Journal of Organometallic Chemistry, 259 (1983) 119–125
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF COORDINATED CYCLIC POLYOLEFINS. THE SYNTHESIS AND CYCLOADDITION REACTIONS OF TRICARBONYL[(1,2,3,4-η)-3,7,7-TRIMETHYLCYCLOHEPTATRIENE]IRON

ZEEV GOLDSCHMIDT* and SHLOMO ANTEBI

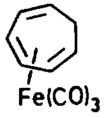
Department of Chemistry, Bar-Ilan University, Ramat Gan 52100 (Israel)

(Received July 8th, 1983)

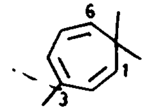
Summary

The synthesis of tricarbonyl[(1–4-η)-3,7,7-trimethylcycloheptatriene]iron (III) by two independent routes is reported. The regiospecificity of the reactions is considered in terms of frontier molecular orbitals. Complex III reacts with tetracyanoethylene to form a mixture of 1,3- and 1,6-cycloadducts in 4/1 ratio. Diphenylketene (DPK) forms a 2 + 2 adduct with III at room temperature. At 80°C an acylated addition product is obtained. In general, steric hindrance increases the yield of products formed via bipolar reactions at the expense of those formed via concerted pathways.

Recent interest in tricarbonyl(cycloheptatriene)iron (I) and derivatives as model compounds for studies of the reactivity of cyclic polyolefin transition metal complexes [1] prompts us to examine simple cycloheptatrienes bearing nonfunctional substituents. Of particular interest is the readily available 3,7,7-trimethylcycloheptatriene (II) [2]. This unsymmetrically substituted hydrocarbon contains two distinct methyl-substituted diene moieties available for tricarbonyliron complexation, the C(3)–C(6) diene in which the methyl occupies the terminal position C(3) and the C(1)–C(4) diene having the methyl group at the internal position C(3). The hydrocarbon II may thus afford two isomeric η^4-Fe(CO)$_3$ π-complexes, III and IV, with geminal methyl groups at C(7) which prevent the undesirable metal hydride shift isomerizations commonly observed in discontinuously conjugated cyclic complexes [3].



(I)



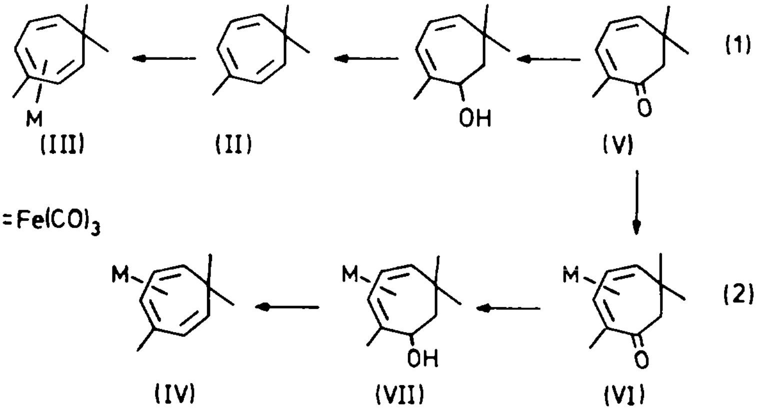
(II)

0022-328X/83/$03.00

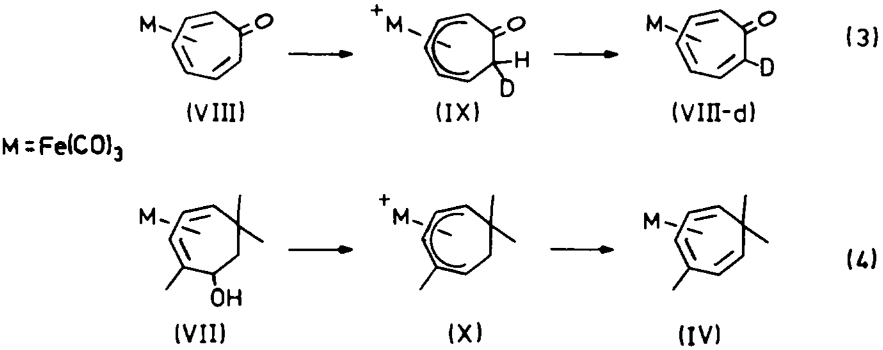
Our attempts to prepare the isomeric complexes III and IV resulted in the successful synthesis only of III. These experiments and some cycloaddition reactions of III form the subject of this paper.

Synthesis

To make the isomers III and IV selectively we devised two independent routes starting from the readily available eucarvone (V) [4]. In route 1 eucarvone is first converted into the cycloheptatriene(II) by reduction and dehydration followed by treatment with $Fe_2(CO)_9$. Earlier reports had indicated that tricarbonyliron transfer agents react with alkyl-substituted dienes to give predominantly the internally substituted complexes [5], and so we expected isomer III to be formed in preference to IV via this route. In fact, the reaction of II with $Fe_2(CO)_9$ at 60°C gave complex III as the sole product, in 53% yield.



Regioselective formation of IV via route 2 was expected. Here eucarvone V is first complexed to VI, and this is followed by reduction and dehydration to IV. Our expectation was based on a previous report by Eisenstadt [6] that (tropone)$Fe(CO)_3$ (VIII) underwent selective deuteration at the uncoordinated double bond via intermediate IX (eq. 3). Analogously, since acid treatment of alcohol VII is likely to give intermediate X, formation of complex IV was expected in the dehydration reaction 4. However, treatment of VII with *p*-toluenesulphonic acid in refluxing benzene for 1 h gave a single product, in 70% yield, which was identified as the isomer III. Attempts to effect the elimination within VII under mild conditions, using $POCl_3$ or $SOCl_2$ in pyridine, failed to give the desired product IV.



The ^1H NMR spectrum clearly distinguishes III from its isomeric IV, since it displays three low field signals at δ 4.87 (H(6)), 5.10 (H(2)) and 5.65 (H(5)) ppm, and two proton signals at higher field, δ 2.85 (H(4)) and 3.00 (H(1)) ppm. The remaining three methyl singlets appear at δ 1.02, 1.15 (geminal C(7) methyls) and 2.05 (C(3) methyl).

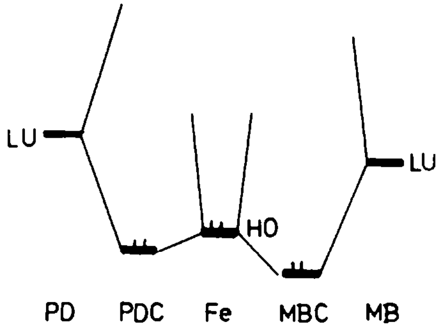
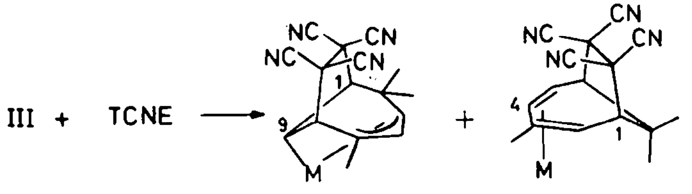


Fig. 1. Interaction diagram for the HOMO of Fe(CO)$_3$ with the LUMOs of methyl-substituted butadiene. PD = 1,3-pentadiene, PDC = PD complex, MB = 2-methylbutadiene, MBC = MB complex.

The site preference exhibited by tricarbonyliron toward the C(1)–C(4) diene moiety of II may be ascribed to the stronger bonding of metal to the organic ligand in III compared to IV. Frontier molecular orbital theory predicts an increase in the energy of butadiene LUMO upon methyl substitution which is greater for the end-substituted 1,3-pentadiene than for the internally-substituted 2-methylbutadiene [7]. Consequently, the back-bonding interaction of the HOMO of the Fe(CO)$_3$ fragment [8] with the low lying LUMO of 2-methylbutadiene is likely to be stronger than the interaction with the high lying LUMO of 1,3-pentadiene. Thus the analogous back-bonding interaction in III is expected to be more stabilizing than that in IV (Fig. 1). Furthermore it would also appear that IV, being unstable under the dehydration conditions used in route 2, underwent a direct metal shift isomerization [9] to the more stable isomer III.

Cycloadditions

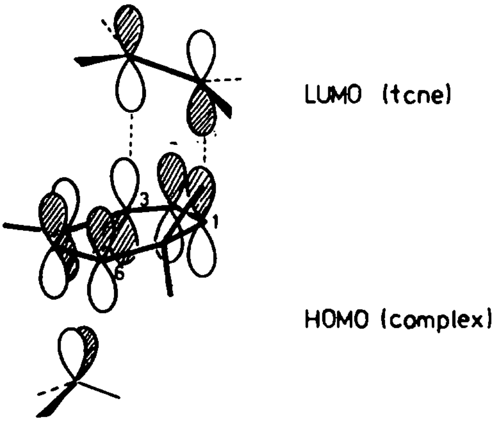
Tetracyanoethylene (TCNE) is a powerful uniparticulate electrophile which reacts regiospecifically with a variety of tricarbonyl(cycloheptatriene)iron derivatives to afford 1,3-σ,π-allylic cycloadducts [10]. The reaction of TCNE with III in CH_2Cl_2 at room temperature was complete within 10 min. The elemental analysis of the crystalline product corresponded to a 1/1 adduct. However, the ^1H NMR spectrum revealed the presence of a 4/1 mixture of isomers, identified as the 1,3 (XI) and 1,6 (XII) adducts (eq. 5). The ^1H NMR spectrum of XI was that expected for a 1,3 adduct, characterized by a high field resonance of H(9) at δ 1.84 ppm, which appeared as a doublet of doublets (J(19) 9.3 Hz, J(69) 6.9 Hz), and a group of four proton doublets at δ 3.00 (H(6)), 4.13 (H(1)), 4.21 (H(4)) and 4.47 (H(3)) ppm. The three methyl singlets resonate at δ 1.53, 1.66 and 2.15 ppm. On the other hand, the 1,6-adduct XII exhibits only one low field resonance at δ 5.29 (H(4)) ppm and four higher field signals at δ 2.60 (H(1)), 2.87 (H(6)), 3.17 (H(2)) and 3.77 (H(5)) ppm. The three methyl singlets appear at δ 1.24, 1.42 and 2.38 ppm.



(XI) (XII)

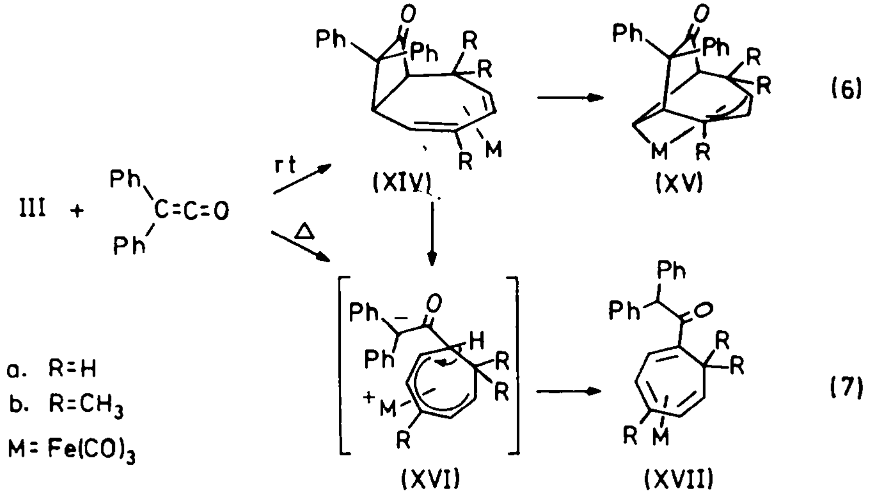
(5)

The formation of 1,3 adducts is commonly observed and there is only one reported precedent for a 1,6 cycloaddition, namely that of TCNE with tricarbonyl(*N*-ethoxycarbonylazepine)iron [10c]. Mingos [10c,11] has recently shown that 1,3 and 1,6 cycloadditions can be treated as symmetry-allowed reactions which are topologically related to Woodward–Hoffmann's $4s + 2s$ $(\pi 2s + \pi 2a + \sigma 2a)$ and $8s + 2s$ $(\pi 2s + \pi 2a + \sigma 2s + \pi 2s + \sigma 2a)$ cycloadditions, respectively [12]. Qualitative frontier molecular orbital considerations also predict a concerted 1,3 cycloaddition. This is illustrated in XIII as the interaction of HOMO cycloheptatriene complex and LUMO TCNE, whereby TCNE attacks the ring *exo* to the metal coordination site [10]. It is clear, however, that applying the same analysis to 1,6 cycloadditions leads to the conclusion that these reactions are symmetry forbidden and thus must have a nonconcerted dipolar mechanism [13]. Furthermore, inspection of molecular models of III reveals a substantial steric crowding around the *exo* face by the *exo*-methyl substituent, which prevents an efficient orbital overlap of TCNE and III at positions 1 and 6. It is thus reasonable to suggest that 1,6-cycloadditions follow a zwitterionic mechanism, presumably via a 'tight' transient ion pair [10c,13].



(XIII)

Finally it was of interest to examine the question of whether 1,3 or 2 + 2 cycloaddition is favoured in reactions of III with ketenes. We have previously shown that diphenylketene (DPK) reacts periselectively with I to give the 2 + 2 adduct XIVa, which rearranges upon heating to the 1,3 adduct XVa (eq. 6) [14]. The reaction of III with DPK at room temperature gave a low yield of the expected cyclobutanone (XIVb). Unlike XIVa however, XIVb did not rearrange thermally to the analogous 1,3-adduct XVb, and instead ketone XVIIb was obtained as the only isolated product. Furthermore, heating a mixture of III and DPK again gave ketone XVIIb, with no detectable 1,3 adduct. The parent acylcycloheptatriene complex XVIIa was previously obtained by acid- (or base)-catalyzed ring opening of the corresponding cyclobutanone XIVa [15]. Ketone XVII is evidently formed by proton transfer within the dipolar intermediate XVI (eq. 7).



In conclusion, we have shown that methyl substitution at the unsaturated part of cycloheptatriene confines the site of metal coordination to the internally substituted diene moiety, producing the isomer with the stronger back-bonding interaction. Methyl substitution at the saturated cycloheptatriene carbon causes steric hindrance, thus effecting the selectivity of cycloadditions in such a way as to increase the amount of products formed via a nonconcerted bipolar mechanism, i.e. acylation and 1,6 cycloaddition, at the expense of those formed in the concerted 1,3 cycloaddition reactions.

Experimental

General. ^{1}H NMR spectra were recorded on Varian Model EM-360A and 300 MHz Brucker WX spectrometers, with TMS as internal standard. IR spectra were recorded on a Perkin–Elmer Model 257 spectrometer. Mass spectra were determined with a GC/MS Finnigan Model 4000 spectrometer. Column chromatographic separations were performed under slight positive nitrogen pressure using Merck Kieselgel 60. Elemental analyses were determined at the analytical laboratories of the Hebrew University, Jerusalem. All reactions were conducted under nitrogen.

Tricarbonyl(η^4-eucarvone)iron (VI) [16]. $Fe_2(CO)_9$ (52 g, 0.14 mol) was gradually added during 4 h to stirred eucarvone [4] (22 g, 0.14 mol) at 60°C. Stirring was continued at 60°C for another 10 h. Pentane was added and the precipitate was filtered off. The solvent and excess $Fe(CO)_5$ were removed under vacuum at room temperature and the residue distilled at 43°C (0.3 mmHg) to give VI (16 g, 37% yield) as an orange oil, which solidified on standing, m.p. 46°C. IR (CCl_4): 2040, 1960 (br), 1650 cm^{-1}; Anal.: Found C, 53.88; H, 4.79. $C_{13}H_{14}FeO_4$ calcd.: C, 53.82; H, 4.86%. ^{1}H NMR (CCl_4): δ 1.13 (3H, s), 1.20 (3H, 2), 1.55 (3H, s), 1.80 (2H, bs), 2.80 (1H, d J 8 Hz), 5.13 (1H, dd, J 8 and 5 Hz), 5.77 (1H, d, J 5 Hz) ppm.

Tricarbonyl[(1–4-η)-3,7,7-trimethylcycloheptatriene]iron (III). (a) From II. A mixture of trimethylcycloheptatriene (II) [2] (2.2 g, 16.4 mmol), $Fe_2(CO)_9$ (7.0 g, 19.3 mmol) and $Fe(CO)_5$ (5 ml) was stirred at 62°C for 12 h. Pentane was added and the precipitate filtered. The solvent and excess $Fe(CO)_5$ were removed under vacuum and the residual oil was distilled (Kugelrohr) at 150°C (0.1 mmHg) to give III (2.5 g, 53% yield). CIMS: m/e (CH_4) 275 ($M+1$), 247, 219, 191, 135. IR ($CHCl_3$): 2050, 1970 cm^{-1}. Anal.: Found C, 57.19; H, 5.38. $C_{13}H_{14}FeO_3$ calcd.: C, 56.97; H, 5.15%. ^{1}H NMR ($CDCl_3$) δ 1.02 (3H, s), 1.15 (3H, s), 2.05 (3H, s) 2.85 (1H, dd, J 8 and 2 Hz), 3.00 (1H, bd, obscured), 4.87 (1H, dd, J 11 and 2 Hz), 5.10 (1H, dd, J 7 and 2 Hz), 5.65 (1H, dd, J 11 and 8 Hz) ppm.

(b) From VI. A solution of eucarvone complex VI (2.0 g, 6.9 mmol) in dry ether (10 ml) was added dropwise to a slurry of $LiAlH_4$ (0.8 g, 21 mmol) in dry ether (20 ml) cooled in a dry ice–acetone mixture. The mixture was stirred for 1 h, then treated with EtOAc followed by 10% aq. HCl. The aqueous solution was extracted with ether and the combined ethereal solutions were washed with brine and dried over Na_2SO_4. Removal of the solvent and chromatography (toluene/$CHCl_3$) gave the crude alcohol VII (0.8 g, 40% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.98 (3H, s), 1.30 (3H, s, +2H obscured), 1.65 (3H, s), 2.68 (1H, d, J 7 Hz), 3.85 (1H, bs), 4.90 (1H, dd, J 7 and 6 Hz), 5.12 (1H, d, J 6 Hz) ppm. A solution of VII (650 mg, 2.2 mmol) in benzene (25 ml) containing p-TsOH (10 mg) was refluxed for $1\frac{1}{2}$ h, stirred with anhydrous Na_2CO_3 and filtered. Removal of the solvent gave III (430 mg, 70% yield), the spectroscopic properties of which were identical to those of the product obtained by method a.

Reactions of III. (a) with TCNE. A solution of equimolar quantities of III (0.5 g, 1.74 mmol) and TCNE (0.22 g) in CH_2Cl_2 (6 ml) was stirred at room temperature for 10 min. The solvent was removed in vacuum and the residue was recrystallised from CH_2Cl_2/hexane to give bright yellow crystals (0.24 g, 35% yield), m.p. 135°C (dec.). CIMS: m/e (CH_4) 403 ($M+1$), 375, 347, 319, 263, 135. Anal.: Found C, 56.85; H, 3.80; N, 14.28. $C_{19}H_{14}N_4FeO_3$ calcd.: C, 56.74; H, 3.51; N, 13.93%. ^{1}H NMR ($CDCl_3$): adduct XI: δ 1.53 (3H, s), 1.66 (3H, s), 2.15 (3H, s), 1.84 (1H, dd, J 9.3 and 6.9 Hz), 3.00 (1H, d, J 6.9 Hz), 4.13 (1H, d, J 9.6 Hz), 4.21 (1H, d, J 9.6 Hz), 4.47 (1H, d, J 9.3 Hz) ppm; adduct XII: δ 1.24 (3H, s), 1.44 (3H, s), 2.38 (3H, s), 2.60 (1H, d, J 8.2 Hz), 2.87 (1H, d, J 3.0 Hz), 3.17 (1H, d, J 8.2 Hz), 3.77 (1H, dd, J 3.0 and 9.6 Hz), 5.29 (1H, d, J 9.6 Hz) ppm.

(b) With DPK (at room temperature). A mixture of III (1.25 g, 4.3 mmol) and DPK (1.26 g, 6.5 mmol) in dry benzene (25 ml) was kept at room temperature for one week. The solvent was removed in vacuum and the residue was treated with hexane and filtered. Slow evaporation of the hexane solution gave a precipitate which was recrystallised from CH_2Cl_2/hexane to give bright yellow crystals of XIVb (0.1 g, 5% yield); m.p. 141–142°C. IR ($CHCl_3$): 2035, 1970 (br) 1770 cm^{-1}. Anal.: Found: C, 68.91; H, 5.06. $C_{27}H_{24}FeO_4$ calcd.: C, 69.24, H, 5.17%. ^{1}H NMR ($CDCl_3$): δ 1.00 (3H, s), 1.30 (3H, s), 1.38 (3H, s), 2.59 (1H, d, J 8.0 Hz), 2.92 (1H, d, J 9.8 Hz), 3.09 (1H, bs), 3.83 (1H, dd, J 9.8 and 3.1 Hz), 4.96 (1H, d, J 8 Hz), 7.2–7.8 (10H, m) ppm.

(c) With DPK (at 80°C). A solution of III (1.25 g, 4.3 mmol) and DPK (1.26 g, 6.5 mmol) in dry benzene (25 ml) was refluxed for 12 g. Removal of solvent and chromatography (hexane/CH_2Cl_2) gave crystals of XVIIb (0.25 g, 12% yield); m.p. 117–118°C (from MeOH). IR ($CHCl_3$): 2050, 1975 (br), 1655 cm^{-1}. Anal.: Found C, 69.29; H, 5.35. $C_{27}H_{24}FeO_4$ calcd.: C, 69.24; H, 5.17%. ^1H NMR ($CDCl_3$): δ 1.13 (3H, s), 1.44 (3H, s), 2.04 (3H, s), 2.96 (2H, m), 5.13 (1H, bd, J 8 Hz), 5.56 (1H, s), 7.2 (11H, m, aromatic + 1 vinyl) ppm.

References

1 Review: G. Deganello, P. Uguagliati, L. Calligaro, P.L. Sandrini and F. Zingales, Inorg. Chim. Acta, 13 (1975) 247; G. Deganello, Transition Metal Complexes of Cyclic Polyolefins, Academic Press, New York, 1979.

2 K. Alder, K. Kaiser and M. Schumacher, Justus Liebigs Ann. Chem., 602 (1957) 80.

3 T.H. Whitesides and J.P. Neilan, J. Am. Chem. Soc., 98 (1976) 63; M. Brookhart and K.J. Karel, J. Organomet. Chem., 140 (1977) 203; W. Lamanna and M. Brookhart, J. Am. Chem. Soc., 102 (1980) 3490; J.M. Brown, I. Midgley and W.J. Albery, J. Chem. Soc., Perkin Trans. 2, (1981) 767 and ref. therein.

4 W.A. Ayer and L.M. Browne, Can. J. Chem., 52 (1974) 1352.

5 G.F. Emerson, J.E. Mahler and R. Pettit, J. Org. Chem., 29 (1964) 3620; M. Brookhart and G. Nelson, J. Organomet. Chem., 164 (1979) 193; A.J. Birch, B.M.R. Bandara, K. Chamberlain, B. Chauncy, P. Dahler, A.I. Day, I.D. Jenkins, L.F. Kelly, T.-C. Khor, G. Kretschmer, A.J. Liepa, A.S. Narula, W.D. Raverty, E. Rizzardo, C. Sell, G.R. Stephenson, D.T. Thompson and D.H. Williamson, Tetrahedron, Suppl., 37 (1981) 289.

6 A. Eisenstadt, J.M. Guss and R. Mason, J. Organomet. Chem., 8 (1974) 245.

7 K.N. Houk, Acc. Chem. Res., 8 (1975) 361; K.N. Houk, J. Sims, R.E. Duke, R.W. Strozier and J.K. George, J. Am. Chem. Soc., 95 (1973) 7287.

8 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058; T.A. Albright, Tetrahedron, 38 (1982) 1339.

9 K.J. Karel, T.A. Albright and M. Brookhart, Organometallics, 1 (1982) 419.

10 (a) M. Green, S. Heathcock and D.C. Wood, J. Chem. Soc., Dalton Trans., (1973) 1564; (b) Z. Goldschmidt and Y. Bakal, Tetrahedron Lett., (1976) 1229, (1977) 955; (c) M. Green, S.M. Heathcock, T.W. Turney and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 204; (d) Z. Goldschmidt and Y. Bakal, J. Organomet. Chem., 168 (1979) 215; (e) S.K. Chopra, M.J. Hynes and P. McArdle, J. Chem. Soc., Dalton Trans., (1981) 586.

11 D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977), 20, 26, 31.

12 R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie- Academic Press, New York, 1969.

13 S.K. Chopra, G. Moran and P. McArdle, J. Organomet. Chem., 214 (1981) C36.

14 Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 271.

15 Z. Goldschmidt and S. Antebi, J. Organomet. Chem., 206 (1981) C1.

16 E.J. Forbes, M.K. Sultan and P.C. Uden, Anal. Lett., 5 (1972) 927.