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A study of the Basicity of the Metal–metal bond in $[\mu\text{-}SCH_3Fe(CO)_2L]_2$ Complexes. IV. Interaction with Sulfur Dioxide and Reactivity of the Coordinated Sulfur Dioxide toward Oxygen

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Introduction

During the course of the study of the basicity of $[\mu\text{-}SCH_3Fe(CO)_2L]_2$ complexes we have shown that the metal–metal bond is the nucleophilic center toward a proton [1] or mercuric chloride [2]. Moreover the nucleophilicity of the metal–metal bond toward H^+ is strongly dependent on the basicity of ligand L but is less dependent for mercuric chloride. We have extended this study to the case of SO_2 to see if its behaviour toward the metal–metal bond resembles that of proton or of mercuric chloride.

Results and Discussion

Addition of SO_2 to a solution of $[\mu\text{-}SCH_3Fe(CO)_2L]_2$ [3] in toluene induces a slow colour change from red to violet in the case of $L = P(CH_3)_3$ and $L = P(CH_3)_2C_6H_5$. For $L = P(C_6H_5)_2CH_3$ and $P(C_6H_5)_3$ no reaction occurs. The adducts are isolated by adding pentane to the toluene solution. The analytical data and the infrared data for the ν(CO) and ν(SO) stretching frequencies are gathered in Table I.

Three infrared active bands are observed in the ν(CO) stretching region from which we can conclude that the C_2v point group of the starting molecule is preserved [4]. The increase in frequencies compared with the starting material is about 50 cm^{-1} which is slightly superior to that found for mercuric chloride complexes [2].

Proton nmr spectra in CH_2Cl_2 confirm the structural hypothesis; one doublet is observed for the $P(CH_3)$ resonance of the ligands (τ = 8.70 ppm; J = 9 Hz, $L = P(CH_3)_3$, τ = 8.50, J = 8 Hz, $L = P(CH_3)_2C_6H_5$) and one resonance for the δSCH_3 (τ = 7.30, $L = P(CH_3)_3$; τ = 7.50, $L = P(CH_3)_2C_6H_5$). From these observations we can conclude that the SO_2 is inserted into the metal–metal bond. Furthermore, the νSO stretching frequencies are in the usual area for the νSO stretching frequencies of a

TABLE I. Analytical Data and Infrared Spectra for $(\mu\text{-}SCH_3Fe(CO)_2L)_2SO_2$ Complexes and $(\mu\text{-}SCH_3Fe(CO)_2P(CH_3)_3)_2SO_4$.

	Yields	Analysis										νCO	νSO_2
		calcd				Found							
	%	C	H	P	S	C	H	P	S	Colour	MP	a	b
$(\mu\text{-}SCH_3Fe(CO)_2P(CH_3)_3)_2SO_2$	80	26.96	4.49	11.61	17.97	27.32	4.73	11.25	17.78	Dark violet	100° dec	2031m 2012s 1975s	1128s 1005s
$(\mu\text{-}SCH_3Fe(CO)_2P(CH_3)_2C_6H_5)_2SO_2$	75	40.12	4.25	9.42	14.58	39.87	4.23	9.36	14.33	violet	140° dec	2031m 2014s 1975s	1132s 1002sh 995s
$(\mu\text{-}SCH_3Fe(CO)_2P(CH_3)_3)_2SO_4$	60	25.44	4.24	–	16.96	22.14	4.22		16.34	yellow	–	2042m 2028s 1987s	

[a] Measured in CH_2Cl_2. [b] Measured in KBr pellets.

sulfur dioxide which acts as a Lewis acid. So the geometry about sulfur atom is tetrahedral as has been found in other mononuclear [5, 6] or dinuclear [7] transition metal complexes sulfur dioxide adducts.

One of the characteristics of this type of bonding for SO_2 molecule is its ability to react with oxygen fo give sulfato complexes [8]. Indeed, when oxygen is bubbled in a toluene solution of $(\mu\text{-}SCH_3Fe(CO)_2\text{-}P(CH_3)_3)_2SO_2$ a yellow solid precipitates. After 24 h the supernatant solution is eliminated and the yellow solid is washed with pentane and dried. Its low solubility prevents further purification but it has been characterised by infrared spectroscopy and its chemical analysis is in good agreement with the formula $(FeSCH_3(CO)_2P(CH_3)_3)_2SO_4$. It is a very hygroscopic compound. In the νCO stretching region there are always three infrared active bands slightly displaced toward high frequencies compared with the SO_2 adduct, and in the νSO stretching region three bands are denoted (1219, 1100, 1012 cm^{-1}). These three bands are attributed to the splitting of the degenerate mode ν_3 of $SO_4^{--}$for a C_2v point group [9]. Other frequencies of the SO_4^{--}group are obscured by the other vibrations of the complex. So we can propose the structure depicted in Fig. 1.

In conclusion SO_2 acts as a Lewis acid toward the metal–metal bond of the $(\mu\text{-}SCH_3Fe(CO)_2L)_2$ complexes if L = $P(CH_3)_3$ or $P(CH_3)_2C_6H_5$. It does not react when L = $P(C_6H_5)_2CH_3$ or $P(C_6H_5)_3$, a result which is very similar to the observations done in the protonation reaction [1]. Furthermore it reacts with oxygen to give a sulfato complex which seems to be, to our knowledge, the first case of oxidation of sulfur dioxide inserted into two metals.

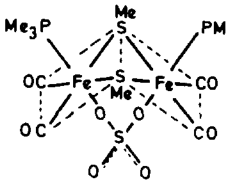

Fig. 1. Proposed structure for $(\mu\text{-}SCH_3Fe(CO)_2P(CH_3)_3)_2\text{-}SO_4$.

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