*Journal of Organometallic Chemistry*
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

# ORGANOMETALLIC COMPOUNDS
# 4*. THE CONSTITUTION OF THE ETHYLZINC HALIDES**

M. H. ABRAHAM AND P. H. ROLFE
*The Joseph Kenyon Laboratories, Battersea College of Technology, London, S.W.11 (Great Britain)*

(Received April 21st, 1966)

## INTRODUCTION

The action of ethyl iodide on a Zn/Cu couple leads to a white, crystalline solid known[3] as ethylzinc iodide***. The empirical formula of this solid has been established to be $C_2H_5ZnI$[4,5], and it has also been shown[4] that the action of diethylzinc on zinc iodide, in absence of solvent, yields the same solid material. The nature of the species existing in solutions of ethylzinc iodide has been the subject of a number of investigations, and various chemical species, based on the empirical formula $C_2H_5ZnI$, have been postulated.

Job and Reich[5] considered as possible structures EtZnI (I) and $Et_2Zn \cdot ZnI_2$ (II); they reasoned that the action of a Grignard reagent RMgI (where $R \neq Et$) on (I) would lead to an unsymmetrical dialkylzinc, EtZnR, but that a mixture of two symmetrical dialkylzincs, $Et_2Zn$ and $R_2Zn$, would be formed if ethylzinc iodide existed as (II). Although their experiments were not very successful, Job and Reich obtained some evidence for the formation of EtZnMe and EtZnBu from ethylzinc iodide and MeMgI or BuMgI respectively; they concluded that (I) was more probable than (II) in solvent ether. Since then, unsymmetrical dialkylzincs have been prepared[1,7–9] several times. Kocheshkov and his co-workers[7] obtained EtZnBu in 71% yield from ethylzinc iodide and a butyl Grignard reagent in solvent ether and, as Job and Reich, concluded[7] that (I) was the species existing in ethereal solution. They did not, however, consider species such as $(EtZnI)_2$ (III) or $(EtZnI)_n$ (IV); neither did they consider the possibility of two or more species[†] existing in equilibrium with each other in solution. Kocheshkov and his co-workers[5,10] have also suggested that ethylzinc iodide might be obtained by three different routes:

$$EtI + Zn/Cu \rightarrow \quad (1)$$

$$Et_2Zn + ZnI_2 \rightarrow \quad (2)$$

$$EtMgI + ZnI_2 \rightarrow \quad (3)$$

They showed that the products from (1), (2), and (3) when dissolved in ether all

---

[*] Part 3, see ref. 1.

[**] A preliminary account of this work has been published, see ref. 2.

[***] We shall use the term ethylzinc iodide to describe this material, either as the solid or in solution, without regard to the chemical constitution of this material, and we shall use formulae to describe the chemical constitution of the species that are considered to be present in solutions of this material.

[†] For instance the species (I) to (IV).

precipitated out identical crystalline dioxanates on addition of dioxane. These dioxanates analysed correctly for $C_2H_5ZnI \cdot C_4H_8O_2$, but as the authors pointed out[10], this is an empirical formula, and a molecular formula such as $Et_2Zn \cdot ZnI_2 \cdot 2\,C_4H_8O_2$ is obviously possible. Evans and Maher[11] studied the proton magnetic resonance spectra of ethereal solutions of diethylzinc and ethylzinc iodide; they observed very similar spectra in both cases and concluded[11], in contrast to Kocheshkov[7], that ethylzinc iodide in solvent ether should be formulated as $Et_2Zn \cdot ZnI_2$.

Neither ethyl bromide nor ethyl chloride react with a Zn/Cu*, and hence studies in these cases are limited to the action of zinc bromide or zinc chloride on diethylzinc (*cf.* eqn. 2). Garrett and his co-workers[12] examined the solubility of zinc bromide in hexane solutions of diethylzinc and concluded that the species present in (hexane) solution was $Et_2Zn \cdot ZnBr_2$**. The zinc chloride/diethylzinc system has also been studied; Dessy and Coe[13] allowed mixtures of zinc chloride and diethylzinc in solvent ether and in solvent tetrahydrofuran (THF) to stand for 120 hours. On addition of bipyridine (bipy), the complex $ZnCl_2 \cdot$bipy was precipitated out from both the ether and the THF systems. As Dessy and Coe observed a statistical exchange of $^{65}Zn$ when $^{65}ZnCl_2$ was used, they considered the possibility that a species EtZnCl existed in ethereal and in THF solutions of diethylzinc plus zinc chloride. Molecular weight determinations[13] on a mixture of diethylzinc and zinc chloride in solvent THF corresponded[13] either to (*a*) no interaction at all between diethylzinc and zinc chloride or to (*b*) a monomer EtZnCl. Dessy and Coe rejected (*a*) thus, presumably, accepting (*b*), but gave no indication of why, if a monomer EtZnCl was present, bipyridine did not precipitate the complex EtZnCl·bipy, rather than $ZnCl_2 \cdot$bipy.

The nature of the species existing in solutions of ethylzinc halides is thus still not clear, and in view of the recent demonstrations[14] that Grignard reagents, in solvents ether and THF, may exist as monomeric RMgX, coupled with the well-known existence[15] of the alkylmercury halides, RHgX, we decided to re-investigate the ethylzinc halide systems.

## DISCUSSION

### *The ethylzinc iodide system*

Solutions of ethylzinc iodide were prepared by addition of ether or THF to the solid product from reaction (1) without analysing this solid product. The solid has been shown[4,5] to have an empirical formula $C_2H_5ZnI$, and we have shown, by analysis of solutions of ethylzinc iodide, that this is also true for the species existing in solution. Thus we may limit discussion to species whose empirical formula is $C_2H_5ZnI$, or to combinations of species giving rise to an equivalent empirical formula (*e.g.* a 1:1 mixture of $Et_2Zn$ plus $ZnI_2$).

We have determined the molecular weight of ethylzinc iodide in solvent THF by ebullioscopic measurements. Over the concentration range (in EtZnI) 0.03 to 0.41 *M*, the average molecular weight found was 268, which corresponds to $(EtZnI)_{1.21}$; significantly, there was no variation of observed molecular weight with concentration and hence the possibility of monomeric and dimeric species existing

---

* Except in solvents such as dimethylformamide.

** The results of Garrett are also consistent with $(EtZnBr)_2$ or, indeed, a mixture of $(EtZnBr)_2$ and $Et_2Zn \cdot ZnBr_2$ as the species present in solution, but neither of these possibilities was considered by Garrett.

in equilibrium with each other is excluded. It is known[16] that traces of air and moisture result in an increase in the observed molecular weights of alkylmagnesium halides and other metal alkyls, and we suggest that the species present in THF solutions of ethylzinc iodide has an "average" molecular formula of EtZnI. The only possibilities are (*a*) monomeric EtZnI, (*b*) an unassociated mixture of $Et_2Zn$ and $ZnI_2$, and (*c*) an equilibrium as in equation (4). Addition of N,N,N',N'-tetramethylethylenediamine

$$Et_2Zn + ZnI_2 \rightleftarrows 2\ EtZnI \qquad (4)^*$$

(TMED) to THF solutions of ethylzinc iodide resulted in precipitation of the hitherto unknown complex EtZnI·TMED; this complex was obtained both from freshly-prepared solutions of ethylzinc iodide, and from solutions kept for several days. When TMED was added to an equimolar mixture of diethylzinc and zinc iodide in solvent THF, two hours after preparation of the mixture, the complex $ZnI_2$·TMED was obtained, but if the mixture of diethylzinc and zinc iodide in THF was allowed to stand at 25° for seven days** before addition of TMED, the complex EtZnI·TMED was once again obtained. It is thus demonstrated that equilibrium (4) lies well to the right in solvent THF, that ethylzinc iodide cannot be represented as a mixture of diethylzinc and zinc iodide, and that the species existing in THF solutions of ethylzinc iodide is monomeric EtZnI.

The solubility of the complexes $Et_2Zn$·TMED, EtZnI·TMED, and $ZnI_2$·TMED in solvents ether and THF decrease markedly along this series; thus $ZnI_2$·TMED is not only the "strongest" complex but also the most insoluble. This is of some consequence if equilibrium (4) or analogous equilibria with zinc bromide and zinc chloride, can be approached only from the left hand side, as precipitation of a complex $ZnX_2$·TMED from a mixture of diethylzinc and zinc halide in a given solvent could be due to (*a*) the equilibrium lying entirely on the left hand side or (*b*) the equilibrium being rapid in both directions and addition of TMED merely displacing the equilibrium as the most insoluble complex is precipitated. We shall use these conclusions later on.

By the same procedure as above, the molecular weight of ethylzinc iodide in ether over the concentration range (in EtZnI) 0.02 to 0.11 *M* corresponded to $(EtZnI)_{1.27}$, and again there was no variation in this association constant with concentration. We conclude that ethylzinc iodide in solvent ether must also have an "average" molecular formula of EtZnI. Addition of TMED to ethereal solutions of ethylzinc iodide gave the complex EtZnI·TMED both from freshly prepared solutions and those kept for several days. The same complex was isolated on addition of TMED to a mixture of diethylzinc and zinc iodide, prepared using refluxing ether. Although the comparative insolubility of zinc iodide in ether prevented us from examining the $Et_2Zn/ZnI_2$ system as fully as with THF solvent, we can again conclude that ethylzinc iodide in ether is present as monomeric EtZnI, and that the position of equilibrium in (4) lies well to the right. Evans and Wharf[17] have recently described

---

* Eqn. (4) reading from left to right is known as a syn-proportionation, and reading from right to left as a symmetrisation.

** This period is probably excessive; in one experiment the mixture of $Et_2Zn$ and $ZnI_2$ in THF became warm, inadvertently, on addition of TMED. The resulting precipitate was a mixture of $ZnI_2$·TMED and EtZnI·TMED, even though addition was made only two hours after the solution had been prepared. Syn-proportionation of $Et_2Zn$ and $ZnI_2$ is thus quite rapid in solvent THF.

some Raman and infra-red studies on ethereal solutions of ethylzinc iodide, and have confirmed our conclusions[2] that the species in solution is monomeric EtZnI, and that the earlier suggestion of Evans and Maher[11] (that the species in solution is $Et_2Zn \cdot ZnI_2$) appears to be incorrect.

This latter suggestion[11] was based on the similarity of the proton magnetic resonance (PMR) spectra of diethylzinc and ethylzinc iodide, both in solvent ether. We have examined the PMR spectra of THF solutions of diethylzinc, ethylzinc iodide, and an equimolar mixture of diethylzinc and ethylzinc iodide. In all three cases, the spectra were very similar, with a sharp triplet at $\tau$ 8.95 ppm and a sharp quartet at $\tau$ 9.92 ppm. We thus agree with Evans and Wharf[17] that PMR cannot distinguish between species such as $Et_2Zn$ and EtZnI, although we can offer no explanation. The possibility that in a mixture of $Et_2Zn$ and EtZnI there is a rapid exchange of ethyl groups (eqn. 5) we feel is remote, as this would require the three-alkyl

$$Et_2Zn + Et^{\circ}ZnI \rightleftharpoons EtZnI + Et^{\circ}ZnEt \tag{5}$$

zinc exchange (5) to be very much faster than the two-alkyl zinc exchange (4), the latter being very slow (on the PMR time-scale).

### *The ethylzinc bromide system*

Equilibrium (6), in solvents ether and THF, can only be approached from the left hand side. Addition of TMED to an equimolar solution of diethylzinc and

$$Et_2Zn + ZnBr_2 \rightleftharpoons 2\ EtZnBr \tag{6}$$

zinc bromide in solvent THF, both after the solution had been kept for two hours and for seven days at 25° yielded the complex $ZnBr_2 \cdot$TMED in each case. Hence we cannot distinguish between the two situations (*a*) equilibrium (6) lying entirely to left and (*b*) equilibrium (6) being very labile* and addition of TMED resulting in the equilibrium being disturbed and the most insoluble complex precipitated out. A third possibility is that the syn-proportionation (6) is kinetically very slow. However Rausch and Van Wazer[18] have determined the reaction rate constants for (7) to be 1.05 (X = Cl), 0.30 (X = Br), and 0.05 (X = I) in solvent methanol and 0.0026 (X = Cl), 0.0035 (X = Br) and 0.0015 (X = I) in solvent dioxane, all in $l \cdot mol^{-1} \cdot sec^{-1}$ at 36°. If there is any analogy at all between (4) and (6) compared to (7), we would

$$Me_2Hg + HgX_2 \rightarrow 2\ MeHgX \tag{7}$$

not expect the syn-proportionation (6) to be much slower than syn-proportionation (4) in solvent THF, the reverse being true for the corresponding alkyl mercury syn-proportionations in solvent dioxane. Furthermore, syn-proportionation (6) proceeds quite rapidly in solvent ether and we would expect it to be even faster in solvent THF. Thus we are left with only the first two situations, (*a*) and (*b*), above.

Addition of TMED to an equimolar solution of diethylzinc and zinc bromide in solvent ether yielded the new complex EtZnBr·TMED. We have not determined the molecular weight of the $Et_2Zn/ZnBr_2$ mixture in solvent ether, so our immediate conclusion that equilibrium (6) lies well to the right must be tempered with the proviso that the species in solution could be a polymeric species $(EtZnBr)_n$ rather

---

* By "labile" we mean rapid in both directions.

than the monomeric EtZnBr. In view of the similarity of this system to the corresponding EtZnI systems, though, it is quite possible that monomeric EtZnBr is the species present in ethereal solution.

### *The ethylzinc chloride system*

After the experiments of Dessy and Coe[13], there seemed little point in extending our work to this system, but in the light of our own experiments we interpret their results as either (*a*) equilibrium (8) lies well to the left hand side or (*b*) equilibrium (8) is labile and addition of bipyridine precipitates the most insoluble complex, $ZnCl_2 \cdot$ bipy.

$$Et_2Zn + ZnCl_2 \rightleftarrows 2\ EtZnCl \qquad (8)$$

## CONCLUSIONS

We have shown that ethylzinc iodide, in solvents ether and THF, exists as monomeric EtZnI, and we are thus in agreement with the views of Job and Reich[6], Kocheshkov and his co-workers[5,7,10], and Evans and Wharf[17] regarding the constitution of ethylzinc iodide in ethereal solution. No direct comparison is possible between our results and those of Garrett and his co-workers[12] on the ethylzinc bromide system, although it is reasonable that more associated species, as found by Garrett, might exist in the non-solvating medium hexane than in the solvating media ether and THF.

The results of our experiments on the action of diethylzinc on zinc halides may be satisfactorily interpreted in terms of the syn-proportionation/symmetrisation equilibria (4) and (6), where the equilibrium lies strongly on the side of the syn-proportionation species (EtZnX) for the three systems $Et_2Zn/ZnI_2$/ether, $Et_2Zn/ZnI_2$/THF, and $Et_2Zn/ZnBr_2$/ether. In the fourth system studied by us, $Et_2Zn/ZnBr_2$/THF, and in the two systems studied by Dessy and Coe[13], $Et_2Zn/ZnCl_2$/ether and $Et_2Zn/ZnCl_2$/THF, it is possible that the equilibria (6) and (8) also lie strongly on the side of the syn-proportionation species, but that the equilibrium is now much more labile. Alternatively, it is possible that in these systems, there is in fact but little interaction between the diethylzinc and zinc halide. It is known[18,19] that dialkylmercurys and mercuric halides invariably yield the syn-proportionation products, alkylmercury halides, and it is tempting to suggest that all the six diethylzinc/zinc halide systems so far studied lead to the corresponding syn-proportionation products, the ethylzinc halides EtZnX, but that in the three ambiguous cases the equilibrium is very labile*.

Of the Group II elements, Be, Mg, Zn, Cd and Hg, three, Mg, Zn, and Hg, are thus now known to form monomeric alkylmetal halides of type RMX, and it would seem to be of some interest to investigate the corresponding systems in beryllium and cadmium compounds in some detail.

---

* *Note added June 8th*, 1966. Recent work by D. F. Evans and I. Wharf indicates the existence of the species EtZnX (X = Cl, Br, I) in solvent THF (personal communication from Dr. D. F. Evans). Our results can thus indeed best be interpreted in terms of this labile equilibrium, at least for the two systems $Et_2Zn/ZnBr_2$/THF and $Et_2Zn/ZnCl_2$/THF.

## EXPERIMENTAL

All operations involving diethylzinc, and ethylzinc halides and their complexes, were carried out under dry, oxygen-free nitrogen. Ether was distilled, dried over $CaCl_2$, again distilled and stored over sodium. THF was stored over sodium and distilled from $LiAlH_4$ under nitrogen immediately prior to use. TMED was dried over KOH pellets, fractionated, and stored over KOH pellets. Zinc was analysed for by the EDTA method[20], and halide was analysed for by Volhard's method. Hydrolysable alkyl was determined[1] as before. Diethylzinc was prepared[1] as before; the present sample had b.p. 50–52°/74 mm. (Found: Zn, 52.78; hydrolysable alkyl 1.98. $C_4H_{10}Zn$ calcd.: Zn, 52.94%; hydrolysable alkyl 2.00.) All b.p.'s and m.p.'s are uncorrected.

### *Ethylzinc iodide preparations*

Small batches were prepared as follows. Ethyl iodide (15.5 g) was added in one portion to a Zn/Cu couple, made from Zn (13 g) and CuO (1 g) by Noller's method[21], in a 100-ml two-necked flask and the mixture stirred magnetically. Reaction was initiated, if necessary, by gentle warming. After reaction the pressure was reduced to 0.2 mm. to remove any unreacted EtI or any $Et_2Zn$, and then either ether or THF was added to the solid residue. The mixture was stirred magnetically, the excess of couple allowed to settle, and the supernatant liquid filtered through a fine glass sinter and then sealed off into glass capsules. Analyses of solutions of ethylzinc iodide were consistent with the stoichiometry EtZnI for the species in solution, and gave ratios close to 1 : 1 for molarity of zinc to molarity of iodide ion, *e.g.*: sample (1), molarity of Zn 1.216, molarity of I 1.200; sample (2), molarity of Zn 0.582, molarity of I 0.580. In addition, PMR spectra of solutions of ethylzinc iodide showed, apart from solvent peaks, only the spectrum expected for an ethyl group attached to zinc.

### *$ZnI_2 \cdot$TMED complex*

An excess of TMED was added to $ZnI_2$ in methanol. The precipitate, on recrystallisation from methanol had m.p. 201–202°. (Found: I, 58.00; Zn, 15.09. $C_6H_{16}I_2N_2Zn$ calcd.: I, 58.29; Zn, 15.01%.) An identical material was prepared using THF as solvent. On recrystallisation from THF it had m.p. 201°. (Found: I, 58.30; Zn, 15.07%.)

### *$ZnBr_2 \cdot$TMED complex*

Prepared as for the iodide complex using methanol it had m.p. 179° (lit.[22,23] 178° and 182° resp.). (Found: Br, 46.63; Zn, 19.06. $C_6H_{16}Br_2N_2Zn$ calcd.: Br, 46.81; Zn, 19.15%.) Using THF the product had m.p. 178°. (Found: Br, 46.44; Zn, 19.01%.)

### *EtZnI·TMED complex*

An excess of TMED was added to an ethereal solution of ethylzinc iodide. Heat was evolved and as the solution cooled, crystals were deposited. On recrystallisation from ether they had m.p. 103°. (Found: I, 37.64; Zn, 19.94. $C_8H_{21}IN_2Zn$ calcd.: I, 37.60; Zn, 19.37%.) An identical material was prepared from a solution of ethylzinc iodide in THF; on recrystallisation from THF it had m.p. 102°. (Found: I, 37.98; Zn, 19.53%.)

*$Et_2Zn$ plus $ZnI_2$ in THF*

TMED (7.0 mmole) in few ml purified hexane was added to a solution of $Et_2Zn$ (4.9 mmole) and $ZnI_2$ (5.0 mmole) in THF (1.5 ml) 2 h after the solution had been made up. The crystalline product was filtered off and washed with hexane. It had m.p. 164°. (Found: I, 58.50; Zn, 15.97%.) On recrystallisation from THF it had m.p. 201°, undepressed on admixture with authentic $ZnI_2 \cdot$TMED. (Found: I, 58.33; Zn, 15.14%.) The above was repeated exactly on a solution of $Et_2Zn$ (4.9 mmole) and $ZnI_2$ (5.0 mmole) in THF (1.5 ml) after this solution had been kept for seven days at 25°. The crystalline product, after washing with hexane, had m.p. 103°. (Found: I, 38.43; Zn, 18.97%.)

*$Et_2Zn$ plus $ZnI_2$ in ether*

$ZnI_2$ (4.8 mmole) was refluxed with a solution of $Et_2Zn$ (5.0 mmole) in ether (50 ml) for 2 h. The solution was filtered to remove undissolved zinc iodide, and to the clear filtrate was added TMED (11.6 mmole). As the solution cooled, crystals were deposited. They were filtered off and washed with ether, after which they had m.p. 100–101°. (Found: I, 37.92; Zn, 19.87%.)

*$Et_2Zn$ plus $ZnBr_2$ in THF*

TMED (27 mmole) in a few ml purified hexane was added to a solution of $Et_2Zn$ (26 mmole) and $ZnBr_2$ (26 mmole) in THF (12.5 ml) 2 h after the solution had been prepared. The resulting precipitate was washed with hexane and had m.p. 175°. (Found: Br, 44.71; Zn, 20.33%.) On recrystallisation from THF it had m.p. 178°, undepressed on admixture with authentic $ZnBr_2 \cdot$TMED. (Found: Br, 45.25; Zn, 20.05%.) The experiment was repeated exactly except that the solution of $Et_2Zn$ and $ZnBr_2$ was kept for seven days at 25° before addition of TMED. The crude product had m.p. 173°. (Found: Br, 42.35; Zn, 20.14%.) On recrystallisation from THF it had m.p. 178°, undepressed on admixture with authentic $ZnBr_2 \cdot$TMED. (Found: Br, 45.31; Zn, 19.72%.)

*$Et_2Zn$ plus $ZnBr_2$ in ether*

TMED (39 mmole) was added to a solution of $Et_2Zn$ (19 mmole) and $ZnBr_2$ (18.6 mmole) in ether (30 ml), 15 min after the solution had been prepared. The crystalline precipitate, after washing with hexane, had m.p. 46°. (Found: Br, 28.32; Zn, 21.29. $C_8H_{21}BrN_2Zn$ calcd.: Br, 27.51; Zn, 22.50%.)

*Molecular weight measurements*

The apparatus used was a Cottrell-type ebulliometer fitted with a Beckmann thermometer. After a determination using the pure solvent, a capsule of a standard solution of ethylzinc iodide in the same solvent was broken in a side-arm of the apparatus and the elevation of the b.p. recorded. The ebullioscopic constant for ether was taken[24] as 2.02 and that for THF was determined as 2.29, using phenanthrene as the solute. Hashimoto and his co-workers[25] have recently found these constants to be 2.03 (ether) and 2.18 (THF). If we had used the latter constant, our observed molecular weight for ethylzinc iodide in solvent THF would have been reduced to 254, and the association constant correspondingly reduced to 1.15.

*PMR measurements*

These were recorded on a Varian HA 100 spectrometer. Spectra of THF solutions of $Et_2Zn$, EtZnI, and a 1 : 1 mixture of $Et_2Zn$ and EtZnI were as far as we could tell identical, with a triplet ($J = 8$ cps) at $\tau$ 8.95 ppm and a quartet ($J = 8$ cps) at $\tau$ 9.92 ppm, due to the methyl and methylene protons of the ethylzinc group respectively.

## ACKNOWLEDGEMENTS

We thank the Governing body of the College for a research studentship (to P.H.R.). We are grateful to the Director of the National Physical Laboratory for permission to use the Varian HA 100 nuclear magnetic resonance spectrometer, and to Dr. K. A. McLauchlan for his kind help with the operation of this machine.

## SUMMARY

We have shown, by ebullioscopic measurements and by the isolation of N,N,N',N'-tetramethylethylenediamine complexes, that ethylzinc iodide in solvents ether and tetrahydrofuran exists as the monomeric species EtZnI and that ethylzinc bromide in ethereal solution probably also exists as the corresponding species EtZnBr.

The action of diethylzinc on zinc iodide in solvents ether and tetrahydrofuran, and on zinc bromide in solvent ether, results in formation of the syn-proportionation products EtZnI and EtZnBr, isolated as their N,N,N',N'-tetramethylenediamine complexes. Observations on the diethylzinc/zinc bromide system in solvent tetrahydrofuran can be explained by (*a*) a labile equilibrium is set up between diethylzinc and zinc bromide and the species EtZnBr or (*b*) diethylzinc does not react with zinc bromide in this solvent.

## REFERENCES

1 M. H. Abraham and J. A. Hill, *J. Organometal. Chem.*, 7 (1967) 23.

2 M. H. Abraham and P. H. Rolfe, *Chem. Commun.*, (1965) 325.

3 A. E. Goddard and D. Goddard, in J. Newton Friend, *Text-book of Inorganic Chemistry*, Vol. XI, Part I, Griffin, London, 1928, p. 25.

4 G. Jander and L. Fischer, *Z. Electrochem.*, 62 (1958) 971.

5 I. E. Paleeva, N. I. Sheverdina, L. V. Abramova and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 159 (1964) 609; *Proc. Acad. Sci. USSR*, 159 (1964) 1230.

6 A. Job and R. Reich, *Bull. Soc. Chim. France*, 33 (1923) 1414.

7 K. A. Kocheshkov, N. I. Sheverdina and J. E. Paleeva, *Bull. Soc. Chim. France*, (1963) 1472.

8 M. H. Abraham and J. A. Hill, *Proc. Chem. Soc.*, (1964) 175.

9 E. Krause and W. Fromm, *Ber.*, 59 (1926) 931.

10 N. I. Sheverdina, L. V. Abramova and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 124 (1959) 602; *Proc. Acad. Sci. USSR*, 124 (1959) 65.

11 D. F. Evans and J. P. Maher, *J. Chem. Soc.*, (1962) 5125.

12 A. B. Garrett, A. Sweet, W. L. Marshall, D. Riley and A. Touma, *Record Chem. Progr.*, 13 (1952) 155.

13 R. E. Dessy and G. R. Coe, *J. Org. Chem.*, 28 (1963) 3592.

14 A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, 82 (1963) 453, 461; 83(1964) 1096; E. C. Ashby and W. E. Becker, *J. Am. Chem. Soc.*, 85 (1963) 118; E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, 86 (1964) 4363.

15 Ref. 3, p. 39.

16 A. D. VREUGDENHIL AND C. BLOMBERG, *Rec. Trav. Chim.*, 84 (1965) 39; N. MULLER AND A. L. OTERMAT, *Inorg. Chem.*, 2 (1963) 1075; 4 (1965) 296.

17 D. F. EVANS AND I. WHARF, *J. Organometal. Chem.*, 5 (1966) 108.

18 M. D. RAUSCH AND J. R. VAN WAZER, *Inorg. Chem.*, 3 (1964) 761.

19 Ref. 3, p. 29 *et seq.*,

20 M. H. ABRAHAM, *J. Chem. Soc.*, (1960) 4130.

21 C. R. NOLLER, *Org. Synt.*, *Collective Vol.*, 2 (1943) 185, procedure (*a*).

22 G. E. COATES AND D. RIDLEY, *J. Chem. Soc.*, (1964) 166.

23 J. G. NOLTES AND J. W. G. VAN DEN HURK, *J. Organometal. Chem.*, 1 (1964) 377.

24 *Handbook of Chemistry and Physics*, 44th ed., Chemical Rubber Publishing Co., Cleveland, 1962, p. 2392.

25 H. HASHIMOTO, T. NAKANO AND H. OKADA, *J. Org. Chem.*, 30 (1965) 1234.