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REACTIONS OF GROUP IVB METAL DIHALIDES WITH η^1 -ALLYL COMPLEXES
OF η^5 -CYCLOPENTADIENYLDICARBONYLIRON[†]

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Summary

The reactions of tin(II) chloride in tetrahydrofuran with the η^1 -allyl systems, $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe allyl}]$, have been reexamined, and an extension made to SnBr_2 and GeCl_2 .dioxan. The insertion compounds, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_2 \text{ allyl}]$, which contain the Group IVB element bound to iron, are the major products, but, in the presence of excess metal dihalide, these slowly react to form the trihalometal compounds $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_3]$. The insertion reactions are inhibited by small amounts of a radical scavenger, and occur initially with allylic rearrangement. In methanol, the process is more complex; an unknown species, possibly an iron-olefin dipolar intermediate, and substantial amounts of trihalometal-iron compounds are formed additionally. A mechanistic scheme for the processes is discussed.

Introduction

The reactions, in tetrahydrofuran, of tin(II) chloride with the η^1 -allyl systems, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeR}]$, ($\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CMe}=\text{CH}_2$,

[†] No reprints available.

$\text{CH}_2\text{CH}=\text{CHMe}$, and $\text{CH}_2\text{CH}=\text{CMe}_2$), which primarily yield the insertion products, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_2\text{R}]$, have recently been studied [1] and interpreted in terms of the reaction scheme proposed [2] for the reactions of electrophiles such as SO_2 and $\text{C}_2(\text{CN})_4$ with similar systems. The insertion reactions are similar, in stoichiometric terms, to those we have studied [3] for GeCl_2 .dioxan, SnCl_2 , and SnBr_2 in a series of corresponding iron-alkyl compounds, but are different in that for $\text{R} = \text{CH}_2\text{CMe}=\text{CH}_2$, with SnCl_2 , or if the reaction is carried out in methanol, the organic ligand is displaced, yielding the trichlorotin complex, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_3]$ as the major product.

Our initial interest in this area was in the form of a routine extension from alkyl to allyl systems to study the electrophilic properties of GeCl_2 .dioxan, but several observations made during this work prompted us also to reexamine the reactions of tin(II) halides. The results of our work are reported here, together with some qualifying comment on the proposed mechanism.

Experimental

All handling operations were carried out under nitrogen, or preferably argon, using standard Schlenk techniques. Reactions were monitored by IR (P.E. 457 spectrophotometer), with solution extracts being evaporated to dryness and redissolved in cyclohexane, and ^1H NMR spectroscopy (Varian EM360). The standard procedure involved the preparation of an approximately 0.35 M solution of the iron-allyl compound, in either THF or methanol, to which was added the metal(II) halide. In the investigation of the initial stages of reaction (up to 1 hour), the resultant solution was quickly syringed into NMR tubes which were capped under nitrogen or argon. For the studies over longer reaction times, the solutions were carefully degassed in NMR tubes which were then evacuated and sealed. The allyl

compounds, $[(\eta^5\text{-Cp})(\text{CO})_2\text{FeR}]$, ($\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CMe}=\text{CH}_2$, and $\text{CH}_2\text{CH}=\text{CHMe}$), were prepared by reactions of $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}]^-$ with the appropriate allyl halide. Purification for $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$ involved chromatography, in hexane on alumina (Grade II/III), followed by short-path distillation ($50^\circ\text{C}/10^{-2}$ mm); for $\text{R} = \text{CH}_2\text{CMe}=\text{CH}_2$ (which decomposed under the chromatographic conditions), distillation alone; and, for $\text{R} = \text{CH}_2\text{CH}=\text{CHMe}$ (a mixture (NMR) of cis and trans isomers), chromatography followed by removal of hexane from the thermally sensitive product at room temperature. Small amounts (up to 5%) of the η^3 -allyl compounds, $[\eta^5\text{-Cp}(\text{CO})\text{Fe}(\eta^3\text{-allyl})]$ were inevitably present (NMR) as impurities. GeCl_2 .dioxan was prepared by the established procedure [4]. Anhydrous SnCl_2 (Ajax) and SnBr_2 (ROC-RIC) were dried ($100^\circ\text{C}/10^{-2}$ mm) commercial samples. Methanol- d^1 was dried by reflux with magnesium and distilled, under nitrogen, onto molecular sieve 3A^0 . Tetrahydrofuran was distilled from calcium hydride. Reactants and products were identified in solution by their characteristic chemical shifts in the $\eta^5\text{-Cp}$ region and by their infrared spectra in the carbonyl stretching region [e.g. $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_2\text{-(CH}_2\text{CH}=\text{CH}_2)]$, δ (in THF, referenced to internal TMS), 5.17 ppm; ν_{CO} 2030 m, 2024 s, 1990 sh, 1983 s cm^{-1} in C_6H_{12} ; compare $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CH}_2)]$, δ (in THF) 4.72 ppm; ν_{CO} 2014 s, 1961 s cm^{-1} in C_6H_{12} , and $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_3]$, δ (in THF) 5.37 ppm; ν_{CO} 2045 s, 2004 s cm^{-1} in C_6H_{12}]. The SnCl_2 insertion compounds have been fully characterized elsewhere [1]. Only small differences were noted for the corresponding GeCl_2 and SnBr_2 compounds (e.g. $[\eta^5\text{-Cp}(\text{CO})_2\text{FeGeCl}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$, δ (in THF) 5.12 ppm; ν_{CO} 2037 m, 2029 s, 1992 m, 1985 s cm^{-1} in C_6H_{12}) and were unexceptional. NMR proved the more sensitive probe (peaks, interestingly, were sharp especially in the presence of excess metal(II) halide which appears to act as an anti-oxidant), but was unfortunately unable to

distinguish the possible presence of small amounts of materials such as $[\eta^5\text{-Cp}(\text{CO})_2\text{FeCl}]$ and $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$, the $\eta^5\text{-Cp}$ peaks for which are very close to those of the insertion compounds.

Results

The reactions, in THF at room temperature, of equimolar amounts of SnCl_2 , SnBr_2 , and GeCl_2 .dioxan with $[\eta^5\text{-Cp}(\text{CO})_2\text{FeR}]$, ($\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CH}_2\text{CMe}=\text{CH}_2$), straightforwardly and very rapidly gave the insertion compounds in essentially quantitative yields. The reactions were fastest for GeCl_2 .dioxan (complete within 10 minutes), but even the slower tin(II) halide reactions were complete within 20 minutes. These observations contrast markedly with the 24 hour reaction periods described elsewhere [1]. In each reaction, a small amount of a side product, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_3]$, was also noted; for SnCl_2 and GeCl_2 .dioxan this was in less than 5% yield, but $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnBr}_3]$ was formed in appreciably higher ($\sim 10\%$) amounts. No change in this initial reaction course was observed, for SnCl_2 and GeCl_2 .dioxan, with both allyl derivatives up to molar ratios Fe allyl: MX_2 of 1:3, and no change was noted for the reaction of SnBr_2 with the iron-allyl compound. However, the reaction of excess SnBr_2 with $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CMe}=\text{CH}_2)]$ gave larger amounts of the tribromostannyl-iron compound (e.g. 50% yield for a 1:3 molar ratio which increased in proportion to the amount of excess SnBr_2). We attribute this to a hydrolytic side reaction associated with our failure completely to dry the SnBr_2 , and have observed a similar production of the trichlorostannyl compound in reactions of excess moist SnCl_2 , but again only for the 2-methylallyl substituent.

The presence of excess GeCl_2 .dioxan and SnBr_2 promoted a separate and very slow "dark" reaction, with both allyl compounds, again to form $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_3]$. Thus, for $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CMe}=\text{CH}_2)]$

and GeCl_2 .dioxan, in a molar ratio of 1:2.5, an approximately 19% yield of $[\eta^5\text{-Cp}(\text{CO})_2\text{FeGeCl}_3]$ build up after 5 days, as the amount of the first-formed insertion compound proportionately decreased. For the allyl system, a 37% yield was observed at a similar time. With SnBr_2 , this further reaction was slightly slower, but, for $\text{R} = \text{CH}_2\text{CMe}=\text{CH}_2$, was obscured by the extent of the hydrolysis reaction which gives the same product. The reaction with excess SnCl_2 was insignificant for the iron-allyl compound, and exceedingly slow (8% of $[\eta^5\text{-Cp}(\text{CO})_2\text{-FeSnCl}_3]$ after 24 days) for the 2-methallyl derivative. For each metal(II) halide, the formation of the trihalometal-iron compounds was faster if plastic-capped, rather than sealed and evacuated, NMR tubes were used, but this probably reflects additional reactions induced by oxygen and water impurities.

Interestingly, the insertion reaction was completely inhibited by the addition of a small amount (~ 5 mole %) of the radical scavenger, 1,1-diphenylpicrylhydrazyl. For example, in the attempted reaction of $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CH}_2)]$ with SnCl_2 in THF under these conditions, only traces of $[\eta^5\text{-Cp}(\text{CO})_2\text{FeCl}]$ were detected (IR) after 24 hours at room temperature.

Reactions of GeCl_2 .dioxan, SnCl_2 , and SnBr_2 with the 2-butenyl (crotyl) complex, $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CHMe})]$, were distinctly slower than with the other allyl systems. Interestingly, the rearranged insertion product $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_2(\text{CHMeCH}=\text{CH}_2)]$ was formed first, which then converted, at a rate which was proportional to the excess of metal(II) halide present, to the unrearranged form, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_2(\text{CH}_2\text{CH}=\text{CHMe})]$. The process could be clearly followed from observation of the ^1H NMR spectra, in which the different chemical shift associated with the CH_2 protons in each group is the most characteristic feature. The general changes in the spectra were similar to those observed in rearrangement reactions in SO_2 insertion

into η^1 -allyl-iron [5] and allyl-tin [6] systems, and were incompatible with a cis-trans isomerization of the crotyl group [5]. Thus, for GeCl_2 .dioxan in d^8 -THF, the characteristic resonances of the mixed cis-trans crotyl starting material (δ (ppm): 1.3 (m, CH_3); 1.9 (m, CH_2); 4.50 (s, Cp); 4.56 (s, Cp); 5.2 m $\text{CH} = \text{CHMe}$) disappeared within 3 minutes and were replaced by those of a mixture of the rearranged insertion product [δ : 1.34 (br d, $J \sim 7\text{Hz}$, CH_3); 4.53 (m, CH_2 ?); 5.13 (s, Cp); 5.93 (m, $\text{CH} = \text{CH}_2$, width $\sim 40\text{ Hz}$)], which predominated initially, and the unrearranged form [δ : 1.62 (br d, $J \sim 5\text{ Hz}$, CH_3); 2.49 (m, CH_2); 5.11 (s, Cp); 5.53 (m, $\text{CH} = \text{CHMe}$, width $\sim 14\text{Hz}$)] which became the major product as the reaction proceeded. The extent of isomerization was conveniently monitored simply by observation of the single η^5 -Cp resonance for each form; for equimolar amounts in the above reaction it was about 50% complete after one hour, but, for a crotyl-iron complex to GeCl_2 .dioxan ratio of 1:2.5, isomerization was 75% complete within 3 minutes. In a reaction mixture with a 40% deficiency of GeCl_2 .dioxan, the rearranged product was stable indefinitely. Similar observations, largely of the η^5 -Cp peaks and the low field CH multiplet were made in the reactions with SnCl_2 and SnBr_2 in THF. In these cases the rate of insertion (reaction $\sim 50\%$ complete after 10 minutes) was comparable with the rate of isomerization, and it was therefore not possible to stabilize the rearranged form in reaction mixtures which had a deficiency of tin(II) halide. Interestingly, the insertion reaction with SnCl_2 in d^8 -THF was much slower (50% complete after 1 hour) and only the unrearranged product is observed [δ (ppm): 1.58 (br d, $J \sim 6\text{Hz}$, CH_3); 2.60 (m, CH_2); 5.12 (s, Cp); 5.52 (m, $\text{CH} = \text{CHMe}$)]. The rate reduction is probably related to the observed inhibition by radical scavengers, which could be present as impurities in the d^8 -THF sample.

The interaction of all three allyl-iron compounds with SnCl_2 and SnBr_2 was also studied in CH_3OD , but GeCl_2 .dioxan was not investigated because of its reaction with the solvent [3]. The reactions had comparable rates to those observed earlier in THF. For $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CH}_2)]$ mixed with deficiency of SnCl_2 (molar ratio 1.0:0.4), the insertion compound (δ , 5.23 ppm, $\eta^5\text{-Cp}$) was the major product but an additional species ($\sim 20\%$ yield), associated with a singlet resonance at 5.66 ppm, was also observed. This unknown material was stable in solution over several hours. In similar reactions with excess SnCl_2 , the formation of $[\eta^5\text{-Cp}(\text{CO})_2\text{-FeSnCl}_3]$, (δ , 5.36 ppm), also occurred. Its amount increased slowly at the expense of the unknown low-field product which disappeared completely after 1 hour. The yield of the trichlorotin-iron compound also increased as the molar excess of SnCl_2 increased, reaching about 25% for a 100% excess. It should be noted that accurate assessment of yields was impossible because of slow precipitation of $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_3]$. Similar observations were made with SnBr_2 although these reactions were further complicated by the limited solubility of SnBr_2 .

The addition of SnCl_2 to $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CMe}=\text{CH}_2)]$ in CH_3OD resulted in almost immediate precipitation of $[\eta^5\text{-Cp}(\text{CO})_2\text{-FeSnCl}_3]$, even with deficiencies of SnCl_2 , and quantitative analysis of the system by NMR was impossible. However the insertion product (δ , 5.22 ppm) and the unknown (δ , 5.68 ppm) remained in solution; the latter, as in the previous system, slowly decreased in amount if excess SnCl_2 was present.

One experiment between the crotyl-iron complex and SnCl_2 (1:1) was also carried out in CH_3OD . As was observed for THF, this reaction was significantly slower (50% complete after 30 minutes) than with the other allyl-iron complexes. The major product

initially was the insertion product in the rearranged form (δ , 5.25 ppm, η^5 -Cp) which progressively isomerized to the unrearranged form (δ , 5.21 ppm). The unknown (δ , 5.71 ppm) was again observed; its resonance increased to a maximum of about 20% of the combined insertion product peaks, but then slowly disappeared, over 5 hours, with a concomitant increase in the amount of $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_3]$. About 10% of starting material remained unreacted.

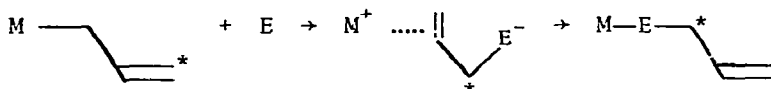
Discussion

Our results differ significantly from those previously reported [1] for this system with respect to the reaction rates, the inhibition of reaction by a radical scavenger, the observation of allylic rearrangement in the insertion process, and the conditions under which the side-product, $[\eta^5\text{-Cp}(\text{CO})_2\text{FeMX}_3]$, is formed.

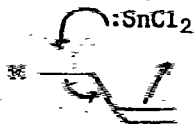
The indication of free-radical involvement, (possibly in a chain process, on the basis of the small amounts of scavenger required), parallels our observation for similar reactions in the $[\eta^5\text{-Cp}(\text{CO})_2\text{Fealkyl}]$ system, and is interesting in view of a recent proposal of a free-radical pathway in the oxidative-addition of alkyl or phenyl halides to $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ [7]. Working from the mechanism suggested for these reactions, the propagation step in the oxidative-addition of the allyl-iron group would involve the formation of $\cdot\text{SnCl}_2\text{allyl}$ radicals.

Although the details of free-radical intervention in the mechanism are clearly unknown at this stage, their involvement necessarily introduces a qualification to any reaction scheme of the type proposed by Magatti and Giering in their earlier study. Their mechanism was reasonably based on the general pathways suggested [2] for the reactions of electrophilic reagents, such as sulfur dioxide and tetracyanoethylene, with η^1 -allyl ligands bound to transition

metals, particularly in the complexes $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\eta^1\text{-allyl})]$. In this reaction, two distinct routes, insertion and cycloaddition, are operative, both based on the initial formation of a dipolar η^2 -olefin complex. When the electrophile (E) is sulfur dioxide, the olefin-metal complex (which in this case has been intercepted and characterized [8]) rearranges to a chain-inverted metal sulfone [5]. With tetra-cyanoethylene, the dipolar intermediate collapses through the attack of the anionic terminus on the coordinated olefin, to generate the cyclic product [2]. Only the former route is relevant to the metal(II) halide reactions and can be represented by:



There is no direct evidence from our work for the dipolar intermediate, but the observation of a low field resonance (δ , 5.7 ppm) in the cyclopentadienyl region of the ^1H NMR spectrum, for reactions in CH_3OD , gives tenuous support for its existence. The resonance corresponds closely to that found (δ , 5.6-5.7 ppm) for the dipolar intermediate formed in the reactions of a number of $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\eta^1\text{-allyl})]$ complexes in neat SO_2 [8], and to that observed (δ , \sim 5.6 ppm) in the cationic species $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-olefin})]^+$ which are generated by protonation of η^1 -allyl systems [9]. The very much enhanced rates observed for the reactions of the metal(II) halides with the η^1 -allyl compared with the η^1 -alkyl iron compounds are, in themselves, indirect evidence for an electrophilic attack of the style depicted above, and the observed allylic rearrangement is consistent with the scheme. However, both of the latter points could be equally well accommodated by a concerted process.

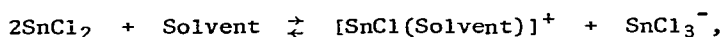


Additional to any mechanistic discussion of this type, whether or not free-radicals are involved, is the problem of the nature of the MX_2^- species in solution. For $SnCl_2$, for example, there are several possibilities. Unsolvated molecules and solvated species such as $SnCl_2 \cdot MeOH$ (note that adducts of this type are isolable with, for example, dioxan and DMSO [10]) are probably present, and there has been a report of the existence of moieties such as $[ClSnL]^+$ and $[SnCl_3]^-$ in donor solvents. [11] Although this uncertainty makes definitive mechanistic comment impossible, the possible existence of ionic species does allow for an interpretation of the side reactions to form $[\eta^5-Cp(CO)_2FeMX_3]$. These reactions appear to proceed by at least three routes, which may be mechanistically connected. Omitting the possibility of their promotion by atmospheric oxidation (which reaction could be deliberately induced and controlled), the process can be described stoichiometrically as a nucleophilic displacement of $RSnCl_2^-$ by $SnCl_3^-$ from the preformed insertion product. As suggested by Magatti and Giering [1], a basically similar displacement could take place from the dipolar intermediate. (Our observations of the inverse relationship between the amount of the unknown species (possibly the dipolar intermediate) and the amount of $[\eta^5-Cp(CO)_2FeSnCl_3]$ in reactions in CH_3OD , would tend to support the latter view). By either picture, the slow further reaction of excess $SnCl_2$, $SnBr_2$, and $GeCl_2 \cdot dioxan$ with the preformed insertion products in THF, can be rationalized by the generation, and subsequent reaction, of smaller amounts of a MX_3^- anionic species, e.g. by the process



Although the ligand displaced in each case, $[\text{RX}_2\text{M}]^-$, is unknown, it could be regarded, in solution, as X^- and RMX . The characterization of associated molecules such as RGeCl [12] and CpSnCl [13] provides some evidence for the latter. The tendency for these further reactions to occur, i.e. $\text{GeCl}_2 \cdot \text{dioxan} > \text{SnBr}_2 > \text{SnCl}_2$, may reflect the general thermodynamic stability of the RMX species.

The peculiar sensitivity of the $[\eta^5\text{-Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{CMe}=\text{CH}_2)]$ reactions, with SnCl_2 and SnBr_2 in THF, to water impurity probably has a similar explanation. The presence of water would promote the hydrolysis of SnCl_2 and SnBr_2 , and increase the concentration of the SnX_3^- ion. This would then compete more extensively via the nucleophilic displacement reaction (which can, in this case, be more easily pictured on the basis of the intermediacy of the dipolar metal-olefin complex). The relative increase in the production of $[\eta^5\text{-Cp}(\text{CO})_2\text{FeSnCl}_3]$ in the reactions in CH_3OD , particularly in the 2-methallyl-iron system, could be similarly interpreted; in the more polar solvent, the equilibrium,



will lie more to the right.

Finally we note the fact that in the crotyl insertion reactions, the rearranged product isomerizes to the thermodynamically favoured unrearranged form at a rate which is proportional to the excess of metal(II) halide present. Although at this stage we can offer no definitive interpretation, the observation suggests that a further electrophilic attack, this time of MX_2 on the η^1 -allyl ligand attached to the Group IVB metal, could be involved. The observation of only the thermodynamically favoured unrearranged insertion product in the earlier study [1] probably reflects simply the longer time scale involved.

Acknowledgements

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References

- 1 C.V. Magatti and W.P. Giering, *J. Organometal. Chem.*, 73 (1974) 85.
- 2 W.P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 93 (1971) 5299.
- 3 J.D. Cotton and G.A. Morris, *J. Organometal. Chem.*, 145 (1977) 245.
- 4 S.P. Kolesnikov, V.I. Shiryayev, and O.M. Nefedov, *Izv. Akad. Nauk, SSSR., Ser. Khim.*, (1966) 584.
- 5 R.L. Downs and A. Wojcicki, *Inorg. Chim. Acta*, 27 (1978) 91.
- 6 C.W. Fong and W. Kitching, *J. Organometal. Chem.*, 22 (1970) 107.
- 7 M.J.S. Gynane, M.F. Lappert, S.J. Miles and P.P. Power, *J. Chem. Soc. Chem. Commun.*, 1976, 256; *ibid*, 1978, 192
- 8 L.S. Chen, S.R. Su, and A. Wojcicki, *J. Amer. Chem. Soc.*, 96 (1974) 5655.
- 9 M.L.H. Green and P.L.I. Nagy, *J. Chem. Soc.*, (1963) 189.
- 10 J.S. Morrison and H.M. Haendler, *J. Inorg. Nucl. Chem.*, 29 (1967) 393.
- 11 T.N. Sumarokova and D.E. Surpina, *Izv. Akad. Nauk. Kaz. SSR. Ser. Khim.*, (1969) 16; *Chem. Abstr.*, 72 (1970) 27926e.
- 12 M. Massol, J. Satgé, P. Rivière, and J. Barrau, *J. Organometal. Chem.*, 22 (1970) 599.
- 13 K.D. Bos, E.J. Bulten, J.G. Noltes, and A.L. Spek, *J. Organometal. Chem.*, 99 (1975) 71.