichio *et al.* obtained cationic complex [PtCl(C_2H_4){$(CH_3)_2NCH_2CH_2N(CH_3)_2$}]$ClO_4$, the structure determined by the X-ray diffraction method,[10] and proposed the decomposition mechanism. They found that the cationic complex is stable enough to be characterized by recrystallization from water, and IR and ^1H NMR spectra.

We have synthesized a cationic optically active platinum(II) complex containing prochiral 2-methyl-2-butene (mbn) and *o*-benzenediamine (*o*-bzda) for the first time and compared the CD spectrum and the kinetics of olefin exchange reaction with those of related complexes.[1-5] The influence of various ligands *cis* and *trans* on the asymmetric olefin as well as of the overall charge of the complex is discussed.

Experimental

Preparation. The cationic optically active complex containing *o*-benzenediamine (*o*-bzda) and 2-methyl-2-butene (mbn), [PtCl(*o*-bzda)(*S*-mbn)]$B(C_6H_5)_4$, was prepared from optically active *trans*(*N*, mbn)-[PtCl(*S*-pro)(*S*-mbn)][3] (pro, prolinate) by the following method with retention of configuration. The original complex was converted into $P(C_6H_5)_4$-[$PtCl_3$(*S*-mbn)] by the method of Miya *et al.*[11] The complex (3.0×10^{-4} mol) was dissolved in methanol (25 cm^3) and treated with $NaB(C_6H_5)_4$ (3.0×10^{-4} mol) and *o*-bzda (3.0×10^{-4} mol). The white precipitate was removed to leave a yellow filtrate which was treated with $NaB(C_6H_5)_4$ (3.0×10^{-4} mol). Dripping of water first gave a small amount of yellowish precipitate, which was filtered off. Further dripping of water gave colorless crystals, which were washed with cold water, recrystallized from methanol and dried *in vacuo*. Found: C, 57.74; H, 5.26; N, 3.85%. Calcd for $C_{35}H_{38}N_2PtBCl$: C, 58.00; H, 5.40; N, 3.73%.

cis and *trans*(*N*, tbn)-[PtCl(*S*-pro)(*S,S*-btn)] (*S*-pro, (*S*)-prolinate; tbn, *trans*-2-butene),[3] *trans*-[$PtCl_2$(4-X-py)(*S*-mbn)][11] (4-X-py, 4-substituted pyridine; X=NH_2, H, and Cl), *trans*-[$PtCl_2$(4-X-ani)(*S*-mbn)][11] (4-X-ani, 4-substituted aniline; X=H, Cl, and CH_3) and *cis*-[$PtCl_2$((*S*)-α-methylbenzylamine)(*S*-mbn)][12] were synthesized by the methods reported. The solvents were purified by the usual methods.

Measurement. The visible and ultraviolet absorption and CD spectra were recorded with a Hitachi 323 spectrophotometer and a JASCO J-40 spectropolarimeter, respectively, at room temperature in acetone, acetonitrile, benzene, dichloromethane or ethanol. The rate of olefin exchange between [PtCl(*o*-bzda)(*S*-mbn)]$^+$ (3.0×10^{-3} mol dm^{-3}) and 1,2-dichloroethylene (dce) (0.1 to 5 mol dm^{-3}) was measured by recording the change in CD strength at 28170 cm^{-1} with time at 17.0 °C in acetone. Since the complex decomposes slightly with lapse of time, freshly prepared sample solutions were used. The results were analysed by a method previously reported.[11]

Results and Discussion

Synthesis. The formation of [$PtCl_3$(*S*-mbn)]$^-$ from the (*S*)-prolinato complex proceeds with full retention of configuration in HCl.[11] The substitution of *o*-bzda for the two chloride ions proceeded quickly in methanol. The white precipitate first formed on the addition of $NaB(C_6H_5)_4$ was $(C_6H_5)_4P^+\cdot B(C_6H_5)_4^-$. The CD measurement suggests that the substitution causes no significant inversion of the coordinated olefin. (*vide infra*) The colorless product is stable in crystalline state. It is insoluble in benzene and dichloromethane, and soluble in acetone and ethanol. The solutions turn slowly yellow, giving a black precipitate after a few days. However, the decomposition rate is amazingly smaller than that of the bpy[7] and en[8] complexes. It is remarkable that *o*-bzda gives a stable cationic platinum(II) complex containing η^2-olefin in spite of the fact that the diamine is believed to be a poor bidentate ligand to metal ions. The stability of this cationic complex might be comparable to that of $[PtCl(C_2H_4)\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}]ClO_4$ prepared by Maresca *et al.*[9]

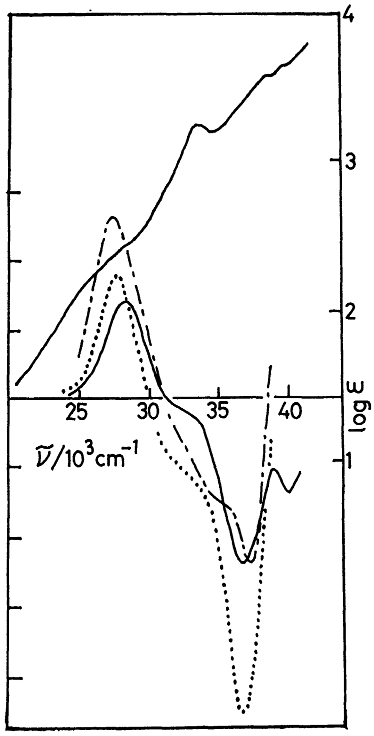

Fig. 1. Absorption and CD spectra in visible and UV region, 1) $[PtCl(o\text{-bzda})(S\text{-mbn})]B(C_6H_5)_4$ in ethanol (——), 2) The differential CD between *cis*(*N*, tbn)-[PtCl(L-pro)(*S*,*S*-tbn)] and *cis*(N, ethylene)-[PtCl(L-pro)(ethylene)] in acetonitrile (······), 3) The differential CD between *cis*-$[PtCl_2((S)\text{-}\alpha\text{-methylbenzylamine})(S,S\text{-tbn})]$ and *cis*-$[PtCl_2((S)\text{-}\alpha\text{-methylbenzylamine})(ethylene)]$ in acetone (—·—·—).

Absorption and CD Spectra. The spectra are shown in Fig. 1 together with those of related complexes. The absorption spectrum of [PtCl(*o*-bzda)(*S*-mbn)]$^+$ changes slowly, the CD intensity decreasing in line with absorption change. However, the apparent rate constant is *ca.* 4×10^{-6} s^{-1} at 17.0 °C, affecting neither the spectroscopic measurement nor the kinetic study of olefin exchange with dce. (*vide infra*) The UV absorption gives a peak at 33000 cm^{-1} with log $\varepsilon=3.22$ and some peaks in the region 36000—39000 cm^{-1}. There is no absorption peak in the range 20000—30000 cm^{-1}, assigned to that of d-d transitions in platinum(II) olefin complexes,[3] but only a shoulder at *ca.* 28000 cm^{-1}. Such broad absorption spectra in the whole range would provide no useful means in investigation on the detailed spectroscopic properties.

On the other hand, the CD spectrum shows distinct strong peaks at 28300 and 37000 cm^{-1}. The former can be attributed to the d-d transition and the latter to the charge transfer between the metal and ligands, or intraligand transitions. The CD spectral data are summarized in Table 1 together with those of related complexes. CD spectra in the d-d transition region are generally affected by environmental changes around a metal ion. On the basis of the additivity rule held in platinum(II) olefin complexes,[4] we can estimate the contribution of asymmetric olefin in various types of complexes. Two cases are shown in Fig. 1, for L-prolinate and α-methylbenzylamine complexes, the differential CD spectra between the complexes containing (*S*,*S*)-*trans*-2-butene and ethylene being calculated. Although the solvents are not common because of the solubility of the complexes, the three CD patterns in Fig. 1 are very similar to each other, despite the big difference in overall charge and the donating atoms. The three complexes have Cl and N in common at the *cis* positions to the olefin, and N, O, and Cl at the *trans* site. The *trans* ligand appears to give only a minor contribution to the CD pattern and even to the peak energy, so far as the ligating atom at the *cis* site remains unchanged.

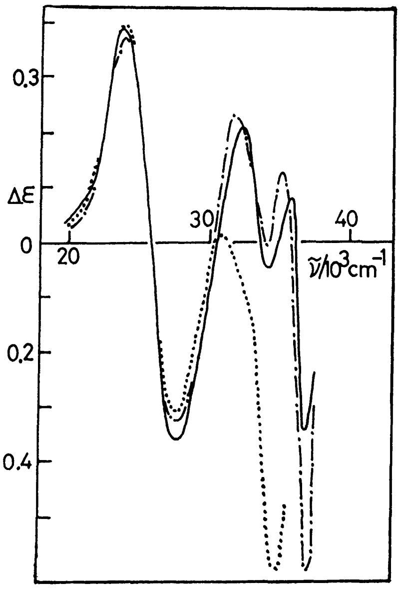

Fig. 2. CD spectra of *trans*-$[PtCl_2(4\text{-X-py})(S\text{-mbn})]$ in dichloromethane, X=NH_2 (······), X=H (——), X=Cl (—·—·—).

This is also supported by the CD pattern of the complexes *trans*(*N*,mbn)-$[PtCl_2(4\text{-X-py})(S\text{-mbn})]$ and *trans*(*N*,mbn)-$[PtCl_2(4\text{-X-ani})(S\text{-mbn})]$. (Figs. 2 and 3) The changes of substituents X on both pyridine and aniline derivatives give no significant influence on the CD spectra, peak positions and strengths in the d-d transition region. In the higher frequency region, only the 4-aminopyridine complex shows a different spectrum from the other two. The strong peak of the 4-aminopyridine complex at 35000 cm^{-1} corresponds to the peaks of the aniline derivatives at the same position. The 4-aminopyridine ligand has two coordinate functions to a metal ion, the amino group and the pyridine

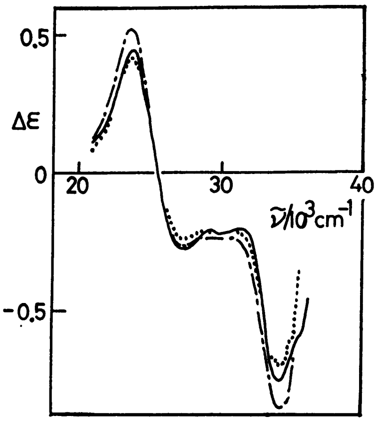

Fig. 3. CD spectra of *trans*-[$PtCl_2$(4-X-ani)(*S*-mbn)] in benzene, X=CH_3 (······), X=H (——), X=Cl (—·—).

nitrogen atom. We have no definite evidence for the coordination mode, but the coordination through the pyridine nitrogen atom is highly probable from the fact that the CD spectrum of the 4-aminopyridine complex is in fair agreement with those of other pyridine derivative complexes in the d-d transition region (Table 1).

Comparison of the CD spectra between *cis*[2] and *trans*(*N*,C_2H_4)-[PtCl(*S*-pro)(C_2H_4)],[3] and between [$PtCl_3$(*S*,*S*-tbn)]$^-$ [4] and *cis*-[$PtCl_2$(α-methylbenzylamine)(*S*,*S*-tbn)][12] also indicates that the change in ligating atoms at the *cis* position to the olefin causes a big difference in the CD pattern, while that at the *trans* site gives only a slight difference. Since, the η^2-olefin gives a very remarkable *trans* influence, the variety of the ligating atom at the *trans* site should be cancelled, whereas change in atoms at the *cis* site causes a significant difference.

CD peaks at around 37000 cm^{-1} (Fig. 1) are also similar to each other despite the difference of the ligating atoms, so that the CD components might be due to the charge transfer between platinum(II) and olefins which are common in these three complexes.

Kinetics of Olefin Exchange. The rate of the following reaction was followed by recording the decrease in CD strength at 28170 cm^{-1} in the presence of a large excess of free *cis*-1,2-dichloroethylene(dce).

$$[PtCl(o\text{-bzda})(S\text{-mbn})]^+ + \text{dce} \longrightarrow [PtCl(o\text{-bzda})(\text{dce})]^+ + \text{mbn} \qquad (1)$$

The observed rate constant is independent of the initial concentration of the complex ($\simeq 10^{-3}$ mol dm^{-3}) (Table 2), and proportional to that of free dce without intercept as shown in Fig. 4. Hence, the rate is expressed by,[11]

$$\text{Rate} = k_2[\text{complex}][\text{dce}]. \qquad (2)$$

The concentration of free *o*-bzda added does not affect the rate in the concentration range 0—2.4×10^{-4} mol dm^{-3} (Table 2). We see that addition of $NaB(C_6H_5)_4$ does not affect the rate of olefin exchange. The complex seems to be in ion-paired in acetone, the observed rate

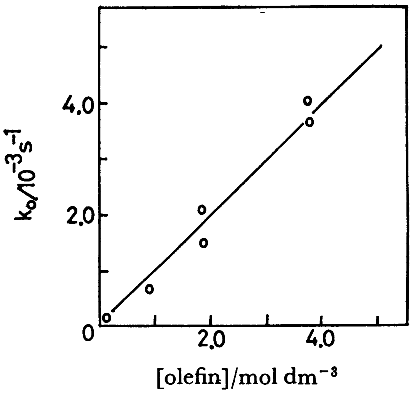

Fig. 4. Dependence of the observed first order rate constant for the substitution of *cis*-1,2-dichloroethylene for the (*S*)-2-methyl-2-butene in *trans*-[PtCl(*o*-bzda)-(*S*-mbn)]$B(C_6H_5)_4$ in acetone at 17 °C, [complex]= 0.0030 mol dm^{-3}.

TABLE 1. CD SPECTRAL DATA OF PLATINUM(II) COMPLEXES CONTAINING η^2-OLEFIN

Complex	CD peaks, $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)				
[PtCl(*S*-mbn)(*o*-bzda]$B(C_6H_5)_4$[a]		28.3(+0.36)	32.8(−0.03)	37.0(−0.59)	40.3(−0.35)
cis-[$PtCl_2$(*S*,*S*-tbn)(mba)][b,c]		27.3(+1.32)	35.0(−0.72)	37.4(−1.19)	
cis(*N*,olefin)-[PtCl(pro)(*S*,*S*-tbn)][d,e]		27.6(+0.92)	33.2(−0.57)	37.0(−2.26)	
trans(*N*,olefin)-[PtCl(pro)(*S*,*S*-tbn)][e,f]		26.8(+1.08)	34.3(−1.90)		39.7(−0.54)
$P(C_6H_5)_4$[$PtCl_3$(*S*-mbn)][g]	22.9(+0.46)	26.5(−0.21)	29.4(+0.13)	34.3(−1.05)	
$P(C_6H_5)_4$[$PtCl_3$(*S*,*S*-tbn)][e]	24.0(+0.76)	28.0(−0.14)		35.1(−1.32)	39.5(+3.20)
trans-[$PtCl_2$(*S*-mbn)(4-Cl-ani)][h]	23.6(+0.51)	27.0(−0.28)		34.7(−0.86)	
trans-[$PtCl_2$(*S*-mbn)(4-CH_3-ani)][h]	23.6(+0.41)	27.1(−0.26)		34.5(−0.70)	
trans-[$PtCl_2$(*S*-mbn)(ani)][h]	23.6(+0.44)	27.2(−0.30)		34.3(−0.76)	
trans-[$PtCl_2$(*S*-mbn)(4-Cl-py)][g]	24.1(+0.35)	27.8(−0.34)	31.8(+0.26) 33.8(−0.01)	35.2(+0.17) 36.8(−0.60)	
trans-[$PtCl_2$(*S*-mbn)(py)][g]	24.0(+0.39)	27.8(−0.37)	32.4(+0.21) 34.4(−0.06)	35.7(+0.09) 37.1(−0.35)	
trans-[$PtCl_2$(*S*-mbn)(4-NH_2-py)][g]	24.0(+0.39)	27.8(−0.31)	30.8(+0.02) 32.4(−0.09)	35.0(−0.60)	

a) In ethanol. b) Differential CD between *cis*(*N*,olefin)-[$PtCl_2$(*S*,*S*-tbn)(*S*-mba)] and *cis*(*N*,olefin)-[$PtCl_2$(C_2H_4)(*S*-mba)], (mba, α-methylbenzyl amine). c) In acetone. d) Differential CD between *cis*(*N*,olefin)-[PtCl(*S*-pro)(*S*,*S*-tbn)] and *cis*(*N*, olefin)-[PtCl(*S*-pro)(C_2H_4)]. e) In acetonitrile. f) Differential CD between *trans*(*N*, olefin)-[PtCl(*S*-pro)(*S*,*S*-tbn)] and *trans*(*N*,olefin)-[PtCl(*S*-pro)(C_2H_4)]. g) In dichloromethane. h) In benzene.

Table 2. Dependence of the observed first order rate constant for the substitution of *cis*-1,2-dichloroethylene for the (*S*)-2-methyl-2-butene in [PtCl(*S*-mbn)(*o*-bzda)]B$(C_6H_5)_4$ in acetone at 17 °C on various factors, [dce]=1.89 mol dm^{-3}.

[complex] 10^{-3} mol dm^{-3}	[*o*-bzda] 10^{-4} mol dm^{-3}	NaB$(C_6H_5)_4$ 10^{-2} mol dm^{-3}	k_0 10^{-3} s^{-1}
1.50	0	0	1.44
3.00	0	0	1.48
4.45	0	0	1.47
3.00	1.24	0	1.57
3.00	2.50	0	1.60
3.00	0	0.32	1.42
3.00	0	1.21	1.42
3.00	0	2.41	1.44

constants reflecting those of the ion-pairs rather than those of the free complex cation. The counter anions play an important role to stabilize the cationic complex. Bulky anions such as perchlorate or tetraphenylborate are good counter anions to stabilize the cationic complex, but not small ones such as chloride.[9] Strong ion-paired interactions between the complex cation and bulky anions might be a key effect to prevent nucleophilic attacks by reacting species such as solvent molecules or halides, stabilizing cationic olefin complexes.

The k_2 in Eq. 2 reflects the rate of direct olefin exchange, which should proceed by the S_N2 mechanism. The *o*-bzda ligand remains coordinated throughout the olefin exchange reaction, and the contribution of solvolysed species[11] being ignored. The result is compared with those of the related complexes in Table 3.

Table 3. Second order rate constants of the substituon of 1,2-dichloroethylene for some 2-methyl-2-butene complexes of platinum(II)

Complex	k_2/dm^3 mol^{-1} s^{-1}	pK_a
[PtCl(*o*-bzda)(*S*-mbn)]$^+$ [a]	1.09×10^{-3}	4.6
trans(*N*,olefin)-[PtCl(*S*-pro)(*S*-mbn)][a]	1.03×10^{-3}	10.6
trans-[PtCl$_2$(py)(*S*-mbn)][b]	4.66×10^{-2}	5.2

a) In acetone at 17.0 °C; k_2 for Eq. 2. b) From Ref. 11.

The basicity of the nitrogen base *trans* to the olefin in [PtCl$_2$(4-X-py)(*S*-mbn)] and [PtCl$_2$(4-X-ani)(*S*-mbn)] is the most important factor ruling the rate of olefin exchange.[11] The *o*-bzda complex has a much smaller k_2 than that of the pyridine complex, despite their similar pK_a values. Difference in the ligating atom at the *cis* site (Cl and N) could be responsible for the difference. However, the kinetic *cis* effect is understood to be in the percentage range of tens to hundreds and can not account for the big difference by 40 times. The difference may be ascribed to the presence of overall charge or of the chelate ring. The (*S*)-proline has pK_a 10.6 and the chargeless complex with one chelate gives $k_2=1.03\times10^{-3}$ dm^3 mol^{-1} s^{-1}. Its log k_2 *vs.* pK_a plot falls almost on the common straight line for *trans*-[PtCl$_2$(4-X-py)(*S*-mbn)] and *trans*-[PtCl$_2$(4-X-ani)(*S*-mbn)] (figure in Ref. 11); *i. e.* the (*S*)-prolinato ligand does not seem to give significant effect on the rate expressed by Eq. 2.

The positive charge of the complex would decrease the effective electron density on platinum(II), and the nucleophilic attack of dce can be facilitated rather than retarded. Thus the overall plus charge cannot be the cause of slow substitution. Neither is its instability in organic solvents responsible for the slow exchange of olefin. Coordinated aniline derivatives in *trans*-[PtCl$_2$(ani)(*S*-mbn)] are replaced by donating solvent molecules to give *e. g.*, *trans*-[PtCl$_2$(S)(*S*-mbn)] (S, solvent molecule), which also participated in the olefin exchange.[11] If such a replacement had taken place prior to the attack of the nucleophilic olefin, the observed rate constant should have depended on the added free *o*-bzda concentration, as was the case for the complexes containing aniline derivatives.[11]

The *o*-bzda chelate may have a significant steric stress due to the rigid aromatic ring, particularly in the transition state; the trigonal bipyramidal intermediate may be formed with difficulty to decrease the second order rate constant. It is interesting that bulky ligands such as *N*,*N*,*N'*,*N'*-tetramethylethylenediamine stabilize the cationic platinum(II) olefin complex, probably preventing the nucleophilic attack by reacting species on a η-bonded olefin.[9] The *o*-bzda ligand might also have this effect.

The work was carried out with a Grant-in-Aid (No. 400016) from the Ministry of Education, Science and Culture.

References

1) I. Kinoshita, Y. Terai, K. Kashiwabara, H. Kido, and K. Saito, *J. Organomet. Chem.*, **127**, 237 (1977).

2) Y. Terai, H. Kido, and K. Saito, *Bull. Chem. Soc. Jpn.*, **50**, 3265 (1977).

3) K. Konya, J. Fujita, and K. Nakamoto, *Inorg. Chem.*, **10**, 1699 (1971).

4) Y. Terai and K. Saito, *Bull. Chem. Soc. Jpn.*, **51**, 503 (1978).

5) Y. Terai, H. Kido, K. Kashiwabara, and K. Saito, *Bull. Chem. Soc. Jpn.*, **51**, 3245 (1978).

6) M. Herberhold, "Metal π-Complexes," Elsevier, Amsterdam, (1972), Vol. 2, pp. 183—189.

7) P. Uguagliati, U. Belluco, U. Croatto, and R. Pietropaolo, *J. Am. Chem. Soc.*, **89**, 1336 (1967).

8) T. Theophanides and P. C. Kong, *Can. J. Chem.*, **48**, 1084 (1970).

9) L. Maresca, G. Natile, and G. Rizzardi, *Inorg. Chim. Acta*, **38**, 53 (1980).

10) A. Tiripichio, M. T. Camelini, L. Maresca, G. Natile, and G. Rizzard, *Cryst. Struct. Commun.*, **8**, 689 (1979).

11) S. Miya, K. Kashiwabara, and K. Saito, *Inorg. Chem.*, **19**, 98 (1980).

12) P. Corradini, G. Paiaro, and A. Panunzi, *J. Am. Chem. Soc.*, **88**, 2836 (1966).