

Aminecyclopentadienyltungsten Carbonyls and Manganesetungsten Bonded Carbonyls

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Amines like benzylamine, piperidine and morpholine reacted with π -cyclopentadienyltungsten tricarbonyl dimer, $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$, and yielded amine derivatives, $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5\text{Am}](\text{Am} = \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2, \text{C}_5\text{H}_{11}\text{N}, \text{C}_4\text{H}_9\text{NO})$. These amine derivatives were reduced with sodium amalgam (Na/Hg) and further reacted with $[\text{Mn}(\text{CO})_5\text{Br}]$ thus producing Mn-W (manganese-tungsten) bonded carbonyls, $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Am}]^-\text{[Mn}(\text{CO})_5]^+$. All the six compounds are characterised by elemental analysis and IR spectra.

INTRODUCTION

Several reactions¹⁻⁴ of $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ (M=Mo and W) with phosphorus, arsenic and sulphur donor ligands have been studied earlier. Mainly two kinds of products were synthesised *viz.*, $[\pi\text{-C}_5\text{H}_5](\text{CO})_3\text{Mo-Mo}(\text{CO})_2\text{L}(\pi\text{-C}_5\text{H}_5)]$ (L=phosphorus and arsenic donor)¹⁻³ and $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{L}]$ (L=sulphur donor)⁴. Several amine derivatives of molybdenum and tungsten hexacarbonyl have been synthesised and characterised by infrared spectra⁵⁻⁷. Here an attempt has been made to study the reaction between some of the amines with $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$. The products thus obtained are further reacted with $\text{Mn}(\text{CO})_5\text{Br}$ and yielded amine substituted Mn-W bonded carbonyls. Although, unsubstituted Mn-W bonded carbonyls compound, $[(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{W-Mn}(\text{CO})_5]$, is already reported in the literature⁸ earlier.

RESULTS AND DISCUSSION

Cyclopentadienyltungsten tricarbonyl dimer was prepared by the reaction of dicyclopentadiene and tungsten hexacarbonyl in an evacuated sealed hard glass tube at high temperature. It was characterised by IR and chemical analysis. This dimeric compound, $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$, reacted with some amines like benzylamine, piperidine and morpholine under mild condition and yielded mono-substituted amine derivative, $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5\text{Am}]$. These compounds are prepared by refluxing $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ with amines in benzene for about 10 minutes. Long time refluxing yielded unidentified black sticky product. The amine derivatives are quite stable and decompose above 200°C. They are orange red to dark red crystalline solids. These compounds are soluble in aromatic hydrocarbons, tetrahydrofuran, carbon tetrachloride, and chloroform but insoluble in aliphatic hydrocarbons, alcohols, acetone and petroleum ether.

The infrared spectra of $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5\text{Am}]$ show six ν_{CO} bands in solid state spectra. The compounds should be in C_2 symmetry and should show five ν_{CO} bands due to $3\text{A}' + 2\text{A}''$ modes of vibrations. One weaker excess ν_{CO} band may be due to crystal effect in the solid state spectra (Table 1).

These amine derivatives, $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5\text{Am}]$, on reduction with sodium amalgam, (Na/Hg), and subsequent reaction with manganese pentacarbonyl-bromide, $[\text{Mn}(\text{CO})_5\text{Br}]$, yielded $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Am}]^- [\text{Mn}(\text{CO})_5]^+$ and $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$. The Mn-W bonded derivatives, $[(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{Am})\text{W}-\text{Mn}(\text{CO})_5]$, were reddish solid and decompose without melting. They were soluble in aromatic hydrocarbons but insoluble in alcohols, hexane and light petroleum. Five ν_{CO} bands have been recorded in infrared spectra of these compounds (nearly at 2060, 2025, 1987, 1955 and 1905 cm^{-1}). The weak band at 2133 cm^{-1} observed in $\text{Mn}(\text{CO})_5\text{Br}$ is not observed in the above W-Mn bonded derivatives. Another ν_{CO} band observed at 2055 cm^{-1} in $\text{Mn}(\text{CO})_5\text{Br}$ is shifted towards higher wave number side in W-Mn bonded compounds and is observed nearly at 2060 cm^{-1} . The ν_{CO} band at about 2000 cm^{-1} in $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5\text{Am}]$ derivatives disappear in W-Mn bonded derivatives while another band at about 1980 cm^{-1} is observed in both type of derivatives. The infrared spectra of W-Mn bonded derivatives in ν_{CO} region is also given in Table 1.

TABLE 1
CO STRETCHING BANDS IN $[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5\text{Am}]$ AND
 $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Am}][\text{Mn}(\text{CO})_5]$ DERIVATIVES

Compound	CO (solid phase) (cm^{-1})
$[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2)]$	2008, 1982, 1974, 1940, 1923, 1902,
$[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5(\text{C}_5\text{H}_{11}\text{N})]$	2000, 1975, 1970, 1937, 1924, 1910.
$[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5(\text{C}_4\text{H}_9\text{NO})]$	2001, 1985, 1975, 1947, 1935, 1900
$[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2)][\text{Mn}(\text{CO})_5]$	2062, 2025, 1987, 1965, 1916
$[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{C}_5\text{H}_{11}\text{N})][\text{Mn}(\text{CO})_5]$	2055, 2020, 1975, 1950, 1890
$[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{C}_4\text{H}_9\text{NO})][\text{Mn}(\text{CO})_5]$	2060, 2025, 1987, 1960, 1920

EXPERIMENTAL

Preparation of Bis-(π -Cyclopentadienyl) Benzylamineditungsten Pentacarbonyl

Cyclopentadienyltungsten tricarbonyl dimer (0.2g) and benzylamine (1.0 ml) were refluxed in benzene (10 ml) for 10 minutes under an inert atmosphere of nitrogen. After this period the purple colour of the solution

turned red. On cooling, benzene was removed in vacuo. The solid residue, so obtained, was washed several times with hexane to remove unreacted benzylamine. A dark red product was obtained which was recrystallised in benzene and was dried in vacuo. It was identified to the above product. The product was obtained in 68% yield. Analysis (Found: C 36.7, H 2.6, N 3.4% and calculated for the above compound: C 35.4, H 2.5 and N 3.0%). The dark red crystals were insoluble in water, sparingly soluble in petroleum ether, hexane, methanol and ethanol but completely soluble in benzene, toluene, xylene, THF, ether, acetone, chloroform and carbon tetrachloride. It melted at 140–142°C with decomposition.

Preparation of (π -Cyclopentadienylbenzylaminetungsten Dicarbonyl) Manganese pentacarbonyl

$[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2)]$ (0.2g. in 10 ml benzene) was treated with sodium amalgam for one hour under nitrogen atmosphere. The red colour of the solution turned light brown on completion of the reaction. The solution was transferred in another flask under nitrogen atmosphere. It was refluxed (bath temperature, 100°C) with a solution of manganese pentacarbonyl bromide (0.15g. in 10 ml. benzene) in nitrogen atmosphere for two hours. The colour of solution turned dark red. Benzene was removed in vacuo to give a dark red residue which was washed first with water to remove sodium bromide and then with excess of hexane to remove any manganese pentacarbonyl bromide left unreacted. The dark red solid, so obtained, was washed again with 5 ml. light petroleum (40–60°C). The washings on evaporation yielded $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ (0.005g). The light petroleum washed solid was identified as above compound. It was found in 75% yield. It was analysed correctly. Analysis (Found: C 37.1, H 2.2, N 2.3%; calculated: C 37.5, H 2.3, N 2.3%). It was nearly insoluble in alcohols, hexane, light petroleum (all fractions) and diethyl-ether but soluble in all aromatic hydrocarbons. It decomposed without melting at 138°C.

Preparation of bis-(π -Cyclopentadienyl) Piperidineditungsten Pentacarbonyl, ($\pi\text{-C}_5\text{H}_5$)₂W₂(CO)₅(C₅H₁₁N)

Cyclopentadienyltungsten tricarbonyl dimer (0.2g) and piperidine (1.5 ml) were refluxed in benzene (15 ml) for 10 min. under an inert atmosphere of nitrogen. After this period the purple colour of the solution changed to dark red. The reaction mixture was cooled to room temperature and benzene was removed in vacuo. Unreacted piperidine was removed by washing several times with hexane. The residue, so obtained, was recrystallised in benzene to yield dark red crystals of bis-(π -cyclopentadienyl) piperidineditungsten pentacarbonyl (yield 85%). It was analysed

and identified as above. Analysis (found: C 33.4, H 3.0, N 2.2%; calculated: C 33.2, H 2.9, N 1.9%). The compound was similar in solubility and stability to its benzylamine analogue. It melted at 110°C with decomposition.

Preparation of (π -Cyclopentadienylpiperidinetungsten Dicarboxyl)-Manganese Pentacarbonyl

$[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5(\text{C}_5\text{H}_{11}\text{N})]$ (0.2g in 10 ml benzene) was treated with sodium-amalgam for one hour under nitrogen. The red colour of the solution turned purple on completion of the reaction. The solution was filtered and transferred to a flask under nitrogen. It was refluxed (at 100°C) with a solution of manganese pentacarbonyl bromide (0.15g. in 10 ml. benzene) for two hours under nitrogen. The colour of solution turned dark brown red. Benzene was removed in vacuo to obtain a brownish red residue which was washed with water to remove sodium bromide and then with hexane to remove excess of manganese pentacarbonyl bromide (if any). The brownish red solid, so obtained, was washed again with 5 ml. of light petroleum (40–60°). The washings on evaporation yielded traces of $[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$. The washed solid was identified as above compound desired. Analysis (found: C 34.6; H 2.7; N 2.4%; calculated: C 34.8; H 2.7; N 2.3%). It resembled in solubility with its benzylamine analogue. It decomposed at 149° without melting.

Preparation of Bis- π Cyclopentadienylmorpholinetungsten Pentacarbonyl

π -Cyclopentadienyltungsten tricarbonyl dimer (0.2g) and morpholine (1.0 ml) were refluxed in benzene (10 ml) for 10 min. under nitrogen atmosphere. The purple colour of the reaction mixture changed to orange after completion of the reaction. Solvent benzene was removed in vacuo and dark orange residue was obtained which on recrystallisation in benzene yielded orange red crystals of the desired product (yield 66%). Analysis (found: C 32.0, H 2.4, N 2.2%; calculated: C 31.4, H 2.6, N 1.9%). It resembled in solubility with its benzylamine analogue. It melted at 110–112° with decomposition.

Preparation of (π -Cyclopentadienylmorpholinetungsten Dicarboxyl)-Manganese Pentacarbonyl

$[(\pi\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5(\text{C}_4\text{H}_9\text{NO})]$ (0.2g in 10 ml benzene) was treated with sodium amalgam for one hour under nitrogen atmosphere. A red coloured solution was observed after completion of the reaction. The compound was recovered as in previous analogous derivative. The yielded was 76%. Analysis (found: C 32.9, H 2.4, N 2.3%; calculated: C 32.7, H 2.3, N 2.3%). It had the same solubility as its benzylamine analogue. It decomposed at 140° without melting.

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