Journal of Organometallic Chemistry, 63 (1973) 329–337
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FRIEDEL–CRAFTS REACTIONS CATALYZED BY ARENETRICARBONYLMOLYBDENUM*

JAMES F. WHITE and MICHAEL F. FARONA
Department of Chemistry, The University of Akron, Akron, Ohio 44325 (U.S.A.)

(Received April 18th, 1973)

SUMMARY

Arenemolybdenum tricarbonyl is an active homogeneous catalyst in such Friedel–Crafts reactions as alkylation, acylation and sulfonylation of aromatic systems, as well as dehydrohalogenation and polymerization reactions. A variety of experiments provide strong evidence that the type of reaction promoted by $ArMo(CO)_3$ with organic halides is ionic, rather than free radical, in nature. The molybdenum catalysts offer some advantages over $AlCl_3$ in Friedel–Crafts reactions, particularly in ease of handling and storage, reaction work up, recoverability of the catalyst, and in their being somewhat milder than $AlCl_3$.

INTRODUCTION

Friedel–Crafts catalysts, whether homogeneous or heterogeneous, are all Lewis acids, and are capable of promoting carbonium ion formation from certain organic molecules. It might at first appear that $ArMo(CO)_3$ (Ar = arene), being a coordinatively saturated molecule, would not show Lewis acid properties. However, in a previous communication,[1] we reported some preliminary results wherein $ArMo(CO)_3$ was shown to be an active catalyst in promoting Friedel–Crafts and related reactions.

The question arises as to the nature of these reactions, *i.e.*, ionic or free radical, since related molecules such as $Mo(CO)_6$ and $ArCr(CO)_3$ have been shown to promote free-radical reactions with certain organic systems. For example, Bamford and coworkers[2] have shown that $Mo(CO)_6$ reacts with organic halides via a free-radical mechanism, and Frankel *et al.*[3,4], have reported that $ArCr(CO)_3$ can function as an effective hydrogenation catalyst. This report is primarily concerned with two main aspects of the reaction described herein: the nature of the active catalyst and the type of reaction. Evidence in the elucidation of these aspects is now presented.

RESULTS

A summary of alkylation, acylation, and sulfonylation reactions are shown in

---

* Based on the Ph.D. thesis submitted by J. F. W. to The University of Akron, December 1972, and presented in part at the Fifth International Symposium on Organometallic Chemistry, Moscow, August, 1971

TABLE 1

ALKYLATION AND POLYMERIZATION REACTIONS

Aromatic substrate	*Organic halide*	*Added catalyst*	*Reactions conditions*	*Yield*	*Comments*
1 Toluene (100 ml)	t-butyl chloride (12.6 g)	$Mo(CO)_6$ (0.20 g)	Reflux 5 h	17.9 g (88%)	Exclusively *para* substitution
2 Toluene (100 ml)	t-butyl chloride (12.6 g)	$TolMo(CO)_3$ (0.20 g)	Reflux 1 h	16.7 g (81.8%)	
3 Toluene (160 ml)	Cyclohexyl chloride (10 g)	$Mo(CO)_6$ (0.05 g)	Reflux 6 h	19.7 g (84.5%)	
4 Toluene (200 ml)	Benzyl chloride (12.6 g)	$Mo(CO)_6$ (0.03 g)	Reflux 12 h	16.4 g (90%)	100% alkylation, 10% polymer, 90% tolylphenylmethane
5 Toluene (50 ml)	n-propyl chloride (8.9 g)	$TolMo(CO)_3$ (0.20 g)	130° 6 h	7.8 g (50.5%)	Carried out in glass-lined Parr bomb, product exclusively *p*-cymene
6 t-Butyl benzene (55 ml)	n-chloroheptane (8.8 g)	$Mo(CO)_6$ (0.01 g)	140° 24 h		Only secondary alkylates obtained
7 Toluene (75 ml)	Cyclohexyl fluoride (11.2 g)	$TolMo(CO)_3$ (0.1 g)	Reflux 6 h	12.8 g (67.3%)	
8 Toluene (80 ml)	Cyclohexyl bromide (26.4 g)	$TolMo(CO)_3$ (0.1 g)	Reflux 8 h	6.7 g (23.4%)	Extensive catalyst decomposition
9 Anisole (150 ml)	t-butyl chloride (6.8 g)	$Mo(CO)_6$ 0.03 g	135° 24 h	9.5 g (79%)	
10 Phenol	t-butyl chloride (12.0 g)	$Mo(CO)_6$ (0.01 g)	Reflux 18 h	18.8 g (96%)	120 ml heptane solvent 93% *p*-t-butylphenol, 3% 2,6-di-t-butylphenol
11 Benzyl chloride (neat)		$Mo(CO)_6$ (0.1 g)	110° 1 h	(100%)	
12 Durene	*p*-xylylene-dichloride	$Mo(CO)_6$ 0.01 g	110° 3 h	9.6 g (98%)	Copolymer nearly insoluble in common organic solvents
13 Benzyl fluoride (neat)		$TolMo(CO)_3$	140°	(100%)	

Tables 1,2, and 3, respectively. Also included in the tables are polymerizations of the appropriate types.

DISCUSSION

The two main areas of concern in this study are elucidation of the nature of the active catalyst or catalyst precursor, and elucidation of the nature of the type of reaction, ionic or free radical. These are now discussed separately.

A. Active catalyst

Although $Mo(CO)_6$ was added as the catalyst in many of the table entries, $ArMo(CO)_3$ appears to be the true catalyst, or catalyst precursor, in all reactions.

TABLE 2

ACYLATION REACTIONS

Aromatic substrate	*Organic halide*	*Added catalyst*	*Reaction conditions*	*Yield*	*Comments*
1 Toluene (100 ml)	acetyl chloride (7.8 g)	$Mo(CO)_6$ (0.15 g)	Reflux 24 h	1.2 g (9 %)	Only *p*-methyl acetophenone isolated
2 Toluene (160 ml)	propionyl chloride (6.35 g)	$Mo(CO)_6$ (0.05 g)	Reflux 24 h	1.85 g (18 %)	Only *para* acylation obtained
3 Toluene (160 ml)	benzoyl chloride (6.05 g)	$Mo(CO)_6$ (0.15 g)	Reflux 18 h	2.5 g (29.7 %)	Only *p*-methyl benzophenone isolated
4 Toluene (160 ml)	benzoyl chloride (6.05 g)	$TolMo(CO)_3$ (0.02 g)	Reflux 12 h	5.65 g (67 %)	Same product as 3
5 Anisole (125 ml)	acetyl chloride (7.8 g)	$Mo(CO)_6$ (0.02 g)	100° 36 h	10.2 g (68 %)	90 %-*p*-methoxyacetophenone, 4 % *o*-methoxyacetophenone
6 Anisole (150 ml)	benzoyl chloride (7.0 g)	$TolMo(CO)_3$ (0.15 g)	100° 18 h	7.34 g (70 %)	Only *p*-methoxybenzophenone isolated

TABLE 3

SULFONYLATION REACTIONS

Aromatic substrate	*Organic halide*	*Added catalyst*	*Reaction conditions*	*Yield*	*Comments*
1 Toluene (160 ml)	Tosyl chloride (3.8 g)	$Mo(CO)_6$ (0.02 g)	Reflux 36 h	2.1 g (43 %)	Product is 4,4'-ditolylsulfone
2 Anisole (160 ml)	Tosyl chloride (3.8 g)	$Mo(CO)_6$ (0.02 g)	135° 24 h	1.15 g (22 %)	Product is 4-methyl-4'-methoxydiphenylsulfone
3 Anisole (160 ml)	Tosyl chloride (3.8 g)	$TolMo(CO)_3$ (0.03 g)	115° 18 h	1.3 g (25 %)	Same as 2
4 Diphenyl ether (2.6 g)	Benzene-1,3-disulfonylchloride (4.3 g)	$Mo(CO)_6$ (0.1 g)	110° 3 h	1.4 g (22 %)	Tan-colored copolymer
5 Diphenyl ether (2.6 g)	Benzene-1,3-disulfonylchloride (4.3 g)	$TolMo(CO)_3$ (0.1 g)	110° 3 h	2.1 g (32 %)	Same as 4

This view is supported by several observations. First of all, $Mo(CO)_6$ does not promote the dehydrohalogenation of t-butyl chloride on reflux for 20 h. Conversely, $TolMo(CO)_3$ (Tol = toluene) reacts rapidly with the same organic halide resulting in dehydrohalogenation and polymerization. Secondly, neither $Mo(CO)_6$ nor $TolMo(CO)_3$ will promote any type of Friedel–Crafts reactions in this work under CO pressure. This, of course, is due to the reversibility of the replacement of the arene ring by three CO groups[10]; indeed, only $Mo(CO)_6$ is isolated from alkylation reactions using $TolMo(CO)_3$ as the catalyst under CO pressure. Furthermore, in most reactions in which $Mo(CO)_6$ was added, $ArMo(CO)_3$ was recovered at the end of the reaction.

During the course of most reactions, a certain amount of catalyst decomposition takes place. Whereas the exact nature of the decomposition products has not been determined, they do contain molybdenum. However, these compounds do not catalyze Friedel–Crafts reactions; hence, it is concluded that the presence of $ArMo(CO)_3$ is necessary to promote reaction in these systems.

However, $Mo(CO)_6$ can be used directly because it is converted *in situ* to $ArMo(CO)_3$ when heated in the presence of aromatic solvents[10,11]. Furthermore, when $Mo(CO)_6$ is added as the catalyst, it is observed that the heated solution gradually turns yellow (the color of $ArMo(CO)_3$) and a short induction period occurs before any alkylation reaction begins, as evidenced by the evolution of HCl. This induction period is reduced considerably when $ArMo(CO)_3$ is used. Apparently, the additional time required for commencement of the reaction is the time necessary for the formation of $ArMo(CO)_3$ to occur, which is slow in the absence of ultraviolet light[12] or donor solvents[13].

B. Type of reaction

A wide variety of inorganic compounds in intermediate or high oxidation states are known to promote Friedel–Crafts reactions, and these reactions are all presumed to be ionic in nature[14]. However, metal complexes in low oxidation states have been shown to produce radical reactions with organic halides[2,15]. Therefore, it was necessary to determine whether $ArMo(CO)_3$ promotes the reactions in this study by carbonium ion or free-radical generation.

Whereas the observation that identical products are obtained from alkylation of toluene by t-butyl chloride catalyzed by $AlCl_3$ and $TolMo(CO)_3$ is not particularly convincing evidence for an ionic reaction, the following experiments provide much stronger support for carbonium ion generation by $ArMo(CO)_3$ in these reactions.

If the reactions are free radical in nature, the addition of substantial amounts of radical-trapping agents would be expected to poison the system. When the polymerization of benzyl chloride was carried out in the presence of large amounts of galvinoxyl[16], iodine, and 2,2-diphenyl-1-picrylhydrazyl[17] the polymerization proceeded unhindered yielding 100% polybenzyl[18] in less than 1 h at 140° in all cases. On the other hand, benzyl chloride could not be induced to polymerize when heated with well-known radical initiators such as azobis(isobutyronitrile), dibenzoyl peroxide, and cumene hydroperoxide.

Only *ortho-* and *para-*substitution was detected in the products when the reactions were catalyzed by $ArMo(CO)_3$. Since the directional properties of substituents on an aromatic ring are not operating in free-radical reactions, a substantial amount of *meta-*substitution would be expected; yet no *meta-*substituted product was observed, indicating that the reaction proceeds by way of an ionic mechanism.

When n-propyl chloride was used as the alkylating agent, only isopropyl substitution was observed. $ArMo(CO)_3$ was found not to dealkylate or rearrange n-propyl benzene on prolonged heating as $AlCl_3$ and some other Friedel–Crafts catalysts are known to do[19]. Alkylation of toluene with n-chloroheptane also leads to secondary products. Apparently, carbonium ions are formed from the primary halides, and rearrangement to secondary carbonium ions before substitution takes place. Primary substitution would be expected for radical reactions.

An interesting rearrangement promoted by $AlCl_3$ is the conversion of octachloro[3.2.0]bicyclohepta-2,6-diene to octachlorocycloheptatriene in 80 to 85% yield[6]. It was speculated that the reaction probably proceeds by abstraction of an allylic chloride to form an ionic intermediate. MesMo$(CO)_3$ (Mes = mesitylene) was also found to induce this rearrangement, albeit in lower yield, presumably by means of a carbonium ion intermediate.

Since it appears that ArMo$(CO)_3$ is capable of generating carbonium ions from organic halides, it must be that arenemetal tricarbonyls are Lewis acids. Strong evidence for this contention was found in the reaction of TolMo$(CO)_3$ with free halide and pseudohalide ions including F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, N_3^-, and OH^- [20]. The Lewis acid properties could arise from coordinate unsaturation in a number of ways. The arene ring in Group VIB metal carbonyl complexes is known to undergo exchange with other aromatic systems[21,22,23,24]. Perhaps during the exchange, there is interaction between the organic halide and the metal; alternately, the organic halide might interact with the metal in a manner similar to that of another arene ring.

Another possibility in which a coordinatively unsaturated center can arise is through partial dissociation of the arene ring, such that the arene ring acts as a bi- or monodentate[25-28]. This would expose a vacant site for nucleophilic attack.

In some preliminary kinetics experiments to obtain some insights into the mechanism of the reaction, the alkylation of toluene by benzyl chloride, using TolMo$(CO)_3$ as the catalyst, was studied by following the disappearance of benzyl chloride by NMR. First order dependence was found for benzyl chloride and catalyst, with an average rate constant of 0.13 $l \cdot mole^{-1} \cdot min^{-1}$. The results are similar to those found for the alkylation of benzene using a $GaCl_3$ catalyst[29] and for alkylations with various benzyl halides using $AlCl_3$[30].

While we are not prepared at this time to propose a detailed mechanism for the generation of carbonium ions from organic halides it is possible to speculate on some feasible mechanisms based on our findings of first order dependence and some related mechanisms reported in the literature. For example, since the arene can act as a mono-, bi-, or tridentate ligand, it can be envisioned that under influence of nucleophilic attack by RX, the arene partially dissociates to create a coordinatively unsaturated center. An analogous situation has been invoked for certain reactions of (LL)M$(CO)_4$ (M = Cr, Mo, W; LL = a bidentate ligand) with Lewis bases in which reversible dissociation of only one end of the bidentate ligand occurs, followed by attack of the nucleophile at the vacated coordination site[31,32].

Another possibility is dissociation of the arene ring, followed by attack on the metal atom by RX. Frankel claimed to have observed free methylbenzoate when (methylbenzoate)chromium tricarbonyl was used as a homogeneous hydrogenation catalyst[3,4]. However, Cais[33] pointed out that the arene ligand remains partially coordinated to the metal, at least during the initial stages of hydrogenation. Convincing evidence of this is found in the observation that both the length of the induction period and the rate of hydrogenation are affected by variation of substituents on the coordinated arene ring. If complete dissociation of the arene ring was required, only the length of the induction period should be affected and no effect should be noted on the rate of hydrogenation.

We have observed variations in both the induction periods and rates of alkylation, particularly on studies with ArCr$(CO)_3$[34] with also functions as a Friedel–

Crafts catalyst but promotes the reactions at a much slower rate than the analogous Mo catalysts. This evidence, therefore, tends to indicate that the arene ring is still attached to the metal during the course of the reaction, but functions as a mono- or bidentate during generation of carbonium ions.

Another possibility which cannot be ruled out at this time is a mechanism based on an oxidative addition intermediate. For this case, the intermediate would be $ArMo(CO)_3R^+$; subsequent transfer of R^+ to the substrate would lead to the alkylated product. Still another mechanism based on oxidative addition could come from dissociation of CO from $ArMo(CO)_3$ followed by addition of RCl to give the intermediate $ArMo(R)(Cl)(CO)_2$, similar to that isolated in the reaction of benzenetricarbonylchromium with trichlorosilane[35].

Further details on specific steps in the mechanism of the reaction are not warranted at this time, but must await the results of future studies.

Certain advantages of $ArMo(CO)_3$ over $AlCl_3$ have been observed, and these are related to storage, handling, and recoverability of the catalyst at the end of the reaction. It should also be noted that in acylation reactions, $ArMo(CO)_3$ is used in catalytic amounts whereas $AlCl_3$ is not. However, the organometallic catalysts do not necessarily promote electrophilic substitution reactions at rates faster than those of $AlCl_3$ nor are the yields any higher. To all intents and purposes, these latter factors appear to be somewhat comparable with respect to the reactions studied in this work.

EXPERIMENTAL

Starting materials. Molybdenum hexacarbonyl was kindly donated by Climax Molybdenum Corporation and used as received. Arene molybdenum tricarbonyls were prepared according to the method of Nicholls and Whiting[5]. Octachloroheptatriene was prepared according to the method of Kusada *et al.*[6]

Reactions catalyzed by $ArMo(CO)_3$. The procedure for alkylation, acylation and sulfonylation reactions is similar, and all reactions carried out along with their conditions, percent yields and other features are summarized in Tables 1–3. Therefore detailed descriptions are given below for only one of each type of reaction, all of which are typical.

Unless otherwise noted, all reactions or manipulations involving metal carbonyl compounds or reagents were carried out under an atmosphere of pre-purified nitrogen. In addition, all solvents, reagents or solutions which were to come in contact with metal carbonyl compounds were deoxygenated prior to use by purging with dry nitrogen.

Alkylation of toluene with t-butyl chloride. A solution of 160 ml of toluene, 13.9 g (0.15 mol) of t-butyl chloride and 0.17 g (0.07 mmol) of $Mo(CO)_6$ was refluxed until the evolution of HCl gas ceased. The reaction vessel was equipped with a reflux condenser connected in series to two traps. The first trap contained 0.1*N* NaOH while the second was immersed in dry ice–acetone. After 8 h of reflux, 0.9 g of liquid was found in the cold trap; it was identified as isobutylene by NMR.

Titration of the 0.1 *N* NaOH in the first trap with standard acid indicated that 0.067 mol of HCl had been evolved. Therefore, the ratio of all t-butyl chloride which reacted to $Mo(CO)_6$ was approximately 10^3. The ratio of all t-butyl chloride reacted to that which was dehydrochlorinated was 4.2.

Isolation of the alkylated product by vacuum distillation yielded 7.2 g of material which boiled at 105°/57 mm. The product was identified by NMR to be *p*-t-butyltoluene. The yield was 72.5 % based on the amount of t-butyl chloride which reacted, or 32 % based on the initial amount.

To determine if only the *para* isomer was present, the compound was oxidized with $KMnO_4$ to the benzene dicarboxylate[7], and converted to the *p*-nitrobenzyl ester derivative[8]. The only product obtained was identified as terephthalic acid di-*p*-nitrobenzoate by melting point (262–264°)[8]. Therefore, the sole isomer from the alkylation reaction was *p*-t-butyltoluene.

Acylation of anisole with acetyl chloride. A solution containing 7.8 g (0.1 mole) of acetyl chloride, 0.02 g (0.08 mmole) of $Mo(CO)_6$ and 125 ml of anisole was heated at 100° for 36 h. Isolation of the product by filtration, water washing, and removal of anisole on a rotary evaporator yielded 10.2 g (68 %) of a semi-solid, acylated product. Two fractions were obtained on vacuum distillation. The first, b.p. 118–120°/10 mm, weighed 0.4 g and the second, b.p. 138–145°/10 mm, weighed 9.2 g. Semicarbazide derivatives (m.p. 180–183° and 198–199°, respectively) were consistent with the properties of *o*- and *p*-methoxyacetophenone, respectively. This corresponds to a product distribution of 90 % *para* and 4 % *ortho*. Other acylations are summarized in Table 2.

Sulfonylation of anisole with toluenesulfonyl chloride.

A solution of 3.8 g (0.02 mol) of tosyl chloride, 0.02 g (0.08 mmole) of $Mo(CO)_6$ and 100 ml of anisole was heated at 135° for 24 h. The reaction solution was cooled, filtered, and washed successively with 50 ml of 5 % Na_2CO_3 and two 100 ml portions of water. The toluene was evaporated and the light-tan crystals remaining were recrystallized from 80 % aqueous ethanol to give 1.2 g (22 %) of 4-methyl-4′-methoxydiphenylsulfone, m.p. 102–103° (lit.[9] 101–103°). Other sulfonylation reactions are summarized in Table 3.

Attempted isomerization of n-propylbenzene. Freshly distilled n-propylbenzene, 25 ml, was heated for 36 h in the presence of 0.3 g of $Mo(CO)_6$. At the end of that time, the only product which could be isolated was (n-propylbenzene)$Mo(CO)_3$, and the rest of the n-propylbenzene was recovered unchanged (NMR).

Attempted alkylations and polymerizations under CO pressure. Several of the alkylation and polymerization reactions were attempted using catalytic amounts of $Mo(CO)_6$ or $TolMo(CO)_3$ under 1500 psig of CO. In all cases no alkylated product was recovered, but $Mo(CO)_6$ was isolated nearly quantitatively, even where TolMo-$(CO)_3$ was used as the catalyst.

Reaction of $Mo(CO)_6$ with t-butyl chloride. A slurry of 50 ml of freshly distilled t-butyl chloride and 0.5 g of $Mo(CO)_6$ was refluxed with stirring for 6 h. During that time no evolution of HCl was observed and $Mo(CO)_6$ was recovered quantitatively.

Reaction of $TolMo(CO)_3$ with t-butyl chloride. A solution of 30 g (0.32 mol) of freshly distilled t-butyl chloride and 0.39 g (14.3 mmol) of $TolMo(CO)_3$ was refluxed for 4 h in a 100 ml flask arranged so that any evolved HCl could be trapped in 200 ml of 0.5 *N* NaOH. HCl evolution proceeded briskly during the initial hour of reaction accompanied by an apparent increase in viscosity and deposition of a brown, solid precipitate.

Titration of the NaOH solution with standard acid indicated that 0.07 mole (21.8 %) of the t-butyl chloride had been dehydrochlorinated. This also indicates that the ratio of t-butyl chloride which reacted to $TolMo(CO)_3$ is approximately 43.

Filtration of the reaction solution yielded a brown powder which did not show carbonyl absorption in its infrared spectrum and was inactive for the polymerization of benzyl chloride.

Vacuum distillation of the filtrate, after removal of t-butyl chloride on a rotary evaporator, yielded two fractions. Studies on these fractions (NMR, elemental analysis) indicated the compounds to be oligomers of isobutene end-capped with HCl. The first fraction, b.p. 78–80°/10 mm analyzed for $(isobutene)_5 \cdot HCl$ whereas the second fraction, b.p. 75–80°/0.1 mm, was equivalent to $i\text{-}Bu_8 \cdot HCl$.

Attempted alkylation of $TolMo(CO)_3$ with t-butyl chloride. A mixture of 8.15 g (0.03 mole) of $TolMo(CO)_3$ and 2.75 g (0.03 mol) of t-butyl chloride was heated for 2 h at 70°. After cooling, 25 ml of acetone was added and the flask opened to the atmosphere for 24 h to decompose any $TolMo(CO)_3$. The solution was filtered and acetone removed on a rotary evaporator leaving a trace of clear liquid which was shown to be toluene by NMR. No alkylated product was detected.

Polymerization of benzyl chloride in the presence of radical traps with $Mo(CO)_6$. Four test tubes were prepared containing 10 ml of benzyl chloride and 0.05 g of $Mo(CO)_6$. Tubes 2, 3, and 4 also contained 0.5 g of galvinoxyl, 0.5 g of 2,2′-diphenyl-1-picrylhydrazyl and 0.3 g of iodine, respectively. The tubes were heated at 110° and polymerization of benzyl chloride to polybenzyl proceeded qualitatively at the same rate to completion (100% yield) in all four tubes.

Conversely, benzyl chloride could not be induced to polymerize by heating with azobis(isobutyronitrile), dibenzoyl peroxide or cumene hydroperoxide, all of which are common initiators of radical polymerization.

Preparation of octachlorocycloheptatriene catalyzed by $MesMo(CO)_3$. An intimate mixture of 0.75 g (2.5 mmol) of $MesMo(CO)_3$ (Mes = mesitylene) and 1.10 g (3 mmol) of octachlorobicyclo[3.2.0]hepta-2,6-diene was prepared at −80° and then heated at 150° for 30 min. After work-up and chromatography on a Florisil column using hexane as the eluting solvent, 0.27 g (24.5% yield) of octachlorocycloheptatriene (m.p. 85–86°) was obtained.

ACKNOWLEDGEMENT

We are grateful to the Climax Molybdenum Corporation for a generous gift of molybdenum hexacarbonyl.

REFERENCES

1 M F Farona and J. F. White, *J. Amer. Chem. Soc*, 93 (1971) 2826

2 C H Bamford, G. C. Eastmond and F J T Fildes, *Chem Commun.*, (1970) 144, 146 and references contained therein

3 E N Frankel, E Selke, and C A Glass, *J Amer Chem. Soc*, 90 (1968) 2446

4 E N Frankel and R. O. Butterfield, *J Org. Chem*, 34 (1969) 3930

5 B. Nicholls and M C Whiting, *J Chem. Soc.*, (1959) 551

6 K Kusada, R West and V N M Rao, *J Amer Chem Soc*, 93 (1971) 3627

7 A Vogel, *Textbook of Practical Organic Chemistry*, 3rd ed., Wiley, New York, 1957, p 570

8 N D Cheronis and J. B Entrikin, *Identification of Organic Compounds*, Interscience publishers, New York, 1963, p. 248

9 M E B. Jones, *British Patent* 979, 111 (1965).

10 E O. Fischer and K. Ofele, *Chem. Ber.*, 90 (1957) 2532, *ibid*, 91 (1958) 2763
11 E. O. Fischer and K Ófele, *Angew Chem*, 69 (1957) 715
12 W. Strohmeier, *Chem. Ber.*, 94 (1961) 3337.
13 R. P. M Werner and T H Coffield, *Chem. Ind* (*London*), (1960) 936
14 G Olah, *Friedel–Crafts and Related Reactions, Vol.* 1, Interscience Publishers, New York, 1963, p 31–32, 202–203
15 C H Bamford, G C. Eastmond and D. Whittle, *J Organometal Chem*, 17 (1969) 33
16 P D Bartlett and T. Funahashi, *J Amer Chem Soc*, 84 (1962) 2596.
17 P D Bartlett and H Kwart, *J Amer Chem Soc.*, 72 (1950) 1051.
18 H C Haas, D I Livingston and M Saunders, *J Polymer Sci*, 15 (1955) 503
19 L Fieser and M. Fieser, *Advanced Organic Chemistry*, Reinhold Publishing Corp., New York, 1963, p 36–39
20 J F White and M F Farona, *J Organometal Chem.*, 37 (1972) 119.
21 D. A. Brown, N J Gogan and H Sloan, *J Chem Soc.*, (1965) 6873
22 H. Werner and R. Prinz, *J Organometal Chem*, 5 (1966) 79
23 W Strohmeier and D. V. Hobe, *Z. Naturforsch*, 186 (1963) 981
24 W Strohmeier, *Angew Chem International Ed.*, 2 (1963) 270.
25 F. Zingales, A. Chresa, and F Basolo, *J Amer Chem Soc*, 88 (1966) 2707
26 F Calderazzo, *Inorg Chem*, 3 (1964) 1207
27 F Calderazzo, *Inorg. Chem*, 4 (1965) 223
28 I. W. Stolz, H Haas and R. K. Sheline, *J Amer Chem Soc.*, 87 (1965) 716
29 H Ulick and G. Heyne, *Z. Elektrochem.*, 41 (1935) 509.
30 H. C Brown and M Grayson, *J. Amer. Chem. Soc.*, 75 (1953) 6285,
31 R. J. Angelici and J. R. Graham, *J Amer. Chem. Soc*, 87 (1965) 5586, *J Amer Chem Soc.*, 87 (1965) 5590, *Inorg Chem*, 6 (1967) 2082.
32 G. R Dobson and G C. Faber, *Inorg Chem.*, 7 (1968) 584; *Inorg. Chim Acta*, 4 (1970) 87.
33 M Cais and A. Rejoan, *Inorg Chim. Acta*, 4 (1970) 509
34 G. Linden, P. Woon and M. F. Farona, unpublished results
35 W. Jetz and W. A G. Graham, *Inorg. Chem.*, 10 (1971) 4