Journal of Organometallic Chemistry, *447* (1993) 197–201

JOM 23201

Manganese carbonyl complexes of 2,5-dimethylbismolyl. The crystal and molecular structure of (η^1-2,5-dimethylbismolyl) manganese pentacarbonyl

Arthur J. Ashe, III, Jeff W. Kampf and Dhananjay B. Puranik

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055 (USA)

(Received June 29, 1992; in revised form August 24, 1992)

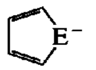
Abstract

(η-^{1}-2,5-Dimethylbismolyl)manganese pentacarbonyl (**8**) has been obtained from the reaction of 1-phenyl-2,5-dimethylbismole with lithium followed by $BrMn(CO)_5$. Heating **8** to its melting point causes the loss of CO to produce (η^5-2,5-dimethylbismolyl)manganese tricarbonyl. Compound **8** crystallizes in the monoclinic crystal system, space group $P2_1$ (No. 4) with $a = 6.838(2)$ Å, $b = 6.424(1)$ Å, $c = 15.787(4)$ Å, $\beta = 95.68(2)°$, $V = 690.1(2)$ Å^3 and $Z = 2$. A full structure has been determined and is compared with those of analogous compounds.

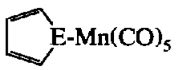
1. Introduction

Heterocyclopentadienides of the Group 15 elements (**1–5**) are versatile ligands towards transition metals [1]. $Mn(CO)_5$-complexes (**6**), in which the heteroatom is η^1-coordinated, are known for tetraphenyl derivatives of **2**, **3** and **4** [2]. Similarly $Mn(CO)_3$-complexes (the heterocymantrenes) (**7**) have been reported for derivatives of **1** [3], **2** [4], **3** [5] and **4** [6]. The absence of analogous d_6-Mn^I complexes of bismolyl (**5**) makes their synthesis desirable in order to complete the series.

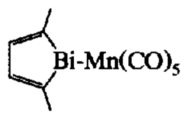
We now wish to report on the preparation of (η^1-2,5-dimethylbismolyl)$Mn(CO)_5$ (**8**) and (η^5-2,5-dimethylbismolyl)$Mn(CO)_3$ (**9**). Since there are no prior structural data for (η^1-heterolyl)$Mn(CO)_5$ complexes and relatively few structural data on organobismuth transition metal complexes [7], we have obtained a crystal structure for **8**.



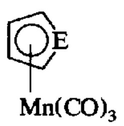
1, E = N
2, E = P
3, E = As
4, E = Sb
5, E = Bi



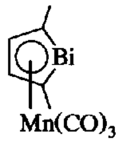
(**6**)



(**8**)



(**7**)



(**9**)

2. Results and discussion

The reaction of 1-phenyl-2,5-dimethylbismole (**10**) [8] with lithium in THF at 25°C gave a green-brown solution of (2,5-dimethylbismolyl)lithium and phenyllithium, which on sequential reaction with NH_3 to remove the phenyllithium, followed by $BrMn(CO)_5$,

---

Correspondence to: Professor A.J. Ashe, III.

0022-328X/93/$6.00

TABLE 1. Structure determination summary of **8** [a]

Crystal data	
Empirical formula	$C_{11}H_8O_5MnBi$
Formula weight (amu)	484.10_2
Crystal colour and habit	Orange rectangular plate
Crystal dimensions (mm^3)	0.14 × 0.42 × 0.34
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4) [b,c]
Z	2
Unit cell dimensions from 25 reflections	($20° \le 2\theta \le 32°$)
a (Å)	6.838(2)
b (Å)	6.424(1)
c (Å)	15.787(4)
β (°)	95.68(2)
Volume ($Å^3$)	690.1(2)
Density (calc.) ($g\ cm^{-3}$)	2.32_9
$F(000)$	444 electrons
Linear absorption coefficient (μ) (cm^{-1})	135.85
Data collection	
Diffractometer	Siemens R3m/v
Radiation type	Mo K$\bar{\alpha}$ λ = 0.71073 Å, Lp corrected, graphite monochromator
Temperature	Ambient
Scan type	θ–2θ scan
2θ scan range (°)	5–60
Octants used	$+h, \pm k, \pm l$ (h 0/10; k $\overline{10}$/10; l $\overline{23}$/23)
Scan rate (° min^{-1})	1.5–5.0, variable
Scan width	0.8° below Kα1 to 0.8° above Kα2
Background/scan ratio	0.5
Standard reflections	3 measured every 97 reflections, linear decay ~ 9%
Number of data collected	4505
Number of unique reflections	4034, $R_{int.} = 0.0234$
Absorption correction	Semi-empirical, psi scans
R merge before/after correction	0.1495/0.0489
Max/min transmission	0.101/0.036
Solution and refinement	
System used	Siemens SHELXTL PLUS VAXStation 3500
Solution	Patterson
Refinement method	Full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_o - F_c \rvert)^2$
Hydrogen atoms	Riding model, $d_{C-H} = 0.96$ Å, common isotropic U_H refined to 0.10(2)
Refined reflections with $(F_o) \ge 0.6\sigma(F)$	3878
Number of parameters refined	163
Data/parameter ratio	23.8
$R = \Sigma(\lvert F_o - F_c \rvert)/\Sigma \lvert F_o \rvert)$	0.0518
$R_w = [\Sigma(w \lvert F_o - F_c \rvert)^2/\Sigma w(F_o)^2]^{1/2}$	0.0676
$w^{-1} = \sigma^2(F_o) + 0.003755\ (F_o)^2$	
GOF	0.92
Mean shift/error	< 0.001
Maximum shift/error	< 0.001
Secondary extinction	10 reflections excluded from refinement
Residual electron density (e $Å^{-3}$)	+4.10/ − 2.98 [d]

---

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, U_{eq} defined as $1/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. [b] The other enantiomorph was checked with refinement leading to significantly higher residuals ($R = 0.0756$, $R_w = 0.1058$). [c] Systematic absences in the data gave centric $P2_1/m$ (No. 11) and acentric $P2_1$ (No. 4) as space group choices. Counting statistics strongly favoured an acentric distribution. However, since the presence of heavy atoms can modify these statistics, initial attempts were made to solve the structure in $P2_1/m$. After no chemically reasonable solutions could be found in the centric space group, solution and refinement in $P2_1$ proceeded smoothly without the problems typically associated with space group misassignment (severe correlations, unusual bond distances/angles, poor agreement of chemically equivalent bonds). [d] All of the large residual electron density peaks/holes are associated with the Bi atom (< 0.8 Å from Bi). There are no chemically significant peaks/holes in the final difference Fourier.

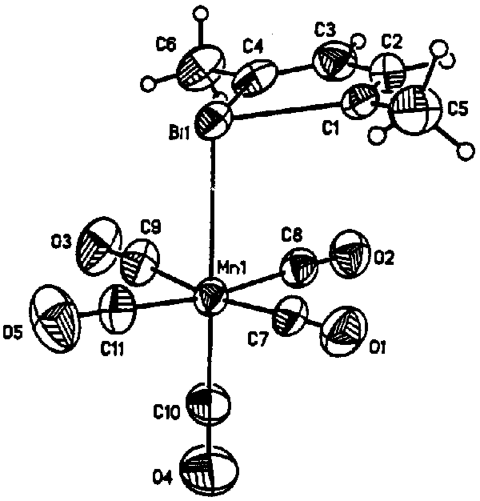
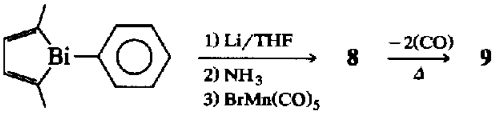


Fig. 1. ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for non-hydrogen atoms of **8**.

TABLE 2. Atomic coordinates and isotropic thermal parameters for **8**

Atom	*x*	*y*	*z*	u_{eq}
Bi1	0.00489(4)	0.00000	0.19318(2)	0.0429(1)
Mn1	0.1963(2)	−0.1241(3)	0.35202(9)	0.0433(4)
O1	0.557(2)	0.076(2)	0.2950(8)	0.067(3)
O2	0.299(1)	−0.511(2)	0.2635(6)	0.071(3)
O3	−0.188(2)	−0.305(2)	0.3884(9)	0.091(5)
O4	0.398(3)	−0.255(3)	0.5181(8)	0.111(6)
O5	0.070(3)	0.287(2)	0.4171(9)	0.097(6)
C1	0.238(1)	−0.086(2)	0.1076(6)	0.050(3)
C2	0.193(2)	−0.268(3)	0.0738(8)	0.060(4)
C3	0.026(2)	−0.385(2)	0.0922(8)	0.062(4)
C4	−0.095(2)	−0.317(2)	0.1475(8)	0.055(3)
C5	0.400(2)	0.058(3)	0.086(1)	0.073(5)
C6	−0.274(2)	−0.428(2)	0.171(1)	0.070(5)
C7	0.418(1)	0.006(3)	0.3151(6)	0.048(2)
C8	0.256(2)	−0.367(2)	0.2956(7)	0.052(3)
C9	−0.046(2)	−0.239(2)	0.3730(9)	0.061(4)
C10	0.318(2)	−0.204(2)	0.4550(8)	0.066(4)
C11	0.115(2)	0.124(2)	0.3920(8)	0.057(4)

afforded **8** in 54% yield. Compound **8** forms orange crystals which are thermally stable up to the m.p. 124–125°C. However, on melting, **8** rapidly loses CO to form π-complex **9**.



(10)

Crystals of **8** suitable for X-ray diffraction were obtained by recrystallization from acetone. Crystal data and data collection parameters are summarized in Table 1. An ORTEP drawing of the molecular structure of **8** showing the numbering scheme used in the refinement is illustrated in Fig. 1. Table 2 gives the positional values, while Table 3 gives the more important bond distances and angles. A table of observed and calculated structure factors is available from AJA on request.

The structure of **8** consists of a near planar 2,5-dimethylbismolyl moiety in which the pyramidal Bi atom is η^1-bonded to the $Mn(CO)_5$ group. The geometry about Mn is that of a distorted octahedron with the equatorial carbonyl groups slightly oriented towards the bismuth atom. The Mn atom is 0.143(3) Å below the plane of the equatorial carbon atoms. Similar distortions are found for $Ph_2BiMn(CO)_5$ (**11**) [9] and indeed for many main group/transition metal carbonyl compounds.

The Bi, Mn, and the axial carbonyl carbon atom are collinear. The Bi–Mn distance of 2.827(1) Å is only slightly shorter than that of the more hindered $Ph_2BiMn(CO)_5$ (2.842(2) Å) [9] but considerably shorter than the Bi–Mn bond lengths of the very crowded $Bi(Mn(CO)_5)_3$ (2.88–2.92 Å) [10].

The bond angles and lengths of the dimethylbismolyl moiety of **8** are identical to those found for 2,2′,5,5′-tetramethylbibismole (**12**) [11]. However the C(1)–Bi–Mn and C(4)–Bi–Mn bond angles (99.8°,

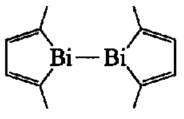
TABLE 3. Selected bond distances (Å) and angles (°) for **8**

Bond lengths			
Bi1–Mn1	2.827(1)	O2–C8	1.11(2)
Bi1–C1	2.26(1)	O3–C9	1.10(2)
Bi1–C4	2.25(1)	O4–C10	1.14(2)
Mn1–C7	1.87(1)	O5–C11	1.17(2)
Mn1–C8	1.86(1)	C1–C2	1.31(2)
Mn1–C9	1.87(1)	C1–C5	1.51(2)
Mn1–C10	1.82(1)	C2–C3	1.42(2)
Mn1–C11	1.82(1)	C3–C4	1.33(2)
O1–C7	1.12(2)	C4–C6	1.50(2)
Bond angles			
Bi1–Mn1–C7	85.1(3)	C1–Bi1–C4	78.2(4)
Bi1–Mn1–C8	85.2(3)	C1–C2–C3	123(1)
Bi1–Mn1–C9	86.0(4)	C2–C1–C5	127(1)
Bi1–Mn1–C10	179.5(5)	C2–C3–C4	121(1)
Bi1–Mn1–C11	86.1(4)	C3–C4–C6	126(1)
Bi1–C1–C2	108.1(8)	C7–Mn1–C8	90.2(6)
Bi1–C1–C5	124.6(9)	C7–Mn1–C9	171.0(5)
Bi1–C4–C3	108.6(9)	C7–Mn1–C10	95.3(6)
Bi1–C4–C6	125.5(9)	C7–Mn1–C11	90.0(6)
Mn1–Bi1–C1	99.8(3)	C8–Mn1–C9	89.6(6)
Mn1–Bi1–C4	97.3(3)	C8–Mn1–C10	95.1(6)
Mn1–C7–O1	176(1)	C8–Mn1–C11	171.2(5)
Mn1–C8–O2	177(1)	C9–Mn1–C10	93.6(7)
Mn1–C9–O3	177(1)	C9–Mn1–C11	88.9(6)
Mn1–C10–O4	178(1)	C10–Mn1–C11	93.6(6)
Mn1–C11–O5	178(1)		

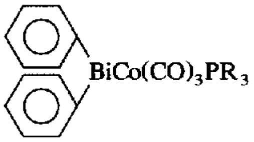
97.3°) are significantly larger than the corresponding C–Bi–Bi bonds angles (88.8°, 90.0°) of **12**. It seems likely that this increase in the angles at Bi is due to steric repulsion between the carbonyl and bismolyl groups. It might be noted that a similar increase in the C–Bi metal bond angles occurs between Ph_4Bi_2 [12] and metal carbonyl complexes $Ph_2BiMn(CO)_5$ [9] and $Ph_2BiCo(CO)_3PPh_3$ (**13**) [13].

That the bond angles about Bi are substantially smaller than tetrahedral suggests that the Bi lone pair is essentially s in character and consequently should have a low availability for bonding. This is consistent with the failure of **8** to form the hypothetical bismolyl bridged complex **14** on heating. The corresponding As- and P-bridged complexes **15** are formed from tetraphenyl derivatives of **7** [2].

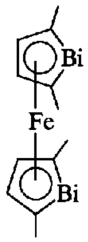
(11)



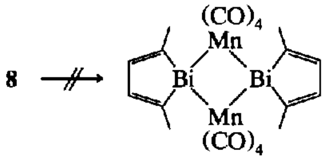
(12)



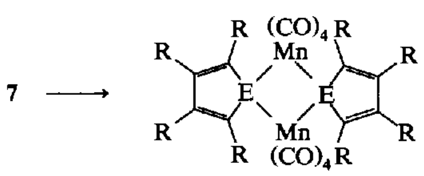
(13)



(16)



(14)



(**15**, E = P, As; R = C_6H_5)

TABLE 4. The IR spectra of the complexes (η^1-heterolyl)$Mn(CO)_5$ in the carbonyl stretching region [a]

Complex	ν(CO) (cm^{-1})				Ref.
$Mn(CO)_5(PC_4Ph_4)$	2111	2032	2024	2002	2
$Mn(CO)_5(AsC_4Ph_4)$	2105	2026	2017	1999	2
$Mn(CO)_5(SbC_4Ph_4)$	2096	2016	2002	1992	2
$Mn(CO)_5(BiC_4Me_2H_2)$	2085s		2023w	1995s	This work

[a] All spectra recorded in hexane.

The availability of **8** allows a comparison of the IR spectra for the series of (η^1-heteroyl)$Mn(CO)_5$ complexes (Table 4). The ν(CO) values decrease in the sequence P > As > Sb > Bi. This trend differs from that observed for the usual dative bonded series ($R_3E \leftarrow M$), where the ν(CO) values change little with atomic number [13,14]. The decrease in the ν(CO) values in the covalently bonded series (R_2E–M, **6**) is consistent with an increase in the donor character of the pnictogen atoms with increasing atomic number. However, this trend does not appear to be due to any particularity of the heterolyl ring systems since the ν(CO) values of **8** are nearly identical to those of **11** [9]. Indeed similar trends of decreases in ν(CO) values from lighter to heavier donor atoms have been observed for metal carbonyl complexes with Group 16 [15] and 17 ligands [16].

The crystals obtained for **9** were not of crystallographic quality. The assignment of the structure as (η^5-C_6H_8Bi)$Mn(CO)_3$ is based on spectroscopic data. Metal π-coordination of the dimethylbismacyclopentadienyl ring of **9** is indicated by the large upfield shift of the CH-carbon ring signals relative to those of **8** in the ^{13}C NMR spectrum. Indeed both the ^1H and ^{13}C NMR spectra of **8** are very similar to those of 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (**16**), the structure of which shows η^5-ring coordination [11].

A comparison of the IR spectra of the (η^5-heterolyl)$Mn(CO)_3$ complexes shows that the ν(CO) values decrease with N > P > As > Sb ≈ Bi (Table 5). These data suggest that the heterolyl ligands become better π-donors to $Mn(CO)_3$ as the heteroatoms increase in atomic number. A similar trend for the group 15 (η^6-heterobenzene)$Mo(CO)_3$ complexes [17] has been associated with the decreasing ionization potentials of the free ligands [18]. We suggest that the heavier heterocyclopentadienyl groups are good π-bases for the same reasons [19].

TABLE 5. The IR spectra of the complexes (η^5-heterolyl)$Mn(CO)_3$ in the carbonyl stretching region

Complex	ν(CO) (cm^{-1})			Ref.
$Mn(CO)_3(NC_4H_4)$	2062	1980		3b
$Mn(CO)_3(PC_4H_2\alpha\text{-}Ph_2)$ [a]	2030	1961	1950	4d
$Mn(CO)_3(PC_4H_2\beta\text{-}Me_2)$ [a]	2032	1958	1954	4a
$Mn(CO)_3(AsC_4H_2\alpha\text{-}Me_2)$ [b]	2020	1948	1942	5b
$Mn(CO)_3(SbC_4H_2\alpha\text{-}Me_2)$ [c]	2010 [e]	1948br		6
$Mn(CO)_3(BiC_4H_2\alpha\text{-}Me_2)$ [d]	2011s	1942s	1937s	This work

[a] Solvent, decalin. [b] Solvent, hexadecane. [c] Solvent, cyclohexane. [d] Solvent, hexane. [e] Misquoted as 2100 cm^{-1} in ref. 5b.

3. Experimental details

3.1. General remarks

All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using either a Brucker WH-360 or AM-300 spectrometer on solutions in $CDCl_3$ or C_6D_6 as noted. The ^1H NMR and ^{13}C NMR spectra were calibrated using signals from the solvents referenced to Me_4Si. The IR spectra were recorded using a Nicolet 5DX spectrometer. The combustion analyses were determined by Galbraith Laboratory, Knoxville, TN.

3.2. (η^1-2,5-Dimethylbismolyl)Mn(CO)$_5$ (8)

An excess (0.5 g) of lithium wire cut into small pieces was added to a solution of 1-phenyl-2,5-dimethylbismole (1.0 g, 2.0 mmol) in 20 ml of THF at 0°C. The colour changed to green-brown and stirring was continued for 4 h. The solution was filtered from the excess lithium and cooled at −35°C. Gaseous NH_3 was bubbled through for 5 min and the reaction mixture was allowed to warm to 0°C. Excess NH_3 was removed by bubbling N_2 through the solution and 10 ml of THF was added. The solution was then cooled to −78°C and cannulated into a suspension of $BrMn(CO)_5$ (2 g, 7.30 mmol) in 20 ml of THF at −78°C. The brown solution was stirred at −78°C for 4 h and then allowed to warm to 0°C for 1 h. After removal of the solvent, the residue was extracted with 70 ml of hexane. After filtration, the hexane extracts were orange. Cooling to −15°C gave orange shiny needles which were recrystallized from acetone to give 0.70 g (54%) of **8**, m.p. 124–125°C. Anal. Found: C, 22.29; H, 2.39. $C_{11}H_8BiMnO_5$ calc.: C, 22.73; H, 2.54%. ^1H NMR ($CDCl_3$): δ 2.33 (s, 6H); 8.16 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 27.7 (CH_3); 150.8 (CH); 166 br (CBi); CO not observed. MS m/e (intensity): 484 (15, M^+ for $C_{11}H_8BiMnO_5$); 344 (100). MS exact mass (EI): Found: 483.9548. $C_{11}H_8BiMnO_5$ calc.: 483.9556.

3.3. (η^5-2,5-Dimethylbismolyl)Mn(CO)$_3$ (9)

(η^1-2,5-Dimethylbismolyl)Mn(CO)$_5$ (99 mg, 0.23 mmol) was heated to 125°C for 5 h affording a dark brown solid, which was taken up in hexane. The solution was filtered and solvent was removed to afford 80 mg (90%) of **8** as black crystals, m.p. 78–80°C. ^1H NMR (C_6D_6): δ 1.89 (s, 6H); 8.32 (s, 2H). ^{13}C NMR (C_6D_6): δ 26.7 (CH_3); 111.5 (CH); CBi and CO not observed. MS (EI) m/z (intensity): 428 (40, M^+ for $C_9H_8BiMnO_3$), 264 (100). MS exact mass: Found: 427.9653. $C_9H_8BiMnO_3$ calc.: 427.9658.

Acknowledgements

We are grateful to the Research Corporation, to NATO Scientific Affairs, and to the donors of the Petroleum Research Fund administered by The American Chemical Society for partial support of this work.

References

1 For a review of phospholyl complexes see: F. Mathey, *Nouv. J. Chim.*, *11* (1987) 585.

2 E. W. Abel and C. Towers, *J. Chem. Soc., Dalton Trans.*, (1979) 814.

3 (a) K. K. Joshi and P. L. Pauson, *Proc. Chem. Soc.*, (1962) 326; (b) K. K. Joshi, P. L. Pauson, A. R. Qazi and W. H. Stubbs, *J. Organomet. Chem.*, *1* (1964) 471.

4 (a) F. Mathey, *Tetrahedron Lett.*, (1976) 4155; (b) F. Mathey and J.-P. Lampin, *J. Organomet. Chem.*, *128* (1977) 297; (c) F. Mathey, A. Mitschler and R. Weiss, *J. Am. Chem. Soc.*, *100* (1978) 5748; (d) A. Breque, F. Mathey and C. Santini, *J. Organomet. Chem.*, *165* (1979) 129.

5 E. W. Abel, I. W. Nowell, A. G. J. Modinos and C. Towers, *Chem. Commun.*, (1973) 258;
(b) G. Thiollet, R. Poilblanc, D. Voigt and F. Mathey, *Inorg. Chim. Acta*, *30* (1978) L294.

6 A. J. Ashe, III and T. R. Diephouse, *J. Organomet. Chem.*, *202* (1980) C95.

7 N. C. Norman, *Chem. Soc. Rev.*, *17* (1988) 269.

8 A. J. Ashe, III and F. J. Drone, *Organometallics*, *3* (1984) 495.

9 J. M. Cassidy and K. H. Whitmire, *Inorg. Chem.*, *30* (1991) 2788.

10 J. M. Wallis, G. Müller and H. Schmidbaur, *Inorg. Chem.*, *26* (1987) 458.

11 A. J. Ashe, III, J. W. Kampf, D. B. Puranik and S. M. Al-Taweel, *Organometallics*, *11* (1992) 2743.

12 F. Calderazzo, A. Morvillo, G. Pelizzi and R. Poli, *J. Chem. Soc., Chem. Commun.*, (1983) 507.

13 F. Calderazzo, R. Poli and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, (1984) 2535.

14 D. Benlian and M. Bigorgne, *Bull. Soc. Chim. Fr.*, (1963) 1583.

15 J. L. Atwood, I. Bernal, F. Calderazzo, L. G. Canada, R. Poli, R. D. Rogers, C. A. Veracini and D. Vitali, *Inorg. Chem.*, *22* (1983) 1797.

16 H. D. Kaesz, R. Bau, D. Hendrickson and J. M. Smith, *J. Am. Chem. Soc.*, *89* (1967) 2844.

17 (a) A. J. Ashe, III and J. C. Colburn, *J. Am. Chem. Soc.*, *99* (1977) 8099; (b) J. C. Colburn, Ph.D. Thesis, University of Michigan, 1978.

18 (a) C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe, III, D. T. Clark, U. T. Cobley, D. Kilcast and I. Scanlan, *J. Am. Chem. Soc.*, *95* (1973) 928; (b) J. Bastide, E. Heilbronner, J. P. Maier and A. J. Ashe, III, *Tetrahedron Lett.*, (1976) 411.

19 For a MO treatment of phosphacymantrene see: G. Guimon, G. Pfister-Guillouzo and F. Mathey, *Nouv. J. Chim.*, *3* (1979) 725.