265. *Some π-Cyclopentadienyl-molybdenum and -tungsten Carbonyls.*

By E. W. ABEL, APAR SINGH, and G. WILKINSON.

Some substituted binuclear cyclopentadienyl-molybdenum and -tungsten carbonyls have been made from the metal carbonyls and fulvenes. The corresponding mononuclear iodides and some alkyl derivatives have been obtained. π-Cyclopentadienylmolybdenum-π-cyclopentadienyltungsten hexacarbonyl is the first reported complex with a metal–metal bond between different transition-metal atoms.

MOLYBDENUM and tungsten form[1,2] binuclear di(cyclopentadienylmetal tricarbonyls) $[\pi\text{-}C_5H_5M(CO)_3]_2$, and a methyl-substituted derivative was prepared[3] from methylcyclopentadiene. We now report the preparation of other substituted binuclear di(cyclopentadienylmetal carbonyls) from the simple carbonyls and various fulvenes; fulvenes were recently used as starting materials for the preparation of substituted ferrocenes.[4] Whereas the formation of the π-cyclopentadienyl compounds from cyclopentadiene required the loss of hydrogen in a manner as yet not fully understood, the formation of substituted π-cyclopentadienylmetal compounds from the fulvenes requires the uptake of hydrogen:

$$2C_5H_4{=}CRR' + 2M(CO)_6 + 2H \longrightarrow [RR'HC{\cdot}C_5H_4M(CO)_3]_2 + 6CO \quad . \; . \; . \; . \; . \quad (1)$$

Since high yields are obtained only with solvents, such as ethylene glycol dimethyl ether, from which hydrogen can be abstracted, the hydrogen is most likely derived from the solvent, though some abstraction from the excess of fulvene is also a possibility. The compounds prepared in this manner are listed in Table 1.

TABLE 1. *Di(substituted π-cyclopentadienylmetal tricarbonyls)* $[R{\cdot}C_5H_4M(CO)_3]_2$.

R	M	M. p.	Colour	CO stretching modes (cm.$^{-1}$) (all strong)
Pr^n	Mo	200° *	Red	1967, 1916
Pr^i	Mo	163	Red	1964, 1916
CHMeEt	Mo	170	Red	1964, 1913
$CHEt_2$	Mo	152	Red	1962, 1916
$CHMePr^n$	Mo	117—119	Red	1962, 1912
CHPhMe	Mo	125 *	Dark red	1962, 1912
$CHPh_2$	Mo	203—205	Brown	1961, 1916
$p\text{-}MeO{\cdot}C_6H_4{\cdot}CH_2$	Mo	103 *	Brown	1961, 1916
Cyclohexyl	Mo	180	Red	1961, 1911
Pr^i	W	195	Red	1958, 1906
$CHEt_2$	W	184	Red	1960, 1905

* Decomposition point.

The tricarbonyl-π-cyclopentadienylmolybdenum halides have previously been made indirectly,[2] but we have now found that the metal–metal bond[5] in bis(tricarbonyl-π-cyclopentadienylmolybdenum) is immediately cleaved by iodine in solution. In this way we have prepared some monomeric iodides (Table 2):

$$[R{\cdot}C_5H_4Mo(CO)_3]_2 + I_2 \longrightarrow 2R{\cdot}C_5H_4Mo(CO)_3I \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

The metal–metal bond can also be cleaved by sodium in tetrahydrofuran to give the corresponding sodium salts.

Many compounds are now known in which an alkyl group is σ-bonded to the metal of

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[1] Wilkinson, *J. Amer. Chem. Soc.*, 1954, **76**. 209.

[2] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[3] Reynolds and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86.

[4] Knox and Pauson, *Proc. Chem. Soc.*, 1958, 289.

[5] Wilson and Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

the tricarbonyl-π-cyclopentadienylmolybdenum residue.[2] No compounds were known, however, in which alkyl groups were attached directly to the metal, and also substituted on the π-cyclopentadienyl ring. A number of these compounds have been obtained (Table 3) by the interaction of the sodium salts of the substituted tricarbonyl-π-cyclopentadienylmolybdenum and alkyl halides.

TABLE 2. *Tricarbonyl-(substituted π-cyclopentadienyl)molybdenum iodides* $\mathrm{R{\cdot}C_5H_4Mo(CO)_3I}$.

R	M. p.	CO stretching modes (cm.$^{-1}$) (all strong)	R	M. p.	CO stretching modes (cm.$^{-1}$) (all strong)
$\mathrm{Pr^i}$ ………………	92—94°	2052, 1974	CHPhMe ………	76°	2052, 1974
CHMeEt ………	75	2051, 1974	p-$\mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2}$	78	2055, 1975
$\mathrm{CHEt_2}$ …………	45	2050, 1976	$\mathrm{CHMePr^n}$ ………	Oil	2050, 1973

The ring-substituted compounds described are very similar to the parent cyclopentadienyl compounds. There is a general tendency, however, for the ring substituent to cause a lowering in melting point, and even some liquid compounds were obtained. This trend has already been noted on methyl substitution.[3]

The infrared spectra of all the compounds have only two strong modes in the metal–carbonyl stretching region, this despite the presence of substituent groups on the cyclopentadienyl ring; it confirms the view [3,6] that the number of infrared-active modes is dependent upon the local symmetry of the $\mathrm{M(CO)_3}$ group and not on the total symmetry of the molecule, owing essentially to free rotation about the metal–ring bond.[7,8] The small variations observed in the CO stretching frequency may be explained by the variations in electron density on the ring and the metal atom, caused by substituents on the π-cyclopentadienyl ring.

TABLE 3. *Alkyl-(substituted π-cyclopentadienyl)molybdenum tricarbonyls* $\mathrm{R{\cdot}C_5H_4{\cdot}MoR'(CO)_3}$.

R	R	M. p.	CO stretching modes (cm.$^{-1}$) (all strong)	R	R′	M. p.	CO stretching modes (cm.$^{-1}$) (all strong)
$\mathrm{Pr^i}$ ……	Me	~−25°	2030, 1938	$\mathrm{CHEt_2}$ …	Et	Oil	2021, 1927
$\mathrm{Pr^i}$ ……	Et	~−15°	2025, 1931	CHPhMe	Me	Oil	2021, 1931
$\mathrm{CHEt_2}$ …	Me	Oil	2028, 1931				

Reaction of the sodium salt of tricarbonylcyclopentadienylmolybdenum with tricarbonylcyclopentadienyltungsten iodide gave π-cyclopentadienyltungsten-cyclopentadienylmolybdenum hexacarbonyl:

$$\pi\text{-}\mathrm{C_5H_5Mo(CO)_3Na} + \pi\text{-}\mathrm{C_5H_5W(CO)_3I} \longrightarrow \mathrm{NaI} + \pi\text{-}\mathrm{C_5H_5(CO)_3Mo{\cdot}W(CO)_3}\pi\text{-}\mathrm{C_5H_5}$$

We believe this is the first carbonyl complex with a metal–metal bond between different transition metals. That it was not a mixture of the corresponding Mo–Mo and W–W compounds was evident as the compound was chromatographed twice (as a single band) and then shown to give the same analytical results. Further, the ultraviolet spectra of the binuclear π-cyclopentadienyl-molybdenum and -tungsten carbonyls have sharp absorption maxima at 386 and 360 mμ, respectively. An equimolar mixture of the compounds exhibits both of these peaks, whereas the molybdenum-tungsten compound has only one maximum at 374 mμ.

EXPERIMENTAL

Microanalyses and Rast molecular-weight determinations were by the Microanalytical Laboratory of Imperial College. Infrared spectra were recorded on a Perkin-Elmer model 21

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[6] Cotton, Liehr, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

[7] Wilkinson and Cotton, " Progress in Inorganic Chemistry," Interscience Publishers Inc., New York, 1959, Vol. I, Chap. 1.

[8] Waugh and Cotton, personal communication.

double-beam spectrophotometer, in carbon tetrachloride and disulphide solution, and ultraviolet spectra were recorded in chloroform solution on a Perkin-Elmer model 4000 Spectracord.

Dimethyl-, diethyl-, ethylmethyl-, and methylphenyl-fulvenes,[9] diphenylfulvene,[10] *p*-methoxybenzylidenefulvene,[11] cyclohexylidene-, cyclopentadiene-,[12] and ethyl-fulvene [13] were prepared by previously described methods. All reactions were carried out under nitrogen, and purifications were by crystallisation, vacuum-sublimation, and chromatography on alumina.

Interaction of Fulvenes with Molybdenum Hexacarbonyl.—The carbonyl (*ca.* 0·01 mole, 1 mol.), the fulvene (1·5 mol.) and ethylene glycol dimethyl ether (50 ml.) were refluxed for 6 hr., considerable amounts of carbon monoxide being evolved and the mixture becoming deep red. Volatile material was removed (60°/10^{-3} mm.), and the red residue extracted with petrol–benzene. After purification by chromatography on alumina the substituted *bis(tricarbonylcyclopentadienylmolybdenum)* formed fine red crystals from light petroleum (Table 4).

Interaction of Fulvenes with Tungsten Hexacarbonyl.—In the same way as described above for the molybdenum analogues, we have prepared *bis[tricarbonyl-π-(isopropylcyclopentadienyl)-tungsten]* (10%) (Found: C, 34·6; H, 3·4; W, 48·2%; *M*, 723. $C_{22}H_{22}O_6W_2$ requires C, 35·2; H, 2·9; W, 49·1%; *M*, 750) and *bis[tricarbonyl-π-(1-ethylpropylcyclopentadienyl)tungsten]* (8%) (Found: C, 38·8; H, 2·8; W, 46·1%; *M*, 806. $C_{26}H_{30}O_6W_2$ requires C, 38·6; H, 3·7; W, 45·7%; *M*, 795).

Preparation of the Substituted Tricarbonylcyclopentadienylmolybdenum Iodides.—The substituted bis(tricarbonyl-π-cyclopentadienylmolybdenum) (0·005 mole, 1 mol.) in chloroform was added dropwise to iodine (1 mol.) in chloroform with constant shaking. The chloroform solution was then shaken with aqueous sodium thiosulphate; after separation, the chloroform was removed (20°/10 mm.), and the residue crystallized from light petroleum (Table 5).

TABLE 4. $[R\cdot C_5H_4Mo(CO)_3]_2$.

	Yield	*M*		Found (%)				Reqd. (%)			
R	(%)	Found	Reqd.	C	H	Mo	O	C	H	Mo	O
Pr^n	20	588	574	46·0	3·7	33·2	—	45·9	3·8	33·5	—
Pr^i	42	619	574	45·5	4·2	33·6	16·9	45·9	3·8	33·5	16·7
CHMeEt	70	614	602	48·3	4·1	32·8	15·9	47·8	4·3	31·9	15·9
$CHEt_2$	45	678	630	50·0	4·8	30·9	14·9	49·5	4·8	30·5	15·2
CHMePr^n	62	645	630	50·4	5·1	30·5	15·2	49·5	4·8	30·5	15·2
CHPhMe	30	702	698	55·4	4·0	27·8	13·8	55·0	3·7	27·5	13·8
$CHPh_2$	30	862	822	61·5	4·3	22·9	—	61·3	3·7	23·4	—
p-$MeO\cdot C_6H_4\cdot CH_2$	60	717	730	53·2	4·1	26·4	—	52·6	3·6	26·3	—
Cyclohexyl	20	670	654	51·5	4·9	29·1	14·5	51·4	4·6	29·4	14·7

TABLE 5. $R\cdot C_5H_4Mo(CO)_3I$.

	Yield	*M*		Found (%)					Reqd. (%)				
R	(%)	Found	Reqd.	C	H	Mo	O	I	C	H	Mo	O	I
Pr^i	69	422	414	32·1	2·6	23·5	11·5	—	31·9	2·7	23·2	11·6	—
CHMeEt	70	450	428	32·7	2·8	22·6	—	29·7	33·7	3·0	22·4	—	29·7
$CHEt_2$	43	476	442	34·6	3·5	22·0	—	29·2	35·3	3·4	21·7	—	28·7
CHPhMe	59	488	476	40·8	3·2	20·0	—	27·5	40·3	2·7	20·2	—	26·7
p-$MeO\cdot C_6H_4\cdot CH_2$	70	510	492	39·5	3·2	14·5	—	25·8	39·0	2·7	19·5	—	25·8
CHMePr	40	416	442	34·0	3·8	22·1	—	29·0	35·3	3·4	21·7	—	28·7

Preparation of the Metal–Alkyl Derivatives of Substituted-cyclopentadienylmolybdenum Tricarbonyls.—Bis[tricarbonyl-π-(isopropylcyclopentadienyl)molybdenum] (1·7 g., 1 mol.) in tetrahydrofuran (25 c.c.) was added to sodium shot (0·4 g.; 5 mol.) suspended in tetrahydrofuran (75 c.c.), and the solution refluxed gently with stirring (3 hr.); during this time a strong yellow coloration developed. After cooling, methyl iodide (2 ml.) was added dropwise and the mixture was refluxed for another hour. Removal of volatile matter (at 20°/10 mm.) left a dark oil which on sublimation gave pure *tricarbonyl-π-(isopropylcyclopentadienyl)(methyl)molybdenum* (70%) (Found: C, 48·1; H, 4·7; Mo, 30·8%; *M*, 295. $C_{12}H_{14}MoO_3$ requires C, 47·7; H, 4·6; Mo, 31·7%; *M*, 302). In a similar manner were prepared *tricarbonylethyl-π-(isopropylcyclopentadienyl)molybdenum* (60%) (Found: C, 50·2; H, 5·2; Mo, 29·8%; *M*, 298. $C_{13}H_{16}MoO_3$

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[9] Crane, Boord, and Henne, *J. Amer. Chem. Soc.*, 1945, **67**, 1237.

[10] Thiele, *Ber.*, 1900, **33**, 672.

[11] Thiele and Balhorn, *Annalen*, 1906, **348**, 10.

[12] Kohler and Kable, *J. Amer. Chem. Soc.*, 1935, **57**, 917.

[13] Engler, *Z. Elektrochem.*, 1912, **18**, 946.

TABLE 6. *Ultraviolet absorption spectra of the bis(substituted-π-cyclopentadienylmetal tricarbonyls)* $[R\cdot C_5H_4M(CO)_3]_2$.

		Absorption maximum		Absorption maximum	
R	M	λ (mμ)	$\varepsilon_{max.}$	λ (mμ)	$\varepsilon_{max.}$
H	Mo	386	22,000	510	2150
Pr^i	Mo	393	15,070	510	3123
$CHEt_2$	Mo	395	15,050	515	1645
CHMeEt	Mo	400	18,060	517	1982
$CHMePr^n$	Mo	398	19,240	512	3436
$CHPh_2$	Mo	394	13,900	512	2978
CHMePh	Mo	390	18,750	513	2360
$MeO\cdot C_6H_4\cdot CH_2$	Mo	395	16,340	513	2340
H	W	360	16,700	490	1540
Pr^i	W	365	26,250	492	4000
$CHEt_2$	W	365	31,300	493	3793
$\pi\text{-}C_5H_5(CO)_3Mo\cdot W(CO)_3\pi\text{-}C_5H_5$		374	17,000	498	2540

requires C, 49·4; H, 5·1; Mo, 30·4%; *M*, 316); and *tricarbonyl-π-(1-ethylpropylcyclopentadienyl)-methylmolybdenum* (60%) (Found: C, 52·1; H, 5·9; Mo, 28·2%, *M*, 315. $C_{14}H_{16}MoO_3$ requires C, 50·9; H, 5·5; Mo, 28·1%; *M*, 330).

Preparation of π-Cyclopentadienylmolybdenum-π-Cyclopentadienyltungsten Hexacarbonyl.—Bis(tricarbonylcyclopentadienylmolybdenum) (1·30 g., 1 mol.) was added to sodium shot (0·49 g., 4 mol.) in tetrahydrofuran (100 c.c.) and the mixture refluxed (2 hr.). After cooling, the yellow solution was filtered from the excess of metal and added to tricarbonyl-π-cyclopentadienyltungsten chloride (1·96 g., 1 mol.) in tetrahydrofuran (30 c.c.). The yellow mixture gradually became red, and after 2 hours' refluxing and subsequent cooling, volatile matter was removed (20°/10 mm.) and the crude product recrystallized from chloroform–petroleum. After chromatography (twice) in petroleum red crystals of *π-cyclopentadienylmolybdenum-π-cyclopentadienyltungsten hexacarbonyl* (1·0 g., 65%), m. p. 250° (Found: C, 32·0; H, 1·8; Mo, 16·75; W, 32·1%; *M*, 528. $C_{16}H_{10}MoWO_6$ requires C, 33·2; H, 1·7; Mo, 16·6; W, 31·8%; *M*, 578, were obtained.

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INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

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