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ORGANOMETALLIC DERIVATIVES OF THE TRANSITION ELEMENTS

IV *. FERROCENES VIA THE REACTION OF IRON ATOMS WITH ALKYNES **

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Summary

Iron atoms react with disubstituted alkynes to produce iron complexes and alkyne oligomers. The oligomers are cyclic trimers and/or cyclic tetramers of the starting alkynes. Structural characterization of iron complexes shows an unusual rearrangement to substituted ferrocenes.

Introduction

Our continued interest in the interaction of transition metal atoms with unsaturated organic substrates [1,2,3] has prompted us to investigate further the reactions of iron atoms with alkynes. Early experiments [4] indicated that iron atoms react with disubstituted alkynes to produce iron complexes having the stoichiometry of one iron atom with five alkyne ligands. Oligomers of the starting alkynes are formed as the organic products. We now report the characterization of two of the iron complexes in addition to further information concerning the oligomeric products.

Experimental techniques and results

Reactions were conducted using the metal atom synthesis technique [5] wherein iron atoms, produced from a resistively heated crucible, were cocondensed under high vacuum conditions (circa 10^{-5} Torr) with alkynes and hydrocarbon diluents on the liquid nitrogen cooled walls of the reaction vessel. For the most part, reactions appear to occur in the frozen ligand matrix after the liquid nitrogen bath is removed,

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* For part III see ref. 4.

** Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983.

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but before the matrix melts. Reaction mixtures were handled using conventional vacuum line techniques. Separation of iron complexes from organic products was done by thermal gradient vacuum sublimation and/or column chromatography. Typical reactions include:

Iron/2-butyne. Iron atoms (0.54 g, 9.7 mmol) and 2-butyne (10 g, 0.185 mol) were cocondensed with 50 g of pentane diluent to produce a dark brown suspension upon warming to room temperature. Filtration under nitrogen and removal of solvent under vacuum at room temperature gave a dark residue. Sublimation at 65°C (10^{-2} Torr) first produced a white solid which became yellow as a volatile iron complex condensed. Thermal gradient vacuum sublimation separated the sublimed product to yield 0.58 g of white, crystalline hexamethylbenzene identified by its melting point of 160–162°C (lit. 164–166°C), mass spectrum, and proton NMR spectrum; 22 mg of tiny yellow crystals of an iron complex were also isolated. High resolution mass spectrometry showed the composition of the iron complex to be $C_{20}H_{30}Fe$.

Iron/2-pentyne. Iron atoms (0.62 g, 11.1 mmol) and 2-pentyne (10 g, 0.147 mol) and 45 g of hexane diluent were cocondensed at liquid nitrogen temperature to give a red-brown coloration in the frozen matrix. Warming to room temperature produced a brown-black solution which became semi-solid upon standing. Extraction of the material with dry, deoxygenated benzene and filtration under nitrogen gave a brownish solution from which the solvent was removed under vacuum. Molecular distillation of the residue (50°C, 10^{-2} Torr) first produced a pale, yellow liquid which became red as an iron complex condensed. A gradual increase in temperature to 70°C insured removal of all volatiles. Separation of the hydrocarbon and iron-containing products was accomplished by column chromatography on alumina. Pentane was used to elute the oligomer (0.45 g) and diethyl ether eluted the burgundy-red liquid iron complex (66 mg). Proton and carbon-13 NMR spectra of the hydrocarbon product identify it as 1,2,4,7-tetramethyl-3,5,6,8-tetraethylcyclooctatetraene (both bond shift isomers), the identical oligomeric product to that obtained by reaction of nickel atoms with 2-pentyne [4]. The oligomer was liquid at room temperature but solidified around 10–15°C upon cooling. Analysis of the burgundy-red liquid iron complex by high resolution mass spectrometry showed its composition to be $C_{25}H_{40}Fe$.

Iron/3-hexyne. Iron atoms (0.66 g, 11.8 mmol) and 3-hexyne (8.7 g, 0.106 mol) were cocondensed with 50 g hexane/heptane diluent to produce a dark liquid after removal of the liquid nitrogen bath. This liquid became semi-solid upon warming to room temperature. Extraction with deoxygenated benzene/hexane gave a fine, dark suspension after filtration under nitrogen. After removal of solvent under vacuum, the dark residue was sublimed (70–100°C, 10^{-2} Torr) to give brownish-orange solids. Repeated thermal gradient vacuum sublimations were used to isolate 1.40 g of white, crystalline hexaethylbenzene, identified by its melting point of 126–127°C (lit. 129°C), carbon-13 and proton NMR spectra; 57 mg of a yellow, crystalline iron complex was also isolated. Analysis of the iron complex by high resolution mass spectrometry showed its composition to be $C_{30}H_{50}Fe$.

Iron/methylphenylacetylene. Iron atoms (0.43 g, 7.7 mmol) and methylphenylacetylene (5.8 g, 0.050 mol) were cocondensed with 50 g of hexane diluent to give a dark brown liquid after warming to room temperature. Extraction with ether/hexane and removal of solvent under vacuum gave dark solids which were sublimed to

140°C (10^{-2} Torr) to yield 0.73 g of white, oligomeric product. Sublimation at 170°C (10^{-2} Torr) then yielded 96 mg of a red-orange iron complex. Analysis of the oligomeric product by carbon-13 and proton NMR spectrometry and mass spectrometry indicated the products to be 1,3,5-trimethyl-2,4,6-triphenylbenzene and 1,2,4,7-tetramethyl-3,5,6,8-tetraphenylcyclooctatetraene (both bond shift isomers). Integration of the methyl resonances in the proton NMR spectra gave the molar ratio of cyclic trimer to cyclic tetramer to be 5 to 3. Analysis of the red-orange iron complex by mass spectrometry indicated a composition of $C_{45}H_{40}Fe$.

Iron/propyne. Iron atoms (0.31 g, 5.5 mmol) and propyne (81 g, 2.04 mol) were cocondensed at liquid nitrogen temperature, then the reaction mixture was warmed to −45°C. Unreacted propyne (b.p. − 23°C) was removed under vacuum leaving a brown residue. Extraction with pentane and filtration under nitrogen gave a yellow-brown solution. Only a small amount of polymeric hydrocarbon material was detected after removal of solvent. In this reaction, no oligomers or iron complexes were observed.

Discussion

Each reaction of iron atoms with disubstituted alkynes produced iron complexes having the stoichiometry pentaalkyneiron along with cyclic trimers or cyclic tetramers of the starting alkyne as organic products. While low-valent transition metal compounds frequently induce cyclic trimerization [6] in reactions with alkynes, the formation of cyclic tetramers is uncommon [3], particularly in the case of substituted alkynes. Identification of hexamethyl- and hexaethyl-benzene oligomers from reactions of iron atoms with 2-butyne and 3-hexyne, respectively, was simplified by comparison with known compounds. In the case of 2-pentyne, however, the proton NMR spectrum (Fig. 1) shows a compound with two types of methyl groups and two types of ethyl groups which, along with the mass spectrum, indicates the product to be a symmetrical tetramethyltetraethylcyclooctatetraene. The carbon-13 NMR spectrum (Fig. 2) shows the correct number of methyl and ethyl resonances (13 to 25 ppm) but twice the expected number of ring carbon resonances (130 to 140 ppm). Paquette [7] has elegantly demonstrated that cyclooctatetraenes having four or more contiguous methyl groups can exist as shelf-stable bond shift isomers. Thus, the cyclic tetramer of 2-pentyne, having eight contiguous alkyl groups, is identified as an equimolar mixture of 1,2,4,7-tetramethyl-3,5,6,8-tetraethylcyclooctatetraene and its bond shift isomer 1,3,6,8-tetramethyl-2,4,5,7-tetraethylcyclooctatetraene (Fig. 3).

In the proton NMR spectrum of the oligomers of methylphenylacetylene (Fig. 4)

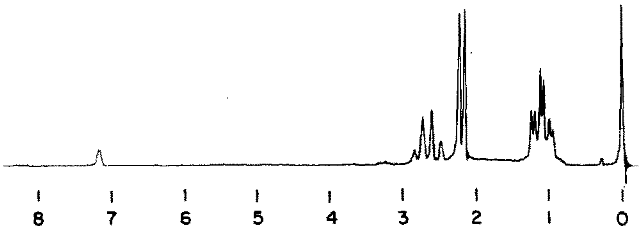

Fig. 1. 60 MHz PMR spectrum of tetramethyltetraethylcyclooctatetraene in benzene-d_6 versus TMS.

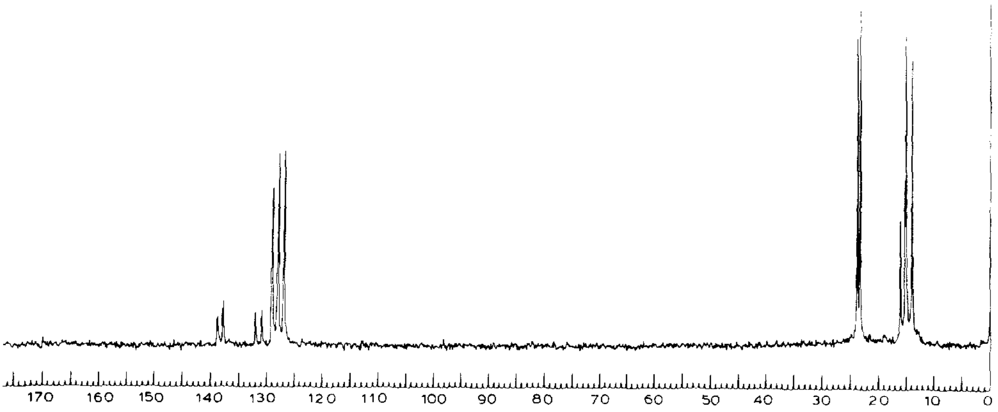

Fig. 2. Carbon-13 NMR spectrum of the bond shift isomers of tetramethyltetraethylcyclooctatetraene in benzene-d_6 versus TMS. Spectrum recorded at 73°C.

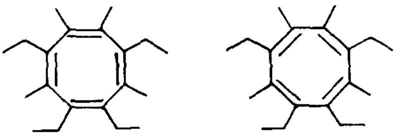

Fig. 3. Bond shift isomers of tetramethyltetraethylcyclooctatetraene.

methyl resonances are sharp for the tetramer (δ 1.8 ppm) and trimer (δ 2.1 ppm) while phenyl resonances (δ 7.0–7.5 ppm) are broadened. Analysis of the carbon-13 NMR spectrum (Fig. 5) indicates two methyl resonances (ca. 18 ppm) for the tetramer with the methyl group of the trimer at 19.3 ppm. In the quaternary carbon region (131–143 ppm) more types of ring carbons are indicated than expected for a single compound, so the cyclic tetramer is again believed to be an equimolar mixture of shelf-stable bond shift isomers. The trimer is identified as 1,3,5-trimethyl-2,4,6-tri-

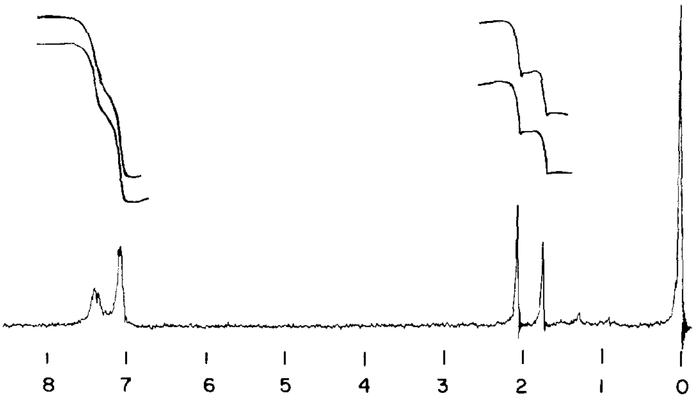

Fig. 4. 60 MHz PMR spectrum of the trimer and tetramer of methylphenylacetylene in deuterochloroform versus TMS.

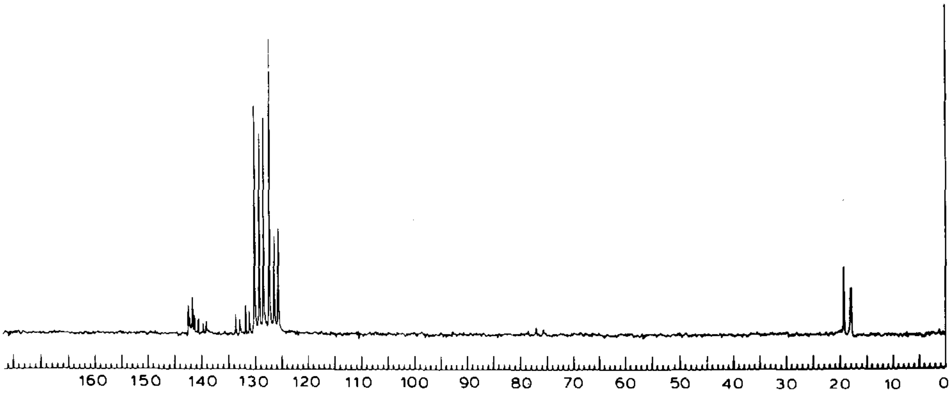

Fig. 5. Carbon-13 NMR spectrum of the oligomers of methylphenylacetylene in deuterochloroform and carbon disulfide versus TMS.

phenylbenzene, and the cyclic tetramer is identified as an equimolar mixture of 1,2,4,7-tetramethyl-3,5,6,8-tetraphenylcyclooctatetraene and its bond shift isomer 1,3,6,8-tetramethyl-2,4,5,7-tetraphenylcyclooctatetraene (Fig. 6). Data for oligomers formed in iron atom reactions is summarized in Table 1.

The isolated iron complexes from reactions with disubstitued alkynes have the stoichiometry of one iron atom with five alkyne ligands (Table 2). With this stoichiometry, a number of different structures seemed possible including π-bonded alkynes, three and five member metallocycles, cyclobutadienes, cyclooctatetraenes, and combinations of these ligand types. Infrared analyses, however, indicated no

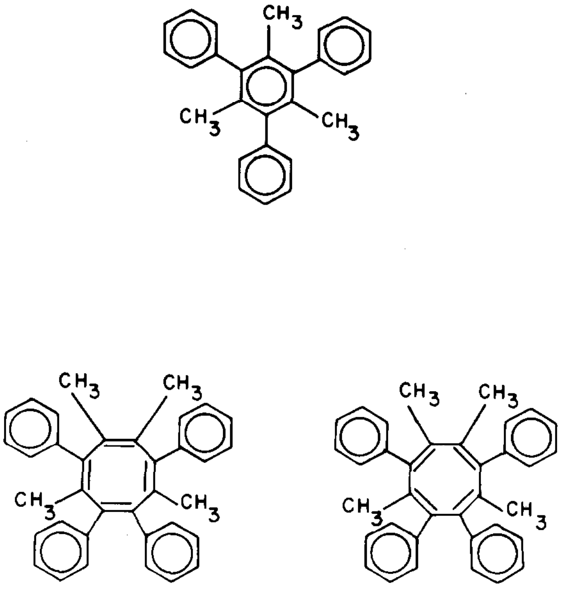

Fig. 6. Oligomers of methylphenylacetylene.

TABLE 1

OLIGOMERS FORMED IN IRON ATOM-ALKYNE COCONDENSATION REACTIONS

Substrate	Diluent	Weight of oligomers Isolated, g.	Oligomer composition (%)	
			Cyclic trimer	Cyclic tetramer
2-Butyne	pentane	0.58	100	–
2-Pentyne	hexane	0.45	–	100
3-Hexyne	hexane/heptane	1.40	100	–
Methylphenylacetylene	hexane	0.73	62	38
Propyne	None	None	–	–

significant bands between 1550 and 2400 cm^{-1}, a region in which one would observe vibrations associated with metallocycles [8] or coordinated alkynes [9]. NMR spectra of the complexes showed sharp solvent and TMS resonances; however, the resonances for the complexes themselves were very broad and difficult to interpret (Fig. 7 and 8). The spectral results, therefore, gave little positive information about molecular structure. Transparent yellow crystals of the 2-butyneiron complex were then submitted for structure determination by X-ray diffraction.

The X-ray data, analyzed by Riley and Davis [10], indicated that the isolated complex is decamethylferrocene! The space group and unit cell dimensions for this decamethylferrocene were the same as those reported a short time later by Raymond et al. [11] who prepared their sample by conventional means. The isolated complex is then the result of an unusual rearrangement in which each metallocene ring is derived from two and one-half 2-butyne ligands which further implies that cleavage of a carbon–carbon triple bond must have occurred.

We then reasoned that an alkyneiron complex incorporating more bulky substituents may not undergo such a remarkable rearrangement. Unfortunately, the complex of iron with methylphenylacetylene could not be well crystallized, so the case with diethyl substituents, the 3-hexyneiron complex, was pursued. After thermal gradient vacuum sublimation and recrystallization from hexane, the complex was in the form of thin, transparent yellow plates which melted at 226–229°C. Literature reports on the preparation of decaethylferrocene indicate, in one case, that the red material melts at 210–230°C, but the authors suggest that this compound might be

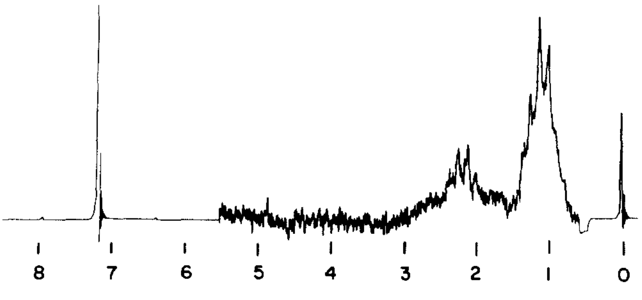

Fig. 7. 60 MHz PMR spectrum of the penta-3-hexyneiron complex in benzene versus TMS.

TABLE 2

COMPLEXES FORMED IN IRON ATOM-ALKYNE COCONDENSATION REACTIONS

Substrate	Diluent	Complex	Molecular weight		Melting point (°C)	Isolated yield (%)[a]	Physical state.
			Found	Theory			
2-Butyne	pentane	$C_{20}H_{30}Fe$	326.1707	326.1697	220[b]	0.69	yellow crystals
2-Pentyne	hexane	$C_{25}H_{40}Fe$	396.247	396.248	5–10	1.63	burgundy red liquid
3-Hexyne	hexane/heptane	$C_{30}H_{50}Fe$	466.3272	466.3262	226–229	1.03	yellow crystals
Methylphenylacetylene	hexane	$C_{45}H_{40}Fe$	636[c]	–	140–150[d]	1.94	red-orange solid
Propyne	None	Not Detected	–	–	–	–	–

[a] Based on moles of iron vaporized. [b] Sublimes. [c] With iron isotope pattern. [d] Softening range.

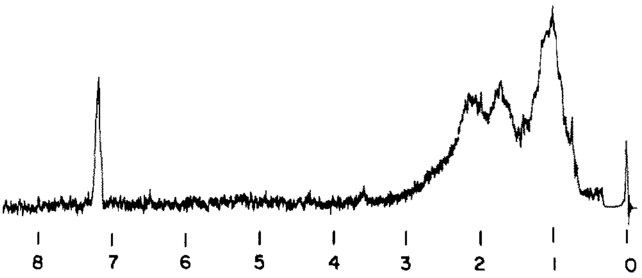

Fig. 8. 60 MHz PMR spectrum of the penta-2-pentyneiron complex in benzene-d_6 versus TMS.

contaminated with nonaethylferrocene [12]. The other report [13], indicates that, after purification by preparative gas chromatography, decaethylferrocene melts at 323–324°C. In this report, Bublitz also describes a normal proton magnetic resonance spectrum for decaethylferrocene with a triplet centered at δ 1.04 ppm and a quartet centered at δ 2.33 ppm. Our 3-hexyneiron complex exhibits broad multiplets centered at δ 1.13 and 2.18 ppm (Fig. 7). These proton resonances and a melting point about 97°C different from that reported for purified decaethylferrocene strongly suggest that the complex prepared from iron atoms and 3-hexyne had not rearranged to the mass equivalent decaethylferrocene. On this basis, the determination of molecular structure by single crystal X-ray analysis was undertaken.

Riley and Davis [10] reported that, although the structure was crystallographically disordered, the molecule isolated is indeed decaethylferrocene!

This second completely unexpected structural result prompts several observations concerning the iron atom-alkyne complexes. It now seems likely that all the isolated complexes have substituted ferrocene structures. Since ferrocene derivatives are strictly diamagnetic, the non-homogeneous paramagnetism exhibited by the alkyne-derived complexes must result from traces of paramagnetic material which affect the resonances for the complexes without significantly affecting solvent or TMS resonances. Further, the paramagnetic impurities must have properties very similar to those of the complexes in order to still be present after purification of the alkyneiron complexes by column chromatography and/or vacuum sublimation.

The substituted ferrocene structure requires the elements of two and one-half alkyne ligands to form each of the five-member rings. This rearrangement means that cleavage of at least one carbon–carbon triple bond must have occurred to generate the two five-member rings. Other examples of transition metal mediated alkyne cleavage reactions have been observed. Hübel and Merényi [14] obtained bis(pentaphenylcyclopentadienyl)molybdenum as one of the products of the reaction between diphenylacetylene with diglymemolybdenum tricarbonyl. Wilke et al. [15] isolated hexamethylbenzene(pentamethylcyclopentadienyl)chromium from the reaction of 2-butyne with $CrCl_3$ and $Al(C_2H_5)_3$. Fritch and Vollhardt [16] have reported high yield syntheses of carbynecobalt clusters by reaction of disubstituted alkynes with cyclopentadienylcobalt dicarbonyl.

Isolation of carbyne complexes suggests that a route to substituted ferrocenes from iron atoms and alkynes might involve an alkyne-bis(metallocycle)iron complex in which the iron inserts in the carbon–carbon triple bond to give a carbyne complex. The carbyne could then add to the metallocycle to generate the pentasubstituted cyclopentadienyl ring. Alternatively, the five-member ring could arise by addition of a carbyneiron to a coordinated cyclobutadiene, a type of reaction documented by Pettit [17] in several instances. Thus, coordinated cyclobutadiene may also have played a role in the formation of the ferrocenes obtained from the interaction of iron atoms and alkynes.

Acknowledgment

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References

1 L.H. Simons, P.E. Riley, R.E. Davis, and J.J. Lagowski, J. Amer. Chem. Soc., 98 (1976) 1044.
2 P.E. Riley and R.E. Davis, Inorg. Chem., 15 (1976) 2735.
3 L.H. Simons and J.J. Lagowski, J. Org. Chem., 43 (1978) 3247.
4 L.H. Simons and J.J. Lagowski in Y. Ishii and M. Tsutsui (Eds.), Fundamental Research in Homogeneous Catalysis, Vol. 2, Plenum Press, New York, N.Y., 1978, pp. 73–80.
5 (a). V. Graves and J.J. Lagowski, Inorg. Chem., 15 (1976) 577; (b) J.R. Blackborow and D. Young, Metal Vapor Synthesis in Organometallic Chemistry, Springer-Verlag, New York, N.Y., 1979.
6 K.P.C. Vollhardt, Acc. Chem. Res., 10 (1977) 1 and ref. therein.
7 (a) L.A. Paquette, J.M. Gardlik, L.K. Johnson and K.J. McCullough, J. Amer. Chem. Soc., 102 (1980) 5026; (b) L.A. Paquette, J.M. Photis and G.D. Ewing, J. Amer. Chem. Soc., 97 (1975) 3538.
8 J.P. Collman, J.W. Kang, W.F. Little, and M.F. Sullivan, Inorg. Chem., 7 (1968) 1298.
9 N.M. Boag, M. Green, D.M. Grove, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Dalton, (1980) 2170.
10 P.E. Riley and R.E. Davis, X-ray Diffraction Studies.
11 D.P. Freyberg, J.L. Robbins, K.N. Raymond and J.C. Smart, J. Amer. Chem. Soc., 101 (1979) 892.
12 K. Schlögl and M. Peterlik, Monatsh. Chem., 93 (1962) 1328.
13 D.E. Bublitz, J. Organometal. Chem., 16 (1969) 149.
14 W. Hübel and R. Merényi, J. Organometal. Chem., 2 (1964) 213.
15 H. Benn, G. Wilke and D. Henneberg, Angew. Chem. Int. Ed. Eng., 12 (1973) 1001.
16 J.R. Fritch and K.P.C. Vollhardt, Angew. Chem. Int. Ed. Eng., 19 (1980) 559.
17 R. Pettit, J. Organometal. Chem., 100 (1975) 205.