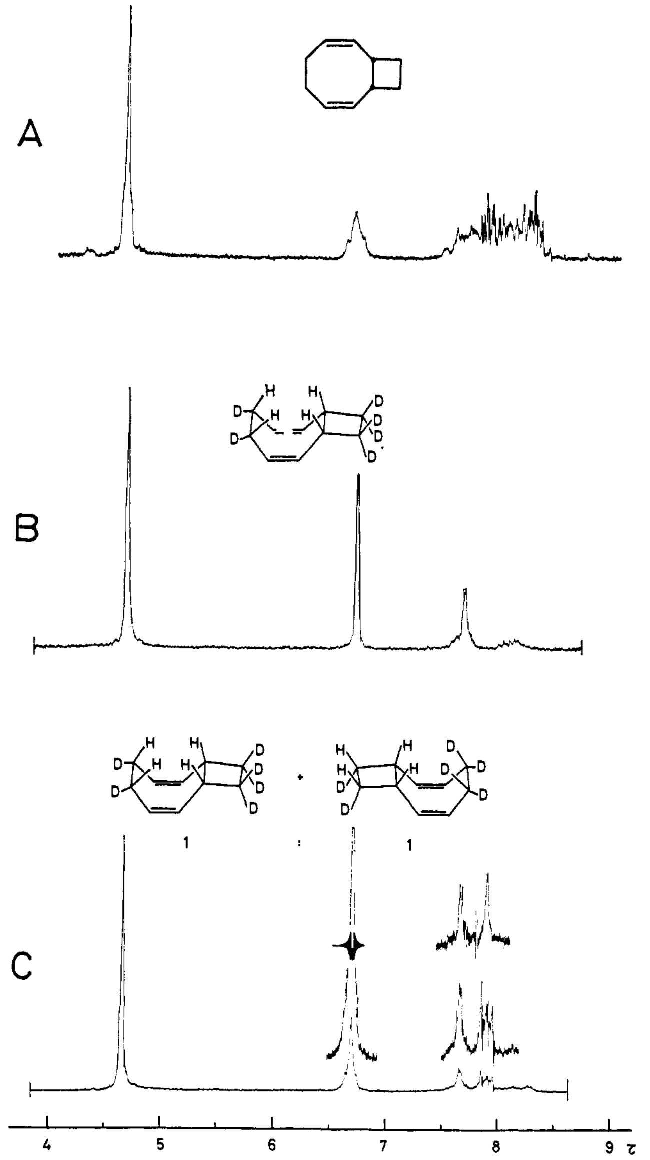
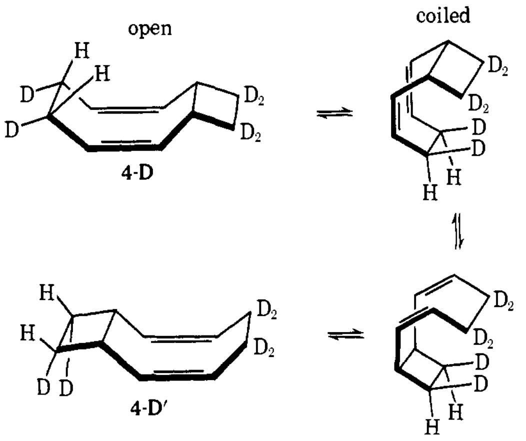


Figure 1. Proton nmr spectra of variously labeled *cis*-bicyclo-[6.2.0]deca-2,6-dienes (CCl_4, 100 MHz, TMS as internal standard): A, spectrum of **4**; B, spectrum of **4-D**, H,D decoupled; C, spectrum of the equilibrium mixture of **4-D** and **4-D′**, H,D decoupled (of the inserted enlargements the upper one is with decoupled bridgehead protons).

singlet of the bridgehead protons of **4-D**. Irradiation with the frequency of the bridgehead protons causes the triplet of the cyclobutane protons to collapse to a singlet, thus confirming the assigned coupling and indicating the presence of only one kind of methylene proton in the cyclobutane ring. Their strong coupling (5 Hz) with the bridgehead protons manifests the mutual cis configuration.[10] Accordingly, the reversible Cope rearrangement proceeds stereospecifically in such a way that the methylene hydrogens trans to the cyclobutane ring in **4-D** become trans to the cyclooctadiene ring in **4-D′**; or more generally, the individual methylene hydrogens retain their geometry with respect to the attached ring.



The observed stereochemistry cannot be rationalized by the reaction occurring in the stable open conformation, for here the trans hydrogens in **4-D** are pointing inward and after ring closure between C_3 and C_6 they must appear cis to the newly formed eight-membered ring. In the coiled conformation, on the other hand, the trans-methylene hydrogens have the correct orientation to remain trans on the cyclobutane ring to be formed. Moreover, this latter conformation is ideal in all respects for the electron reorganization of the Cope rearrangement to occur with the least motion of atoms, but it suffers from a severe compression between the two pairs of cis deuterium atoms.

The stereochemistry of the reaction proves unambiguously that the coiled conformation is a prerequisite for the transition state and the higher temperature required (about 100°) than for the Cope rearrangement of *cis*-1,2-divinylcyclobutane[11] adequately reflects the high strain involved. A substantial rate enhancement should be experienced, then, by a *cis*-bicylo[6.2.0]deca-2,6-diene with direct bonding between C_4 and C_{10} and between C_5 and C_9, *i.e.*, by an analog of semibullvalene.[12,13]

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(10) *Cf.* the coupling constants between the cyclobutane protons in *endo-cis*-5,6-dimethylbicyclo[2.2.0]hex-2-ene (4 Hz) and in the exo isomer (1 Hz). The nmr spectra of both compounds were kindly provided by Professor W. R. Roth, Ruhr-Universität, Bochum.

(11) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964); R. Sundermann, Dissertation, University of Cologne, 1966.

(12) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966).

(13) This expectation has been verified very recently by the synthesis of hypostrophane: J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *ibid.*, **93**, 4957 (1971).

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A New Mode of Sulfur Dioxide Attachment to Halogenated Transition Metal Complexes

Sir:

The considerable interest in sulfur dioxide reactions with metal complexes[1] prompts us to report our study

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(1) (a) C. G. Hull and M. H. B. Stiddard, *J. Chem. Soc. A*, 710 (1968); (b) W. Stromeier and J. F. Gutterberger, *Chem. Ber.*, **97**, 1871 (1964); (c) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 5377 (1967); (d) J. J. Levinson and S. D. Robinson, *Chem. Commun.*, 198 (1967); (e) A. Wojcicki,

Table I. SO_2 Infrared Stretching Frequencies (cm^{-1})

Compound	ν_1 symmetric stretch	ν_3 antisymmetric stretch	Ref
1. SO_2[a]	1150	1340	5
2. $KI\cdot 4SO_2$[a]	1116	1294	5
3. $Pt(PPh_3)_2CH_3I\text{-}SO_2$[a]	1138	1322	This work
4. $Pt(PPh_3)_2CH_3I\text{-}SO_2$[b]	1127	1305	This work
5. $PtCl(SO_2CH_3)(PPh_3)_2$[b]	1070	1215	This work
6. $O_2S\text{-}Ir(PPh_3)_2(CO)Cl$[b]	1057	1214, 1188[d]	1g
7. $O_2S\text{-}Ir(PPh_3)_2(CO)I\text{-}SO_2$[b]	1040, 1140[c]	1323, 1185, 1156[c,e]	This work

[a] Acetonitrile solution. [b] Nujol mull. [c] Medium; all other peaks are strong. [d] Rhodium analog has only a single peak in this region at 1208 cm^{-1} (ref 8). [e] Uncertain assignment.

of the adduct $Pt(PPh_3)_2CH_3I\text{-}SO_2$.[2] We anticipated an unusual five-coordinated platinum(II) species, but X-ray structural analysis shows SO_2 attachment to iodine. Adducts of SO_2 with halide ions have been known since 1916[3] and their spectral and equilibrium properties are now well characterized.[4,5] No structural data have been reported, but this adduct of the platinum complex serves as a good structural model for the halide complexes and provides a warning that SO_2 may attach to sites other than the metal of metal complexes. Indeed we find that the new compound $O_2S\text{-}Ir(PPh_3)_2(CO)I\text{-}SO_2$ has attachments to both iridium and iodine, whereas in $O_2S\text{-}Ir(PPh_3)_2(CO)Cl$ only a bond to iridium is formed.[1g,6]

Liquid sulfur dioxide dissolves $Pt(PPh_3)_2CH_3I$ (**1**) giving a yellow solution. Evaporation of the solution yields yellow crystals, analysis of which agrees with that of the monoadduct. On exposure to air the adduct reverts to pale cream **1** at a rate dependent on crystal size; those larger than fine powder stay yellow for weeks exposed to air. The same yellow crystals were obtained from a benzene solution of **1** saturated with SO_2. They are triclinic, space group $P\bar{1}$ with a reduced cell of $a = 11.853$ (6), $b = 16.610$ (9), $c = 9.738$ (5) Å; $\alpha = 98.12$ (2), $\beta = 108.17$ (1), and $\gamma = 69.90$ (2)°; and $Z = 2$ ($\lambda_{MoK\alpha_1}$ 0.7093 Å, $\mu = 52.9$ cm^{-1}). The absorption corrected data (3143 reflections with $I > 3\sigma(I)$) gave $R = 0.027$ (based on F) on full-matrix least-squares refinement. The iodine to sulfur distance (Figure 1) is significantly shorter than the van der Waals radii sum (3.80 Å)[7] but longer than their single bond covalent radii sum (2.37 Å). The angle O-S-O is 116.1 (5)°, and the I-S vector makes an angle of 21.3 (5)° with the normal to the SO_2 plane. This orientation of the SO_2 molecule is not very different from that in other adducts. Thus in $O_2S\text{-}M(PPh_3)_2(CO)Cl$ the M-S vector makes an angle of 30.3 (3)° (M = Rh)[8] and 31.6 (1.5)° (M = Ir)[6] with the normal to the SO_2 plane. The corresponding angle in the adduct $(CH_3)_3N\text{-}SO_2$[9] is 22°. In the metal complexes short nonbonded intramolecular distances to the oxygens of SO_2 are present. In the absence of these steric constraints these angles in excess of 30° could be expected to approach 20° as found in the adduct of **1** where such constraints are not present. The Rh-SO_2 and N-SO_2 distances represent a much greater contraction from their van der Waals radii sums than is the case with I-SO_2. The stronger bonds implied in the former cases are consistent with larger shifts of their S-O infrared stretching frequencies (Table I, ref 10).

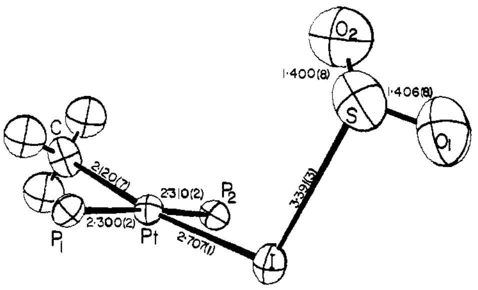

Figure 1. Structure and bond lengths of $Pt(PPh_3)_2CH_3I\text{-}SO_2$ (phenyl groups omitted for clarity).

The uv spectrum of $[(C_2H_5)_4N]^+I^-\text{-}SO_2$ displays an intense absorption at 378 mμ ($\epsilon \approx 9900$)[4] in acetonitrile solution. Similar absorptions are also found in spectra of the bromide and chloride salts progressively shifted to higher energies. The difference spectrum at a concentration of 0.33×10^{-4} M of the adduct of **1** against **1** displays a similar absorption centered at the same wavelength ($\epsilon \approx 15{,}000$) in this solvent. These data together with the infrared spectra (Table I) provide evidence that the nature of the bonding interactions in $Pt(PPh_3)_2CH_3I\text{-}SO_2$ and $[I\text{-}SO_2]^-$ are the same. We strongly anticipate that these spectral results would be unaffected by reasonable variation of the groups on the platinum center. Employing the same conditions[1g,8] used to prepare the monoadduct $O_2S\text{-}Ir(PPh_3)(CO)Cl$, we have prepared the adduct $O_2S\text{-}Ir(PPh_3)_2(CO)I\text{-}SO_2$ from the corresponding iodide complex. The stoichiometry is supported by elemental analysis and this formulation by the infrared spectra. Thus the spectrum of this species (7, Table I) is nearly the sum of that of species 3 and 6 where $O_2S\text{-}I$ and $O_2S\text{-}Ir$ bonds have been established by X-ray structure analysis.

It was possible to show that the hypothetical SO_2 insertion compound $PtI(SO_2CH_3)(PPh_3)_2$ was not formed on adding SO_2 to **1**. The chloro species $Pt(PPh_3)_2(SO_2CH_3)Cl$ formed from $Pt(PPh_3)_4$ and CH_3-

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Accounts Chem. Res., **4**, 344 (1971); (f) L. Vaska, *ibid.*, **1**, 335 (1968); (g) L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, **88**, 1338 (1966).

(2) We have departed from IUPAC ligand order notation to show the site of attachment of the SO_2.

(3) T. C. Waddington, "Non-Aqueous Solvent Systems," Academic Press, London and New York, 1965, pp 256-259, and references therein.

(4) E. J. Woodhouse and T. H. Norris, *Inorg. Chem.*, **10**, 614 (1971).

(5) E. R. Lippincott and F. E. Welsh, *Spectrochim. Acta*, **17**, 123 (1961).

(6) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

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(9) D. Van der Helm, J. D. Childs, and S. D. Christian, *Chem. Commun.*, 887 (1969).

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SO_2Cl has a distinctly different infrared spectrum from $Pt(PPh_3)_2CH_3I\text{-}SO_2$ (3, Table I). Comparison of the spectra of compounds 5 and 6, however, shows that it would not have been possible to eliminate from consideration the unknown five-coordinate platinum(II) species $O_2S\text{-}Pt(PPh_3)_2CH_3I$ on this basis.

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Phosphoranylperoxy Radicals[1]

Sir:

The existence of phosphoranylperoxy radicals, $X_4POO\cdot$, has been postulated to account for the products observed in the autoxidation of alkanes in the presence of phosphorus trichloride,[2] for the deoxygenation of pyridine *N*-oxide by trialkyl phosphites,[3] and for the photoinduced oxidation of benzenoid compounds by trialkyl phosphites.[4] The radical is assumed to be formed by reaction of a phosphoranyl radical with oxygen.

$$X_4P\cdot + O_2 \longrightarrow X_4POO\cdot \qquad (1)$$

The epr spectra of phosphoranyl radicals, generated by the photolysis of di-*tert*-butyl peroxide in the presence of trialkyl phosphites or trialkylphosphines, have been observed recently.[5-7] The spectra are characterized by a doublet separated by 700–900 G.

We wish to report that *tert*-butoxy trialkoxyphosphoranyl radicals obtained in the above manner from trialkyl phosphites [$(R'O)_3P$, R′ = Me, Et, *i*-Pr, *tert*-Bu] in cyclopropane solution below −40°, will react with oxygen. The doublet due to the phosphoranyl radical disappears and is replaced by a doublet with a somewhat broader line width. The hyperfine coupling of the new doublet is ~9 G and there is no further resolvable fine structure. The radical has a *g* value of 2.022 which is between the value of 2.025 found for group IV trialkylmetalperoxy radicals[8] and the values of ~2.014–2.016 found for alkylperoxy radicals. Since the phosphoranyl radical reappears when the oxygen has been consumed (see below) we have assigned this new radical the structure *tert*-$BuO(R'O)_3POO\cdot$. We believe this to be the first direct observation of phosphoranylperoxy radicals. The coupling constants and *g* values are summarized in Table I.

Table I. Hyperfine Coupling Constants and *g* Values of Phosphoranylperoxy Radicals in Cyclopropane at −80°

Radical	a_P, G	g
tert-$BuO(MeO)_3POO\cdot$	9.2	2.022
tert-$BuO(EtO)_3POO\cdot$	9.5	2.022
tert-$BuO(i\text{-}PrO)_3POO\cdot$	8.9	2.022
(*tert*-$BuO)_4POO\cdot$[a]	9	2.02

[a] The doublet due to this peroxy radical is obtained together with a broad asymmetric unresolved signal (~400 G wide) so that measurements of its physical constants are imprecise. This signal may be due to impurities in the original phosphite since it can only be obtained in ~90% purity (V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964)).

Under continuous irradiation the phosphoranylperoxy radicals survived for several minutes at −90° but only for about 30 sec at −50°, after which they were, of course, replaced by phosphoranyl radicals. Clearly the dissolved oxygen is rapidly depleted by a chain reaction at the higher temperatures and the scheme suggested by Walling and Rabinowitz[9] seems not unreasonable. Reaction 4 is reasonably fast even

$$RO\dot{P}(OR')_3 \longrightarrow R\cdot + OP(OR')_3 \qquad (2)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (3)$$

$$ROO\cdot + P(OR')_3 \longrightarrow ROO\dot{P}(OR')_3 \qquad (4)$$

$$ROO\dot{P}(OR')_3 \longrightarrow RO\cdot + OP(OR')_3 \qquad (5)$$

$$RO\cdot + P(OR')_3 \longrightarrow RO\dot{P}(OR')_3 \qquad (6)$$

at low temperatures.[10] However, the scission of a *tert*-butyl radical from *tert*-$BuO\dot{P}(OEt)_3$ is not a particularly rapid reaction[11] and therefore at low temperatures and/or at high oxygen concentrations the Walling and Rabinowitz chain is probably replaced by

$$RO\dot{P}(OR')_3 + O_2 \longrightarrow RO(R'O)_3POO\cdot \qquad (7)$$

$$RO(R'O)_3POO\cdot + P(OR')_3 \longrightarrow RO(R'O)_3POO\dot{P}(OR')_3 \qquad (8)$$

$$RO(R'O)_3POO\dot{P}(OR')_3 \longrightarrow RO(R'O)_3PO\cdot + OP(OR')_3 \qquad (9)$$

$$RO(R'O)_3PO\cdot \longrightarrow RO\cdot + (R'O)_3PO \qquad (10)$$

$$RO\cdot + P(OR')_3 \longrightarrow RO\dot{P}(OR')_3 \qquad (6)$$

The phosphoranylperoxy radicals from trimethyl, triethyl, and triisopropyl phosphite[12] decayed with second-order kinetics at temperatures below −85°.

$$2\,tert\text{-}BuO(R'O)_3POO\cdot \xrightarrow{2k_t} \text{nonradical products} \qquad (11)$$

At peroxy radical concentrations in the range $0.5\text{–}1.0 \times 10^{-5}\ M$ the measured values of $2k_t$ at −90° were $6 \times 10^4\ M^{-1}\ sec^{-1}$ for R′ = Me, 1×10^4 for Et, and 3×10^4 for *i*-Pr. These differences are within the probable experimental error. Over the temperature range from −89 to −116° $2k_t$ for R′ = Me is given by $2k_t = 10^{10} \exp(-4500/RT)\ M^{-1}\ sec^{-1}$.

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[9] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1243 (1959).

[10] The rate constant for the reaction of *tert*-butyl peroxy radicals with trimethyl phosphite is $1.0\ M^{-1}\ sec^{-1}$ at −100°; J. A. Howard and G. B. Watts, unpublished results.

[11] For this radical,[7] $k_2 = 2.4 \times 10^{13} \exp(-9340/RT)\ sec^{-1}$.

[12] The second radical obtained with tri-*tert*-butyl phosphite (footnote *a*, Table I) decayed slowly and prevented kinetic studies on the peroxy radical. A similar broad signal, but of much reduced intensity, was present in the other phosphoranylperoxy radicals and made kinetic studies rather difficult. The measurement of peroxy radical concentrations was also a problem because of the relatively short lifetime of the radical under continuous irradiation.