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AMINE COMPLEXES OF CYCLOPENTADIENYLTUNGSTEN CARBONYL AND THE SYNTHESIS OF SOME W—Mn BONDED COMPOUNDS

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Summary

Ethyl-, isopropyl-, diethyl-, butyl- and cyclohexyl-amines reacted with cyclopentadienyltungsten tricarbonyl dimer at ambient temperatures to give $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ (L = amines). Potential chelating bidentate ligands like ethylenediamine, *o*-phenanthroline and 2,2′-bipyridine also displaced only one CO group under identical conditions. Examination of the IR spectra of these derivatives in the C—O stretching region indicated a slight distortion from the local C_2 symmetry.

$(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ derivatives after reduction with sodium amalgam and subsequent treatment with manganese pentacarbonyl bromide yielded a mixture of $[(\pi\text{-}C_5H_5)W(CO)_2L]Mn(CO)_5$ and $[(\pi\text{-}C_5H_5)W(CO)_3]Mn(CO)_5$. The two different constituents have been separated by column chromatography.

Introduction

Several studies [1—5] have been made on the CO exchange reactions of cyclopentadienylmolybdenum tricarbonyl dimer with phosphorus and sulphur donor ligands; relatively little attention has been paid to the reactions of its tungsten analogue. Further, the reactions between these dimers and nitrogen donor ligands are almost uninvestigated. We describe here a study of the ligand behaviour of some mono- and bi-dentate nitrogen donor ligands in the CO displacement reaction of cyclopentadienyltungsten tricarbonyl dimer. A number of $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ ($L = C_2H_5NH_2$, $i\text{-}C_3H_7NH_2$, $(C_2H_5)_2NH$, $C_4H_9NH_2$ and $C_6H_{11}NH_2$) derivatives have been prepared by these reactions. Potential bidentate ligands like ethylenediamine, *o*-phenanthroline and 2,2′-bipyridine acted as monodentate in these cases. The reactions of the anions, which are obtained by sodium amalgam reduction of $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$, with manganese pentacarbonyl bromide have also been investigated. These reactions provide a good route for the synthesis of some novel W—Mn bonded complexes.

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Results and discussion

Cyclopentadienyltungsten tricarbonyl dimer reacted with ethyl-, diethyl-, isopropyl-, butyl- and cyclohexyl-amine at ambient temperature to give monosubstituted, $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$, derivatives. To achieve more substitution, the reactions were performed at higher temperatures for longer time but they yielded the products which did not contain amines. Under all the conditions studied, not more than one CO group could be displaced. Potential bidentate ligands like ethylenediamine, *o*-phenanthroline and 2,2′-bipyridine also could not displace more than one CO group. In the case of *o*-phenanthroline and 2,2′-bipyridine gentle warming is preferable. The monosubstituted derivatives were separated from the parent dimer by column chromatography on an alumina column. Elution with hexane gave red or orange air-stable crystalline di-π-cyclopentadienyl-(amine)ditungsten(I) pentacarbonyl complexes. In all cases a second fraction, which could not be eluted with hexane, was obtained by elution with tetrahydrofuran. Evaporation of the solvent yielded a greyish product which was identical to the product obtained by high temperature reactions (and which did not contain amines).

$(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ derivatives dissolved in almost all common organic solvents. They were non-electrolytes in benzene (mol. cond. < 1 ohm^{-1} cm^2 mol^{-1}). After reduction with sodium amalgam in dry benzene they yielded faint red or colourless anions * which were used as such (without isolation from the solution) in further reactions with manganese pentacarbonyl bromide. Two different types of W—Mn bonded compounds, $[(\pi\text{-}C_5H_5)W(CO)_2L]Mn(CO)_5$ and $[(\pi\text{-}C_5H_5)W(CO)_3]Mn(CO)_5$, were obtained in these reactions. The detailed separation technique is given in the experimental section. $[(\pi\text{-}C_5H_5)W(CO)_2L]Mn(CO)_5$ derivatives dissolved in aromatic hydrocarbons, tetrahydrofuran, diethyl ether, acetone, chloroform, carbon tetrachloride but were insoluble in alcohols, aliphatic hydrocarbons and light petroleum (all fractions).

Infrared spectra

In the IR spectra of $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ derivatives five to eight C—O stretching bands were recorded (Table 1). If the substitution in cyclopentadienyltungsten tricarbonyl dimer is considered to occur in the plane of symmetry, the appearance of five bands due to $3A' + 2A''$ modes is expected. The appearance of more bands indicates a slight distortion from local C_2 symmetry in the solid state. A very weak or shoulder band ~2000 cm^{-1} in the IR spectra of some derivatives indicates that the Raman active mode of C_{2h} symmetry in cyclopentadienyltungsten tricarbonyl dimer gained some intensity in the distorted C_2 symmetry of these molecules and appeared in the IR spectra. Other bands were of identical nature as reported for the other similar tertiary phosphine and phosphite substituted complexes [5].

The IR spectra of $[(\pi\text{-}C_5H_5)W(CO)_2L]Mn(CO)_5$ derivatives showed five C—O stretching bands (Table 2). The weak band at 2133 cm^{-1} of manganese pentacarbonyl bromide disappeared when $Mn(CO)_5$ was added to the anions obtained by

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* Colourless anions for derivatives containing *o*-phenanthroline or 2,2′-bipyridine and faint red for others.

TABLE 1

C—O STRETCHING FREQUENCIES OF $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ COMPLEXES

Compound	ν(CO)(cm^{-1})
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_2H_5NH_2)$	2010vw, 1975vs, 1947s(sh), 1902s 1885s(sh), 1870(sh), 1855m
$(\pi\text{-}C_5H_5)_2W_2(CO)_5\{(C_2H_5)_2NH\}$	1970s, 1947m, 1910s, 1885s(sh), 1855w(sh)
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(i\text{-}C_3H_7NH_2)$	2001w, 1973s, 1935s(sh), 1900(br), 1885s(sh) 1852m
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_4H_9NH_2)$	1974s, 1940vs(sh), 1902(br), 1885(sh), 1876(sh)
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_6H_{11}NH_2)$	1970s, 1937s(sh), 1924(sh), 1910s, 1885s(sh)
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_2H_8N_2)$	2000w(sh), 1975s, 1934m, 1920(sh), 1902(br), 1862m, 1848mw
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_{10}H_8N_2)$	1970s, 1937vs(sh), 1900(br), 1885(sh), 1852vs(sh)
$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_{12}H_8N_2)$	2000vw, 1975vs, 1935(sh), 1921(sh), 1903vs, 1894ms, 1873(sh), 1858w

the reduction of $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ derivatives with sodium amalgam. There is a little effect on the band at 2050 cm^{-1} of manganese pentacarbonyl bromide since a band around this frequency always appeared in the W—Mn bonded compounds. A very strong band between 2008-2019 cm^{-1} in the IR spectra of W—Mn bonded derivatives may be the same as 2006 cm^{-1} of $Mn(CO)_5Br$ with a slight shift in higher frequency region. Except for a band at ~1855 cm^{-1} which did not appear in the spectra of W—Mn bonded compounds, the other bands might be due to the $(\pi\text{-}C_5H_5)W(CO)_2L$ moiety; they were invariably present in the spectra of $(\pi\text{-}C_5H_5)_2W_2(CO)_5L$ derivatives. Since these complexes are the first of this type to be reported we reproduce the spectrum of the C—O stretching region of a typical cyclohexylamine substituted derivative $[(\pi\text{-}C_5H_5)W(CO)_2(C_6H_{11}NH_2)]Mn(CO)_5$ (Fig. 1).

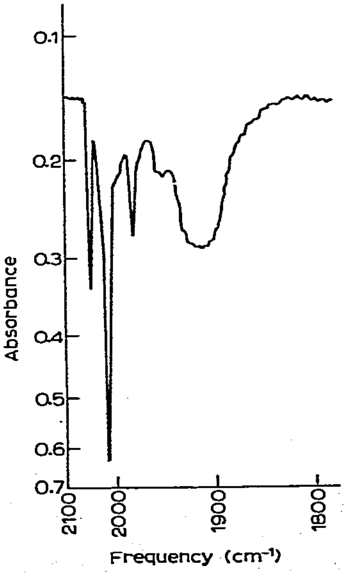

Fig. 1. C—O stretching region of the IR spectrum of $[(\pi\text{-}C_5H_5)W(CO)_2(C_6H_{11}NH_2)]Mn(CO)_5$.

TABLE 2

C—O STRETCHING FREQUENCIES OF [(π-C_5H_5)W$(CO)_2$L]Mn$(CO)_5$ COMPLEXES

Compound	ν(CO) (cm^{-1})
[(π-C_5H_5)W$(CO)_2$($C_2H_5NH_2$)] Mn$(CO)_5$	2040s, 2008vs, 1973m, 1948w, 1900
[(π-C_5H_5)W$(CO)_2${$(C_2H_5)_2NH$}]Mn$(CO)_5$	2060s, 2010vs, 1972m, 1950w, 1902
[(π-C_5H_5)W$(CO)_2$(i-$C_3H_7NH_2$)]Mn$(CO)_5$	2052s, 2002vs, 1970m, 1944w, 1902(br)
[(π-C_5H_5)W$(CO)_2$($C_4H_9NH_2$)]Mn$(CO)_5$	2050s, 2016vs, 1975m, 1955w, 1910
[(π-C_5H_5)W$(CO)_2$($C_6H_{11}NH_2$)]Mn$(CO)_5$	2050s, 2016vs, 1983m, 1955w, 1916(br)
[(π-C_5H_5)W$(CO)_2$($C_2H_8N_2$)]Mn$(CO)_5$	2042s, 2019vs, 1975m, 1930w, 1910(br)
[(π-C_5H_5)W$(CO)_2$($C_{10}H_8N_2$)]Mn$(CO)_5$	2056s, 2016vs, 1969m, 1937w, 1910(br)
[(π-C_5H_5)W$(CO)_2$($C_{12}H_8N_2$)]Mn$(CO)_5$	2055s, 2010vs, 1976m, 1940w, 1912(br)

Experimental

Tungsten hexacarbonyl was sublimed before use. Cyclopentadienyltungsten tricarbonyl dimer was prepared by heating [6] tungsten hexacarbonyl and dicyclopentadiene in an evacuated sealed tube at 250°C for 4 h. Manganese pentacarbonyl bromide was prepared by the established method [7]. All the experiments were performed in a nitrogen atmosphere or in vacuo. Except for ethyl- and isopropyl-amine, which were used as 70% aqueous solutions, all the amines were used neat. IR spectra were measured on mulls using Perkin—Elmer spectrophotometer model 621.

Preparation of ethylamine(di-π-cyclopentadienyl) ditungsten(I) pentacarbonyl

Ethylamine (2.0 ml) was mixed in a benzene solution of cyclopentadienyltungsten tricarbonyl dimer (0.2 g in 15 ml). After mixing, the pink colour of the solution of the dimer rapidly changed to red-brown. The reaction mixture was

TABLE 3

REACTION TIMES, YIELDS AND ANALYSES OF SUBSTITUTED (π-C_5H_5)$_2$$W_2(CO)_5$L COMPLEXES

Compound	Reaction time (min)	M.p. [a] (°C)	Yield (%)	Analysis Found (calcd.) (%)		
				C	H	N
(π-C_5H_5)$_2$$W_2(CO)_5${$(C_2H_5)_2NH$}	50	95	66	31.8 (32.0)	2.7 (2.9)	1.8 (1.9)
(π-C_5H_5)$_2$$W_2(CO)_5$(i-$C_3H_7NH_2$)	50	96	68	30.2 (30.9)	2.8 (2.7)	2.1 (2.0)
(π-C_5H_5)$_2$$W_2(CO)_5$($C_4H_9NH_2$)	50	100	65	31.6 (32.0)	2.6 (2.9)	2.0 (1.9)
(π-C_5H_5)$_2$$W_2(CO)_5$($C_6H_{11}NH_2$)	45	104	55	33.2 (34.1)	3.0 (3.1)	1.7 (1.8)
(π-C_5H_5)$_2$$W_2(CO)_5$($C_2H_8N_2$)	30	122	70	29.0 (29.2)	2.3 (2.5)	3.8 (4.0)
(π-C_5H_5)$_2$$W_2(CO)_5$($C_{10}H_8N_2$)	75	125	60	37.1 (37.7)	2.1 (2.2)	3.6 (3.5)
(π-C_5H_5)$_2$$W_2(CO)_5$($C_{12}H_8N_2$)	75	112	56	39.0 (39.7)	2.3 (2.2)	3.3 (3.4)

[a] The crystals shrink at the temperature specified.

TABLE 4

COLOURS, YIELDS AND ANALYSES OF $(\pi\text{-}C_5H_5)W(CO)_2LMn(CO)_5$ COMPLEXES

Compound	Colour	M.P. (°C)	Yield (%)	Analysis Found (calcd.) (%)		
				C	H	N
$[(\pi\text{-}C_5H_5)W(CO)_2\{(C_2H_5)_2NH\}]Mn(CO)_5$	orange	110	42	33.5 (34.1)	2.7 (2.8)	2.2 (2.4)
$[(\pi\text{-}C_5H_5)W(CO)_2(i\text{-}C_3H_7NH_2)]Mn(CO)_5$	orange	112	44	31.6 (32.2)	2.3 (2.5)	2.4 (2.5)
$[(\pi\text{-}C_5H_5)W(CO)_2(C_4H_9NH_2)]Mn(CO)_5$	Brick-red	115	48	33.4 (34.1)	2.6 (2.8)	2.1 (2.4)
$[(\pi\text{-}C_5H_5)W(CO)_2(C_6H_{11}NH_2)]Mn(CO)_5$	dark brown	130	40	35.4 (36.0)	2.8 (3.0)	2.2 (2.3)
$[(\pi\text{-}C_5H_5)W(CO)_2(C_2H_8N_2)]Mn(CO)_5$	Yellowish brown	135d	42	29.2 (30.0)	2.2 (2.3)	4.6 (5.0)
$[(\pi\text{-}C_5H_5)W(CO)_2(C_{10}H_8N_2)]Mn(CO)_5$	Yellowish brown	170d	58	40.0 (40.2)	1.9 (1.9)	4.1 (4.2)
$[(\pi\text{-}C_5H_5)W(CO)_2(C_{12}H_8N_2)]Mn(CO)_5$	Yellow	196d	55	41.5 (42.3)	1.8 (1.9)	3.8 (4.1)

left at room temperature * (35°C) for 45 min. After this period, benzene and excess of amine were removed in vacuo. The product was washed with water and extracted in benzene (2 ml). The solution was poured on an alumina column for chromatographic separation. After elution with hexane and evaporating the solvent, a red substance was obtained (0.12 g). It was shown to be ethylaminedi-π-cyclopentadienylditungsten(I) pentacarbonyl. (Found: C, 29.3; H, 2.3; N, 1.9. $W_2C_{17}H_{17}NO_5$ calcd.: C 29.9; H, 2.4; N, 2.0%) m.p. 98°C (crystals shrink).

The second portion was eluted with dry tetrahydrofuran which on evaporation gave a small quantity of an unidentified product. This product did not contain amine molecules. Reaction times, yields and analyses of other substituted complexes are given in Table 3.

Preparation of ethylaminedicarbonyl-π-cyclopentadienyl-tungsten(I) manganese-(I) pentacarbonyl

$(\pi\text{-}C_5H_5)_2W_2(CO)_5(C_2H_5NH_2)$ in benzene (0.2 g in 10 ml) was refluxed with sodium amalgam (1%) for 1 h under nitrogen. The red colour of the solution discharged after this time. The supernatent liquid was decanted out under nitrogen. To this solution a benzene solution of manganese pentacarbonyl bromide (0.16 g in 10 ml) was added. The reaction mixture was refluxed for 2 h. After cooling, benzene was removed in vacuo. The solid mass was washed with a small quantity of water (to remove sodium bromide formed as a result of the reaction) and then with ethanol and a small quantity of diethyl ether. The product was extracted in benzene (2 ml). The solution was poured on an alumina column for chromatographic separation. After elution with hexane and evaporating the solvent, a pink substance was obtained. It was shown to be the reported complex $[(\pi\text{-}C_5H_5)W(CO)_3]Mn(CO)_5$ [8,9] m.p., 93°C.

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* The identical product was obtained after refluxing the reaction mixture for 10 min but the quantity of the decomposition product was larger in this case.

The second portion was eluted with dry tetrahydrofuran which on evaporation gave a reddish-brown coloured substance (0.09 g) which was shown to be ethylamine dicarbonyl(π-cyclopentadienyl)tungsten(I) pentacarbonyl manganese(I) (Found: C, 29.9; H, 2.0; N, 2.3. $MnWC_{14}H_{12}NO_7$ calcd.: C, 30.8; H, 2.2; N, 2.5%) m.p. 106°C.

Colours, yields and analyses of other complexes are given in Table 4.

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References

1 R.G. Hayter, Inorg. Chem., 2 (1963) 1031.
2 W.R. Cullen and R.G. Hayter, J. Amer. Chem. Soc., 86 (1964) 1030.
3 R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc. A, (1968) 43.
4 R.B. King, J. Amer. Chem. Soc., 85 (1963) 1587.
5 S.C. Tripathi, S.C. Srivastava and R.D. Pandey, J. Inorg. Nucl. Chem., 35 (1973) 457.
6 G. Wilkinson, J. Amer. Chem. Soc., 76 (1954) 209.
7 E.W. Abel and G. Wilkinson, J. Chem. Soc., (1959) 1501.
8 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.S. Beschastnov, Dokl. Akad. Nauk SSSR, 159 (1964) 377.
9 A.N. Nesmeyanov, G.G. Dvoryantseva, Yu. N. Sheinker, N.E. Kolobova and K.N. Anisimov, Dokl. Akad. Nauk SSSR, 169 (1966) 843.