

Journal of Organometallic Chemistry, 187 (1980) 341–347
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

X-RAY PHOTOELECTRON SPECTRA OF INORGANIC MOLECULES

XXVI *. COMPLEXES OF MOLYBDENUM(0) AND MOLYBDENUM(II) CONTAINING THE DICARBONYL MOLYBDENUM MOIETY

B.J. BRISDON,

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY (Great Britain)

W.S. MIALKI and R.A. WALTON **

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

(Received September 20th, 1979)

Summary

The Mo 3d binding energies of sixteen complexes of Mo^{II} containing the [(η^3 -allyl)Mo(CO)₂] moiety have been recorded. These data are compared with that available for dicarbonyl molybdenum derivatives of Mo⁰ and with literature data for complexes of the types Mo(CO)₅L, Mo(CO)₄L₂ and Mo(CO)₃L₃. In contrast to the conclusions of other workers, the present work shows that the Mo 3d energies are not dependent in any simple way upon the number of carbonyl groups bound to molybdenum. The dependence of the Mo 3d binding energies upon the nature of the ligands and the metal oxidation state is discussed.

Introduction

Studies on the X-ray photoelectron spectra (XPS) of well defined molybdenum compounds [2–14] have included a few on organometallic derivatives of this element [3–7,14]. However, in only one instance [4] has an extensive series of organometallic complexes been investigated, the studies of Grim and Matienzo [4] having concentrated on Mo⁰ derivatives which contain the Mo(CO)₅, Mo(CO)₄ and Mo(CO)₃ moieties. One of their more important observations [4] concerned the decrease in the average Mo 3d binding energies of complexes of the type Mo(CO)_{6-x}L_x (where L = phosphorus or nitrogen donor and x = 3, 4

* For part XXV see ref. 1.

** Address any correspondence to this author.

or 5) in the order $\text{Mo}(\text{CO})_5\text{L} > \text{Mo}(\text{CO})_4\text{L}_2 > \text{Mo}(\text{CO})_3\text{L}_3$. Grim and Matienzo concluded [4] that this "indicates a higher electron density on Mo with increasing substitution for CO by better σ donors and poorer π acceptors than CO".

One important group of complexes not previously investigated were those containing the dicarbonyl molybdenum unit. These species are of considerable interest in the light of the conclusions of Grim and Matienzo [4]. As a consequence of our recent interest in the XPS of derivatives of Mo^{II} [8,10–12,14] and the availability of a variety of (η^3 -allyl)dicarbonylmolybdenum(II) complexes from previous studies devoted to their synthesis, structure and dynamic properties [15–19], we have measured the Mo 3d binding energies of sixteen of these complexes and combined this study with one involving Mo^0 derivatives of the type $\text{Mo}(\text{CO})_2\text{L}_4$, species which are conveniently prepared using the allyl derivatives as synthetic precursors. Our results are compared with those expected on the basis of the previous interpretations of Grim and Matienzo [4] and lead, we believe, to the need to reassess their conclusions.

Experimental

X-ray photoelectron spectra were recorded using a Hewlett-Packard Model 5950A ESCA spectrometer. Monochromatic aluminum $K_{\alpha 1,2}$ radiation (1486.6 eV) was used as the X-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface. An electron "floodgun" was used in conjugation with this instrument to eliminate, or at least reduce to a minimum, surface changing effects. Additional experimental details are described fully elsewhere [20,21].

The complexes studied in the present investigation were prepared by literature methods or extensions thereof [15–17,22–26]. All samples were of acceptable analytical purity and their identity was further confirmed by their spectroscopic properties. In the subsequent discussion of these complexes the following ligand abbreviations will be used (see Table 1): py = pyridine; bipy = 2,2'-bipyridyl; dpa = 2,2'-dipyridylamine; dppe = 1,2-bis(diphenylphosphino)ethane; arphos = 1-diphenylphosphino-2-diphenylarsinoethane; dpae = 1,2-bis(diphenylarsino)ethane; acac = acetylacetonate; sal = NPh = *N*-phenylsalicylaldimine (OC₆H₄CHNPh).

Results and discussion

Complexes of the types $\text{Mo}(\text{CO})_2\text{L}_4$ and $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)\text{XL}_2$

The Mo $3d_{5/2}$ binding energies of the dicarbonyl molybdenum derivatives of Mo^0 and Mo^{II} are presented in Table 1 and the spectra of representative examples of the two groups of complexes are shown in Fig. 1. In all instances, the Mo $3d_{3/2}$ spin-orbit component occurs at ~ 3.1 eV to the high binding energy side of the Mo $3d_{5/2}$ peak. Additional core electron binding energies have been recorded for certain of the complexes and these are also listed in Table 1. However, since the latter data have little direct bearing on the objectives of the present investigation they will not be considered further other than to note that these binding energies (N 1s, Cl 2p, S 2p, P 2p, Br 3d and I 3d) are quite normal for the ligands in question.

TABLE 1

X-RAY PHOTOELECTRON SPECTRA OF COMPLEXES CONTAINING THE DICARBONYLMOLYB-DENUM MOIETY ^a

Complex	Mo 3d _{5/2}	N 1s ^b	Cl 2p _{3/2}	Other B.E.'s
I Mo(CO) ₂ (MeCN) ₂ (PPh ₃) ₂	227.8(1.8)			
II Mo(CO) ₂ (MeCN)(P-n-Bu ₃) ₃	227.8(1.4)			
III Mo(CO) ₂ (MeCN)(PPh ₂ Me) ₃	227.9(1.8)			
IV Mo(CO) ₂ (dppe) ₂	227.3(1.4)			
V Mo(CO) ₂ (bipy)(PPh ₃) ₂	227.3(1.4)	400.0(2.6)		P 2p _{3/2} = 131.0
VI Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)Cl	228.7(1.4)		197.5	
VII Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)Br	228.8(1.7)	400.0(1.8)		Br 3d _{5/2} = 69.1
VIII Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)I	228.5(1.7)	399.5(1.9)		I 3d _{5/2} = 618.8
IX Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)NCS	228.7(1.7)	399.2(2.2) ^c 397.7(1.6) ^{c, d}		S 2p _{3/2} = 162.2 ^d
X Mo(CO) ₂ (η ³ -C ₃ H ₅)(dpa)Cl	229.1(1.6)	400.0(1.8)	198.2	
XI Mo(CO) ₂ (η ³ -C ₃ H ₅)(dpa)Br	228.6(1.8)	399.7(2.6)		Br 3d _{5/2} = 68.4
XII Mo(CO) ₂ (η ³ -C ₃ H ₅)(dpae)Cl	228.9(1.2)		197.9	
XIII Mo(CO) ₂ (η ³ -C ₃ H ₅)(arphos)Cl	228.9(1.6)			
XIV Mo(CO) ₂ (η ³ -C ₃ H ₅)(dppe)Cl	228.9(1.2)		197.9	
XV Mo(CO) ₂ (η ³ -C ₃ H ₅)(py)(acac)	229.4(1.8)			
XVI Mo(CO) ₂ (η ³ -C ₃ H ₅)(py)-(sal=NPh)	229.2(1.6)	399.7(2.4)		
XVII Mo(CO) ₂ (η ³ -2MeC ₃ H ₄)-(P(OMe) ₃) ₂ Cl ^e	228.9(1.2)		198.5	
XVIII [Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)-(P(OMe) ₃)I ⁺ BF ₄ ⁻ ^e	228.7(1.3)			
XIX [Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)-(P(OEt) ₃)I ⁺ BF ₄ ⁻ ^e	228.7(1.4)			
XX [Mo(CO) ₂ (η ³ -C ₃ H ₅)(bipy)-(py)I ⁺ BF ₄ ⁻ ^e	228.6(1.7)	399.5(1.8)		
XXI [Ph ₃ PC ₃ H ₅] [Mo ₂ (CO) ₄ (η ³ -C ₃ H ₅) ₂ Cl ₃] ⁻	228.9(1.3)		198.3	

^a Binding energies are referenced to a C 1s binding energy of 285.0 eV for the organic ligands (this is taken as the most intense peak in the C 1s spectrum); full-width half-maximum values for the Mo 3d_{5/2} and N 1s peaks are given in parentheses. ^b A peak at ~395 eV, to the low binding energy side of the N 1s photoline, is due to the Mo 3p_{3/2} photoemission. ^c The intensity ratio of the peak at 399.2 eV to that at 397.7 eV is 2 : 1 in accord with the stoichiometric ratio of different nitrogen atoms. ^d These binding energies are characteristic of thiocyanate [31]. ^e These complexes show a C 1s peak at ~286 eV, assigned to the α-carbon atoms of the P(OR)₃ ligands, in addition to the main C 1s peak at 285.0 eV.

The binding energy referencing procedure we have chosen to use is the one most commonly employed in earlier XPS studies on complexes of this type, namely, a C 1s energy of 285.0 eV for the organic ligands [3,6,7,9,11–14]. Although several of the complexes contain carbon atoms whose C 1s energies differ (for example, the C 1s value for the P(OMe)₃ ligand differs from that for 2,2'-bipyridyl), if reference is made to the most intense C 1s peak (that close to 285.0 eV) which arises from those aromatic (or aliphatic) carbon atoms which are not subject to any marked inductive effects, then this procedure is quite satisfactory. With this reference procedure we estimate the Mo 3d binding energies given in Table 1 to be accurate to ±0.2 eV. To compare the present data with that available for some molybdenum halide complexes, for which a graphite reference (C 1s 284.0 eV) [8,10] had been used, and with the data reported by Grim and Matienzo [4], who used a Au 4f_{7/2} reference of 83.0 eV,

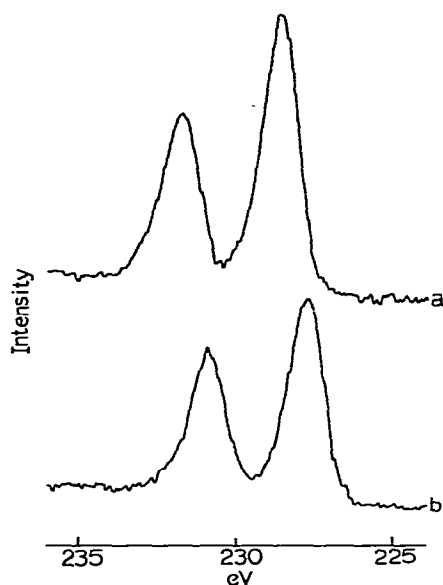


Fig. 1. Mo 3d binding energy spectra of (a) $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})\text{Cl}$ and (b) $\text{Mo}(\text{CO})_2(\text{MeCN})(\text{P-n-Bu}_3)_3$.

the literature data should be "corrected" by either +0.3 eV (for references [8] and [10] or +0.8 eV (for reference [4]) to make it compatible with the normal reference values for these two standards [27]. This has been done in all subsequent discussions concerning the literature data.

A comparison of the data for the η^3 -allyl derivatives of Mo^{II} with those for the Mo^0 species (see Table 1), shows that the Mo $3d_{5/2}$ binding energies occur in the ranges 229.4–228.5 eV and 227.9–227.3 eV, respectively. Assuming that differences in relaxation energy and Madelung-type potentials are small then the data imply that the molybdenum atom is more positively charged in the Mo^{II} complexes, than in the Mo^0 derivatives which are formed from the η^3 -allyl derivatives by the reductive elimination of the appropriate allyl-halide. The range of Mo $3d_{5/2}$ energies for the η^3 -allyl complexes are in turn similar to those reported previously for an assortment of organometallic and non-organometallic derivatives of Mo^{II} . These include $\text{Mo}(\text{CO})_3\text{Cl}_2(\text{PPh}_3)_2$ (228.0 eV) [3], $[\text{Mo}(\text{CNR})_7](\text{PF}_6)_2$ (229.1 eV) [14], $\text{MoCl}_2(\text{dppe})_2$ (228.3 eV) [7] and $\text{Mo}_2\text{-X}_4\text{L}_4$, where X = Cl, Br or NCS, (229.2–228.6 eV) [8,10,11].

Within the group of sixteen complexes which contain the $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)$ unit, there is no obvious correlation of the Mo 3d energies with variations in the ligand sets, indeed, these energies are remarkably similar. Furthermore, we observe no dependence of the binding energies upon the detailed molecular geometries of the complexes, of which three different types have so far been identified [18,19,23,28–30]. One possible correlation which we checked was that between the Mo 3d chemical shifts, which monitor (in part) the charge variations which occur at the metal center, and the infrared active $\nu(\text{CO})$ modes, which reflect differences in the M–CO bonding. In all instances, the two CO groups are *cis* to one another. The $\nu(\text{CO})$ modes for the crystalline

complexes are listed in Table 2. In the case of the Mo⁰ species (complexes I–V) there is no correlation. Indeed, the complexes which possessed the highest and lowest energies for their $\nu(\text{CO})$ modes, Mo(CO)₂(dppe)₂ (IV) and Mo(CO)₂-(bipy)(PPh₃)₂ (V), had indistinguishable Mo 3d energies. Accordingly, the similarity in the electron density at the central metal atom in IV and V, in spite of their greater degree of Mo–CO π -back bonding in V, may reflect differences in the donor abilities of the other ligands (bipy, PPh₃ and dppe). In the case of IV and V, this correlates with nitrogen being a better σ donor and/or a poorer π acceptor than phosphorus in dicarbonyl derivatives of Mo⁰, a conclusion which agrees with that of Grim and Matienzo [4] for carbonyl derivatives of the types Mo(CO)₄L₂ and Mo(CO)₃L₃.

For the Mo^{II} complexes VI–XXI there is again no correlation between the Mo 3d energies and variations in $\nu(\text{CO})$. In this series, the complex with the lowest energy $\nu(\text{CO})$ modes, XV, possesses the highest Mo 3d_{5/2} energy, while the complex with the next lowest values for $\nu(\text{CO})$, VIII, has the lowest Mo 3d_{5/2} energy.

Comparison of Mo 3d binding energies with literature data

Grim and Matienzo [4] had previously observed that the average Mo 3d binding energies of Mo⁰ carbonyl derivatives decrease in the order Mo(CO)₅L > Mo(CO)₄L₂ > Mo(CO)₃L₃. The interpretation of these results [4] in terms of an increase in electron density at the molybdenum upon the substitution of CO by ligands which are better σ donors and poorer π acceptors than CO, leads to the expectation that the Mo 3d energies for Mo(CO)₂L₄ will be lower than those of Mo(CO)₃L₃. In fact, the average value for the five complexes of the type Mo(CO)₂L₄ is 227.6 eV, a value which is significantly greater than the average value reported [4] for Mo(CO)₃L₃. Actually, the use of an average value of the Mo 3d energy for these different groups of complexes [4] is questionable because of the widely different numbers of complexes within each group which were studied. Instead, we prefer to consider the ranges of binding energy values

TABLE 2

INFRARED ACTIVE $\nu(\text{CO})$ MODES OF COMPLEXES CONTAINING THE DICARBONYLMOLYB-
DENUM MOIETY ^a

Complex	$\nu(\text{CO})$ (cm ⁻¹)	Ref ^b	Complex	$\nu(\text{CO})$ (cm ⁻¹)	Ref ^b
I	1807 1740	32	XII	1935 1850	17
II	1811 1741	c	XIII	1935 1850	c
III	1838 1754	c	XIV	1940 1852	16
IV	1858 1778	c	XV	1918 1830	15
V	1792 1723	c	XVI	1926 1848	c
VI	1934 1845	22	XVII	1980 1849	26
VII	1927 1845	22	XVIII	1940 1859	c
VIII	1923 1845	22	XIX	1942 1850	c
IX	1943 1855	c	XX	1938 1876	22
X	1928 1842	15	XXI	{ 1927 1850br 1942	17
XI	1930 1844	15			

^a Spectra are for nujol mulls; ^b reference to the source of the infrared spectral data. ^c New data or redetermination of literature data.

within each group. When this is done, we find that for $\text{Mo}(\text{CO})_5\text{L}$, $\text{Mo}(\text{CO})_4\text{L}_2$, $\text{Mo}(\text{CO})_3\text{L}_3$ and $\text{Mo}(\text{CO})_2\text{L}_4$ the ranges are 227.7–227.0, 227.8–226.1, 227.0–226.0 and 227.9–227.3 eV, respectively*. Unfortunately, there is no series of complexes of the type $\text{Mo}(\text{CO})_{6-x}\text{L}_x$, where $x = 1, 2, 3$ or 4, in which L remains the same and for which the Mo 3d binding energies have been measured. The closest we come to this situation is within the series $\text{Mo}(\text{CO})_5(\text{PPh}_3)$, $\text{Mo}(\text{CO})_4(\text{dppe})$, $\text{Mo}(\text{CO})_3(\text{dppe})[\text{P}(\text{O}i\text{Bu})_3]$ and $\text{Mo}(\text{CO})_2(\text{dppe})_2$ for which the Mo 3d_{5/2} values are 227.6 [3], 226.7 [4], 227.0 [4] and 227.3 eV, respectively. Accordingly, for the substituted carbonyl derivatives of Mo⁰, it is clear that there is no simple correlation between the Mo 3d binding energies and the number of carbonyl groups, a result which contrasts with the earlier conclusions of Grim and Matienzo [4].

One further way of considering the Mo 3d binding energies for the η^3 -allyl derivatives $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)\text{XL}_2$ (Table 1) is in terms of a comparison with the data for the related Mo⁰ tetracarbonyls $\text{Mo}(\text{CO})_4\text{L}_2$ [4]. In so doing, we are effectively considering the net electron withdrawing effect of two CO groups versus an η^3 -allyl ligand and a halogen (assuming that the effects of the remaining ligands remain constant). Thus, if we determine the chemical shift within the pairs $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})\text{Cl}$ – $\text{Mo}(\text{CO})_4(\text{bipy})$ and $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dppe})\text{Cl}$ – $\text{Mo}(\text{CO})_4(\text{dppe})$, the values of 2.6 and 2.2 eV, respectively, which are obtained reflect a considerable decrease in the electron density at the metal in going to the species with the higher formal oxidation state.

The preceding discussion has indicated that there is no simple correlation between the metal charge (as reflected by changes in the Mo 3d binding energies) and a variation in the number of carbonyl groups. The relative insensitivity of these binding energies to such a change is further shown by a comparison of the Mo 3d energies for the Mo^{II} complexes $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$ (Mo 3d_{5/2} 229.0–228.5 eV) [8,10] and $\text{Mo}(\text{CO})_3\text{Cl}_2(\text{PPh}_3)_2$ (Mo 3d_{5/2} 229.0 eV) [3], where the electron withdrawing effect of three CO groups is clearly minimal. On the other hand, the isoelectronic dinitrosyl derivatives $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{PR}_3)_2$ have Mo 3d binding energies (Mo 3d_{5/2} 230.6–230.2 eV) [3,12] which reveal the dramatic electron withdrawing influence of two NO groups.

A final comparison is that between $\text{Mo}(\text{CO})_2(\text{dppe})_2$ (Table 1) and $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ [6]. These complexes have essentially identical binding energies (227.3 and 227.2 eV, respectively) and their oxidation to the Mo^I derivatives $[\text{Mo}(\text{CO})_2(\text{dppe})_2]\text{ClO}_4$ [7] and $\text{Mo}(\text{N}_2)\text{Cl}(\text{dppe})_2$ [6] lead to similar Mo 3d chemical shifts (+1.4 and +1.0, respectively).

Acknowledgements

R.A.W. thanks the National Science Foundation (Grant CHE74-12788) for research support and the University of Bath for its hospitality. Several of the samples used in this study were kindly provided by Kathleen E. Paddick, University of Bath.

* As mentioned previously, the data of Grim and Matienzo [4] has been corrected by +0.8 eV to make it compatible with our data.

References

- 1 R.R. Gagné, J.L. Allison, C.A. Koval, W.S. Mialki, T.J. Smith and R.A. Walton, *J. Amer. Chem. Soc.*, in the press.
- 2 W.E. Swartz, Jr., and D.M. Hercules, *Anal. Chem.*, 43 (1971) 1774.
- 3 W.B. Hughes and B.A. Baldwin, *Inorg. Chem.*, 13 (1974) 1531.
- 4 S.O. Grim and L.J. Matienzo, *Inorg. Chem.*, 14 (1975) 1014.
- 5 D. Briggs, D.T. Clark, H.R. Keable and M. Kilner, *J. Chem. Soc. Dalton*, (1973) 2143.
- 6 P. Brant and R.D. Feltham in P.C.H. Mitchell, (Ed.), *Proceedings of the Climax Second International Conference on the Chemistry and Uses of Molybdenum*, Climax Molybdenum Co. Ltd. 1976, p. 39.
- 7 P. Brant, Ph. D. Thesis, University of Arizona, 1977.
- 8 R.A. Walton in P.C.H. Mitchell (Ed.), *Proceedings of the Climax Second International Conference on the Chemistry and Uses of Molybdenum*, Climax Molybdenum Co. Ltd., 1976, p. 35.
- 9 J. Chatt, C.M. Elson, G.J. Leigh, J.A. Connor, *J. Chem. Soc. Dalton*, (1976) 1351.
- 10 S.A. Best, T.J. Smith and R.A. Walton, *Inorg. Chem.*, 17 (1978) 99.
- 11 T. Nimry and R.A. Walton, *Inorg. Chem.*, 17 (1978) 510.
- 12 T. Nimry, M.A. Urbanic and R.A. Walton, *Inorg. Chem.*, 18 (1979) 691.
- 13 Yu.M. Shul'ga, A.P. Pivovarov, V.D. Makhaev and A.P. Borisov, *J. Organometal. Chem.*, 164 (1979) 47.
- 14 P. Brant, W.S. Mialki and R.A. Walton, *J. Amer. Chem. Soc.*, 101 (1979) 5453.
- 15 B.J. Brisdon and G.F. Griffin, *J. Chem. Soc. Dalton*, (1975) 1999.
- 16 B.J. Brisdon, *J. Organometal. Chem.*, 125 (1977) 225.
- 17 B.J. Brisdon and K.E. Paddick, *J. Organometal. Chem.*, 149 (1978) 113.
- 18 B.J. Brisdon and A.A. Woolf, *J. Chem. Soc. Dalton*, (1978) 291.
- 19 M.G.B. Drew, B.J. Brisdon, D.A. Edwards and K.E. Paddick, *Inorg. Chim. Acta*, 35 (1979) L381.
- 20 A.D. Hamer and R.A. Walton, *Inorg. Chem.*, 13 (1974) 1446.
- 21 A.D. Hamer, D.G. Tisley and R.A. Walton, *J. Inorg. Nucl. Chem.*, 36 (1974) 1771.
- 22 C.G. Hull and M.H.B. Stiddard, *J. Organometal. Chem.*, 9 (1967) 519.
- 23 J.W. Faller, D.A. Haitko, R.D. Adams and D.F. Chodosh, *J. Amer. Chem. Soc.*, 99 (1977) 1654.
- 24 H. Friedel, I.W. Renks and H. tom Dieck, *J. Organometal. Chem.*, 26 (1971) 247.
- 25 J. Powell, *J. Organometal. Chem.*, 129 (1977) 175.
- 26 B.J. Brisdon, D.A. Edwards, K.E. Paddick and M.G.B. Drew, *J. Chem. Soc. Dalton*, in the press.
- 27 G. Johansson, J. Hedman, A. Berndtsson, M. Klasson and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, 2 (1973) 295.
- 28 M.G.B. Drew and G.F. Griffin, private communication.
- 29 A.J. Graham and R.H. Fenn, *J. Organometal. Chem.*, 17 (1969) 405.
- 30 A.J. Graham and R.H. Fenn, *J. Organometal. Chem.*, 37 (1972) 137.
- 31 S.A. Best and R.A. Walton, *Isr. J. Chem.*, 15 (1978) 160.
- 32 F. Hohman and H. tom Dieck, *J. Organometal. Chem.*, 85 (1975) 47.