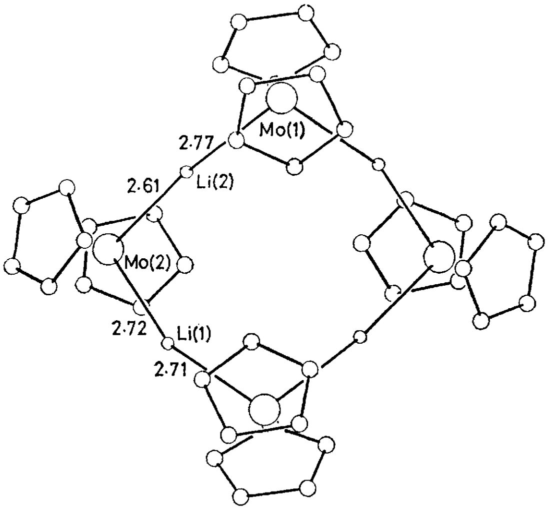
Electron-deficient Transition-metal Compounds: a Lithiobis-π-cyclopentadienylmolybdenum Tetramer: Crystal Structure and Properties

By Frank W. S. Benfield, Roger A. Forder, Malcolm L. H. Green,* Glenn A. Moser, and Keith Prout*
(*Inorganic Chemistry and Chemical Crystallography Laboratories, South Parks Road, Oxford*)

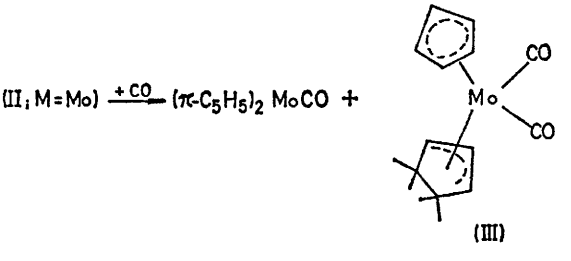
Summary The crystal structure and some properties of the tetramer $[(\pi\text{-}C_5H_5)_2Mo(H)Li]_4$ are described.

TREATMENT of the dihydrides $(\pi\text{-}C_5H_5)_2MH_2$ (I; M = Mo or W) in toluene at 50° with n-butyl-lithium gives yellow-orange crystalline products(II), $[(\pi\text{-}C_5H_5)_2M(H)Li]_4$, M = Mo or W. These highly reactive, pyrophoric compounds and some of their unusual chemistry have been previously communicated.[1]



The tetramer (II; M=Mo) in projection down the *y*-axis; there is a two-fold axis through the centre of the ring.
σ(Mo–Li) = 0·04 Å
Li–Mo(1)–Li = 98(1)° Li–Mo(2)–Li = 100(1)°
Mo–Li(1)–Mo = 158(2)° Mo–Li(2)–Mo = 173(2)°

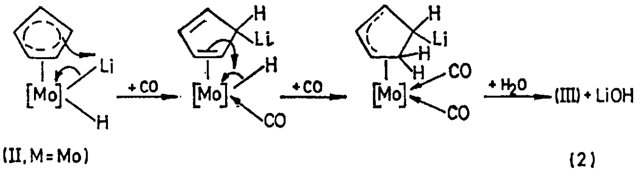
The structure of the product from n-butyl-lithium and $(\pi\text{-}C_5H_5)_2MoH_2$ has been determined by single-crystal X-ray diffraction. *Crystal Data:* $C_{40}H_{44}Li_4Mo_4$; monoclinic, a = 26·39, b = 7·72, c = 22·43 Å, β = 124·8°; space group $C2/c$; Z = 4. 1624 independent reflections were measured on a Hilger and Watts linear diffractometer, using Mo-K_α radiation and balanced filters. All crystals examined were twinned, but corrections were made for the systematic overlap of reflections which occurred in the $hk0$ zone. The structure was solved by the heavy atom method and refined by full-matrix least-squares; R is 0·071.



(1)

The molecule consists of eight-membered Mo–Li rings, the molybdenum atoms being part of bis (π-cyclopentadienyl)-molybdenum groups (see Figure 1). The ring has crystallographic C_2 symmetry; the angle between the planes Mo(1)–Mo(2)–Mo(1′) and Mo(1)–Mo(2′)–Mo(1′) is 135°. The long Mo–Li bonds (mean 2·70 Å) are presumably a reflection of the electron-deficient nature of the compound: lithium appears to have a surprisingly large effective radius in such systems.[2,3]

The geometry of the $(\pi\text{-}C_5H_5)_2Mo$ groups differs somewhat from that observed in other molecules.[4,5] The mean perpendicular distance of the molybdenum from the rings is 1·91 Å compared with the more usual 1·96—1·99 Å, and the mean angle between the ring normals is 148° compared with *ca.* 133° for known $(\pi\text{-}C_5H_5)_2MoX_2$ systems, except the dihydride[6] where the angle is 146°. The shortest lithium–carbon contacts from each ring are in the range 2·6—2·8 Å, but their directions are not consistent with any rational co-ordination sphere for the lithium.



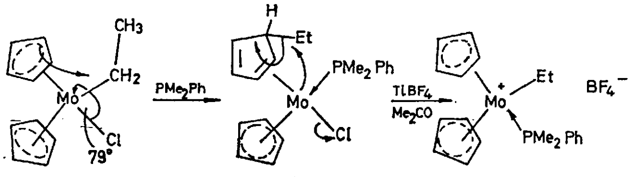
(2)

The crystals are isomorphous with those of the corresponding yellow tungsten compound (II; M = W).

The *X*-ray structure analysis gave no indication of hydrogen atom positions, but there is evidence that there may be one hydrogen atom associated with each molybdenum, in addition to those of the cyclopentadienyl rings; the stoicheiometry of the synthesis would certainly permit this:

$$4(\pi\text{-}C_5H_5)_2MoH_2 + 4LiC_4H_9 \rightarrow [(\pi\text{-}C_5H_5)_2Mo(H)Li]_4 + 4C_4H_{10}$$

In a number of its reactions, the compound yields hydrides,[1] and the i.r. spectrum shows a broad band at 1847 cm^{-1} which may be assigned to ν(Mo–H). The wide Li–Mo–Li angles (mean 99°), which are not dictated by the ring geometry and are much larger than those observed in free $(\pi\text{-}C_5H_5)_2MoX_2$ systems,[4] indicate that the hydrogen may be placed in this angle by analogy with the recently postu-



(IV) (V) (VI)

(3)

lated Mo–H–Al,[7] and Ti–H–Al systems.[8] It may even be that the hydrogen is involved in multicentre bonding with both molybdenum and lithium.

A particularly interesting reaction of the tetramer (II; M=Mo) which indicates the presence of an Mo–H system is that with carbon monoxide which, in addition to yielding $(\pi\text{-}C_5H_5)_2MoCO$, yields up to 5% of a cyclopentenyl derivative (III) [reaction (1)]. The formation of (III) may be envisaged to proceed as in reaction (2). Evidence that the shift of lithium and hydrogen to the π-C_5H_5 ring is a reasonable proposal is provided by the reaction sequence (3). The crystal structure of (IV) has been determined,[9] and (V) and (VI) have been isolated and fully characterised.

Acknowledgement is made to the S.R.C. and the donors of the Petroleum Research Fund administered by the American Chemical Society for partial financial support.

(*Received*, 19*th July* 1973; *Com.* 1039.)

[1] B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Comm.*, 1971, 1290.
[2] H. Dietrich, *Acta Cryst.*, 1963, **16**, 681.
[3] E. Weiss and G. Hencken. *J. Organometallic Chem.*, 1970, **21**, 265.
[4] J. C. Green, M. L. H. Green, and C. K. Prout, *J.C.S. Chem. Comm.*, 1972, 421.
[5] C. K. Prout, G. B. Allison, L. T. J. Delbaere, and E. Gore, *Acta Cryst.*, 1972, **B28**, 3043.
[6] M. Gerlock and R. Mason, *J. Chem. Soc.*, 1965, 296.
[7] R. A. Forder, M. L. H. Green, R. E. MacKenzie, J. S. Poland, and C. K. Prout, *J.C.S. Chem. Comm.*, 1973, 426.
[8] F. N. Tebbe and L. J. Guggenberger, *J.C.S. Chem. Comm.*, 1973, 227.
[9] R. A. Forder and C. K. Prout, to be published.