At the second step, ethylene enters a position which is trans to the Cl atom rather than to the NH_2 group of the amino acid anion, since the order of trans effect is Cl > NH_2. Once the *cis*-dichloro complex (III) is obtained, the O-trans isomer (II) can be derived from it through hydrolysis. We have succeeded in the preparation of the *cis*-dichloro complexes containing glycine, L-alanine, and sarcosine. However, the corresponding O-trans isomers were not isolated for the sarcosine and glycine complexes due to their high solubility in aqueous solution.

Uv Spectra.—As is shown in Figure 1, the uv spectrum of *N-trans*-$PtCl(C_2H_4)$(L-ala) in 3 *N* HCl is almost identical with that of Zeise's anion. This result suggests that the L-alanino ligand in this compound is completely dissociated in 3 *N* HCl solution to give the $PtCl_3(C_2H_4)^-$ ion, as is shown in the first reaction scheme. The strong trans effect of ethylene is responsible for the cleavage of the Pt–N bond trans to it. In fact, (glyH)[$PtCl_3(C_2H_4)$] was isolated from a 3 *N* HCl solution of *N-trans*-$PtCl(C_2H_4)$(gly).

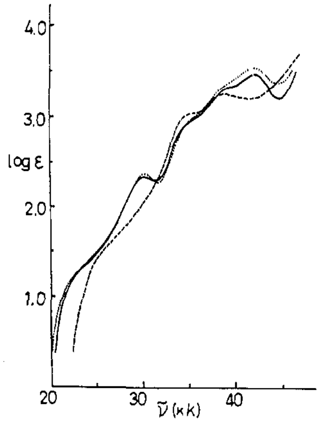

Figure 1.—Absorption spectra of *N-trans*-$PtCl(C_2H_4)$(L-ala) (-----) in H_2O, *N-trans*-$PtCl(C_2H_4)$(L-ala) (——), and K[$PtCl_3$-(C_2H_4)] (......) in 3 *N* HCl.

Figure 2 shows that the uv spectrum of *O-trans*-$PtCl(C_2H_4)$(L-ala) in 3 *N* HCl is almost identical with that of *cis*-$PtCl_2(C_2H_4)$(glyH) in the same solvent. This result indicates that the Pt–O bond of the O-trans isomer is cleaved due to the strong trans effect of ethylene but its Pt–N bond remains intact because it is trans to chlorine. Thus, the present uv study supports the validity of the N-trans and O-trans structures proposed for the two isomers of $PtCl(C_2H_4)$(L-ala).

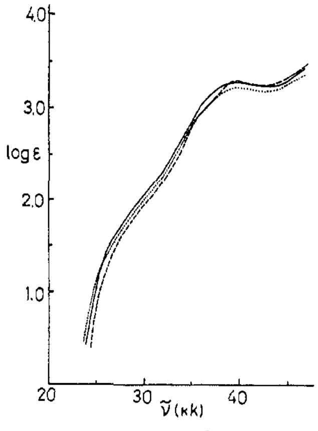

Figure 2.—Absorption spectra of *O-trans*-$PtCl(C_2H_4)$(L-ala) (-----) in H_2O, *O-trans*-$PtCl(C_2H_4)$(L-ala) (——), and *cis*-$PtCl_2$-(C_2H_4)(glyH) (......) in 3*N* HCl.

Infrared Spectra.—The cis structures of the $PtCl_2$-(C_2H_4)(amH) type of complexes (am = gly, sar, and L-ala) are supported by the appearance of two strong Pt–Cl stretching bands in the region from 350 to 300 cm^{-1}.[6] These compounds also exhibit strong COOH bands of un-ionized amino acids near 1720 cm^{-1} which are characteristic of the unidentate coordination.[5a]

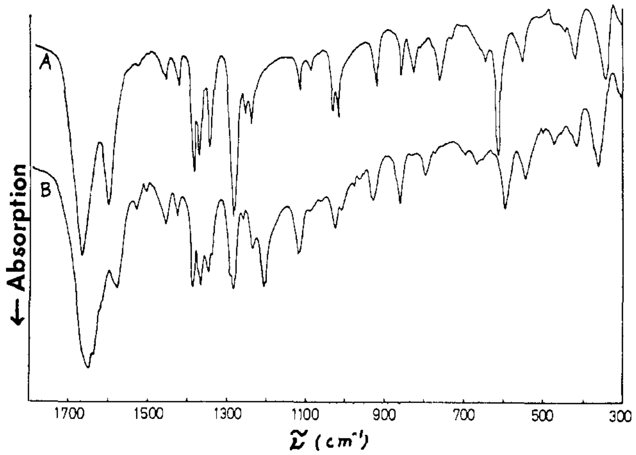

Figure 3.—Infrared spectra of (A) O-trans isomer and (B) N-trans isomer of $PtCl(C_2H_4)$(L-ala).

Figure 3 shows that the spectra of the N-trans and O-trans isomers of $PtCl(C_2H_4)$(L-ala) are essentially similar in the whole frequency region. They can be distinguished, however, by comparing the detailed features of the spectra. It is interesting to note that the Pt–Cl stretching frequency of the O-trans isomer (340 cm^{-1}) is definitely lower than that of the N-trans isomer (360 cm^{-1}). This is because the Pt–Cl bond of the O-trans isomer is weaker than that of the N-trans isomer since the trans effect of the NH_2 group in the former is stronger than that of the COO^- group in the latter. Thus, our ir study again confirms the proposed N-trans and O-trans structures for the two isomers of $PtCl$-(C_2H_4)(L-ala) prepared in this investigation.

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Perfluorodimethyl Sulfoxide and Bis(trifluoromethyl)sulfur Difluoride

By Edward W. Lawless

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Perfluorodimethyl sulfoxide, $(CF_3)_2SO$, has recently been synthesized in this laboratory and is believed to be the first known example of a perfluorodialkyl sulfoxide. Previous studies of the fluorination of sulfoxides electrochemically[1,2] with IF_5[3] or with AgF_2[3] failed to give the perfluoroalkyl sulfoxides, and efforts to oxidize $(CF_3)_2S$ were without success.[4] The $(CF_3)_2SO$ has been obtained by a two-step reaction *via* the reactive intermediate bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$

$$(CF_3)_2S + F_2 \xrightarrow[C_2F_6]{-78°} (CF_3)_2SF_2 \xrightarrow[\text{or glass}]{H_2O} (CF_3)_2SO$$

Experimental Section

Synthesis.—The $(CF_3)_2S$ (10 mmol) prepared by the method of Lawless and Harman[4] and C_2F_6 (92 mmol) were transferred through a vacuum line into a valved 425-ml stainless steel cylinder (pretreated with 200 mm of warm F_2) and then cooled to −196°. Fluorine, which had been passed through NaF and −196° traps, was added until the pressure was 120 mm in the reactor ($\lesssim 10$ mmol). The reactor was placed in a dewar of Dry Ice and allowed to warm to room temperature over 40 hr. The C_2F_6 was removed at −78° and shown by infrared analysis to contain small amounts of CF_2O and SF_2O (from adventitious moisture or metal oxides), $(CF_3)_2SF_2$, and unreacted $(CF_3)_2S$. The reactor retained 5.6 mmol of volatile product which was shown by infrared analysis to be $(CF_3)_2SF_2$ contaminated with hydrolysis byproduct $(CF_3)_2SO$. The $(CF_3)_2SF_2$ was stored overnight in a 1-l. glass bulb to complete the conversion to $(CF_3)_2SO$. By-product SiF_4 was pumped off at −78°. Upon warming the product, about 0.5 ml of liquid was obtained which was shown by the analyses described below to be $(CF_3)_2SO$, containing only a few per cent total of $(CF_3)_2SO_2$, CF_3SFO, residual $(CF_3)_2S$, and possibly C_2F_6 as impurities.

Characterization of $(CF_3)_2SO$.—The $(CF_3)_2SO$ was identified by its molecular weight (calcd, 186.1; found, 185.5 by the vapor density method), mass spectrum, ^{19}F nmr spectrum, and infrared spectrum. The mass spectrum at 70 eV had the following ion intensities: $(CF_3)_2SO_2^+$ trace, $(CF_3)_2SO^+$, 0.4; $(CF_3)_2S^+$, 1.0; $CF_3SCF_2^+$, 0.1; CF_3SCF^+, 0.1; $C_2F_5^+$, 2.5; CF_3SO^+, 1.0 CF_3S^+, 5.6; CF_2SO^+, 5.9; *m/e* 96, 0.1; CF_2S^+, 3.1; *m/e* 81 ($C_2F_3^+$?), 1.3; CSO_2^+, 0.5; CF_3^+, 100.0; SFO^+ 3.5; SO_2^+, 1.5; CFS^+, 1.7; CSO^+, 5.2; SF^+, 1.6; CF_2^+, 1.8; SO^+, 4.4; CS^+, 6.9; S^+, 5.2; CF^+, 2.0. The ^{19}F nmr spectrum showed a single strong resonance at 70.0 ppm (*vs.* external $CFCl_3$) as expected for equivalent fluorines in the CF_3 groups. (Detectable as trace impurities in the nmr sample were $(CF_3)_2S$ at 40.1 ppm,[4] CF_3SFO at 23.8 and 84.1 ppm,[5] and a third impurity suspected to be either $(CF_3)_2SO_2$ or C_2F_6 superimposed at 84.1 ppm.) The infrared spectrum of $(CF_3)_2SO$, obtained on a sample purified by vacuum line fractionation, shows (Figure 1) very strong bands at 1245 (S→O), 1182 (C–F asym), 1122, and 1102 cm^{-1} (C–F sym) and medium-intensity bands at 1283, 775 (C–S and/or CF_3 def), 593, 558, and 471 cm^{-1}.

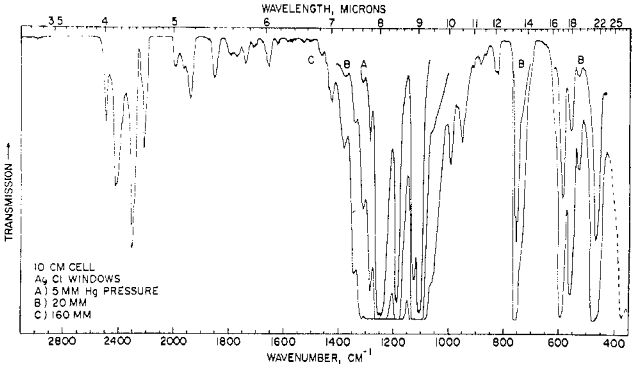

Figure 1.—Infrared spectrum of perfluorodimethyl sulfoxide.

The $(CF_3)_2SO$ is a white solid and a colorless liquid, mp −52°. Equilibrium vapor pressures were determined at 10 temperatures over the range −63.5–25° (using a 0–760-mm gauge). The data fit the equation $\log P_{Torr} = 7.592 - (1.456/T) \times 10^3$ over the range −30–25°, yielding an extrapolated normal boiling point of 36°, a heat of vaporization of 6.65 kcal/mol, and a Trouton constant of 21.5 eu.

No reaction was observed when moist air was admitted to a sample of $(CF_3)_2SO$ in an infrared cell and allowed to stand overnight. No reaction was observed between $(CF_3)_2SO$ and BF_3 at −78 or at 25°. Although $(CF_3)_2SO$ appears to be quite stable at room temperature, partial decomposition was observed after 100 mm of $(CF_3)_2SO$ was heated for 2 hr at 200° in a Pyrex tube. Infrared and mass spectroscopic analysis of the products (all of which appeared to be gaseous) indicated the presence of SiF_4, CF_2O, CF_2S, CO_2 $(CF_3)_2S$, and materials of molecular weights of 202 (possibly $(CF_3)_2S_2$) and 250 (possibly $CF_3SO_2S(O)CF_3$, as suggested also by a strong unidentified infrared band at 1425 cm^{-1} in the SO_2 region).

Bis(trifluoromethyl)sulfur Difluoride.—No attempt was made to obtain a high-purity sample of $(CF_3)_2SF_2$, but its appearance upon fluorination of $(CF_3)_2S$ and disappearance upon hydrolysis of the fluorination product to $(CF_3)_2SO$ were observed by infrared studies. Rapid hydrolysis is known to occur with SF_4[6] and its derivatives, CF_3SF_3[5,7,8] and $C_6H_5SF_3$.[7] (In contrast, $[(CF_3)_2CF]_2SF_2$ was reported[9] to be hydrolytically stable[10] even at 100° in the vapor phase, while $(CF_3)_2CFSF_3$ has been reported both to hydrolyze[9] and to be hydrolytically stable.[11]) The $(CF_3)_2SF_2$ has a very strong infrared band at 678 cm^{-1} (S–F stretch) and a medium-intensity band at 507 cm^{-1} (SF_2 bend).[12] Other bands appear to be at 1216 (s), 1080 (s), and 760 cm^{-1} (w).

The tentative identification of perfluorodimethyl sulfone[2] as a minor by-product in the preparation of $(CF_3)_2SO$ was confirmed as follows. $(CF_3)_2SO$ was condensed into the cold finger of an infrared cell and treated at −80° with an F_2–N_2 mixture. Fractionation of the reaction mixture and infrared analysis revealed the formation of several known degradation products, a small amount of $(CF_3)_2SO_2$, and two unidentified products, which were not successfully separated. The $(CF_3)_2SO_2$ was again observed mass spectrometrically and identified by infrared analysis (strong S→O band at 1433 cm^{-1}, compared to bands at 1476 cm^{-1} for[13] CF_3SO_2F and 1425 cm^{-1} for[14] $(C_2F_5)_2SO_2$).

Equipment.—The nmr and mass spectra were obtained using Varian Associates HA-100 and Atlas CH-4B spectrometers, respectively. The infrared spectra were recorded on a Beckman IR-12 spectrophotometer, employing a Kel-F cell[15] with AgCl windows for the glass-reactive $(CF_3)_2SF_2$ samples. Materials were handled in a glass-free vacuum line.

Discussion

A comparison of the structures of $(CF_3)_2SO$ and dimethyl sulfoxide (DMSO) is of interest. The infrared spectra indicate a shortened S→O bond in $(CF_3)_2SO$ (S→O stretch at 1245 cm^{-1}) compared to that (1.48 Å) in DMSO (S→O stretch[16] at 1102 cm^{-1}). It is, how-

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(12) The bands appear analogous to the 708- and 517-cm^{-1} bands[6] of CF_3SF_3.

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ever, longer than that (1.412 Å) in SF_2O (S→O stretch[17] at 1331 cm^{-1}) and near that (1.45 Å) of Cl_2SO (S→O stretch[18] at 1229 cm^{-1}) and that of CF_3SFO (S→O stretch[5] at 1269 cm^{-1}). The boiling point, 36°, of $(CF_3)_2SO$ is slightly higher than one would have expected based on the value of 15.6° for $(CF_3)_2SO_2$ mentioned by Banks and Haszeldine[19] and the much lower values of perfluorosulfur compounds of comparable molecular weights (*e.g.*, CF_3SF_5: mol wt 196; bp −20°). The Trouton constant, however, indicates that $(CF_3)_2SO$ is, unlike DMSO,[17] an unassociated liquid. The $(CF_3)_2SO$ therefore appears to have a sizable dipole moment, but it is probably nearer those[20] of Cl_2SO (1.452 D) and SF_2O (1.618 D) than that (4.3 D) of DMSO.[17] The $(CF_3)_2SO$ should prove to have some interesting solvent properties.

Acknowledgment.—The nmr and mass spectra were obtained by Mrs. Hope Miller and Mr. George Vaughn.

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Mechanism of the Tris(triphenylphosphine)platinum(0)-Catalyzed Oxidation of Triphenylphosphine

BY JACK HALPERN*[1] AND A. L. PICKARD

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We have previously interpreted the $Pt(P(C_6H_5)_3)_3$-catalyzed oxidation of $P(C_6H_5)_3$ in terms of the stepwise mechanism depicted by[2]

$$Pt(P(C_6H_5)_3)_3 + O_2 \xrightarrow{k_1} Pt(P(C_6H_5)_3)_2O_2 + P(C_6H_5)_3 \quad (1)$$

$$Pt(P(C_6H_5)_3)_2O_2 + P(C_6H_5)_3 \xrightarrow{k_2} [Pt(P(C_6H_5)_3)_3O_2] \xrightarrow[\text{fast}]{2P(C_6H_5)_3} Pt(P(C_6H_5)_3)_3 + 2(C_6H_5)_3PO \quad (2)$$

$$2P(C_6H_5)_3 + O_2 \xrightarrow{Pt(P(C_6H_5)_3)_3} 2(C_6H_5)_3PO \quad (3)$$

Our conclusions were based upon kinetic investigations of the two separate component reactions, each of which was followed spectrally by monitoring the concentration of $Pt(P(C_6H_5)_3)_3$. The kinetic results yielded by these investigations are summarized by the two rate laws

$$-d[Pt(P(C_6H_5)_3)_3]/dt = k_1[Pt(P(C_6H_5)_3)_3][O_2] \quad (4)$$

$$d[Pt(P(C_6H_5)_3)_3]/dt = k_2[Pt(P(C_6H_5)_3)_2O_2][P(C_6H_5)_3] \quad (5)$$

These results are consistent with the mechanism postulated above but do not unambiguously establish (i) whether the initial reaction between $Pt(P(C_6H_5)_3)_3$ and O_2 involves the displacement of $P(C_6H_5)_3$ as depicted above or (as has been suggested elsewhere),[3] in part at least of $(C_6H_5)_3PO$, in accord with the alternative overall stoichiometry of

$$Pt(P(C_6H_5)_3)_3 + 1.5O_2 \longrightarrow Pt(P(C_6H_5)_3)_2O_2 + (C_6H_5)_3PO \quad (6)$$

or (ii) whether the formation of $Pt(P(C_6H_5)_3)_2O_2$ results exclusively from the reaction of O_2 with $Pt(P(C_6H_5)_3)_3$ in accord with eq 1 (or eq 6) or whether there is an *additional* contribution (eq 7) from a reaction with $Pt(P(C_6H_5)_3)_2$ which is known to coexist in solution in equilibrium with $Pt(P(C_6H_5)_3)_3$.[2,4] Since the reactions of several other molecules, *e.g.*, acetylenes, with $Pt(P(C_6H_5)_3)_3$ to form adducts such as $Pt(P(C_6H_5)_3)_2$(acetylene) have been shown to proceed through mechanisms of the latter type, it is not unreasonable to expect a similar reactive path for O_2. The obvious criterion for distinguishing between these two alternative pathways, namely, the dependence of the rate on the $P(C_6H_5)_3$ concentration, could not be adequately examined in our earlier study because, when excess $P(C_6H_5)_3$ was added, the simultaneous occurrence of reaction 2 interfered with the study of reaction 1.

$$Pt(P(C_6H_5)_3)_3 \xrightleftharpoons{-P(C_6H_5)_3} Pt(P(C_6H_5)_3)_2 \xrightarrow{O_2} Pt(P(C_6H_5)_3)_2O_2 \quad (7)$$

In order to resolve these residual mechanistic questions concerning this important system, we have performed the additional experiments described in this paper in which the kinetics of reaction 3 were examined (under conditions of the simultaneous occurrence of eq 1 and 2) by monitoring the consumption of O_2. The results support the mechanism described by eq 1–3.

Experimental Section

Solutions of $Pt(P(C_6H_5)_3)_3$ were prepared by dissolving $Pt(P(C_6H_5)_3)_4$ (synthesized as described earlier[4]) in deoxygenated reagent grade benzene, the dissociation of $Pt(P(C_6H_5)_3)_4$ to $Pt(P(C_6H_5)_3)_3 + P(C_6H_5)_3$ having previously been shown to be complete.[2,4]

The kinetic experiments were performed at 25.0 ± 0.3° by measuring the volume of oxygen taken up at constant pressure, using the gas buret apparatus and procedure described previously.[5] The same apparatus was also used to determine the solubility of oxygen in benzene, by measuring the successive volumes of oxygen taken up as the partial pressure was incrementally increased.[5] The solubility of O_2 in benzene at 25° was thus determined to be $(6.5 \pm 0.4) \times 10^{-3}$ mol l.$^{-1}$ atm^{-1}.

Results and Discussion

Our earlier kinetic studies of the reaction that we interpreted as corresponding to eq 1 were based on spectral measurements of the rates of consumption of $Pt(P(C_6H_5)_3)_3$ by reaction with O_2.[2] The initial $Pt(P(C_6H_5)_3)_3$ concentrations in these experiments, ranging from 2×10^{-3} to 8×10^{-3} *M*, were at least 20 times greater than the O_2 concentration, so that the small overall decrease in the $Pt(P(C_6H_5)_3)_3$ concentration (which could be accurately measured at wavelengths in the 420–450-nm range, using the expanded scale of a Cary 14 spectrophotometer) exhibited pseudo-first-

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