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μ-Bi-η:η-CYCLOPENTADIENYLDIMOLYBDENUM CHEMISTRY: SOME LITHIO, ALKYL, HALO, HYDRIDO AND ALKYLTHIOLATO DERIVATIVES

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Summary

The syntheses of the new compounds $\{[(\eta\text{-}C_5H_5)MoR]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$, where R = CH_2SiMe_3, CH_2Ph and Me, Br, $\{[(\eta\text{-}C_5H_5)MoR_2]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$ where R = H, S-n-Bu and SMe, and $\{[\eta\text{-}C_5H_5)MoH_2](\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))[(\eta\text{-}C_5H_5)MoH(SnX_3)]\}$, where X = Me or n-Bu, are described.

Introduction

We have set out upon a synthetic programme towards binuclear metal compounds which we anticipate will have the following properties. Firstly, that the two metal atoms will be held firmly by a bridging ligand system that will be relatively non-labile under a variety of reaction conditions. Secondly, that the bridging ligands will allow the metal atoms to come close enough together to form metal—metal interactions. Thirdly, that the bridging ligand should be suitably compact so that it will not restrict access of other potential ligands to the metal atoms. Fourthly, that the electronic effect of the bridging ligands should be such that the metal centre should be reasonably electron rich. It is hoped that a study of such systems will lead towards understanding of binuclear transition metal catalysts.

A ligand that seems attractive within these requirements is the system $\mu(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)$ ligand. We have previously described the synthesis of dimolybdenum compounds containing this ligand [1]. Smart and co-workers have also made dimolybdenum compounds [2] with this ligand as well as with several other first row transition metals [3]. Here we describe our efforts to develop the chemistry of the molecule $\{[(\eta\text{-}C_5H_5)MoH]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$ [1]. A communication of part of this work has appeared [4].

Chemical studies

Treatment of I with n-butyllithium gave a fine yellow-green precipitate, II, which, by analogy with the synthesis of $[Mo(\eta\text{-}C_5H_5)_2HLi]_4$ [5], may be presumed to contain Mo—Li bonds. Hydrolysis of the precipitate reforms I immediately and quantitatively, as would be expected. Further, addition of trimethylsilylmethyl chloride to the yellow-green precipitate gives deep green crystals, III, which the data in the Table in ref. 4 shows to be a binuclear bis-trimethylsilylmethyl derivative. The ^{1}H NMR spectrum of III shows the presence of two η-C_5H_5 rings and two C_5H_4 rings acting as ABCD spin systems. The data do not distinguish between the possibilities that the two C_5H_4 units occur as two η^1:η^5-C_5H_4 groups or as a η-C_5H_4-η-C_5H_4 group. Since II reforms I readily upon hydrolysis we assumed II to contain the η-C_5H_4-η-C_5H_4 system which is present in I [1]. Therefore, we argue that the bi-η:η-cyclopentadienyl system is also likely to be present in III, i.e. $\{[Mo(\eta\text{-}C_5H_5)(CH_2SiMe_3)]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$.

Treatment of II with benzyl chloride or benzyl bromide gave the expected bis-benzyl derivative $\{[Mo(\eta\text{-}C_5H_5)(CH_2Ph)]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$, IV. Similarly, reaction between II and methyl bromide gives the compound $\{[Mo(\eta\text{-}C_5H_5)Me]_2\text{-}(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$, V. We note that, unlike I, which is a fluxional molecule and exhibits an A_2B_2 spin system, the bis-alkyl compounds, III, IV and V show *ABCD* systems for C_5H_4 groups and thus these compounds are not fluxional at room temperature.

Acetonitrile solutions of I react readily with 1,2-dibromoethane giving purple crystal stoicheiometry $C_{20}H_{18}Br_2Mo_2$, VI. However, these too were insufficiently soluble, even in dimethylsulphoxide, for solution NMR study. Treatment of a refluxing acetonitrile solution of I with iodine in the mole ratio 1 : 0.98 has been shown to give light brown crystals of $\{[(\eta\text{-}C_5H_5)MoI]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$ [1]. However when I was treated with excess of iodine, light brown crystals separated which consistently analysed giving the stoicheiometry $C_{20}H_{18}I_4Mo_2$, 1/3 MeCN, VII. These crystals are virtually insoluble in all solvents investigated, including dimethylsulphoxide, dichloromethane and acetonitrile. Compound VII is also formed by addition of an excess of iodine to the compound $[Mo(\eta\text{-}C_5H_5)\text{-}(\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4))]_2$.

Treatment of VII with sodium n-butylthiolate gives bright red crystals which are soluble in ethanol and dichloromethane and liquid sulphur dioxide. The data in Table 1 show the compound to be $\{[Mo(\eta\text{-}C_5H_5)(S\text{-n-Bu})_2]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$, VIII. When VIII was treated with excess of hydrogen iodide small brown crys-

TABLE 1

MASS SPECTRAL DATA

Data presented as: Compound number: *m/e* (relative intensity) assignment; where *P* represented the parent ion.

III	624(35)*P*; 537(75)$[P - Me_3SiCH_2]^+$; 450(100)$[P - 2\ Me_3SiCH_2)]^+$; 224(50)$[(C_{10}H_8Mo)_2]^{2+}$.
IV	632(15)*P*; 54(40)$[P - PhCH_2]^+$; 450(100)$[P - (PhCH_2)_2]^+$; 224(30)$[(C_{10}H_8Mo)_2]^{2+}$.
V	480(15)*P*; 465(100)$[P - Me]^+$; 450(35)$[P - Me_2]$; 235(20)$[P - Me]^{2+}$; 224(5)$[C_{10}H_8Mo)_2]^{2+}$.
VI	610(15)*P*; 531(40)$[P - Br]^+$; 540(100)$[P - 2\ Br]^+$.
VIII	692(10)$[P - 3\text{-n-Bu}]^+$; 450(100)$[P - 4\ S\text{-n-Bu}]^+$.
IX	497(10)$[P - 3\ SMe]^+$; 482(100)$[P - S_3Me_4]^+$; 450(20)$[P - S_4Me_4]^+$; 241(10)$[P - S_3Me_4]^{2+}$.
X	450(100)$[P - H_4]^+$; 224(30)$[P - H_4]^{2+}$.
XI	615(10)$[P - H_3]^+$; 600(40)$[P - H_3, Me]^+$; 585(30)$[P - H_3, Me_2]^+$; 570(80)$[P - H_3, Me_3]^+$.
XII	450(100)$[P - H_3, SnMe_3]^+$; 285(25)$[P - H_3, Me_3]^{2+}$; 224(15)$[C_{10}H_8Mo)]^{2+}$.

tals were formed which were shown by the IR spectrum to be essentially identical to VII. Sodium methylthiolate also reacts with VII giving red crystals of low solubility. Analysis, the mass spectrum and analogy with VIII suggest the compound to be $\{[Mo(\eta\text{-}C_5H_5)(SMe)_2]_2(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))\}$, IX.

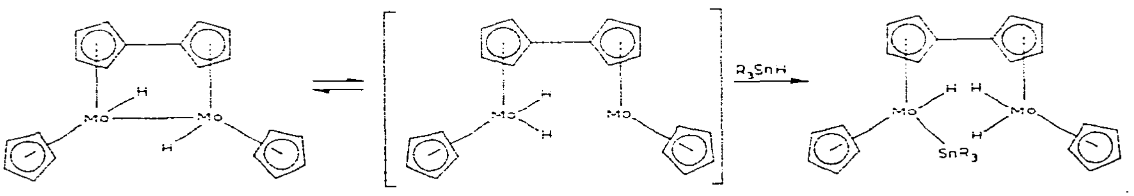
The tetraiodide VII reacts with sodium tetrahydridoborate giving a pale yellow solid. Rapid recrystallisation from toluene gives yellow plates of empirical stoicheiometry $C_{10}H_{11}Mo$, X. The IR spectrum of X shows broad bands at 1815 cm^{-1} and 1841 cm^{-1}. These were absent in the spectrum of the deuterio analogue of X, prepared from VII and sodium tetradeuterioborate. The deuterio analogue X-*d* showed new bands at 1303 cm^{-1} and 1328 cm^{-1}. Thermolysis of X at 130°C/10^{-5} mmHg gives I in high yield.

Treatment of I with tri-n-butylhydridotin gives yellow crystals soluble in petroleum ether. The partial data in the Experimental section suggest that the compound is $\{[Mo(\eta\text{-}C_5H_5)H_2](\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))[Mo(\eta\text{-}C_5H_5)H(Sn\text{-}n\text{-}Bu_3)]\}$, XI. Trimethylhydridotin also reacts readily with I giving yellow needles of stoicheiometry $C_{23}H_{30}SnMo_2$ which, by analogy with XI, may be formulated as $\{[Mo(\eta\text{-}C_5H_5)H_2](\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4))[Mo(\eta\text{-}C_5H_5)H(SnMe_3)]\}$, XII.

Discussion

The structure proposed for the compounds II—XII are shown in the Scheme in ref. 4, or in Scheme 1. Low solubility or thermal instability prevented full structural characterisation of some of the compounds. However, the interconvertability of the compounds, as shown in the Schemes, provides very strong circumstantial evidence of the proposed structures. For example, the interconversion of VIII to VII and the reduction of VII to X and the thermal decomposition of X to I when taken together with the available spectroscopic evidence clearly indicate the structures shown.

Scheme 1



A

(XI, R = n-Bu;
XII, R = Me)

In the light of the discussion given elsewhere [1] for the mechanism of hydrogen migration in some molybdenocene dimers, we propose the mechanism shown in Scheme 1 for the formation of XI and XII from I, via intermediate A. Similarly the formation of I from X may be envisaged to proceed via initial loss of dihydrogen from X giving the intermediate A which then rearranges to I.

This study shows that the $\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)$ ligand has many of the desired properties. However, in these particular systems the low solubility of the compounds restricted their study.

Experimental

All reactions and manipulations were carried out under dinitrogen or in vacuo. All solvents were dried and distilled. ^1H NMR spectra were determined using a Bruker 90 MHz or JEOL 60 MH instrument. Infrared spectra were determined as mulls using a Perkin—Elmer 457 instrument, calibrated with polystyrene film. Mass spectra were determined using an AEIMS 9 spectrometer at 70 eV. Compound I was prepared as described [1].

[(μ-Bi-η⁵:η⁵-cyclopentadienyl)bis(trimethylsilylmethyl-η-cyclopentadienylmolybdenum)], II

The compound I (0.4 g, 0.88 mmole) in toluene (50 cm^3) was treated with an excess of n-butyllithium (1.6 *M* in hexane). A fine yellow-green precipitate of II settled from the solution after 2 h. The mother liquor was then decanted and the precipitate was washed with toluene (20 cm^3) and dried under reduced pressure. The solid is pyrophoric and insoluble in aromatic solvents. Addition of acetone, ethanol or water reforms I. The freshly prepared precipitate of II (from 0.4 g of I) in toluene (75 cm^3) at −78° C was treated with chloromethyltrimethylsilane (1 cm^3, 7.0 mmole). The mixture was stirred, allowed to warm to room temperature and then heated to 50° C for 30 min. The resulting intense yellow solution was filtered and alumina (2.0 g) was added to the filtrate. The solvent was removed under reduced pressure. The product-coated alumina was placed on an alumina column made up in light petroleum ether (30—40° C). Elution with light petroleum ether (40—60° C) gave a bright yellow band which was collected. The eluate was concentrated under reduced pressure until crystals appeared.

The concentrate was then cooled to −78° C for 2 h and then to −95° C for 3 h. Dark green crystals separated which were washed with light petroleum ether (20 cm^3 at −78° C) and finally dried in vacuo, yield 0.14 g (26%).

[(μ-Bi-η⁵:η⁵-cyclopentadienyl)bis(benzyl-η-cyclopentadienylmolybdenum)], IV

The procedure was essentially identical to that used for the synthesis of III. Benzyl chloride (1 cm^3, 7 mmole) or benzyl bromide (0.8 cm^3, 6.5 mmole) were used. The product was eluted from the alumina column using toluene and was recrystallised from toluene/light petroleum ether 1/1 at room temperature; yield 0.48 g (85%).

[(μ-Bi-η:η-cyclopentadienyl)bis(bromo-η-cyclopentadienylmolybdenum)], VI

The compound 1 (0.9 g, 1.77 mmole) in acetonitrile (180 cm^3) at 85° C was treated with 1,2-dibromoethane (1 cm^3, 12 mmole). The initially deep green solution turned light brown and slow cooling to room temperature gave purple crystals which were washed with cooled acetonitrile (2 × 10 cm^3) and dried in vacuo, yield 0.3 g. Concentration of the mother liquor and cooling to 0° C gave a second crop of product, 0.51 g. The combined yield was 0.81 g (75%).

[(μ-Bi-η:η-cyclopentadienyl)bis(diiodo-η-cyclopentadienylmolybdenum)], VII

Iodine (0.53 g, 2.1 mmole) in acetonitrile (50 cm^3) was added to a refluxing solution of I (0.34 g, 0.75 mmole) in acetonitrile (10 cm^3). The resulting dark brown solution was immediately filtered and allowed to cool slowly (12 h) to room temperature giving light brown crystals. These were washed with acetonitrile (2 × 10 cm^3) and dried in vacuo; yield 0.68 g (95%).

[(μ-Bi-η:η-cyclopentadienyl)bis(di(n-butylthiol)-η-cyclopentadienylmolybdenum], VIII

n-Butylthiol (1.5 cm^3, 52 mmole) was added to a solution of sodium ethoxide in ethanol (prepared from sodium (0.2 g) in ethanol (40 cm^3)). The resulting solution was added to a suspension of compound VII (0.6 g, 0.63 mmole) in ethanol (30 cm^3). The mixture was stirred under reflux for 30 min. The solid dissolved giving a deep red solution. Slow removal of the solvent under reduced pressure and cooling to room temperature gave red microcrystals. These collected and recrystallised from hot ethanol as red needles; yield 0.33 g (65%).

[(μ-Bi-η:η-cyclopentadienyl)bis(di(methanethiol))-η-cyclopentadienylmolybdenum], IX

Methanethiol was passed through a solution of sodium ethoxide (from 0.2 g of sodium in ethanol (25 cm^3)). The resulting solution was added to a suspension of the compound VII in ethanol (40 cm^3). The mixture was refluxed for 30 min giving a bright orange solution. On cooling to room temperature purple microcrystals separated (2 h). These were collected, washed with ethanol (2 × 15 cm^3) and dried in vacuo; yield 0.33 g (71%).

[(μ-Bi-η:η-cyclopentadienyl)bis(methyl-η-cyclopentadienylmolybdenum)], V

A freshly prepared suspension of II (from 0.4 g of I) in toluene (50 cm^3) at —78°C was treated with bromoethane (1 cm^3, 15 mmole) and the mixture was stirred and allowed to warm to room temperature. After 1 h the mixture was filtered and the filtrate was passed through a short alumina column (5 cm^3) made up in light petroleum ether. The eluate and column washings (2 × 5 cm^3 of toluene) were combined and the solvent was removed under reduced pressure. The resulting green solid was extracted with petroleum ether (100—120°C) and the deep green extract was filtered and concentrated. Cooling to —30°C gave deep green crystals which were washed with petroleum ether (30—40°C) and dried in vacuo; yield 0.29 g (70%).

{(μ-Bi-η:η-cyclopentadienyl)(η-cyclopentadienyldihydridomolybdenum)-(η-cyclopentadienylhydrido(trimethyltin)molybdenum)}, XII

A solution of I (0.1 g, 0.22 mmole) in toluene (30 cm^3) was treated with trimethylhydridotin (0.4 cm^3, 2.1 mmole) and the mixture was stirred at 90°C for 30 min. The solvent was removed under reduced pressure from the bright yellow solution giving yellow crystals. These were recrystallised from hot benzene/light petroleum ether (60—80°C) (1/2). The resulting yellow plates were washed with cold (0°C) light petroleum ether (30—40°C) and dried in vacuo; yield 0.09 g (68%). Anal.: Found: C, 45.1; H, 5.0. $C_{23}H_{30}SnMo_2$ calcd.: C, 44.8; H, 4.9%. The IR spectrum shows bonds assignable to γ-Mo—H at 1831s(br) and 1813(sh) cm^{-1}. The ^{1}H NMR spectrum in C_6D_6 showed: 5.26 τ, 2 (c) 2(H_A, H_B); 5.54 τ, 9 (c) C_5H_5 + 4(H_A, H_B); 4.73 τ, 7 (c) C_5H_5 + 2(H_A, H_B); 9.48 τ, 9 (d) $SnMe_3$ (J^{119}Sn) 36 Hz); 18.03 τ, 2 (s) MoH_2; 18.09 τ, 1 (s) MoH(Sn).

The compound XI was prepared in a similar manner from tri-n-butylhydridotin (1 cm^3, 2.73 mmole). Recrystallisation was from hot petroleum ether (40—60°C): yield 0.24 g (73%). Anal.: Found: C, 51.8; H, 6.4. $C_{32}H_{48}SnMo_2$ calcd.: C, 51.6; H, 6.45%. ^1H NMR spectrum in C_6D_6: 5.50 τ, 11 (c) C_5H_5 + 6(H_A, H_B); 5.64 τ, 7 (c) C_5H_5 + 2(H_A, H_B); 8.31 τ, 12 (c) $SnCH_2CH_2$; 8.83 τ, 15 (c) Et_3; 17.97 τ, 1 (s) MoH(Sn); 18.20 τ, 2 (s) MoH_2. The H_A and H_B hydrogens are of the μ-(η^5-C_5H_4-η^5-C_5H_4) group and are not fully assignable.

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