Journal of Organometallic Chemistry, 148 (1978) C27—C30
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

$\eta^5:\eta^5$-BICYCLOPENTADIENYLMOLYBDENUM CHEMISTRY: SOME ALKYL, HALO AND THIOL DERIVATIVES

MALCOLM L.H. GREEN[*] and STEPHEN J. SIMPSON
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR (Great Britain)

(Received January 11th, 1978)

Summary

The preparation of the compounds $\{(\eta\text{-}C_5H_5)MoX\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (X = Me, $PhCH_2$, Me_3SiCH_2, Br) and $\{(\eta\text{-}C_5H_5)MoY_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (Y = H, I, SMe, S-n-Bu) is described. Photolysis of $\{(\eta\text{-}C_5H_5)MoH\}_2\{\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)\}_2$ and $\{(\eta\text{-}C_5H_5)MoH\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ in benzene leads to a compound of stoichiometry $C_{20}H_{18}Mo_2$.

Recently we communicated the synthesis and some reactions of the molybdenocene dimers $\{\{(\mu\text{-}C_5H_5)MoH\}_2\{\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)\}_2\}$ (I) and $\{\{(\eta\text{-}C_5H_5)MoH\}_2\text{-}\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}\}$ (II) the latter contains the $\eta^5:\eta^5$-bicyclopentadienyl ligand [1]. Here we report further derivatives of these compounds. In particular we were interested in the extent to which the chemistry of these systems resembled that of the well explored monomeric bis(cyclopentadienylmolybdenum) compounds [2] or showed evidence for a cooperative binuclear chemistry.

Treatment of II with n-butyllithium in toluene yields a pale green-yellow pyrophoric solid (III) which on hydrolysis gives the parent compound II. By analogy with the formation of $[(\eta\text{-}C_5H_5)_2Mo(H)Li]_4$ from n-butyllithium and $[(\eta\text{-}C_5H_5)_2MoH_2]$ [3], we assume compound III to be dimolybdenumdilithio derivative. Treatment of solid III in toluene suspension with alkyl halides, RX, (R = CH_3, $C_6H_5CH_2$ or $(CH_3)_3SiCH_2$) leads to the formation of the corresponding dialkyls $\{\{(\eta\text{-}C_5H_5)MoR\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}\}$ where R = CH_3 (IV), R = $C_6H_5CH_2$ (V) and R = $(CH_3)_3SiCH_2$ (VI).

The dibenzyl compound V is also obtained from the reaction of benzyl chloride with the lithio derivative formed from n-butyllithium and the dihydride I. The diastereotopic methylene protons in compounds V and VI form an AB spin system.

Addition of 1,2-dibromoethane to an acetonitrile solution of II leads to the formation of the purple crystalline dibromide VII in good yield.

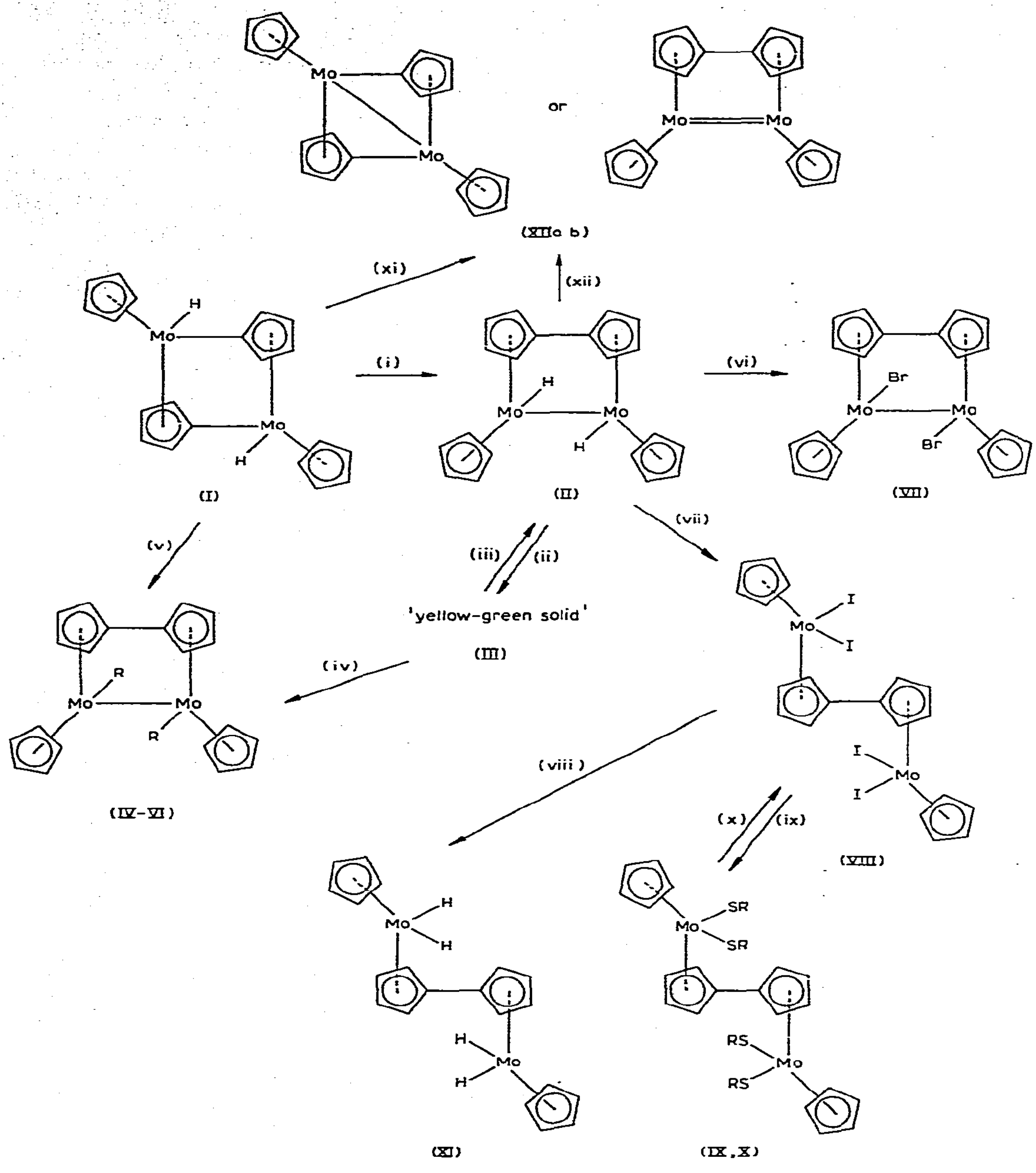
Treatment of a refluxing acetonitrile solution of II with excess iodine gives light brown crystals of a tetraiodo compound VIII, which when treated with

(continued on p. C 30)

TABLE 1. ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analysis (found (calcd.)(%)) C	H	Other	m/e[a]	^{1}H NMR[b] (τ)
$\{(\eta\text{-}C_5H_5)Mo(CH_3)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (IV)	Green	55.21 (55.00)	5.18 (5.00)		480P	4.87,2,c,C_5H_4; 5.58,10,s,C_5H_5; 6.66,2,c,C_5H_4; 7.00,2,c,C_5H_4; 7.48,2,c,C_5H_4; 11.20,6,s,CH_3.
$\{(\eta\text{-}C_5H_5)Mo(CH_2Ph)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (V)	Light green	64.47 (64.55)	5.24 (5.06)		632P	2.95,10,c,C_6H_5; 5.45,2,c,C_5H_4; 5.70,10,s,C_5H_5; 6.55,2,c,C_5H_4; 6.81,2,c,C_5H_4; 7.65,2,c,C_5H_4; 8.75,2,d,CH_2,(J 11 Hz) 10.55,2,d,CH_2,(J 11 Hz).
$\{(\eta\text{-}C_5H_5)Mo(CH_2SiMe_3)\}_2\{(\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}(C_5H_4)\}$ (VI)	Dark green	54.13 (53.95)	6.64 (6.43)		624P	4.43,2,c,C_5H_4; 5.61,10,s,C_5H_5; 6.55,2,c,C_5H_4; 6.95,2,c,C_5H_4; 7.60,2,c,C_5H_4; 9.81,18,s,SiMe; 11.71,2,d,CH_2,(J 14 Hz); 12.93,2,d,CH_2,(J 14 Hz).
$\{(\eta\text{-}C_5H_5)MoBr\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (VII)	Purple	39.23 (39.35)	3.22 (2.95)	Br. 25.88 (26.23)	610P	c
$\{(\eta\text{-}C_5H_5)MoI_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}\cdot\frac{1}{3}CH_3CN$ (VIII)	Light brown	25.46 (25.52)	1.98 (1.96)	I 52.66 (52.28) N 0.84 (0.48)	d	c
$\{(\eta\text{-}C_5H_5)Mo(SMe)_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (IX)	Purple	44.83 (45.00)	4.72 (4.70)	S 19.40 (20.05)	497[e]	c
$\{(\eta\text{-}C_5H_5)Mo(S\text{-}n\text{-}Br)_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (X)	Dark red	53.67 (53.60)	7.15 (6.70)	S 15.63 (15.88)	692[f]	4.76,8,c,C_5H_4; 4.88,10,s,C_5H_5; 7.82,8,c,S-CH_2; 8.48,16,c,CH_2; 9.03,12,c,CH_3[g]
$\{(\eta\text{-}C_5H_5)MoH_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$ (XI)	Pale yellow	52.95 (52.86)	4.81 (4.85)		452[h]	c. $\nu_{Mo\text{-}H}$ = 1815, 1841 cm^{-1}
$C_{20}H_{18}Mo_2$ (XIIa,b)	Dark red	53.50 (53.30)	4.47 (4.05)		448[j]	4.48,2,c,C_5H_4; 5.03,2,c,C_5H_4; 5.30,10,s,C_5H_5; 5.81,2,c,C_5H_4; 6.74,2,c,C_5H_4.

[a] ^{96}Mo peak tabulated. P = parent ion. [b] 90 MHz, $C_6H_6\text{-}d_6$. [c] Not soluble enough to obtain spectrum. [d] No spectrum at 360°C. [e] Highest peak corresponds to $C_{21}H_{21}Mo_2S^+$. [f] Highest peak corresponds to $C_{28}H_{36}Mo_2S_4^+$. [g] 90 MHz, liquid SO_2. [h] Highest peak corresponds to $C_{20}H_{20}Mo_2^+$. [j] Highest peak corresponds to



SCHEME 1. (i) Toluene, 70°C, 2 h, 100%; (ii) BuLi, toluene, 50°C, 30 min; (iii) H_2O, toluene, RT, 1 min; (iv) RX, toluene, −50°C, 1 h; R = CH_3, X = Br, 70% (IV), R = $C_6H_5CH_2$, X = Cl, Br, 85% (V), R = $(CH_3)_3SiCH_2$, X = Cl, 25% (VI); (v) (1) BuLi, toluene, −10°C, 2 h; (2) $C_6H_5CH_2Cl$, 0°C, 2 h, 80%; (vi) CH_2BrCH_2Br, MeCN, 50°C, 10 min, 60%; (vii) I_2, MeCN, 80°C, 5 min, ca. 95%; (viii) $NaBH_4$, THF, 50°C, 1 h, 70%; (ix) NaSR, EtOH, 70°C, 1 h, R = Me, 70% (IX), R = n-Bu, 65% (X); (x) R = n-Bu, HI, toluene, RT, 2 h, 90%; (xi) hν, benzene, 0°C, 20 h, 80%; (xii) hν, benzene, RT, 20 h, 85%.

sodium alkylthiolates, NaSR, (R = CH_3, n-C_4H_9) in ethanol gave the crystalline compounds $\{\{(\eta\text{-}C_5H_5)Mo(SR)_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}$, R = CH_3 (IX) and R = n-C_4H_9 (X). Treatment of X in toluene with hydrogen iodide reforms complex VIII, which we propose to have the structure shown in Scheme 1.

The mass spectrum of the compounds IX and X did not show the parent ion, the thioalkyl ligands revealing lability and complex decomposition modes under the conditions used. Treatment of VIII with sodium borohydride in THF leads to the isolation of a pale yellow microcrystalline compound XI. Low solubility and thermal instability above ca. 70°C prevented determination of its ^1H NMR spectrum. The mass spectrum shows the highest peak at *m/e* 452, corresponding to $C_{20}H_{20}Mo_2$. The IR spectrum shows broad bands at 1815, 1841 cm^{-1} assignable to ν(Mo—H). The IR spectrum of the dideuterio analogue of XI prepared from VIII and sodium borodeuteride shows bands corresponding to ν(Mo—D) at 1303, 1328 cm^{-1}.

The mass spectrum of $[(\eta\text{-}C_5H_5)_2MoH_2]$ shows that dihydrogen loss is a favoured process, since the parent ion peak is very small compared to the strong base peak at *m/e* 226 corresponding to $C_{10}H_{10}Mo^+$.

Since compound XI is prepared from the tetraiodo derivative VIII and is clearly different from the previously described *cis—trans* yellow isomers (I) [1], we propose that XI is the tetrahydrido compound shown in Scheme 1.

Irradiation of I and II in benzene leads to the isolation of a red crystalline compound of stoichiometry $C_{20}H_{18}Mo_2$ (XII) identical to that prepared from the irradiation of $[(\eta\text{-}C_5H_5)_2MoH_2]$ in benzene [4]. ^1H NMR and IR of XII suggests either of the two structures shown in Scheme 1. The ABCD spin system for the η^5-C_5H_4 hydrogens are consistent with tetrahedral symmetry at the metal atoms arising in XIIa. Structure XIIb could also show the same spectral pattern if there is no plane of symmetry containing the $\{(\eta\text{-}C_5H_5)Mo\}_2$ system. This could arise if the two η-C_5H_5 rings of XIIb are sterically distorted from the appropriate Mo_2-plane. Smart and Curtis [5] have described the compound $\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)Mo\}_2$ from which it follows that a very close approach of the (η-C_5H_5) rings in XIIb could in principle arise. On the other hand the ^1H NMR spectrum shows no evidence for broadening of the η-C_5H_5 band which might be expected to reflect a severe steric constraint.

All the above reactions are shown in Scheme 1 and data for the compounds are shown in Table 1. We are grateful to Dr. Smart who has informed us that compounds II, III, V and VI have recently been independently synthesised by him [6].

We thank the S.R.C. for support (to SJS) and the Petroleum Research Fund administered by the American Chemical Society for partial support.

References

1 N.J. Cooper, M.L.H. Green, C. Couldwell and K. Prout, J. Chem. Soc. Chem. Commun., (1977) 145.
2 M.L.H. Green, J. Less Common Metals, 54 (1977) 159.
3 B.R. Francis, M.L.H. Green, N.-T. Luong-thi and G.A. Moser, J. Chem. Soc. Dalton, (1976) 1339.
4 M. Berry, S.G. Davies and M.L.H. Green, J. Chem. Soc. Chem. Commun., (1978) in press.
5 J.C. Smart and C.J. Curtis, J. Amer. Chem. Soc., 99 (1977) 3518.
6 J.C. Smart and C.J. Curtis, personal communication.