University of Groningen

Phenylethynyl Complexes of Titanocene and Vanadocene

Teuben, J.H.; Liefde Meijer, H.J. de

Published in:
Journal of Organometallic Chemistry

DOI:
[10.1016/S0022-328X\(00\)88039-0](https://doi.org/10.1016/S0022-328X(00)88039-0)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1969

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Teuben, J. H., & Liefde Meijer, H. J. D. (1969). Phenylethynyl Complexes of Titanocene and Vanadocene. *Journal of Organometallic Chemistry*, 17(1). [https://doi.org/10.1016/S0022-328X\(00\)88039-0](https://doi.org/10.1016/S0022-328X(00)88039-0)

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

PHENYLETHYNYL COMPLEXES OF TITANOCENE AND VANADOCENE

J. H. TEUBEN AND H. J. DE LIEFDE MEIJER

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Bloemsingel 10, Groningen (The Netherlands)

(Received January 24th, 1969)

SUMMARY

The syntheses and properties of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$, $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)$, $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ and of a diamagnetic complex of composition $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$ are reported. In the first three compounds the $C\equiv CC_6H_5$ groups are σ -bonded to the metal atoms, while in $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$ the $C\equiv CC_6H_5$ groups are probably bridging ligands. The isolation of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ strongly supports our hypothesis^{1,2} that the failure to obtain other complexes $(C_5H_5)_2V^{IV}R_2$ (R = alkyl, aryl) is due to steric reasons. The stability of the compound $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$, which is in marked contrast with the instability of other complexes $(C_5H_5)_2Ti^{III}R$, supports our hypothesis that in stable complexes containing the $(C_5H_5)_2Ti$ group the metal atom is coordinated by two ligands (or one bidentate ligand) in addition to the two C_5H_5 groups^{1,2}.

INTRODUCTION

In our laboratory systematic studies are being undertaken on the preparation and stability of compounds of the general formula $(\pi-C_5H_5)_2MR_m$, where M is a transition metal and R an alkyl or aryl group, which is σ -bonded to the metal.

While titanium forms stable compounds of composition $(C_5H_5)_2Ti^{IV}R_2$, compounds of composition $(C_5H_5)_2Ti^{III}R$ (R = alkyl, aryl) are extremely unstable and could not be isolated^{1,2}. [In $(C_5H_5)_2Ti^{III}(C_3H_5)$ and homologues the allyl group is π -bonded to the metal³.] It has been suggested^{1,2}, that complexes containing the $(C_5H_5)_2Ti$ group are stable only if two coordination places of the metal are occupied (in addition to the C_5H_5 groups). Accordingly, $[(C_5H_5)_2Ti^{III}Cl]_2$, where chlorine forms bridges between the titanium atoms, is a stable compound. Since alkyl and aryl groups are far less effective as bridging groups, stabilization of $(C_5H_5)_2Ti^{III}R$ by dimerization is not possible. Probably for these reasons compounds of this type have not so far been isolated.

In the case of vanadium several stable compounds of composition $(C_5H_5)_2V^{III}R$ ^{1,5} have been isolated, but no compounds of the type $(C_5H_5)_2V^{IV}R_2$, have yet been prepared^{2,4}. The instability of $(C_5H_5)_2V^{IV}R_2$, in contrast to the corresponding titanium and niobium compounds *viz.* $(C_5H_5)_2Ti^{IV}R_2$ and $(C_5H_5)_2Nb^{IV}R_2$ ⁶, was ascribed to steric effects since the atomic radius of vanadium (1.22 Å) is smaller than

that of titanium (1.32 Å) or niobium (1.34 Å)⁷. To test this hypothesis we tried to prepare a compound $(C_5H_5)_2V^{IV}R_2$ with a ligand R with minimum sterical requirements in the neighbourhood of the metal. The phenylethynyl group seemed to be a ligand which best meets these conditions.

The present paper reports the syntheses and properties of the compounds $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$, $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)$, $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ and of a complex of composition $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$, probably with bridging phenylethynyl ligands. The isolation and the stability of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ strongly support our hypothesis^{1,2} that the failure to obtain other complexes $(C_5H_5)_2V^{IV}R_2$ (with R = alkyl, aryl) is due to steric reasons. The great stability of the complex $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$, on the other hand, indicates that the phenylethynyl group is far more apt to act as a bridging ligand than alkyl or aryl groups.

EXPERIMENTAL

All experiments were carried out in an atmosphere of purified nitrogen. Solvents were purified by conventional methods; before use they were freed from oxygen by repeated degassing and saturating with nitrogen. Phenylethynylsodium was prepared by a modification of a synthesis described in the literature⁸: a mixture of finely divided sodium in ether and phenylacetylene (20% excess) was stirred until the evolution of hydrogen had ceased. The insoluble product was filtered, washed with ether and dried *in vacuo*. Phenylethynylsodium was stored under nitrogen in ampoules. Yield (based on Na): 64%.

All other starting materials were prepared according to published procedures^{9-11,14}. Analyses of C, H, Ti and V were carried out at the Microanalytical Department of this University under supervision of Mr. W. M. Hazenberg; Ti was weighed as TiO_2 , V as V_2O_5 . The uncorrected melting points were determined under nitrogen in sealed glass capillaries. Spectra in the visible range were recorded on a Unicam SP 800 spectrophotometer. IR spectra were recorded on a Hitachi EPI-G spectrophotometer. The samples were embedded in KBr discs excluding oxygen as described previously³. Magnetic susceptibilities were determined by the Faraday method; the measurements were carried out by Miss A. H. C. Bruining. The derived magnetic moments are corrected for induced diamagnetism. Mass spectra were recorded by Dr. W. D. Weringa by means of an AEI mass spectrometer type MS9 operating at 70 eV. NMR spectra were measured with a Varian A60 instrument, using TMS as internal standard. Gas chromatographic analyses were performed by means of a F & M model 720 gas chromatograph.

Bis(phenylethynyl)dicyclopentadienyltitanium(IV), $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ ^{1,12}

5.23 g (42.2 mmol) of $NaC\equiv CC_6H_5$ were added to a mixture of $(C_5H_5)_2Ti^{IV}Cl_2$ (5.21 g, 20.9 mmol) and 250 ml of ether at room temperature. After stirring for 3 h the reaction mixture was filtered and the solution was concentrated to about 50 ml. Pentane (150 ml) was added. $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ separated as orange crystals. The crude product was filtered and dried *in vacuo*. Yield 7.73 g (20.3 mmol, 97%). The product is somewhat sensitive to light and air. The IR spectrum (Fig. 1), the absorption spectrum in the visible range and the NMR spectrum were identical with those recently described by Köpf and Schmidt¹².

Fig. 1. IR spectra of a) $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$; b) $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$; c) $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)_2$ and d) $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$ in KBr discs.

Bis(phenylethynyl)dicyclopentadienylvanadium(IV), $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$

2.99 g (24.2 mmol) of $NaC\equiv CC_6H_5$ were added with stirring to 3.08 g (12.2 mmol) of $(C_5H_5)_2V^{IV}Cl_2$ in 100 ml of tetrahydrofuran. After one hour the solvent was removed *in vacuo*. The brown-red reaction product was extracted three times with 100 ml of *n*-hexane in order to remove soluble by-products. Continuous extraction of the residue under reduced pressure with about 100 ml of ether gave tiny dark-red crystals. These crystals were filtered, washed with small portions of ether and dried *in vacuo*. The temperature had to be kept below 0° during the reaction and purification. The crystals were stored in ampoules under nitrogen at -25° . Yield 1.33 g (3.48 mmol, 29%). (Found: C, 81.31; H, 5.24; V, 13.25. $C_{26}H_{20}V$ calcd.: C, 81.45; H, 5.26; V, 13.29%). M.p. $74-75^\circ$ (decompn.); λ_{max} (in ether) 547, 486 and 400 m μ . The IR spectrum is given in Fig. 1 [$\nu(C\equiv C)$ 2060 cm^{-1}]. The magnetic moment of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ (measured from 96–274° K) is 1.54 B.M. The mass spectrum of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ is a superposition of the spectra of $(C_5H_5)_2V^{13}$ and $C_6H_5C\equiv C-C\equiv CC_6H_5$. Probably the high temperature of the ion source caused decomposition of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$. No peaks with $m/e > 202$ ($C_6H_5C\equiv C-C\equiv CC_6H_5^+$) were present in the spectrum.

(Phenylethynyl)dicyclopentadienylvanadium(III), $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)$

2.26 g (10.4 mmol) of $(C_5H_5)_2V^{III}Cl$ in 200 ml of ether were stirred at 0° with 1.29 g (10.4 mmol) of $NaC\equiv CC_6H_5$. After 3 h the dark green solution was concentrated to 100 ml at room temperature and filtered. Further concentration to about 25 ml and cooling yielded small black crystals. The mother liquor was removed. The product was dried *in vacuo* and stored in ampoules under nitrogen. Because of decomposition of the product in solution no attempts were made to purify the crystals. Yield 1.27 g (4.5 mmol, 43%). (Found: C, 75.59; H, 5.60; V, 17.68. $C_{18}H_{15}V$ calcd.: C, 76.59; H, 5.36; V, 18.05%). Upon heating under nitrogen decomposition of the compound started at about 80° , fast decomposition with melting at 135° . λ_{max} (in

ether) 703, 525 (sh) μm . The IR spectrum is shown in Fig. 1 [$\nu(\text{C}\equiv\text{C})$ 2060 cm^{-1}]. The compound appeared to be very sensitive to air.

(Phenylethynyl)dicyclopentadienyltitanium(III), $[(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}(\text{C}\equiv\text{CC}_6\text{H}_5)]_2$

Phenylethynylsodium (1.90 g, 15.3 mmol) was added to a mixture of $[(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}\text{Cl}]_2$ (3.29 g, 7.7 mmol) and 100 ml of benzene. After stirring at room temperature for 2 h the reaction mixture was pumped to complete dryness. The reaction product was washed with 300 ml of n-hexane. The green residue was extracted continuously with about 100 ml of dichloromethane. The product was obtained as small dark-green crystals which were filtered and dried *in vacuo*. Yield 2.30 g (4.1 mmol, 54%). (Found: C, 76.72, 76.70; H, 5.47, 5.39; Ti, 17.22, 17.04. $\text{C}_{18}\text{H}_{15}\text{Ti}$ calcd.: C, 77.43; H, 5.42; Ti, 17.15%). M.p. > 200°; λ_{max} in dichloromethane 745 (sh), 655, 435 μm . The IR spectrum is shown in Fig. 1. A $\text{C}\equiv\text{C}$ stretching band is absent. The mass spectrum indicates the compound to be dimeric; the peak with the highest m/e value in the spectrum ($m/e = 558$) corresponds to $[(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}(\text{C}\equiv\text{CC}_6\text{H}_5)]_2^+$. The peaks with relative intensities higher than 10% are listed in Table 1. The isotopic pattern of these peaks is as expected.

TABLE 1

MAJOR PEAKS OF THE MASS SPECTRUM OF $[(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}(\text{C}\equiv\text{CC}_6\text{H}_5)]_2$.

m/e value	Rel. abundance	Ion
558	19	$[(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}(\text{C}\equiv\text{CC}_6\text{H}_5)]_2^+$
279	81	$(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}(\text{C}\equiv\text{CC}_6\text{H}_5)^+$
202	21	$\text{C}_6\text{H}_5\text{C}\equiv\text{C}-\text{C}\equiv\text{CC}_6\text{H}_5^+$
178	100	$(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{III}}^+$
113	46	$(\text{C}_5\text{H}_5)\text{Ti}^{\text{III}}^+$
102	19	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}^+$

The compound is diamagnetic. Because of the very low solubility of the compound in common organic solvents no NMR spectrum could be obtained.

Reaction of the compounds with hydrogen chloride

The compounds $(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{IV}}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ and $(\text{C}_5\text{H}_5)_2\text{V}^{\text{IV}}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ reacted with hydrogen chloride in ether with formation of $(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{IV}}\text{Cl}_2$, $(\text{C}_5\text{H}_5)_2\text{V}^{\text{IV}}\text{Cl}_2$ and phenylacetylene according to:

The yield of phenylacetylene depended on the reaction temperature, probably because of partial polymerisation.

By reaction of $(\text{C}_5\text{H}_5)_2\text{V}^{\text{III}}(\text{C}\equiv\text{CC}_6\text{H}_5)$ with hydrogen chloride in ether at -50° phenylacetylene and $(\text{C}_5\text{H}_5)_2\text{V}^{\text{III}}\text{Cl}$ were formed. The latter compound was oxidized by an excess of hydrogen chloride and oxygen:

yield determined by weighing. Phenylacetylene was quantitatively determined by gas chromatographic methods and characterized by its retention time. The results are given in Table 2.

TABLE 2

REACTION OF THE COMPLEXES $(C_5H_5)_2M(C\equiv CC_6H_5)_2$ WITH HYDROGEN CHLORIDE

Complex	Reaction temp. ($^{\circ}C$)	Yield of $(C_5H_5)_2M^{IV}Cl_2$ (%)	Yield of $C_6H_5C\equiv CH$ (%)
$(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$	20	97	+ ^a
$(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$	20	94	50
	-28	99	61
	-50	99	68
$(C_5H_5)_2V^{III}(C\equiv CC_6H_5)_2$	-50	99	63

^a Not quantitatively determined.

The reaction of $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$ at 20° with an excess of hydrogen chloride in ether followed by oxidation by air gave $(C_5H_5)_2TiCl_2$ (93%) and *trans*-1,4-diphenylbutenyne ($C_6H_5CH=CHC\equiv CC_6H_5$) (69%) according to:

trans-1,4-Diphenylbutenyne was characterized by the melting point $96-98^{\circ}$ (reported¹⁵ m.p. 96°); by the NMR spectrum in $CDCl_3$ (phenyl protons at τ 2.73 ppm; olefinic protons at τ 2.87, 3.13, 3.58, 3.84 ppm; intensity ratio phenyl/olefinic protons 5/1) and by the mass spectrum (parent ion at $m/e=204$). The IR spectrum does not show absorptions in the $C\equiv C$ stretching frequency range; a sharp intensive peak at 947 cm^{-1} is in accordance with a *trans*-olefinic structure.

DISCUSSION

The complexes $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ and $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)_2$ are compounds of the well-known types $(\pi-C_5H_5)_2Ti^{IV}(\sigma-R)_2$ ¹⁶ and $(\pi-C_5H_5)_2V^{III}(\sigma-R)_2$ ⁵. The IR spectra (Fig. 1) show peaks characteristic for π -bonded C_5H_5 -groups, whereas vibrations of σ -bonded C_5H_5 -groups are absent¹⁷. The presence of σ -bonded phenylethynyl groups is indicated by the observation of absorption bands characteristic for monosubstituted phenyl groups and of the $C\equiv C$ stretching band for $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ at 2066 cm^{-1} and for $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)_2$ at 2060 cm^{-1} . The reaction of the complexes with hydrogen chloride in ether, their thermal stability, their behaviour towards air and the results of the elementary analyses are in accordance with the proposed structures.

The IR spectrum of $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ (Fig. 1) is closely similar to those of $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ and $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)_2$; the $C\equiv C$ stretching band is observed at 2060 cm^{-1} , indicating that the $C\equiv C$ moiety is not coordinated to a metal atom. Therefore, the compound is formulated as $(\pi-C_5H_5)_2V^{IV}(\sigma-C\equiv CC_6H_5)_2$. The chemical behaviour and the magnetic properties (found: 1.54 B.M.; calculated

spin only 1.73 B.M.) are in agreement with the proposed structure. $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ is the first compound of the type $(\pi-C_5H_5)_2V^{IV}(\sigma-R)_2$ that has been isolated. The isolation and stability of $(\pi-C_5H_5)_2V^{IV}(\sigma-C\equiv CC_6H_5)_2$ strongly supports our hypothesis^{1,2} that the instability of compounds $(\pi-C_5H_5)_2V^{IV}R_2$, where R = alkyl, aryl or perfluorophenyl, is due to steric reasons; the steric requirements (in the neighbourhood of the metal) of the ligands $\sigma-C\equiv CC_6H_5$ are much less stringent than those of the other groups R mentioned.

The mass spectrum of the green compound, isolated from the reaction of $[(C_5H_5)_2Ti^{III}Cl]_2$ with $NaC\equiv CC_6H_5$, suggests that this compound has a dimeric structure of the formula $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$. Its IR spectrum (Fig. 1) and the formation of $(C_5H_5)_2Ti^{IV}Cl_2$ after reaction with hydrogen chloride and oxygen indicate that the compound contains $(\pi-C_5H_5)_2Ti$ groups. The formation of *trans*-1,4-diphenylbutenyne in this reaction and the absence of the C≡C stretching band (around 2060 cm^{-1}) show that the bonding of the phenylethynyl groups in $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$ and in the other complexes discussed is different*. It seems most likely that the phenylethynyl groups in $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$ are bridging ligands bonded to the two metal atoms in the dimeric molecule. Two structures seem to be possible (Fig. 2).

Fig. 2. Possible structures for the complex $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$.

- (i). A symmetrical structure (I), as has been proposed for $[R_2Al(C\equiv CC_6H_5)]_2$ ¹⁸, $[(C_5H_5)_2Ti^{III}Cl]_2$ ¹¹ and $[(C_5H_5)_2Ti^{III}(PR_2)]_2$ ¹⁹. The capacity of the phenylethynyl group for acting as a bridging ligand has recently been discussed by Jeffery and Mole¹⁸.
- (ii). An alternative structure (II), in which each of the phenylethynyl ligands is σ -bonded to one titanium atom while the C≡C moiety is π -coordinated to the other metal atom; phenylethynyl ligands bonded in a comparable way are found in phenylethynylcopper, $[Cu(C\equiv CC_6H_5)]_\infty$ ²⁰.

Since the compound is diamagnetic a spin pairing between the metal atoms via a titanium–titanium bond is assumed. Such a bond is possible in both structures, (I) and (II). The same type of interaction has been assumed in $[(C_5H_5)_2Ti^{III}Cl]_2$ ²² and in $[(C_5H_5)_2Ti^{III}(PR_2)]_2$ ¹⁹.

* The IR spectra (Fig. 1) of $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$, $(C_5H_5)_2V^{IV}(C\equiv CC_6H_5)_2$ and $(C_5H_5)_2V^{III}(C\equiv CC_6H_5)_2$ show a sharp, intensive absorption at 1200 cm^{-1} . This peak and the C≡C stretching band are absent in $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$. Probably the 1200 cm^{-1} band is correlated with the first type of compounds.

Our present results do not allow us to decide between the structures (I) and (II) for the compound $[(C_5H_5)_2Ti^{III}(C\equiv CC_6H_5)]_2$. Both structures are in agreement with our hypothesis^{1,2}, that in stable complexes containing the $(C_5H_5)_2Ti$ group the metal atom is coordinated by two monodentate ligands (for instance in $(C_5H_5)_2Ti^{IV}R_2$ ¹⁶, $(C_5H_5)_2Ti^{IV}RCl$ ¹⁶, $[(C_5H_5)_2Ti^{III}Cl]_2$ ¹¹, $[(C_5H_5)_2Ti^{III}(PR_2)]_2$ ¹⁹) or by one bidentate ligand (*e.g.* in $(C_5H_5)_2Ti^{III}(\pi\text{-allyl})$ ³, $(C_5H_5)_2Ti^{III}(\text{carboxylate})$ ²¹) in addition to the two π -cyclopentadienyl groups.

ACKNOWLEDGEMENTS

The authors are much indebted to Prof. F. JELLINEK for his stimulating interest and Dr. W. D. WERINGA for recording and interpreting the mass spectra. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the advancement of Pure Research (ZWO). Financial support to one of the authors (J.H.T.) by the Dutch State Mines (Geleen, the Netherlands) is gratefully acknowledged.

REFERENCES

- 1 H. J. DE LIEFDE MEIJER AND F. JELLINEK, *3rd International Symposium on Organometallic Chemistry*, Munich, 1967, p. 250.
- 2 H. J. DE LIEFDE MEIJER *et al.*, to be published.
- 3 H. A. MARTIN AND F. JELLINEK, *J. Organometal. Chem.*, 12 (1968) 149.
- 4 H. J. DE LIEFDE MEIJER AND G. J. M. VAN DER KERK, *Rec. Trav. Chim. Pays-Bas*, 85 (1966) 1015.
- 5 F. W. SIEGERT AND H. J. DE LIEFDE MEIJER, *J. Organometal. Chem.*, 15 (1968) 131.
- 6 F. W. SIEGERT AND H. J. DE LIEFDE MEIJER, *Rec. Trav. Chim. Pays-Bas*, 87 (1968) 1445.
- 7 C. F. BELL AND K. A. K. LOTT, *Modern Approach to Inorganic Chemistry*, 2nd Ed., Butterworths, London, 1966, p. 87.
- 8 H. GILMAN AND R. V. YOUNG, *J. Org. Chem.*, 1 (1936) 315.
- 9 E. O. FISCHER, S. VIGOUREUX AND P. KUZEL, *Chem. Ber.*, 93 (1960) 701.
- 10 G. WILKINSON AND J. M. BIRMINGHAM, *J. Amer. Chem. Soc.*, 76 (1954) 4281.
- 11 G. NATTA, G. DALL'ASTA, G. MAZZANTI, U. GIANNINI AND S. CESCA, *Angew. Chem.*, 71 (1959) 205.
- 12 H. KÖPF AND M. SCHMIDT, *J. Organometal. Chem.*, 10 (1967) 383.
- 13 J. MÜLLER AND L. D'OR, *J. Organometal. Chem.*, 10 (1967) 313.
- 14 F. STRAUß, *Justus Liebigs Ann. Chem.*, 342 (1905) 223.
- 15 J. H. PINCHARD, B. WILLE AND L. ZECHMEISTER, *J. Amer. Chem. Soc.*, 70 (1948) 1938.
- 16 G. A. RAZUVAEV AND V. N. LATYAEVA, *Organometal. Chem. Rev.*, 2 (1967) 349.
- 17 H. P. FRITZ, in F. G. A. STONE AND R. WEST (Eds.), *Advan. Organometal. Chem.*, Vol. 1, Academic Press, New York, 1964.
- 18 E. A. JEFFERY AND T. MOLE, *J. Organometal. Chem.*, 11 (1968) 393.
- 19 K. ISSLEIB AND H. HÄCKERT, *Z. Naturforsch.*, B, 21 (1966) 519.
- 20 G. E. COATES, M. L. H. GREEN AND K. WADE, *Organometallic Compounds*, Vol. 2, 3rd Ed., Methuen, London, 1968, p. 275.
- 21 R. S. P. COUTTS AND P. C. WAILES, *Aust. J. Chem.*, 20 (1967) 1579.
- 22 R. L. MARTIN AND G. WINTER, *J. Chem. Soc.*, (1965) 4709.