April, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 54, 1015—1018 (1981)* 1015

Hydrodimerization of Methyl Acrylate Catalyzed by Halogenotris(triphenylphosphine)cobalt

Hiroyoshi Kanai* and Keiji Ishii

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received September 4, 1980)

Methyl acrylate was hydrodimerized in a methanolic solution by $CoX(PPh_3)_3$ (X=halogen) into dimethyl adipate. The *in situ* prepared cobalt complexes from cobalt halides, triphenylphosphine, and zinc gave higher yields of the hydrodimer in the presence of alkali halides. A mechanism is proposed which involves the protonation of Co(I)–methyl acrylate π-complex to give (2-methoxycarbonylethyl)cobalt complex, followed by a further addition of methyl acrylate.

Olefins substituted with electron-withdrawing groups are dimerized to head-to-head or head-to-tail dimers by bases,[1,2] electrolytic coupling,[3] and transition metal complexes.[4,5] The head-to-head hydrodimerization has been extensively studied because head-to-head dimers are of considerable interest as starting materials for the preparation of monomers.[3,5] We have previously reported that acrylic esters were hydrodimerized by cobalt(I)–triphenylphosphine complexes and that the addition of alkali halides and zinc increased the yield.[5j] We wish to report our subsequent work on the development of good catalysts for and the mechanism of the hydrodimerization of methyl acrylate.

Experimental

All reagents were used directly as obtained commercially unless otherwise noted. Tetrahydrofuran (THF) and alcohols were refluxed over sodium and sodium alkoxides, respectively, distilled, and stored under an atmosphere of nitrogen. Methyl acrylate was distilled and stored under N_2 in a refrigerator. ^1H NMR spectra were obtained on a JEOL PM-60 spectrometer. A Shimadzu 6A gas chromatograph with a FID detector was used for most GLC analyses [PEG 20M (25% on celite 545), 4 m × 3 mm i.d. column, 175°]

Cobalt Complexes. Cobalt (I) complexes were prepared by modifying the procedure used by Aresta *et al.*[6] slightly. A solution of cobalt iodide (0.30 g, 1 mmol) and triphenylphosphine (0.93 g, 3.5 mmol) in THF (15 ml) and ethanol (1 ml) was treated with zinc dust (0.36 g, 5.5 mmol) under stirring at room temperature for 1 h. The resulting green suspension was filtered and the filtrate was concentrated almost to dryness. Ethanol (25 ml) was added and the precipitate was washed with three portions of ethanol (6 ml) and dried. The yield was 0.69 g (60%). Anal. Found: C, 66.79; H, 4.66%. Calcd for $C_{54}H_{45}ICoP_3$: C, 66.68; H, 4.66%. Bromo- and chlorotris(triphenylphosphine)cobalt were obtained similarly. The yields were 42 and 22%, respectively. Their elementary analyses were in fair agreement with the calculated values.

Reactions. The complex (*ca.* 0.2 mmol) was placed in a 100-ml flask which was flushed with nitrogen. Tetrahydrofuran (8 ml), methanol (2 ml), and methyl acrylate (1.5 ml, 16.4 mmol) were added by syringes. The reaction mixture was stirred for 16—20 h at room temperature.

Reactions with in Situ *Prepared Complexes.* In a 100-ml flask were placed cobalt halide (1 mmol), triphenylphosphine (3 mmol), and zinc (8 mmol). Tetrahydrofuran (8 ml) and methanol (2 ml) were added and the solution was stirred for half an hour. To the resulting yellow-green solution was added methyl acrylate (16.4 mmol) and the reaction mixture was stirred for an adequate interval. The determination of yields was carried out by gas chromatography using an internal standard.

Results and Discussion

Stoichiometric Reactions. When methyl acrylate (MA) was treated with $CoX(PPh_3)_3$ (X=halogen) in THF–methanol, the yellow-green solution turned brown and finally blue. The former color change suggests an interaction between the Co(I) complex and MA. The products were identified as dimethyl adipate and methyl 2-methoxypropionate. The yield of dimethyl adipate is dependent upon halides and decreases in the order I>Br>Cl, as shown in Table 1. The higher concentration of MA causes the increase of Co(I)–MA complex, resulting in the higher yield of the hydrodimer.

Table 1. Hydrodimerization of methyl acrylate catalyzed by $CoX(PPh_3)_3$[a)]

X / mmol	MA / mmol	Yield of dimethyl adipate Co base mol/g atom
Cl 0.26	16.4	0.15(0.15)[b)]
Br 0.20	16.4	0.26(0.18)[b)]
I 0.23	2.2	0.18
I 0.22	16.4	0.31(0.30)[b)]

a) KX 5 mmol, THF 8 ml, CH_3OH 2 ml, r.t., 16—20 h.
b) In the absence of KX.

$$2\,CH_2{=}CHCO_2CH_3 + 2\,CH_3OH + CoX(PPh_3)_3 \longrightarrow H_3CO_2C(CH_2)_4CO_2CH_3 + XCo(OCH_3)_2(PPh_3)_n \quad (1)^{7)}$$

$$CH_2{=}CHCO_2CH_3 + CH_3OH \xrightarrow{XCo(OCH_3)_2(PPh_3)_n} H_3COCH_2CH_2CO_2CH_3. \quad (2)$$

The hydrodimerization was little affected by the addition of potassium halides. A Michael reaction (Eq. 2) is responsible for the catalysis of the cobalt methoxide formed.

Use of in Situ *Prepared Cobalt(I) Complexes in the Presence of Alkali Halides and Zinc.* Cobalt(I) complexes were prepared by the reaction of cobalt halides, triphenylphosphine (PPh_3), and zinc in THF–methanol at room temperature. If methoxyl group in $XCo(OCH_3)_2(PPh_3)_n$ is replaced by halogens, Co(I) complexes are expected to be regenerated in the presence of zinc. Catalytic hydrodimerization of MA was, in fact, carried out successfully by cobalt complexes in the

$$\mathrm{CoX_2 + 3\,PPh_3 + \frac{1}{2}Zn \longrightarrow CoX(PPh_3)_3 + \frac{1}{2}ZnX_2} \qquad (3)$$

presence of alkali halides and zinc, as shown in Table 2. The addition of zinc affords dimethyl adipate in more than 100% yields, based on cobalt complexes, even in the absence of alkali halides. The reaction of $\mathrm{XCo(OCH_3)_2(PPh_3)_n}$ and $\mathrm{ZnX_2}$ in the presence of zinc might regenerate a Co(I) complex. The trend in the reactivity of $\mathrm{CoX(PPh_3)_3}$ in the presence of zinc is the same as that in the isolated complexes. Alkali iodides and lithium chloride are effective and potassium iodide is the most effective among the alkali halides investigated. Although lithium salts are more soluble,[8] none of them exert any positive effect toward the hydrodimerization. It is not clear why potassium iodide is the most effective even though it is less soluble. Counter ions also play an important role in the hydrodimerization.[9]

Table 2. Effects of the addition of alkali halides on the hydrodimerization of methyl acrylate by $\mathrm{CoX(PPh_3)_3}$ in the presence of zinc[a]

X	Alkali halide	mmol	Conv. %	Yield of dimethyl adipate[b] Co base[c] mol/g atom
Cl[d]	—			1.51
Cl	LiCl	8.1	75	4.30 (70)[e]
Cl	KCl	8.0	25	0.54 (26)
Cl	$\mathrm{NH_4Cl}$	7.9	50	2.97 (72)[f]
Cl[d]	$\mathrm{AgClO_4}$	1.0		3.02
Cl[g]	KI	5.2		5.47
Br[h]	—			2.25
Br	LiBr	8.0	43	1.44 (41)[i]
Br	KBr	8.0	27	0.81 (36)
I	—		39	1.98 (62)
I[d]	LiI	4.8		4.12[j]
I	LiI	8.0	57	1.55 (33)[k]
I[d]	NaI	5.0		3.86
I	NaI	8.0	62	3.54 (69)
I	KI	5.0	55	4.09 (91)
I	KI	8.0	81	6.56 (98)
I	KI	15	80	5.16 (78)
I[d]	RbI	5.1		3.35
I	RbI	8.0	43	2.42 (69)
I[d]	CsI	5.0		3.48
I	CsI	8.0	54	3.91 (88)
I[d]	$\mathrm{NH_4I}$	5.1		4.87
I	$\mathrm{NH_4I}$	8.0	66	3.56 (66)[l]

a) $\mathrm{CoX(PPh_3)_3}$ was prepared *in situ* from $\mathrm{CoX_2}$ (1 mmol), $\mathrm{PPh_3}$ (3 mmol), and Zn (10 mmol) in THF (10 ml) and $\mathrm{CH_3OH}$ (2 ml). MA (16.4 mmol), 20 °C, 2 h. b) The number in parentheses is the yield based on MA consumed. c) Yield based on cobalt complex. d) r.t., 20—24 h. e) Methyl 2-methoxypropionate 20%. f) Methyl propionate 12%. g) r.t., 2 d. h) r.t., 4 d. i) Methyl 2-methoxypropionate 5.4%. j) Methyl 2-methoxypropionate 50%. k) Methyl 2-methoxypropionate 2.7%. l) Methyl propionate 16%.

The yield of the hydrodimer is dependent upon the amount of alkali halides. The excess of alkali halides lowers both yield and selectivity. The appropriate amount of alkali halides nearly corresponds to that of the dimethyl adipate to be produced. A considerable amount of methyl 2-methoxypropionate and propionate were formed in the presence of lithium and ammonium salts, respectively.

Table 3. Effects of temperature and additives on the hydrodimerization of methyl acrylate[a]

Temp °C	Additive KI mmol	Additive MeOH ml	Time h	Conv. %	Yield of dimethyl adipate[b] Co base mol/g atom
0	5.0	2	6	92	7.54 (99)
20	—	—	2	40	1.13 (34)
	5.0	—	2	68	1.61 (29)
	5.0	2	2	55	4.09 (91)
	5.0	2	6	83	5.87 (86)
40	5.0	2	6	46	2.81 (75)

a) Catalysts prepared *in situ* from $\mathrm{CoI_2}$ (1 mmol), $\mathrm{PPh_3}$ (3 mmol), and Zn (10 mmol) in THF (8 ml). MA 16.4 mmol. b) Yields are the same as those in Table 2.

The effects of methanol and temperature were examined as shown in Table 3. Even in the absence of methanol, hydrodimerization occurred, but the addition of methanol appreciably increased the yield of the hydrodimer. Low temperatures are preferable because catalytic species are so thermally unstable as to be easily decomposed.[6]

Table 4. Solvent effects on the hydrodimerization of methyl acrylate by $\mathrm{CoX(PPh_3)_3}$[a]

X	Solvent ml	Yield of dimethyl adipate Co base mol/g atom
Cl	THF 8, MeOH 2	1.51
	DMF 8, MeOH 2	2.89
	$\mathrm{CH_3CN}$ 8, MeOH 2	2.18
	MeOH 10	2.23
I	THF 8, MeOH 2	5.26
	THF 10	0.56
	$\mathrm{CH_3CN}$ 8, MeOH 2	0.67
	$\mathrm{CH_3CN}$ 10	1.20
	MeOH 10	0.45

a) $\mathrm{CoX(PPh_3)_3}$ prepared *in situ* from $\mathrm{CoX_2}$ (1 mmol), $\mathrm{PPh_3}$ (3 mmol), and Zn (8—10 mmol) in solvents. MA 16.4 mmol, r.t., 20—90 h.

Tetrahydrofuran and *N*,*N*-dimethylformamide were found to be the most suitable solvents among several investigated in the catalysis of $\mathrm{CoI(PPh_3)_3}$ and $\mathrm{CoCl(PPh_3)_3}$, respectively (Table 4). Polar solvents are preferable. The reduction to the Co(I) complexes occurred in all solvents listed in Table 4, but it was accelerated by the addition of methanol. The effects of methanol on the hydrodimerization of MA in THF–methanol are shown in Fig. 1. The appropriate mole ratio of methanol to MA is 4—5. The Michael reaction took place in preference to the hydrodimerization in a large excess of methanol : methyl 2-methoxypropionate was obtained in a 52% yield in methanol as the sole solvent. Ethanol functions similarly to methanol in the hydrodimerization, but ester exchange occurs in it.

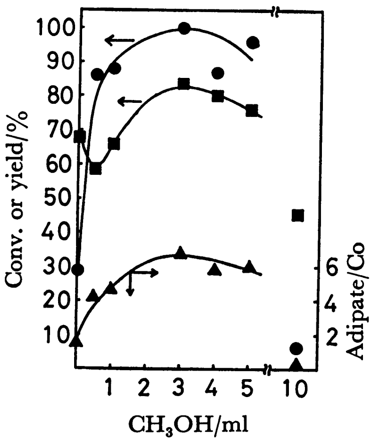


Fig. 1. Effects of the amount of methanol on the hydrodimerization of methyl acrylate by *in situ* prepared $CoI(PPh_3)_3$ in THF (8 ml)-methanol. (Methanol (10 ml) without THF.)
■: Conversion, ●: yield based on MA consumed, ▲: yield based on the cobalt complex.

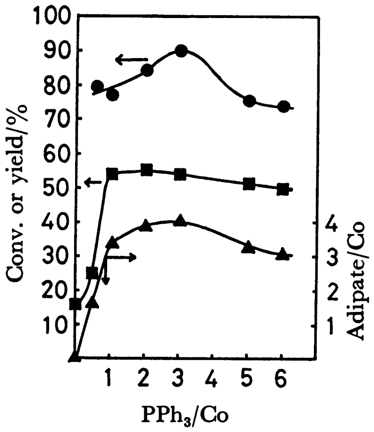


Fig. 2. Effects of the ratio of triphenylphosphine to cobalt on the hydrodimerization of methyl acrylate by *in situ* prepared $CoI(PPh_3)_3$. Symbols are the same as those in Fig. 1.

The effects of the ratio of PPh_3 to a cobalt complex are shown in Fig. 2. The optimum ratio is 3, which is in accord with the ratio of the isolated complexes. The excess of PPh_3 did not affect the conversion of MA, but lowered the yield of the hydrodimer. The coordination of MA is blocked by excess PPh_3 which, however, does not inhibit the Michael reaction.

Mechanism. The hydrodimer obtained in deuterated compounds was analyzed by ^1H NMR as shown in Table 5. Most of the hydrogen added originates from the hydroxyl hydrogen in methanol. The rest seems to be from solvents and MA itself, because we have not detected ortho-hydrogen of PPh_3 in the hydrodimer. No hydrogen attached to β-carbon of MA exchanged with that of solvents such as THF and benzene, but a part of the hydrogen exchanged with that of acetonitrile. Acetonitrile is sometimes split to H and CH_2CN radicals by oxidative addition to low-valent transition metal complexes.[10] Since $CoX(PPh_3)_3$, one of the low-valent d^8 complexes, is susceptible to oxidative addition,[11] deuterium incorporation into the hydrodimer may occur *via* deuterium atom abstraction of acetonitrile-d_3 by the Co(I) complex and the transfer of the deuterium.

Table 5. ANALYSIS OF HYDROGEN OF DIMETHYL ADIPATE PRODUCED BY THE REACTION OF MA WITH *IN SITU* PREPARED $CoX(PPh_3)_3$ IN DEUTERATED COMPOUNDS

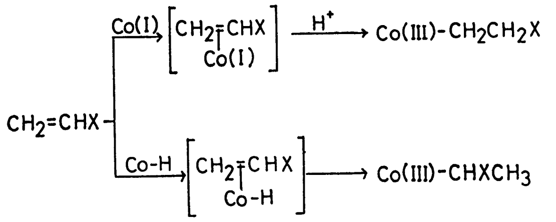
Catalytic system[a]	Deuterium source	Solvent	^1H NMR analysis[b]	
			β-C	α-C
CoI_2P_2-P-Zn	CH_3OD	THF	2.05	1.24
$CoCl_2$-3P-Zn	CH_3OD-D_2O[c]	THF	2.06	1.22
CoI_2-P-Zn	CH_3OD	CH_3CN	2.03	1.68
CoI_2-3P-Zn	CH_3OD	C_6H_6	1.96	1.78
CoI_2-3P-Zn	$P(C_6D_5)_3$	CH_3CN	2.11	1.94
CoI_2-3P-Zn	CD_3CN	CD_3CN	1.76	1.95
CoI_2-3P-Zn	CH_3OD	CH_3CN	1.35	1.59

a) P=PPh_3. b) Based on the assumption that the number of hydrogens of the methoxy group is 3.00. c) Before the end of the reaction, D_2O was added.

Hydrodimerization of acrylonitrile by iron carbonyls and ruthenium complexes has been extensively investigated by Misono *et al.*,[5a-e] McClure *et al.*,[5f] and Billig and coworkers.[5g] They explained the reaction involving insertion of acrylonitrile into an M–H or M–cyanoethyl or an M–vinyl bond (M=Fe, Ru), some of which were isolated and characterized. The products are not only a hydrodimer but also propionitrile, 2-methylglutaronitrile, and *cis*- and *trans*-2-hexenedinitrile. The products from the reaction of MA with Co(I) complexes are a head-to-head hydrodimer, Michael adduct, and methyl propionate. We could not observe 2-methylglutarate and *cis*- and *trans*-2-hexenedioate at all. The products of the latter reaction are very similar to those derived from the electrolytic coupling.[3] The difference in products suggests that the hydrodimerization of MA by $CoX(PPh_3)_3$ proceeds by a mechanism different from that of the hydrodimerization of acrylonitrile by iron carbonyls and ruthenium complexes. Another characteristic feature is that the hydrogen incorporated into the hydrodimer in the Co(I) complex systems originates mainly from alcohols, but that in the ruthenium complex systems comes from atmospheric hydrogen.

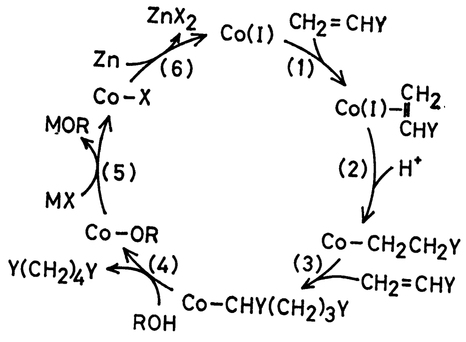
The addition of MA to $CoX(PPh_3)_3$ in methanolic solution produces a red-brown color from a yellow-green one. A similar color change was observed between cobaloxime(I) and ethyl acrylate or acrylonitrile.[12] Spectroscopic study showed an interchange between the cobaloxime–ethyl acrylate π-complex and (2-ethoxycarbonylethyl)cobaloxime.[12b] However, a hydride $HCo(dmg)_2P(n\text{-}C_4H_9)_3$ (dmg=dimethylglyoximato) reacted with acrylonitrile or acrylates to yield the α-substituted ethylcobaloxime derivatives,[13] in contrast with β-substituted isomers from the protonation of the cobaloxime(I)–olefin π-complex (Scheme 1). The latter has been exemplified by the work on the rhodium–olefin complexes.[14]

We postulate a mechanism for the hydrodimerization of methyl acrylate by Co(I) complexes (Scheme 2). Red-brown species are responsible for the formation



Co=cobaloxime, X=CN, CO_2R.

Scheme 1.



Co=$CoX(PPh_3)_n$, X=halogen,
Y=CO_2CH_3, M=alkali metal.

Scheme 2.

of Co(I)–MA π-complex. A β-substituted ethylcobalt complex is formed from the protonation of the Co(I)–MA π-complex with alcohol. Further addition of MA to the ethylcobalt complex gives 1,4-bis(methoxycarbonyl)butylcobalt complex, which is protonated to yield dimethyl adipate. No reverse reaction in (2) occurs because hydrogen exchange between MA and alcohol has not been observed. The susceptibility of protonation of the 1,4-bis(methoxycarbonyl)butylcobalt complex, in comparison with that of the β-substituted ethylcobalt complex, is correlated with the stability of the cobalt-carbon: alkylmetal complexes bearing primary carbons are more stable than those bearing secondary carbons.[15] The Co(I) complex can be regenerated by the reduction of the cobalt halide complex which is formed by replacing the alkoxyl group with alkali halides. Cobalt alkoxide or alkali metal alkoxide released in (5) causes the Michael reaction to occur.

The present work was partially supported by Grants-in-Aid for Scientific Research (Nos. 065100, 265235) from the Ministry of Education, Science and Culture.

References

1) H. R. Snyder and R. E. Putnam, *J. Am. Chem. Soc.*, **76**, 33 (1954); M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965); M. F. Semmelhack and R. D. Stauffer, *ibid.*, **40**, 3619 (1975); J. Shabtai, E. Ney-Igner, and H. Pines, *ibid.*, **43**, 4086 (1978); T. Miyakoshi, H. Omichi, and K. Saito, *Nippon Kagaku Kaishi*, **1978**, 473.

2) Y. Arad, M. Levy, and D. Vofsi, *J. Org. Chem.*, **34**, 3709 (1969).

3) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964); M. M. Baizer and J. D. Anderson, *ibid.*, **111**, 223 (1964); M. M. Baizer, *Chemtech*, **1980**, 161; D. E. Danly *ibid.*, **1980**, 302.

4) J. Kwiatek, I. L. Mador, and J. K. Seyler, *Adv. Chem. Ser.*, **37**, 201 (1963); T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965); Y. Kobayashi and S. Taira, *Tetrahedron*, **24**, 5763 (1968); T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *Bull. Chem. Soc. Jpn.*, **43**, 877 (1970); G. Oehme and H. Pracejus, *Tetrahedron Lett.*, **1979**, 343.

5) a) A. Misono, Y. Uchida, K. Tamai, and M. Hidai, *Bull. Chem. Soc. Jpn*, **40**, 931 (1967); b) A. Misono, Y. Uchida, M. Hidai, and H. Kanai, *J. Chem. Soc., Chem. Commun.*, **1967**, 357; c) A. Misono, Y. Uchida, T. Saito, and M. Hidai, *Kogyo Kagaku Zasshi*, **70**, 1890 (1967); d) A. Misono, Y. Uchida, M. Hidai, H. Shinohara, and Y. Watanabe, *Bull. Chem. Soc. Jpn*, **41**, 396 (1968); e) A. Misono, Y. Uchida, M. Hidai, and I. Inomata, *J. Chem. Soc., Chem. Commun.*, **1968**, 704; f) J. D. McClure, R. Owyang, and L. H. Slaugh, *J. Organomet. Chem.*, **12**, P8 (1968); g) E. Billig, C. B. Strow, and R. L. Pruett, *J. Chem. Soc., Chem. Commun.*, **1968**, 1307; h) S. Hosaka and S. Wakamatsu, Japan Patent, 46-5689, *Chem. Abstr.*, **74**, 124867 (1971); i) G. Agnès, G. P. Chiusoli, and G. Cometti, *J. Chem. Soc., Chem. Commun.*, **1968**, 1515; j) H. Kanai and M. Okada, *Chem. Lett.*, **1975**, 167.

6) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).

7) The authors wish to thank a referee who kindly suggested the structure of the cobalt complex produced after the reaction.

8) E. Price, "The Chemistry of Non-aqueous Solvents," ed by J. J. Lagowski, Academic Press, New York and London (1966), Chap. 2, p. 70; J. Burgess, "Metal Ions in Solutions," Ellis Horwood Ltd. (1978), pp. 219—223.

9) Lithium iodide and sodium iodide are the most effective additives in the hydrodimerization of methyl acrylate by Co(I)–fumarate complexes and in that of methyl vinyl ketone by Co(I)–bipyridyl complexes, respectively. The congeniality has not been simply explained.

10) B.-K. Teo, A. P. Ginsberg, and J. C. Calabrese, *J. Am. Chem. Soc.*, **98**, 3027 (1976); J. A. Sofranko, R. Eisenberg, and J. A. Kampmeier, *ibid.*, **102**, 1163 (1980).

11) J. K. Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York (1978), pp. 156—177.

12) G. N. Schrauzer, *Angew. Chem.*, **88**, 465 (1976); G. N. Schrauzer, J. H. Weber, and T. M. Beckham, *J. Am. Chem. Soc.*, **92**, 7078 (1970).

13) G. N. Schrauzer and R. J. Holland, *J. Am. Chem. Soc.*, **93**, 1505 (1971).

14) L. P. Seiwell, *Inorg. Chem.*, **15**, 2560 (1976).

15) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 (1971); M. Tamura and J. K. Kochi, *J. Organomet. Chem.*, **29**, 111 (1971).