JOURNAL OF CATALYSIS **138**, 611–616 (1992)

Oxidation of Styrene Catalyzed by μ-Oxotrinuclear Mixed Valence and Mixed Metal Carboxylate Complexes

HIROYOSHI KANAI,* HIROKATSU HAYASHI,† TATSUYA KOIKE,† MAKOTO OHSUGA,†
AND MASAKATSU MATSUMOTO‡

**Faculty of Living Science, Kyoto Prefectural University, Shimogamo, Sakyo-ku, Kyoto 606, Japan;*
†Division of Molecular Engineering, School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan;
and ‡Central Research Laboratory, Fuji Rebio Co. Ltd., Komiyacho, Hachioji 192, Japan

Received August 29, 1990; revised August 13, 1991

Catalytic oxidation of styrene and cumene was carried out in the absence of solvent with μ-oxotrinuclear mixed valence and mixed metal carboxylate complexes as catalysts. Main products from styrene are styrene oxide and benzaldehyde. Among these complexes tested, the μ-oxo mixed metal acetate complexes $Fe^{III}_2Zn^{II}$, $Co^{III}_2Co^{II}$, and $Cr^{III}_2Fe^{II}$ are superior for both reactivity and epoxide selectivity to monomeric or trinuclear homometal complexes. Moderately high temperatures (80–95°C) and decreased O_2 pressure result in increased epoxide selectivity. Cumene was oxidized by all the complexes tested, but the $Fe^{III}_2Mn^{II}$ complex had no activity for the oxidation of styrene. Electron transfer between metals via a μ-oxo atom is considered to be responsible for the effective catalytic feature.

INTRODUCTION

Biochemical studies of catalytic oxidations with transition metal compounds have been focussed on selectivity and catalytic species (*1*). It is generally accepted that metal-oxo species participate in the homogeneous oxidations of olefins as mono-oxygen transfer agents to give epoxides (*2*).

Holm (*3*) discussed stoichiometric and catalytic aspects of metal-catalyzed oxygen transfer reactions revealing diverse metal–oxygen species. Recently, μ-oxotrinuclear metal complexes have become of interest in connection with biomimetic model complexes (*4*) and with magnetic and electronic properties (*5*). Especially, interatomic interactions in both static and dynamic states have been studied for mixed valence complexes (*5*). μ-Oxoiron(II)iron(III) complexes have been shown to work as dual catalysts for oxidation (*6*) and reduction reactions (*7*). μ-Oxotrinuclear ruthenium complexes were effective for oxidations of inorganic (*8*) and organic substrates (*9*) although it is not certain that these reactions are intrinsically related to μ-oxotrinuclear metal species.

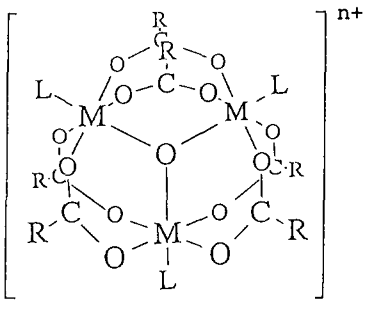
We have been investigating oxidation of styrene by μ-oxotrinuclear mixed valence and mixed metal complexes (Fig. 1) from the viewpoint that centered oxo species might be labile due to the key atom for an electron transfer process in the mixed valence complexes and that the electronic interaction between trinuclear metals including mixed valence and mixed metals can take a significant role in the oxidations.

EXPERIMENTAL

Materials

$[Fe^{III}_2M^{II}O(CH_3CO_2)_6L_3]nL$ (M = Mg, Mn, Fe, Co, Ni, Zn, L = H_2O, py), $[M^{II}Cr^{III}_2O(CH_3CO_2)_6(py)_3]n(py)$ (M = Fe, Co), and $[Co^{II}Fe^{III}Cr^{III}O(CH_3CO_2)_6(py)_3]n$ (py) were prepared according to the method of Blake *et al.* (*10*) Trinuclear iron (III) complexes with aliphatic and aromatic carboxylate ligands were prepared from iron (III) chloride and sodium carboxylate by the method of Earnshaw *et al.* (*11*). $V_3O(CH_3CO_2)_6(CH_3CO_2)_{2/2}(CH_3CO_2H)$

0021-9517/92 $5.00



M = V, Cr, Mn, Fe, Co, Ni, Zn
R = CH_3, C_6H_5, 2,5- and 3,4-$(CH_3)_2C_6H_3$
L = H_2O, py
n = 0, 1

FIG. 1. μ-Oxotrinuclear metal-complexes used as catalysts.

(*12*), $[Mn_3O(CH_3CO_2)_6CH_3CO_2H](CH_3CO_2)$ (*13*), and $[Co_3O(CH_3CO_2)_6(CH_3CO_2H)_3]$ (*14*) were prepared according to the methods given in the literature. Commercially available styrene and cumene were distilled at reduced pressures in the presence of sulfur powder and the distillates were stored under N_2 in a refrigerator.

Catalytic Oxidation

A two-necked 50 ml flask containing 0.04 mmol of μ-oxotrinuclear complex was filled with an O_2 atmosphere. Two milliliters of styrene were added and the flask was immersed in a thermostated bath followed by stirring of the reaction mixture. After an induction period oxygen began to be absorbed. The subsequent constant O_2 uptake was adopted as an oxidation rate (Fig. 2).

Products were analyzed by a Shimadzu GC-6A gas chromatograph (25% Ucon LB 550X/Celite 545, 2.5 m, 140°C) at 8–10% conversion of styrene. Benzaldehyde, phenylacetaldehyde, styrene oxide, acetophenone, and 1- and 2-phenylethanol were successively eluted in that order. Reaction products were separated with a preparative gas chromatograph (20% SE30/Celite 545, 2 m, 120°C) followed by analysis with ^1H and ^{13}C NMR. The identification was confirmed by comparison of the NMR data of the products with those of authentic samples. No phenylacetaldehyde was observed in the elutes. Since styrene oxide was found to be isomerized into phenylacetaldehyde in the inlet or the column oven (*15*), the amount of styrene oxide was estimated as the sum of itself and phenylacetaldehyde isomerized in the column. We detected paraformaldehyde on top of the flask which should be formed by polymerization of formaldehyde equivalent to the benzaldehyde produced.

RESULTS

Styrene Oxidation by μ-Oxotrinuclear Metal Carboxylate Complexes

Oxidation of styrene was carried out in neat styrene since we could not find any suitable solvents which had relatively low vapor pressure and solubility for μ-oxotrinuclear metal complexes. μ-Oxotrinuclear iron(III) complexes with aromatic carboxylate ligands dissolve in styrene, but those with acetic acid derivatives are less soluble even at the concentration of 0.02 mol/liter.

Oxidation occurred slowly at room temperature in the presence of μ-oxotrinuclear iron complexes, products were mainly benzaldehyde and formaldehyde. Appreciable O_2 uptake was detected above 60°C in the presence of complexes and products were a mixture of styrene oxide, benzaldehyde, and a small amount of acetophenone and

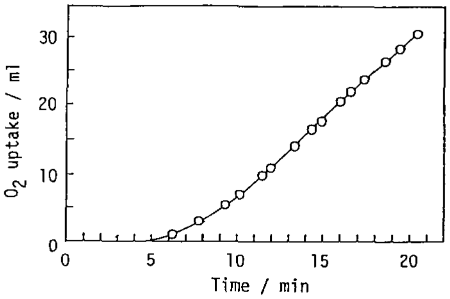


FIG. 2. Oxidation of styrene catalyzed by $[Fe_2ZnO(OAc)_6(H_2O)_3]3H_2O$ at 70°C.

TABLE 1

Oxidation of Styrene Catalyzed by μ-Oxotrinuclear Mixed-Valence and Mixed-Metal Complexes at 85°C

Complex M^{II}	Rate of O_2 uptake (ml_{STP} min^{-1})	Selectivity of styrene oxide (%)
$[Fe^{III}_2M^{II}O(CH_3CO_2)_6(H_2O)_3]n(H_2O)$		
Mg	1.8	11.8
Mn	0	
Fe	2.2	21.8
Co	1.3	6.7
Ni	0.82	4.3
Zn	3.3	37.3
Fe^{III}	1.1	4.8
$[M_a^{II}M_b^{III}M_c^{III}O(CH_3CO_2)_6(py)_3]n(py)$		
M_a M_b M_c		
Fe Cr Cr	3.0	31.0
Co Fe Cr	2.8	10.3
Co Cr Cr	3.6	5.0

1- and 2-phenylethanol (total yields of the latter three products were less than 0.5%).

After an induction period constant O_2 uptake continued below 15% conversion (Fig. 2). The rate was taken as the slope of the linear part. The induction period is not necessarily correlated with reactivity, but relatively fast reactions have short induction periods. The ratios of the total amount of oxygen atoms incorporated into the products to that of O_2 uptake are 0.86–1.0, indicating that material balance nearly satisfies stoichiometry.

A mixed valence complex, $[Fe^{III}_2Fe^{II}O(CH_3CO_2)_6(H_2O)_3]2(H_2O)$, revealed somewhat different catalytic behavior from that of homovalent triiron(III) complex (Table 1). Electron transfer between iron atoms via a centered oxygen atom averaging their valences into 2.67 (*16*) increases epoxide selectivity. Mixed metal trinuclear iron– or chromium–acetate complexes were prepared by mixing iron(III) or chromium(III) compounds with divalent metal compounds (*10*). $[Cr^{III}_2Fe^{II}O(OAc)_6(py)_3]$ was prepared from mixing of $[Fe^{III}_2Fe^{II}O(OAc)_6(H_2O)_3]$ and $Cr_2(CH_3CO_2)_4$, where Cr(II) is oxidized into Cr(III) to replace Fe(III) to maintain Fe(II) in the original oxidation state. Among divalent metals in $[Fe^{III}_2M^{II}O(OAc)_6(H_2O)_3]$ nH_2O, zinc exerts the most active and selective epoxide forming abilities at 80°C. No oxidation occurred with Mn^{II}-mixed iron complex during 2 h.

Increasing temperature facilitates reactivity and epoxide selectivity, which reach maxima between 85 and 95°C (Fig. 3). Smooth curves are observed for aqua complexes, while sudden reactions start above certain temperatures for pyridine complexes containing Co(II) and Fe(II). Thermal capacity measurements indicate that the pyridine molecule is coordinated to each iron and residual pyridine molecules are rotated about C_3 axes (*5*). Iron atoms when coordinatively saturated are difficult for substrates to attack. Heat treatment takes off pyridine molecules for the coordination of styrene. DTA and DTG of trinuclear mixed metal complexes suggest that coordinated water or pyridine molecules begin to desorb around 80°C. Although there are dif-

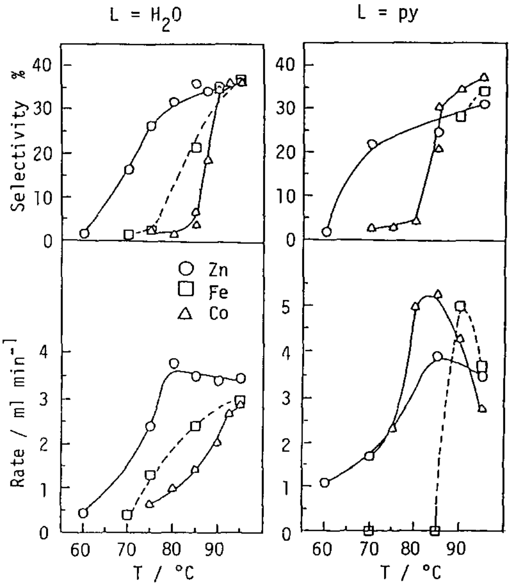


FIG. 3. Effects of temperature on the rates and epoxide selectivity in the oxidation of styrene catalyzed by μ-oxotrinuclear mixed metal acetate complexes.

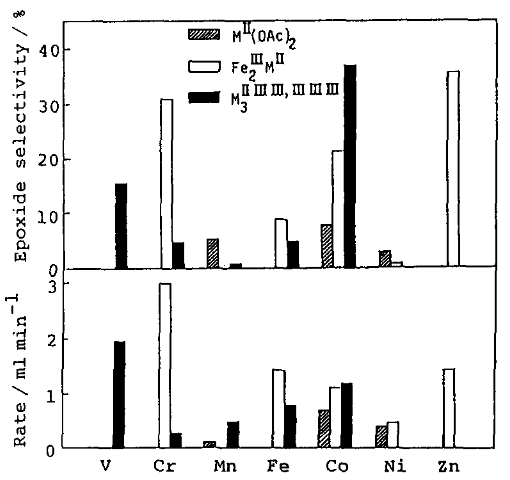


FIG. 4. Comparison of styrene oxidation catalyzed by mononuclear, μ-oxotrinuclear mixed valence, homometal, and mixed-metal complexes (80°C).

ferences in activity and selectivity in epoxide formation among mixed metal complexes at low temperatures, they diminish with increasing temperature (Fig. 3).

Oxidation of styrene was carried out with three types of metal acetate complexes: mononuclear, μ-oxotrinuclear homometal, and μ-oxotrinuclear mixed metal complexes. Not all types are known for each metal of the first transition series (*17*). Oxidation rates and epoxide selectivity were compared between some known members of the three types of acetate complexes (Fig. 4). A mixed valence and mixed metal complex, μ-oxo-$\mathrm{Fe^{II}Cr^{III}_2}$ complex, is superior in both reactivity and selectivity to μ-oxo-$\mathrm{Cr^{III}_3}$ and $\mathrm{Fe^{III}_2Fe^{II}}$ complexes. Replacement of the $\mathrm{Fe^{II}}$ atom with $\mathrm{Zn^{II}}$ and $\mathrm{Co^{II}}$ in $\mathrm{Fe^{III}_2Fe^{II}}$ brings about an increase of epoxide selectivity, but replacement with $\mathrm{Ni^{II}}$ does not. It is very strange that monomeric Mn(II) acetate and μ-oxotrinuclear manganese(III) acetate complex exhibited a little activity, but no reaction occurred with μ-oxo-$\mathrm{Fe^{III}_2Mn^{II}}$ complex. Figure 4 suggests that the original structure of μ-oxo mixed valence and mixed metal complexes is maintained during oxidation.

Effect of Oxygen Pressure

A decrease of oxygen pressure reduces conversion, but increases epoxide selectivity (Fig. 5). Dependences of styrene oxide and benzaldehyde formation on oxygen pressure are different for different complexes. With $[\mathrm{Fe^{III}_2ZnO(OAc)_6(H_2O)_3}]$ at 85°C the reaction orders for the production of styrene oxide and benzaldehyde are 0.58 and 0.80, respectively. The epoxide selectivity increased up to 50% at less than 13 kPa of O_2, but reactivity was reduced to $\frac{1}{5}$ of that at total pressure of 1 atm. With $[\mathrm{Fe_3O(2,5\text{-}(CH_3)_2C_6H_3CO_2)_6(H_2O)_3}]^+$ at 70°C the orders for epoxide and benzaldehyde are 1.1 and 1.3, respectively. Almost the same epoxide selectivity (50%) was obtained at 4 kPa of O_2, but the rate decreased to $\frac{1}{20}$ of that at total pressure of 1 atm.

Oxidation of Cumene

Cumene was oxidized with any of the μ-oxotrinuclear complexes tested (Table 2). $\mathrm{Fe^{III}_2Mn^{II}}$ complex easily initiated oxidation to give almost the same products as those from other complexes. Oxidation with $\mathrm{Fe^{III}_2Mn^{II}}$ and $\mathrm{Fe^{III}_2Co^{II}}$ complexes

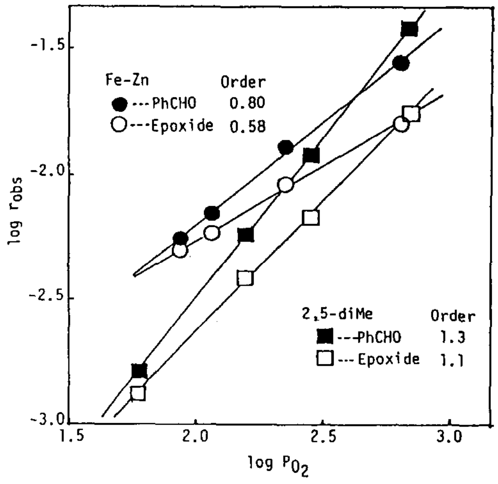
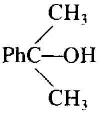
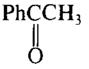
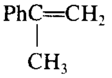


FIG. 5. Effects of O_2 pressure on the rates and epoxide selectivity in the oxidation of styrene catalyzed by $[\mathrm{Fe_2ZnO(OAc)_6(H_2O)}]$ (85°C) and $[\mathrm{Fe_3O(2,5\text{-}(CH_3)_2C_6H_3CO_2)_6(H_2O)_3}]^+$ (70°C).

TABLE 2

Oxidation of Cumene Catalyzed by μ-Oxotrinuclear Metal Complexes at 80°C

Complex	Rate of O_2 uptake[a] (ml_{STP} min^{-1})	Products (%)		
		 $PhC(CH_3)_2OH$	 $PhC(=O)CH_3$	 $PhC(CH_3)=CH_2$
	$[Fe_3O(RCO_2)_6(H_2O)_3]^+$			
R = C_6H_5	0.38(37)	77	21	1.8
3,4-$(CH_3)_2C_6H_3$	0.38(40)	77	21	1.4
	$[Fe^{III}{}_2M^{II}O(CH_3CO_2)_6(H_2O)_3]n(H_2O)$			
M^{II} = Mn	0.66(12)	78	19	2.4
Fe	0.25(67)	72	27	1.6
Co	0.85(7.6)	79	20	0.8
Zn	0.23(17)			

[a] The number in parentheses is the length of the induction period (min).

proceeded rather rapidly with short induction periods. Co–Mn acetate is known as a typical initiator for radical-type oxidation (*18*). Oxidation of cumene has rather longer induction periods than that of styrene with any other complexes except $Fe^{III}{}_2Mn^{II}$ and $Fe^{III}{}_2Co^{II}$. When a mixture of styrene and cumene was reacted with $Fe^{III}{}_2Mn^{II}$ acetate complex, styrene was oxidized to give benzaldehyde exclusively, although styrene alone could not be oxidized.

DISCUSSION

Catalytic Species

Induction periods were always observed in the oxidations of styrene and cumene with μ-oxotrinuclear metal complexes and ranged from 2 to 60 min. The oxidation rate tends to increase in parallel with the shortening of the induction period for the oxidation of styrene. When the oxidation of styrene is induced by radical initiators, an oxygen atom is incorporated into styrene to give oxygenated products including polymeric materials (*19*). Even oxygen can initiate the reaction with a long induction period (*20*). Reaction initiated by radical initiators concomitantly leads to C=C bond cleavage, epoxide formation, *cis–trans* isomerization, and rearrangement, where O_2 facilitates C=C bond cleavage to give aldehydes (*19, 20*). Oxidations by μ-oxotrinuclear metal complexes are somewhat different from radical-initiated oxidations; a considerable amount of epoxide was formed depending largely on type of catalyst, temperature, and O_2 pressure. Styrene oxide and benzaldehyde are the main products in the oxidation of styrene in O_2 with μ-oxotrinuclear metal complexes. The tendency for the increase of O_2 pressure to facilitate C=C bond cleavage suggests the participation of radical-type oxidation. Maximum epoxide selectivity in the radical-type oxidation was attained in a very narrow range of O_2 pressure around 0.13 kPa (*21*). Dependence of epoxide selectivity on the kind of μ-oxotrinuclear metal complexes is explained by the fact that the oxidation was initiated by metal complexes which also decomposed peroxy species into epoxide similarly to styrene oxidation by ruthenium, palladium, and other noble metal complexes (*22*).

After oxidation of styrene was carried out with $[Fe^{III}{}_2ZnO(OAc)_6(H_2O)_3]$ at 75°C, the complex was isolated and analyzed by IR, which identified it to be the original one (*23*). The complex was not decomposed to monomeric species during the oxidation.

Cumene was oxidized to 2-phenyl-2-propanol, acetophenone, and 2-phenylpropylene with all of the μ-oxotrinuclear iron complexes tested including Mn-mixed iron complex which has no catalytic activity toward styrene. After O_2 uptake started, the addition of 2,6-di-*tert*-butyl-4-methylphenol entirely inhibited oxidation. Also coupled with an induction period μ-oxotrinuclear complex can serve not only as an initiator for the oxidation to form radical species but also to control the product formation.

Catalysis by μ-Oxotrinuclear Metal Complexes

The metal–metal distance of ca. 3.3 Å in μ-oxotrinuclear iron complexes (*24*) is too long for direct orbital overlap between metals. Magnetic and spectroscopic studies have revealed that there is a superexchange interaction between metals which is provided by a μ-oxo atom (*10*). The replacement of M^{III} with M^{II} results in the increase of the interaction between remaining M^{III}–M^{III} which, however, is not influenced by M^{II} species on the Mössbauer timescale (*25*). It should be noted that μ-oxotrinuclear mixed valence and mixed metal complexes can affect reactivity and epoxide selectivity. The comparison of catalysis among mononuclear, μ-oxotrinuclear mixed-metal and mixed-valence metal complexes shows that $Cr^{III}{}_2Fe^{II}$, $Co^{III}{}_2Co^{II}$, and $Fe^{III}{}_2Zn^{II}$ acetate complexes are superior in both activity and epoxide selectivity (Fig. 4). We are now studying how mixed-valence and mixed-metal complexes exert an additional effect and also how the μ-oxo atom can participate in the oxidation.

ACKNOWLEDGMENT

One of the authors (H.K.) thanks the Ministry of Education for Scientific Research Grant-in-Aid 02650586.

REFERENCES

1. Sheldon, R. A., and Kochi, J. K., "Metal-Catalyzed Oxidation of Organic Compounds." Academic Press, New York, 1981.

2. (a) Collman, J. P., Brauman, J. I., Meunier, B., Hayashi, T., Kodadek, T., and Raybuck, S. A., *J. Am. Chem. Soc.* **107,** 2000 (1985); (b) Collman, J. P., Kodadek, T., and Brauman, J. I., *J. Am. Chem. Soc.* **108,** 2588 (1986).

3. Holm, R. H., *Chem. Rev.* **87,** 1401 (1987).

4. Lippard, S. J., *Chem. Br.,* **1986,** 222.

5. (a) Oh, S. M., Hendrickson, D. N., Hassett, K. L., and Davis, R. E., *J. Am. Chem. Soc.* **107,** 8009 (1985); (b) Jang, H. G., Geib, S. J., Kaneko, Y., Nakano, M., Sorai, M., Rheingold, A. L., Montez, B., and Hendrickson, D. N., *J. Am. Chem. Soc.* **111,** 173 (1989).

6. (a) Ito, S., Inoue, K., and Matsumoto, M., *J. Am. Chem. Soc.* **107,** 6450 (1982); (b) Barton, D. H. R., Boivin, J., Gastiger, M., Morzycki, J., Hay-Motherwell, R. S., Motherwell, W. B., Ozbalik, N., and Schwartzentruber, K. M., *J. Chem. Soc. Perkin Trans. 1,* 1986, 947.

7. Murata, S., Miura, M., and Nomura, M., *Chem. Lett.,* 1988, 361.

8. Spencer, A., and Wilkinson, G., *J. Chem. Soc. Dalton Trans.,* 1972, 1570.

9. Davis, S., and Drago, R. S., *Inorg. Chem.* **27,** 4759 (1988).

10. Blake, A. B., Yavari, A., Hatfield, W. E., and Sethulekshmi, C. N., *J. Chem. Soc. Dalton Trans.,* **1985,** 2505.

11. Earnshaw, A., Figgis, B. N., and Lewis, J., *J. Chem. Soc. A,* **1966,** 1656.

12. Allin, B. J., and Thornton, P., *Inorg. Nucl. Chem. Lett.* **9,** 449 (1973).

13. Nippon Kagakukai [Chemical Society of Japan], Ed., "New Chemical Experimentals, Vol. 8, Synthesis of Inorganic Compounds II," p. 981. Maruzen, 1969.

14. Ziółtkowski, J. J., Pruchnik, F., and Szymanska-Buzar, T., *Inorg. Chim. Acta* **7,** 473 (1973).

15. Watson, J. M., and Young, B. L., *J. Org. Chem.* **39,** 116 (1974).

16. Lupu, D., Barb, D., Filoti, G., Morariu, M., and Tarina, D., *J. Inorg. Nucl. Chem.* **34,** 2803 (1972).

17. Mehrotra, R. C., and Bohra, R., "Metal Carboxylates," Academic Press, New York, 1983.

18. Kamiya, Y., *Bull. Chem. Soc. Jpn.* **43,** 830 (1970).

19. Mayo, F. R., *Acc. Chem. Res.* **1,** 193 (1968).

20. Miller, A. A., and Mayo, F. R., *J. Am. Chem. Soc.* **78,** 1017 (1956).

21. Mayo, F. R., *J. Am. Chem. Soc.* **80,** 2465 (1956).

22. (a) Takao, K., Fujiwara, Y., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Jpn.* **43,** 1153 (1970); (b) Lyons, J. E., and Turner, J. O., *Tetrahedron Lett.* **1972,** 2903.

23. Meesuk, L., Jayasooriya, U. A., and Cannon, R. D., *J. Am. Chem. Soc.* **109,** 2009 (1987).

24. Blake, A. B., and Fraser, L. R., *J. Chem. Soc. Dalton Trans.* 1975, 193.

25. Dzibkowski, C. T., Wrobleski, J. T., and Brown, D. B., *Inorg. Chem.* **20,** 679 (1981).