Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AUTOXIDATION OF ARYLCOPPER(I) COMPOUNDS

A. CAMUS and N. MARSICH
Institute of Chemistry and CNR Center, University of Trieste, 34127, Trieste (Italy)

(Received July 25th, 1972)

SUMMARY

The autoxidations of arylcopper(I) compounds (R = phenyl-, *o*-, *m*-, *p*-tolyl-, *o*-anisyl) have been studied in several solvents, and the yields of the main products have been determined. The results are compared with those obtained for the corresponding copper(I) lithium-ate complexes and lithium derivatives. Possible mechanisms of the autoxidation are discussed.

INTRODUCTION

Although the reactions of organometallic compounds with molecular oxygen have been studied systematically for the derivatives of many elements[1], very little is known about organocopper autoxidation. Information is limited to a study of the autoxidation of methylcopper in methanol[2], a brief account of the behaviour of fluorinated arylcopper compounds[3,4], and a few papers on the oxidative coupling of copper(I) lithium-ate complexes in the presence of organic halides[5,6].

This paper is concerned with the behaviour of suspensions of phenylcopper, *o*-, *m*-, *p*-tolylcopper and *o*-anisylcopper in ether, hydrocarbons, methanol and pyridine when treated with molecular oxygen. The study was mainly confined to determination of the reaction products, since the heterogeneous systems are not suitable for kinetic investigation. The autoxidations of ethereal solutions of some "ate" complexes of the above compounds and of the corresponding lithium derivatives are also considered. Aryllithium autoxidations have been studied several times previously[7], but the different experimental conditions precluded useful comparison with our results.

RESULTS AND DISCUSSION

(1). *Autoxidation products*

The autoxidation products consist of both soluble organic compounds and insoluble copper-containing compounds. The average yields of the main products in different solvents, their ratios, and the total combined yield of identified aromatic products are listed in Tables 1 and 2.

The main soluble products from the arylcopper autoxidations are diarenes (RR), arenes (RH), and diaryl ethers (R_2O), along with traces of other compounds. Reactions in methanol give, in addition, anisole, methylanisoles, and *o*-methoxy-

(*continued on p.* 388)

TABLE 1

AVERAGE YIELDS[a] AND RATIOS OF THE MAIN AUTOXIDATION PRODUCTS FROM RCu IN SEVERAL SOLVENTS AT 0° (AFTER HYDROLYSIS)

Solvent	*R*	$[RR]/[Cu]$	$[ROH]/[Cu]$	$[R_2O]/[Cu]$	$[RH]/[Cu]$	$[ROCH_3]/[Cu]$	$[R_T]^b/[Cu]$	$[RR]/[ROH]$
Ether	Phenyl	0.265	0.28	0.023	0.095		0.95	0.95
	o-Tolyl	0.16	0.255	0.071	0.074		0.79	0.63
	m-Tolyl	0.305	0.28		0.020		0.91	1.1
	p-Tolyl	0.325	0.28	0.004	0.035		0.97	1.2
	o-Anisyl	0.19	0.30	N.d.[c]	0.12		0.80	0.63
Pentane	Phenyl	0.255	0.25	0.009	0.030		0.81	1.0
	o-Tolyl	0.165	0.24	0.065	0.069		0.77	0.69
	m-Tolyl	0.265	0.23		0.028		0.79	1.1
	p-Tolyl	0.31	0.215	0.007	0.015		0.86	1.4
	o-Anisyl	0.16	0.26	N.d.	0.10		0.68	0.61
Xylene	Phenyl	0.24	0.24	0.013	0.077		0.80	1.0
	o-Tolyl	0.155	0.25	0.096	0.060		0.81	0.62
	m-Tolyl	0.31	0.24		0.053		0.91	1.3
	p-Tolyl	0.26	0.17	0.009	0.10		0.81	1.5
	o-Anisyl	0.21	0.27	N.d.	0.088		0.78	0.78
MeOH	Phenyl	0.098	0.205	0.003	0.44	0.11	0.96	0.48
	o-Tolyl	0.06	0.16	0.005	0.60	0.085	0.97	0.37
	m-Tolyl	0.175	0.20		0.36	0.11	1.0	0.88
	p-Tolyl	0.14	0.13		0.485	0.086	0.98	1.1
	o-Anisyl	0.11	0.18	N.d.	0.53	0.10	1.0	0.61
Pyridine	Phenyl	0.16	0.09	0.003	0.35		0.77	1.8
	o-Tolyl	0.085	0.03	0.019	0.395		0.63	2.8
	m-Tolyl	0.16	0.06		0.37		0.75	2.7
	p-Tolyl	0.21	0.045		0.31		0.77	4.7

[a] Average values of 2–4 experiments on different preparations. [b] $[R_T] = 2[RR] + 2[R_2O] + [ROH] + [RH] + $[other identified aryl derivatives]. [c] N.d. = not determined.

TABLE 2

AVERAGE YIELDS AND RATIOS OF MAIN AROMATIC AUTOXIDATION PRODUCTS FROM ETHEREAL SOLUTIONS OF "ATE" COMPLEXES AND LITHIUM DERIVATIVES AT 0° (AFTER HYDROLYSIS)

	$[RR]/[Li]$[a]	$[ROH]/[Li]$	$[R_2O]/[Li]$	$[RH]$[b]$/[Li]$	$[MeRCHOH]/[Li]$	$[RBr]/[Li]$	$[R_T]/[Li]$[c]	$[RR]/[ROH]$	$[RH]/[ROH]$
From CuBr + 2 Phenyllithium	0.265	0.335		0.044		N.d.[d]	0.91	0.79	0.13
From CuBr + 2 *o*-Tolyllithium	0.29	0.295	0.001	0.042		N.d.	0.92	0.98	0.14
From CuBr + 2 *m*-Tolyllithium	0.31	0.325		0.048		0.005	0.99	0.95	0.14
From CuBr + 2 *p*-Tolyllithium	0.31	0.305		0.072		0.002	1.00	1.01	0.24
From CuBr + 2 *o*-Anisyllithium	0.23	0.365	0.011	0.048		N.d.	0.90	0.63	0.13
Phenyllithium	0.043	0.335		0.34	0.16	N.d.	0.92	0.13	1.01
o-Tolyllithium	0.048	0.335	0.005	0.38	0.17		0.99	0.14	1.13
m-Tolyllithium	0.038	0.29		0.375	0.15		0.89	0.13	1.29
p-Tolyllithium	0.063	0.285		0.37	0.175		0.96	0.22	1.30
o-Anisyllithium	0.047	0.36	0.003	0.26	0.075		0.80	0.13	0.73

[a] Original concentration of organic lithium = [Cu] + [Li] in the "ate" complexes. [b] Small amounts of RH were present in the starting reagents, so the uncorrected values in this column may be too high. [c] $[R_T] = 2\,[RR] + [ROH] + 2\,[R_2O] + [RH] + [\text{other identified aromatic derivatives}]$. [d] N.d. = not determined.

anisole. Diaryl ethers are formed in only very small amounts from "ate" complexes, and never from aryllithium compounds; the latter give numerous unidentified additional by-products.

At the end of the reaction copper is present as copper(II), in insoluble form. The IR spectra of the suspensions isolated after autoxidation of arylcopper derivatives in ether or hydrocarbons show clear analogies with those of copper phenates[8], while the solid residue isolated after autoxidation in methanol is mainly Cu^{II} methoxide. Cupric oxide and tars are also present among the solid products.

Tars are formed in significant amounts, especially in the autoxidations of the pyridine *ortho*-substituted phenyl derivatives, in agreement with the rather low total combined yields of identified products from the aromatic radical. Their IR spectra and solubilities suggest that they could be mixtures of polyhydroxy and polymeric phenols*.

On hydrolysis of the oxidized suspensions, large amounts of phenols (ROH) are liberated; aryllithium compounds give also (methyl)(aryl)carbinols (MeRCHOH) and ethanol**. From a quantitative point of view the principal feature of the results for the organocopper compounds is the dramatic decrease in dimer formation when *ortho*-substituted compounds are used, whatever the solvent. Aryl ether yields, on the contrary, are at a maximum for the *ortho*-derivatives. The best phenol yields are obtained in ether. "Ate" complexes and lithium derivatives*** give comparable phenol yields, higher than those of arylcopper compounds, but differ clearly in that the ratios of diarenes and arenes are inverted.

(2). *Autoxidation rate*

Typical oxygen uptakes for phenylcopper, *o*-, *m*-, *p*-tolylcopper and *o*-anisylcopper in ether are plotted against time in Fig. 1. Radical scavengers (1–2 mmoles % of hydroquinone or *N*-tetramethyl-*p*-phenylendiammine) do not much affect the reaction rate, which largely depends on the purity of the sample: the purer the reacting compounds, the slower the autoxidation. LiBr (but not LiCl or LiI), added to the pure organocopper compound suspended in ether eliminates the induction period, and increases the initial autoxidation rate markedly.

The order of the reaction rate, *viz.*, *p*-tolyl > *m*-tolyl > *o*-tolyl ≫ phenyl ≫ *o*-anisyl, applies also in the other solvents, with a decreasing rate in the order: pyridine > MeOH > xylene > ether > pentane. In pyridine and MeOH, however, arylcopper compounds clearly undergo competing solvolyses.

The autoxidations of ethereal solutions of "ate" complexes and lithium derivatives are complete in a few minutes. However, it should be noted that, having been prepared *in situ*, they both contain large amounts of LiBr, which may exercise a considerable influence.

(3). *Oxygen uptake*

Average oxygen uptake values for the autoxidation of arylcopper compounds,

---

* Pyrocatechol was identified among the products from the phenylcopper reaction, while the tar isolated from *p*-tolylcopper contained also at least two oxygen atoms for each aromatic ring.

** The formation of products of this kind has been reported frequently in the autoxidation of lithium derivatives[9a] or Grignard reagents[9b].

*** Under the experimental conditions used, the reported difference between the behaviour of phenyl- and tolyllithium compounds[10] was not observed.

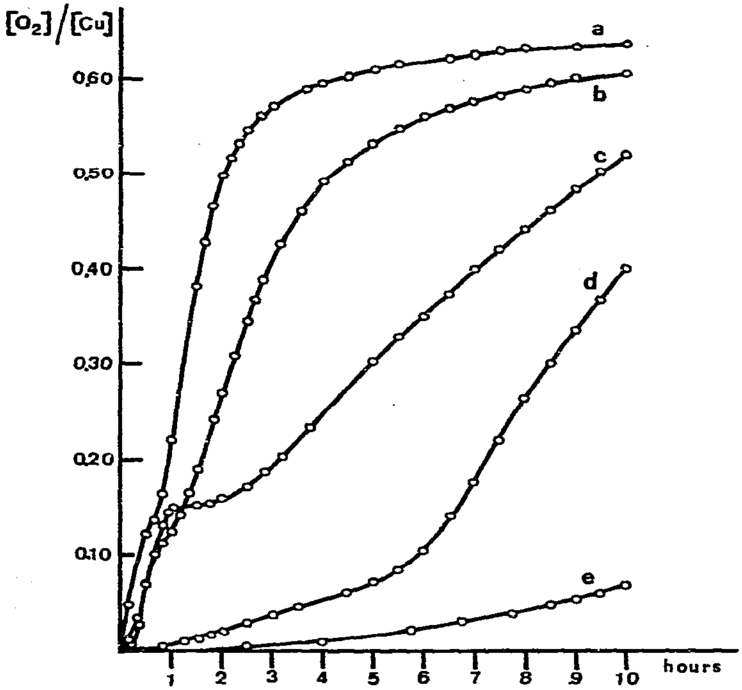

Fig. 1. The variation of the oxygen uptake with time for RCu in ether: R = a) *p*-tolyl, b) *m*-tolyl, c) *o*-tolyl, d) phenyl, e) *o*-anisyl.

TABLE 3

A. Average oxygen uptake: $[O_2]/[Cu]$, *in RCu oxidation in different solvents at* 0°

R	*Ether*	*Pentane*	*Xylene*	*MeOH*	*Pyridine*
Phenyl	0.52	0.55	0.62	0.51	>0.60
o-Tolyl	0.53	0.58	0.71	0.47	>0.96
m-Tolyl	0.60	0.63	0.73	0.54	>0.84
p-Tolyl	0.61	0.58	0.72	0.48	>0.91

B. Average oxygen uptake[a]: $[O_2]/[Li]^b$, *in "ate" complexes and lithium derivatives in ethereal solutions at* 0° *(not isolated compounds)*

CuBr + 2 Phenyllithium	(0.50)	0.49	Phenyllithium	(0.41)	0.39
CuBr + 2 *o*-Tolyllithium	(0.52)	0.48	*o*-Tolyllithium	(0.40)	0.39
CuBr + 2 *m*-Tolyllithium	(0.48)	0.47	*m*-Tolyllithium	(0.41)	0.39
CuBr + 2 *p*-Tolyllithium	(0.50)	0.48	*p*-Tolyllithium	(0.40)	0.39
CuBr + 2 *o*-Anisyllithium	(0.48)	0.46	*o*-Anisyllithium	(0.40)	0.39

[a] The absorption curves show a maximum indicated by the value in parentheses. [b] Original concentration of organic lithium = [Cu] + [Li] in "ate" complexes.

"ate" complexes and lithium derivatives are listed in Table 3. In inert solvents they amount to about 0.6 moles of oxygen for each metal atom in the organocopper compounds, while lower values were found for the other derivatives, probably owing

TABLE 4

AUTOXIDATION PRODUCTS AFTER VARIOUS TIMES FOR REACTIONS IN PENTANE AT 0°

Compound	(*h*)	$[O_2]/[Cu]$	*RCu in solution*	$[RR]/[Cu]$	$[ROH]/[Cu]$	$[R_2O]/[Cu]$	$[RH]/[Cu]$ *Before* (*after*) *hydrolysis*	$[RR]/[ROH]$	$[R_2O]/[ROH]$	$[R_T]^a/[Cu]$
o-Tolylcopper	1½	0.11	Present	0.095	0.049	0.056	0.044 (0.616)	1.96	1.16	0.97
o-Tolylcopper	3	0.16	Traces	0.119	0.073	0.061	0.041 (0.553)	1.63	0.83	0.99
o-Tolylcopper	6½	0.25		0.134	0.126	0.067	0.045 (0.401)	1.06	0.53	0.93
o-Tolylcopper	9	0.41		0.155	0.175	0.074	0.050 (0.246)	0.89	0.42	0.88
o-Tolylcopper	36	0.71		0.150	0.224	0.077	0.049 (0.050)	0.66	0.34	0.73
m-Tolylcopper	2½	0.08	Present	0.117	0.036		0.023 (0.725)	3.23		0.99
m-Tolylcopper	4	0.22	Traces	0.276	0.100		0.030 (0.219)	2.76		0.87
m-Tolylcopper	6	0.44		0.274	0.166		0.020 (0.047)	1.64		0.76
m-Tolylcopper	9	0.62		0.270	0.203		0.020 (0.028)	1.33		0.77

[a] $[R_T] = 2[RR] + [ROH] + 2[R_2O] + [RH \text{ after hydrolysis}]$.

to competing side-reactions with the solvent (*e.g.*, methylcarbinol formation in the case of lithium derivatives). In most of the reactions, the oxygen uptake clearly shows two steps. The point of inflection corresponds experimentally to the disappearance of the organometallic compound in solution; however, at this point large amounts of arene are still formed on hydrolysis. After this stage the oxygen uptake increases again, but the gas is partly used in secondary reactions, which show up in tar formation.

(4). *Autoxidation mechanisms*

The autoxidation of organometallic compounds has often been assumed to proceed by a polar mechanism, involving coordination of oxygen to the metal, followed by a nucleophilic rearrangement, to form first, an organoperoxymetallic derivative and then, in the presence of an excess of the original product, an alkoxide[11]. Recently, however, to account for the formation of RH and RR, which has been repeatedly observed in these processes, it has been suggested that the reaction takes place wholly or partly by a free radical mechanism[12], and this is confirmed by recent new evidence[13]. The reaction of the free radicals with themselves or with the solvent becomes particularly important for arylmetallic derivatives, because either oxygen does not add to aryl radicals or any aryl peroxides formed undergo rapid decomposition.

Both homolytic* and polar mechanisms are probably involved in the autoxidation of organocopper compounds**. For arylcopper derivatives in inert solvents, neglecting diaryl ether formation, the reaction has the following approximate stoichiometry:

$$6\,\mathrm{CuR} + \tfrac{7}{2}\,\mathrm{O_2} \rightarrow 2\,\mathrm{RR} + \mathrm{Cu(OR)_2} + 5\,\mathrm{CuO}$$

In some experiments, samples were analyzed at various times before completion of the oxygen uptake. In pentane (Table 4) and in the other solvents, the diarene/phenol ratio was found to be high at the beginning of the reaction and to decrease with time. The amounts of arene, on the other hand, are constant during the whole process, and hence not relevant to the autoxidation. The amount of RH is negligible in comparison with that of the dimer, which suggests the existence of an intermediate compound between at least two arylcopper molecules and O_2, from which aryl groups would be expelled in pairs to give diarene. The evidence is not sufficient, however, to indicate whether the dimer and phenol are formed in consecutive or competing reactions***.

"Ate" complexes and lithium derivatives show very similar patterns of oxygen uptake, which implies that similar mechanisms are probably involved. Arenes and methylcarbinols, which are formed in large amounts from the aryllithium compounds,

---

* The negligible influence of radical scavengers on the reaction rate does not rule out a free radical mechanism, because they may be ineffective in reactions with the chain-carrying species and/or be deactivated by direct reaction with the organocopper compounds.

** Ligand transfer oxidations[14] may also be involved in the side-reactions, *e.g.*, in the formation of methoxy derivatives in methanol, which requires the intermediate formation of $\mathrm{Cu^{II}}$ dimethoxide.

*** *Note added in proof.* On the basis of a recent structural study[18] there could be a cluster of six copper atoms in a distorted octahedral arrangement. The non equivalence of the axial and planar metal atoms could explain, in quantitative agreement with the experimental results, the different fate of the aryls bonded to them.

are, however, formed in only very small or undetectable amounts from the "ate" complexes. They are probably formed by a free radical mechanism, and in the "ate" complexes, in which two R's are bonded to the same metal atom, the dimer formation will be favoured by cage effect***. With both arylcopper compounds and "ate" complexes, the dimer formation thus appears to occur preferentially within the organometallic compound, without intervention of long-lived free radicals.

The increase in the reaction rate for the arylcopper in the presence of LiBr is probably due to partial formation of an easily oxidizable mixed "ate" complex. In agreement with this, the mixture obtained from ethereal suspensions of the organometallic in the presence of the halide shows a marked basic reaction after hydrolysis, and the ratios of the autoxidation products are shifted towards the values obtained for "ate" complexes.

EXPERIMENTAL

Materials

Arylcopper compounds were prepared and isolated as previously described[15]. Lithium derivatives were not isolated, but the solutions were filtered before use. "Ate" complexes were prepared *in situ* by the reaction at 0° between copper(I) bromide and aryllithium compounds in 1/2 ratio. The absence of an excess of lithium derivative in the "ate" complexes was confirmed by the Gilman test[16].

Dry, freshly redistilled solvents were used. Research-grade oxygen was further purified and dried by passage through a column of KOH pellets and through a vessel cooled in an acetone/CO_2 bath.

Autoxidation procedure

The organocopper compounds (3–4 mmoles) were suspended with vigorous stirring in 5 ml of solvent*. After cooling at $-80°$ the container was evacuated, immersed in ice and connected to a thermostatted burette, containing oxygen at atmospheric pressure. Reactions were carried on until the oxygen uptake became negligible. The uptake of gas with time was measured. Corrections were made for the amount of oxygen necessary to saturate the solvent.

During the reactions the yellow colour of the arylcopper suspensions turned to brown-black, or to blue-grey in methanol, while the viscosity increased, reaching a maximum corresponding with the point of inflection (see Fig. 1) and then decreased slowly. With the "ate" complexes, black suspensions were immediately formed, while solutions of lithium derivatives became deep yellow.

Analytical part

The oxidized sample was analysed by GLC. It was then quenched with 2 ml of water**, and the analysis was repeated in order to ascertain which low boiling

---

* Autoxidation in absence of solvent caused explosions.

** Direct hydrolysis with HCl gave also small amounts of chloro derivatives. Since they are not formed from the original organocopper compounds, they probably come from secondary reactions of the phenols[17].

*** *Note added in proof.* This suggestion is confirmed by the first newly reported structure of a copper(I)-lithium-ate complex[19].

products had been formed by hydrolysis, and to check the amount of arene, which increases in incomplete reactions. 10 ml HCl 1/1 were subsequently added, the aqueous layer was extracted four times with 20 ml portions of ether, and the extracts were subjected again to GLC, to determine the nature of the high-boiling hydrolysis products.

The main products were separated chemically or by GLC, and identified by elemental analysis and/or IR spectrophotometry. In particular the identity of diarenes, cresols, *o,o*-ditolyl ether, and *p*-methylanisole was confirmed. The other components were identified by TLC and GLC by comparison with the retention times of authentic samples on two columns of different polarity.

Quantitative analyses were carried out with 2 m columns of Carbowax 20M or Silicone OS 200, with a temperature-programmed C. Erba Model GT gas chromatograph in the range 120–200°. Suitable internal standards were used, and response factors determined for the major components.

The total amount of copper in the sample was determined by weighing the organometallic compound before the autoxidation, a check of the copper content of the stock having been previously made.

ACKNOWLEDGEMENTS

Financial support by CNR (Rome) is gratefully acknowledged. We thank Prof. G. Costa for helpful discussions.

REFERENCES

1 G. Sosnowski and J. H. Brown, *Chem. Rev.*, 66 (1966) 529 and references therein; T. G. Brilkina and V. A. Shushunov, *Reaction of organometallic compounds with oxygen and peroxides*, Iliffe Books Ltd., London, 1969.

2 G. Costa, A. Camus and N. Marsich, *J. Inorg. Nucl. Chem.*, 27 (1965) 281.

3 A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, 90 (1968) 2186.

4 R. J. de Pasquale and C. Tamborski, *J. Org. Chem.*, 34 (1969) 1736.

5 G. M. Whitesides, J. San Filippo, C. P. Casey and E. J. Panek, *J. Amer. Chem. Soc.*, 89 (1967) 5302.

6 G. M. Whitesides, W. F. Fischer, J. San Filippo, R. W. Bashe and H. O. House, *J. Amer. Chem. Soc.*, 91 (1969) 4871.

7 H. Hock, H. Kropf and F. Ernst, *Angew. Chem.*, 71 (1959) 541 and references therein; G. A. Razuvaev and G. G. Petukhov, *Tr. Khim. Khim. Tekhnol.*, 4 (1961) 150; *Chem. Abstr.*, 55 (1961) 27169 g; G. A. Razuvaev, E. V. Mitrofanova and G. G. Petukhov, *Zh. Obshch. Khim.*, 31 (1961) 2343; *Chem. Abstr.*, 56 (1962) 4786 b; H. S. Chang and J. T. Edward, *Can. J. Chem.*, 41 (1963) 1233.

8 A. Camus and N. Marsich, unpublished work.

9a H. Hock and F. Ernst, *Chem. Ber.*, 92 (1959) 2732 and references therein;

9b M. S. Kharash and O. Reinmuth, *Grignard reactions of non metallic substances*, Prentice Hall, New York, 1954, p. 1268–1269; C. Walling and S. A. Buchler, *J. Amer. Chem. Soc.*, 77 (1955) 6032.

10 E. Müller and T. Töpel, *Chem. Ber.*, 72 (1939) 273.

11 A. G. Davies, *Organic peroxides*, Butterworths, London, 1961 p. 124–126; T. G. Brilkina and V. A. Shushunov, *Russ. Chem. Rev.*, 35 (1966) 613.

12 E. Müller (Ed.), Houben-Weyl, *Methoden der organischen Chemie*, vol XIII/1, G. Thieme, Stuttgart, 1970, p. 553.

13 A. G. Davies, K. V. Ingold, B. P. Roberts and R. Tudor, *J. Chem. Soc. B*, (1971) 698 and references therein; R. V. Winchester, *Can. J. Chem.*, 49 (1971) 1748.

14 C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 94 (1972) 856.

15 G. Costa, A. Camus, L. Gatti and N. Marsich, *J. Organometal. Chem.*, 5 (1966) 568; A. Camus and N. Marsich, *J. Organometal. Chem.*, 14 (1968) 441.
16 H. Gilman and R. Jones, *J. Amer. Chem. Soc.*, 62 (1940) 1243.
17 H. P. Crocker and R. Walser, *J. Chem. Soc. C*, (1970) 1982.
18 J. M. Guss, R. Mason, K. M. Thomas, G. van Koten and J. G. Noltes, *J. Organometal. Chem.*, 40 (1972) C79.
19 G. van Koten and J. G. Noltes, *Chem. Commun.*, (1972) 940.

JOURNAL OF ORGANOMETALLIC CHEMISTRY, VOL. 46 (1972)

AUTHOR INDEX