Inorganica Chimica Acta, 12 (1975) 93–97
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Kinetics of the Addition Reactions of Tetracyanoethylene towards Rhodium(I) Cationic Isocyanide Complexes

MASA-AKI HAGA, KATSUHIKO KAWAKAMI and TOSHIO TANAKA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received July 2, 1974

The kinetics of the addition reactions of tetracyanoethylene (TCNE) to trans-$[Rh(RNC)_2(PR'_3)_2]ClO_4$*, where R =* p-$CH_3OC_6H_4$*,* p-ClC_6H_4*, and* C_6H_{11} *and R' =* C_6H_5 *and* C_6H_5O*, in acetonitrile, acetone, and tetrahydrofuran (THF) have been investigated employing stopped-flow techniques. The reaction is first order with respect to both complex and TCNE. The reaction rate increases with increasing solvent polarity in the order of THF < acetone < acetonitrile. The activation parameters for the reactions of* $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ *in the three solvents were:* ΔH^**, 7.6, 3.5, 2.2 kcal* mol^{-1}*;* ΔS^**, –15.2, –27.7, –28.3 e.u. The nature of the transition state and ligand effects on the rate of reaction are discussed.*

Introduction

In recent years highly activated olefins such as tetracyanoethylene (TCNE) have been shown to react with low-valent transition metal complexes to give stable adducts.[1,2] These reactions are of interest because of their resemblance to fundamental steps in homogeneous catalytic processes.[3,4] Related work includes stereochemical and kinetic studies of the reactions of *trans*-$IrCl(CO)(PPh_3)_2$ and $Ru(CO)_3L_2$ (L = phosphite ligands) with *trans*-$CF_3(CN)C{=}C(CF_3)CN$.[5,6]

Kinetic studies of the oxidative addition reactions of hydrogen,[7] oxygen,[8,9] methyl iodide,[8,10,11] and substituted silanes[12] toward four-coordinated rhodium(I) and iridium(I) complexes have been reported from several laboratories.

Recently we have reported that TCNE added to $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ to form $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(TCNE)]ClO_4$ quantitatively.[13] The present work was undertaken to study the kinetics of reactions of TCNE with several isocyanide cationic complexes of rhodium(I), $[Rh(RNC)_2L_2]ClO_4$, where RNC is alkyl or aryl isocyanide and L is triphenylphosphine or -phosphite in various solvents.

Experimental

All experimental manipulations were performed under nitrogen. Solvents were distilled twice, and saturated with nitrogen. Tetrahydrofuran (THF) was dried over activated alumina and lithium aluminum hydride, acetonitrile over phosphorus pentoxide, and acetone over Drierite. Commercial TCNE was recrystallized twice from 1,2-dichloroethane and sublimed.

Infrared spectra were recorded in Nujol mulls on a Hitachi-Perkin–Elmer 225 grating spectrophotometer. Electronic spectra were obtained by using a 1-cm quartz cell on a Hitachi 124.

Preparation of Starting Materials

$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ was prepared according to the literature;[14] $\nu(NC)$ 2124 cm^{-1}, λ_{max} (CH_3CN) 419 mμ(ε 4720) and 478 mμ(ε 560). *Anal.* Calcd for $C_{52}H_{44}N_2O_6P_2ClRh$: C, 62.88; H, 4.46; N, 2.82. Found: C, 62.90; H, 4.38; N, 2.89.

The corresponding cyclohexylisocyanide complex was similarly prepared: cyclohexylisocyanide (0.16 g, 1.5 mmol) in CH_2Cl_2 (10 ml) was added slowly to $[Rh(1,5\text{-}C_8H_{12})(PPh_3)_2]ClO_4$[15] (0.60 g, 0.73 mmol) in CH_2Cl_2 (10 ml). The solution was stirred under nitrogen for 30 min, during which time the color of the solution changed from orange to yellow. The solvent was removed under reduced pressure, and the resulting product was recrystallized from CH_2Cl_2–petroleum ether to give $[Rh(C_6H_{11}NC)_2(PPh_3)_2]ClO_4$ (0.55 g, 80% yield); $\nu(NC)$ 2156 cm^{-1}, $\lambda_{max}(CH_3CN)$ 401 mμ (ε 5170) and 458 mμ(ε 230). *Anal.* Calcd for $C_{50}H_{50}N_2O_4P_2ClRh$: C, 63.53; H, 5.54; N, 2.96. Found: C, 63.24; H, 5.45; N, 3.18.

$[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ was similarly obtained from a reaction of $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ with p-methoxyphenylisocyanide (98% yield); $\nu(NC)$ 2154 cm^{-1}, $\lambda_{max}(CH_3CN)$ 398 mμ(ε 6310) and 455 mμ(ε 485). *Anal.* Calcd for $C_{52}H_{44}N_2O_{12}P_2ClRh$: C, 57.34; H, 4.07; N, 2.57. Found: C, 57.25; H, 4.16; N, 2.70.

$[Rh(p\text{-}ClC_6H_4NC)_2(PPh_3)_2]ClO_4$ was prepared as mentioned above (80% yield); $\nu(NC)$ 2145 cm^{-1},

$\lambda_{max}(CH_3CN)$ 427 mμ(ε 3300) and 485 mμ(ε 370). *Anal.* Calcd for $C_{50}H_{38}N_2O_4P_2Cl_3Rh$: C, 59.93; H, 3.82; N, 2.79. Found: C, 59.63; H, 3.79; N, 2.80.

Isolation of the Addition Products

TCNE (25 mg, 0.19 mmol) was added to $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ (0.2 g, 0.18 mmol) in acetone (10 ml) at room temperature; the yellow color of the solution disappeared immediately. The solvent was evaporated under reduced pressure and the product was recrystallized from CH_2Cl_2–diethyl ether to give $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ (0.20 g, 91% yield); ν(NC) 2206 cm^{-1} and ν(CN) 2232 cm^{-1}. *Anal.* Calcd for $C_{58}H_{44}N_6O_{12}P_2ClRh$: C, 57.23; H, 3.64; N, 6.90. Found: C, 57.16; H, 3.71; N, 7.24.

$[Rh(C_6H_{11}NC)_2(PPh_3)_2(TCNE)]ClO_4 \cdot 1/2CH_2Cl_2$ was similarly obtained (90% yield) with a half mole of dichloromethane in the crystals; ν(NC) 2212 cm^{-1} and ν(CN) of TCNE is obscured by the strong isocyanide vibration. *Anal.* Calcd for $C_{56.5}H_{53}N_6O_4P_2Cl_2Rh$: C, 60.82; H, 4.79; N, 7.53. Found: C, 60.43; H, 4.70; N, 7.57.

$[Rh(p\text{-}ClC_6H_4NC)_2(PPh_3)_2(TCNE)]ClO_4$ was analogously prepared (81% yield); ν(NC) 2193 cm^{-1} and ν(CN) 2227 cm^{-1}. *Anal.* Calcd for $C_{56}H_{38}N_6O_4P_2Cl_3Rh$: C, 59.51; H, 3.39; N, 7.44. Found: C, 59.26; H, 3.17; N, 7.58.

Kinetic Measurements

Reaction rates were followed by measuring the transmittance in the vicinity of 400 mμ with a Union RA-1100 stopped-flow spectrophotometer and a 2 mm quartz cell. The instrument was thermostated to ± 0.2 °C. The temperature at the cell was measured with a corrected thermometer. Concentrations of the complexes in solution varied between 1.2×10^{-3} and $1.0 \times 10^{-4} M$. Lambert–Beer's law was shown to be valid in the case of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$–TCNE in acetonitrile and THF, and was assumed in the other systems. All reactions were carried out under pseudo-first-order conditions, using at least a tenfold excess of TCNE. Solutions were stored in a constant temperature bath at the reaction temperature under nitrogen, and were transferred into the driving syringe of the stopped-flow apparatus. A glass syringe fitted with a 30 cm stainless steel needle was used for transferring solutions of metal complexes. Glass pipettes were used for solutions of TCNE, because the color turned yellow when a stainless steel needle was used. Solutions were allowed to stand for 15 min to ensure thermal equilibration before kinetic runs.

The changes in transmittance as a function of time were monitored by a memoryscope; a typical reaction curve is shown in Figure 1. Five or six measurements were carried out for each run. Plots of $\ln(A_t - A_\infty)$ *vs.* time were found to be linear, and the pseudo-first-order rate constant, k_{obs}, was calculated by the method of least-squares, where A_t and A_∞ are absorbances at the times "t" and infinity. Rate constants were reproducible within ± 5%.

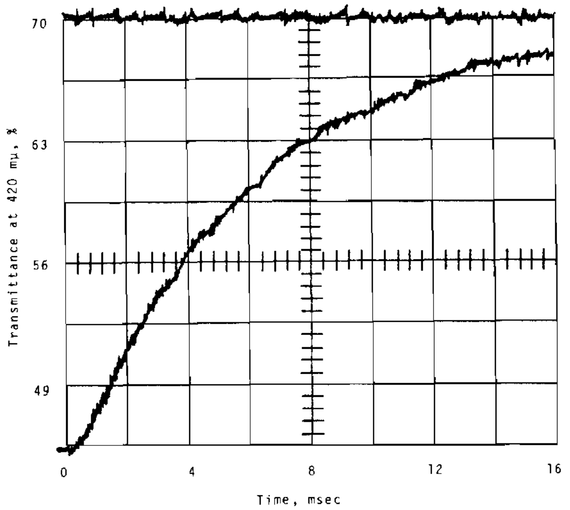


Figure 1. A typical oscillogram showing disappearance of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ (monitored at 420 mμ) in reaction with TCNE in CH_3CN; [Rh] = $1.67 \times 10^{-4} M$ and [TCNE] = $1.77 \times 10^{-3} M$ at 35.0 °C.

Results and Discussion

Stoichiometries of reaction 1 were established by the essentially quantitative isolation of products and by the

$$trans\text{-}[Rh(RNC)_2(PR'_3)_2]ClO_4 + TCNE \rightarrow [Rh(RNC)_2(PR'_3)_2(TCNE)]ClO_4 \quad (1)$$

spectrophotometric titration of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ with TCNE (Figure 2). Approximate equilibrium constants ($[[Rh(p\text{-}CH_3OC_6H_4NC)_2L_2(TCNE)]ClO_4]$ / $[[Rh(p\text{-}CH_3OC_6H_4NC)_2L_2]ClO_4][TCNE]$) were 3.3×10^4 for L = PPh_3 in 1,2-dichloroethane and $4.0 \times 10^3 M^{-1}$ for L = $P(OPh)_3$ in CH_3CN (25 °C).

Kinetic studies were carried out in THF, $(CH_3)_2CO$, and CH_3CN. They are good solvents for the rhodium substrates and do not react with TCNE. In the kinetic runs the reactions proceeded essentially to completion. The results at 25 °C are given in Table I. Plots of the pseudo-first-order rate constant, k_{obs}, against [TCNE] were linear with a zero intercept; a representative one is shown in Figure 3. This shows a simple second-order rate law:

$$-\frac{d[Rh]}{dt} = k_2[Rh][TCNE] \quad (2)$$

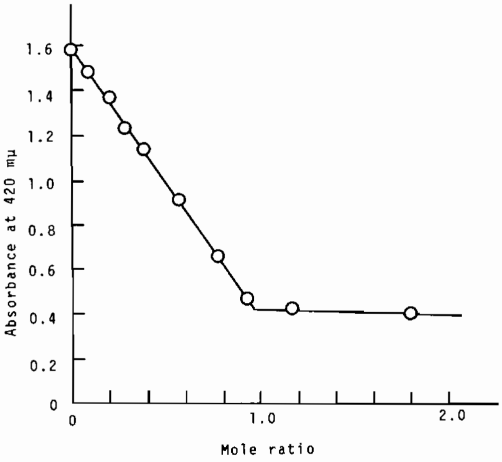


Figure 2. A plot of the absorbance at 420 mμ to the mole ratio of [TCNE]/[[Rh(p-$CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$] in CH_2ClCH_2Cl; [Rh] = 3.38×10^{-4} *M*.

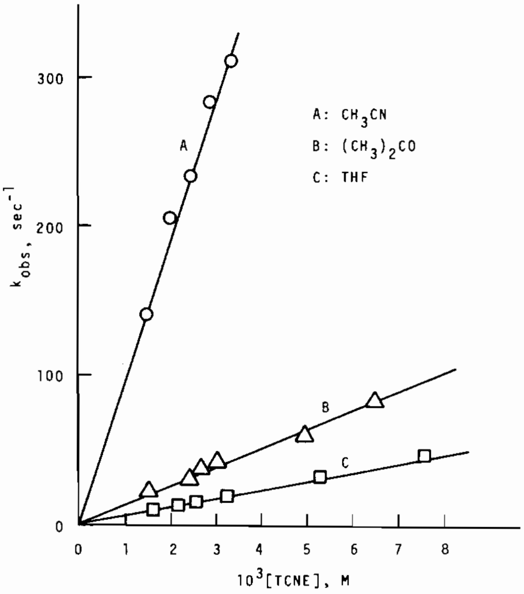


Figure 3. Second-order rate plots for the reactions of [Rh(p-$CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ with TCNE at 25°C, [Rh] = 1.6×10^{-4} *M*.

Kinetic data at various temperatures are given in Table II.

The reaction of [Rh(p-$CH_3OC_6H_4NC)_2(PR'_3)_2$] ClO_4 ($R' = C_6H_5$ or C_6H_5O) has a large solvent effect; the reaction becomes faster in the order of THF < $(CH_3)_2CO$ < CH_3CN, which is consistent with increasing solvent polarity. Similar solvent effects have been reported for the reactions of methyl iodide with π-$C_5H_5M(CO)L$ (where M = Co, Rh, and Ir)[11] and

TABLE I. Rates of Reactions of $[Rh(RNC)_2L_2]ClO_4$ with TCNE at 25°C. Effects of Variation in Solvent and Ligand.

Solvent	10^3[TCNE] *M*	k_{obs} sec^{-1}	$10^{-4}k_2$ M^{-1} sec^{-1}
	$R = p$-$CH_3OC_6H_4$, $L = PPh_3$		
CH_3CN	1.57	140	8.92
	2.04	197	9.67
	2.57	234	9.11
	2.98	284	9.53
	3.47	310	8.94
$(CH_3)_2CO$	1.65	23.1	1.40
	2.48	34.4	1.39
	2.78	40.3	1.45
	3.04	42.1	1.38
	5.00	60.8	1.22
	6.50	85.8	1.32
THF	1.68	10.2	0.61[a]
	2.25	13.3	0.59
	2.69	15.6	0.58
	3.30	18.8	0.57[b]
	5.37	31.7	0.59
	7.65	46.7	0.61
	$R = p$-$CH_3OC_6H_4$, $L = P(OPh)_3$		
CH_3CN	1.48	134	9.05
	1.90	178	9.37
	2.12	201	9.48
	2.64	232	8.79
$(CH_3)_2CO$	1.61	37.9	2.35
	2.13	60.2	2.83
	2.94	71.3	2.43
THF	1.64	23.9	1.46
	2.14	33.2	1.55
	2.63	37.8	1.44
	2.82	40.6	1.44
	3.33	47.6	1.43
	R = *cyclo*-C_6H_{11}, $L = PPh_3$		
CH_3CN	1.50	459	30.6
	1.70	450	26.5
	2.04	598	29.3
	2.31	777	33.6
	$R = p$-ClC_6H_4, $L = PPh_3$		
CH_3CN	2.20	51.4	2.34
	2.72	62.8	2.31
	3.20	83.6	2.61
	4.44	94.2	2.12

[a] The influence of the addition of sodium perchlorate to the reactants on the reaction rate was investigated: [$NaClO_4$] = 1.64×10^{-2} *M*, $k_2 = 0.58 \times 10^4$ M^{-1} sec^{-1}; [$NaClO_4$] = 8.31×10^{-2} *M*, $k_2 = 0.53 \times 10^4$ M^{-1} sec^{-1}. [b] k_2 at 25°C in changing the counter anion ClO_4^- into PF_6^-: 0.45×10^4 M^{-1} sec^{-1}.

TABLE II. Second-order Rate Constants for the Reactions of $[Rh(RNC)_2L_2]ClO_4$ with TCNE at Various Temperatures.

Solvent	T (°C)	10^{-4} k_2 M^{-1} sec^{-1}
	R = p-$CH_3OC_6H_4$, L = PPh_3	
CH_3CN	5.0	6.32 ± 0.35
	15.0	7.61 ± 0.30
	25.0	9.23 ± 0.34
	35.0	10.4 ± 0.1
$(CH_3)_2CO$	5.0	0.83 ± 0.02
	15.0	1.11 ± 0.01
	25.0	1.36 ± 0.08
	35.0	1.71 ± 0.04
THF	5.0	0.22 ± 0.01
	15.0	0.39 ± 0.02
	25.0	0.59 ± 0.01
	35.0	0.94 ± 0.01
	R = p-$CH_3OC_6H_4$, L = $P(OPh)_3$	
CH_3CN	5.0	5.18 ± 0.02
	15.0	6.96 ± 0.06
	25.0	9.17 ± 0.30
	35.0	11.9 ± 0.2

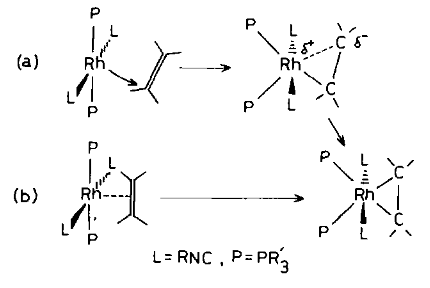
with *trans*-$IrCl(CO)(PPh_3)_2$.[16] Our complexes are ionic and it may be possible that they exist as ion pairs in media of low dielectric constant. Ion pairing alone, however, cannot account for the observed solvent effects. The addition of sodium perchlorate, up to 500 times the concentration of complex in THF, or changing the counter ion from ClO_4^- to PF_6^- has only a slight effect on the rate. In addition, good second-order kinetics were observed in each solvent for the reaction of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$.

Plots of $\ln k_2$ *vs.* 1/T(°K) give a straight line, from which activation parameters (Table III) were calculated using the Eyring equation. They also show a strong solvent dependence. ΔH^* and ΔS^* decrease in the order of THF $\gg$ $(CH_3)_2CO \geqq CH_3CN$. Although the ΔH^* values in $(CH_3)_2CO$ and CH_3CN are small, they are similar to values reported for reactions of this kind.[9, 17]

Two different transition state shown in Scheme I may be considered: (*a*) an asymmetric one with a dipole formed by nucleophilic attack of the metal at one end of the TCNE, and (*b*) a symmetric one with little charge separation.

TABLE III. Activation Parameters for Reactions of $[Rh(p\text{-}CH_3OC_6H_4NC)_2L_2]ClO_4$ with TCNE.

L	Solvent	ΔH^* Kcal mol^{-1}	ΔS^* e.u.
PPh_3	CH_3CN	2.2 ± 0.1	−28.3 ± 3.2
PPh_3	$(CH_3)_2CO$	3.5 ± 0.2	−27.7 ± 3.4
PPh_3	THF	7.6 ± 0.2	−15.2 ± 2.2
$P(OPh)_3$	CH_3CN	4.1 ± 0.1	−22.0 ± 2.5



Scheme I.

The mechanism *b* predicts that a dipole is induced mainly by a prerequisite deformation of the square-planar rhodium complexes as suggested for the reactions of $[Ir(Ph_2PCH_2CH_2PPh_2)_2]BPh_4$ with $(CH_3)_n(C_2H_5O)_{3-n}SiH$.[12] The change in the ΔS^* values in this work is consistent with the mechanism *b* because of an increased solvation due to the increased dipole. This mechanism, however, predicts that ΔH^* will be mainly governed by the prerequisite deformation and so remain rather constant regardless of the nature of solvents. This is contrary to a strong dependence of ΔH^* values (Table III) found in this work. In addition, little electron density on the rhodium atom may be transferred to TCNE, so the activated complex cannot have a sufficiently large dipole to account for the rate effect. Thus, the mechanism *b* is not likely to be predominant in the present reaction.

On the other hand, the mechanism *a* involving a dipolar intermediate will be consistent with the fact that the reaction rate is accelerated by polar solvents, and that the ΔH^* and ΔS^* values show marked solvent dependences as described in the following discussion. In a polar solvent such as acetone or acetonitrile, the solvent molecules may be strongly oriented surrounding the cationic complex, and a charge separation induced by the formation of a dipolar intermediate will cause stronger orientation of the solvent molecules for the activated complex than for the reactants. Thus, a negative ΔS^* will be observed in a polar solvent and a small ΔH^* can be expected as the dipolar intermediate is stabilized by solvation. We propose, therefore, that the reaction is more likely to proceed *via* the mechanism *a*, in which the transition state is similar to those suggested recently for the reactions of *trans*-$IrCl(CO)(PPh_3)_2$ with $CF_3(CN)C{=}C(CF_3)CN$[5] and of the related Ir(I) complexes with alkyl halides.[18] The transition state in our case involves a tight binding of one carbon atom of the ethylene and a loose interaction of the other olefinic carbon with the rhodium. It may be noted that the metal attack does not proceed symmetrically into a heteropolar bond such as the carbon–

halogen bond in methyl iodide nor into a homopolar bond such as the electron-deficient carbon–carbon bond in TCNE which is a strong π-acid.

The dependence of the reaction rate on the ligands attached to the rhodium atom was investigated in a few cases. Changing the isocyanide ligands in $[Rh(RNC)_2(PPh_3)_2]ClO_4$ increases the rate in the order of p-$ClC_6H_4 < p$-$CH_3OC_6H_4 <$ *cyclo*-C_6H_{11}, as expected for increasing electron density on the metal.

On the other hand, the substitution of triphenylphosphite for triphenylphosphine in $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ causes little change in reaction rate. This cannot be interpreted as an electronic effect only, since $\nu(NC)$ is lower in the PPh_3 complex. Recently it was suggested that $\nu(CO)$ in Vaska's type complexes is related to their reactivity.[19] It is safe to assume that a similar relation holds for our isocyanide complexes. We interpret the similar rates on replacing PPh_3 with $P(OPh)_3$ as a near cancellation of steric and electronic effects. Larger steric hindrance to TCNE approach is expected for PPh_3 because of its larger cone angle.[20]

References

1 W.H. Baddley, *Inorg. Chim. Acta Rev., 2,* 5 (1968).
2 W.H. Baddley, *J. Am. Chem. Soc., 88,* 4545 (1966).
3 W.H. Baddley and M.S. Fraser, *J. Am. Chem. Soc., 91,* 3661 (1969).
4 J.P. Collman and W.R. Roper, *Advan. Organometal. Chem., 7,* 53 (1968).
5 J. Ashley-Smith, M. Green and D.C. Wood, *J. Chem. Soc. (A),* 1847 (1970).
6 M. Cooke and M. Green, *J. Chem. Soc. (A),* 651 (1969).
7 L. Vaska and M.F. Werneke, *Trans. New York Academy of Science,* 70 (1971).
8 P.B. Chock and J. Halpern, *J. Am. Chem. Soc., 88,* 3511 (1966).
9 V.J. Choy and C.J. O'Connor, *J. Chem. Soc. (Dalton),* 2017 (1972).
10 M. Kubota, G.W. Kiefer, R.M. Ishikawa and K.E. Bencala, *Inorg. Chim. Acta, 7,* 195 (1973).
11 A.J. Hart-Davis and W.A.G. Graham, *Inorg. Chem., 9,* 2658 (1970).
12 J.F. Harrod and C.A. Smith, *J. Am. Chem. Soc., 92,* 2699 (1970).
13 T. Kaneshima, K. Kawakami and T. Tanaka, *Inorg. Chem., 13,* 2198 (1974).
14 L. Vallarino, *Gazz. Chim. Ital., 89,* 1632 (1959).
15 R.R. Schrock and J.A. Osborn, *J. Am. Chem. Soc., 93,* 2397 (1971).
16 H. Stieger and H. Kelm, *J. Phys. Chem., 77,* 290 (1973).
17 L. Vaska, L.S. Chen and W.V. Miller, *J. Am. Chem. Soc., 93,* 6671 (1971).
18 R. Ugo, A. Pasini, A. Fusi and S. Cenini, *J. Am. Chem. Soc., 94,* 7364 (1972).
19 L. Vaska and L.S. Chen, *Chem. Commun.,* 1080 (1971).
20 C.A. Tolman, *J. Am. Chem. Soc., 92,* 2956 (1970).