JOURNAL OF CATALYSIS 63, 175–181 (1980)

Ethylene Hydrogenation Catalyzed by Polymer-Bound Tetraruthenium Clusters

Z. OTERO-SCHIPPER, J. LIETO,[1] AND B. C. GATES[2]

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711

Received July 25, 1979; revised November 26, 1979

Metal clusters with unique structures have been attached to solid polymeric supports and used to catalyze ethylene hydrogenation at 1 atm and 50–90°C. Polymer-bound analogs of $[H_4Ru_4(CO)_{12-x}(PPh_3)_x]$ (with $x = 1$, 3, or 4) were synthesized by ligand exchange between $[H_4Ru_4(CO)_{12}]$ and poly(styrene-divinylbenzene) membranes functionalized with phosphine ligands. Rates of ethylene hydrogenation were measured with a flow reactor allowing simultaneous recording of the infrared spectra of the functioning catalyst. Each catalyst was stable, exhibiting undiminished activity after thousands of turnovers and presenting a carbonyl spectrum unchanged during catalysis and indistinguishable from that of the membrane incorporating the originally bound tetraruthenium cluster. The catalysts incorporating tri- and tetrasubstituted clusters exhibited the same form of kinetics, indicating saturation in ethylene and a reaction order in H_2 of 0.8. The catalytic activity increased, the activation energy decreased, and the strength of bonding of ethylene to the catalyst increased with increasing substitution by electron-donor phosphine ligands on the cluster. The results suggest that the Ru_4 framework provided the catalytic sites, perhaps by reversible Ru–Ru bond breaking to form coordinatively unsaturated metal centers.

INTRODUCTION

The dispersed aggregates of metal atoms on typical supported-metal catalysts are difficult to characterize, presenting a variety of structures and catalytic activities. Metal clusters—polynuclear metal compounds—have unique structures and are therefore attractive model catalysts, but characterization of catalysis by metal clusters in solution is hindered by the difficulties associated with fragmentation and aggregation of the clusters—all but a few (*1–4*) of the reported studies of catalysis by soluble metal clusters have involved unidentified catalytic species. Not surprisingly, most attempts to support metal-cluster species on solids have led to the formation of aggregated and/or mononuclear (*5–8*) metal species, and only recently have researchers (*9, 10*) succeeded in preparing unique metal clusters on supports.

The work described here develops the theme of preparation and catalytic characterization of supported metal clusters having unique structures. We have used tetraruthenium clusters, since many clusters in this family are known and some of them evidently have catalytic activity for isomerization of alkenes and for hydrogenations of alkynes, alkenes, and ketones carried out homogeneously (*11–16*). Further, from the known solution chemistry of $[H_4Ru_4(CO)_{12}]$ (*17, 18*), we expected this cluster to lend itself readily to bonding to supports by simple ligand exchange involving pendant phosphine groups on the support and CO ligands on the cluster.

The following paragraphs summarize (i) the preparation of polymer-supported derivatives of $[H_4Ru_4(CO)_{12}]$, with the substitution by phosphine ligands having been varied systematically, (ii) characterization of the supported clusters by carbonyl infra-

---

[1] Present address: Institut de Pétroléochimie et de Synthèse Organique Industrielle, Centre de St. Jérome, Rue Henri-Poincaré, 13397 Marseille Cedex 4, France.

[2] To whom correspondence should be addressed.

0021-9517/80/050175-07$02.00/0

red spectroscopy, and (iii) characterization of the catalytic nature of the polymers by the kinetics of a simple reaction, ethylene hydrogenation.

NOTATION

a	Exponent in reaction rate equation
b	Exponent in reaction rate equation (reaction order in H_2)
c	Exponent in reaction rate equation
E	Ethylene
k	Reaction rate constant, variable dimensions
K_E	Temperature-dependent parameter in reaction rate equation (interpreted as an equilibrium constant for the bonding of ethylene to the catalyst), atm^{-1}
P	Partial pressure, atm
r	Catalytic reaction rate, molecules of ethane/Ru atom · sec.

EXPERIMENTAL METHODS

Catalyst Preparation

The parent cluster $[H_4Ru_4(CO)_{12}]$ was synthesized by the method of Kaesz *et al.* (*19*). The reaction was monitored by infrared spectroscopy, the results indicating product yields of 85–90%.

Two types of polymer-membrane supports incorporating phosphine groups were synthesized (*9, 20, 21*), the first prepared by copolymerization of styrene, divinylbenzene (DVB), and *p*-styryldiphenylphosphine, and the second by copolymerization of styrene, DVB, and *p*-bromostyrene; the –Br groups in the latter polymer were partially converted into phosphines by reaction with lithium diphenylphosphide (*22*). The first kind of support was a block copolymer having high local concentrations of $-PPh_2$ groups in the polymer matrix, and the second kind was a nearly random copolymer having almost uniformly distributed $-PPh_2$ groups (*23*). All the membranes were crosslinked with 2 mole% DVB.

The tetraruthenium carbonyl clusters were incorporated in the polymers by ligand exchange involving CO and the polymer-bound $-PPh_2$ groups. Many of the preparations gave mixtures of supported tetraruthenium species having various degrees of phosphine substitution. Nearly pure supported tetraruthenium species were prepared by proper choice of the synthesis conditions, determined by trial. These conditions are reported in the following paragraphs.

A membrane of the nearly random copolymer (prepared from a mixture of monomers containing 4 mole% *p*-bromostyrene) was protected by encasement in stainless-steel mesh and contacted with $[H_4Ru_4(CO)_{12}]$ in hexane–diethyl ether solution. With the temperature maintained at 45°C, the ligand-exchange reaction was allowed to proceed for 2 hr. The membrane was washed with diethyl ether, with *n*-hexane, and again with diethyl ether. The metal species on the membrane was identified by its carbonyl infrared spectrum (Table 2) as the analog of the cluster $[H_4Ru_4(CO)_{11}(PPh_3)]$, referred to as $[H_4Ru_4(CO)_{11}(PPh_2)–Ⓟ]$, where Ⓟ designates the polymer support.

The synthesis of $[H_4Ru_4(CO)_9(PPh_2)_3–Ⓟ]$ was carried out with a block copolymer membrane prepared from a mixture of monomers containing 0.3 mole% *p*-styryldiphenylphosphine. The ligand exchange with $[H_4Ru_4(CO)_{12}]$ was allowed to proceed for 3 hr at 45°C, but otherwise the preparation method was the same as that used for $[H_4Ru_4(CO)_{11}(PPh_2)–Ⓟ]$. The product was identified by its carbonyl infrared spectrum (Table 2).

The tetrasubstituted cluster, $[H_4Ru_4(CO)_8(PPh_2)_4–Ⓟ]$, was synthesized with a block copolymer membrane prepared from a mixture of monomers containing 0.5 mole% *p*-styryldiphenylphosphine. The membrane was brought in contact with a solution of $[H_4Ru_4(CO)_{12}]$ in a dry hexane–tetrahydrofuran (THF) solution. The ligand-exchange reaction was allowed to proceed for 10 hr at 48°C, and the product was washed with THF, *n*-hexane, and THF. Again, the product was identified by its carbonyl infrared spectrum (Table 2).

Elemental analyses of the membranes, performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y., are given in Table 1.

Details of the syntheses and analyses are given in Otero-Schipper's thesis (*23*).

Catalytic Kinetics Measurements and Infrared Spectroscopy

The polymers incorporating tetraruthenium clusters were evaluated as catalysts for ethylene hydrogenation at 52–95°C and 1.0–1.2 atm using a flow reactor system described previously (*6, 21*). Ethylene (Linde, research grade) was used without further purification. H_2 (Linde, research grade) and He (Linde, research grade) flowed through a bed of supported copper, held at 300°C, to remove traces of oxygen, and through a bed of zeolite 5A (Linde), to remove traces of water. The reactant stream flowed into a reactor which was also an infrared cell, allowing measurement of the spectra of functioning catalysts. The product gas stream flowed steadily through a gas sampling valve and was analyzed with a gas chromatograph equipped with a thermal conductivity detector. Ethane was the only observed product.

The kinetics data were obtained over the following ranges of partial pressures: $0.2 \leq P_{H_2} \leq 0.85$; $0.15 \leq P_E \leq 0.9$ atm. Helium was used as a diluent to allow variation of the partial pressure of each reactant while the partial pressure of the other was held nearly constant. In a typical experiment, the system was flushed with helium for 5 hr prior to the flow of reactants. Steady state was attained in approximately 9 hr. Subsequent changes in the partial pressures of the reactants were followed by the attainment of a new steady state, typically in about 30 min. The conversions of reactant were shown experimentally to be differential, giving reaction rates directly (*23*).

TABLE 1

Elemental Analyses of the Catalysts

Catalyst	wt% Br	wt% P	wt% Ru
$[H_4Ru_4(CO)_{11}(PPh_2)$–Ⓟ$]$	0.19	0.13	0.25
$[H_4Ru_4(CO)_9(PPh_2)_3$–Ⓟ$]$	—	0.14	0.11
$[H_4Ru_4(CO)_8(PPh_2)_4$–Ⓟ$]$	—	0.17	0.49

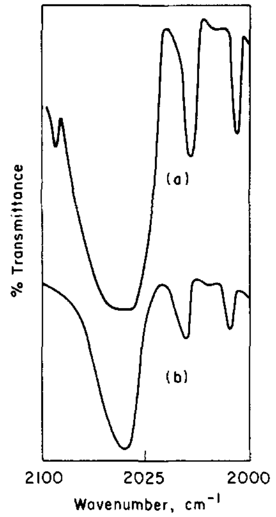

FIG. 1. Carbonyl infrared spectra of (a) $[H_4Ru_4(CO)_{11}(PPh_3)]$ and (b) the polymer-supported analog $[H_4Ru_4(CO)_{11}(PPh_2)$–Ⓟ$]$.

RESULTS

The supported ruthenium species were identified by comparison of their carbonyl infrared spectra with the spectra of the analogous molecular clusters, which are reported in the literature (Table 2). The band locations and the relative intensities of the molecular and supported clusters are in good agreement, as demonstrated by the comparison of Fig. 1 for $[H_4Ru_4(CO)_{11}(PPh_3)]$ and its supported analog. The only observable species obtained by the preparation methods reported here are the unique tetraruthenium clusters.

The polymers containing tetraruthenium clusters were found to be active catalysts for ethylene hydrogenation. The rate data (Fig. 2) indicate saturation kinetics and, in the case of the monosubstituted cluster, inhibition of reaction by ethylene at the

TABLE 2

Carbonyl Infrared Spectra of Molecular and Polymer-Supported Tetraruthenium Clusters

Cluster	ν_{CO} (cm^{-1})	Ref.
[$H_4Ru_4(CO)_{11}(PPh_3)$]	2094 m, 2086 w, 2067 s, 2057 s, 2053 sh, 2038 w, 2032 m, 2027 s, 2015 m, 2008 s, 1998 w, 1994 w, 1966 mw	(*17*)
[$H_4Ru_4(CO)_{11}(PPh_3)$] (in CH_2Cl_2)	2095 mw, 2064 vs, 2027 s, 2020 w, 2006 s	This work
[$H_4Ru_4(CO)_{11}(PPh_2)$-Ⓟ]	2062 vs, 2030 s, 2018 w, 2006 s	This work
[$H_4Ru_4(CO)_9(PPh_3)_3$]	2068 s, 2024 vs, 2003 s, 1993 s, 1987 sh, 1963 s, 1945 sh, 1940 m	(*17*)
[$H_4Ru_4(CO)_9(PPh_2)_3$-Ⓟ]	2063 s, 2024 vs, 2005 s, 1995 s, 1972 s	This work
[$H_4Ru_4(CO)_8(PPh_3)_4$]	2015 s, 1984 m, 1952 m, 1930 w	(*17*)
[$H_4Ru_4(CO)_8(PPh_2)_4$-Ⓟ]	2024 s, 1982 m, 1953 s[a]	This work

[a] Coincides with a band of the crosslinked polystyrene support.

higher partial pressures. The data were therefore fitted to equations of the following form:

$$r = \frac{kK_EP_E{}^aP_{H_2}^b}{[1 + K_EP_E]^c}. \qquad (1)$$

The several equations best fitting the data for each catalyst were determined with a standard nonlinear least-squares regression technique (*24*). Details are given elsewhere (*23*). Table 3 lists the equations giving the best fit and the best values of the kinetics parameters obtained for each of the three catalysts at various temperatures; also listed are the energy of activation (determined from the dependence of k on temperature) and the enthalpy of adsorption of ethylene (determined from the dependence of K_E on temperature) for each. Figure 2 shows the fit of some representative data to the rate equation giving the best fit for each of the three catalysts.

The catalysts were stable, showing unchanged activity after >100 hr under reaction conditions and after thousands of turnovers. CO was a strong reaction inhibitor; even traces of CO in the feed stream led to a complete loss of activity of the monosubstituted catalyst, but the activity was fully regained after about 7 hr in flowing reactants.

The infrared spectrum of each catalyst was indistinguishable from that of the originally prepared polymer under all the observed reaction conditions. It follows that the predominant form of the metal in each catalyst was the originally prepared tetraruthenium carbonyl cluster.

DISCUSSION

The synthesis described here provides the means for attachment of a wide variety of metal clusters to supports. The method simply requires a parent cluster which readily undergoes ligand exchange with the support. To allow formation of uniquely substituted clusters, the support must provide an environment having an appropriate uniformity and concentration of ligands. The polymers are therefore especially useful

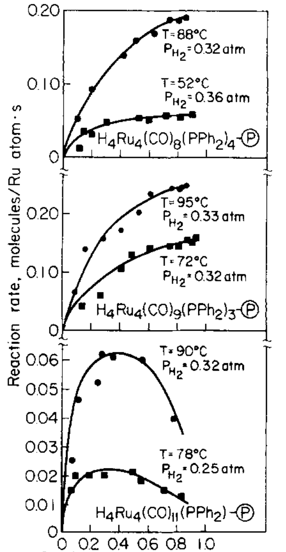

FIG. 2. Kinetics of ethylene hydrogenation catalyzed by polymers incorporating tetraruthenium carbonyl clusters: dependence of rate on ethylene partial pressure. The curves are the predictions of the equations of Table 3 with the parameter values given there.

TABLE 3

Kinetics of Ethylene Hydrogenation Catalyzed by Polymers Incorporating Tetraruthenium Clusters

Catalyst	Rate equation	Temperature (°C)	$10 \cdot k^{a}$	K (atm^{-1})	E_{act} (kcal/mole)	ΔH_E (kcal/mole)
$H_4Ru_4(CO)_{11}(PPh_2)$–Ⓟ	$r = \frac{kK_EP_EP_{H_2}^{1.5}}{(1 + K_EP_E)^3}$	62	3.1 ± 0.2	3.1 ± 0.2	12.3 ± 0.7	−6 ± 1
		78	8.2 ± 1.0	2.7 ± 0.2		
		90	12.8 ± 1.0	1.5 ± 0.1		
$H_4Ru_4(CO)_9(PPh_2)_3$–Ⓟ	$r = \frac{kK_EP_EP_{H_2}^{0.8}}{1 + K_EP_E}$	52	0.33	—	15	−6
		72	1.5 ± 0.1	10.5 ± 0.6		
		95	4.7 ± 0.3	6.2 ± 0.4		
$H_4Ru_4(CO)_8(PPh_2)_4$–Ⓟ	$r = \frac{kK_EP_EP_{H_2}^{0.8}}{1 + K_EP_E}$	52	1.5 ± 0.2	12 ± 1.0	9 ± 2	−10 ± 2
		69	4.9 ± 0.4	5.3 ± 0.6		
		88	6.2 ± 1.0	2.3 ± 0.2		

[a] The dimensions of k are molecules/Ru atom · sec · atm^b, where b equals 1.5 for [$H_4Ru_4(CO)_{11}(PPh_2)$– P] and 0.8 for the other two catalysts.

supports, since various polymer syntheses can give wide variations in the local concentration of pendant ligands. Inorganic solids like silica can easily be functionalized with ligands like mono- and diphosphines, which can be used for attachment of metal clusters (*4*), but precise control of the uniformity of surface ligand density is relatively difficult, and the inorganic solids lend themselves less readily than the polymers to preparation of series of variously substituted supported metal clusters having unique structures.

The preparation of the supported mono-, tri-, and tetrasubstituted phosphine derivatives of [$H_4Ru_4(CO)_{12}$] has allowed us, following established patterns of study of homogeneous metal-complex catalysts, to determine the effect of the phosphine ligands on catalytic activity. The results, typified by the data of Fig. 3, show that increasing the phosphine ligand substitution on the Ru_4 framework increased the activity of the catalyst. This pattern parallels that observed by Frediani *et al.* (*13*) for cyclohexanone hydrogenation catlayzed in solution by tetrahydridotetraruthenium clusters substituted with phosphine groups.

On the basis of this result, we suggest that the Ru_4 framework provided the catalytic sites and that the role of the electron-donor phosphine ligands—besides anchoring the clusters—was to activate ethylene, also bonded to the metal framework.

The kinetics data—showing saturation in ethylene and, in the case of [$H_4Ru_4(CO)_{11}$ PPh_2–Ⓟ], inhibition of reaction by ethylene—confirm the hypothesis that ethylene

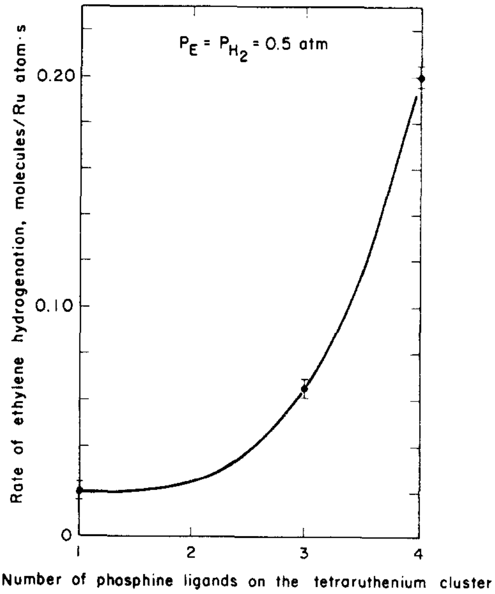

FIG. 3. Effect of the number of phosphine substituents bonded to the tetraruthenium carbonyl cluster on the rate of ethylene hydrogenation at 72°C. Points were determined by interpolation of the data.

(like hydrogen) was coordinated to the metal framework. Comparing the results of Table 3 for $[H_4Ru_4(CO)_9(PPh_2)_3$–Ⓟ$]$ and $[H_4Ru_4(CO)_8(PPh_2)_4$–Ⓟ$]$, for which the observed rate equations were of the same form, we observe that the increased substitution by phosphine decreased the activation energy for the catalytic reaction from 15 to 9 kcal/mole and increased the strength of bonding of ethylene to the metal by about 4 kcal/mole (as indicated by the temperature dependence of K_E). These results are in accord with the interpretation given above, providing further support for the suggestion of increased back donation to and increased activation of the π-acceptor ethylene ligand with an increasing number of donor phosphine ligands on the metal framework.

We caution that the possibility that the catalytic sites were provided by undetectably low concentrations of mononuclear Ru complexes or aggregates of Ru atoms cannot be ruled out; however the suggestion that the tetraruthenium clusters provided the catalytic sites is consistent with all the observations, being supported specifically by (i) the infrared spectra, showing that tetraruthenium clusters were the only observed metal species, (ii) the systematic variation of catalytic activity with changes in the ligand environment of the clusters, and (iii) the stability of the catalysts and the reproducibility of the catalytic activity measured for separately synthesized membranes (*23*).

Proceeding under the assumption that the tetraruthenium clusters indeed provided the catalytic sites in each catalyst, we recognize several possibilities for generation of sites by generation of coordinatively unsaturated metal centers.[3] The possibilities include (reversible) breaking of Ru–CO, Ru–H, Ru–P, and Ru–Ru bonds. Since the infrared spectra of the attached clusters remained unchanged even after >100 hr under reaction conditions, we exclude the possibility that dissociation of Ru–CO bonds was responsible for the formation of the active sites. If CO had been dissociated, CO would have flowed out in the effluent stream, and changes in the infrared spectra of the clusters would have been observed. Further, since the donor phosphine ligands increase the Ru–CO bond strength, an increasing number of phosphine ligands would have decreased the rate of reaction if Ru–CO bond breaking had been the slow step in the catalytic cycle; the data show the opposite trend (Fig. 3).

The possibility that Ru–H bond dissociation was responsible for the formation of the active sites seems unlikely since hydrogen did not inhibit the catalytic reaction under any observed conditions. Further, flowing pure ethylene over the supported tetrahydridotetraruthenium clusters produced no ethane and no change in the spectra even after 100 hr at 90°C,[4] confirming the stability of the Ru–H bonds in the cluster.

There is no information available about the bond strengths of the ruthenium carbonyl clusters, and it is therefore difficult to ascertain whether Ru–P or Ru–Ru bond dissociation is more likely to be responsible for the formation of active sites. Examples of both metal–phosphorus and metal–metal bond dissociation mechanisms in metal cluster chemistry are cited in the literature (e.g. (*25–27*)).

We speculate that Ru–Ru bond breaking is the more important step, since there is evidence suggesting that Ru–Ru bond breaking may occur when olefins are bonded to $[H_4Ru_4(CO)_{12}]$ (*28*).[5] There is

---

[3] Any mechanism involving coordinative unsaturation at a metal center would account for the observed inhibition of reaction by CO.

[4] This observation indicates that an olefin insertion mechanism on the saturated cluster can be ruled out.

[5] The cited work fails to provide conclusive evidence, since it was carried out with "$[\alpha$-$H_4Ru_4(CO)_{12}]$," which is now recognized to be a mixture of $[H_4Ru_4(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ (*29*); it is therefore not clear whether the Ru–Ru bond breaking occurred in the tetraruthenium cluster.

also evidence that Ru–Ru bond cleavage occurs when alkynes are bonded to $Ru_3(CO)_{12}$ (*30*). More structural information is needed before concrete ideas about the catalytic intermediates can be developed. Whatever the intermediates were, they were present in the functioning catalysts in concentrations too low to detect by infrared spectroscopy—the coordinatively saturated tetraruthenium clusters were the only metal species detected.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation.

REFERENCES

1. Deeming, A. J., and Hasso, S., *J. Organomet. Chem.* **112**, C39 (1976).

2. Botteghi, C., Gladiali, S., Bianchi, M., Matteoli, U., Frediani, P., Vergamini, P. G., and Benedetti, E., *J. Organomet. Chem.* **140**, 221 (1977).

3. Bianchi, M., Frediani, P., Matteoli, U., Menchi, G., Piacenti, F., Botteghi, C., and Gladiali, S., paper presented at First International Symposium on Homogeneous Catalysis, Corpus Christi, Texas, 1978.

4. Smith, A. K., Abboud, W., Basset, J. M., Reimann, W., Rempel, G. L., Bilhou, J. L., Bilhou-Bougnol, V., Graydon, W. F., Dunogues, J., Ardoin, N., and Duffaut, N., *in* "Fundamental Research in Homogeneous Catalysis," (M. Tsutsui, ed.), Vol. 3, p. 621. Plenum, New York, 1979.

5. Collman, J. P., Hegedus, L. S., Cooke, M. P., Norton, J. R., Dolcetti, G., and Marquardt, D. N., *J. Amer. Chem. Soc.* **94**, 1789 (1972).

6. Jarrell, M. S., and Gates, B. C., *J. Catal.* **54**, 81 (1978).

7. Ichikawa, M., *J. Chem. Soc. Chem. Commun.*, 366 (1978).

8. Anderson, J. R., Elmes, P. S., Howe, R. F., and Mainwaring, D. E., *J. Catal.* **50**, 3 (1977).

9. Rafalko, J. J., Lieto, J., Gates, B. C., and Schrader, G. L., Jr., *J. Chem. Soc. Chem. Commun.*, 540 (1978); Lieto, J., Rafalko, J. J., Minkiewicz, J. V., Rafalko, P. W., and Gates, B. C., *in* "Fundamental Research in Homogeneous Catalysis," (M. Tsutsui, ed.), Vol. 3, p. 637. Plenum, New York, 1979.

10. Brown, S. C., and Evans, J., *J. Chem. Soc. Chem. Commun.*, 1063 (1978).

11. Vaglio, G. A., and Valle, M., *Inorg. Chim. Acta* **30**, 161 (1978).

12. Valle, M., Osella, D., and Vaglio, G. A., *Inorg. Chim. Acta* **20**, 213 (1976).

13. Frediani, P., Matteoli, U., Bianchi, N., Piacenti, F., and Menchi, G., *J. Organomet. Chem.* **150**, 273 (1978).

14. Lausaroti, P. M., Vaglio, G. A., and Valle, M., *Inorg. Chim. Acta* **25**, L107 (1977).

15. Laine, R. M., *J. Amer. Chem. Soc.* **100**, 20 (1978).

16. Laine, R. M., Rinker, R. G., and Ford, P. C., *J. Amer. Chem. Soc.* **99**, 1 (1977).

17. Piacenti, F., Bianchi, M., Frediani, P., and Benedetti, E., *Inorg. Chem.* **10**, 2759 (1971).

18. Wilson, R. D., Wu, S. M., Love, R. A., and Bau, R., *Inorg. Chem.* **17**, 5 (1978).

19. Kaesz, H. D., Knox, S. A. R., Koepke, J. W., and Saillant, J. R., *J. Chem. Soc. Chem. Commun.*, 477 (1971).

20. Jarrell, M. S., Ph.D. Thesis, University of Delaware, 1978.

21. Lieto, J., Ph.D. Thesis, University of Delaware, 1979.

22. Tamborski, C., Ford, F. E., Lehn, W. L., Moore, G. S., and Soloski, E. J., *J. Org. Chem.* **27**, 619 (1962).

23. Otero-Schipper, Z., M.Ch.E. Thesis, University of Delaware, 1979.

24. Marquardt, D. W., *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).

25. Bingham, D., Webster, D. E., and Wells, P. B., *J. Chem. Soc. Dalton,* 1928 (1972).

26. Bingham, D., Webster, D. E., and Wells, P. B., *J. Chem. Soc. Dalton,* 1514 (1974).

27. Bör, G., Dielter, U. K., Pino, P., and Poë, A., *J. Organomet. Chem.* **154**, 301 (1978).

28. Canty, A. J., Johnson, B. F. G., Lewis, J., *J. Organomet. Chem.* **43**, C35 (1972).

29. Knox, S. A. R., Koepke, J. W., Andrews, M. A., and Kaesz, H. D., *J. Amer. Chem. Soc.* **97**, 3947 (1975).

30. Johnson, B. F. G., Lewis, J., and Schorpp, K. T., *J. Organomet. Chem.* **91**, C13 (1975).