Preparation and Reactions of *cyclo*-Tetra-μ-lithio-tetrakis[bis(η-cyclopentadienyl)hydrido-molybdenum] and -tungsten] and some Bis(η-cyclopentadienyl) Derivatives of Molybdenum and Tungsten

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The dihydrides $[M(\eta\text{-}C_5H_5)_2H_2]$(M = Mo or W) react in toluene with n-butyl-lithium to give the tetramers $[\{M(\eta\text{-}C_5H_5)_2HLi\}_4]$. The tetramers react with $PhCH_2Br$ or PhCOX [X = Cl, OMe, or (M = W)H] giving $[M(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$ or $[M(\eta\text{-}C_5H_5)_2(COPh)H]$ respectively. With carbon dioxide the monocarbonyls $[M(\eta\text{-}C_5H_5)_2(CO)]$ are formed in high yield. The tetramer (M = W) reacts with acetyl chloride or benzophenone giving the compounds $[W(\eta\text{-}C_5H_5)_2(COMe)H]$ or $[W(\eta\text{-}C_5H_5)_2\{C_6H_4(COPh\text{-}p)\}H]$ respectively. These compounds in carbon tetrachloride give the chloro-analogues $[W(\eta\text{-}C_5H_5)_2(COMe)Cl]$ and $[W(\eta\text{-}C_5H_5)_2\{C_6H_4(COPh\text{-}p)\}Cl]$. The molybdenum tetramer with carbon monoxide gives both the monocarbonyl $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ and the cyclopentenyl compound $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(CO)_2]$. The products of reaction between the dihydrides $[M(\eta\text{-}C_5H_5)_2H_2]$ and methyl- or phenyl-lithium appear to be identical to those formed from $LiBu^n$. With ZnR_2 (R = Et or Bu^n) the dihydrides give polymeric compounds $[\{M(\eta\text{-}C_5H_5)_2Zn\}_n]$. The compounds $[M(\eta\text{-}C_5H_5)_2(COPh)Cl]$ (M = Mo or W), $[W(CH_2SiMe_3)_2(\eta\text{-}C_5H_5)_2]$, $[M(\eta\text{-}C_5H_5)_2(C_6F_5)_2]$ (M = Mo or W), and $[Mo(\eta\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_4Me)][PF_6]$ are also described.

THE energy of the d^n electrons in a transition-metal compound depends on the nature of the metal M and on the nature of the ligands. When the d^n electrons have unusually low ionisation potentials the metal centre may be described as electron rich.[1] We set out to prepare electron-rich metal compounds in the expectation that they would lead to new areas of reactivity, possibly to hydrocarbon activation. The general requirement of an electron-rich compound is that the ligands should not prevent effective build up of electron density on the metal.[1] Zero-valent compounds are not necessarily electron rich, for example, the carbonyl ligand is a strong π acceptor so that even binary metal carbonyls may accept electrons forming carbonylate anions, $[M(CO)_n]^{x-}$. In contrast, the hypothetical molecule $[Mo(NH_3)_6]$ would be expected to be extremely electron rich and, as such, not stable to isolation. Clearly isolable electron-rich compounds require ligands which have neither extreme donor nor extreme acceptor properties.

There is a body of evidence which suggests that the η-cyclopentadienyl ligand is not a strong π acceptor compared with two or three carbonyl ligands. For example, the anion $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ is a much stronger nucleophile than the isoelectronic $[Mn(CO)_5]^-$. Further, salts of the anions $[M(\eta\text{-}C_5H_5)_2]^-$ are unknown and it may be that they are too electron rich to be readily isolable. Photoelectron spectra of the dihydrides $[M(\eta\text{-}C_5H_5)_2H_2]$ (I; M = Mo or W) show that the first ionisation potentials arising from the d^4 electrons are very low, and, for example, they are lower than the first ionisation potential of molybdenum itself.[2]

Transition-metal compounds which do not form discrete anions $[M]^-$ may be likened to simple alkyl or aryl groups R, for which discrete anions R^- are rare or unknown. Anionic or nucleophilic character is most marked for groups R when they are covalently bonded to electropositive atoms such as Li, Mg, or Al. By analogy, highly electron-rich compounds of transition metals would be anticipated when covalent systems [M–M′] are formed (M′ = Li, Mg, or Al). We have found that covalent bonds [M–M′] (M = Mo or W) may be formed by the alkane-elimination reaction. In this paper we

$$M\text{-}H + MR' \longrightarrow M\text{-}M' + RH$$

describe the preparation and reactions of molybdenum- and tungsten–lithium derivatives; some of this work has been briefly communicated.[3,4]

RESULTS

Chemical Studies.—Treatment of the compounds $[M(\eta\text{-}C_5H_5)_2H_2]$, (I; M = Mo or W), in toluene with either an equimolar quantity of or excess of n-butyl-lithium in hexane at 60 °C caused smooth precipitation of yellow-orange crystals. Analysis, i.r. spectra, and especially the *X*-ray structure determination show the products, which are isomorphous, to be the tetramers $[\{M(\eta\text{-}C_5H_5)_2HLi\}_4]$ [M = Mo (II) or W (III)].[4,5] The structures of compounds (II) and (III) are shown in the Scheme. The compounds are insoluble in aliphatic or aromatic hydrocarbons and they react with most other solvents, including tetrahydrofuran (thf). On exposure to air they normally char or darken immediately and they are instantly hydrolysed giving the parent compounds (I). Thermal decomposition *in vacuo* at *ca.* 150 °C gives small quantities of the hydrides (I). The occurrence of metal–hydrogen bonds in (II) is shown by comparison of the i.r. spectrum of (II) with that of the deuteriated analogue prepared from $[Mo(\eta\text{-}C_5H_5)_2D_2]$. Compound (II) showed a band at 1 670 cm^{-1} which was absent in the spectra of the deuteriated analogue which had a new band at 1 210 cm^{-1}. The ratio of ν(Mo–H) : ν(Mo–D) is 1.38 : 1 and supports the assignment.

Compounds (II) and (III) react readily with a variety of alkyl and aryl halides and related compounds. Thus, treatment of a freshly prepared toluene suspension of (III) with bromobenzene gave the previously described[6] hydride

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[1] M. L. H. Green and P. Powell, 'Comprehensive Inorganic Chemistry,' Pergamon Press, 1973, vol. 1, ch. 14, p. 1295.

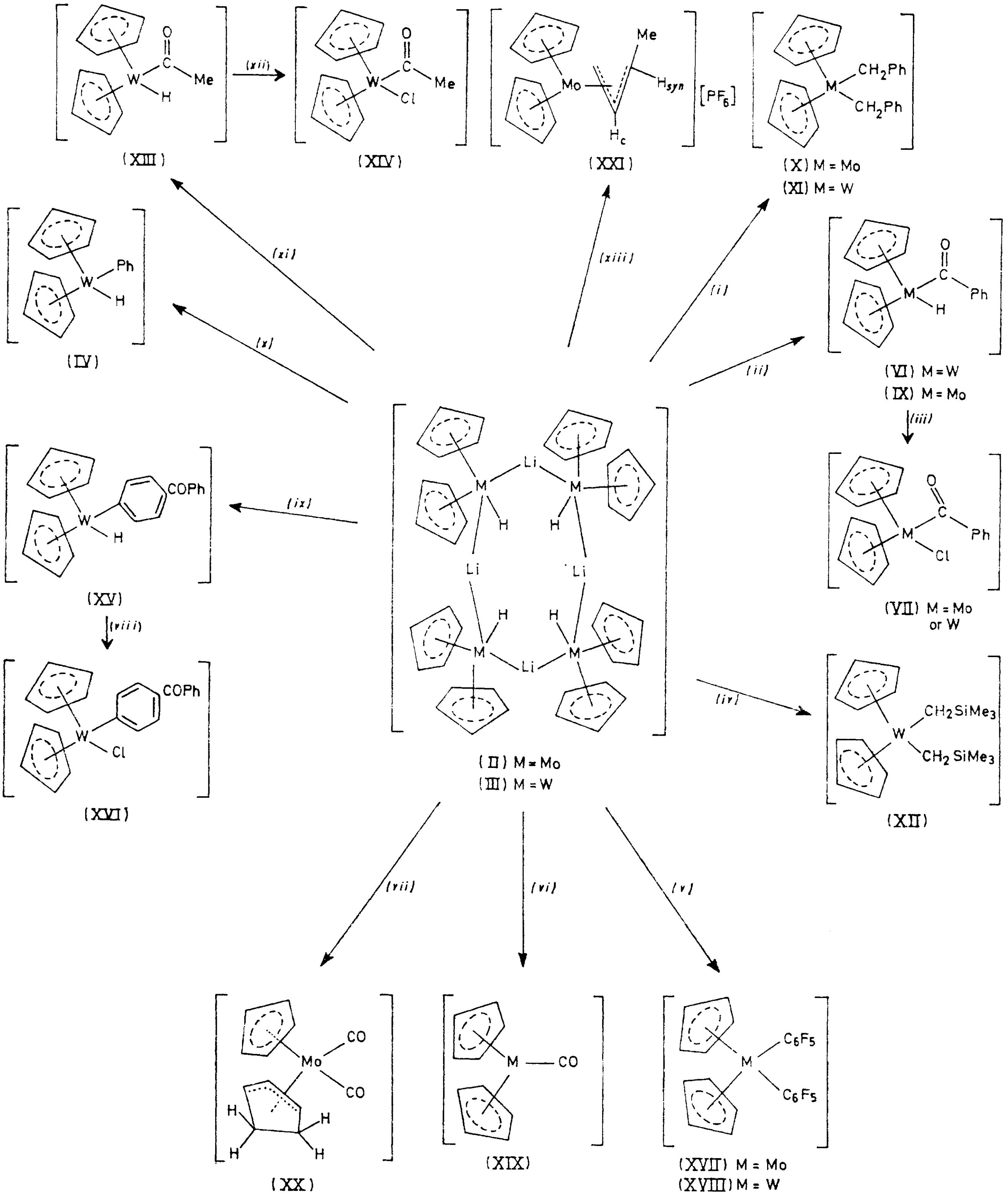
[2] J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1975, 403.

[3] B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Comm.*, 1971, 1290.

[4] F. W. S. Benfield, B. R. Francis, M. L. H. Green, N.-T. Luong-thi, G. A. Moser, J. S. Poland, and D. M. Roe, *J. Less-Common Metals*, 1974, **36**, 187.

[5] R. A. Forder and C. K. Prout, *Acta Cryst.*, 1974, **B30**, 2318.

[6] M. L. H Green and P. J. Knowles, *J. Chem. Soc.* (*A*), 1971, 1508.



SCHEME (*i*) $PhCH_2Br$; (*ii*) PhCOX (X = OMe, Cl, or H); (*iii*) CCl_4; (*iv*) M = W, Me_3SiCH_2Cl; (*v*) C_6F_5Br; (*vi*) M = Mo or W, CO_2; (*vii*) M = Mo, CO; (*viii*) CCl_4; (*ix*) M = W, PhCOPh; (*x*) M = W, PhBr; (*xi*) M = W, MeCOCl; (*xii*) CCl_4; (*xiii*) M = Mo, butadiene, $[NH_4][PF_6]$

$[W(\eta\text{-}C_5H_5)_2(Ph)H]$, (IV), together with a small yield of the corresponding *p*-tolyl analogue $[W(\eta\text{-}C_5H_5)_2(C_6H_4Me\text{-}p)H]$, (V).[6] The latter product is presumably formed from the toluene solvent. The yield of (IV) increased to *ca.* 50% when reactions were carried out *in situ* with $LiBu^n$ being added to (I; M = W) in pure bromobenzene. Substantial quantities of the parent (I; M = W) were also formed in the above reaction and, indeed, this is the case with all the reactions of compound (III). Preliminary studies of the reaction between (III) and chlorobenzene or iodobenzene show that iodobenzene reacts much more rapidly than chlorobenzene. Neither reaction gave yields of (IV) as good as those for the bromobenzene reaction. Attempts to prepare the molybdenum analogue of (IV) from (II) and bromobenzene under a variety of conditions were unsuccessful.

Treatment of the tetramer (III) with PhCOX (X = Cl, OMe, or H) gave the yellow benzoyl compound $[W(\eta\text{-}C_5H_5)_2(COPh)H]$, (VI). This is slightly soluble in non-polar hydrocarbons such as benzene and the solutions are only slowly decomposed in air. It is moderately soluble in dichloromethane, dimethyl sulphoxide, or thf. With carbon tetrachloride, (VI) gave green crystals which the data show to be the air-stable chloro-derivative $[W(\eta\text{-}C_5H_5)_2(COPh)Cl]$, (VII; M = W). This is moderately soluble in thf and slightly soluble in dichloromethane. Treatment of the latter solutions with hydrogen chloride rapidly gave benzaldehyde and the dichloro-compound $[W(\eta\text{-}C_5H_5)_2Cl_2]$, (VIII). Compound (II) also reacted readily with PhCOX (X = Cl or OMe) giving the benzoyl derivative $[Mo(\eta\text{-}C_5H_5)_2(COPh)H]$, (IX); however, the yields were poorer than for the tungsten analogue. With carbon tetrachloride, (IX) gave $[Mo(\eta\text{-}C_5H_5)_2(COPh)Cl]$, (VII; M = Mo), which is generally similar to its tungsten analogue. Both (II) and (III) reacted readily with benzyl bromide giving the bis(benzyl) derivatives $[M(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$ [M = Mo (X) or W (XI)] in high yields. These compounds are soluble in benzene and the solutions are only slowly oxidised in air. The compounds are stable up to *ca.* 130 °C.

The tetramer (III), with (chloromethyl)trimethylsilane gave orange, slightly air-sensitive, crystals of stoicheiometry $[W(CH_2SiMe_3)_2(\eta\text{-}C_5H_5)_2]$, (XII), soluble in light petroleum. Compound (XII) may also be prepared from the dichloride $[W(\eta\text{-}C_5H_5)_2Cl_2]$ and the Grignard reagent $MgBr(CH_2SiMe_3)$. Addition of acetyl chloride to a suspension of (III) in toluene gave mainly the dihydride (I; M = W) together with small quantities of an acetyl compound $[W(\eta\text{-}C_5H_5)_2(COMe)H]$, (XIII). Compound (XIII) reacted rapidly in carbon tetrachloride giving the chloro-derivative $[W(\eta\text{-}C_5H_5)_2(COMe)Cl]$, (XIV).

An unexpected reaction product resulted from treatment of (III) with benzophenone. The initially green solution eventually gave purple-red crystals which the data in the Table show to be the *p*-benzoylphenyl derivative $[W(\eta\text{-}C_5H_5)_2\{C_6H_4(COPh\text{-}p)\}H]$, (XV). This is soluble in aromatic solvents and is only moderately stable to oxidation. With carbon tetrachloride a smooth reaction gave the chloro-analogue $[W(\eta\text{-}C_5H_5)_2\{C_6H_4(COPh)\text{-}p\}Cl]$, (XVI). Treatment of (III) with acetophenone or acetone gave the dihydride (I; M = W) rapidly and quantitatively. The tetramers (II) and (III) with bromopentafluorobenzene at −78 °C gave small yields of orange compounds which the data show to be the bis(pentafluorophenyl) derivatives $[M(\eta\text{-}C_5H_5)_2(C_6F_5)_2]$ [M = Mo (XVII) or W (XVIII)].

When a suspension of tetramer (II) in toluene was treated with carbon monoxide (1 atm),* after methanolysis, three carbonyl compounds were isolated and could be separated by chromatography on alumina. The major product, apart from (I; M = Mo), was the green crystalline monocarbonyl $[M(\eta\text{-}C_5H_5)_2(CO)]$, (XIX; M = Mo).[7] The second product was the dicarbonylcyclopentenyl compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_7)(CO)_2]$, (XX). Trace amounts of a red compound were also found which the i.r. and the mass spectra suggest to be the dimer $[(\eta\text{-}H_5C_5)(OC)_2MoMo(\eta\text{-}C_5H_5)(CO)_2]$. Both compounds (II) and (III) reacted rapidly with carbon dioxide to give the monocarbonyls (XIX; M = Mo or W) in high yields. This is certainly the most convenient route to compounds (XIX). The reaction between (II) and butadiene gave the η-but-2-enyl compound $[Mo(\eta\text{-}C_3H_4Me)(\eta\text{-}C_5H_5)_2][PF_6]$, (XXI), in *ca.* 15% yield.

The dihydrides (I) reacted with methyl- or phenyl-lithium in a similar manner to that found for $LiBu^n$ giving yellow powders. For example reaction between (I; M = Mo) in toluene and LiMe at 55 °C occurred within a few minutes. Where comparative studies were made, these yellow powders behave in an essentially identical manner to either (II) or (III). Thus the adduct from (I; M = Mo) and LiMe with benzyl bromide gave the bis(benzyl), (X). This same adduct with 1-mesitylprop-2-en-1-one gave $Me_3C_6H_2{\cdot}CO{\cdot}CHMe{\cdot}(CH_2)_2{\cdot}C_6H_2Me_3$.

We also explored the reactions between the dihydrides (I; M = Mo or W) and the dialkylzinc compounds ZnR_2 ($R = Bu^n$ or Et). Compound (I; M = Mo) reacted smoothly at 80 °C with $ZnEt_2$. A gas was evolved and red-brown crystals separated of stoicheiometry $[\{Mo(\eta\text{-}C_5H_5)_2Zn\}_n]$, (XXII). Compound (XXII) is insoluble in all the common solvents. It is readily hydrolysed giving the dihydride (I; M = Mo). Suspensions in toluene showed no reaction with $PhCH_2Cl$, MeCOCl, or MeI. Thermal decomposition occurred *in vacuo* at *ca.* 180 °C giving small quantities of (I; M = Mo) and a zinc mirror. The i.r. spectrum showed bands assignable to a bent bis(η-cyclopentadienyl)molybdenum system but no bands assignable to a Mo–H group were observed. Compound (XXI) was also formed from $ZnBu^n_2$ in a similar manner. Compound (I; M = W) also reacted smoothly with both dialkylzinc compounds giving brown-red crystals which are essentially identical in their appearance and behaviour to compound (XXII). Total analysis shows the stoicheiometry to be $[\{W(\eta\text{-}C_5H_5)_2Zn\}_n]$, (XXIII).

DISCUSSION

The approximately linear, two-co-ordinate, environment about the lithium in compounds (II) and (III) is unique, and these compounds constitute the first examples of covalent lithium–transition-metal bonds. Tetramers (II) and (III) show strongly nucleophilic behaviour which bears similarity to both carbonylate anions and organolithium reagents. The extreme nucleophilicity of the metal centre is exemplified by the reactions with carbon dioxide giving metal carbonyls, and with bromobenzene giving phenyl derivatives.

The ease of reduction of carbon dioxide to carbon

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* 1 atm = 101 325 Pa.

[7] H. H. Brintzinger and J. L. Thomas, *J. Amer. Chem. Soc.*, 1972, **94**, 1386; F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometallic Chem.*, 1972, **44**, C13.

monoxide by (II) and (III) is of some interest. Insertions of carbon dioxide into transition-metal–carbon bonds has been observed for rhodium,[8] titanium,[9] zirconium,[10] cobalt,[11] copper,[12] and zinc.[13] Reduction of carbon dioxide to carbon monoxide has been observed for some ruthenium and rhodium hydrides[14] and for transition-metal–aluminium or –magnesium[15] systems. In these latter compounds it is thought that the intermediate includes a system MCOOM′ which may then undergo hydrolysis.[15]

Analytical and spectroscopic data

Compound	Colour	θ_c[a] / °C	Analytical data (%)[b]		Mass spectra (P)	^{1}H N.m.r. data[c]	Selected i.r. data[d]	
			C	H			ν(M–H)	ν(CO)
$[\{Mo(\eta-C_5H_5)_2HLi\}_4]$ (II)	Yellow-orange		53.1 (53.1)	4.8 (4.7)[e]			1 670	
$[\{W(\eta-C_5H_5)_2HLi\}_4]$ (III)	Yellow-brown		39.0 (37.3)	3.7 (3.4)				
$[W(\eta-C_5H_5)_2(COPh)H]$ (VI)	Red	100 (decomp.)	49.2 (48.6)	4.1 (3.8)	420	2.7 , *5*, **c**, Ph; 5 2;[g] 20.1, *1*, **s**, W–H[h]	1 928m	1 537s
$[W(\eta-C_5H_5)_2(COPh)Cl]$ (VII)	Red-brown	180 (decomp.)	44.6 (44.8)	3.3 (3.3)	454			1 564s
$[Mo(\eta-C_5H_5)_2(COPh)H]$ (IX)	Red	70 (decomp.)	61.9 (61.5)	4.6 (4.8)	334	2.9, *5*, **c**, Ph; 5.3;[g] 17.4, *1*, **s**, Mo–H[h]	1 861m	1 564s
$[Mo(\eta-C_5H_5)_2(COPh)Cl]$ (VII)	Red-brown	140 (decomp.)	52.9 (53.1)	3.8 (4.4)				1 596s, 1 581s 1 572s
$[W(CH_2Ph)_2(\eta-C_5H_5)_2]$ (XI)	Orange	200 (decomp.)	57.9 (58.1)	5.1 (4.8)	496	3.23, *10*, **c**, Ph_2; 5 7;[g] 8.25, *4*, **s**, $(CH_2)_2$[h]		
$[Mo(CH_2Ph)_2(\eta-C_5H_5)_2]$ (X)	Orange-red	150 (decomp.)	69.8 (70.2)	6.0 (5.8)	410	3.18, *10*, **c**, Ph_2; 5.59;[g] 8.15, *4*, **s**, $(CH_2)_2$[i]		
$[W(\eta-C_5H_5)_2\{C_6H_4(COPh-p)\}H]$ (XV)	Red-purple	92	55.35 (55.6)	4.05 (4.0)	496	2.1, *4*, **c** (A_2B_2 pattern), C_6H_4; 2.8, *5*, **c**, Ph; 5.60;[g] 20.2, *1*, **s**, W–H[i]	1 800m	1 638s
$[W(\eta-C_5H_5)_2\{C_6H_4(COPh-p)\}Cl]$ (XVI)	Red-brown	90	52.6 (51.9)	4.1 (4.6)	530			1 637s
$[W(\eta-C_5H_5)_2(COMe)H]$ (XIII)	Orange		40.6 (40.2)	4.2 (3.9)	358		1 908m	1 598s
$[W(\eta-C_5H_5)_2(COMe)Cl]$ (XIV)	Red-brown	140 (decomp.)	35.9 (36.6)	3.5 (3.3)	392			1 617s
$[W(\eta-C_5H_5)_2(CH_2SiMe_3)_2]$ (XII)	Orange		43.5 (44.2)	6.8 (6.55)	488	5.86, *10*, **brs**, $(\eta-C_5H_5)_2$; 9.68, *4*, **s**, $(CH_2)_2$; 9.80, *18*, **s**, Me_6[i]		
$[Mo(\eta-C_5H_5)(\eta^3-C_5H_7)(CO)_2]$ (XX)	Yellow	120 (decomp.)	50.4 (50.7)	4.3 (4.22)	286	5.42;[g] 6.5, *3*, **c**, $(CH)_3$; 8.23, *4*, **c**, $(CH_2)_2$[i]		1 882s, 1 952[j]
$[W(\eta-C_5H_5)_2(C_6F_5)_2]$ (XVII)	Yellow	110 (decomp.)	40.5 (40.8)	1.7 (1.6)				
$[Mo(\eta-C_5H_5)_2(C_6F_5)_2]$ (XVII)	Yellow-orange	108 (decomp.)	47.3 (47.2)	1.9 (1.8)	395[k]			
$[\{Mo(\eta-C_5H_5)_2Zn\}_n]$ (XXII)	Red-brown	>150 (decomp.)	41.0 (41.2)	3.6 (3.5)				
$[\{W(\eta-C_5H_5)_2Zn\}_n]$ (XXIII)	Red-brown	>150 (decomp.)	31.5 (31.7)	2.2 (2.7)[m]				
$[Mo(\eta-C_5H_5)_2(\eta^3-C_3H_4Me)][PF_6]$ (XXI)	Red	120 (decomp.)	39.5 (39.4)	4.1 (4.0)		4.46, *5*, **s**, $\eta-C_5H_5$; 4.48, *5*, **s**, $\eta-C_5H_5$; 5.3—5.8, *1*, **c**, CH_c; 6.5—6.8, *2*, **c**, H_{2syn}; 7.98, *3*, **d** [J(Me-H_c) 6.6], Me; 8.3, *1*, **c**, H_{anti}[n]		

[a] M.p. or decomposition temperature. [b] Calculated values are given in parentheses. [c] Given as: chemical shift (τ), *relative intensity*, **multiplicity** (J in Hz), assignment, *etc.* [d] In cm^{-1}, calibrated with polystyrene film. [e] Li, 2.8 (3.0); Mo, 38.8 (41.0%). [f] Li, 1.9 (2.2); W, 54.3 (57.2%). [g] As *10*, **s**, $(\eta-C_5H_5)_2$. [h] In $S(CD_3)_2O$. [i] In C_6D_6. [j] In C_6H_{12} solution. [k] Parent ion not seen: assigned to $[Mo(\eta-C_5H_5)_2(C_6F_5)]^+$. [l] Mo, 32.9 (32.9); Zn, 22.5 (24.3%). [m] W, 48.6 (48.45); Zn, 19.1 (17.2%). [n] In $(CD_3)_2CO$, see Scheme for labelling.

The addition of (III) to benzophenone giving a η-sub-

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[8] I. S. Kolomnikov, A. O. Gusev, T. S. Belopotopova, M. Kh. Grigoryan, T. V. Lysyak, Yu. T. Struchkov, and M. E. Volpin, *J. Organometallic Chem.*, 1974, **69**, C10.

[9] I. S. Kolomnikov, T. S. Lobeeva, and M. E. Volpin, *Zhur. obshchei. Khim* , 1972, **41**, 2231; I. S. Kolomnikov, T. S. Lobeeva, M. E. Gurbachevskaja, G. G. Aleksandrov, Yu. T. Struchkov, and M. E. Volpin, *J.C.S. Chem. Comm.*, 1972, 972.

[10] G. N. Schrautzer and J. V. Siberts, *J. Amer. Chem. Soc.*, 1970, **92**, 3510; I. S. Kolomnikov, H. Stepovoska, S. Tyrlik, and M. E. Volpin, *Zhur. obshchei Khim.*, 1972, **42**, 1652.

[11] A. Miyashita and A. Yamamoto, *J. Organometallic Chem.*, 1973, **49**, C57.

[12] S. Inoue and Y. Yokoo, *J. Organometallic Chem.*, 1972, **39**, 11.

[13] S. Svoboda, T. S. Belopotapova, and J. Hetflejs, *J. Organometallic Chem.*, 1974, **65**, C37 and refs. therein.

[14] I. S. Kolomnikov, T. S. Belapotapova, T. U. Lysyak, and M. E. Volpin, *J. Organometallic Chem.*, 1974, **67**, C25.

[15] H. Felkin and P. J. Knowles, *J. Organometallic Chem.*, 1972, **37**, C14.

stituted phenone has a parallel in the reaction of bulky Grignard reagents with benzophenone.[16]

The yellow powders formed from (I) and LiR (R = Me or Ph) may be identical to (II) or (III) or they may have a related linear polymeric structure. Certainly they show closely analogous reactivity. The zinc compounds (XXII) and (XXIII) could be either cyclic tetramers or ' linear ' (zig-zag) polymers.

EXPERIMENTAL

Operations were made under dry nitrogen. Hydrogen-1 n.m.r. spectra were recorded on JEOL (60 MHz) or Varian spectrometers (100 MHz). All the solvents were dried and distilled before use. The reaction vessels were Schlenk tubes and these were dried before use. Chromatography was carried out in all cases using alumina columns, 100—120 mesh (grade III) made up in light petroleum (b.p. 30—40 °C). After the material had been placed on the column, elution was first attempted with light petroleum and then with other solvents, as illustrated in the text. All the solvents and the alumina column were flushed with nitrogen before and during chromatography. Low-resolution mass spectra were recorded on an MS9 spectrometer. I.r. spectra were obtained for mulls using a Perkin-Elmer 457 instrument. The compounds $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{H}_2]$, (I; M = Mo or W), were prepared as described.[17] n-Butyl-lithium in hexane (*ca.* 2 mol dm^{-3}) was supplied by Alpha Inorganic Co. Ltd.

cyclo-*Tetra-μ-lithio-tetrakis[bis(η-cyclopentadienyl)hydridomolybdenum]*, (II).—Pure (I; M = Mo) (0.5 g) in toluene (100 cm^3) at 65 °C was treated with a slight excess of n-butyl-lithium (1.0 g in hexane, 2 mol dm^{-3}) and the mixture was allowed to cool over 2 h. Yellow-orange crystals separated which were collected, washed with toluene (2 × 50 cm^3), and dried *in vacuo*, *ca.* 90%. The same product was formed when a substantial excess of stoicheiometric quantities of LiBu^n were used. When the reaction temperature was either that of the room or 100 °C, smaller microcrystals were obtained.

Reactions between the dihydride (I; M = Mo) and methyl- or phenyl-lithium were carried out in the same manner and the products, irrespective of reaction temperature, were yellow powders or microcrystalline.

cyclo-*Tetra-μ-lithio-tetrakis[bis(η-cyclopentadienyl)hydridotungsten]*, (III).—Pure (I; M = W) (0.5 g) in toluene (100 cm^3) at room temperature was treated with a slight excess of LiBu^n (1.0 g in hexane, 2 mol dm^{-3}). After a few minutes small yellow crystals separated and the reaction appeared to be complete after 2 h. The crystals were collected, washed with toluene (2 × 50 cm^3), and dried *in vacuo*, *ca.* 90%. Reactions with methyl- or phenyl-lithium were carried out in the same way giving yellow microcrystalline products.

Bis(η-cyclopentadienyl)hydridophenyltungsten, (IV).—*Method A*. Pure (I; M = W) (0.7 g, 2.21 mmol) in bromobenzene (50 cm^3) at 5 °C was treated with LiBu^n in hexane (4.4 mmol). The initial yellow-green solution became brown and a precipitate appeared. The mixture was cooled in order to maintain the temperature below 35 °C. After 1 h the mixture was hydrolysed by careful addition of water (2 cm^3), the toluene layer was separated, and then concentrated. Chromatography as previously described [6] gave the pure compound, *ca.* 50%.

Method B. Tetramer (III) (1.0 g) in suspension in toluene was treated with bromobenzene (0.5 cm^3) in a dropwise manner with stirring. The mixture became warm and brown-yellow. After 30 min water (5 cm^3) was added slowly giving an orange-brown toluene layer. This was separated, concentrated (3 cm^3), and chromatographed, as described. The orange band was shown to contain both compounds (IV) and $[\mathrm{W}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)\mathrm{H}]$, (V), from the n.m.r., i.r., and mass spectra, *ca.* 20%. Only partial separation could be achieved by crystallisation from light petroleum.

Benzoylbis(η-cyclopentadienyl)hydridomolybdenum, (IX).—A stirred suspension of tetramer (II) (1.3 g) in toluene (100 cm^3) at room temperature was treated with freshly distilled methyl benzoate (1.2 cm^3). Immediately a yellow-brown colour developed and after 30 min water (5 cm^3) was added giving a dark red toluene layer. This was separated and concentrated by removal of the solvent under reduced pressure (to 3 cm^3). This concentrate was placed on an alumina column made up in light petroleum. Elution with light petroleum–diethyl ether (1 : 2) gave first a yellow band, shown to contain the dihydride (I; M = Mo), a second narrower orange band of an unidentified material, and then a wide red band. The last band was collected, concentrated under reduced pressure, and cooled giving red crystals which were collected and recrystallised from light petroleum–diethyl ether. The resulting red crystals were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 20%.

Benzoylchlorobis(η-cyclopentadienyl)molybdenum, (VII).—Pure (IX) (0.3 g) in toluene (20 cm^3) and dichloromethane (10 cm^3) was treated with carbon tetrachloride (2 cm^3). The initial red solution darkened giving slow precipitation of purple-red crystals (6 h). These were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 90%.

Benzoylbis(η-cyclopentadienyl)hydridotungsten, (VI).—*Method A*. Tetramer (III) (1.0 g) in suspension in toluene (50 cm^3) was treated with freshly distilled benzoyl chloride (0.55 cm^3) in a dropwise manner with stirring. A red colour developed rapidly and after 30 min water (5 cm^3) was added. The toluene layer was separated, concentrated under reduced pressure (3 cm^3), and placed on an alumina column made up in light petroleum. Elution with light petroleum–diethyl ether (1 : 1) gave first a yellow band, identified as the dihydride (I; M = W), then a second red band which was collected. The solvent was removed under reduced pressure and the residue was extracted with light petroleum (50 cm^3). The extract was filtered, concentrated under reduced pressure, and cooled to −20 °C giving orange needles of the pure compound, *ca.* 35%.

Method B. The reaction was carried out as described above except that methyl benzoate was used instead of benzoyl chloride, *ca.* 35%.

Method C. The reaction was carried out as described in method *A* except that benzaldehyde was used instead of benzoyl chloride, *ca.* 10—12%.

Benzoylchlorobis(η-cyclopentadienyl)tungsten, (VII).—Pure (VI) (0.3 g) in dichloromethane (10 cm^3) was treated with carbon tetrachloride (3 cm^3) and the mixture was warmed to 30 °C for 2 h. The initial orange solution darkened giving dark red-brown needles which were collected, washed with light petroleum, and dried under reduced pressure, *ca.* 90%.

Acetylbis(η-cyclopentadienyl)hydridotungsten, (XIII).—Tetramer (III) (1.2 g) in toluene (60 cm^3) was treated with freshly distilled acetyl chloride (2.0 g). Immediate reaction

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[16] R. C. Fuson and R. Tull, *J. Amer. Chem. Soc.*, 1949, **71**, 2543.

[17] M. L. H. Green and P. J. Knowles, *J.C.S. Perkin I*, 1973, 989.

occurred giving a red solution and after 30 min water (5 cm^3) was added. The solvent was removed under reduced pressure and the residue was extracted with benzene (10 cm^3). The extract was concentrated under reduced pressure (3 cm^3) and placed on an alumina column made up in light petroleum. Elution with light petroleum–diethyl ether (10 : 1) separated two bands. A wide yellow band was shown to be the dihydride (I; M = Mo), *ca.* 60%, and a second orange band was collected and the solvent removed under pressure. The residue was extracted with light petroleum (b.p. 60—80 °C) forming a red solution which was filtered, concentrated, and cooled giving bright red crystals. The latter were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 3—10%.

Acetylchlorobis(η-cyclopentadienyl)tungsten, (XIV).—Compound (XIII) (0.2 g) in dichloromethane (15 cm^3) was treated with carbon tetrachloride (1.0 cm^3). The initial orange solution became red and after 4 h light petroleum was added (100—120 °C, 15 cm^3). The solution was slowly concentrated under reduced pressure giving red-brown crystals which were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 90%.

Bis(benzyl)bis(η-cyclopentadienyl)molybdenum, (X).—Tetramer (II) (1.3 g) in toluene (60 cm^3) was treated with benzyl bromide (0.8 cm^3) giving immediately a clear red solution. After 30 min water (3 cm^3) was added and the toluene layer was separated, concentrated under reduced pressure, and chromatographed on an alumina column made up in light petroleum. Elution with light petroleum–benzene (1 : 1) gave first an orange band; this was collected, the solvent was removed under reduced pressure, and the residue was crystallised from toluene–light petroleum giving orange crystals. These were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 30%. Further elution of the column with pure benzene gave a yellow band from which the dihydride (I; M = Mo) was isolated, *ca.* 30%.

Compound (X) was similarly prepared from the yellow powder formed from the hydride (I; M = Mo) and methyl-lithium, *ca.* 22%, and from the yellow powders from (I; M = Mo) and phenyl-lithium, *ca.* 30%. The analogue bis(benzyl)bis(η-cyclopentadienyl)tungsten, (XI), was similarly prepared from compound (III) as orange needles. Recrystallisation was from benzene–light petroleum (b.p. 100—120 °C), *ca.* 40%.

(p-*Benzoylphenyl)bis(η-cyclopentadienyl)hydridotungsten*, (XV).—Tetramer (III) (1.2 g) in suspension in toluene (50 cm^3) was treated with benzophenone (1.0 g) at room temperature. Immediately a deep blue-green colour developed and after 30 min water (2 cm^3) was added, giving a deep red toluene layer. This was separated and solvent was removed under reduced pressure. The residue was extracted with benzene and the extract was concentrated (3 cm^3) and chromatographed on an alumina column made up in light petroleum. Elution with benzene–light petroleum (1 : 3) gave a deep red-purple band, and a yellow band which was shown (i.r.) to contain the hydride (I; M = W). The red-purple band was collected, the solvent was removed under reduced pressure, and the residue was recrystallised from toluene–hexane as deep red crystals. These were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 20%.

(p-*Benzoylphenyl)chlorobis(η-cyclopentadienyl)tungsten*, (XVI).—Compound (XV) (0.1 g) in dichloromethane (20 cm^3) was treated with carbon tetrachloride (1 cm^3). The initial red-orange solution turned deep red and after 6 h the solvent was removed under reduced pressure giving red-brown needles which were collected, washed with light petroleum, and dried *in vacuo*, *ca.* 90%.

Reaction between the Tetramers (II) *and* (III) *and Carbon Dioxide*.—A suspension of the tetramer (II) (2.19 g) in toluene (80 cm^3) was treated with a stream of carbon dioxide at 1 atm and room temperature for 30 min. The solvent was removed from the resulting green solution under reduced pressure and the residue was treated with a little methanol (2 cm^3) and then extracted with toluene (2 × 20 cm^3). The extract was concentrated (4 cm^3) and chromatographed on an alumina column in light petroleum. Elution with light petroleum–toluene (1 : 1) gave first a yellow band, identified as the dihydride (I; M = Mo), *ca.* 20%. Further elution with pure toluene gave a green band which was collected and the solvent was removed under reduced pressure. The green residue was recrystallised from benzene–heptane as deep green crystals, *ca.* 78%. Tetramer (III) reacted with carbon dioxide in a similar manner giving the monocarbonyl $[W(\eta\text{-}C_5H_5)_2(CO)]$, *ca.* 80%.

Reaction between the Tetramer (II) *and Carbon Monoxide*.—A suspension of the tetramer (2.0 g) in toluene (100 cm^3) was treated with a stream of carbon monoxide at room temperature for 1 h. The solvent was removed from the resulting green reaction mixture and the residue was treated with methanol (5 cm^3). The methanol was removed under reduced pressure and the residue was extracted with toluene (5 cm^3) and chromatographed. Elution with hexane gave trace amounts of (I; M = Mo). Further elution with hexane–toluene gave a yellow band and a small red band; with pure toluene a green band was eluted. The solvent was removed from the yellow band under reduced pressure and the yellow residue was recrystallised from cyclohexane as yellow crystals. These were washed with light petroleum (b.p. 30—40 °C) and dried *in vacuo* giving the pure compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_7)(CO)_2]$, (XX), *ca.* 10%. Mass spectrum for ^{98}Mo: *m/e* 286 $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(CO)_2]^+$ and 258 $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_7)CO]^+$. The green band was shown to contain the compound $[Mo(\eta\text{-}C_5H_5)_2(CO)]$, (XIX), *ca.* 65%. The red band gave a small yield, *ca.* 2%, of red crystals (XXI).

Bis(η-cyclopentadienyl)bis(pentafluorophenyl)molybdenum, (XVII).—A stirred suspension of (II) (2.2 mmol) in toluene (50 cm^3) was cooled to −80 °C and bromopentafluorobenzene (1.23 g, 5.0 mmol) was added. The mixture was allowed to warm to room temperature, methanol (2 cm^3) was added, and the mixture was concentrated under reduced pressure to 3 cm^3. The concentrate was chromatographed on an alumina column and elution with benzene–light petroleum developed a yellow-orange band which was collected. The solvent was removed under reduced pressure and the residue was crystallised from light petroleum, 0.31 g (*ca.* 25%). Further elution of the alumina column gave compound (I; M = Mo) in 42% yield. The tungsten analogue $[W(\eta\text{-}C_5H_5)_2(C_6F_5)_2]$, (XVIII), was similarly prepared in 18% yield.

Bis(η-cyclopentadienyl)bis(trimethylsilylmethyl)tungsten, (XII).—*Method A*. The dichloride $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (1.0 g) in suspension in dry toluene (50 cm^3) was treated with freshly prepared $MgCl(CH_2SiMe_3)$ in diethyl ether (6 cm^3 of 2 mol dm^{-3}). The mixture was stirred at room temperature for 12 h giving a red solution, and this was cooled to −196 °C and ethanol (10 cm^3) was slowly added. The mixture was warmed to room temperature, the solvent was removed under reduced pressure, and the residue was extracted with benzene. The extract was chromatographed on an alumina column. Elution with light petroleum gave an orange band which was collected, the solvent was removed under reduced pressure, and the residue was crystallised from light petroleum at −40 °C, *ca.* 20%.

Method B. A suspension in toluene (50 cm^3) of the freshly prepared tetramer (III) (0.5 g) was treated with (chloromethyl)trimethylsilane (0.4 cm^3) at room temperature with stirring. A red solution formed immediately and after addition of water (1 cm^3) the toluene layer was separated, chromatographed, and the product was isolated as described in *A*, *ca.* 30%.

Bis(η-cyclopentadienyl)molybdenum–Zinc Polymer, (XXII).—The dihydride (I; M = Mo) (0.5 g) in toluene (50 cm^3) was treated with excess of diethylzinc (or di-n-butylzinc) in toluene (typically 2 g in 50 cm^3) and the mixture was heated to 110 °C for 30 h giving well formed brown crystals. These were washed with toluene and dried *in vacuo*, *ca.* 80%. The tungsten analogue, (XXIII), was similarly prepared, *ca.* 80%.

(1—3-η-*But-2-enyl)bis(η-cyclopentadienyl)molybdenum Hexafluorophosphate*, (XXI).—A toluene suspension of (II) (0.5 g in 50 cm^3) and butadiene (5 cm^3) in a sealed glass tube was warmed to 50 °C for 24 h. The reaction mixture was concentrated and placed on an alumina column. Elution with ethanol gave a red band which was collected and treated with excess of aqueous ammonium hexafluorophosphate. Concentration under reduced pressure gave red crystals of compound (XXI), which were washed with water and dried, *ca.* 25%.

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