new rapid modification for the analysis of silane hydrogen *in liquids*, applicable even to n-C_4H_9-SiH_3, b.p. 56°, if one delivers the contents of the micropipet into bulb E from a nearly horizontal position. Little true comparison with results of other investigators[13] appears possible at present; uncertainties in the work of numerous others may involve the purity of the compound, the analytical method or both.

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE ETHYL CORPORATION]

Reductive Carbonylation Synthesis of Metal Carbonyls. II. Synthesis of Manganese Carbonyl and Group VI-B Metal Carbonyls by the Alkylaluminum Method[1]

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Manganese and Group VI-B metal carbonyls may be prepared by reductive carbonylation of an appropriate salt of the metal employing an alkylaluminum compound, generally triethylaluminum, as the reducing agent. Manganese carbonyl thus can be prepared conveniently in 55–60% yield by employing a 4:1 mole ratio of triethylaluminum to manganese acetate in isopropyl ether at 80–100°, 3000 p.s.i.g. carbon monoxide pressure. Similarly, chromium, molybdenum and tungsten carbonyl can be prepared readily in high yield (90%) from the corresponding metal chlorides. The effect of various reaction variables on the yield is discussed, and the results are compared with those of the Grignard method. The differences can be explained in terms of the lower reactivity and hence the greater selectivity of an alkylaluminum compound compared to a Grignard reagent in its reaction with a transition metal salt. A mechanism is proposed for the formation of metal carbonyls by the alkylaluminum method which involves essentially the formation of an alkyl transition metal intermediate in a rate-determining step and then its facile reaction with carbon monoxide.

Introduction

It was reported recently by Closson, Buzbee and Ecke[2] of our Laboratories that the relatively inaccessible manganese carbonyl can be prepared in 32% yield by treating manganese chloride with two equivalents of the sodium ketyl of benzophenone in tetrahydrofuran (THF), with subsequent carbonylation and hydrolysis to produce manganese carbonyl. This represented the first satisfactory method developed for the preparation of manganese carbonyl in appreciable quantity.[3]

In the course of investigating other new methods for preparing manganese carbonyl a novel and superior method was discovered which involved the use of triethylaluminum (TEA) as a "selective reducing agent." This method then was extended to the synthesis of the carbonyls of chromium, molybdenum, tungsten and iron. The generality of this method, which we have referred to as involving a reductive carbonylation reaction, and its differences from the Grignard method were described briefly in a communication[1] from this Laboratory. Shortly before this communication appeared, L. I. Zakharkin, *et al.*,[4] reported the use of TEA and diisobutylaluminum hydride as reducing agents for the preparation of chromium, molybdenum and tungsten carbonyl. Inadvertently, we failed to acknowledge this paper in our previous communication.[5]

There are now available several adequate laboratory methods for preparing the Group VI-B metal carbonyls and in particular chromium carbonyl. The Grignard method is perhaps the best known and most common method for preparing chromium carbonyl.[6–10] This method, however, is not well adapted for the preparation of manganese[3] or molybdenum and tungsten carbonyls.[7,8] In contrast to the Grignard method for manganese[11] and the Group VI-B metal carbonyls, the metal carbonyl was found to be produced directly as such in the alkylaluminum method without requiring hydrolysis to liberate it and little or no free metal was produced as a side product. Consequently, it was concluded that TEA behaves as a more selective reducing agent than does the Grignard reagent for the preparation of metal carbonyls. It also appeared likely that since the product is formed directly without requiring hydrolysis, there might not be a theoretical limitation on the yield (below 100%) due to disproportionation,[8,10] such as imposed by the Grignard method.

Results

Effect of Manner of Contact on Yield.—Typical results are summarized in Table I. It was found that in those cases where the metal salt reacted with TEA at room temperature in the particular solvent employed, the subsequent yield of metal carbonyl was greatly reduced. This was evident in the case of manganese acetate in benzene and for molybdenum pentachloride and tungsten hexachloride in ethers and benzene. To minimize this difficulty for the purpose of the reaction variable study, the metal salt was enclosed in a glass am-

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(1) H. E. Podall, THIS JOURNAL, **80**, 5573 (1958).

(2) R. D. Closson, L. R. Buzbee and G. C. Ecke, *ibid.*, **80**, 6167 (1958).

(3) Manganese carbonyl, $Mn_2(CO)_{10}$, was first predicted by Hieber, *et al.*, *Ber.*, **65**, 1090 (1932), and its formation by the Grignard method was indicated by D. T. Hurd, G. W. Sentell, Jr., and F. J. Norton, THIS JOURNAL, **71**, 1899 (1949). Its preparation in sufficient quantity (in about 1% yield) for characterization was first reported by E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *ibid.*, **76**, 3831 (1954).

(4) L. I. Zakharkin, V. V. Gavrilenko and O. Yu. Okhlobystin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 100 (1958).

(5) It is of interest to note that no mention was made by these workers of the applicability of this method to the preparation of manganese carbonyl—the compound, curiously enough, for which our independent discovery of the alkylaluminum method was first made.

(6) A. Job and A. Cassal, *Compt. rend.*, **183**, 392–4 (1926).

(7) A. Job and J. Rouvillois, *Bull. soc. chim.*, **41**, 1041 (1927).

(8) W. Hieber and E. Romberg, *Z. anorg. Chem.*, **221**, 321 (1935).

(9) B. B. Owen, J. English, Jr., H. G. Cassidy and C. V. Dundon, THIS JOURNAL, **69**, 1723 (1947).

(10) W. M. Cumming, J. A. Horn, and P. D. Ritchie, *J. Appl. Chem.*, **2**, 624 (1952).

(11) V. Hnizda (to Ethyl Corporation) U. S. Patent 2,822,247 (1958).

TABLE I

EFFECT OF MANNER OF CONTACT ON YIELD[a]

MX, moles		TEA, moles	Solv., ml.	CO,[b] p.s.i.g.	Mode of contact[c]	Temp., °C.	Time, hr.	% Yield
$Mn(OAc)_2$	0.010	0.040	Ether, 40	3500	A	100	3	40
	.010	.040	Ether, 40	3500	B	100	3	40
	.010	.040	Benzene, 40	3500	A	100	3	0[d]
	.010	.040	Benzene, 40	3500	B	100	3	31
$CrCl_3$	.075	.45	Ether, 73	1000	A	115	7	92
	.010	.060	Ether, 40	1100	B	115	5	85
	.20	1.20	Benzene, 300	1000	C	110	1	72
$MoCl_5$	.010	0.040	Ether, 40	3000	A	100	4.3	65
	.010	.040	Benzene, 40	3000	A	100	5	15
	.010	.040	Benzene, 40	3000	B	100	4	38
	.20	.80	Benzene, 300	1000	C	65	1	76
WCl_6	.01	.05	Ether, 40	3000	A	100	5	30
	.01	.05	Ether, 40	3000	B	25	24	34
	.01	.05	Benzene, 40	3000	B	25	24	40
	.20	.60	Benzene, 300	1000	C	50	1	92

[a] Details on the procedures used are described in the Experimental part. [b] Initial pressure at 25°. [c] A was a two-step procedure, B was the sealed ampoule procedure and C was the simultaneous contact procedure at the desired reaction temperature. [d] In this run complete reduction to manganese metal occurred prior to carbonylation.

poule which was broken at the appropriate time in the presence of the alkylaluminum compound and carbon monoxide. The order of reactivity of the transition metal salts with TEA in benzene, as measured by the temperature at which reduction products were first observed, and by the rate of gas evolution, was

$WCl_6 > MoCl_5 > Cr(AA)_3 > Mn(OAc)_2 > CrCl_3 > MnCl_2$

where AA is acetylacetonate.

Effect of Anion.—The yields of manganese carbonyl obtained with different salts of manganese, employing a 4:1 mole ratio of TEA to manganese salt in diethyl ether at 100°, 3000 p.s.i.g. of CO for 3 hr. were

$Mn(OAc)_2 = Mn(O_2C\phi)_2 > Mn(O\textit{i}Pr)_2 > Mn(AA)_2 >$
40% 38% 35%
$Mn(OCHO)_2 > MnI_2 > MnCl_2$
7% 3% <1%

Effect of Solvent.—The yield of manganese carbonyl obtained from the carbonylation of manganese acetate in different solvents at a 4:1 mole ratio of TEA to manganese acetate at 100°, 3000 p.s.i.g. of CO for 3 hr., was

$i\text{-}Pr_2O$ > anisole > Et_2O > C_6H_6 >
56% 45% 40% 31%
THF > diglyme > pyridine
20% 10% <1%

In the case of chromium, employing a 6:1 mole ratio of TEA to chromic chloride at 115°, the yields of chromium carbonyl were

Et_2O > THF > $i\text{-}Pr_2O$ > diglyme >
85% 71% 60% 37%
C_6H_6 > pyridine > C_8H_{18}
20% 10% 9%

where C_8H_{18} is 2,4,4-trimethylpentane. Similar results were obtained for molybdenum pentachloride and tungsten hexachloride, except that the differences were not as marked.

Effect of Mole Ratio of TEA to Metal Salt.—Typical results are illustrated in Table II. In the case of manganese, the optimum mole ratio of TEA to $Mn(OAc)_2$ at 100° in ether was 9:1, giving a maximum yield of 79%. For preparative purposes, however, it was found most convenient to employ a 4:1 mole ratio of TEA to $Mn(OAc)_2$ in isopropyl ether; with this ratio the yield of manganese carbonyl averaged 55–60% at 100°, 3000 p.s.i.g. CO, 3 hr. For chromium carbonyl, the optimum mole ratio of TEA to $CrCl_3$ in either ether or benzene at 115° was 5:1. For molybdenum carbonyl, the optimum mole ratio of TEA to $MoCl_5$ in benzene at 65° was 4:1, and for tungsten carbonyl the optimum mole ratio of TEA to WCl_6 in benzene at 50° was 3:1.

TABLE II

EFFECT OF MOLE RATIO OF TEA/$Mn(OAc)_2$ ON YIELD[a]

Mole ratio	% Yield $[Mn(CO)_5]_2$
0.9	10
1.8	15
2.7	29
3.6	40
5.4	49
7.2	55
9.0	79, 76[b]
12.7	54

[a] In ether at 100°/3 hr., unless otherwise noted. [b] In ether at 100°/6 hr.

Effect of Different Alkylaluminum Compounds.—The yield of manganese carbonyl obtained with different alkylaluminum compounds in benzene employing 12 alkylaluminum groups (*e.g.*, 3 moles of $NaAlEt_4$) per mole of manganese acetate at 100° was

TIBA > TEA > $NaAlEt_4$ > Et_2AlH > TMA > $Et_3Al_2Cl_3$
45% 35% 30% 25% 10% <1%

where TIBA is triisobutylaluminum and TMA is trimethylaluminum. In diethyl ether at 100°, under the same conditions the results were

TIBA > TEA > Et_2AlH > $NaAlEt_4$ > TMA $\approx$ $(C_6H_5)_3Al$
65% 40% 30% 3% <1%

In the case of chromic chloride, the effectiveness of different trialkylaluminum compounds in either ether or benzene on the yield of chromium carbonyl was

$$\mathrm{TMA} > \mathrm{TEA} > \mathrm{TIBA}$$

The results for different chromium and molybdenum compounds are summarized in Table III.

TABLE III

EFFECT OF DIFFERENT ALKYLALUMINUM COMPOUNDS ON YIELD OF CHROMIUM AND MOLYBDENUM CARBONYLS[a]

R_3Al	MCl_x	Solvent	% Yield
TMA	$CrCl_3$	Ether	81
TEA	$CrCl_3$	Ether	78
TIBA	$CrCl_3$	Ether	74
TMA	$CrCl_3$	Benzene	47
TEA	$CrCl_3$	Benzene	20
TEA	$Cr(AA)_3$[b]	Benzene	61
TIBA	$Cr(AA)_3$[b]	Benzene	60
TEA	$CrCl_2$	Ether	64
TMA	$CrCl_2$	Ether	62
TMA	$MoCl_5$	Benzene	58
TEA	$MoCl_5$	Benzene	38
TMA	$MoCl_3$	Ether	9
TEA	$MoCl_3$	Ether	6

[a] The sealed ampoule procedure was used in each case. The charge consisted of 0.010 mole of metal salt in the ampoule, 0.060 mole of R_3Al, and 40 ml. of solvent, except in the case of $MoCl_5$ where 0.040 mole of R_3Al was employed. The reaction conditions were 115°, 3500 p.s.i.g. CO (initial pressure at 25°) for 5 hr., except for $MoCl_5$ where 100° for 4 hr. was employed. [b] $Cr(AA)_3$ denotes chromic acetylacetonate.

Effect of Temperature and Pressure.—In the case of manganese, the yield increased with temperature when employing benzene as solvent up to 165°, with no further increase in yield evident beyond this temperature. In anisole and isopropyl ether the optimum temperature was 145°. In diethyl ether, it was noted that there was a tendency toward a sudden exothermic reaction between manganese acetate and TEA in the presence of carbon monoxide, generally occurring at 85°, particularly in the larger scale preparations. In benzene it was found that beyond a 6-hr. reaction time at 165° the conversion to manganese carbonyl decreased.

The yield of chromium carbonyl from chromic chloride in benzene increased up to 190° with no evidence of metallic chromium being formed as a side product. In isopropyl ether the optimum temperature was about 150° with no further increase in yield resulting at higher temperatures. In general, it appeared that the more soluble the transition metal salt was in the solvent employed and the more readily it reacted with TEA, the lower was the temperature at which carbonylation set in.

In the case of manganese acetate, the conversion to metal carbonyl was essentially independent of the CO pressure above 2500 p.s.i.g. In the case of chromic chloride, the conversion to metal carbonyl was essentially independent of the CO pressure in the range of 1000–3500 p.s.i.g. Below these pressures, the conversions gradually decreased.

Stoichiometry and Side Reactions.—Analysis of the reaction mixtures by hydrolysis for active ethyl groups of the TEA and other ethylaluminum moieties showed that in the best case no less than 15 ethyl groups were consumed per mole of manganese pentacarbonyl produced from manganese acetate. Very little ethane or ethylene was present in the vent gas. The uptake of carbon monoxide corresponded to about 12 moles of CO per mole of $Mn(CO)_5$. In accord with this result it was found that some aldehydes or ketones also were formed in this reaction.

In the case of chromic chloride, about 7 ethyl groups were consumed per mole of $Cr(CO)_6$ at an 82% yield in diethyl ether at 115°, and about 9 ethyl groups were consumed per mole of $Cr(CO)_6$ at a 67% yield in isopropyl ether at 130°. Little or no ethane or ethylene was present in the vent gas. The CO uptake corresponded to about 7 moles of CO per mole of $Cr(CO)_6$. In each of these runs positive 2,4-DNP tests also were obtained, indicative of the presence of aldehydes or ketones.

The number of ethyl groups per TEA molecule utilized in the synthesis of a metal carbonyl was found to increase in going from manganese to tungsten as shown

$$\begin{array}{lccccccc} & \mathrm{Mn(OAc)_2} & < & \mathrm{CrCl_3} & < & \mathrm{MoCl_5} & < & \mathrm{WCl_6} \\ \mathrm{Et/TEA} & <<1 & & \approx 1.0 & & \approx 1.5 & & \approx 2.0 \end{array}$$

Thus, in the synthesis of manganese carbonyl from manganese acetate less than 1 ethyl group/TEA molecule is effectively utilized for reductive purposes, while in the synthesis of tungsten carbonyl from tungsten hexachloride approximately 2 ethyl groups/TEA molecule are effectively utilized.

Discussion

It was found that the conditions under which the transition metal salt, alkylaluminum compound and carbon monoxide are contacted are not so critical for the alkylaluminum method as for the Grignard method for preparing metal carbonyls in high yield. Thus, whereas it is necessary to contact chromic chloride with the Grignard reagent at a low temperature (−70°) prior to carbonylation in order to obtain consistently high yields of chromium carbonyl,[9] in the case of the alkylaluminum method the chromic chloride could be contacted directly with TEA in a coördinating or noncoördinating solvent at room temperature prior to carbonylation. This evidently is due to the lower reactivity of TEA compared to a Grignard reagent with chromic chloride. It should be noted that, whereas manganese acetate reacts rapidly with TEA in benzene at 25° to produce metallic manganese, this reaction is greatly retarded in the presence of carbon monoxide despite the fact that the rate of formation of manganese carbonyl is very slow at this temperature. It appears therefore that carbon monoxide stabilizes the intermediate from the reduction step against decomposition to the free metal.

The relative rates of conversion of the different transition metal salts to metal carbonyl, as indicated by the temperature and rate of CO uptake, were

$$\mathrm{WCl_6} > \mathrm{MoCl_5} > \mathrm{CrCl_3} >> \mathrm{MnCl_2}$$

Preliminary experiments with ferric chloride indicate it to be even more reactive than tungsten hexachloride. The indicated order parallels roughly the solubility of these salts, as well as the relative reactivity of the metals themselves with carbon monoxide. It should be emphasized, however, that the free metals produced from the reactions of the metal salts with TEA carbonylate much less readily or not at all. This is particularly true for manganese and chromium.

The anion was found to have a very marked effect upon the yield of manganese carbonyl from a manganese salt. Thus, whereas the manganese halides gave only very low yields, the carboxylic acid salts and the isopropoxide gave very good yields. Since all of these salts are practically insoluble in the solvents employed, it would appear difficult to account for the differences simply in terms of solubility, although the differences are in the order of the expected solubility. An alternate and perhaps more likely explanation takes into account the lattice structure of the manganese salt. Thus whereas the ions in the halides may be tightly packed, the opposite would seem to be true in the case of the carboxylic acid salts and the isopropoxide—presumably because of the greater steric requirements of the latter anions in the crystalline lattice. In the case of the latter salts, therefore, the alkylaluminum compound has apparently a greater opportunity to react with the manganese ion.

In the case of chromium, the greater reactivity of the acetylacetonate compared to the chloride can be accounted for simply in terms of its greater solubility.

In contrast to the Grignard method where chromous chloride is ineffective for the preparation of chromium carbonyl,[8,9] good yields of metal carbonyl were obtained by the alkylaluminum method (see Table III). The ineffectiveness of chromium, molybdenum and tungsten in oxidation states other than +3, +5 and +6, respectively, in the Grignard method suggests that there is perhaps something unique about these oxidation states for the respective metals in this reaction.[7–10] The results obtained here, with chromous chloride in particular, indicate that the +3 oxidation state of chromium is not required, although it may be preferred yieldwise. It appears that the differences obtained with these metals in different oxidation states can for the most part be explained in terms of the solubility of their respective compounds. A rather interesting fact is that no chromium or chromous chloride could be detected in the alkylaluminum process for preparing chromium carbonyl from chromic chloride. It would appear therefore that the reductive carbonylation of chromic chloride does not occur *via* chromous chloride or the subchloride, CrCl.

In every case, mole ratios of TEA to metal salt which were higher than what was considered to be stoichiometric (*e.g.*, one TEA per $CrCl_3$) were required to produce high yields of metal carbonyl. The highest mole ratio was required for manganese, a 9:1 mole ratio of TEA to manganese acetate providing a 79% yield (see Table II). The mole ratio requirement, however, decreased in going from manganese to chromium to molybdenum to tungsten, with an apparent concurrent decrease in the carbon monoxide uptake per mole of metal carbonyl produced. In view of the latter result, it would appear that the requirement of a high mole ratio of TEA to metal salt is due mainly to a side reaction of the TEA with carbon monoxide and that the metal salt employed influences the extent of this reaction.

The solvent was found to play an important role in this reaction. In general, solvents of moderate polarity or coördinating strength gave the best results. In the case of manganese, it appears that the principal role of the solvent is to moderate the reducing action of the alkylaluminum compound. Thus, in highly coördinating solvents such as diglyme or pyridine, the alkylaluminum compound, *viz.*, TEA, may be too strongly coördinated, whereas in non-coördinating solvents, such as benzene, reduction to the free metal may be an important side reaction. In the case of chromium, it was found that some chromic chloride was present at the end of the reaction in every solvent except THF, diglyme and pyridine. It seems plausible that in these strongly coördinating solvents the chromic chloride, as well as the TEA, may be tightly bonded. In this connection it should be noted that whereas higher yields of chromium carbonyl were obtained in diethyl ether than in isopropyl ether, the reverse was true in the case of manganese. This suggests that to obtain a facile conversion of a transition metal salt to the corresponding carbonyl a balance is required between the ability of the solvent to coördinate with the transition metal salt and its ability to coördinate with the alkylaluminum compound. Thus in the case of manganese acetate the degree or strength of coördination of the solvent with the TEA may be the controlling factor, whereas in the case of chromic chloride solubilization of the latter may be controlling in determining the extent of conversion to metal carbonyl.

The yield of manganese carbonyl from manganese acetate with different alkylaluminum compounds was found to correspond roughly to their reactivity with manganese acetate at 25° in the absence of carbon monoxide. It appears therefore that the observed order of effectiveness of the alkylaluminum compounds on the yield of manganese carbonyl parallels their reducing strength. In the case of chromic chloride, the reverse order of effectiveness on the yield of chromium carbonyl was obtained, *i.e.*, TMA > TEA > TIBA. The latter order corresponds to the increasing steric requirements of the alkylaluminum compound. Accordingly, it would seem reasonable that steric effects are more important in the reactions involving trivalent chromium and pentavalent molybdenum than in reactions involving divalent manganese.

The stoichiometry of the alkylaluminum process for preparing metal carbonyls appears to be rather complex, being complicated by side reactions of the alkylaluminum compound with carbon monoxide and quite possibly by chain growth reactions of the olefins arising from the disproportionation of the alkyl radicals. The increase in the ethyl group utilization per TEA molecule in going from manganese to chromium to molybdenum to tungsten parallels the ease and extent of conversion of the respective metal salt to carbonyl and indicates that the side reactions of the TEA become less important as the rate of conversion to metal carbonyl increases. However, even in the best case, *viz.*, tungsten carbonyl from tungsten hexachloride, further details on the fate of the alkyl groups are required before one can assign a specific stoichiometry to this process.

The Question of Mechanism.—The various mechanisms which have been proposed for the Grignard route to chromium carbonyl have been very nicely reviewed by Cumming, *et al.*[10] In agreement with Owen, *et al.*,[9] they conclude that none of these mechanisms is satisfactory, and they suggest instead a modification of the organochromium mechanism.[8] In essence it is assumed that the reaction proceeds *via* an organochromium (III) dichloride, the steps being

$$CrCl_3 + C_6H_5MgBr \longrightarrow C_6H_5CrCl_2 + {}^1/_2MgCl_2 + {}^1/_2MgBr_2 \quad (1)$$

$$C_6H_5CrCl_2 + 2C_6H_5MgBr + 4CO \longrightarrow (C_6H_5)_2Cr(CO)_4 + MgCl_2 + MgBr_2 + C_6H_5\cdot \quad (2)$$

$$(C_6H_5)_2Cr(CO)_4 + C_6H_5\cdot \rightleftarrows (C_6H_5)_3Cr(CO)_3 + CO \quad (3)$$

$$3(C_6H_5)_2Cr(CO)_4 + 3H^+ \longrightarrow 2Cr(CO)_6 + Cr^{+3} + {}^3/_2H_2 + 6C_6H_5\cdot \quad (4)$$

The difficulty with this mechanism, as well as the others, lies in the fact that neither diphenylchromium tetracarbonyl nor triphenylchromium tricarbonyl has been found in the reaction mixtures.

Most of the differences between the alkylaluminum and Grignard methods for preparing metal carbonyls, such as the higher yields, less side product metal and the requirement of higher temperatures in the former method, can be explained in terms of the lower reactivity and hence greater selectivity of an alkylaluminum compound compared with a Grignard reagent in its reaction with a transition metal salt. Perhaps the most striking difference between the two methods is the fact that whereas hydrolysis of the reaction mixture is required in order to liberate the metal carbonyl in the Grignard method, in the alkylaluminum method the metal carbonyl is obtained without hydrolysis. This difference also can be rationalized in terms of the differences in reactivity of the organometallic compounds as reducing agents. Thus it is conceivable that in the Grignard method the reagent reacts further with the metal carbonyl or with the metal carbonyl intermediate, thereby tying it up. The nature of the latter reaction is presently being investigated.

On the basis of the results here obtained, we wish to propose a reaction scheme for the formation of metal carbonyls by the alkylaluminum route, illustrated with chromic chloride and TEA.

$$\begin{tikzcd}
CrCl_3 + Et_3Al \arrow[r, "k_1"] & {[I]} \arrow[r, "CO", "k_2"'] \arrow[d, "k'_2"] & {[II]} \\
 & Cr &
\end{tikzcd}$$

$$[II] \xrightarrow[k_3]{Et_3Al/CO} Cr(CO)_6 \quad (5)$$

In this scheme the results would seem to indicate that the relative rates are in the order $k_2 > k_2' > k_1$. In other words, the production of the intermediate [I], believed to be an ethylchromium compound, appears to be the slow or rate-determining step. Formation of [II] is considered to be very rapid and minimizes the degradation of chromic chloride to chromium metal. Step 3 very likely occurs in a sequence of steps and is undoubtedly affected more by steric effects than is Step 1. In the absence of further information concerning kinetics and the exact nature of the intermediates, further discussion of the mechanism is best deferred.

Experimental[12]

Materials.—Manganese acetate (Fisher Certified reagent) was dried by azeotroping the water with toluene, and then vacuum drying the filtered product at 75°. Manganese iodide, formate and benzoate were prepared by conventional methods. The iodide was about 95% pure while the formate was better than 99.5% pure. The benzoate was dried only to the monohydrate stage and was used as such. Manganous acetylacetonate was prepared by the reaction of an aqueous solution of 0.20 mole of manganese chloride with an aqueous solution of 0.40 mole of sodium acetylacetonate (prepared from 0.40 mole of acetylacetone and 0.40 mole of sodium hydroxide in water) and then filtration of the yellow product under nitrogen. The product was dried at 100° under vacuum to produce a fine white powder. *Anal.* Calcd. for $C_{10}H_{14}O_4Mn$: Mn, 21.7. Found: Mn, 21.5. Manganese isopropoxide was prepared by treating manganese cyclopentadienide with excess isopropyl alcohol under nitrogen and then vacuum drying of the filtered product at 80°. *Anal.* Calcd. for $C_6H_{14}O_2Mn$: Mn, 31.8. Found: Mn, 28.0. Manganese(III) acetylacetonate was prepared according to the procedure of Cartledge.[13]

Chromic chloride, anhydrous purified, was obtained from Fisher Scientific Company. Chromous chloride, anhydrous (same source) was analyzed and found to be 90–92% pure. Chromic acetylacetonate (Union Carbide) was analyzed and found to be 99% pure or better. Molybdenum pentachloride (Matheson, Coleman and Bell) and tungsten hexachloride (Union Carbide) were used without further purification.

Trimethylaluminum and triethylaluminum (Ethyl Corp., Orangeburg, S. Carolina) were 95% pure or better. Triisobutylaluminum (Hercules Powder Co.) was about 90% pure. Triphenylaluminum was obtained from Orgmet Chemical Co. and was used without further purification. Ethylaluminum sesquichloride was prepared by reaction of equimolar quantities of triethylaluminum and aluminum chloride. Sodium tetraethylaluminum was prepared by treating ethylsodium with triethylaluminum. All of the manipulations involving these compounds were handled under Seaford grade nitrogen.

The solvents were of the highest purity commercially available and were dried over calcium hydride or by the sodium–benzophenone procedure.[14] The carbon monoxide (Matheson) was 99.5% pure or better.

Analysis.—For the reaction variable study, the metal carbonyls were analyzed in appropriate organic solvents by infrared analysis; manganese carbonyl was analyzed in benzene and the Group VI-B metal carbonyls in carbon tetrachloride. The method was accurate generally to within 0.02 mg. of metal carbonyl/ml. The procedure consisted of quenching the reaction mixture with alcohol, water and dilute hydrochloric acid at 0°, extracting with the appropriate organic solvent, drying the extract over Drierite and diluting an aliquot with the same solvent to an appropriate concentration (0.2–1.8 mg./ml.) for infrared analysis. The metal carbonyl bands at about 5 μ were used for the analysis.

Methods of Contact.—Three methods of contacting and carrying out the reactions were used: A—a two-step pro-

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[12] All melting points uncorrected, in a sealed capillary.

[13] G. H. Cartledge (to Cornell Aeronautical Laboratory, Inc.), U. S. Patent 2,556,316, June 12, 1951.

[14] Procedure of Dr. G. V. D. Tiers described in M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 25.

cedure consisting of adding the alkylaluminum compound in a chosen solvent to the metal salt in the same solvent at 0–25° under dry nitrogen, followed by transferring the reaction mixture to an autoclave, pressurizing with carbon monoxide and heating to the desired reaction temperature; B—a sealed ampoule procedure consisting of adding the metal salt in a sealed ampoule to a 100-ml. Magne–Dash autoclave containing the alkylaluminum compound in a chosen solvent, pressurizing with carbon monoxide, breaking the ampoule at room temperature and heating to a desired temperature; C—a simultaneous contact procedure consisting of gradually adding the alkylaluminum compound in a chosen solvent to the metal salt in the same solvent in the presence of carbon monoxide at the desired temperature. When superatmospheric pressures of carbon monoxide were employed in conjunction with procedure C, the alkylaluminum solution was pumped in under dry nitrogen pressure.

Procedure B was generally employed for the reaction variable study. For preparative purposes, procedures A or C are best for preparing manganese carbonyl in ethers, procedure C for preparing manganese carbonyl in benzene, procedure A or C for preparing chromium carbonyl and procedure C for preparing molybdenum or tungsten carbonyl.

Preparation of Manganese Carbonyl.—A typical procedure is described: to 34.6 g. (0.20 mole) of anhydrous manganese acetate suspended in 150 ml. of dry isopropyl ether was added dropwise with stirring a solution consisting of 120 ml. (0.80 mole) of triethylaluminum and 290 ml. of isopropyl ether at 0° under a dry nitrogen atmosphere. The addition time was about 2.5 hr. With the aid of 40 ml. of isopropyl ether, the mixture then was transferred (in a nitrogen dry box) to a one-liter Magne–Dash autoclave. After assembly, the autoclave was purged twice with 600 p.s.i.g. of C.P. carbon monoxide. The autoclave then was pressured with 3000 p.s.i.g. of CO and heated by means of a steam-bath (with an alternate cold water supply) to 80–85° with stirring. It is important to maintain this temperature constant during the initial stage of the reaction to prevent a violent reaction between the manganese acetate and triethylaluminum. After the initial reaction occurred, the autoclave was heated to and maintained at 100° for 5 hr.

After the autoclave cooled to room temperature, it was carefully vented and the reaction mixture was transferred to a 2-liter three-neck flask equipped with a Dry Ice condenser, dropping funnel, and stirrer and was kept under a dry nitrogen blanket. The mixture then was carefully quenched by dropwise addition of 400 ml. of water and 100 ml. of concentrated hydrochloric acid at 0°. The mixture was distilled at atmospheric pressure into a three-neck round-bottomed flask which had an outlet at the bottom and condensers at the receiving and exit necks of the flask. This receiver was cooled in an ice-bath throughout the distillation. A forecut, mainly solvent, was taken at 92° and the manganese carbonyl steam distilled (static) at 92–100°. The product was filtered and allowed to dry in air for several hours (preferably in the dark under nitrogen). The yield was 21.0 g. (54% conversion) of yellow solid, m.p. 153–155°.

At 1000 p.s.i.g. of CO pressure under otherwise comparable conditions a 33% conversion to manganese carbonyl was obtained.

Preparation of Chromium Carbonyl.—Into a 250-ml. Magne–Dash autoclave in a dry nitrogen box was added 73 ml. of anhydrous diethyl ether, 67 ml. (0.45 mole) of triethylaluminum and 11.9 g. (0.075 mole) of chromic chloride. After assembly, the autoclave was purged twice with 600 p.s.i.g. CO and pressurized to 1000 p.s.i.g. The autoclave then was heated with stirring to 115° and maintained there for 7 hr.

After the autoclave had cooled to room temperature, it was vented slowly and the reaction mixture was carefully quenched with 20 ml. of 1:1 methanol–benzene, 100 ml. of water and 100 ml. of 1:1 water:concentrated hydrochloric acid. An additional 100 ml. of water was added and the reaction mixture then was distilled under nitrogen. The chromium carbonyl steam distilled (static) at 90–100°. The product then was filtered and allowed to dry in air. Yield was 15.2 g. (92%) of white crystalline product, m.p. 154–155°.

Preparation of Molybdenum Carbonyl.—To a 1-liter autoclave (Autoclave Engineers) fitted with stainless steel baffles and a turbine-type stirrer was added 54.8 g. (0.20 moles) of molybdenum pentachloride and 100 ml. of dry benzene. To a 700-ml. capacity reservoir (50 mm. diameter Pyrex tube) was added 200 ml. of benzene and 120 ml. (0.80 moles) of triethylaluminum under dry nitrogen. The autoclave was purged twice with 600 p.s.i.g. of CO, pressurized to 1000 p.s.i.g. of CO and heated with stirring to 50°. The triethylaluminum solution then was pumped in under slight nitrogen pressure *via* a Lapp Microflow Pulsafeeder in the course of about 1 hr. The reaction was exothermic and heating was not required during the addition of the triethylaluminum solution (maximum temperature was 68°). The mixture then was maintained at 65° an additional 2 hr.

The reaction mixture was worked up by the procedure described for the preparation of manganese carbonyl. The yield of snow-white crystalline molybdenum carbonyl was 40 g. (76% yield), m.p. 150–151° dec.

Preparation of Tungsten Carbonyl.—The same procedure as described for molybdenum carbonyl was used. The charge to the autoclave consisted of 79.4 g. (0.20 mole) of tungsten hexachloride and 100 ml. of benzene. The reservoir was charged with 200 ml. of benzene and 89.4 ml. (0.60 mole) of triethylaluminum. The initial reaction temperature was 50° and the temperature rose to 94° during the addition of the triethylaluminum solution. The mixture then was stirred an additional 2 hr. at 50°. Yield of snow-white crystalline tungsten carbonyl was 65 g. (92% yield), m.p. 169.5–170°.

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BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY]

The Preparation and Properties of Boron Phosphides and Arsenides[1]

BY FORREST V. WILLIAMS AND ROBERT A. RUEHRWEIN

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Four methods of preparation of cubic boron phosphide, BP, are described. The chemical and physical properties of BP and BAs are reported. The formation of lower phosphides and arsenides is noted.

Introduction

The semiconducting properties of silicon and germanium have generated considerable interest in the Group III-A-Group V-A compounds. The antimonides, arsenides and phosphides of indium, gallium and aluminum crystallize in the cubic zinc-blende structure, which is closely related to the diamond structure of the Group IV-A elements. Welker[2] was the first to show that these compounds

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[1] Presented in part at the 135th meeting of the American Chemical Society, Boston, Mass., April 7, 1959.

[2] H. Welker, *Naturforsch.*, 7a, 744 (1952).