Table I[a]

ESF_4		$E(CF_3)_2SF_2$		comments
$E–S–F_a$	93.4_5	$E–S–F_a$	93.0_5	equal within exptl error
$E–S–F_e$	129.2_5	$E–S–C$	131.3_5	$\Delta_1 = 2.1°$; sign in agreement with the prediction of VSEPR model, 2 such interactions
$F_e–S–F_e$	101.5	$C–S–C$	97.3	$\Delta_2 = -4.2°$; sign in disagreement with the prediction of VSEPR model, 1 such interaction
$F_a–S–F_e$	87.8	$F_a–S–C$	88.0	equal within exptl error

[a] All angles given in degrees.

work[10] have been in agreement with the prediction from this simple approach indeed.

The consideration of the quadruple-average angles has also shown[7] the series of SF_4, OSF_4, and $H_2C{=}SF_4$ molecules to have structural consistency in spite of rather differing bond angles. The special advantage of utilizing quadruple-average angles in these trigonal-bipyramidal systems is that they can be simply calculated from the bond angles by virture of symmetry.

Recently the molecular geometry of $(CF_3)_2SF_2$ has been reported by Oberhammer et al.[11] from electron diffraction. The structure is characterized by a trigonal-bipyramidal configuration with the fluorine ligands in axial positions. The following bond angles described the geometry: C–S–C = 97.3 (8)° and $F_a–S–F_a$ = 173.9 (8)°. The values cited in parentheses were given as error limits representing 3σ from a least-squares analysis. Comparing the structures of SF_4[12] and $(CF_3)_2SF_2$, Oberhammer et al. noted that the bond angles involving the axial ligands were equal in the two molecules within experimental error. They also stated the following: "The decrease of the equatorial bond angle from 101.5 (5)° in SF_4 to 97.3 (8)° in $(CF_3)_2SF_2$ is incompatible ith the VSEPR model."[11]

When considering, however, the variations of *all* angles around the sulfur atom, as is shown below, they appear to be fully compatible with the VSEPR model. Indeed, the SF_4 and $(CF_3)_2SF_2$ structures provide an excellent example for the applicability of this model.

In both molecules there are two kinds of interactions that have to be taken into account, viz., E/b and b/b. The only difference in the two systems is that the two ligands in the equatorial positions are less electronegative[13] in $(CF_3)_2SF_2$ than the corresponding ones in SF_4.

Consider now first the quadruple-average angles of the lone pairs of electrons:

	SF_4	$(CF_3)_2SF_2$
$\tilde{\alpha}_Y$	$111.3_5°$	112.2°

Although the difference in the two quadruple-average angles is small, its direction is in complete agreement with the prediction of the VSEPR model postulating the E/b repulsions to be greater when involving bonds to less electronegative ligands.[1] Here the $E/S–F_a$ repulsions in the two molecules are assumed to be equal.

Consider now the individual bond angles given in Table I. It is obvious that $2|\Delta_1|$ and $|\Delta_2|$ are equal. It is also obvious that there are two competing effects acting in the equatorial plane of $(CF_3)_2SF_2$ as compared with the case for SF_4. One of them is that the $E/S–CF_3$ repulsion is greater than the $E/S–F_e$ repulsion, thus tending to increase the E–S–C angles. The other effect is that the $S–CF_3/S–CF_3$ repulsion is greater than the $S–F_e/S–F_e$ one, thus tending to increase the C–S–C bond angle.

All angles being in the equatorial plane, either the E–S–C angles or the C–S–C angle can increase and can do so only at the expense of the other. The relative magnitude of the two competing effects decides which of them prevails. The experimentally observed decrease of the C–S–C angle in $(CF_3)_2SF_2$ as compared with the $F_e–S–F_e$ angle in SF_4 unambiguously indicates the $E/S–CF_3$ repulsions to prevail, in complete agreement with the VSEPR model.

Registry No. SF_4, 7783-60-0; $(CF_3)_2SF_2$, 30341-38-9.

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Communications

Photochemical Fragmentation Kinetics of Triruthenium Dodecacarbonyl

Sir:

The photochemical fragmentation reaction (1) is known to

$$\mathrm{Ru_3(CO)_{12}} \xrightarrow[\mathrm{CO}]{h\nu} \mathrm{Ru(CO)_5} \qquad (1)$$

proceed smoothly, without detectable side reactions.[1] In spite of the considerable current interest in photofragmentation of metal–metal-bonded carbonyls,[2,3] no detailed investigation of reaction 1 has been reported. We have studied it as a function of [CO], irradiation wavelength (λ), solvent, and the intensity, I_a, of absorbed light. Some of the results are reported in Table I.

Studies of reactions in deoxygenated cyclohexane and isooctane under $CO–N_2$ mixtures containing from 5 to 100% CO invariably showed a pronounced dependence of the quantum yield, ϕ_{obsd}, on [CO]. Plots of ϕ_{obsd} against [CO][4] always showed quite appreciable curvature (Figure 1), suggesting that ϕ_{obsd} would tend to a limiting value, ϕ_l, at sufficiently high values of [CO]. Plots of $1/\phi_{obsd}$ against 1/[CO] are closely

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(4) Solubilities of CO under 1-atm pressure are taken as follows: isooctane, 0.012 M;[5] cyclohexane, 0.0092 M;[6] Decalin, 0.0059 M;[7] benzene, 0.0075 M.[6] Henry's law has been shown[5] to hold for isooctane at 25 °C.

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Table I. Disappearance Quantum Yields for the Reaction

$$Ru_3(CO)_{12} \xrightarrow[CO]{h\nu} 3Ru(CO)_5$$

λ, nm	solvent	% CO[a]	$10^2\phi_{obsd}$[b]	$10^2\phi_l$[c]
366	cyclohexane	5.1	0.27	
		15.3	0.71	
		25.4	0.98	
		40.5	1.62	
		100	2.60 ± 0.08[d]	5.1 ± 0.8
436	cyclohexane	15.3	0.60 ± 0.04[e]	
436	isooctane	100	3.5 ± 0.4[f]	5.6 ± 0.7
366	isooctane	100	4.4	10.5 ± 2.2
313	isooctane	100	3.9	8.5 ± 1.5
436	Decalin	100	0.84	
436	benzene	100	0.14	
366	benzene	100	0.13	

[a] In CO-N_2 mixtures. [b] Incident light intensities, I_0, were measured by ferrioxalate actinometry. Reactions were followed in 10-mm path length silica cuvettes that were completely enveloped by the light beam, and the progress of the reaction was followed by absorbance measurements at 390 nm. Quantum yields were constant to within a standard deviation of 3% or less over the course of up to 50% reaction and were constant to ca. 10% between separately measured runs. [c] Limiting quantum yields from plots of $1/\phi$ against $1/[CO]$. [d] Over the range of absorbed light intensity $10^7 I_a = 3.6\text{-}23$ einsteins L^{-1} s^{-1}. [e] Over the range $10^7 I_a = 2.0\text{-}14$ einsteins L^{-1} s^{-1}. [f] Over the range $10^7 I_a = 3\text{-}6$ einsteins L^{-1} s^{-1}.

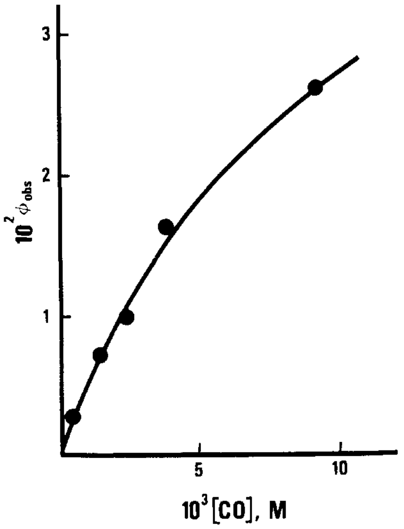


Figure 1. Dependence of the disappearance quantum yield, ϕ_{obsd}, on [CO][4] for the reaction of $Ru_3(CO)_{12}$ in cyclohexane under CO upon irradiation at λ = 366 nm.

linear (Figure 2), and the inverses of the intercepts provide values of ϕ_l (Table I).

Quantum yields do not depend on I_a down to $I_a = 2 \times 10^{-7}$ einstein L^{-1} s^{-1}, nor do they depend in any significant way on λ. They do, however, depend appreciably on the nature of the solvent.

The increase of ϕ_{obsd} with increasing [CO] implies the existence of a reactive intermediate or intermediates that can either revert to stable $Ru_3(CO)_{12}$ or react further with CO to form $Ru(CO)_5$ in one or more steps. The reaction in cyclohexane under 15% CO and with λ = 436 nm demonstrates the absence of any dependence of ϕ_{obsd} on I_a at values of ϕ_{obsd} much less than ϕ_l. This shows conclusively that the reactive intermediate is still a Ru_3 species and that fragmentation of $Ru_3(CO)_{12}$ has not occurred by the time competitive attack by CO takes place. If fragmentation had occurred, then the recombination reaction of the fragments would have an order greater than unity and ϕ_{obsd} would have decreased steadily as I_a increased.[8] It seems most likely that the reactive intermediate is an isomeric form of $Ru_3(CO)_{12}$. Any photochemically induced dissociation of CO would be expected to be reversed at a rate much more rapid than any alternative mode of attack by CO that leads to fragmentation. The overall reaction can therefore be described by the mechanism shown in eq 2 and 3, for which the corresponding rate equation is given by eq 4. Inverse plots such as that shown in Figure 2

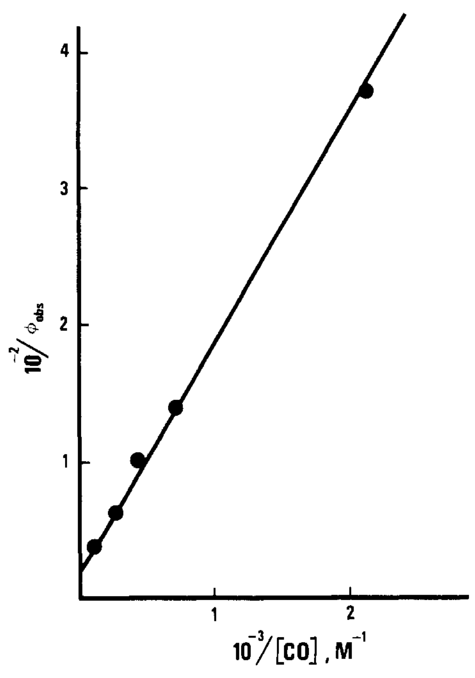


Figure 2. Dependence of $1/\phi_{obsd}$ on $1/[CO]$ for the reaction of $Ru_3(CO)_{12}$ in cyclohexane under CO (λ = 366 nm).

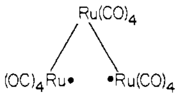
$$Ru_3(CO)_{12} \underset{k_r}{\overset{\phi_l}{\rightleftharpoons}} Ru_3(CO)_{12}^* \qquad (2)$$

$$Ru_3(CO)_{12}^* \xrightarrow[k_f]{CO} \text{intermediate(s)} \xrightarrow{\text{fast}} 3Ru(CO)_5 \qquad (3)$$

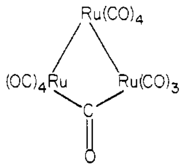
$$\phi_{obsd} = \phi_l\, k_f[CO]/(k_r + k_f[CO]) \qquad (4)$$

provide values of $\phi_l k_f/k_r$ (the inverse of the gradient) in addition to values of ϕ_l.

It has been suggested that excitation of $Ru_3(CO)_{12}$ by light in the 400-nm region would lead to homolytic fission of one of the Ru–Ru bonds in the cluster to give a reactive intermediate such as I.[10] If this does occur, however, the diradical



I



II

must be much less reactive than related five-coordinate 17-electron metal-centered radicals[2] since the disappearance quantum yield in CCl_4 under N_2 is very small (ca. 0.001).

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(8) At higher intensities fragments would be generated in higher concentrations so that their second-order recombination is favored relative to their pseudo-first-order reaction with CO. Only when the latter is sufficiently fast to scavenge all the fragments before their recombination, i.e., when $\phi = \phi_l$, will the intensity dependence of such reactions disappear. Relevant rate equations have been reported.[9]

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Reaction 1 does occur in CCl_4 with a quantum yield ca. 20 times greater than for reaction in the absence of CO. It seems somewhat improbable that reaction with quite low concentrations of CO, leading to fission of a Ru–Ru bond in the diradical, should be more rapid than chlorine abstraction from the CCl_4 solvent. The existence of a diradical intermediate should, therefore, not be assumed without question and nonradical, reactive isomeric forms of $Ru_3(CO)_{12}$ (e.g., II) can easily be postulated. Reaction of II with CO to form $Ru_3(CO)_{13}$ followed by rapid fragmentation is not unreasonable to contemplate. Similar processes have been proposed to occur during the thermal fragmentation reactions of $Co_4(CO)_{12}$[5] and $Ru_3(CO)_9(PPh_3)_3$[11] as well as in reactions of dinuclear complexes.[12]

The values of ϕ_{obsd} for reaction in isooctane under 100% CO show no perceptible dependence on irradiation wavelength. The values of ϕ_l are necessarily less precise than those of ϕ_{obsd} because of the extrapolation involved, but those obtained for isooctane are also consistent with a wavelength-independent value of 0.065 ± 0.006 obtained from the weighted average of the three individual values. Similar wavelength independence is shown in cyclohexane and benzene. The limiting quantum yield for reaction 5 has been found to be over 3 times

$$\mathrm{Ru_3(CO)_{12}} \xrightarrow[\text{methyl acrylate}]{h\nu} \mathrm{3Ru(CO)_4(methyl\ acrylate)} \qquad (5)$$

higher when λ = 313 nm than when λ = 395 nm, and this enhanced value was ascribed to photochemically induced dissociation of CO.[13] Our studies show that 313-nm excitation can lead to formation of a reactive isomeric form of $Ru_3(CO)_{12}$ such as I or II, the additional CO dissociative process being reversed in the presence of free CO.

The solvent dependence of the reaction can best be indicated by the relative values of the parameter $\phi_l(k_f/k_r)$, which is equal to the initial slope of the plot of ϕ_{obsd} against [CO]. These fall in the relative order isooctane (100) > cyclohexane (90) > Decalin (30) > benzene (3). It is not obvious from these data whether the variation is due to a solvent dependence of ϕ_l or k_f/k_f or both, but we believe that it is most likely to be due to a dependence on k_f/k_r. This represents a chemical selectivity on the part of the reactive intermediate as opposed to what is more likely to be a photophysical selectivity if ϕ_l were solvent dependent. This is supported by data for reaction with other ligands.[13,14]

Finally, the data in Table I suggest that there is a dependence of ϕ_l on the nature of the attacking nucleophile. The weighted average of 0.065 ± 0.006 for ϕ_l in isooctane over the range λ = 313–436 nm can be compared with the value of 0.038 ± 0.002 for methyl acrylate in hexane with λ = 395 nm[13] or 0.031 for ethyl acrylate in benzene with λ = 436 nm.[14] This is of interest since it cannot readily be explained by a simple competitive reaction of a single reactive intermediate. In that case ϕ_l would be reached when the reaction was driven in the forward direction every time the intermediate was formed (i.e., $k_f[L] >> k_r$) and ϕ_l would then be independent of the nature of the ligand. This aspect of the photochemical behavior is receiving further attention.

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Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_5$, 16406-48-7; CO, 630-08-0; cyclohexane, 110-82-7; isooctane, 540-84-1; Decalin, 91-17-8; benzene, 71-43-2.

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Antiferromagnetic Ruthenium(III)

Sir:

We report here what appears to be the first example of antiferromagnetism in a discrete ruthenium(III) coordination compound, chloropentaammineruthenium(III) chloride, $[Ru(NH_3)_5Cl]Cl_2$.

The high-temperature susceptibility of this compound has been reported[1] and shows that this 4d^5 compound is low spin. That means, according to Bleaney and O'Brien,[2] that the ground state in the temperature range of our measurements (below 4.2 K) therefore should be an effective $S = {}^1/_2$ ground state with anisotropic g values. Introducing the axial crystal field splitting parameter v and spin–orbit parameter ζ (which is estimated to be of the order of 1000 cm^{-1}), one calculates that

$$g_\parallel = 2|(1 + k)\cos^2\alpha - \sin^2\alpha|$$

$$g_\perp = 2|2^{1/2}k\cos\alpha\sin\alpha + \sin^2\alpha|$$

where $\tan 2\alpha = 2^{1/2}({}^1/_2 - v/\zeta)^{-1}$ and k is the orbital reduction factor; the latter is generally expected to take a value slightly smaller than 1. One can see from the relationships for the g values that they can be quite anisotropic and differ widely in value from compound to compound, depending on the local crystalline field. This can in turn lead to highly anisotropic magnetic ordering phenomena. EPR measurements at 77 K of $[Ru(NH_3)_5Cl]^{2+}$ doped into $[Co(NH_3)_5Cl]Cl_2$ have yielded[3] the results that $g_x = 0.987 \pm 0.008$, $g_y = 1.513 \pm 0.005$, and $g_z = 2.983 \pm 0.003$, or an average value of 2.013. These results were shown to be consistent with the presence of a well-isolated doublet ground state.

The compound was prepared according to the method of Fergusson and Love[4] and is known to belong to the space group *Pnma*.[5] It is isostructural[6] with $[Co(NH_3)_5Cl]Cl_2$ and contains four molecules in the orthorhombic unit cell. Thus, there are two pairs of magnetically inequivalent complex ions in the cell. Further implications of the crystal structure for the magnetic properties were discussed in the report[3] on the EPR spectra. The zero-field magnetic susceptibility of polycrystalline $[Ru(NH_3)_5Cl]Cl_2$, measured by an ac mutual inductance procedure,[7–9] is illustrated in Figure 1. For comparison,

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