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Interaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgX})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) complexes with $\text{M}'(\text{CO})_3(\text{bipy})$ ($\text{M}' = \text{Mo}, \text{W}$) fragments. Trimetallic compounds containing $\text{M}-\text{Hg}-\text{M}'-\text{X}$ arrays

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Abstract

Reactions of the tricarbonyl mercury complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgX})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) with $[\text{M}'(\text{CO})_3(\text{bipy})(\text{NCMe})]$ ($\text{M}' = \text{Mo}, \text{W}$) give the new mercury-bridged trinuclear complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\mu\text{-HgM}'(\text{X}))(\text{CO})_3(\text{bipy})]$. The formation of $\text{M}-\text{Hg}-\text{M}'-\text{X}$ arrays can be explained assuming that $\text{M}'(\text{CO})_3(\text{bipy})$ fragments are inserted into the $\text{Hg}-\text{X}$ bonds.

Introduction

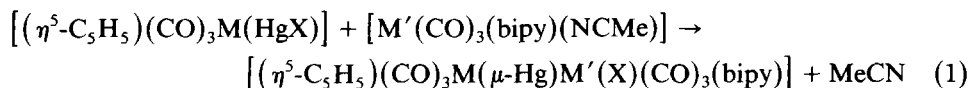
Some of our previous papers [1,2] have been concerned with the reactivity of $[\text{M}'(\text{CO})_3(\text{NN})(\text{NCMe})]$ ($\text{M}' = \text{Mo}, \text{W}$; $\text{NN} = 2,2'$ -bipyridine (bipy), 1,10-phenanthroline, ethylenediamine) complexes towards mercury halides and pseudohalides to give products containing $\text{Hg}-\text{M}'$ bonds. Indeed, the reaction could be interpreted as the insertion of $\text{M}'(\text{CO})_3(\text{NN})$ fragments into the $\text{Hg}-\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) bonds. The concept of insertion of $\text{M}'(\text{CO})_3(\text{NN})$ moieties permitted us to isolate trimetallic compounds with $\text{X}-\text{M}-\text{Hg}-\text{M}'\text{X}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{Fe}-\text{Hg}-\text{M}'-\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{NCS}$) arrays.

As a further extension of the utilization of the above behaviour, here we describe experiments in which the insertion occurs in cyclopentadienyl derivatives $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgX})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) to give new trimetallic complexes. $[\text{M}'(\text{CO})_3(\text{bipy})(\text{NCMe})]$ compounds are used to examine the results of the insertion.

Results and discussion

Treatment of the tricarbonyl mercury complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgX})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) with an equimolar amount of the acetonitrile

compounds $[M'(CO)_3(bipy)(NCMe)]$ ($M' = Mo, W$) in dichloromethane at $-15^\circ C$ affords red solutions, from which the new crystalline $[(\eta^5-C_5H_5)(CO)_3M(\mu-Hg)M'(X)(CO)_3(bipy)]$ products are precipitated by addition of methanol. The reaction can be represented by eq. 1.



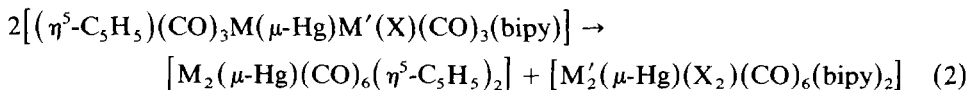
The $[(\eta^5-C_5H_5)(CO)_3M(\mu-Hg)M'(X)(CO)_3(bipy)]$ compounds are orange to red coloured crystalline solids; they are air-stable but decompose in light, producing mercury. They are soluble in solvents such as dichloromethane, chloroform, acetone and benzene; slightly soluble in methanol, and insoluble in light petroleum.

The new compounds appear to have trimetallic $M-Hg-M'-X$ bonding arrangements. The band patterns observed in the infrared carbonyl stretching region (Table 1) show a superimposition of the tricarbonyl $(\eta^5-C_5H_5)(CO)_3MHg$ [3,4] and $HgM'(X)(CO)_3(bipy)$ [1,5] moieties. It is hence inferred that the $M'(CO)_3bipy$ fragments has been inserted into the $Hg-X$ bonds.

The IR spectra of all isolated compounds are characterized by the presence of bands assignable to coordinated 2,2'-bipyridine and cyclopentadienyl ligands. In the spectra of $[(\eta^5-C_5H_5)(CO)_3M(\mu-Hg)M'(N_3)(CO)_3(bipy)]$ complexes the absorption of the azido groups, $\nu(NN)$, is found at ca. 2050 cm^{-1} . The products of the reaction $[(\eta^5-C_5H_5)(CO)_3M(HgSCN)]$ complexes with $[M'(CO)_3(bipy)(NCMe)]$ show distinctive IR bands indicating the existence of isothiocyanate $M'-NCS$ bonds [6]. Thus, the $\nu(CN)$ stretching vibration is localized near 2070 cm^{-1} and the deformation vibrations, $\delta(NCS)$, occur around 480 cm^{-1} .

The electronic spectra in the visible region of complexes with $M'(X)(CO)_3(bipy)$ moieties have been studied previously [2]. These studies have made the assignment of the electronic spectra for our compounds straightforward. The spectra in CH_2Cl_2 of all new compounds reported here exhibit only one broad band in the range from 400 to 500 nm. The position of these absorptions is difficult to evaluate, since such transitions are masked by the more intense transitions arising from the UV. On the basis of the qualitative similarity of the absorption spectra to previously published results on related complexes [2], these lowest energy absorptions are assigned to $bipy(\pi^*) \leftarrow M'(d)$ MLCT.

When deaerated CH_2Cl_2 solutions of the mercury halide complexes $[(\eta^5-C_5H_5)(CO)_3M(\mu-Hg)M'(X)(CO)_3(bipy)]$ are kept in the dark at room temperature, the orange highly light-sensitive substances $[M'_2(\mu-Hg)(X)_2(CO)_6(bipy)_2]$ [1] precipitate within 3–5 min. After filtration, the electronic spectra of the solutions show the presence of $[M_2(\mu-Hg)(CO)_6(\eta^5-C_5H_5)_2]$ [4] complexes. The initially asymmetric mercurial complexes therefore undergo a spontaneous redistribution reaction (eq. 2) to give the symmetric ones, as described by Bonati et al. [7]:



Experimental

All operations were carried out under nitrogen using standard Schlenk line techniques. The compounds $[(\eta^5-C_5H_5)(CO)_3M(HgCl)]$ ($M = Cr, Mo, W$) [3] and

Table 1

Elemental analysis and IR data for the complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\mu\text{-Hg})\text{M}'(\text{X})(\text{CO})_3(\text{bipy})]$

Compound			Analysis (%) ^a					IR (cm ⁻¹) ^b				
M	M'	X	M and M'		C	H	N	$\nu(\text{CO})$				
Cr	Mo	Cl	6.7(6.72)	12.3(12.41)	32.6(32.62)	1.6(1.69)	3.6(3.62)	1970	1945	1900	1875	1820
		Br	6.3(6.36)	11.4(11.73)	30.6(30.84)	1.6(1.60)	3.3(3.43)	1980	1950	1900	1880	1820
		I	6.1(6.01)	10.8(11.09)	29.0(29.17)	1.5(1.52)	3.2(3.24)	1975	1950	1900	1875	1820
		N ₃	6.5(6.67)	12.1(12.30)	32.1(32.34)	1.6(1.68)	9.1(8.98)	1975	1950	1980	1870	1820
		NCS	6.5(6.53)	11.8(12.05)	33.2(33.20)	1.6(1.65)	5.4(5.28)	1975	1950	1910	1875	1935
	W	Cl	6.0(6.04)	21.5(21.35)	29.3(29.29)	1.6(1.52)	3.3(3.25)	1975	1945	1900	1870	1820
		Br	5.8(5.74)	20.1(20.30)	27.8(27.85)	1.5(1.45)	3.0(3.09)	1975	1940	1900	1875	1820
		I	5.6(5.46)	19.2(19.30)	26.3(26.48)	1.5(1.38)	3.0(2.94)	1970	1940	1905	1870	1820
		N ₃	6.1(5.99)	21.0(21.19)	29.2(29.07)	1.5(1.57)	8.1(8.07)	1975	1945	1900	1870	1830
		NCS	5.9(5.88)	20.7(20.80)	29.8(29.90)	1.5(1.48)	4.8(4.75)	1975	1940	1900	1870	1825
Mo	Mo	Cl		23.3(23.48)	31.0(30.86)	1.7(1.60)	3.4(3.43)	1985	1940	1900	1880	1820
		Br		22.4(22.27)	29.1(29.27)	1.5(1.52)	3.3(3.25)	1980	1945	1900	1875	1820
		I		20.9(21.12)	27.8(27.76)	1.4(1.44)	3.1(3.08)	1980	1940	1890	1870	1820
		N ₃		23.2(23.29)	30.6(30.62)	1.6(1.59)	8.6(8.50)	1980	1950	1900	1875	1830
		NCS		22.7(22.85)	31.3(31.46)	1.6(1.56)	5.1(5.00)	1980	1945	1910	1875	1820
	W	Cl			27.9(27.87)	1.4(1.45)	3.1(3.09)	1975	1945	1900	1880	1820
		Br			26.5(26.56)	1.4(1.38)	3.0(2.95)	1975	1940	1905	1880	1830
		I			25.2(25.31)	1.3(1.31)	2.7(2.81)	1980	1940	1900	1875	1825
		N ₃			27.5(27.66)	1.5(1.44)	7.8(7.68)	1980	1945	1910	1880	1830
		NCS			28.6(28.48)	1.5(1.41)	4.6(4.53)	1975	1940	1905	1870	1830
W	Mo	Cl			27.8(27.87)	1.5(1.45)	3.1(3.09)	1990	1935	1890	1860	1820
		Br			26.6(26.56)	1.4(1.38)	3.0(2.95)	1980	1935	1885	1860	1820
		I			25.3(25.31)	1.3(1.31)	2.8(2.81)	1985	1935	1880	1865	1825
		N ₃			27.2(27.66)	1.5(1.44)	7.8(7.68)	1990	1930	1900	1860	1820
		NCS			28.6(28.48)	1.5(1.41)	4.3(4.53)	1990	1930	1880	1865	1825
W	W	Cl		36.7(37.03)	25.3(25.40)	1.4(1.32)	2.9(2.82)	1985	1940	1890	1870	1830
		Br		35.2(35.44)	24.3(24.31)	1.3(1.26)	2.7(2.70)	1985	1945	1890	1870	1820
		I		33.5(33.90)	23.4(23.26)	1.3(1.21)	2.6(2.58)	1980	1940	1900	1860	1825
		N ₃		36.1(36.78)	25.2(25.23)	1.4(1.31)	7.1(7.01)	1980	1935	1900	1865	1825
		NCS		35.9(36.20)	26.0(26.02)	1.3(1.29)	4.2(4.14)	1985	1940	1890	1865	1820

^a Required values are given in parentheses. ^b KBr discs, all bands are strong.

$[\text{M}'(\text{CO})_3(\text{bipy})(\text{NCMe})]$ ($\text{M}' = \text{Mo}, \text{W}$) [1] were prepared by methods similar to those described in the literature. The complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgX})]$ ($\text{X} = \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) were precipitated by treatment of an acetonitrile solution of the complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgCl})]$ with an excess of NaX dissolved in water. The yellow coloured light-sensitive microcrystals were filtered off and washed with water. The IR and electronic spectra were recorded using Perkin-Elmer 577 and Carl Zeiss DMR 22 instruments.

Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\mu\text{-Hg})\text{M}'(\text{X})(\text{CO})_3(\text{bipy})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{M}' = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3, \text{NCS}$)

These compounds were isolated by reaction of the complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}(\text{HgX})]$ and $[\text{M}'(\text{CO})_3(\text{bipy})(\text{NCMe})]$ in dichloromethane. The preparation described below is typical.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cr}(\mu\text{-Hg})\text{Mo}(\text{Cl})(\text{CO})_3(\text{bipy})]$: An ice-salt bath cooled solution of $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{NCMe})]$ (0.106 g, 0.281 mmol) and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cr}(\text{HgCl})]$ (0.123 g, 0.281 mmol) in CH_2Cl_2 (10 ml) was stirred in the dark for 0.50 h. The deep red yellowish solution was then filtered, methanol (15 ml) was added to this solution, and the total volume was then reduced *in vacuo* to ca. one third. From this self-cooled solution an orange precipitate was obtained which was filtered and washed with cool methanol (3×2 ml) to give 0.139 g of the product in form of an orange coloured scaly crystalline solid. The results of the elemental analysis are presented in Table 1.

Acknowledgements

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