chloride with O-coordinated acetone.

Oxidation of **8** by molecular oxygen to the corresponding vanadyl compound occurs in solution; oxo(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(IV) (**12**), isolated by overnight oxygenation of a dichloromethane solution of **8**, was identical with that prepared from vanadyl acetate and **1** by use of a standard method.[15]

Acknowledgment. This research was supported by a grant from the Research Corp. and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. **1**, 97390-85-7; **2**, 97390-86-8; **3**, 407-91-0; **4**, 97390-87-9; **5**, 97390-88-0; **6**, 97390-90-4; **7**, 97390-91-5; **8**, 97403-32-2; **9**, 97403-33-3; **10**, 97403-34-4; **11**, 97390-93-7; **12**, 97390-94-8; **13**, 97390-95-9; (2-cyanoethyl)butylamine, 1789-37-3; butylamine, 109-73-9; acrylonitrile, 107-13-1; (3-aminopropyl)butylamine, 1555-68-6; salicylaldehyde, 90-02-8; (2-cyanoethyl)butylphosphine, 32272-08-5; tris(2-cyanoethyl)phosphine, 4023-53-4; *n*-butyl iodide, 542-69-8; bis(3-aminopropyl)butylphosphine, 6779-39-1; 6-aminocaproic acid, 60-32-2; trifluoroacetic anhydride, 407-25-0; dinicotinoyl chloride, 15074-61-0.

Contribution from the Departments of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, and University of North Dakota, Grand Forks, North Dakota 58202

Reaction of Vaska's Complex with Thionyl Chloride

RICHARD A. VANDERPOOL and HARMON B. ABRAHAMSON[*]

Received December 6, 1984

The title reaction has been studied by using ^{31}P NMR spectroscopy, and the products have been identified. If thionyl chloride is in excess throughout the reaction, only $IrCl_2(CO)(PPh_3)_2(SOCl)$ is formed. If Vaska's complex, $IrCl(CO)(PPh_3)_2$, is present in excess at some point, a substantial amount of decomposition is observed, some of it irreversible. The decomposition is due to attack of the reactive S(O)Cl ligand by Vaska's complex. One of the side products, $IrCl(CO)(PPh_3)_2(SO_2)$, displays a reversible exchange reaction in the presence of free Vaska's complex. Thermodynamic parameters for the exchange have been calculated from variable-temperature ^{31}P NMR data: $\Delta G^* = 40 \pm 8$ kJ mol^{-1}, $\Delta H^* = 74 \pm 5$ kJ mol^{-1}, $\Delta S^* = 113 \pm 20$ J K^{-1} mol^{-1}. These values are consistent with a dissociated intermediate in the exchange.

Few examples of complexes of sulfur monoxide (SO) are known.[1] This analogue of other two-atom ligands like O_2, NO, and CO is unstable in the free state[2] but is a possible intermediate in reactions of sulfur–oxygen compounds. We are currently engaged in the preparation of new complexes of sulfur monoxide, as the chemistry of these complexes can be important in the study of the formation of sulfur oxide pollutants and reagents for their removal.

Iridium complexes have been used as models for reactions important in transition-metal homogeneous catalysis,[3] including oxidative-addition reactions with small molecules.[4] Consequently, as part of a program to prepare new sulfur monoxide complexes, oxidative addition of thionyl chloride to iridium(I) complexes is of interest. The reaction of Vaska's complex,[5] $IrCl(CO)(PPh_3)_2$ (**1**), with thionyl chloride (Cl_2SO) is the first reaction of this series.

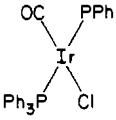
This reaction has been previously reported to yield $IrCl_2(CO)(PPh_3)_2(SOCl)$ (**2**). The addition of Vaska's complex to Cl_2SO in a 1:1 molar ratio reportedly[6] gives a 99% yield of **2**, based on elemental analysis and infrared spectra, but two carbonyl bands are observed. A second report of the synthesis[7] using excess Cl_2SO reaches the same conclusions, but with a simpler infrared spectrum. The confusion over spectra, and the report of dramatic color changes during the reaction,[6] has led us to reexamine this reaction with the aid of ^{31}P NMR spectroscopy. We find the system to be considerably more complex than previously reported and that under many conditions a mixture of products results.

Results and Discussion

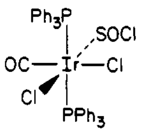
Reaction. Vaska's complex (**1**) reacts with excess thionyl chloride (Cl_2SO) (eq 1) at low temperature as previously described by Blake et al.[7] Pure $IrCl_2(CO)(PPh_3)_2(SOCl)$ (**2**) is isolated

$$IrCl(CO)(PPh_3)_2 + Cl_2SO \rightarrow IrCl_2(CO)(PPh_3)_2(SOCl) \quad (1)$$

as a yellow solid after recrystallization. The ^{31}P NMR spectrum



1



2

of this material in $CHCl_3$ solution shows four lines with the central doublet much more intense than the outer pair of lines (Figure 1G, Table I). Oxidative addition to $IrCl(CO)(PPh_3)_2$ (**1**) normally yields products with *trans*-phosphines, giving a singlet in the ^{31}P NMR spectrum.[8,9] The quartet observed for **2** is due to the phosphine ligands occupying different environments owing to the asymmetrical nature of the pyramidal S(O)Cl ligand; i.e., the phosphines are diastereotopic. This structure (**2**) is also consistent with infrared and ^1H NMR data collected by Blake et al.[7] The values of $^2J_{PP}$ (Table I) are consistent with *trans*-phosphines on iridium.[10a]

In contrast, when a solution of Cl_2SO is slowly added to a solution of **1** at room temperature or 263 K, the reaction proceeds

---

[*] To whom correspondence should be addressed at the University of North Dakota.

(1) (a) Schmid, G.; Ritter, G.; Debaerdemaeker, T. *Chem. Ber.* **1975**, *108*, 3008–3013. (b) Höfler, M.; Baitz, A. *Chem. Ber.* **1976**, *109*, 3147–3150. (c) Markó, L.; Markó-Monostory, B.; Madạch, T.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 226–227. (d) Winter, A.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1982**, *234*, 337–353. (e) Arulsamy, K. S.; Pandey, K. K.; Agarwala, U. C. *Inorg. Chim. Acta* **1981**, *54*, L51. (f) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130–3136.

(2) Schenk, P. W.; Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 402–409.

(3) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53–94.

(4) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335–344.

(5) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 2784–2785.

(6) Schmid, G.; Ritter, G. *Z. Anorg. Allg. Chem.* **1975**, *415*, 97–103.

(7) Markham, S. J.; Chung, Y. L.; Branum, G. D.; Blake, D. M. *J. Organomet. Chem.* **1976**, *107*, 121–127.

(8) Collman, J. P.; Sears, C. T., Jr. *Inorg. Chem.* **1968**, *7*, 27–32.

(9) Al-Jibori, S.; Crocker, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 319–321.

(10) (a) Pregosin, P. S.; Kunz, R. W. "NMR Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: New York, 1979; Vol. 16. (b) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectros.* **1969**, *2*, 345–422.

0020-1669/85/1324-2985$01.50/0

Table I. $^{31}P\{^1H\}$ NMR Data for Vaska's Complex and Reaction Products

complex[a]	$CHCl_3$, 304 K shift, ppm (^2J(PP), Hz)	$CHCl_3$, 213 K shift, ppm (^2J(PP), Hz)	C_6H_6, 304 K shift, ppm (^2J(PP), Hz)
$IrCl(CO)L_2$[b]	+23.8	+23.3	+23.8
$IrCl(CO)L_2(SO_2)$[c]	+9.7	+9.8	+9.7
$IrCl(CO)L_2(O_2)$	+5.2	+8.1	
$IrCl_2H(CO)L_2$	−2.5		−4.0
$IrCl_3(CO)L_2$	−16.0,[e] −17.6	−19.0	−19.4
$IrCl_2(CO)L_2(SOCl)$[d]	−3.7, −15.7 (482)	+2.0, −16.4 (374)	−5.6, −17.1 (460)

[a] L = triphenylphosphine. [b] Lit. +24.1 ppm in $CDCl_3$: Schramm, K. D.; Tulip, T. H.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 3183–3185. [c] Solution saturated with SO_2 gas. [d] Prepared by the method given in ref 7. [e] Second isomer, **3b**.

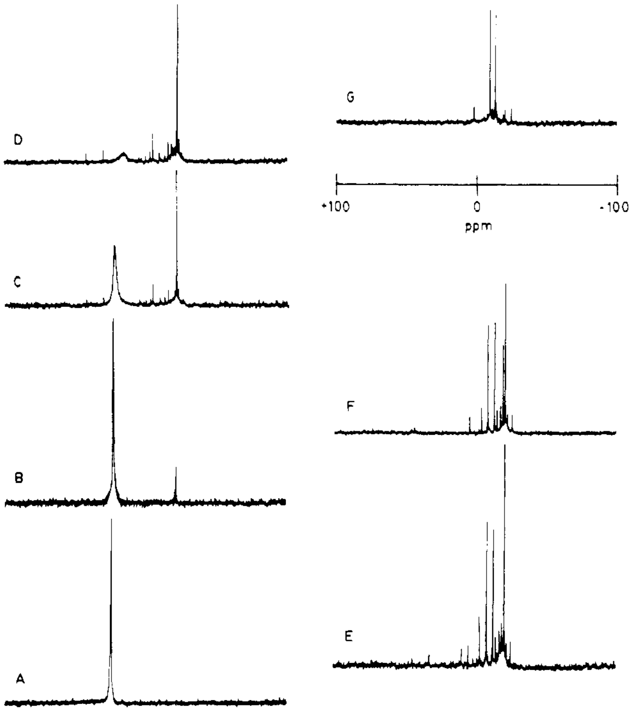


Figure 1. $^{31}P\{^1H\}$ NMR spectra in the region +100 to −100 ppm displaying the progress of the reaction of $IrCl(CO)(PPh_3)_2$ with additions of Cl_2SO, in $CDCl_3$ under nitrogen at 263 K: (A) $IrCl(CO)(PPh_3)_2$ with no Cl_2SO addition, yellow; (B) $^1/_{10}$ equiv of Cl_2SO, yellow; (C) $^1/_4$ equiv of Cl_2SO, green; (D) $^1/_2$ equiv of Cl_2SO, dark green; (E) $^3/_4$ equiv of Cl_2SO, yellow-orange; (F) 1 equiv of Cl_2SO, yellow-orange; (G) sample of **2** prepared by the method in ref 7, yellow. (Resonances for $IrCl_2(CO)(PPh_3)_2(SOCl)$ at 263 K are at +4.7, −7.0, −11.3, and −23.0 ppm; the resonance for $IrCl_3(CO)(PPh_3)_2$ at 263 K is at −18.4 ppm.)

Table II. Infrared Data for Vaska's Complex and Addition Products

complex[a]	ν(CO), cm^{-1} exptl[b]	ν(CO), cm^{-1} lit.[c]	ν(SO), cm^{-1} exptl[b]	ν(SO), cm^{-1} lit.[c]
$IrCl(CO)L_2$	1956	1950		
$IrCl(CO)L_2(SO_2)$	2024	2020	1201 1188 1050	1198 1185 1048
$IrCl(CO)L_2(O_2)$	2000	2000		
$IrCl_2H(CO)L_2$	2028	2024		
$IrCl_3(CO)L_2$	2084	2078		
$IrCl_2(CO)L_2(SOCl)$	2070	2053[d]	1117	1118[d]

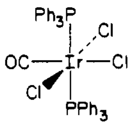
[a] L = triphenylphosphine. [b] This work; KBr. [c] From ref 19 except where noted. [d] Nujol; from ref 7.

through two distinct steps. The initial yellow solution begins turning green upon addition of the first few drops of Cl_2SO. The deepest color is reached at $^1/_2$ equiv of Cl_2SO, and the solution turns yellow-orange only near the end of the addition of a second $^1/_2$ equiv of Cl_2SO. When the reaction is worked up after the addition of a total of 1 equiv of Cl_2SO, the resulting pale yellow product has properties similar to those described previously.[6] However, the presence of a number of compounds is indicated by the ^{31}P NMR spectrum of the material, which contains at least four intense resonances, two identical with the strong lines assigned to **2** and two more at −16.0 and −17.6 ppm (304 K). When compared to spectra of material prepared by Blake's method,[7] infrared spectra (KBr) of this material have broader peaks in the carbonyl stretching region, which are on occasion split into two peaks.

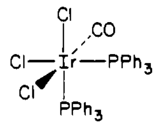
NMR Studies. The observation of a green color at low ratios of thionyl chloride to Vaska's complex is of interest, owing to the fact that it could represent a dinuclear SO-bridged complex.[11] Attempts to isolate the presumed green intermediate have been unsuccessful (see Experimental Section). To obtain a more accurate picture of the progress of the reaction, increments of Cl_2SO were gradually added to a solution of **1** in $CDCl_3$ at 263 K (Figure 1). A resonance due to **1** appears at +23.3 ppm (A) and shifts upfield and broadens with the addition of Cl_2SO (**B**, C). The green coloration seems to be associated with this broad peak, the position and width of which are dependent on the number of scans collected during the FT experiment. Other experiments show (see below) that this broad peak is due, not to any intermediate, but to contaminating side products of the reaction (see below). From the first addition, a peak also appears at −18.4 ppm that increases in intensity as more Cl_2SO is added.

By the time $^1/_2$ equiv of Cl_2SO has been added (D), the low-field resonance (+16 ppm) has become very broad and the most intense resonance is at −18.3 ppm. Addition of more thionyl chloride leads to the appearance of two new peaks at −6.7 and −11.1 ppm (E) and finally yet another (−16.6 ppm) by the time 1 equiv is reached (F). The dominant peaks in the final spectrum are at −18.3, −16.6, −11.0, and −6.6 ppm. The addition of excess Cl_2SO at this point leads to no change in the spectrum. Use of other solvents ($CHCl_3$, benzene) does not appear to affect the course of the reaction; similar changes are seen in ^{31}P NMR spectra of reactions run in these solvents. Positions of the bands are slightly sensitive to solvent and temperature (Table I).

The two high-field peaks in the ^{31}P NMR spectra and the presence of two bands in the carbonyl stretching region of the infrared spectrum point to the presence of additional products formed in preparations where **1** is in excess at some point,[6] as opposed to those where excess thionyl chloride is always present.[7] Several potential impurities have been prepared in order to check their properties and spectra (^{31}P NMR spectra, Table I; infrared spectra, Table II) against those of the contaminants. (The ^{31}P NMR spectra of these compounds has not been previously reported.[10]) It is apparent from the ^{31}P NMR spectra that the likely identity of the major contaminant (Figure 1F; −18.3 ppm resonance) is $IrCl_3(CO)(PPh_3)_2$ (**3a**).[8] Compound **3** is reported to appear as another isomer at times.[12] This isomer may be **3b**,



3a



3b

---

(11) An SO-bridged dinuclear complex of manganese is known.[1b]

(12) (a) Shaw, B. L.; Smithies, A. C. *J. Chem. Soc. A* **1968**, 2784–2787. (b) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983–6994.

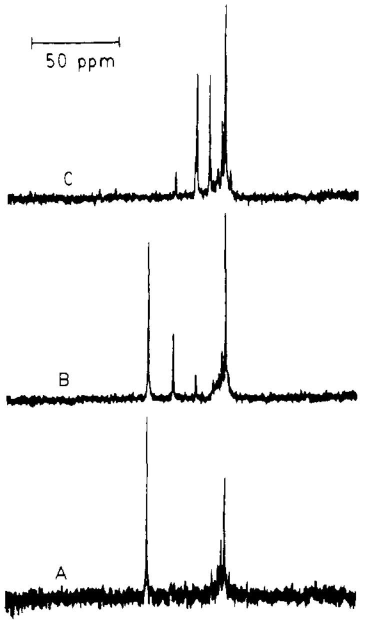
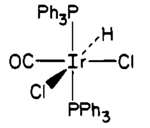


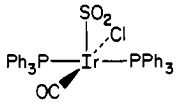
Figure 2. $^{31}P\{^1H\}$ NMR spectra in the region +100 to −100 ppm in $CHCl_3$ at 213 K for the addition of 1 equiv of $IrCl(CO)(PPh_3)_2$ to 1 equiv of $IrCl_2(CO)(PPh_3)_2(SOCl)$: (A) 5 min after mixing; (B) after 1.5 h, sample warmed slightly and recooled to 213 K; (C) after the addition of 10 equiv of Cl_2SO at room temperature and recooling to 213 K.

accounting for the additional high-field resonance (−16.6 ppm). These two peaks always occur together, in similar ratios, and do not disappear when the SOCl adduct **2** is decomposed by air or Vaska's complex. On one occasion, a reaction of **1** with chlorine gas gave both −16.6 and −18.3 ppm peaks, but this result was not consistently reproducible.

Addition of excess **1** to a solution containing a 1:1 stoichiometric ratio of **1** and Cl_2SO regenerates the green color present in the original 1:0.5 solution (Figure 1D). The ^{31}P NMR resonances for product **2** decrease, and new peaks appear at −2.5 and +9.5 ppm ($CHCl_3$, 263 K). These new products correspond to $IrCl_2H(CO)(PPh_3)_2$ (**4**) and $IrCl(CO)(PPh_3)_2(SO_2)$ (**5**) (Table I). The amount of trichloride **3** present also increases slightly.



4



5

To further investigate the nature of the complex(es) responsible for the green color, samples of pure **1** and **2** were mixed in $CHCl_3$ solution. The yellow solutions turn green immediately upon mixing. Room-temperature ^{31}P NMR spectra of this mixture show a resonance at −17.6 ppm, attributable to **3**, and a peak initially at +23.0 ppm. Over a 3-h period this latter peak shifts to +19.9 ppm, and the solution turns a lighter green color. Cooling the solution to 213 K results in a resolution of the shifting peak into two resonances corresponding to Vaska's complex (**1**) and its SO_2 adduct (**5**). Rewarming the solution leads to a coalescence into one average peak. Separate experiments demonstrate that there is intermolecular exchange of SO_2 between **1** and **5** (see below). Thus the broad low-field peak in the slow addition of Cl_2SO to **1** (Figure 1B–D) and the shifting resonance in mixtures of **1** and **2** can be attributed to a mixture of **1** and **5**, with a gradual increase in the amount of **5**.

Because $IrCl_2(CO)(PPh_3)_2(SOCl)$ (**2**) is relatively stable by itself in solution, even at room temperature, the observed decomposition of **2** in the presence of excess **1** indicates that the unsaturated **1** must attack **2**. Even mixing **1** and **2** at low temperature (213 K) results in nearly total reaction of **2** before 5 min has elapsed. The ^{31}P NMR spectrum of such a mixture (Figure 2A) shows little remaining **2**, with peak integrations showing 50% **1**, about 30% **3**, and some small unassigned peaks near those for **3** (20%). Little of the SO_2 adduct **5** is seen at this short time, but more appears as time goes on (Figure 2B), at the expense of Vaska's complex and the unassigned peaks. This behavior is consistent with the generation of sulfur monoxide, which is known to decompose[2] into SO_2 and S. Addition of thionyl chloride at this point results in the formation of the SOCl complex **2** (Figure 2C) from free **1** and from **5**, which is in equilibrium with **1** (see below).

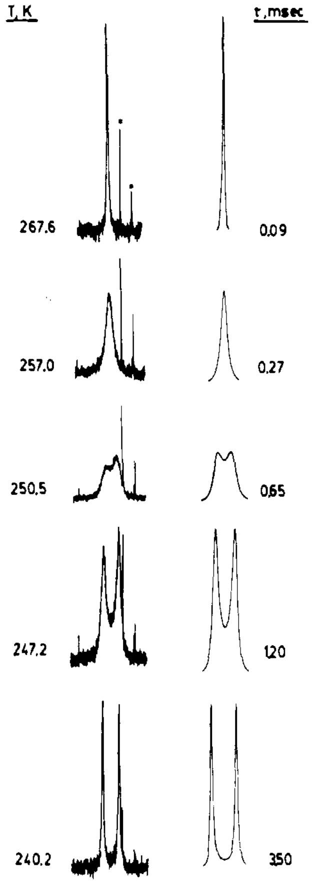


Figure 3. Observed (left) and calculated (right) $^{31}P\{^1H\}$ NMR spectra of an equimolar mixture of $IrCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2(SO_2)$ as a function of temperature. The symbol * represents impurities formed by slow decomposition.

In other contexts, the S–Cl bond in coordinated SOCl and $SOCl_2$ ligands is quite reactive, being susceptible to solvolysis by very weak acids such as methanol[7] and water,[13] which we also observe. The reactivity pattern displayed in the reaction of **1** and **2** is consistent with the attack of **1** on the S(O)Cl ligand to form **3** and SO, with initially no net reaction of added **1**. It cannot be established whether a short-lived dinuclear SO-bridged intermediate is involved (from the oxidative addition of the free S–Cl bond) or whether the decomposition occurs as a result of attack of **1** elsewhere on the SOCl ligand, e.g., at an oxygen or sulfur lone pair. Note that Lewis acid–base adducts are formed[14] with thionyl chloride and, e.g., $SbCl_5$.

SO_2 Exchange Reaction. Because of the formation of SO_2 adduct **5** in the title reaction, the interaction of **1** and **5** was examined via ^{31}P NMR spectroscopy. Whenever the concentration of SO_2 is less than the concentration of **1**, giving a mixture of **5** and **1**, there is a rapid exchange of SO_2 and an averaged NMR spectrum results at room temperature. Addition of 1 equiv of the bright green $IrCl(CO)(PPh_3)_2(SO_2)$ (**5**) to 2 equiv of IrCl-

---

[13] Broomhead, J. A.; Gill, N. S.; Hammer, B. C.; Sterns, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1234–1235.

[14] (a) Brunette, J. P.; Burgard, M.; Leroy, M. J. F.; Lucken, E. A. C. *J. Mol. Struct.* **1977**, *36*, 269–274. (b) Gutmann, V.; Steininger, A.; Wychera, E. *Monatsh. Chem.* **1966**, *97*, 460–467. (c) Lindqvist, I.; Zackrisson, M. *Acta Chem. Scand.* **1960**, *14*, 453–456.

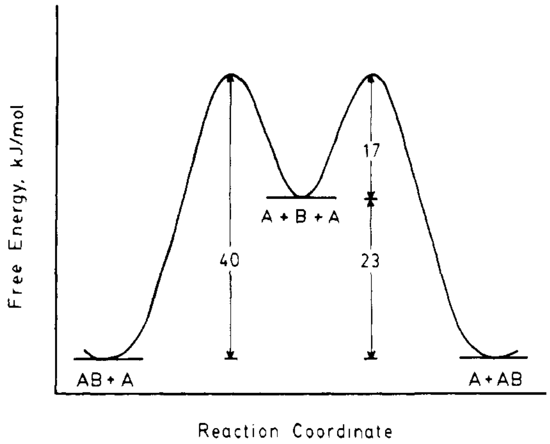


Figure 4. Free energy diagram incorporating the addition of SO_2 to Vaska's complex (eq 3 in text) and the exchange reaction (eq 2 in text). A = $IrCl(CO)(PPh_3)_2$ (**1**), B = SO_2, and AB = $IrCl(CO)(PPh_3)_2(SO_2)$ (**5**).

$(CO)(PPh_3)_2$ (**1**) gives a green solution with a single sharp ^{31}P NMR resonance at +17.5 ppm. Addition of another equivalent of the SO_2 adduct **5**, to make the solution equimolar in both complexes ($Ir:SO_2 = 2:1$), results in a shift of this single resonance to +15.1 ppm. Cooling the solution gives peaks of equal intensity at +23.1 and +9.6 ppm at 213 K. This behavior is consistent with an exchange of SO_2 that is rapid on the NMR time scale at room temperature.

Sulfur dioxide bonding to **1** is known to be reversible.[4,15] However, observation of the exchange using dynamic NMR (DNMR) techniques has not been previously reported. Variable-temperature NMR spectra were collected and analyzed by a complete band shape method (see Experimental Section). Experimental and calculated spectra are shown in Figure 3 for the exchange process shown in eq 2. Temperature-dependent

$$IrCl(CO)(PPh_3)_2 + IrCl(CO)(PPh_3)_2(SO_2) \rightleftarrows IrCl(CO)(PPh_3)_2(SO_2) + IrCl(CO)(PPh_3)_2 \quad (2)$$

rate constants from the analysis were used to calculate activation parameters. The resulting enthalpy of activation ($\Delta H^{\ddagger} = +74 \pm 5$ kJ mol^{-1}) and entropy of activation ($\Delta S^{\ddagger} = +113 \pm 20$ J mol^{-1} K^{-1}) were used to calculate the free energy of activation ($\Delta G^{\ddagger} = +40 \pm 8$ kJ mol^{-1} at 303 K).

Vaska has reported[16] thermodynamic values for the addition of SO_2 to **1** (eq 3). ($\Delta G^{\circ}_{303} = -17.3$ kJ mol^{-1} and $\Delta S^{\circ} = -88$ J mol^{-1} K^{-1}.) The thermodynamic parameters from both the addition and exchange reactions can be used to construct the reaction diagram in Figure 4.

$$IrCl(CO)(PPh_3)_2 + SO_2 \rightleftarrows IrCl(CO)(PPh_3)_2(SO_2) \quad (3)$$

Since the free energy of activation ($\Delta G^{\ddagger}$) for exchange is larger than the free energy of dissociation (ΔG° for the reverse of eq 3), the exchange reaction must pass through a transition state having a free energy larger than the stable states in either the exchange (eq 2) or the addition (eq 3) reaction. This transition state could have one of two limiting structures, a dissociated state consisting of 2 equiv of **1** plus 1 equiv of SO_2 or a bridged ($M-SO_2-M$) structure. Dinuclear complexes bridged through SO_2 are known, e.g. $[IrH(CO)_2L]_2SO_2$,[17] and would tend to support a dinuclear transition state. The value found here for $\Delta S^{\ddagger}$ (for eq 2) is larger than ΔS° for the reverse of eq 3, implying that the transition state has a disorder greater than 2 equiv of **1** plus 1 equiv of SO_2. This rules out a bridged intermediate structure, a conclusion supported by the large positive $\Delta S^{\ddagger}$. The transition state may be pictured as a dissociated one consisting of 2 equiv of **1** plus 1 equiv of SO_2 but must also have additional disorder, perhaps in the solvent sphere, in order to account for the increased entropy. While the intermediate state (A + B + A) shown in Figure 4 is not required for the exchange reaction, reorganization of a solvent sphere to give the dissociated intermediate should be rapid. The resulting small barrier to adduct formation is consistent with the rapid rates reported[4] for reaction 3.

Note that the impurity peaks in Figure 3 (one due to $IrCl(CO)(PPh_3)_2(O_2)$) stay sharp over the whole temperature range. This indicates that exchange of the dioxygen complex with free **1** is slow on the NMR time scale at these temperatures. This is consistent with kinetic data[4] that put the rate constant for the exchange of SO_2 with **1** several orders of magnitude higher than the corresponding rate constants for O_2.

Conclusion. The reaction of **1** with excess Cl_2SO gives **2**. The unsaturated d^8 complex **1** can interact with adduct **2** to immediately generate the trichloride **3** and probably also free SO, which decomposes[2] to SO_2, which can then interact with Vaska's complex to make **5**. The reaction of **1** with **2** can be termed catalytic, because substantially all of the added **1** is regenerated in the early stages of the reaction. These observations correlate well with previous experience. The preparation of Blake et al.[7] uses excess thionyl chloride. At no time is **1** in excess, explaining the lack of contamination of the product. An attempted preparation after the method of Schmid and Ritter[6] results in the presence of excess **1** throughout most of the reaction, leading to decomposition primarily to **3**, since any **5** produced can react with Cl_2SO. The elemental analysis quoted in ref 6 is consistent with a 4:1 mixture of **2** and **3**. Contrary to expectations, no evidence for any binuclear intermediate is found. Exchange between **1** and **5** is observed and likely proceeds through a dissociated intermediate.

Experimental Section

Materials. All reactions were carried out under a nitrogen atmosphere, except where noted. Thionyl chloride was purified by trap to trap distillation and stored under nitrogen in a thick-walled glass ampule closed with a Teflon stopcock. Water and ethanol were removed from chloroform with 4-Å molecular sieves and the chloroform was stored under nitrogen in the dark. Benzene was also dried over 4-Å molecular sieves and stored under a nitrogen atmosphere. Vaska's complex, $IrCl(CO)(PPh_3)_2$, was purchased from Alfa or prepared from $IrCl_3 \cdot 3H_2O$ (Alfa) following literature methods.[18] Other complexes prepared according to literature methods were $IrCl_2H(CO)(PPh_3)_2$[5] and $IrCl_2(CO)(PPh_3)_2(SOCl)$.[6,7]

Preparation of $IrCl(CO)(PPh_3)_2(SO_2)$ (5). Vaska's procedure[19] was modified by using solutions of $IrCl(CO)(PPh_3)_2$ (0.1 g) in degassed benzene or chloroform. Slowly bubbling $SO_2(g)$ (Matheson) into the solution for 15 min produced a green color. Low-temperature (213 K) ^{31}P NMR spectra showed a singlet (Table I) and no $IrCl(CO)(PPh_3)_2$ resonance. After evaporation of the solution to dryness under a nitrogen gas flow, an infrared spectrum of the residue (KBr) showed bands for the SO_2 complex as reported by Vaska[19] and a small amount of starting material (**1**).

Preparation of $IrCl_3(CO)(PPh_3)_2$ (3). The addition of chlorine gas to $IrCl(CO)(PPh_3)_2$ is known[8] to give $IrCl_3(CO)(PPh_3)_2$. After 0.1 g of $IrCl(CO)(PPh_3)_2$ was dissolved in nitrogen-purged C_6H_6 or $CHCl_3$, chlorine gas (Matheson) was bubbled through the solution for 15 min. The ^{31}P NMR spectrum generally showed only one peak, and the infrared spectrum of the evaporated solid matched the literature values (Table II). In one case, two peaks were observed in the ^{31}P NMR spectrum when a published synthesis was used,[8] but the peak at −16 ppm disappeared upon recrystallization and could not be reproduced.

Preparation of $IrCl(CO)(PPh_3)_2(O_2)$. The known oxygen adduct of Vaska's complex[20] was prepared by bubbling oxygen through a nitrogen-purged $CHCl_3$ solution of **1**. During the reaction, the ^{31}P NMR resonance of $IrCl(CO)(PPh_3)_2$ lost intensity while that of $IrCl(CO)(PPh_3)_2(O_2)$ gained intensity. Conversion was ultimately 100% by NMR, giving an orange solution.

Spectroscopy. ^{31}P NMR spectra were recorded on an IBM NR-80B spectrometer at 32.38 MHz with a D_2O external lock, resulting in an approximately ±0.5 ppm error for all reported ^{31}P NMR chemical shift values. Broad-band irradiation to decouple protons was used. Spectra

---

(15) Ashcroft, S. J.; Mortimer, C. T. *J. Organomet. Chem.* **1970**, *24*, 783–786.

(16) Vaska, L. *Inorg. Chim. Acta* **1971**, *5*, 295–300.

(17) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47–100.

(18) Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 844–851.

(19) Vaska, L.; Bath, S. S. *J. Am. Chem. Soc.* **1966**, *88*, 1333–1335.

(20) Vaska, L. *Science (Washington, D.C.)* **1963**, *140*, 809–810.

were recorded in $CHCl_3$, $CDCl_3$, or C_6H_6 and referenced to a 1% H_3PO_4 (0.0 ppm) external secondary reference. A low-field positive chemical shift convention is used in reporting data. In all cases a 10-mm variable-frequency probe was used.

Low-temperature experiments were conducted on the NR-80B using a variable-temperature unit. A nitrogen gas flow, from liquid nitrogen, was passed over a resistance heater and used to obtain the required temperature with a stability of ±0.5 K by use of a thermocouple-regulated temperature-control unit. The temperature reading was calibrated with a low-temperature thermometer held in a $CHCl_3$-filled NMR tube by a septum and read after reaching thermal equilibrium in the probe. Temperature calibration was made after the data collection was concluded for a given temperature.

Infrared spectra were collected by using KBr pellets on Perkin-Elmer 283B and Beckman IR 4250 spectrophotometers. Calibration used polystyrene and carbon monoxide.

Reaction of $IrCl(CO)(PPh_3)_2$ with Cl_2SO at 263 K. A 0.2-g sample of **1** was dissolved in 10 mL of $CDCl_3$, and 5 mL of solution was transferred to a 10-mm NMR tube capped with a rubber septum. The sample was held at 263 K by a constant-temperature bath. A solution of 1:3 Cl_2SO in $CDCl_3$ was prepared, and additions of the Cl_2SO solution were made into the NMR tube through the septum via a syringe. Additions were made so as to obtain the $IrCl(CO)(PPh_3)_2$ to Cl_2SO ratios shown in Figure 1. The solution was rapidly mixed by inverting the tube and then was returned to the low-temperature bath. The sample was taken to the spectrometer in the low-temperature bath and placed into the 263 K NMR probe. Further aliquots of Cl_2SO and **1** were added with the same technique.

Attempts To Isolate the Green Intermediate in the Title Reaction. An experimental procedure for the preparation of $IrCl_2(CO)(PPh_3)_2(SOCl)$[6] was followed, except that the amount of Cl_2SO used was reduced to $^1/_2$ equiv. The mixing of 0.616 g (0.789 mmol) of $IrCl(CO)(PPh_3)_2$ and 0.029 mL (0.40 mmol) of Cl_2SO in benzene gave an emerald green solution. Reduction of the volume by pumping off some of the benzene resulted in the precipitation of an orange solid and left a yellow-orange solution. A hexane precipitation of the filtrate yielded a yellow solid. By infrared spectroscopy, both solids were mixtures of $IrCl_2(CO)(PPh_3)_2(SOCl)$ and $IrCl(CO)(PPh_3)_2$. Other attempts at precipitation or evaporation invariably led to yellow or orange products and disappearance of the green color.

Variable-Temperature Study of $IrCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2(SO_2)$. A sample was prepared under a nitrogen atmosphere in chloroform having equal concentrations of **1** and **5** (0.05 M in each complex). ^{31}P NMR spectra were collected from 213 to 303 K, and nine points from 240.2 to 267.6 K were used in the analysis. For each temperature the mixture of **1** and **5** was allowed to reach thermal equilibrium in the probe (~15 min for small temperature changes) after which FIDs were collected and stored on disk. A sample of **1** (0.05 M in chloroform) was next allowed to equilibrate in the probe and its FID stored. Finally, the temperature was determined as described above.

Experimental spectra for temperatures 240.2, 243.0, 247.0, 250.0, 253.0, 257.0, 260.0, 265.0, and 270.0 K were hand-digitized and subjected to a complete band shape analysis as described by Sandström.[21] The shape function[22] for a noncoupled, equal-population, two-site exchange was used in the nonlinear least-squares program NLLSQ.[23] Nonexchange bandwidths were determined on **1** over the experimental temperature range. It was assumed that the nonexchange bandwidth for **5** was the same as for **1**. The NLLSQ fit parameters were used to calculate a value for the exchange lifetime, τ, for each spectrum. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were then calculated[21] from a plot of ln $(1/T\tau)$ vs. $1/T$. The linear least-squares analysis of this plot using the program LINGEN[24] used weighted values for both x and y.

Acknowledgment. Partial support for this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. We thank Dr. B. M. Fung for his help on the band shape analysis.

Registry No. **1**, 15318-31-7; **2**, 59599-05-2; **3a**, 22788-78-9; **3b**, 24810-96-6; **4**, 26545-07-3; **5**, 15692-64-5; Cl_2SO, 7719-09-7; $IrCl(CO)(PPh_3)_2(O_2)$, 15187-10-7.

---

(21) Sandström, J., "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982.

(22) Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4134–4140.

(23) The program is a local modification by B. M. Fung of the general nonlinear least-squares program NLLSQ written in Apple Basic (Christian, S. D.; Tucker, E. E. *Am. Lab.* (*Fairfield, Conn.*) **1982**, *14* (9), 31–36).

(24) Christian, S. D.; Tucker, E. E. *J. Chem. Educ.* **1984**, *61*, 788.

Contribution from the Department of Chemistry,
University of Calgary, Calgary, Alberta, Canada T2N 1N4

Reactions of Hydride with Tungsten Complexes Containing Organosulfur Ligands: Synthesis and Characterization of (μ-Hydrido)bis(μ-dimethyl sulfide)ditungsten(III) Species[1]

P. MICHAEL BOORMAN,* KELLY J. MOYNIHAN, VIKRAM D. PATEL, and JOHN F. RICHARDSON

Received December 11, 1984

The reaction between $WCl_4(Me_2S)_2$ and an excess of Et_3SiH in CH_2Cl_2 solution was found to produce HCl, H_2, and trace quantities of CH_4; the major tungsten-containing product was identified as the diamagnetic, ditungsten(III) hydrido complex, $Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_2(Me_2S)$ (**1**). X-ray crystallographic analysis of a chloroanionic derivative of **1**, $[Ph_4P][Cl_3W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3]\cdot 2CH_2Cl_2$, revealed that this series of dinuclear compounds possesses a confacial bioctahedral framework distorted by a strong W–W (≈triple) bond. The tetraphenylphosphonium salt crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.620$ (2) Å, $b = 12.841$ (2) Å, $c = 14.667$ (2) Å, $\alpha = 79.45$ (1)°, $\beta = 81.17$ (1)°, $\gamma = 76.45$ (1)°, and $Z = 2$. The structure refined to $R = 0.039$ and $R_w = 0.037$ based on 3413 observed data. The position of the μ-H atom was located in the difference map, but could not be successfully refined. The presence of the hydride ligand is confirmed by infrared and NMR spectroscopic results, including data for corresponding deuterio derivatives for comparison. The ^1H NMR signal for the μ-H in these complexes was observed at relatively low field (δ ~3.7), and this chemical shift was observed to vary in an unusual manner with temperature, moving upfield as the temperature is lowered. Spin coupling between the hydride ligand and ^{183}W nuclei remains constant, with $J(^{183}W\text{–}^1H) = 110 \pm 3$ Hz, over the temperature range −80 to +22 °C. The ^1H NMR spectrum of the neutral complex **1**, over the temperature range −70 to +20 °C, is interpreted on the basis of the existence of a C_s isomer and an enantiomeric pair of C_1 isomers. With increasing temperature the enantiomers interconvert, through a process believed to involve the exchange of two Me_2S ligands between terminal and bridging sites.

Introduction

The activation of C–S bonds in organosulfur species toward cleavage upon coordination of the sulfur atom to a metal center is a topic of potential relevance to the process of catalytic hydrodesulfurization. Most of the mechanisms proposed for this process assume that in the activation of H_2 to enable the hydrogenolysis of the C–S bond, the hydrogen is provided by S–H groups on the metal sulfide catalyst surface.[2,3] Rakowski Dubois

---

(1) Taken in part from: Moynihan, K. J. Ph.D. Thesis, University of Calgary, 1983.

(2) (a) Massoth, F. E.; Kirby, C. L. *J. Catal.* **1977**, *47*, 300. (b) Massoth, F. E. *J. Catal.* **1977**, *47*, 316.