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 $\pi-\pi^*$ 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 $\pi-\pi^*$ 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, $\pi_L-\pi_L^*$ 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 $\pi-\pi^*$ 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$_3$)$_5$H$_2$O^{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$_3$)$_5$py^{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$_3$)$_5$py^{2+}, 21360-09-8.

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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$_7$H$_6$S·$^+$ 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**.
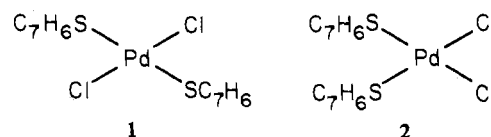
Infrared data indicate that in the solid the cis arrangement **2** is preferred over the trans one **1**. In fact, the 2:1 adduct gives two absorption bands at 304 and 296 cm^{-1} which, being shifted to 264 and 257 cm^{-1} on replacement of chlorine with bromine (Table I), are attributable to the palladium–halogen 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-

Table I. Far-Infrared Spectra for Some Palladium Complexes and Free Ligands

Complex or ligand	Ir absorptions, cm⁻¹
(C₇H₆S)₂PdCl₂[a]	383 w, 361 s, 336 s, 326 m, 304 s, 296 m
(C₇H₆S)₂PdBr₂[a]	383 w, 361 s, 318 m, 264 s, 257 m
(C₇H₆O)₂PdCl₂[a]	429 s, 419 s, 369 m, 344 s, 268 m
Cycloheptatrienone[b]	398 s, 384 s, 327 m

[a] Nujol mull. [b] Liquid film.

composition of the complex during attempted exchange of chlorine with bromine (which is not too surprising in view of the expected poorer coordination ability of the oxygen *vs.* sulfur ligand toward a class b metal) rendered very uncertain any configurational assignment from ir spectra. It is clear in fact that whereas the 429- and 419-cm⁻¹ bands (Table I) are probably due to the ligand, the 369- and 344-cm⁻¹ bands are too far apart from one another, besides showing the reversed order of intensities,[8,10] to be attributable to the cis oxygen analog of **2**. Moreover, while the 369-cm⁻¹ band could arise from the trans oxygen analog of **1**, the very broad 344-cm⁻¹ band could well be in part contributed by a band due to the cis isomer, so that we cannot even exclude it being a mixture of cis and trans isomers.

Dichlorocycloheptatriene. Dichlorocycloheptatriene is a versatile synthetic intermediate which can exist either as chlorotropenylium chloride or as covalent dichlorocycloheptatriene (possibly as a mixture of four isomers).[11]

Stability is insufficient to isolate any of these forms so that trapping with palladium chloride was attempted. Thus, on the mixing of *ca.* 0.15 *M* dichlorocycloheptatriene with *ca.* 0.06 *M* dichlorobis(benzonitrile)palladium in dichloromethane at room temperature (method a, Experimental Section) yellow microcrystals precipitated. These are nearly insoluble in all common solvents and elemental analysis is consistent with the tropenylium structure **3**.

3   4
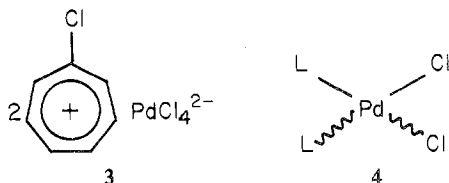
Absorptions at 341 (w), 320 (s), and 349 (m) cm⁻¹, being close to the value, 336 cm⁻¹, expected for the asymmetric stretching mode of PdCl₄²⁻,[12] support structure **3**. Also, the only conceivable alternative to structure **3** is structure **4** which, involving C=C coordination to the metal, has no precedent in olefin coordination chemistry of palladium.[13]

Experimental Section

Jeol PS 100, Unicam SP 800, and Perkin-Elmer 337 or 225 spectrometers were used to record ¹H nmr, uv, and ir spectra, respectively. Nmr data are in δ with respect to Me₄Si.

Dichloromethane was dried first over magnesium sulfate and then over calcium chloride and finally distilled under nitrogen. Cycloheptatrienone,[14] dichlorocycloheptatriene,[15] cycloheptatrienethione,[7] and dichlorobis(benzonitrile)palladium,[16] were prepared according to literature.

Dichlorobis(cycloheptatrienethione)palladium. To an ice-cold solution of dichlorobis(benzonitrile)palladium (0.2 g, 0.6 mmol) in dichloromethane (3 ml) was rapidly added, under N₂ with stirring, 60 ml of a dichloromethane solution of cycloheptatrienethione freshly prepared from 6 mmol of cycloheptatrienone. The mixture was allowed to reach room temperature, whereby red microcrystals precipitated which were filtered under N₂, washed with dichloromethane and pentane, and dried at 1 mm (0.18 g; 70% yield with respect to (C₆H₅CN)₂PdCl₂); mp 180° dec.

Anal. Calcd for C₁₄H₁₂Cl₂S₂Pd: C, 39.8; H, 2.8; Cl, 16.8; S, 15.2; Pd, 25.3. Found: C, 40.0; H, 2.7; Cl, 17.0; S, 14.9; Pd, 25.0. Spectra: δ (DCON(CD₃)₂) 7.7 (4 H, complex multiplet), 8.9 (2 H, complex

multiplet); νmax (KBr pellet) 3035 (w), 3000 (w), 2960 (w), 1610 (m), 1560 (w), 1520 (s), 1470 (s), 1430 (m), 1350 (m), 1270 (s), 1230 (s), 1050 (s), 950 (m), 835 (s), 740 (s), 590 (m), 550 (m) cm⁻¹; νmax (Nujol mull) 383 (w), 361 (s), 336 (s), 304 (s), 296 (s) cm⁻¹; λmax (log ε) 450 (4.05), 315 nm (3.46); *m/e* 124 (0.4), 123 (0.1), 122 (10), 121(8.5), 78(2).

Dibromobis(cycloheptatrienethione)palladium. To a stirred suspension of dichlorobis(cycloheptatrienethione)palladium (0.048 g, 0.11 mmol) in acetone (50 ml) was added, at room temperature, a solution of 0.17 g of LiBr·H₂O in 6 ml of acetone. The mixture was refluxed for 10 min and then stirred at room temperature for 1 hr. The crystalline solid was collected by filtration and an additional crop of crystals was obtained on the addition of water to the mother liquor. The two crops of crystals were mixed together and dried over P₂O₅ at 1 mm to give red microcrystals, mp 184–187° dec.

Anal. Calcd for C₁₄H₁₂S₂Br₂Pd: C, 33.1; H, 2.4; Br, 31.4. Found: C, 33.4; H, 2.7; Br, 30.9. Spectra: νmax (Nujol mull) 1605 (m), 1505 (s), 1420 (m), 1350 (m), 1270 (m), 1230 (w), 1060 (s), 1050 (s), 950 (w), 835 (m), 740 (s), 595 (w), 550 (m), 383 (w), 361 (s), 318 (m), 264 (s), 257 (m) cm⁻¹.

Dichlorobis(cycloheptatrienone)palladium. To a solution of dichlorobis(benzonitrile)palladium (0.125 g, 0.3 mmol) in dichloromethane (2 ml) was rapidly added at room temperature, under N₂ and with stirring, a solution of freshly distilled cycloheptatrienone (0.086 g, 0.8 mmol) in dichloromethane (2.5 ml). A precipitate was soon observed and was filtered, washed with dichloromethane and carbon tetrachloride, and finally dried at 1 mm to give 0.082 g (yield 70% with respect to (C₆H₅CN)₂PdCl₂) of pale yellow microcrystals, mp 172–173° dec.

Anal. Calcd for C₁₄H₁₂Cl₂O₂Pd: C, 43.1; H, 3.1; Cl, 18.2; Pd 27.4. Found: C, 42.8; H, 3.0; Cl, 18.9; Pd, 27.3. Spectra: νmax (Nujol mull) 1620 (s), 1580 (w), 1510 (s), 1250 (s), 1218 (s), 1024 (w), 903 (m), 835 (s), 826 (m), 783 (s), 755 (m), 611 (w), 583 (s), 570 (s), 429 (s), 419 (s), 369 (s) 344 (s), 268 (m) cm⁻¹.

Reaction of Dichlorocycloheptatriene with Dichlorobis(benzonitrile)palladium. Method a. To a solution of dichlorobis(benzonitrile)palladium (0.16 g, 0.4 mmol) in dichloromethane (2.5 ml) was rapidly added, at room temperature, under N₂ and with stirring, a solution of dichlorocycloheptatriene (3.3 ml) which had been freshly prepared from 1 mmol of cycloheptatrienone. A yellow precipitate was immediately obtained, filtered, washed with dichloromethane and pentane under N₂, and finally dried at 1 mm to give 0.17 g of yellow microcrystals, mp 110–115° dec.

Anal. Calcd for C₁₄H₁₂Cl₆Pd: C, 33.9; H, 2.4; Cl, 42.7; Pd, 21.4. Found: C, 33.9; H, 2.5; Cl, 39.3; Pd, 21.0. Spectra: νmax (KBr pellet) 3005 (w), 2980 (m), 2910 (w), 1620 (m), 1540 (s), 1505 (s), 1475 (s), 1440 (s), 1345 (m), 1270 (w), 1245 (m), 1220 (m), 1032 (s), 1010 (w), 945 (w), 780 (m), 735 (s), 580 (s) cm⁻¹; νmax (Nujol mull) 349 (m), 341 (w), 320 (s), 300 (w) cm⁻¹.

Method b. Carrying out the above reaction on the addition of dichlorobis(benzonitrile)palladium to a tenfold excess of a 0.05 *M* solution of dichlorocycloheptatriene under otherwise identical conditions, yellow microcrystals, mp 133–135° dec, were obtained.

Anal. Found: C, 37.3; H, 3.7; Cl, 26.4; O, 9.4; Pd, 20.8. Spectra: νmax (Nujol mull) 1610 (s), 1540 (s), 1510 (s), 1495 (m), 1405 (m), 1350 (m), 1320 (s), 1245 (s), 1225 (s), 1110 (m), 1055 (m), 1007 (s), 920 (m), 890 (s), 880 (m), 780 (s), 720 (w), 590 (m), 500 (w), 320 (s) cm⁻¹. These crystals are insoluble in CHCl₃, CH₂Cl₂, (C₂H₅)₂O, and (CH₃)₂CO, very slightly soluble in CH₃OH and C₂H₅OH, and slightly soluble in water where they showed λmax 230, 305, and 310 nm.

Registry No. (C₇H₆S)₂PdCl₂, 54062-27-0; (C₇H₆S)₂PdBr₂, 54062-28-1; (C₇H₆O)₂PdCl₂, 54062-29-2; 3, 54062-31-6; cycloheptatrienone, 539-80-0; dichlorobis(benzonitrile)palladium, 14220-64-5.

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Spectroscopic Behavior of [(π-C5H5)2Fe2(CO)3P(OCH3)3] and Related Compounds on Protonation of the Metal–Metal Bond[1]

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It has been known[2] for some years that a number of cyclopentadienylmetal carbonyl compounds containing metal–metal bonds can abstract a proton from strong acids to form species containing metal–hydrogen bonds. Early in our investigation of some of these reactions it was concluded that hydrogen-bridged M–H–M linkages, where M is a metal with other ligands attached, are formed. In particular, we were able to prepare a stable salt of the cation **2**.
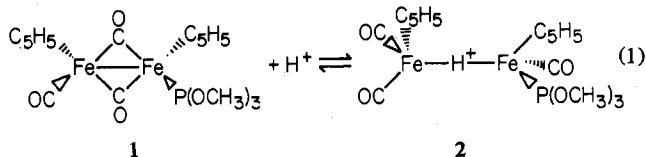
During our work, a report was published[3] in which the same conclusion regarding the structure of [CpFe(CO)2]2H+ (Cp = π-C5H5) was reached. Here we report nmr, ir, and electronic absorption spectra of **1** and **2** and related complexes. The relative basicities of **1**, [CpFe(CO)2]2, and [CpRu(CO)2]2 have been determined.

Experimental Section

General Data. All reactions and all handling of compounds were done under an atmosphere of nitrogen. The compounds [CpM(CO)2]2 (M = Fe, Ru), **1**, and the tetraphenylborate salt of **2** could be handled briefly in the air with no apparent harm but were stored under nitrogen in the dark at –20°. Solvents were generally deoxygenated by nitrogen purging or by several freeze–thaw cycles on a vacuum line. Where water could not be tolerated, benzene was distilled from sodium–benzophenone and acetone for spectra was distilled from P4O10 or from Linde 4A molecular sieves *in vacuo*. Melting points were determined with open capillary tubes and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer. Electronic spectra were obtained using Cary 17 and Cary 14 spectrophotometers. Nmr spectra were obtained with a Varian A-60A instrument.

{(Cp)2(CO)3Fe2[P(OCH3)3]3]H}{B(C6H5)4}. A red solution of 0.25 g of **1** in 7 ml of acetic acid (deoxygenated by nitrogen purging) was treated with 0.70 ml of 98% H2SO4. The H2SO4 need not be degassed

Table I. ^{1}H Nmr Spectra^a

Compd	$\tau(\text{H})^b$	$\tau(\text{C}_5\text{H}_5)$	$\tau(\text{CH}_3)$
[CpFe(CO)$_2$]$_2$		5.11	
{[CpFe(CO)$_2$]$_2$H}{HSO$_4$}	36.3	4.66	
[CpRu(CO)$_2$]$_2$		4.67	
{[CpRu(CO)$_2$]$_2$H}{HSO$_4$}	29.1	4.18	
Cp$_2$Fe$_2$(CO)$_3$P(OCH$_3$)$_3$		5.33, 5.47^d	6.50^e
{Cp$_2$Fe$_2$(CO)$_3$P(OCH$_3$)$_3$H}{HSO$_4$}	36.3^c	4.79, 5.05^d	6.18^f

^{a} All spectra are for acetic acid solutions. Protonated species were formed by adding 98% H$_2$SO$_4$ to these solutions. Chemical shifts are given in ppm. ^{b} Hydride of protonated species. ^{c} $J(^{31}\text{P}-^1\text{H}) = 44$ Hz. ^{d} The high-field cyclopentadienyl group is coupled to ^{31}P and, hence, bound to the iron which is bound to phosphorus. $J(^{31}\text{P}-\text{H}) = 1.5$ Hz. ^{e} $J(^{31}\text{P}-^1\text{H}) = 11$ Hz. ^{f} $J(^{31}\text{P}-^1\text{H}) = 11.5$ Hz.

for this preparation. The resulting green solution was added to a well-stirred solution of 0.28 g NaB(C6H5)4 in 14 ml deoxygenated water. The green powder was filtered in the air, washed with water, and dried. The product can be crystallized from 6 ml hot acetone–4.5 ml ether by slowing cooling to –20°; yield 74%; mp 154–159° dec. *Anal.* Calcd for C40H40O6Fe2PB: C, 62.38; H, 5.23; Fe, 14.50; B, 1.40. Found: C, 62.83; H, 5.14; Fe, 16.11; B, 1.30.

[CpRu(CO)2]2. This was prepared by the method of Blackmore, *et al.*,[5] using [Ru(CO)3Cl2]2 prepared by the method of Cleare and Griffith.[6] The only way we found to obtain pure material from the pyrophoric benzene extract was tedious sublimation of aliquots at 160° (10 μ). The brown-orange sublimate was fractionally resublimed, first at 60° (10 μ) to remove yellow Cp2Ru and then at 160° (10 μ) to produce light orange product. Even purer material can be obtained after a second fractional sublimation; yield 0.17 g, 3%; mp 175–176°.

cis- and *trans-*[CpFe(CO)2]2.[7] The trans isomer was most easily obtained by crystallizing a sample of commercial material from hot ethanol. Crystallizing a sample in ethyl acetate at 0° again produces the trans isomer. By cooling this mother liquor to –78°, the cis isomer is obtained. Comparison of the KBr pellet ir spectra to those of Bryan, *et al.*,[7] showed that the trans compound was formed uncontaminated by the cis form but that the cis form was sometimes contaminated with the trans. Repeated preparations gave enough pure cis isomer for our studies.

Results and Discussion

^{1}H Nmr Spectra. When a solution of [CpFe(CO)2]2 in acetic acid is treated with a large excess of 98% H2SO4 (H2SO4:[CpFe(CO)2]2 > 100), the very dark red-purple solution becomes green and a signal appears in the metal hydride region at τ 36.3 ppm. The very high-field absorption immediately suggests that the hydride is in a bridging position.[8,9] Nmr spectra are summarized in Table I. In all compounds studied, protonation deshields the cyclopentadienyl groups, consistent with the introduction of positive charge. Of particular note, *both* cyclopentadienyl groups of each compound are shifted downfield, indicating a static terminal hydride structure to be very unlikely. The coupling of the bridging hydride and ^{31}P in **2** (44 Hz) is similar in magnitude to that found between bridging phosphorus and terminal hydrogen.[9d]

It was possible to make a quantitative estimate of the base strength of [CpFe(CO)2]2 in acetic acid solution. Addition of successive aliquots of 4.10 M H2SO4 in acetic acid to a solution of [CpFe(CO)2]2 caused the cyclopentadienyl signal at 5.11 ppm to decrease in intensity as the corresponding signal at 4.66 ppm of protonated product grew. These data were fitted to the equilibrium in eq 2. The product was taken as

$$[\text{CpFe(CO)}_2]_2 + \text{H}_2\text{SO}_4 \overset{K_2}{\rightleftharpoons} \{[\text{CpFe(CO)}_2]_2\text{H}^+\}\{\text{HSO}_4{}^-\} \quad (2)$$
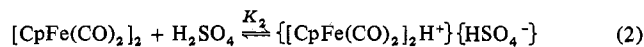
$$K_2 = \frac{[\{[\text{CpFe(CO)}_2]_2\text{H}^+\}\{\text{HSO}_4{}^-\}]}{[[\text{CpFe(CO)}_2]_2][\text{H}_2\text{SO}_4]}$$

an ion pair because of the low dielectric constant of acetic acid.[10] The apparent equilibrium constant increases with increasing H2SO4 concentration, and we estimate that the value of K_2 at zero sulfuric acid concentration is $10^{-0.8}$ l. mol^{-1}.[11]