Table II. Analysis of Dialkyltin Dihalides R₂SnXY

	% found (calcd)		
	C	H	Total halogen (R₂SnClBr)
Me₂SnClBr	8.65 (9.09)	2.51 (2.28)	43.3 (43.6)
Me₂SnClI	7.38 (7.72)	2.06 (1.94)	40.9 (40.8)[a]
Me₂SnBrI	6.68 (6.75)	1.71 (1.70)	b
Et₂SnClBr	16.82 (16.44)	3.42 (3.45)	38.9 (39.4)
Et₂SnBrI	12.94 (12.52)	2.67 (2.62)	b
(n-Bu)₂SnClBr	28.07 (27.64)	5.25 (5.18)	32.6 (33.2)
(n-Bu)₂SnClI	24.76 (24.33)	4.53 (4.56)	31.8 (32.2)[a]
(n-Bu)₂SnBrI	21.88 (21.84)	4.16 (4.12)	b

[a] Iodine only. [b] The analysis figures for total halogen in bromide iodides were unreliable.

Dimethyltin diiodide was prepared similarly (8.3 g, 85%), bp 62° (1 mm), mp 36°. *Anal.* Calcd for C₂H₆SnI₂: C, 5.96; H, 1.50; I, 63.5. Found: C, 6.16; H, 1.52; I, 63.6.

Reaction of Tri-n-butyltin Fluoride with Triethylbromosilane. The bromide (11.44 g, 1 mol) was slowly added, with cooling, to the tin fluoride (18.10 g, 1 mol). The reaction was exothermic and after heating for 6 hr, the mixture was carefully fractionated giving triethylfluorosilane (5.1 g, 68%), bp 109°, $n^{20}D$ 1.3905,[10] and tri-n-butyltin bromide (19.1 g, 88%), bp 104° (0.5 mm), $n^{28}D$ 1.5015.[12]

Reaction of Me₃SiBr and Et₂SnCl₂. The additon of the components in equimolar quantities led to a mildly exothermic reaction. After heating overnight, the chlorosilane was pumped off and distilled (1.1 g, 86%), bp 57°, $n^{18}D$ 1.3900, while the residual diethyltin chloride bromide was recrystallized from dry pentane (3.5 g, 92%), mp 62–63°. *Anal.* Calcd for C₄H₁₀SnClBr: C, 16.42; H, 3.45; total halogen, 39.40. Found: C, 16.82; H, 3.42; total halogen, 38.9.

Reaction of Di-n-butyltin Dichloride and Di-n-butyltin Diiodide. The dichloride (1.68 g, 1 mol) and diiodide (2.7 g, 1 mol) were mixed and warmed. Vacuum distillation yielded di-n-butyltin chloride iodide (3.2 g, 73%), bp 88–89° (0.01 mm), mp 25°, $n^{28}D$ 1.5380. *Anal.* Calcd for C₈H₁₈SnClI: C, 24.33; H, 4.56; I, 32.2. Found: C, 24.76; H, 4.53; I, 31.8.

Registry No. Me₂SnClBr, 54182-25-1; Me₂SnClI, 54182-26-2; Me₂SnBrI, 54182-27-3; Me₂SnCl₂, 753-73-1; Me₂SnBr₂, 2767-47-7; Me₂SnI₂, 2767-49-9; Et₂SnClBr, 54182-28-4; Et₂SnBrI, 54182-29-5; Et₂SnCl₂, 866-55-7; Et₂SnBr₂, 1655-81-8; Et₂SnI₂, 2767-55-7; (n-Bu)₂SnClBr, 54182-30-8; (n-Bu)₂SnClI, 28339-79-9; (n-Bu)₂SnBrI, 54182-31-9; (n-Bu)₂SnCl₂, 683-18-1; (n-Bu)₂SnBr₂, 996-08-7; (n-Bu)₂SnI₂, 2865-19-2; Me₃SiI, 16029-98-4; Me₃SnCl, 1066-45-1; (n-Bu)₃SnF, 1983-10-4; Et₃SiBr, 1112-48-7; Me₃SiBr, 2857-97-8; Me₃SiCl, 75-77-4.

References and Notes

(1) J. C. Lockhart, "Redistribution Reactions," Academic Press, New York and London, 1970, Chapter 7, p 106.
(2) J. G. Riess and S. C. Pace, *Inorg. Chim. Acta*, **9**, 61 (1974).
(3) H. H. Anderson, *J. Amer. Chem. Soc.*, **73**, 5804 (1951); M. Kumada, *J. Inst. Polytech., Osaka City Univ. Ser. C*, **2**, 131 (1952).
(4) J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. S. Poland, *J. Chem. Soc., Dalton Trans.*, 1943 (1972).
(5) B. Aronheim, *Justus Liebigs Ann. Chem.*, **194**, 145 (1878); D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, 2050 (1962); O. H. Johnson and H. E. Fritz, *J. Amer. Chem. Soc.*, **77**, 5857 (1955); G. Hugl, *Kolloid-Z.*, **131**, 4 (1953).
(6) S. A. Kandil and A. L. Allred, *J. Chem. Soc. A*, 2987 (1970); L. E. Levchuk, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 43 (1972).
(7) J. R. Sams, J. N. R. Ruddick, and A. Tarassoli, private communication.
(8) C. Turner and R. F. M. White, private communication.
(9) E. V. Van den Berghe, G. P. Van der Kelen, and Z. Eeckhaut, *Bull. Soc. Chim. Belg.*, **76**, 79 (1967).
(10) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 172.
(11) R. C. Poller, "The Chemistry of Organotin Compounds," Logos Press, London, 1970, p 54.
(12) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).
(13) A. K. Sawyer, "Organotin Compounds," Vol. 1, Marcel Dekker, New York, N.Y., p 130.

Photochemical Reaction Pathways of Ruthenium(II) Complexes.[1] Ultraviolet Irradiation of the Pyridine Complex Ru(NH₃)₅py²⁺

Ray E. Hintze and Peter C. Ford*[2]

Previously, we have reported[3] on the photochemistry resulting when aqueous pentaamminepyridineruthenium(II), Ru(NH₃)₅py²⁺, is irradiated with visible light. The prominent visible range absorption of this complex is a metal-to-ligand charge transfer (MLCT) band (λ_{max} 407 nm, ϵ 7.78 × 10³ M^{-1} cm⁻¹). However, the principal photoreactions observed are substitutional, and ligand field excited states of this 4d⁶ complex have been invoked[3,4] to explain the photoreactivity pattern. Qualitative experiments[5] have shown that ultraviolet irradiation of this complex leads not only to ligand photoaquation but also to photooxidation of ruthenium(II) to ruthenium(III). Reported here is a quantitative study of the photosubstitution and photooxidation quantum yields for the uv photolyses of this complex.

Experimental Section

Photolysis Procedures. Irradiations at 334, 313, and 303 nm were carried out with an apparatus described previously.[3] This apparatus uses a 200-W, short-arc, high-pressure mercury lamp source and a Jarrell-Ash 0.25-m monochromator. Average intensities (I) at the respective wavelengths were 3.0 × 10⁻⁷, 1.4 × 10⁻⁷, and 0.7 × 10⁻⁷ einstein/(l. sec). Irradiations at 253.7 nm used a Philips medium-pressure mercury lamp source and an Oriel 253.7-nm mercury line interference filter (I = 4.3 × 10⁷ einstein/(l. sec)). Each of these apparatus was equipped with a cell holder thermostated at 25°. Ferrioxalate actinometry was used to measure light intensities. The photolysis solutions were prepared by dissolving [Ru(NH₃)₅py](BF₄)₂ in argon-deaerated, aqueous solution (μ = 0.2 M NaCl). Ru(II) concentrations were varied from 0.4 × 10⁻⁴ to 2.3 × 10⁻⁴ M and no relationship between complex concentrations and measured quantum yields was obvious.

Quantum yields were determined by evaluating spectral changes in the reaction solutions as a function of light absorbed.[3] A number of the photolysis runs were analyzed by a difference method where two 2-cm spectrometer cells of the same Ru(II) solution were filled, and one was placed in the sample cell compartment (25°) of a Cary 14 spectrometer while the other was used as photolysis solution. Periodically, irradiation was interrupted, the photolysis solution placed in the reference cell compartment, and the spectrum recorded. Since the photolysis solution is placed in the reference compartment, the difference spectra recorded (Figure 1) show a positive deflection from the t = 0 base line at wavelengths where the optical density of the photolysis is decreased relative to the dark control solution. The difference-spectra method has the advantage of automatically compensating for small spectral changes resulting from the very slow dark reactions. All quantum yields were evaluated as initial quantum yields by extrapolating plots of overall quantum yield values vs. per cent reaction back to 0% reaction.[3]

Results and Discussion

Photolysis of aqueous Ru(NH₃)₅py²⁺ at 405 nm leads principally to photoaquation of coordinated NH₃ and pyridine, although a very low-yield photoexchange of pyridine protons with solvent protons has also been detected.[3] Pyridine aquation (eq 1) leads to major spectral changes since the dominant
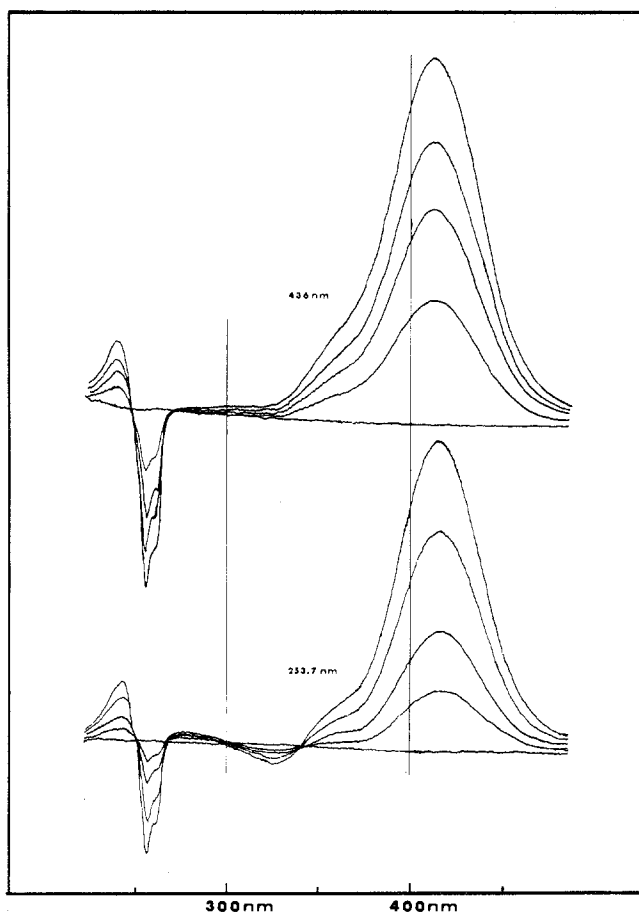
$$Ru(NH_3)_5py^{2+} + H_2O \xrightarrow{h\nu} Ru(NH_3)_5H_2O^{2+} + py \quad (1)$$
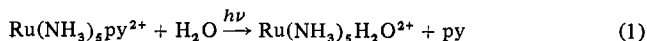
Figure 1. Difference spectra for the photolysis of Ru(NH₃)₅py²⁺ at 436 nm (top) and at 253.7 nm (bottom). The base line is the difference spectrum between the dark solution (sample cell) and the photolysis solution (reference cell) before initiating photolysis. Spectra taken after four successive photolysis intervals are shown (pH 3, $\mu = 0.2\,M$ NaCl).

Table I. Quantum Yields for the Photolysis of Aqueous Ru(NH₃)₅py²⁺ at Different Wavelengths[a]

λ_{irr}, nm	E, kK	10^{-3} ϵ^{b}	Assignment	Φ_{py}	$\Phi_{Ru(III)}{}^{c}$
436[d]	22.9	4.53	MLCT	0.051 ± 0.002 (12)	<0.01 (12)
				0.048 ± 0.002 (7)[e]	<0.01 (7)
405[d]	24.5	7.74	MLCT	0.044 ± 0.002 (4)	<0.01 (4)
				0.043 ± 0.002 (6)[e]	<0.01 (6)
366[d]	27.3	3.54	MLCT	0.043 ± 0.002 (7)[e]	<0.01 (7)
334	29.9	1.19		0.042 ± 0.002 (2)	0.01 (2)
313	31.9	0.77		0.048 ± 0.004 (5)	0.020 ± 0.005 (5)
				0.044 ± 0.002 (5)[e]	0.020 ± 0.002 (5)[e]
303	33.0	0.68		0.041 (1)[e]	0.019 (1)[e]
253.7	39.4	1.69	π_L–$\pi_L{}^*$	0.038 ± 0.002 (2)	0.035 ± 0.002 (2)

a 25°, $\mu = 0.2\,M$ (NaCl), and pH 3 except where noted. *b* Extinction coefficient at λ_{irr} in M^{-1} cm⁻¹. *c* Φ_{py} is quantum yield for pyridine aquation; $\Phi_{Ru(III)}$ is quantum yield for Ru(III) formation; mean value and average deviations reported with number of determinations in parentheses. *d* Reference 3. *e* pH 4.6.

aquation. Optical density decreases in the region 248–210 nm are also a result of eq 1 as the π–π^* band of the coordinated pyridine has a λ_{max} at 244 nm. The resulting appearance of free pyridinium ion is indicated by the increased absorbance between 266 and 248 nm. Photolysis at 254 nm leads to similar difference spectra with one major exception, an increase in the photolysis solution optical density from ~300 to 340 nm, thus indicating Ru(NH₃)₅Cl²⁺ formation as a result of photooxidation.

Quantitative evaluation of $\Phi_{Ru(III)}$ is complicated by the sensitivity of the photoaquation products to traces of oxygen and the fact that virtually all the reactants and products have some absorbance at 328 nm. In a parallel study of the acetonitrile complex,[6] we have shown that the primary photoredox reaction results in Ru(NH₃)₅CH₃CN³⁺. If we assume the analogous photooxidation pathway for the pyridine complex followed by reactions with the photoaquation product Ru(NH₃)₅H₂O²⁺ and Cl⁻ in solution (eq 2–4), then the net

$$\text{Ru(NH}_3)_5\text{py}^{2+} + h\nu \rightarrow \text{Ru(NH}_3)_5\text{py}^{3+} + \text{reduction products} \quad (2)$$

$$\text{Ru(NH}_3)_5\text{py}^{3+} + \text{Ru(NH}_3)_5\text{H}_2\text{O}^{2+} \rightarrow \text{Ru(NH}_3)_5\text{py}^{2+} + \text{Ru(NH}_3)_5\text{H}_2\text{O}^{3+} \quad (3)$$

$$\text{Ru(NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^{-} \xrightarrow[\text{Ru(NH}_3)_5\text{H}_2\text{O}^{2+}]{\text{cat. by}} \text{Ru(NH}_3)_5\text{Cl}^{2+} + \text{H}_2\text{O} \quad (4)$$

spectroscopic consequence of photooxidation is formation of Ru(NH₃)₅Cl²⁺ from the Ru(NH₃)₅H₂O²⁺ generated by eq 1.[3] The photooxidation quantum yield can therefore be calculated from eq 5 where $\Delta\epsilon_{328}$ is the change in the solution's

$$\Phi_{Ru(III)} = \frac{\Delta\epsilon_{328} + 860}{1750}\Phi_{py} \quad (5)$$

molar extinction coefficient, 860 is ($\epsilon_{Ru^{II}py} - \epsilon_{Ru^{II}H_2O}$), and 1750 is ($\epsilon_{Ru^{III}Cl} - \epsilon_{Ru^{II}H_2O}$), all at 328 nm. Photoredox quantum yields determined in this manner are listed in Table I. A realistic evaluation of the complications in using the spectral method places a limit of 0.01 mol/einstein as the minimum value of $\Phi_{Ru(III)}$ that one can be confident that photooxidation is indeed the result of photolysis (Table I). However, ion-exchange studies of aqueous Ru(NH₃)₅py²⁺ solutions which had been irradiated at 405 nm then quenched with deaerated pyridine failed to show Ru(NH₃)₅Cl²⁺ as a reaction product despite its stability to conditions of the quenching procedure.[3,7] The estimated upper limit of detectability by the latter procedure is ~0.005 mol/einstein.

The data for the various λ_{irr} show that photoaquation of pyridine occurs with a relatively constant quantum yield over.

visible region absorption band is a ruthenium-to-pyridine charge transfer and Ru(NH₃)₅H₂O²⁺ is virtually transparent in the visible spectrum ($\Delta\epsilon_{407}$ resulting from eq 1 is 7.71 × 10³ M^{-1} cm⁻¹). The spectra of the Ru(NH₃)₄(H₂O)py²⁺ isomers are very similar to that of Ru(NH₃)₅py²⁺; therefore, changes in the optical density at 407 nm can be used to determine the quantum yield (Φ_{py}) for eq 1.[3] Minor shifts in the MLCT λ_{max} (<10 nm) as the photolysis proceeds are the principal spectroscopic consequence of NH₃ photoaquation. Since these spectral shifts were observed reproducibly at all wavelengths, the ratio of pyridine aquation to NH₃ aquation is apparently not a significant function of λ_{irr}. Pyridine aquation quantum yields for various photolysis wavelengths are listed in Table I.

Quantum yields for Ru(II) photooxidation to Ru(III) were also determined from spectral changes. Under conditions where aquation exceeds oxidation, Ru(III) final products appear as chloroammineruthenium(III) complexes, primarily Ru(NH₃)₅Cl²⁺ which shows a characteristic ligand to metal charge transfer (LMCT) absorption band (λ_{max} 328 nm, ϵ 1.93 × 10³ M^{-1} cm⁻¹). This band appears at a minimum in the Ru(NH₃)₅py²⁺ absorption spectrum (Table I) thus can be monitored easily, and quantum yields ($\Phi_{Ru(III)}$) can be determined from molar extinction coefficient changes. Qualitatively, the wavelength dependence of the Ru(NH₃)₅py²⁺ photoreaction can be seen in Figure 1. Photolysis at 436 nm leads to decrease in optical density at all wavelengths >266 nm (shown as positive deflection from base line) owing to decreased MLCT absorption resulting from pyridine photo-
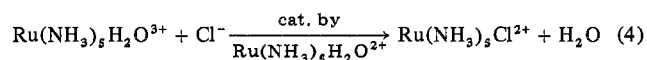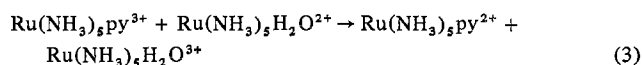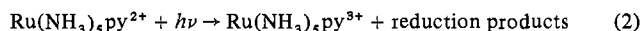
the wavelength range 436–254 nm. Photooxidation is small or nonexistent in the visible region but is detectable for 334-nm irradiation and increasingly important for lower wavelengths. The constant value of Φ_{py} suggests that excitation into upper states, including the π–π^* internal ligand excited state, is followed by relatively efficient interconversion to a lower energy common state. This common state may be either the state responsible for the aquation reactions (proposed to be ligand field in character)[3,4] or one such as the state directly populated by MLCT excitation. The tendency to cascade efficiently to an active lower energy state is not an uncommon photo property of the heavier transition metal complexes.[8] For example the quantum yield of emission from the lowest MLCT state of $Ru(bipy)_3{}^{2+}$ is independent of excitation wavelength,[9] including wavelengths involving excitation of the ligand π–π^* states. However, it is equally easy to point to examples where excitation of upper states leads to photoreaction characteristic of the upper state. For example, π_L–π_L^* excitation of the ruthenium(II) complex $Ru(bipy)_2(stilbazole)_2{}^{2+}$ leads to isomerization reaction of the coordinated stilbazole in a manner similar to that observed with the π–π^* states of the free ligand.[10] What happens to the excited complex depends therefore upon the relative rates of chemical reaction *vs.* deactivation to a lower state.

It can be noted, however, that despite the relatively constant Φ_{py}, reaction does occur from an upper excited state of some manner, *i.e.* the photoredox process. Since $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$ are both susceptible to photooxidation when irradiated in the uv region[5,6] and since H_2 has been shown[5] to be a reaction product in the uv photolysis of $Ru(NH_3)_5py^{2+}$, a charge-transfer-to-solvent state is probably responsible for the photooxidation pathway. If so, the wavelength behavior of $\Phi_{Ru(III)}$ suggests that the population of the CTTS state is principally dependent on the energy of the exciting radiation rather than the specific character of the states initially populated. Another suggestion would be that the molar absorptivities at a particular wavelength include CTTS character, the percentage of which is energy dependent. The relative constancy of Φ_{py}, even at wavelengths where $\Phi_{Ru(III)}$ is comparable in magnitude, indicates that the majority of the initially excited molecules interconvert to the reactive state responsible for the aquation pathways. For the wavelengths studied here, the presence of the CTTS state and the photooxidation pathway apparently does not provide a dominant alternative mechanism for nonradiative deactivation directly to the ground state.

Registry No. $Ru(NH_3)_5py^{2+}$, 21360-09-8.

References and Notes

(1) (a) Presented in part at the Symposium on Inorganic Photochemistry, 164th National Meeting of the American Chemical Society, New York, N.Y., Aug 1972. (b) Taken in part from the Ph.D. dissertation of R.E.H., University of California, Santa Barbara, Calif., 1974.
(2) Camille and Henry Dreyfus Foundation Teacher–Scholar, 1971–1976.
(3) D. A. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *J. Amer. Chem. Soc.*, **94**, 6665 (1972).
(4) G. Malouf and P. C. Ford, *J. Amer. Chem. Soc.*, **96**, 601 (1974).
(5) P. C. Ford, D. H. Stuermer, and D. P. McDonald, *J. Amer. Chem. Soc.*, **91**, 6209 (1969).
(6) R. E. Hintze and P. C. Ford, *J. Amer. Chem. Soc.*, in press.
(7) D. H. Stuermer, unpublished observations.
(8) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N.Y., 1970.
(9) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971).
(10) P. P. Zarnegar, C. R. Bock, and D. G. Whitten, *J. Amer. Chem. Soc.*, **95**, 4367 (1973).

Pseudoaromatic Compounds. XX.[1] Palladium Chloride Complexes of Cycloheptatrienethione, Tropone, and Dichlorocycloheptatriene

Renzo Cabrino, Gino Biggi, and Francesco Pietra*

Only a few thio analogs of cycloheptatrienones have been reported so far.[2] Among these, 2-mercaptotropone[3] and dithiotropolone[4] are sufficiently stable to allow both structural and chemical investigations by ordinary techniques,[2,4] while cycloheptatrienethione was obtained as a (presumably quite impure) unstable red liquid[5] which was trapped as a [8 + 2] cycloadduct with maleic anhydride,[6] diethyl acetylenedicarboxylate,[6] or dichloroketene.[7]

Because of special interest toward cycloheptatrienethione as the parent member of a class of sulfur compounds, we report here on its trapping with palladium chloride or bromide. We report here also on similar studies with the synthetic precursors of the above thioketone.

Results and Discussion

Cycloheptatrienethione. A stable red microcrystalline material, which analyzed for a 2:1 adduct of cycloheptatrienethione with palladium chloride, precipitated on the mixing at 0° of a 10 molar excess of a dichloromethane solution of cycloheptatrienethione (prepared as previously described[7]) with dichlorobis(benzonitrile)palladium, whereas working with only a 5 molar excess of the ligand a less pure adduct was obtained.

That cycloheptatrienethione is the actual ligand is suggested by strong absorptions of the above 2:1 adduct at 450 nm (close to that of the free ligand[8]) and 1050 cm^{-1} (attributable to the coordinated thione group because the neat free ligand shows a rapidly decaying absorption at 1078 cm^{-1}). Also, the ^{1}H Fourier transform nmr spectrum in DMF-d_7 shows two complex absorptions at δ 8.9 (2 H) and 7.7 ppm (4 H) attributable to the 2, 7 and 3, 4, 5, 6 ligand ring protons, respectively. Finally, the mass spectrum shows the molecular ion C_7H_6S·$^+$ and a peak at m/e 78 which probably arises by CS loss from the molecular ion.

All the above data are consistent with either the trans 1 or the cis planar[9] arrangement 2.

1   2
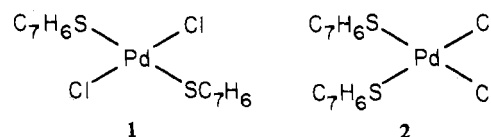
Infrared data indicate that in the solid the cis arrangement 2 is preferred over the trans one 1. In fact, the 2:1 adduct gives two absorption bands at 304 and 296 cm^{-1} which, being shifted to 264 and 257 cm^{-1} on replacement of chlorine with bromine (Table I), are attributable to the palladium–halogen stretching of 2.[9,10] This is confirmed both by the lack of the 357 ± 5 cm^{-1} band expected for the palladium–chlorine stretching mode of 1[9,10] and by the presence of two strong bands at 1050 and 1062 cm^{-1} attributable to the C=S stretching modes of 2. Clearly, for symmetry reasons, only one C=S band would be expected for 1.

Cycloheptatrienone. A stable pale yellow microcrystalline 2:1 adduct of cycloheptatrienone with palladium chloride precipitated on the mixing of dichloromethane solutions of the ligand and dichlorobis(benzonitrile)palladium.

Here not only were dipole moment measurements prevented by the extremely low solubility of the adduct, but also de-