ZINC AND CADMIUM

LITERATURE SURVEY COVERING THE YEAR 1979*

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Introduction

The number of papers dealing with organozinc- and organocadmium chemistry has declined sharply from the annual average of about 50 to 27 in 1979. This is not due to a diminished interest in one or two particular research subjects, but appears to be a general phenomenon. Although this decline might be just an excessive negative fluctuation, it may signify the beginning of a shift of interest away from this research area. It is, however, to early yet to be sure of that.

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*Zinc and Cadmium; Annual Survey covering the year 1978: J. Organometal. Chem. Vol. 189 (1980) p. 1-14.

Only one review has appeared in 1979; i.e. Preparation and reaction of zinc compounds in organic synthesis[1]. It deals with reactions of dialkylzinc compounds, alkylzinc halides, and activated zinc metal (zinc/copper, zinc/silver, and zinc/mercury couples).

I. Preparation of organozinc- and organocadmium compounds

A description of a convenient laboratory-scale synthesis of dimethylzinc has been given by Galyer and Wilkinson[2]. It is based on the reaction of trimethyl aluminium with zinc acetate:

$$2\ Me_3Al + Zn(OCOMe)_2 \longrightarrow Me_2Zn + 2\ Me_2AlOCOMe$$

The authors give a very detailed description of the experimental procedure and of the safety measures necessary in the manipulation of this very volatile, pyrophoric compound.
Klabunde and Murdock have prepared very reactive zinc and cadmium slurries by co-precipitation of zinc and cadmium vapour with organic solvents like toluene, THF, and diglyme[3].
The zinc slurries react with alkyl halides to give quantitative yields of dialkylzinc compounds. The cadmium slurries were hardly reactive towards alkyl bromides, and react with alkyl iodides not beyond the alkylcadmium iodide stage. Unsolvated ethylcadmium iodide was prepared in this way as a colourless precipitate in hexane.
The electrochemical oxidation of cadmium metal in the presence of alkyl- or arylhalides, developed by Tuck and co-workers, has been extended to the preparation of a series of anionic organodihalocadmate species (I)[4]:

$$RCdX_2^-$$

$$R = Me, Et, n\text{-}Bu, CF_3, C_6F_5;\ X = Cl, Br, I$$

Cadmium metal was used as a sacrificial anode in a cell containing as electrolyte a solution of $(nPr)_4NX$ and RX in a methanol/benzene mixture.
The tetra-n-propyl ammonium salts of the organodihalocadmate ions are moisture-sensitive solids which are insoluble in common organic solvents. They are most probably formed via the initial formation of RCdX species which are stabilized by salt formation:

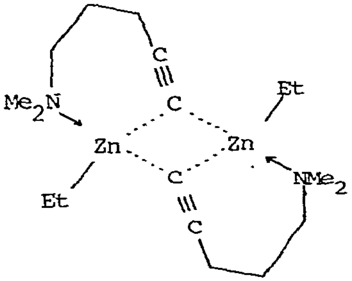
$$RCdX + R^1_4NX \longrightarrow R^1_4N(RCdX_2)$$

The same research group has prepared some triphenyltin-zinc and -cadmium species by the electrochemical oxidation of zinc and cadmium metal in the presence of triphenyltinchloride in a acetonitrile/benzene mixture[5]. The tin-zinc and tin-cadmium compounds were isolated as TMED or Bipy adducts.

ω-Dimethylamino-1-alkynylzinc compounds have been obtained by metalation of the dimethylaminoalkynes $HC{\equiv}C(CH_2)n\ NMe_2 (n = 1\text{-}4)$ with diethylzinc and diphenylzinc[6]:

$$Me_2N(CH_2)_nC{\equiv}CH + Et_2Zn \longrightarrow EtZnC{\equiv}C(CH_2)_nNMe_2$$
$n = 1\text{-}4$
$$2\ Me_2N(CH_2)_nC{\equiv}CH + Ph_2Zn \longrightarrow Zn[C{\equiv}C(CH_2)_nNMe_2]_2$$
$n = 1\text{-}4$

These alkynylzinc compounds are associated into oligomers, the degree of association varying from one to three, with the exception of $EtZnC{\equiv}CCH_2NMe_2$ and $Zn[C{\equiv}CCH_2NMe_2]_2$, which are probably polymeric. The association is brought about by coordinate bonding via dimethylaminogroups and/or bridging alkynyl groups. Structures like:



for dimeric $EtZnC{\equiv}C(CH_2)_3NMe_2$, are proposed.

Liu and Asprey have presented ^1H- and ^{19}F-NMR evidence for the formation of bis(trifluoromethyl)zinc and methyl(trifluoromethyl)zinc in the reaction of dimethylzinc with bis(trifluormethyl)cadmium and bis(trifluoromethyl)mercury[7]. In both cases, exchange reactions occur to give final product distributions depending on the initial concentrations of reactants:

$$2(CF_3)_2M + Me_2Zn \leftrightarrows 2\ Me(CF_3)M + (CF_3)_2Zn$$
$$(CF_3)_2M + 2\ Me_2Zn \leftrightarrows Me_2M + 2\ Me(CF_3)Zn$$
$$3(CF_3)_2M + 2\ Me_2Zn \leftrightarrows 3\ Me(CF_3)M + Me(CF_3)Zn + (CF_3)_2Zn$$
$M = Cd, Hg$

It appeared that the initial exchange between dimethylzinc and

bis(trifluoromethyl)cadmium proceeded much more rapidly than the exchange between dimethylzinc and bis(trifluoromethyl)mercury.
The first alkylsilylzinc and - cadmium compounds $(Me_3Si)_2M$ (M = Zn, Cd) have been prepared by reacting the metal chloride with lithium-tetrakistrimethylsilylaluminium[8].

$$2\ MX + LiAl(SiMe_3)_4.2DME \longrightarrow 2\ (Me_3Si)_2M$$
$$X = Cl,\ OCOMe;\ M = Zn,Cd$$

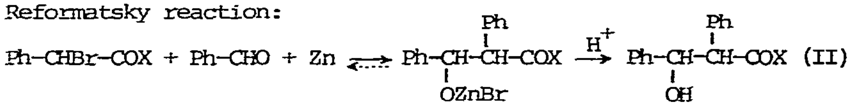
Like their carbon homologs $(tBu)_2Zn$ and $(tBu)_2Cd$, these silyl compounds are thermolabile, the zinc compound decomposing slowly at room temperature and the cadmium compound decomposing completely within two days at -20°.

II. Reactions of organozinc- and organocadmium compounds

A. The Reformatsky reaction and related reactions

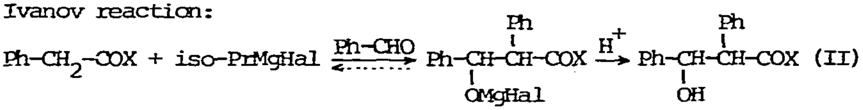
Mladenova and co-workers have continued their comparative studies on the stereochemistry and reversibility of the Reformatsky and Ivanov reactions[9]. They have investigated these reactions using N-substituted amides of phenylacetic acid as substrates. It appeared that, contrary to what happens in the Ivanov reaction, in the Reformatsky reaction the erythro: threo ratio of the product alcohols (II) was hardly affected by differences in the nature of group X and solvent polarity:

Reformatsky reaction:



$$\text{Ph-CHBr-COX} + \text{Ph-CHO} + \text{Zn} \rightleftarrows \text{Ph-}\underset{\text{OZnBr}}{\text{CH}}\text{-}\overset{\text{Ph}}{\text{CH}}\text{-COX} \xrightarrow{H^+} \text{Ph-}\underset{\text{OH}}{\text{CH}}\text{-}\overset{\text{Ph}}{\text{CH}}\text{-COX}\ \text{(II)}$$

Ivanov reaction:



$$\text{Ph-CH}_2\text{-COX} + \text{iso-PrMgHal} \xrightleftharpoons{\text{Ph-CHO}} \text{Ph-}\underset{\text{OMgHal}}{\text{CH}}\text{-}\overset{\text{Ph}}{\text{CH}}\text{-COX} \xrightarrow{H^+} \text{Ph-}\underset{\text{OH}}{\text{CH}}\text{-}\overset{\text{Ph}}{\text{CH}}\text{-COX}\ \text{(II)}$$

$X = NMe_2,\ NHMe$

The reversibility of these reactions was found to be very small, and very much slower than that of the corresponding hydroxyl esters.
As found by Fauvarque and Jutand, the Reformatsky reagent derived from ethylbromoacetate can be arylated and vinylated by simple

aromatic and vinylic halides in the presence of a transition-metal catalyst and a dipolar aprotic solvent[10]:

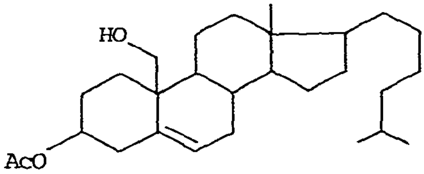
$$ArX + BrZnCH_2COOEt \xrightarrow{Ni(PPh_3)_4} ArCH_2COOEt + ZnBrX$$

HMPT and N-methylpyrrolidone, each mixed with an equal volume of dimethoxymethane, are the best solvents for these reactions since they allow the use of chlorobenzenes with fair to good yields. Soluble triphenylphosphine complexes of Ni^0 and Pd^0 were used as catalysts in 10 mole % amount.

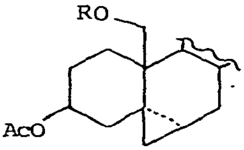
The authors suggest a reaction mechanism consisting of oxidative addition of the aromatic halide to the transition metal, followed by ligand substitution by the Reformatsky reagent, and finally reductive elimination of the product. It was shown that the scope of the reaction can be extended to include the synthesis of functionally substituted arylacetic acid esters.

B. Carbenoid reactions

Fajkoš and Joska have investigated the Simmons-Smith methylenation of 19-hydroxycholesteryl acetate[11] (III).

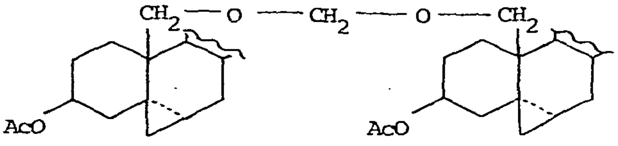


Three main reaction products were identified:



IV: R = H

V : R = CH_2OCH_2OEt

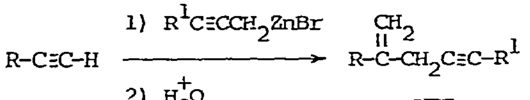


V

The expected product IV has the cyclopropane ring situated at the β-side of the molecule, indicating that the methylenation proceeded stereospecifically.

C. Reactions of alkenyl- and alkynylzinc compounds

When organozinc reagents derived from di-substituted α-acetylenic bromides are reacted with mono-substituted acetylenes and α- or β-acetylenic alcohols, the corresponding β-enynes and β-enynols are formed[12]:



$$\text{R-C}\equiv\text{C-H} \xrightarrow[2)\ H_3\overset{+}{O}]{1)\ R^1C\equiv CCH_2ZnBr} \text{R-}\overset{\overset{CH_2}{\|}}{C}\text{-}CH_2C\equiv C\text{-}R^1$$

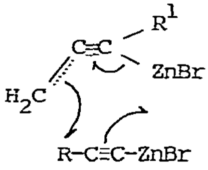
VI VII

R = nC_5H_{11}, $C_2H_5CH(CH_3)CH_2$, $nC_3H_7CH(CH_3)$, C_6H_5, CH_2OH, CH_3CHOH, $CH_3CHOHCH_2$, $C(OH)(CH_3)_2CH_2$.

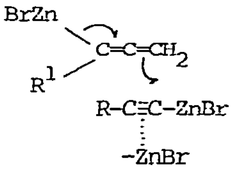
R^1= Me, allyl, C_6H_5

These reactions proceed in a regiospecific way and products (VII) are obtained nearly exclusively. Only when R is n-pentyl and R^1 is allyl, a compound resulting from two-fold addition was formed as a byproduct in low (12%) yield.

The authors assume that the starting acetylenes (VI) are metallated by the zinc reagent and react with another equivalent of reagent via a $S_{E'}i$ or $S_{E'}2$ mechanism:



$S_{E'}i$



$S_E'2$

It is proposed that electrophilic assistance during the addition reaction is rendered by excess reagent, as was found earlier for similar reactions of α-ethylenic organozinc reagents.

L.Miginiac and co-workers have continued their investigations into the reactivity of organometallic reagents derived from alkenyl bromides by studying the preparation and reactivity of organozinc, organomagnesium and organoaluminium reagents derived from primary α-allenic bromides[13,14]:

R-CH=C=$(R^1)CH_2M$

M = ZnBr, MgBr, AlBr

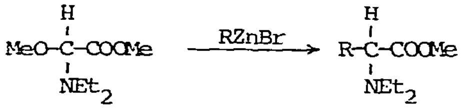
Although the zinc-containing reagents do not react with organic halides, they react readily with the aldehydes $(CH_3)_2CHCHO$ and C_6H_5CHO, but sluggishly with ketones.

In all cases, allenic alcohols:

$R{-}CH{=}C{=}C(R^1)CH_2CHOH\ R^{11}$

$R = H, Me;\ R^1 = H, Me;\ R^{11} = (CH_3)_2CH,\ C_6H_5CH$

are formed exclusively. It was proposed that a S_E2' or S_E2 mechanism is operative in these reactions.
Unsaturated α-aminoesters having a tertiairy amino function have been prepared by reacting the methoxy aminoester derivative (VII) with alkenylzinc bromides[15]:

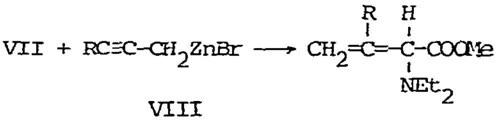


$$\mathrm{MeO{-}\underset{NEt_2}{\overset{H}{C}}{-}COOMe} \xrightarrow{RZnBr} \mathrm{R{-}\underset{NEt_2}{\overset{H}{C}}{-}COOMe}$$

VII

$R = CH_2{=}CH{-}CH_2{-},\ CH_2{=}C{=}CH{-}$

The corresponding reaction with alkynylzinc bromides (VIII) yielded allenic esters:



$$\mathrm{VII} + RC{\equiv}C{-}CH_2ZnBr \longrightarrow CH_2{=}\overset{R}{C}{=}\underset{NEt_2}{\overset{H}{C}}{-}COOMe$$

VIII

$R = Me, Et, Pr, Bu$

D. Miscellaneous reactions

The kinetics and mechanism of the auto-oxidation reactions of dimethylzinc and dimethylcadmium have been studied by Lebedev and Kuznetsova and co-workers [16,17]. In both cases, free-radical chain reactions occur to give the methylperoxy derivatives (IX) and (X).

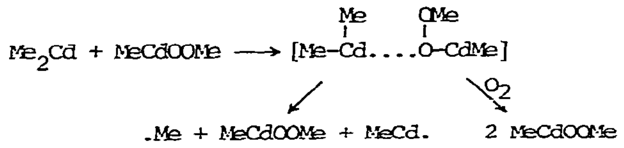
$MeMOOMe$ IX

$MeOOMOOMe$ X

$M = Zn, Cd$

The radical-generation rates decrease with increasing oxygen concentration in the reaction mixtures.
Rate expressions for the initiation stages and for the overall reactions have been determined.

In both auto-oxidation reactions, degenerate branching occurs, e.g.:



$$Me_2Cd + MeCdOOMe \longrightarrow [\overset{Me}{\underset{|}{}}Me\text{-}Cd....O\text{-}CdMe] \quad (Me \text{ on } Cd,\ OMe \text{ on } O)$$

$$\longrightarrow .Me + MeCdOOMe + MeCd. \qquad \xrightarrow{O_2} 2\ MeCdOOMe$$

It was shown that, contrary to earlier beliefs, the rearrangement of peroxides:

$$.MeCdOOMe \text{ --- } Cd(OMe)_2$$

or the oxidation of dimethyl-metal compounds:

$$MeCdOOMe + Me_2Cd \longrightarrow 2\ MeCdOOMe$$

either do not take place, or do not contribute significantly to the reaction products.

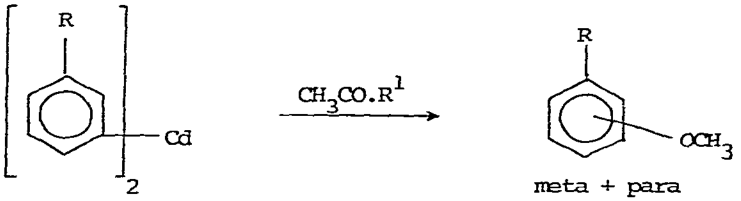
The photolysis of diarylcadmium compounds in benzene has been investigated in view of the potential use of these compounds as synthetic intermediates[18]. The photolysis reactions yielded mainly the symmetric biaryls, together with minor amounts of products resulting from the arylation of benzene:

$$Ar_2Cd \xrightarrow{h\nu} 2\ Ar. + Cd$$

$$2\ Ar. \longrightarrow Ar\text{-}Ar \qquad \text{(main reaction)}$$

$$Ar. + C_6H_6 \xrightarrow{-H.} Ar\text{-}C_6H_5 \quad \text{(side reaction)}$$

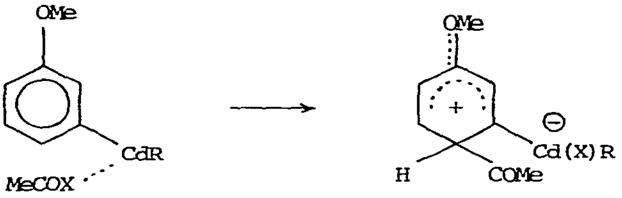
The formation of aryl radicals in the initial step was confirmed by carrying out the photolyses in CCl_4, which yielded chloroarenes in high yield. The photolysis of diarylcadmium compounds derived from polynuclear aromatics yielded no coupling products. Instead, products resulting from hydrogen abstraction were mainly found. Jones and Shelnut have investigated the apparent rearrangement occurring during the addition of some meta-substituted arylcadmium compounds, prepared in situ from the corresponding Grignard reagents, to acetyl derivatives[19]:



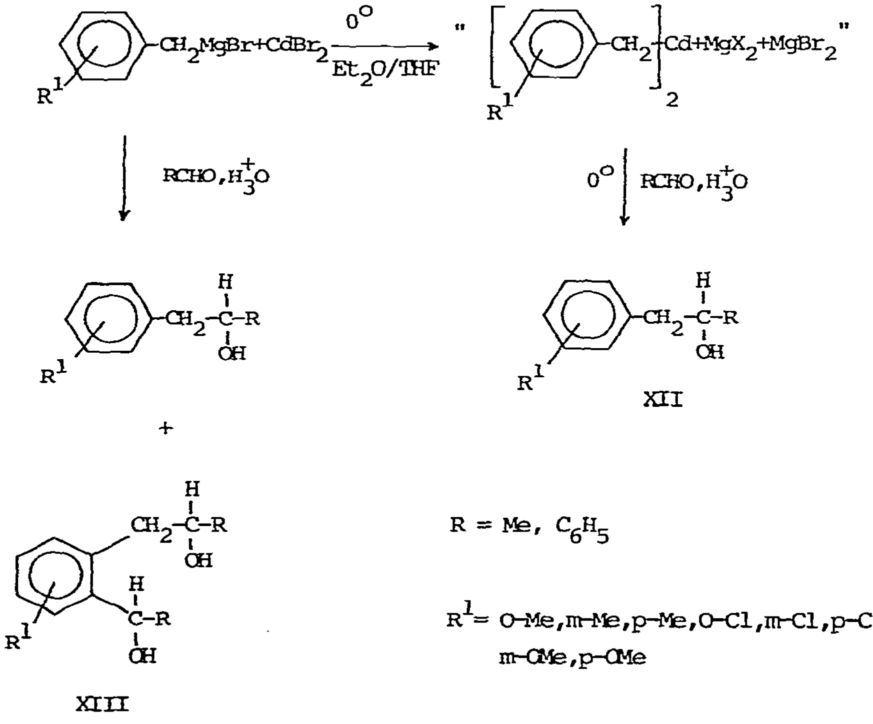
XI

$R = OMe, SMe, Me, F, CF_3$
$R^1 = Cl, Br, OCOMe, SCOMe$

It appeared that only those compounds (XI), in which R = OMe or SMe, yielded both the expected meta- and the unexpected para-substituted product. This phenomenon was interpreted in terms of the directing effect of the substituent meta to the original cadmium and is consistent with the following intermediate species:



Here, the cadmium acts as an internal Lewis acid.
In contrast to non-substituted or substituted benzylic Grignard reagents, the corresponding cadmium compounds react with aldehydes to give exclusively secondary benzylic alcohols (XII) in good yield[20]:

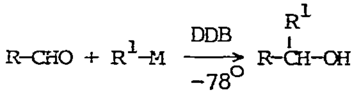


R = Me, C_6H_5

R^1= O-Me,m-Me,p-Me,O-Cl,m-Cl,p-Cl
m-OMe,p-OMe

In the case of acetaldehyde, the use of at least 8 moles of THF

per mole of cadmium reagent was necessary to suppress the formation of diol (XIII). In the other cases, diethylether alone could be used.
The (+) enantiomer of DDB (1,4-dimethylamino-2,3-dimethoxy-butane) has been used as a chiral co-solvent in enantioselective 1,2-additions of, amongst others, lithiumdiorganozincates and Reformatsky reagents to carbonyl compounds[21]:



$$R\text{-}CHO + R^1\text{-}M \xrightarrow[-78^{\circ}]{DDB} R\text{-}\overset{\overset{R^1}{|}}{C}H\text{-}OH$$

$R^1M = Bu_3ZnLi,\ BrZnCH_2COOEt,\ BrZnCH_2COOtBu$

Although the lithium diorganozincate behaved, as far as enantioselectivity was concerned, fully comparable to lithium, magnesium and copper reagents, the Reformatsky reagents showed different behaviour. In the latter cases, the enantiomer excess did not increase when more than one molequivalent of DDB was used. This behaviour had not been observed earlier for this chiral co-solvent.

III Organozinc- and organocadmium compounds as polymerization catalysts

A combination of an diorganozinc compound and polymers containing partially modified functional groups has been claimed as an efficient catalyst for the copolymerization of carbon dioxide and oxiranes[22]. In this way, propylene oxide was co-polymerized with carbon dioxide using a combination of diethylzinc and partially methylated poly(hydroxystyrene) as catalyst.
Bis(triethylgermyl)cadmium has been used as a catalyst to polymerize vinylic monomers to give metal-containing vinyl polymers[23].

IV Physical and spectroscopic studies

Lopatin and co-workers have investigated the electronic absorption spectra of a series of pentafluorophenyl derivatives of group II B and IV A elements, including $[(C_6F_5)_3Sn]_2Cd$[24]. It appeared that the position of the long-wavelength band in the spectra is similar for all compounds, indicating that the electronic transition is almost completely localized on the pentafluorophenyl nucleus. It was also found that in $[(C_6F_5)_3Sn]_2Cd$, intramolecular coordination between the cadmium atom and an ortho fluorine atom occurs.

Perichon and co-workers have carried out zero-current potential measurements on the reaction of zinc and cadmium halides with Grignard reagents in the presence of a halide acceptor-donor system in THF[25]. This was done to establish whether it would be possible to modify in this way the product composition and product reactivity.
It was possible, in the presence of a high, buffered, halide-ion concentration to obtain mixed organocadmium and organozinc species:

$$\underset{(Zn)}{Bu_4NCdX_3} + RMgX \rightleftharpoons \underset{(Zn)}{Bu_4NRCdX_2} + MgX_2$$

With a lower halide-ion concentration, R_2Zn and R_2Cd species were formed. These equilibria lie more to the right for $X = Cl^-$ than for $X = Br^-$.

References

1. I. Nishiguchi, Yuki Gosei Kagaku Kyokaishi, 37 (1979) 996
2. A.L. Galyer and G. Wilkinson, Inorg. Synth., 19 (1979) 253
3. K.J. Klabunde and T.O. Murdock, J. Org. Chem., 44 (1979) 3901
4. A. Osman and D.G. Tuck, J. Organometal. Chem., 169 (1979) 255
5. J.J. Habeeb, A. Osman and D.G. Tuck, Inorg. Chim. Acta, 35 (1979) 105
6. A.J. de Koning, P.E. van Rijn, J. Boersma and G.J.M. van der Kerk, J. Organometal. Chem., 174 (1979) 129
7. E.K.S. Liu and L.B. Asprey, J. Organometal. Chem., 169 (1979) 249
8. L. Rösch and G. Altnau, Angew. Chem., 91 (1979) 62
9. M. Mladenova, B. Blagoev and B. Kurtev, Bull. Soc. Chim. France, Pt. 2 (1979) 77
10. J.F. Fauvarque and A. Jutand, J. Organometal. Chem., 177 (1979) 273
11. J. Fajkos and J. Joska, Collect. Czech. Chem. Comm., 44 (1979) 251
12. M. Bellasoued, Y. Frangin and M. Gaudemar, J. Organometal. Chem., 166 (1979) 1
13. J. Pornet, B. Randrianoelina and L. Miginiac, J. Organometal. Chem., 174 (1979) 1
14. J. Pornet, B. Randrianoelina and L. Miginiac, J. Organometal. Chem., 174 (1979) 15
15. M. Bourhis, R. Golse and J.J. Bosc, C.R. Hebd. Seances Acad. Sci., Ser. C, 289 (1979) 379
16. Y.A. Aleksandrov, S.A. Lebedev, N.V. Kuznetsova and G.A. Razuvaev, J. Organometal. Chem., 177 (1979) 91
17. S.A. Lebedev, N.V. Kuznetsova, Y.A. Aleksandrov and V.E. Lelekov, Zh. Obshch. Khim., 49 (1979) 2263

18. A.M. Osman, A.I. Khodair, A.A. Abdel-Wahab and A.M. El-Khawaga, Can. J. Chem., 57 (1979) 1923

19. P.R. Jones and J.G. Shelnut, J. Org. Chem., 44 (1979) 696

20. C. Bernadon, Tetrahedron Lett., (1979) 1581

21. D. Seebach and W. Langer, Helv. Chim. Acta, 62 (1979) 1701

22. M. Nishimura, M. Kasai and H. Tsuchida, Jpn. Kokai Tokkyo Koho 79, 139, 994

23. Y.O. Sanchikov, N.L. Khvatov, V.G. El'son, V.T. Bychkov and S.N. Titova, U.S.S.R. 707, 929

24. M.A. Lopatin, V.A. Kuznetsov, A.N. Egorochkin and M.N. Bochkarev, Zh. Obshch. Khim., 49 (1979) 2257

25. C. Chevrot, Y. Rollin and J. Perichon, Bull. Soc. Chim. France, Pt. 2 (1979) 266