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(26) All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.
(27) $R_1 = [\sum||F_o| - |F_c||/|F_o|] \times 100\%$ and $R_2 = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100\%$.
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Diagnostic Features of Transition-Metal–SO_2 Coordination Geometries

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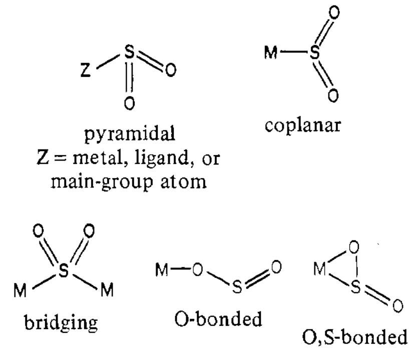
SO_2 complexes have been carefully examined in regard to possible correlations involving their physicochemical properties and SO_2 coordination geometries (coplanar MSO_2, pyramidal MSO_2, bridging MSO_2M, O,S-bonded SO_2, or ligand–SO_2 interaction). On a 1:1 basis, general correlations of geometry with SO infrared stretching frequencies, reversibility of SO_2 binding, and tendency of a complex to undergo the sulfato reaction can be made, but exceptions do exist. However, certain *combinations* of properties have been found to be diagnostic of specific geometries and appear to be useful criteria for identifying modes of SO_2 binding. The synthesis and properties of two new complexes, $Ir(SPh)(CO)(PPh_3)_2(SO_2)$ and $[RhCl(PPh_3)_2(SO_2)]_2$, are described in relation to the above correlations. These species as well as $RhCl(PPh_2Me)_3(SO_2)$ were found to react with atmospheric oxygen to form sulfates, which also were isolated and characterized.

Introduction

Few, if any, small molecules coordinate to a larger variety of substrates in a greater number of modes than sulfur dioxide. Excluding "insertion"-type structures,[1a] five different SO_2 coordination geometries have now been established by X-ray crystallography (Chart I). A complete listing of complexes possessing these structures is given in Table I. Of obvious interest is a means other than X-ray crystallography to determine which of these structural possibilities is most probable in a given transition-metal complex containing SO_2. In the past, efforts to correlate structure and physicochemical properties were primarily limited to the observation that compounds with pyramidal MSO_2 generally possessed a lower set of SO stretching frequencies than those with coplanar MSO_2.[1b] Also, in regard to the question of whether the SO_2 is S-bonded or O-bonded, a diagnostic based on Δ, the observed difference between the two SO stretching frequencies, has been proposed.[2] As part of an ongoing study of SO_2 complexes,[3-15] we have been closely scrutinizing complexes in regard to ν(SO), reversibility of SO_2 attachment, and reactivity with oxygen to form sulfates and have found that, in the majority of cases, correlations of structure with each of these properties can be made on a one-to-one basis. Occasional exceptions, even to the structure–infrared relation, do occur, which make structural predictions based on any one given property unreliable. However, certain *combinations* of properties have been found to be, without exception, diagnostic of specific coordination geometries and appear to be useful for identifying modes of SO_2 binding in newly synthesized complexes.

In the course of the above investigation, new SO_2 adducts have been synthesized and characterized also. The observed properties of these species will be discussed in relation to the proposed diagnostic features.

Chart I



Experimental Section

All reactions except those requiring oxygen as a reactant were carried out in an atmosphere of dry nitrogen. Sulfur dioxide (Matheson, 99.98%), phosphines (Strem Chemicals), and other reagents were purchased commercially and used as received. $MCl(CO)(PPh_3)_2(SO_2)$ (M = Rh, Ir) and $RhCl(PPh_3)_3$ were synthesized according to methods described in *Inorganic Syntheses* (Vol. IX and X, respectively). $Ir(SPh)(CO)(PPh_3)_2$,[16] $RuCl_2(PPh_3)_2(SO_2)$,[17] $CpMn(CO)_2(SO_2)$[18] (Cp = η-C_5H_5), $[Ir(dppe)_2]Cl$[19] (dppe = $Ph_2PCH_2CH_2PPh_2$), $Ni(p_3)(SO_2)$[20] [p_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane], $RhCl(PCy_3)_2(SO_2)$[21] (Cy = cyclohexyl), $Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$[22] (phen = 1,10-phenanthroline), and $RhCl(PPh_2Me)_3(SO_2)$[23] were prepared according to literature methods. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thermogravimetric curves and Nujol mull infrared spectra were recorded using Perkin-Elmer Models TGS-2 and 521, respectively.

Preparation of $RhCl(SO_4)(PPh_2Me)_3\cdot{}^3/_4C_6H_6$. $RhCl(PPh_2Me)_3(SO_2)$ (0.35 g) was dissolved in 50 mL of warm benzene, and the solution was filtered and saturated with oxygen. A yellow-orange crystalline precipitate (0.13 g) formed upon allowing the loosely stoppered solution to stand for 3 days at room temperature. The precipitate was collected on a frit, washed with a small quantity of benzene and then pentane, and dried in air. Infrared and elemental analysis indicated that lattice benzene was present in the sulfate. Anal. Calcd for $C_{43.5}H_{43.5}P_3O_4SClRh$: C, 58.4; H, 4.9; P, 10.4; S, 3.6. Found: C, 58.3; H, 4.8; P, 10.0; S, 3.8.

Thermogravimetric analysis (2.5 °C/min heating rate) of $RhCl(SO)_4(PPh_2Me)_3\cdot{}^3/_4C_6H_6$ indicated loss of benzene at 50–100 °C, loss of one phosphine at 150–225 °C, and further phosphine loss to 500 °C.

Preparation of $Ir(SPh)(CO)(PPh_3)_2(SO_2)\cdot C_7H_8$. $Ir(SPh)(CO)(PPh_3)_2$ was dissolved in toluene (~0.4 g/25 mL). The resulting yellow solution was treated with excess SO_2 gas, giving an immediate color change to deep red. The filtered solution was then reduced to

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Table I. Structurally Characterized Complexes Containing SO_2[a]

	pyramidal ZSO_2	coplanar MSO_2	bridging MSO_2M	S,O-bonded	O-bonded
Z = metal	$IrCl(CO)(PPh_3)_2(SO_2)$[46]	$[RuCl(NH_3)_4(SO_2)]Cl$[40]	$[CpFe(CO)_2]_2SO_2$[51]	$Rh(NO)(PPh_3)_2(\eta^2\text{-}SO_2)$[9]	F_5SbOSO[58]
	$RhCl(CO)(PPh_3)_2(SO_2)$[49]	$MnCp(CO)_2(SO_2)$[18]	$Cp_2Fe_2(CO)_3(SO_2)$[52]	$RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$[26]	
	$Pt(PPh_3)_3(SO_2)$[6]	$RhCp(C_2H_4)(SO_2)$[4]	$Fe_2(CO)_8(SO_2)$[53]	$Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$[27]	
	$Pt(PPh_3)_2(SO_2)_2$[5]	$Ni(p_3)(SO_2)$[20]	$Pd_3(t\text{-}BuNC)_5(SO_2)_2$[54]		
	$[RhCl(PPh_3)_2(SO_2)]_2$[13]	$OsHCl(CO)(PCy_3)_2(SO_2)$[14]	$[IrH(CO)_2(PPh_3)]_2SO_2$[55]		
	$RhCl(ttp)(SO_2)$[39a]	$Ni(PPh_3)_2(SO_2)_2$[50]	$Pt_3(PPh_3)_3(SO_2)_3$[10]		
Z = ligand	$Pt(CH_3)(PPh_3)_2I\text{-}SO_2$[48]	$Co(NO)(PPh_3)_2(SO_2)$[50]	$[IrI_2(CO)(PPh_3)]_2SO_2$[59]		
	$Cu(SPh)(PPh_2Me)_3\cdot SO_2$[12]	$RhCl(PCy_3)_2(SO_2)$[27]	$Pd_2Cl_2(dpm)_2(SO_2)$[43]		
	$Cu_2I_2(PPh_2Me)_4\cdot SO_2$[11]	$Ni(PPh_3)_3(SO_2)$[8]			
Z = nonmetal	$Me_3N\cdot SO_2$[56]				
	$C_6H_4(NMe_2)_2\cdot 2SO_2$[57]				
	$[PPh_3Bz]I\cdot SO_2$[15]				

[a] Ligand abbreviations: p_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane, dpm = $Ph_2PCH_2PPh_2$, phen = 1,10-phenanthroline, ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$.

Table II. Infrared Frequencies

compound	$\nu(SO_2,SO_4)$, cm^{-1}
$RhCl(PPh_2Me)_3(SO_2)$	1163, 1025
$[RhCl(PPh_3)_2(SO_2)]_2\cdot 2CHCl_3$	1166, 1031
$Ir(SPh)(CO)(PPh_3)_2(SO_2)\cdot C_7H_8$[a]	1192, 1042
$[RhCl(SO_4)(PPh_3)_2]_2$	1252, 1065, 958, 667, 623
$Ir(SPh)(SO_4)(CO)(PPh_3)_2$[b]	1295, 1160, 875, 646, 595
$RuCl_2(SO_4)(PPh_3)_2$	1262, 1060, 930, 656, 586
$RhCl(SO_4)(PPh_2Me)_3\cdot {}^3/_4C_6H_6$	1247, 1146, 927, 639, 601

[a] $\nu(CO) = 2007$ cm^{-1}. [b] $\nu(CO) = 2053$ cm^{-1}.

half its volume by solvent removal in vacuo and cooled to −20 °C, resulting in the precipitation of microcrystalline deep red $Ir(SPh)(CO)(PPh_3)_2(SO_2)\cdot C_7H_8$ in good yield. The product was collected on a frit, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_{50}H_{43}O_3P_2S_2Ir$: C, 59.5; H, 4.3; S, 6.3; P, 6.1. Found: C, 61.1; H, 4.4; S, 6.3; P, 6.2.

The solid complex is slowly converted to the orange sulfato species upon standing in air and loses volatiles rapidly upon heating to 100 °C or greater. The evolved toluene and SO_2 were separated by trap-to-trap distillation on a vacuum line and were identified by mass spectroscopy.

Preparation of $IrX(SO_4)(CO)(PPh_3)_2$ (X = Cl, SPh). Toluene solutions of $IrX(CO)(PPh_3)_2(SO_2)$ (X = Cl, SPh) were allowed to stand in air. For X = SPh, precipitation of orange $Ir(SPh)(SO_4)(CO)(PPh_3)_2$ was complete after 1 day, but over 1 week was required for the formation of off-white $IrCl(SO_4)(CO)(PPh_3)_2$. The precipitates were washed with toluene and then air-dried. The sulfates are nearly insoluble in toluene but are soluble in CH_2Cl_2. Infrared bands due to bidentate sulfate were observed for $IrCl(SO_4)(CO)(PPh_3)_2$ at frequencies which agreed well with literature values[24,25] and for $Ir(SPh)(SO_4)(CO)(PPh_3)_2$ at frequencies given in Table II.

Preparation of $[RhCl(PPh_3)_2(SO_2)]_2\cdot 2CHCl_3$. Excess SO_2 was passed through a solution of $RhCl(PPh_3)_3$ (0.4 g) in 15 mL of $CHCl_3$. SO_2-saturated ethanol (50 mL) was then added and the solution was stirred. After several minutes, precipitation of a red-orange microcrystalline solid commenced (supersaturation can occur; rapid cooling induced crystallization in one case). The mixture was allowed to stand in a freezer overnight and then filtered. The ethanol-washed and vacuum-dried product weighed 0.308 g (84% yield). Anal. Calcd for $C_{74}H_{62}O_4P_4Cl_8S_2Rh_2$: C, 52.5; H, 3.7; P, 7.3; S, 3.8; Cl, 16.8. Found: C, 51.6; H, 3.9; P, 7.4; S, 3.0; Cl, 17.0. $[RhCl(PPh_3)_2(SO_2)]_2\cdot 2CHCl_3$ can also be prepared from $RhCl(PPh_3)_2(C_2H_4)$ or $RhCl(PPh_3)_2(H_2)$ in nearly identical fashion.

Heating the complex to 115 °C in vacuo for 1 h resulted in partial loss of volatiles (2.84 mmol of a mixture of $CHCl_3$ and SO_2/mmol of dimer). Thermogravimetric analysis (1.25 °C/min heating rate, N_2 purge) indicated a gradual 20% weight loss at 35–160 °C (theory for loss of $CHCl_3$ and SO_2: 21.7%), immediately followed by slow phosphine loss above 160 °C.

Preparation of $[RhCl(SO_4)(PPh_3)_2]_2$. A solution of $[RhCl(PPh_3)_2(SO_2)]_2\cdot 2CHCl_3$ (0.53 g) in benzene was allowed to stand in air for several hours. A golden-yellow precipitate of the sulfate (0.15 g) formed, which was washed with benzene and air-dried. Anal. Calcd for $C_{72}H_{60}O_8S_2Cl_2Rh_2$: C, 57.0; H, 4.0; P, 8.2; S, 4.2; Cl, 4.7; M_r, 1518. Found: C, 57.0; H, 4.1; P, 7.9; S, 4.0; Cl, 4.6; M_r, 1517 (in $CHCl_3$).

Reaction of $RhCl(CO)(PPh_3)_2(SO_2)$ and Oxygen in Benzene. Over a period of several days, an oxygen-saturated benzene solution of $RhCl(CO)(PPh_3)_2(SO_2)$ underwent a color change from yellow to red and began to precipitate a yellow solid. Several days after the red coloration appeared, the solution became yellow-orange and no further precipitation occurred. The yellow solid was collected on a frit, washed with benzene, and air-dried. The yield was low, and infrared analysis indicated that the precipitate contained a mixture of $RhCl(SO_4)(CO)(PPh_3)_2$ and $[RhCl(SO_4)(PPh_3)_2]_2$.

Reaction of $[Ir(dppe)_2]Cl$ with SO_2 and O_2. $[Ir(dppe)_2]Cl$ did not yield an isolatable SO_2 adduct upon treatment with SO_2 in $CHCl_3$ solution. $[Ir(dppe)_2]Cl$ was recovered unchanged upon solvent removal. However, exposure of the above mixture to oxygen for several days led to decolorization of the solution. Addition of hexane gave an oil which solidified upon trituration with acetone. The infrared spectrum of the white solid indicated that it was $[Ir(SO_4)(dppe)_2]Cl$. Bands due to coordinated sulfate were observed at 1270–1290, 1160, 880–890, and 645 cm^{-1} (lit.[25] 1280–1295, 1170, 885, 655 cm^{-1}).

Determinations of Reversibility or Nonreversibility of SO_2 Binding and Reactivity of Oxygen with Selected SO_2 Complexes

(a) $RuCl_2(PPh_3)_2(SO_2)\cdot CHCl_3$. Recrystallization of $RuCl_2(PPh_3)_2(SO_2)$ from a $CHCl_3$–C_2H_5OH solution yielded a chloroform solvate, a sample (0.159 g, 0.175 mmol) of which was placed in a tube and heated to 130 °C for 2 h on a vacuum line. Volatiles (0.327 mmol) collected in a −196 °C trap were separated via a −83 °C trap into SO_2 (0.145 mmol) and $CHCl_3$ (0.182 mmol) fractions. Mass spectroscopy of the latter indicated that a small amount of ethanol was also present. The molar ratio of recovered SO_2 to initial adduct was 0.83. The residue obtained on cooling the heated solid could not be converted back to $RuCl_2(PPh_3)_2(SO_2)$ upon addition of SO_2 (gas or liquid).

An oxygen-saturated benzene solution of $RuCl_2(PPh_3)_2(SO_2)$ deposited a solid over a period of several hours which gave infrared absorptions characteristic of coordinated bidentate sulfate (Table II).

(b) $CpMn(CO)_2(SO_2)$. Since this compound readily sublimes unchanged at <100 °C, it is presumed that the SO_2 is bound irreversibly.

Within minutes after exposure to oxygen, a benzene solution of $CpMn(CO)_2(SO_2)$ began to precipitate a yellow-brown solid. When the solution was allowed to stand overnight, the supernatant became completely colorless. The solid which proved to be insoluble in organic solvents, was collected, dried, and characterized by infrared spectroscopy. No absorptions due to carbonyl or sulfate were present in the spectrum. Thus, decomposition of the complex occurred rather than sulfate formation.

(c) $Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$. Thermogravimetric analysis (2.5 °C/min heating rate, nitrogen purge) showed rapid loss of volatiles at 170–215 °C corresponding to 20% of sample weight, followed by additional weight loss to 500 °C at a slower rate (38.5% total loss). Since the expected weight loss for removal of SO_2 is 15%, the compound undergoes decomposition rather than reversible SO_2 loss.

$Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$ is nearly insoluble in benzene at room temperature but is somewhat soluble in boiling solvent. Therefore a sample (50 mg) was refluxed in benzene (25 mL) overnight open to the atmosphere. A dark colored precipitate formed which did not show bands due to sulfate. Evaporation of the supernatant solution

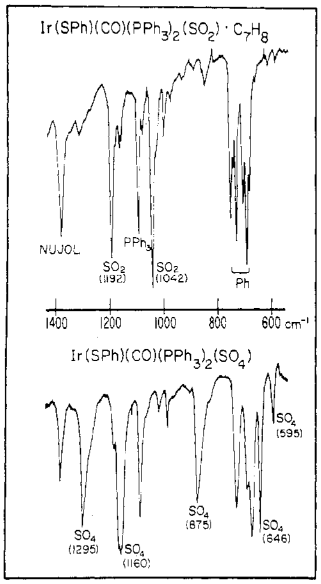


Figure 1. Infrared spectra of typical SO_2 and sulfato complexes (Nujol mulls between CsBr plates).

yielded 15 mg of red needles which proved to be $Mo(CO)_4(phen)$.

(d) $Ni(p_3)(SO_2)$. A sample of $Ni(p_3)(SO_2)$ was heated to 150 °C in vacuo. No loss of volatiles was observed and the infrared spectrum of the cooled residue was unchanged.

Solutions of the complex changed color slightly upon exposure to air. However, no sulfato species precipitated and oil formation occurred upon solvent removal. This agrees with previously reported results of a similar experiment.[20]

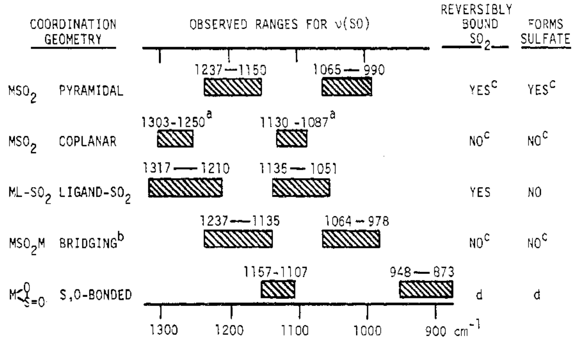
(e) $RhCl(PCy_3)_2(SO_2)$. No loss of volatiles was observed for a sample heated to 200 °C under nitrogen in a thermogravimetric apparatus.

Reaction with oxygen in solution gave results similar to those in (d) and those previously reported.[21] Apparently phosphine and/or metal oxidation occurs which precludes any possibility of sulfate information. However, finely divided solid $RhCl(PCy_3)_2(SO_2)$ underwent a color change from brown to orange-brown on exposure to air in a stoppered vial for several months. Strong infrared absorptions at 1155 and 645 cm^{-1} appeared while absorptions at 1264 and 1112 cm^{-1} due to coordinated SO_2 diminished in intensity. Further exposure to pure oxygen for several weeks resulted in decomposition since all infrared bands became much weaker and broader. Thus apparently the SO_2 complex slowly oxidizes to a sulfate which is itself unstable and is transformed to uncharacterized species.

(f) $RhCl(PPh_2Me)_3(SO_2)$. Thermogravimetric analysis (5 °C/min heating rate, N_2 purge) showed that SO_2 is lost at 150–200 °C but phosphine loss also begins to occur in this range, thus denying strict reversibility to the SO_2 binding. At a heating rate of 1.25 °C/min, SO_2 plus one phosphine is removed at 150–200 °C, followed by loss of remaining phosphines at 200–500 °C.

Results and Discussion

Relation of SO Stretching Frequencies to SO_2 Coordination Geometry. An extensive literature search on transition-metal–SO_2 complexes covering nearly 100 references and 140 compounds has been carried out in order to aid in the correlation of their physicochemical properties. One of the easiest and most definitive characterization methods is infrared spectroscopy since two strong bands due to SO stretching modes are normally present in the spectra of all SO_2 complexes, as exemplified in Figure 1. Furthermore, the peaks rarely overlap in cases where more than one type of SO_2 binding is present in the same complex (e.g., both metal–SO_2 and ligand–SO_2 interactions). The ranges in which $\nu(SO)$ fall for each geometry type known to occur in transition-metal–SO_2 complexes are illustrated in Figure 2. The graph is based on all known data on complexes which either have been structurally characterized or which, in all probability, possess structures which can be assumed to contain a specific substrate–SO_2 geometry. Thus, the structure of $Ir(SPh)(CO)(PPh_3)_2(SO_2)$ undoubtedly is similar to the structure known for $IrCl(CO)(PPh_3)_2(SO_2)$, and $\nu(SO)$ for both of these complexes would be included in the range for pyramidal MSO_2. As it turns out, all but a very few complexes can be categorized. It is clear that some of the ranges for $\nu(SO)$, unlike analogous ranges for $\nu(NO)$ in nitrosyl complexes, are relatively narrow and do not overlap with certain other ranges. This is especially true for the coplanar MSO_2 and pyramidal MSO_2 categories, as expected from previously reported qualitative observations. However, two striking exceptions are known. $Ni(p_3)(SO_2)$[20] and $Ni(PPh_3)_3(SO_2)$[8] have coplanar MSO_2, but $\nu(SO)$'s at 1190 and 1050 cm^{-1} and 1205 and 1055 cm^{-1}, respectively, are well within the region for pyramidal MSO_2. Thus, other criteria are clearly necessary to differentiate between the geometries, especially since some of the frequency ranges, such as those for coplanar MSO_2 and pyramidal ML–SO_2, do overlap. These will be discussed in following sections.



[a] $\nu(SO)$ for $Ni(p_3)(SO_2)$ = 1190, 1050 cm^{-1}.

[b] A molecule must be known to contain at least two metal atoms before it can be assumed to possess this geometry.

[c] In the majority of cases.

[d] Too few examples known to establish a general trend.

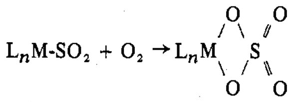
Figure 2. Diagnostic features of SO_2 coordination geometries. The $\nu(SO)$ ranges are based on $\nu(SO)$ observed for compounds given in Table I as well as those reported in ref 17, 24, 29–35, 37, 39, 42, 46, and 60–72.

A more quantitative examination of Figure 2 reveals that the overall frequency spread for the high-frequency SO_2 stretch (ν_1) is 210 cm^{-1} and that for the low-frequency stretch (ν_2) is 262 cm^{-1}. Percentagewise, all of the geometry-specific ranges (the bar graphs in Figure 2) are less than 51% of the total respective spreads (the percentages span 24–51% for ν_1 and 16–33% for ν_2). Interestingly, the ranges for pyramidal MSO_2 and bridging MSO_2M are nearly identical. Although perhaps fortuitous, this coincidence is certainly not surprising since in both instances the SO_2 is S bound and the interaction with the metal(s) is of the "bent" variety (bridging O-bonded or S,O-bonded SO_2 has not been structurally documented as yet). Differentiation between the pyramidal and bridging geometries thus usually will not be possible on the basis of infrared evidence alone, but knowledge of the stoichiometry and molecularity of a complex could easily clarify the situation.

At this time the S,O-bonding mode has been found to occur only in $Rh(NO)(PPh_3)_2(\eta^2\text{-}SO_2)$,[9] $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$,[26] and $Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$,[27] although it is reasonable to expect more examples to eventually be characterized. As can be seen in Figure 2, the SO stretches are significantly lower in energy than those found for S-bonded complexes. Also, the observed differences between the stretching frequencies, Δ, are 190 cm^{-1} for the Rh complex, ca. 250 cm^{-1} for the Ru complex, and 214 cm^{-1} for the Mo species, whereas complexes containing SO_2 bound to transition metals via only sulfur give Δ values in the range 125–184 cm^{-1}.

As has been previously pointed out, trends in the value of Δ appear to be a useful diagnostic feature for the mode of SO_2 coordination (S or O bonding).[2] Values in excess of 190 cm^{-1} (the value for liquid SO_2) appear to be characteristic of O bonding, as in F_5SbOSO which gives $\Delta = 220$ cm^{-1} [ν(SO) $\simeq$ 1320, 1100 cm^{-1}], whereas values lower than 190 cm^{-1} are typical for S bonding.[2] The same criteria found for O bonding thus appear to be applicable for S,O bonding as well. However, these two bonding situations in all likelihood will be resolvable on the basis of ν(SO). Some care must be exercised in applying the Δ criterion since complexes with weak ligand–SO_2 interactions, such as $Cu_mI_m(PR_3)_n{\cdot}xSO_2$,[11] can also give Δ values as high as 190 cm^{-1}. However, species of this type display ν(SO) at frequencies nearly as high as those found in free SO_2 (1340 and 1150 cm^{-1}) and consequently are readily identifiable. On the other hand, complexes with stronger ligand–SO_2 binding, such as $Cu(PR_3)_n(SR'){\cdot}SO_2$,[12] can exhibit ν(SO) and Δ values indistinguishable from those of pyramidal MSO_2 complexes. In these cases, additional criteria, which will be discussed next, are necessary to establish whether the SO_2 is bound to ligand or metal.

Sulfate Formation and Its Relation to SO_2 Coordination Geometries. Quite a number of SO_2-containing five-coordinate rhodium,[24,28–31] iridium,[29,32,33] and ruthenium[7,17,24,34] complexes have been previously observed to undergo the sulfato reaction



$$L_nM\text{-}SO_2 + O_2 \rightarrow L_nM(O)_2S(O)_2$$

Similarly, several d^{10} complexes of nickel,[35] palladium,[36,37] and platinum[5,36,38] readily form bidentate sulfates. The sulfates are easily identifiable by infrared spectroscopy, as can be seen in Figure 1. The strong peak in the 630–680-cm^{-1} region, which is rarely obscured by ligand peaks, is very characteristic. We have found additional examples of sulfate formation. The conversion in solution of $[RhCl(PPh_3)_2(SO_2)]_2$, $RhCl(PPh_2Me)_3(SO_2)$, and $Ir(SPh)(CO)(PPh_3)_2(SO_2)$ to their respective sulfates was relatively rapid and straightforward, the products starting to precipitate from solution within 1 h to 1 day. However, in the case of $IrCl(CO)(PPh_3)_2(SO_2)$, about 1 week was required. This may explain why the latter had been previously reported[24] to be nonreactive toward oxygen in solution. The reaction of oxygen with $RhCl(CO)(PPh_3)_2(SO_2)$ in benzene is interesting in that both $RhCl(SO_4)(CO)(PPh_3)_2$[29] and $[RhCl(SO_4)(PPh_3)_2]_2$ are formed. Apparently the carbonyl is labile enough to be slowly spontaneously lost during the course of the oxidation. Both $RhCl(CO)(PPh_3)_2(SO_2)$ and its iridium analogue had previously been reported to react with oxygen in the solid state for unspecified periods of time to give $MCl(SO_4)(CO)(PPh_3)_2$.[29] In all cases, the d^8 and d^{10} complexes undergoing sulfate formation have been shown to or are expected to possess pyramidal MSO_2 geometry. It is thus tempting to propose that, in general, metal–SO_2 complexes with this geometry will be reactive with oxygen in solution to give sulfates. However, occasional exceptions will occur since $RhCl(ttp)(SO_2)$ (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$), which has now been confirmed[39a] to contain pyramidal MSO_2 as suggested by ν(SO) at 1155 and 1030 cm^{-1}, has been reported to be stable toward oxygen in solution.[39b]

In regard to complexes with coplanar MSO_2 it is apparent that they normally do not form sulfates. $[RhCl(NH_3)_4(SO_2)]Cl$ is air stable in solution,[40] and solutions of $CpMn(CO)_2(SO_2)$, $CpRh(C_2H_4)(SO_2)$,[4] $Ni(p_3)(SO_2)$, and $RhCl(PCy_3)_2(SO_2)$ decompose to non-sulfate-containing products upon atmospheric exposure. However, a d^6 six-coordinate complex, $OsHCl(CO)(PCy_3)_2(SO_2)$, surprisingly has been found to form $OsCl(SO_4)(CO)(PCy_3)_2$.[14] Furthermore, $RuCl_2(PPh_3)_2(SO_2)$, which has not been structured, but apparently possesses coplanar MSO_2 judging by ν(SO) at 1300 and 1130 cm^{-1}, also has been reported to form a sulfate.[17] This has been confirmed by our isolation of the latter, which gives an infrared spectrum typical of bidentate sulfate coordination (Table II).

Complexes with bridging SO_2 have generally not been reported to undergo sulfate formation. The presumably SO_2-bridged species $[Pd(PPh_3)(SO_2)]_3$ will yield $Pd(PPh_3)_2(SO_4)$ provided PPh_3 is present, however.[37] Not surprisingly, oxidation of ligand-bound SO_2 to sulfate has never been observed. Finally, regarding the S,O-bonded complexes, $Rh(NO)(PPh_3)_2(\eta^2\text{-}SO_2)$ and $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ have been found to react with oxygen in solution to give $Rh(NO)(SO_4)(PPh_3)_2$[8,9,24] and $RuCl(NO)(SO_4)(PPh_3)_2$,[41] respectively, but $Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$ does not give a sulfate. Thus it is clear that a compound's metal–SO_2 geometry is in itself not a limiting factor in the ability of the compound to undergo the sulfato reaction, although complexes with pyramidal MSO_2 appear to have by far the greatest proclivity for doing so.

Correlations of Reversibility of SO_2 Binding with SO_2 Coordination Geometry. In a practical sense, a complex can be regarded as containing reversibly bound SO_2 if the SO_2 can be removed upon moderate (<200 °C) heating to give a stable SO_2-free species. In order for the above process to be strictly reversible, the SO_2 complex must be regenerable upon SO_2 readdition. The classic example here is $MCl(CO)(PPh_3)_2(SO_2)$ (M = Rh, Ir),[42] which contains pyramidal MSO_2. Many other five-coordinate d^8 complexes also are known to contain reversibly bound SO_2. $Ir(SPh)(CO)(PPh_3)_2(SO_2){\cdot}C_7H_8$ readily loses both toluene of solvation and SO_2 at 100 °C in vacuo to give $Ir(SPh)(CO)(PPh_3)_2$ and is obviously similar in nature. In addition to the five-coordinate d^8 complexes, d^{10} species with pyramidal MSO_2, e.g., $Pt(PPh_3)_2(SO_2)_2$,[5] also readily lose and readd SO_2. Thus, in general, complexes with pyramidal MSO_2 possess reversible bound SO_2, which is expected since, in this case, the M–S distance is relatively long (2.35–2.50 Å) and the SO_2 is behaving as a Lewis acid. The only known exception thus far is $RhCl(ttp)(SO_2)$, which is stable to 200 °C and begins to decompose on further heating before losing SO_2.[39]

Of the complexes known to contain coplanar MSO_2 (Table I), all retain SO_2 on heating (the Cp compounds are readily sublimable) except $OsHCl(CO)(PCy_3)_2(SO_2)$, which loses SO_2 reversibly at 100 °C to form $OsHCl(CO)(PCy_3)_2$.[14] Also, $RuCl_2(PPh_3)_2(SO_2)$, which has infrared frequencies indicative of coplanar MSO_2, loses SO_2 upon heating, though apparently not in a strictly reversible fashion (formation of chloride-bridged species is likely to occur upon SO_2 removal). Thus, nonreversible SO_2 binding can be correlated with the coplanar geometry in most, but not all, cases. This is in line with the relatively short M–S distances (2.0–2.1 Å) usually observed for the coplanar geometry and the Lewis base behavior of SO_2 in these types of complexes. Interestingly, $OsHCl(CO)(PCy_3)_2(SO_2)$, which has by far the longest M–S distance (2.24 Å) of any complex with coplanar MSO_2, loses SO_2 reversibly, while $RhCl(ttp)(SO_2)$, which has a longer M–S distance (2.33 Å) but a distance which is *short relative to most pyramidal cases*,[39a] does not. Thus, certain gradations of properties *within* structural categories may eventually evolve.

Compounds with bridging MSO_2M geometry have not generally been reported to contain reversibly bound SO_2, as expected. However, reversible insertion of SO_2 into the metal–metal bonds of $Pd_2Cl_2(dpm)_2$ (dpm = $Ph_2PCH_2PPh_2$) and several Pd and Pt analogues has recently been reported.[43] The adducts possess the novel "A-frame" bridging geometry, as shown by the crystal structure of $Pd_2Cl_2(dpm)_2(SO_2)$. Thus, in certain situations involving metal–metal bonding, SO_2 may indeed reversibly bridge two metals.

There are yet too few examples of complexes with η^2-SO_2 to generalize their behavior. Although solid Rh(NO)$(PPh_3)_2(\eta^2$-$SO_2)$ loses SO_2 on heating, the residue, which apparently contains nitrosyl-bridged species judging by a shift of ν(NO) to lower frequency, does not readd SO_2 to form the original complex.[44] $Mo(CO)_3(phen)(\eta^2$-$SO_2)$ is stable to 170 °C, whereupon loss of volatiles ensues. However, thermogravimetric data in the 170–210 °C range show a weight loss exceeding that expected for removal of SO_2, indicating decomposition occurs. Solution studies revealed that the SO_2 in both the Rh and Mo complexes is readily displaceable by neutral donor bases such as phosphines, or, in case of $Mo(CO)_3(phen)(\eta^2$-$SO_2)$, acetonitrile.[9,27] Thus, the SO_2 is clearly labile but not reversibly bound in the strict sense.

In all cases, SO_2 coordinated to ligands has been found to be reversibly bound.

Correlation of SO_2 Reversibility with Sulfate Formation. One correlation can be made which so far appears to have no exceptions: all complexes with reversibly metal-bound SO_2 form bidentate sulfates upon reaction with oxygen. The geometry of the MSO_2 group and other factors apparently have no bearing on this relationship, even for example in the case of the coordinatively saturated complex $OsHCl(CO)(PCy_3)_2(SO_2)$. The latter has been found to lose hydride upon reaction with oxygen to form bidentate-sulfate-containing $OsCl(SO_4)(CO)(PCy_3)_2$.[14]

Since all ligand-bound SO_2 can be reversibly removed but does not oxidize to sulfate, a useful test for the ML–SO_2 structure is readily obvious. Complexes containing both ligand- and metal-bound SO_2 present a more difficult problem, however. Fortunately, infrared studies generally allow differentiation between the two types of SO_2 attachment, although it is conceivable that this may not always be true.

Determination of Probable SO_2 Coordination Geometries in Complexes of Unknown Structure. Although exceptions to the previously discussed structure–property correlations exist, it nonetheless appears possible to identify with a high degree of confidence the type of SO_2 attachment in most transition-metal–SO_2 complexes by correlating *sets* of properties with structure. This can be accomplished by referring to Figure 2, which can be utilized in two ways. If a particular geometry is known or assumed for a complex, then the complex will probably, but not necessarily, exhibit the tabulated properties. However, using the table in a converse sense, accurate predictions of geometry can be made if the observed properties of a SO_2 complex match one of the listed sets of properties. For example, newly synthesized complexes that are found to possess reversibly bound SO_2, form sulfates, and have ν(SO) in the ranges 1237–1150 and 1065–990 cm^{-1} will very likely contain pyramidal MSO_2. No exceptions to predictions of this type have been found thus far.[45] Compounds possessing sets of properties not listed, such as $OsHCl(CO)(PCy_3)_2(SO_2)$, $RhCl(ttp)(SO_2)$, and $Ni(p_3)(SO_2)$, are not as yet amenable to identification of the mode of SO_2 bonding by this method, since they are literally in a class by themselves until further examples are found. Thus, Figure 2 also serves as a means of singling out complexes with unusual properties, assuming that species with the geometries and attendant properties given in Figure 2 will remain predominant. At this time it is difficult to rationalize the singular behavior displayed by the three aforementioned complexes. Ligand considerations may be important, since the Os complex possesses a trans-labilizing hydride and bulky phosphines while the Rh and Ni compounds have constraining phosphine groups. However, $RuCl_2(PPh_3)_2(SO_2)$, which has not been structured crystallographically, exhibits properties similar to $OsHCl(CO)(PCy_3)_2(SO_2)$ but yet does not possess unusual ligands. Also, $Ni(PPh_3)_3(SO_2)$ has proven to have structure and properties quite comparable to those of $Ni(p_3)(SO_2)$.[8] Further synthetic and X-ray structural studies are thus needed to aid in understanding the relation of steric and electronic factors to the physicochemical properties of SO_2 complexes.

Synthesis and Characterization of SO_2 Complexes. Applications of the Structure–Property Correlations. The diagnostics set forth in Figure 2 have proven to be of considerable value in coordinating our synthetic and structural effort to develop bonding principles in transition-metal–SO_2 complexes.[3–15] They have also been useful in singling out occasional misinterpretations of data in the literature by leading to reexaminations of compounds with properties that conflict with their proposed structures. Examples of this and some new synthetic work will now be discussed.

$[Ir(dppe)_2]Cl$ had been reported to give a bis-SO_2 adduct.[19] However, both the white color and ν(SO) (1276, 1163 cm^{-1}) of the solid isolated were indicative of a sulfato complex. Our attempts to isolate an SO_2 adduct were unsuccessful, but a white sulfate, with infrared bands matching the above and also corresponding to $\nu(SO_4)$ reported for $[Ir(SO_4)(dppe)_2]Cl\cdot H_2O$,[23] formed upon reaction of $[Ir(dppe)_2]Cl$ with a mixture of SO_2 and O_2. Thus, it is likely that a similar oxidation had occurred inadvertently in the original study.

The addition of SO_2 to $Ir(SPh)(CO)(PPh_3)_2$ in toluene yielded a mono-SO_2 adduct $Ir(SPh)(CO)(PPh_3)_2(SO_2)\cdot C_7H_8$. This reaction was of interest because of the possibility of attachment of SO_2 to both the metal and the mercaptide sulfur. The latter type of binding has recently been found to occur in SO_2 adducts of organophosphinecopper(I) mercaptides and $Pt(PPh_3)_2(SPh)_2$.[12] In the iridium adduct, it appears that only metal-bound SO_2 is present, since the carbonyl stretching frequency increases from 1950 cm^{-1} for $Ir(SPh)(CO)(PPh_3)_2$ to 2007 cm^{-1} upon SO_2 coordination and ν(SO) is typical for the expected pyramidal MSO_2 geometry. Ligand–SO_2 binding also had been expected especially since $Ir(SPh)(CO)(PPh_3)_2$ had been reported to be monomeric in solution.[16] However, the mercaptide sulfur apparently is too sterically crowded to allow attachment of SO_2. $Ir(SPh)(CO)(PPh_3)_2(SO_2)\cdot C_7H_8$ possesses properties similar to the previously reported[29] SC_6F_5 analogue, including reactivity with O_2 in both solid and solution states to give sulfates. The latter plus the reversibility of the SO_2 coordination clearly supports a structure similar to that of $IrCl(CO)(PPh_3)_2(SO_2)$.[46]

Examples of four-coordinate SO_2 complexes of d^8 metals have been rare and consequently of considerable interest to us. The reaction of solid $IrCl(PPh_3)_2(N_2)$ with SO_2 had been reported to give $IrCl(PPh_3)_2(SO_2)$, which possessed ν(SO) indicative of coplanar MSO_2.[47] However, the complex is unstable in solution and could not be characterized further. Preparation of solution-stable monomeric $RhX(PPh_3)_2(SO_2)$ (X = Cl, Br, I) from $RhX(PPh_3)_3$ and SO_2 in *n*-alkane had been claimed earlier[28] but, in light of the instability of $IrCl(PPh_3)_2(SO_2)$, this report appeared to be in need of further investigation. The reaction of $RhCl(PPh_3)_3$ with SO_2 in $CHCl_3$ solution was thereupon carried out, as well as a similar reaction utilizing $RhCl(PPh_3)_2(C_2H_4)$ as starting material. In both instances, the product was the chloride-bridged dimer $[RhCl(PPh_3)_2(SO_2)]_2\cdot 2CHCl_3$. The structure[13] of the latter (Figure 3) showed axially bound sulfur dioxide ligands and pyramidal $RhSO_2$ geometries. ν(SO) were located at 1166 and 1031 cm^{-1}, in the range expected for pyramidal MSO_2 and in good agreement with the frequencies reported by Levison and Robinson for their "type A" $RhX(PPh_3)_2(SO_2)$ complexes (for X = Cl, ν(SO) = 1172, 1033 cm^{-1}). Thus, it would appear that the "type A" species in all probability are actually halide-bridged dimers. Further evidence for this is

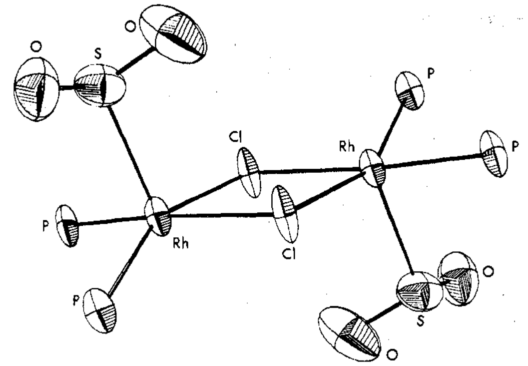


Figure 3. Projection of the Rh coordination sphere in [RhCl(PPh$_3$)$_2$(SO$_2$)]$_2$·2CHCl$_3$.[13]

the observation that [RhCl(PPh$_3$)$_2$(SO$_2$)]$_2$·2CHCl$_3$ reacts with O$_2$ in solution to give a sulfato species with ν(SO$_4$) (Table II) nearly identical with that reported[25] for the sulfato product obtained by Levison and Robinson. Elemental analysis and molecular weight measurements indicate that the sulfate, like the SO$_2$ complex, is also a chloride-bridged dimer, and has the stoichiometry [RhCl(SO$_4$)(PPh$_3$)$_2$]$_2$. The aforementioned authors also obtained in admixture with the "type A" complexes, 30% "type B" RhX(PPh$_3$)$_2$(SO$_2$) (X = Br, I) with ν(SO) at ~1288 and 1124 cm^{-1}. It is possible that these species are indeed monomeric with coplanar MSO$_2$, judging by the ν(SO) positions. However, as can be seen in Figure 2, these frequencies are also characteristic of ligand-bound SO$_2$. Thus it is likely that species containing SO$_2$ bound to both metal and halide ligands (e.g., as in Ir(CO)(PPh$_3$)$_2$(SO$_2$)I–SO$_2$[48]) were formed and interpreted as being a mixture of "type A" and "type B" complexes. This is further amplified by the failure to obtain "type B" complexes for X = Cl, since chloride binds SO$_2$ much more weakly than bromide or iodide. The situation just described is thus an excellent example of the usefulness of the proposed diagnostics in distinguishing between various structural possibilities.

An authentic four-coordinate d^8 SO$_2$ complex, RhCl(PCy$_3$)$_2$(SO$_2$), has now recently been synthesized[21] and structurally characterized.[27] It possesses a coplanar MSO$_2$ geometry as predicted by its properties [ν(SO) = 1266, 1111–1121 cm^{-1}; SO$_2$ is nonreversibly bound; it does not form a sulfate].

Lastly, in contrast to RhCl(PPh$_3$)$_3$, RhCl(PPh$_2$Me)$_3$ was found[23] to add SO$_2$ to form monomeric, five-coordinate RhCl(PPh$_2$Me)$_3$(SO$_2$). The latter possesses ν(SO) (Table II) typical of pyramidal MSO$_2$ and forms a sulfate, RhCl(SO$_4$)(PPh$_2$Me)$_3$, possessing infrared frequencies characteristic of bidentate coordination (Table II). Thus, merely by varying phosphine size and basicity, using essentially identical synthetic procedures, one can obtain (a) a four-coordinate complex with coplanar MSO$_2$, RhCl(PCy$_3$)$_2$(SO$_2$), (b) a five-coordinate species with presumably pyramidal MSO$_2$, RhCl(PPh$_2$Me)$_3$(SO$_2$), or (c) a five-coordinate chloride-bridged dimer with two pyramidal MSO$_2$ moieties, [RhCl(PPh$_3$)$_2$(SO$_2$)]$_2$. The influence of ligand on coordination geometry is quite striking in this system, well illustrating the usefulness of SO$_2$ as a probe to the bonding in transition-metal complexes.

Summary

Diagnostic properties of transition-metal–SO$_2$ complexes have been studied which, when considered in a groupwise fashion, have thus far proven to be quite accurate indicators of the mode of SO$_2$ bonding in a given complex.

In no case does the observed properties of a compound lead to an incorrect diagnosis of the SO$_2$ coordination geometry, although in several instances structural predictions cannot be made because the set of properties is not consistent with any of the "standard" sets. Although SO stretching frequencies may eventually prove to be less geometry dependent than they now appear to be, at this time they are by themselves fairly reliable structural indicators. For example, the third known case of S,O bonding was discovered[27] in Mo(CO)$_3$(phen)(η^2-SO$_2$) primarily due to scanning the literature for unusually low SO stretching frequencies with a separation (Δ) greater than 190 cm^{-1}. In certain systems, such as Rh^{I}–SO$_2$ complexes, predictions of the overall coordination geometry (e.g., five-coordinate bridged dimer vs. square planar) are also possible based on the diagnosed MSO$_2$ coordination geometry.

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Registry No. RhCl(PPh$_2$Me)$_3$(SO$_2$), 59889-13-3; [RhCl(PPh$_3$)$_2$(SO$_2$)]$_2$, 63455-06-1; Ir(SPh)(CO)(PPh$_3$)$_2$(SO$_2$), 68297-99-4; [RhCl(SO$_4$)(PPh$_3$)$_2$]$_2$, 68307-32-4; Ir(SPh)(SO$_4$)(CO)(PPh$_3$)$_2$, 68318-19-4; RuCl$_2$(SO$_4$)(PPh$_3$)$_2$, 68307-33-5; RhCl(SO$_4$)(PPh$_2$Me)$_3$, 68307-34-6; [RhCl(C$_2$H$_4$)$_2$]$_2$, 12081-16-2; RhCl(PPh$_3$)$_3$, 14694-95-2; [Ir(SO$_4$)(dppe)$_2$]Cl, 21519-09-5; Ir(SPh)(CO)(PPh$_3$)$_2$, 51935-95-6; RhCl(CO)(PPh$_3$)$_2$(SO$_2$), 16050-42-3; [Ir(dppe)$_2$]Cl, 15390-38-2; RuCl$_2$(PPh$_3$)$_2$(SO$_2$), 56105-07-8; CpMn(CO)$_2$(SO$_2$), 51508-47-5; Mo(CO)$_3$(phen)(η^2-SO$_2$), 68297-98-3; Ni(p$_3$)(SO$_2$), 58657-89-9; RhCl(PCy$_3$)$_2$(SO$_2$), 63742-63-2.

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Stereochemistry and Mechanisms of Mercury(II) Chloride Cleavage of *threo*-1,2-Dideuteriophenethyl Compounds of Iron, Manganese, and Tungsten

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Mercury(II) chloride cleaves the alkyl ligands from *threo*-PhCHDCHDFe$(CO)_2(\eta^5\text{-}C_5H_5)$ and *trans*-(*threo*-PhCHDCHD)W$(CO)_2(PEt_3)(\eta^5\text{-}C_5H_5)$ with retention of configuration, while that from *cis*-(*threo*-PhCHDCHD)Mn$(CO)_4PEt_3$ is cleaved with inversion of configuration, to give phenethylmercury(II) chloride. The first two reactions are believed to proceed via S_E(oxidative) processes, the last via an S_E2(inversion) mechanism. The differences are rationalized in terms of the expected energy gap between the HOMO and the metal–carbon σ-bonding orbital for each compound.

Cleavage of alkyl–, alkenyl–, or aryl–metal σ bonds by mercury(II) to give the corresponding organomercury(II) compounds (eq 1) is a reaction of great generality and even

$$RML_n + HgX_2 \rightarrow XML_n + RHgX \qquad (1)$$

R = alkyl, alkenyl, aryl L = neutral, anionic ligands

X = halide, acetate, etc.

of environmental importance[1] but one which is surprisingly poorly understood mechanistically when M is a transition metal. Thus although, as Jensen and Rickborn[2] and Matteson[3] have observed, considerable is known about metal-exchange reactions of organometallic compounds of the main-group metals, much less is known about similar reactions or organotransition-metal compounds.[4,5]

A key datum in the elucidation of the mechanism of a reaction such as (1), when the α-carbon atom of R is saturated, is the stereochemistry of the transformation at the α-carbon atom. We have previously demonstrated the advantages of the primary alkyl ligand *threo*-α,β-dideuteriophenethyl (*threo*-PhCHDCHD) in studying the stereochemistry of a variety of olefin elimination,[6,7] alkyl migration,[7,8] halogen cleavage,[9] and sulfination[8] reactions. We now consider the stereochemistry of mercury(II) chloride cleavage reactions of the compounds *threo*-PhCHDCHDFe$(CO)_2(\eta^5\text{-}C_5H_5)$ (I), *cis*-(*threo*-PhCHDCHD)Mn$(CO)_4PEt_3$ (II), and *trans*-(*threo*-PhCHDCHD)W$(CO)_2(PEt_3)(\eta^5\text{-}C_5H_5)$ (III), all of which react with mercury(II) chloride, as in (1), to give PhCHDCHDHgCl. When considered in conjunction with pertinent kinetics studies on similar compounds of the types $\eta^5\text{-}C_5H_5Fe(CO)_2R$,[4,10] $RMn(CO)_5$,[11,12] and $\eta^5\text{-}C_5H_5M(CO)_3R$ (M = Mo, W),[13] the stereochemical data lead to reasonable conclusions concerning the mechanisms of the reactions. Brief mention of some of this work has been made previously.[14,15]

Experimental Section

IR spectra were run on a Perkin-Elmer 180 spectrometer and NMR spectra were taken on a Bruker HX60 spectrometer. Compounds I,[9] II,[8] and III[8] were prepared as described in the literature, by treating *erythro*-PhCHDCHDOTs with the anions $[\eta^5\text{-}C_5H_5Fe(CO)_2]^-$, $[Mn(CO)_4PEt_3]^-$, and $[\eta^5\text{-}C_5H_5W(CO)_2PEt_3]^-$, respectively. All solvents were dried and deoxygenated before use.

Mercuration reactions were carried out by treating each phenethylmetal compound with a slightly more than equimolar amount of $HgCl_2$ in acetone (I) or methylene chloride (II, III). The courses of the reactions could be followed by observing the disappearance of the carbonyl stretching bands of I,[9] II,[8] and III[8] and the appearance of the carbonyl stretching bands of the products $\eta^5\text{-}C_5H_5Fe(CO)_2Cl$, *cis*-$Mn(CO)_4(PEt_3)Cl$, and *trans*-$\eta^5\text{-}C_5H_5W(CO)_2(PEt_3)Cl$, respectively. In all cases, the reactions appeared to proceed very cleanly, with no formation of metal–mercury compounds, as has been observed in some cases.[4] After completion of the reactions, the organomercury products were obtained by removing the solvent under reduced pressure, extracting the solids with petroleum ether, and then recrystallizing the residues from methylene chloride–petroleum ether. Phenethylmercuric chloride is a white, crystalline compound, mp 168–169 °C (lit.[16] 165.5–166 °C).

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