are described, K[Ln(C_8H_8)$_2$] and [(C_8H_8)LnCl·2THF]$_2$. The empirical composition of both series of complexes has been well established by analysis and low-temperature oxidation. The molecular structures of both series are established by comparison of spectral characteristics with the corresponding cerium complex for which in both cases the single crystal X-ray structure has been determined.

The chemical and spectral results demonstrate that these complexes involve no chemically significant amount of covalent interaction with the metal. The ease of hydrolysis and the hydrolysis products are characteristic of ionic salts of C_8H_8 dianion. The facile interconversion of the two series of complexes is also indicative of highly ionic bonding. The near-ir spectra are characteristic of f^n transitions in the central metal ion with only mild perturbation by the ligand field. The magnetic susceptibility results lead to a similar conclusion. The assignment of visible bands as ligand to metal charge-transfer transitions, however, does imply some overlap of ligand π MO's and metal atomic orbitals. Nevertheless, even if the 4f orbitals are involved in such transitions, the actual amount of overlap need only be minute and without chemical significance. Such minute overlap could still correspond to essentially ionic ligand–metal bonding. Furthermore, included among these sandwich complexes is that with yttrium which is not a lanthanide rare earth and which has no 4f electrons or accessible 4f orbitals; yet its complex has properties similar to those of the lanthanide rare earth complexes.

These results provide a valuable contrast to the corresponding actinide complexes and suggest that the actinides do have significant ring–metal covalent bonding. The Raman spectral results show that the M–C bond strength in uranocene is greater than in the corresponding lanthanide complexes.

Finally, the rapid and complete conversion of the cerium complex to uranocene on treatment with UCl_4 also emphasizes the greater thermodynamic stability of the actinide complex. Thus, all of this chemistry is consistent with the simple hypothesis that the lanthanide C_8H_8 complexes are almost wholly ionic whereas the actinide C_8H_8 complexes have significant ring–metal covalent bonding involving metal orbitals; these differences suggest strongly that the actinite orbitals involved in such covalent interaction are 5f orbitals.

Acknowledgment. We thank Dr. Norman Edelstein of the Lawrence Berkeley Laboratory and Professor Gerd M. LaMar of University of California, Davis, who measured preliminary nmr spectra of the paramagnetic complexes. We also thank Professor Kenneth Raymond for his helpful discussions and suggestions.

Pentachlorocyclopentadienylmercurials

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Abstract: The first σ-bonded organometallic derivatives of the pentachlorocyclopentadienide anion, $C_5Cl_5^-$, are reported. The compounds $Hg(C_5Cl_5)_2$, C_5Cl_5HgCl, C_5Cl_5HgBr, and $C_6H_5HgC_5Cl_5$ are prepared either by the reaction of mercuric halides with thallium pentachlorocyclopentadienide or by the reaction of methoxides of mercury with pentachlorocyclopentadiene. Different crystalline phases of these compounds and adducts of these compounds with ethers and with mercuric halides are described and characterized. The presence of a σ-bonded C_5Cl_5 ring rather than a π-bonded ring is deduced from ir, nqr, and uv spectra of the mercurials. The electronic spectra of substituted cyclopentadienes are discussed; those for the mercurials are interpreted in terms of σ–π conjugation between the C–Hg bond and the cyclopentadiene π orbitals.

Organometallic derivatives of chlorocarbons were little known until recently, but this field has grown rapidly in the last few years, as shown in the review by Chivers.[1] Organometallic derivatives of the interesting pentachlorocyclopentadienide anion,[2] $C_5Cl_5^-$ (**1**), were not isolated until 1970, when perchloroferrocene, $Fe(C_5Cl_5)_2$, and perchlororuthenocene, $Ru(C_5Cl_5)_2$, were prepared.[3] This preparation of π-bonded organometallic derivatives of **1** was supplemented in 1971 by the isolation of an ionic organometallic derivative $Tl^+C_5Cl_5^-$ (**1a**).[2] We wish to report a series of σ-bonded organometallic derivatives of mercury including bis(pentachlorocyclopentadienyl)mercury (**2**) and several compounds (**3**–**5**) of the general formula C_5Cl_5HgX, some ether adducts, and double salts.[4]

Synthesis

Compounds **2e** and **3a** were prepared by the action of **1a** on solutions of $HgCl_2$ in tetrahydrofuran at −78°. When 2 mol of **1a** was allowed to react with 1 mol of $HgCl_2$, **2e** was produced as colorless flat crystals. However, use of only 1 mol of **1a** furnished

$$2Tl^+C_5Cl_5^- + HgCl_2 \xrightarrow{\text{THF}} 2TlCl + Hg(C_5Cl_5)_2\text{–THF}$$

3a as lemon-yellow crystals. Mixing of equimolar amounts of **1a** and **3a** in tetrahydrofuran afforded **2e**.

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(1) T. Chivers, *Organometal. Chem. Rev., Sect. A*, 6, 1 (1970).

(2) G. Wulfsberg and R. West, *J. Amer. Chem. Soc.*, 94, 6069 (1972).

(3) F. L. Hedberg and H. Rosenberg, *ibid.*, 92, 3239 (1970); 95, 870 (1973).

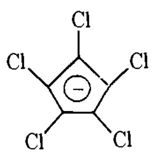
(4) Some of these compounds have been reported in a preliminary communication: G. Wulfsberg and R. West, *ibid.*, 93, 4085 (1971).

Table I. Mercuric Pentachlorocyclopentadienides

No.	Formula	Mp, °C	% C Theory	% C Found	% H Theory	% H Found	% Cl Theory	% Cl Found	% Hg Theory	% Hg Found	% other Theory	% other Found
2a	α-$Hg(C_5Cl_5)_2$	112–113 dec	17.79	17.93	0.00	0.00	52.51	52.32	29.71	29.90		
2b	β-$Hg(C_5Cl_5)_2$	106 dec	17.79	17.76	0.00	0.04	52.51	52.40	29.71	29.90		
2c	γ-$Hg(C_5Cl_5)_2{}^e$											
2d	$Hg(C_5Cl_5)_2 \cdot {}^5/_3C_4H_{10}O_2$										18.20	18.70^a
2e	$Hg(C_5Cl_5)_2 \cdot xC_4H_8O^e$											
3a	α-$ClHgC_5Cl_5$	135–136 dec	12.68	12.95	0.00	0.00	44.94	44.13	42.38	42.24		
3b	β-$ClHgC_5Cl_5{}^e$											
3c	γ-$ClHgC_5Cl_5$	136 dec	12.68	12.95	0.00	0.00	44.94	44.69				
3d	$ClHgC_5Cl_5 \cdot HgCl_2$	160 dec	8.05	8.33	0.00	0.00	38.05	38.29	53.90	54.11		
3e	$ClHgC_5Cl_5 \cdot C_4H_{10}O_2$										15.99	16.04^a
3f	$ClHgC_5Cl_5 \cdot C_6H_{14}O_3$	70–75									22.09	22.5^b
3g	$ClHgC_5Cl_5 \cdot {}^1/_2C_4H_8O$										7.08	5.71^c
4	$BrHgC_5Cl_5$	132 dec	11.60	11.75	0.00	0.00	34.23	34.20			15.43	14.85^d
4a	$BrHgC_5Cl_5 \cdot HgBr_2$	161 dec	6.84	6.88	0.00	0.00	20.18	20.20			27.29	27.05^d
4b	$BrHgC_5Cl_5 \cdot C_4H_{10}O_2$										14.83	14.94^a
5	$C_6H_5HgC_5Cl_5$	120–121 dec	25.65	25.83	0.98	1.08	34.42	34.28	38.95	38.76		

[a] Per cent 1,2-dimethoxyethane (glyme), $C_4H_{10}O_2$. [b] Per cent bis(2-methoxyethyl) ether (diglyme), $C_6H_{14}O_3$. [c] Per cent tetrahydrofuran (THF), C_4H_8O. [d] Per cent bromine. [e] Not analyzed.

The reaction of equimolar amounts of **1a** and C_6H_5HgCl gave colorless crystals of **5**. The synthesis is analogous to the previously reported use of $Tl^+C_5H_5^-$ as a mild reagent for preparing cyclopentadienyl–metal derivatives.[5,6] However, the alkali metal salts of **1** (unlike $Na^+C_5H_5^-$)[7] gave little or no product.



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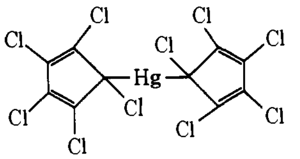

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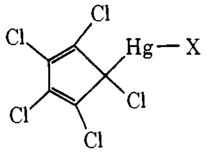
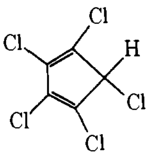
1, $Tl^+C_5Cl_5^-$

crystal modifications; **2a**,**2b**,**2c**, adducts, **2**-glyme (**2d**); **2**-THF (**2e**)



3, X = Cl
4, X = Br
5, X = C_6H_5

crystal modifications; **3a**,**3b**,**3c**, adducts; **3**-$HgCl_2$ (**3d**); **3**-glyme (**3e**); **3**-diglyme (**3f**); **3**-THF (**3g**) **4**-$HgBr_2$ (**4a**); **4**-glyme (**4b**)



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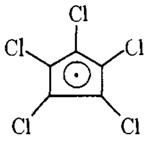

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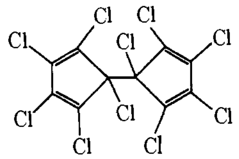

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The use of the very unstable **1a** can be avoided by a second, more convenient method, in which mercury methoxides or hydroxides react directly with 1,2,3,4,5-pentachlorocyclopentadiene (**6**). Treatment of mercuric acetate with 2 mol of lithium methoxide in methanol produced a white air sensitive precipitate.

$$(CH_3COO)_2Hg + 2LiOMe \longrightarrow 2LiOCOCH_3 + \text{“}Hg(OMe)_2\text{”}$$

The precipitate was filtered under nitrogen, washed free of lithium salt, dried, and allowed to react at 0° with 2 mol of **6** in *n*-hexane. The reaction proceeded readily

$$\text{“}Hg(OMe)_2\text{”} + 2C_5Cl_5H \longrightarrow (C_5Cl_5)_2Hg + 2CH_3OH$$

and afforded a mixture of colorless **2a** and pale yellow **2b**. Similarly, treatment of a tetrahydrofuran solution of $HgCl_2$ with lithium methoxide in methanol produced an air-sensitive orange precipitate. Reaction with 1 mol of **6** in pentane at 0° gave **3a**. Reaction of $HgCl_2$ with 2 mol of lithium methoxide followed by treatment with **6** yielded only small amounts of **2**; **3a** was still the major product.

If sodium methoxide is substituted for lithium methoxide, the resulting precipitate must be washed with large volumes of methanol to remove the sparingly soluble chloride, since the presence of sodium chloride decreases the yield of **3a** significantly. Commercial "phenylmercuric hydroxide," when stirred at 0° with **6** in the presence of 2,2-dimethoxypropane (a dehydrating agent) in *n*-hexane, gave **5** in good yield.

These reactions most likely involve methoxides and/or hydroxides of mercury as intermediates, the structures of which are complex and not well understood.[8,9] Proof of the existence of such intermediates, however, has been obtained in the preparation of phenyl(trihalomethyl)mercury compounds.[8] The ease of reaction encountered in the present study is undoubtedly due to the rather high acidity of **6**. The reactions must be carried out in hydrocarbon solvents. More polar solvents such as tetrahydrofuran or glyme apparently favor the formation of unstable **1** in solution which can lead to secondary products.

The desymmetrization reaction

$$(C_5Cl_5)_2Hg + HgBr_2 \longrightarrow 2C_5Cl_5HgBr$$

was used to prepare cream-colored crystals of **4**.[10] A similar reaction between **2** and $HgCl_2$ afforded **3c** in good yield. The adducts of **2**–**4** with tetrahydrofuran (THF, C_4H_8O), 1,2-dimethoxyethane (glyme, $C_4H_{10}O_2$), and bis(2-methoxyethyl) ether (diglyme, $C_6H_{14}O_3$) were prepared by dissolving the appropriate organomer-

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(10) A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Yu N. Sheinker, *Dokl. Chem.*, 159, 1274 (1964).

Table II. Characteristic Infrared Absorptions of Ionic, π-Bonded, and σ-Bonded C_5Cl_5 Groups[a]

Type of absorption	Ionic $C_5Cl_5^-$ [b]	π-bonded $Fe(C_5Cl_5)_2$ [c]	Organic RC_5Cl_5 [d,e]	σ-bonded C_5Cl_5HgX, solid[d]	C_5Cl_5HgX, solution[f]
Ring modes	1410–1415 (s)	1350 (s)	1595–1604 (vs)	1563–1586 (s–vs)	1569–1582 (s–vs)
		1307 (m)	1558–1577 (w–s)	1558–1566 (w, sh)	
			1228–1248 (vs)	1243–1259 (vs)	1240–1249 (vs)
			1152–1196 (m–s)	1187–1204 (m–s)	1192–1199 (m–s)
			1065–1139 (m–vs)	1127–1138 (m–vs)	1127–1135 (w–vs)
			961–976 (m–s)	970–979 (w–m)	970–976 (w–m)
			937–966 (w–s)	946–954 (m)	949–955 (w–s)
			574–675 (s)	647–655 (m–s)	648–660 (m–s)
			502–568 (w–m)	508–519 (vvw–w)	510–522 (vvw–w)
			358–367 (vw)	339–365 (vvw–w)	335–363 (vw)
Allylic C–Cl stretch			717–810 (s–vs)	720–766 (w–vs, multiple)	727–771 (m–s, multiple)
Vinylic/aromatic C–Cl stretch	657–681 (m–s)	702 (s)	676–707 (s–vs)	689–697 (s–vs)	692–695 (s–vs)

[a] Bands due to C_6H_5, C–H, Hg–Cl, etc., are deleted. Frequencies are given in cm^{-1}. [b] Reference 3. [c] Reference 4. [d] Mineral oil mull. [e] Neat liquid or film. [f] Dissolved in CCl_4, $CHBr_3$, or C_6H_6.

Table III. Hg–Cl Infrared Frequencies of C_5Cl_5HgCl and Other Model Compounds

Compd	Mull	CCl_4 soln	C_6H_6 soln
3a	319 (s)		
3c	327 (vs)	369 (m)	
3d	372 (s) ($HgCl_2$) 318 (m) (C_5Cl_5HgCl)		396 (s) ($HgCl_2$) 358 (s) (C_5Cl_5HgCl)
3e	328 (s)		
3f	330 (s)		
3g	335 (s), 308 (s)	367 (sh), 359 (m), 352 (sh)	
CCl_3HgCl	339 (s)		
$HgCl_2$–glyme	357 (vs) (antisym), 294 (m) (sym)		
$HgCl_3$–diglyme	364 (s)		
$HgCl_2$	375 (antisym)		392 (antisym)[a]

[a] G. Allen and G. Warhurst, *Trans. Faraday Soc.*, **54**, 1786 (1958).

curial in the ethereal solvent, adding *n*-heptane and cooling. Large colorless crystals which decrepitate readily were formed. The adducts were analyzed by pumping on weighed samples until a constant weight was obtained.[11] The double salts with mercury halides, **3d** and **4a**, were prepared by combining equimolar solutions of the components in tetrahydrofuran or benzene and subsequently removing solvent under reduced pressure. The physical constants and other pertinent data for these compounds are summarized in Table I.

Crystal Modifications. Bis(pentachlorocyclopentadienyl)mercury exists in three modifications: the white α form **2a**, the yellow β form **2b**, and the 77°K modification of the latter, designated as the γ form, **2c**. The reaction of $Hg(OCH_3)_2$ with **6** produces predominantly **2b** but crystals of **2a** are present and can be separated by hand. Pure **2a** can be obtained from **2d** by pumping off all the 1,2-dimethoxyethane. **2a** can then be isomerized to **2b** by grinding with cyclohexane. Compound **2b** on cooling to 77°K gives a different nqr spectrum, that of **2c**.

Compound **3a**, on cooling to 77°K, changes from yellow to white and gives a qualitatively different nqr spectrum. This low temperature modification is referred to as **3b**. A third modification, **3c**, can be obtained by adding a solution of **3a** in dichloromethane to excess *n*-heptane. Cream-colored **3c** crystallizes rapidly from this solvent mixture. Its nqr spectrum is qualitatively the same at 77 and 301°K. **3c** can also be obtained from a solution of **3a** using seed crystals of **3c**.

Spectra and the Mode of Metal–C_5Cl_5 Bonding

Infrared Spectra. The nature of bonding between a metal and a cyclopentadienyl ring can be distinguished in principle by means of infrared spectra.[12] In an ionic C_5Cl_5 ring (symmetry D_{5h}) only one ring (carbon–carbon) mode is allowed in the infrared, while in π-bonded metallocenes involving C_5Cl_5 (local symmetry at the ring C_{5v}) two ring modes are permitted. In a σ-bonded RC_5Cl_5 (symmetry C_s), however, nine ring modes are allowed. This test is particularly useful for C_5Cl_5 derivatives because C–H bending modes are absent, leading to a clear assignment of ring modes and C–Cl modes.

Table II lists the range in frequencies observed for compounds **2**–**5** both in solid state state and in solution. The frequency range data for RC_5Cl_5 includes a variety of compounds where R = Cl, Br, CCl_3, C_5Cl_5, H, C_2H_5, isopropyl, or *tert*-butyl. The observed frequencies were assigned as ring or C–Cl modes by comparison with assignments for C_5Cl_6[13] and $C_5Cl_5CCl_3$.[14] Omitting the very weak 339–365 band which may be a combination, nine ring mode frequencies are observed.

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(11) T. B. Brill and Z. Z. Hugus, Jr., *Inorg. Chem.*, **9**, 984 (1970).

(12) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(13) H. Gerding, H. J. Prins, and H. Van Brederode, *Recl. Trav. Chim. Pays-Bas*, **65**, 168 (1946).

(14) E. Zeigler, *Z. Anal. Chem.*, **213**, 9 (1965).

Table IV. ^{35}Cl Nqr Frequencies of C_5Cl_5 Groups (MHz at 77 °K)

Compd	Vinylic chlorine resonances (S/N in parentheses)				Allylic res.
$C_5Cl_4H_2$[a]	36.128	*b*	36.298	*b*	
6	36.887 (9)	36.928 (12)	36.951 (5)	37.090 (9)	38.019 (8)[c]
C_5Cl_6[d]	36.953 (9)	37.279 (6)	37.283 (10)	37.454 (10)	38.813 (7) 39.082 (10)
2c	36.431 (7)	36.700 (13)	36.882 (12)	36.980 (5)	38.240 (6)
	36.569 (5)	36.812 (11)	36.925 (11)	36.995 (8)	38.364 (6)
3f	36.543 (12)	36.570 (10)	36.592 (9)	36.613 (10)	38.364 (12)
4b	36.307 (5)	36.540 (6)	36.601 (sh)	36.749 (9)	38.444 (5)
	36.367 (5)	36.549 (sh)	36.610 (7)	36.778 (8)	38.878 (5)
5	36.212 (9)	36.265 (8)	36.737 (10)	36.865 (9)	37.350 (6)
Compd	Aromatic chlorine resonances				
$Bu_4P^+C_5Cl_5^-$ [e]	35.20 (10)	35.28 (10)	35.33 (10)	35.50 (7)	35.68 (8)
$Ru(C_5Cl_5)_2$[e]	38.61 (5)	*b*	38.66 (5)	*b*	38.74 (2)

[a] I. Agranat, D. Gill, M. Hayek, and R. M. J. Loewenstein, *J. Chem. Phys.*, **51**, 2756 (1969). [b] This chlorine is in a position which is crystallographically indistinguishable from another chlorine, hence gives no separate resonance. [c] In C_5Cl_5D this frequency was measured at 38.004 MHz. Vinylic frequencies were unshifted. [d] M. Hayek, D. Gill, I. Agranat, and M. Rabinovitz, *J. Chem. Phys.*, **47**, 3680 (1967). [e] Reference 3.

Based on these observations compounds **2–5** must have a σ-bonded structure both in solution and as solids.

In Table III are listed the Hg–Cl stretching frequencies for **3** and a few other model compounds. These frequencies confirm the presence of the Hg–Cl unit, and show the presence of discrete $HgCl_2$ molecules in **3d** rather than, say, $HgCl_3^-$ and $C_5Cl_5Hg^+$ ions. No absorption was observed which could be assigned to the Hg–C_5Cl_5 stretching mode.

Nuclear Quadrupole Resonance (nqr) Spectra. The nqr spectra of **2–5** have been determined at 77°K. Representative data are given in Table IV along with data for various model C_5Cl_5 compounds.[15] The spectra of the mercurials are complex, but in each case a series of four or more lines are found in the vinyl-Cl region (35.7–37.4 MHz), and one or more lines in the allylic region (37.3–39.7 MHz). The relative intensity of vinyl-Cl:allyl-Cl is nearly 4:1. Similar results are observed for the organic C_5Cl_5 derivatives. These results contrast with the spectra[3] of $Ru(C_5Cl_5)_2$ and the ionic salts of $C_5Cl_5^-$ in which all lines fall within a narrow range of not more than 0.75 MHz. Thus the nqr spectra of the mercurials also indicate that they are σ bonded in the solid state.[16]

σ–π Conjugation in Cyclopentadienes. The electronic structure of cyclopentadiene has been calculated by Del Bene and Jaffe[21] using a modified CNDO method. These calculations indicate the importance of hyperconjugation of the σ bonds in the CH_2 group with the π bonds in the diene portion of the molecule. One σ-bonding orbital in the CH_2 group is not separated by symmetry from the π orbitals, and is involved, along with the C═C π orbitals, in π-type molecular orbitals as shown diagramatically in Figure 1. The effects of such hyperconjugation are to stabilize π_0, destabilize π_1 and π_3*, and leave π_2 and π_4* unchanged (Figure 1). σ–π conjugation removes electron density from the CH_2 system (because of the system's involvement in the unpopulated π_3* orbital) and transfers it to the diene system. We would therefore expect it to occur with substituents of low electronegativity or high polarizability, such as H and Hg, but not with highly electronegative substituents such as $-OCH_3$, $-CCl_3$, and –Cl.

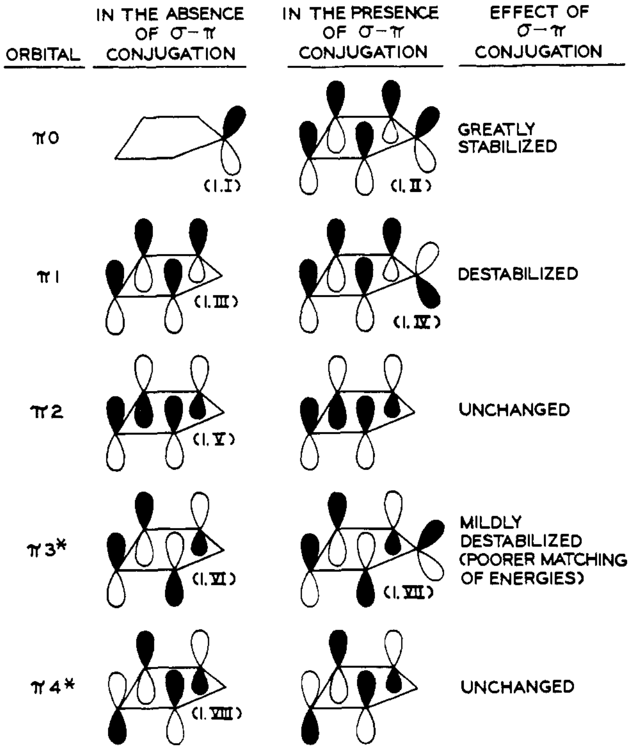

Figure 1. π-molecular orbitals in cyclopentadiene.

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(15) The complete nqr data will be presented and discussed in a separate paper.

(16) The question of fluxional behavior in σ-bonded cyclopentadienyls of many metals has been an area of active research.[17] Thus the cyclopentadienyls of mercury show fluxional behavior[18] while the pentamethylcyclopentadienylmercurials reportedly do not.[19] We have attempted to obtain ^{13}C nmr spectra of 2 and **3**. (Such spectra have been used recently in the study of a fluxional behavior in some metal-substituted cyclopentadienes.)[20] Unfortunately due to the instability of **2** and **3** in solution above 30° for any extended period of time as well as their solubility in preferred solvents, we have not yet been able to obtain satisfactory spectra.

(17) Fluxional organometallics have been reviewed by F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968). A vigorous dissent with respect to the elements of the fifth and sixth periods is contained in the review by E. I. Fedin, L. A. Fedorov, and R. B. Materikova, *J. Struct. Chem.*, **11**, 169 (1970).

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(20) U. K. Grishin, N. M. Sergeyev, and U. A. Ustynuk, *Org. Magn. Resonance*, **4**, 377 (1972).

(21) J. Del Bene and H. H. Jaffe, *ibid.*, **48**, 4050 (1968).

Table V. Uv Spectral Data for Organic Cyclopentadienes[a]

Compd	Solvent	$\pi_1 \rightarrow \pi_3^*$	$\pi_2 \rightarrow \pi_4^*$	$\pi_2 \rightarrow \pi_3^*$	Estimated "$\pi_3^* \rightarrow \pi_4^*$" separation,[b] eV
C_5H_6	Vapor[d]	157	198	257	
$C_5Cl_4H_2$	EtOH[c,e]	End (3.7)	232 (sh, 3.2)	276 (3.6)	0.86
C_5Cl_5H	EtOH[c,e]	End (4.3)	227 (sh, 3.3)	307 (3.3)	1.42
$C_5Cl_5CMe_3$	Isooctane[f]			311 (3.3)	
$C_5Cl_4(OMe)_2$	EtOH[e]			308 (3.4)	
C_5Cl_6	EtOH[c,e]	End (4.0)	235 (sh, 3.4)	322 (3.3)	1.43
$C_5Cl_5CCl_3$	EtOH[c]	204 (4.3)	237 (sh, 3.4)	327 (3.4)	1.44

[a] λ_{max} in nm (log ϵ). [b] Calculated by subtracting $\pi_2 \rightarrow \pi_3^*$ from $\pi_2 \rightarrow \pi_4^*$. [c] This work. [d] G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, New York, N. Y., 1966, p 663. [e] Reference 22. [f] V. Mark, *Tetrahedron Lett.*, 295 (1961).

Ultraviolet data for substituted pentachlorocyclopentadienes has been reported by Idol, Roberts, and McBee.[22] We have extended observation of the uv bands to 200 nm, and summarized pertinent data in Table V. Assignments for the polychlorocyclopentadienes can be made on the basis of that for C_5H_6.[21] The lowest energy transition is assigned to $\pi_2 \rightarrow \pi_3^*$; in the event of σ–π conjugation with the $-CX_2$ group this band would be shifted to higher energy.[23] The $\pi_2 \rightarrow \pi_3^*$ transition occurs at 308 nm (4.03 eV) in $C_5Cl_4(OMe)_2$ in which no hyperconjugation is expected, and at nearly the same value for $C_5Cl_5CMe_3$ (and other alkylpentachlorocyclopentadienes not cited), and in C_5Cl_5H. A small shift to lower energies is observed for C_5Cl_6 and $C_5Cl_5CCl_3$, perhaps due to mixing of chlorine 3d orbitals or C–Cl antibonding orbitals with π_3^*. For $C_5Cl_4H_2$, however, a large shift to higher energy is observed for $\pi_2 \rightarrow \pi_3^*$ (276 nm, 4.49 eV). This value is close to that for C_5H_6 in which hyperconjugation is believed to be important.[21] If the σ–π conjugative model is correct, the data suggest that this interaction is important in $C_5Cl_4H_2$ but not in C_5Cl_5H or C_5Cl_6.

A further indication of σ–π conjugation can be obtained by subtracting the energy of the $\pi_2 \rightarrow \pi_3^*$ transition from that of $\pi_2 \rightarrow \pi_4^*$,[24] thus obtaining an approximate value for the $\pi_3^* \rightarrow \pi_4^*$ separation. This separation should be smaller in the presence of σ–π conjugation (Figure 1). For the $C_5Cl_4R_1R_2$ compounds, this separation is approximately 1.4 eV *except* in $C_5Cl_4H_2$, where it is 0.86 eV, consistent with significant σ–π conjugation in $C_5Cl_4H_2$ and its unimportance in C_5Cl_5H, C_5Cl_6, and $C_5Cl_5CCl_3$.[25]

σ–π Conjugation in Perchlorocyclopentadienylmercurials. In the C_5Cl_5HgX compounds, the electron-releasing nature of mercury substituents may counter the electron-withdrawing nature of the allylic chlorine, allowing σ–π conjugation. It is also possible that the molecule might distort so as to increase the C–Hg bond overlap with the diene π bonds while reducing the unfavorable C–Cl bond overlap.

Ultraviolet and ir data for compounds **2**–**5** are given in Table VI. The lowest energy band resembles in position and intensity the π_2–π_3^* band of C_5Cl_5R compounds. σ–π hyperconjugation is predicted to cause a shift to higher energies. However, it is probable that the unoccupied 6p orbitals on mercury can also interact with π_3^*, producing a red shift and masking the σ–π conjugation effect. The data in any event show a very irregular trend in the $\pi_2 \rightarrow \pi_3^*$ transition energy as a function of X in C_5Cl_5HgX.

The second-lowest energy band does not resemble in position and intensity any band found in organic C_5Cl_5R compounds, in alkylmercurials,[28] phenylmercurials[29] or trichloromethylmercurials,[30] but *does* resemble bands found in allylmercurials,[31] benzylmercurials,[29] and cyclopentadienylmercurials,[32] *i.e.*, in other σ–π conjugated systems. In the cyclopentadienylmercurials this band has been assigned[32] to a transition from the C–Hg σ bond to the diene system, *i.e.*, as $\pi_1 \rightarrow \pi_3^*$ in our terminology (Figure 1.IV; Figure 1.VII). The fact that it is so greatly shifted from the position of $\pi_1 \rightarrow \pi_3^*$ in simple RC_5Cl_5 compounds indicates the importance of hyperconjugation, *i.e.*, the C–Hg σ component is the major part of the π_1 orbital.

We would expect a $\pi_1 \rightarrow \pi_3^*$ transition to show a shift to *lower* energy with increased hyperconjugation, opposite to the trend in $\pi_2 \rightarrow \pi_3^*$. Mercury 6p orbital participation would serve to reinforce this trend, not counteract it as in $\pi_2 \rightarrow \pi_3^*$. In cyclohexane solution the transition energies are in the order $C_5Cl_5HgCl >$ $C_5Cl_5HgBr > C_5Cl_5HgC_6H_5 > (C_5Cl_5)_2Hg$, approximately consistent with predicted ease of σ–π conjugation ($HgCl < HgBr < HgC_5Cl_5 < HgC_6H_5$).

However, the effect of Hg 6p orbitals may not be a uniform variable in this series. We should be able to eliminate most of the effect of 6p orbital participation in π_3^* by subtracting the $\pi_2 \rightarrow \pi_3^*$ energy from the $\pi_1 \rightarrow \pi_3^*$ energy, giving an approximation of the $\pi_1 \rightarrow \pi_2$ separation. As σ–π conjugation increases this separation should decrease (Figure 1 and Table VI).

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(22) J. D. Idol, Jr., C. W. Roberts, and E. T. McBee, *J. Org. Chem.*, 20, 1743 (1955).

(23) This change contrasts with the bathochromic shift of the long-wavelength transition proposed upon hyperconjugation in allyl and benzyl compounds, where the highest occupied MO is not nodal at the CX_2 group.

(24) The second electronic transition in C_5H_6 has been calculated[21] to be principally $\pi_2 \rightarrow \pi_4^*$. This transition involves two orbitals which are nodal at the allylic carbon and so should be unaffected by σ–π conjugation. In fact all of the $C_5Cl_4R_2$ compounds absorb in the relatively narrow range of 5.23–5.46 eV (227–237 nm). The highest energy transition, calculated to be $\pi_1 \rightarrow \pi_3^*$ for C_5H_6, lies outside the spectrophotometric range for most of the compounds in question.

(25) Additional evidence for σ–π conjugation is given by structural studies of C_5H_6[26] and C_5Cl_6.[27] In the former the allylic H–C–H angle is 147°; the spreading of the dihedral HCH angle above the tetrahedral value is consistent with σ–π overlap. In contrast the Cl–C–Cl angle in C_5Cl_6 is 117°.

(26) G. Liebling and R. E. Marsh, *Acta. Crystallogr.*, **19**, 202 (1965).

(27) C. H. Chang and S. H. Bauer, *J. Phys. Chem.*, **75**, 1685 (1971).

(28) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1454 (1955).

(29) Yu. G. Bundel, V. I. Rozenberg, C. V. Garrilova, and O. A. Revtov, *Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1290 (1969).

(30) We have found the first absorption of trichloromethylmercurials to occur at 240 nm (log ϵ 3.7) in CCl_3HgCl and 246 nm (log ϵ 3.7) in CCl_3HgPh (ethanol solution).

(31) P. P. Shorygin, V. A. Petukhov, and L. G. Stolyarova, *Dokl. Chem.*, **154**, 62 (1964).

(32) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2, 32 (1956).

Table VI. *Uv[a] and Ir Spectra of Cyclopentadienylmercury Compounds*

Compd	Solvent	Unassigned	$\pi_1 \rightarrow \pi_3^*$	$\pi_2 \rightarrow \pi_3^*$	$\pi_1 \rightarrow \pi_2$ separation, eV	$\nu_{C=C}$, cm^{-1}
2a or **2b**	Solid mull	220	301	362 (sh)	0.7	1576
2a or **2b**	Cyclohexane	223 (4.2)	298 (4.2)	350 (sh, 3.1)	0.7	1573[b]
2a or **2b**	Glyme	226 (4.2)	301 (4.3)	342 (sh, 3.1)	0.5	1575[c]
3d	Solid mull	230	300	390 (sh)	0.9	1578
3a	Solid mull	222	285	375 (sh)	1.0	1579
3c	Solid mull	220	275	345 (sh)	0.9	1586 (sh), 1581
3a or **3c**	Cyclohexane	215 (4.1)	265 (3.9)	330 (3.1)	0.9	1580[b]
3a or **3c**	Glyme	212 (4.0)	270 (3.9)	323 (sh, 3.1)	0.8	1582[d] 1575[c]
4a	Solid mull	220	290	395 (sh)	1.1	1575
4	Solid mull	215 (sh)	280	360	1.0	1584 (sh), 1580
4	Cyclohexane	217 (4.2)	270 (4.0)	335 (3.1)	0.9	1579[b]
4 or **4a**	Glyme	220 (sh, 4.3)	276 (4.0)	329 (sh, 3.1)	0.7	1579[c]
5	Solid mull	217	286	333 (sh)	0.6	1570
5	Cyclohexane	223 (4.3)	285 (4.0)	329 (sh, 3.1)	0.6	1569
$C_5Cl_5CCl_3$	EtOH		204 (4.3)	327 (3.4)	2.3	1594
C_5H_6	Vapor[e]		157	258		
$(C_5H_5)_2Hg$	EtOH[f]	237 (4.1)	286 (3.9)			
$(C_5Me_5)_2Hg$	N.s.g.[g]		270 (3.9)	248 (sh)		
C_5H_5HgCl	EtOH[f]	208 (4.2)	244 (3.9)			
C_5H_5HgBr	EtOH[f]		252 (sh, 4.3)			

[a] λ_{max} in nm (log ϵ). [b] CCl_4 solution. [c] Solid mull of glyme adduct. [d] Solid mull of diglyme adduct. [e] Footnote *d*, Table V. [f] Reference 10. [g] Reference 19.

This separation shows much clearer trends than either the $\pi_2 \rightarrow \pi_3^*$ or $\pi_1 \rightarrow \pi_3^*$ energies. (1) The $\pi_1 \rightarrow \pi_2$ separation is the *same* within experimental error for the cyclohexane solutions and for the different solid structural forms of each mercurial. (This suggests that the degree of σ–π hyperconjugation is invariant for a given substituent, and that the different colors and properties of the different solid-state forms may be due to different modes of Hg 6p-orbital involvement.) (2) The $\pi_1 \rightarrow \pi_2$ separation *decreases* in the sequence $C_5Cl_5HgCl > C_5Cl_5HgBr > (C_5Cl_5)_2Hg > C_5Cl_5HgC_6H_5$. This corresponds to the expected sequence of ease of σ–π conjugation: $HgCl < HgBr < HgC_5Cl_5 < HgC_6H_5$. (3) The $\pi_1 \rightarrow \pi_2$ separation *decreases* by 0.2 eV upon formation of a glyme adduct (*i.e.*, in the solid state of the adduct or in a solution of the parent mercurial in glyme). This is consistent with the electron-donating properties of the ether, raising the energy of the C–Hg σ bond and making hyperconjugation easier.[33]

Supplementary evidence for σ–π conjugation in **2**–**5** can be obtained from their ir spectra. The C=C stretching frequency, which occurs at 1594–1604 cm^{-1} in organic RC_5Cl_5 compounds, is shifted to 1580 cm^{-1} in **3** and **4**, 1575 cm^{-1} in **2**, and 1570 cm^{-1} in **5** (see Table VI). An analogous trend has been noted among allylmetallic compounds, in which $\nu_{C=C}$ is shifted to lower frequency by 10–20 cm^{-1} in metallic derivatives.[31]

Reactions of Pentachlorocyclopentadienylmercurials

The characteristic reaction of C_5Cl_5Hg compounds is scission of the Hg–C bond to produce the pentachlorocyclopentadienyl radical, **7**. This occurs quite readily: refluxing a solution of **2** in methyl iodide produces mercury metal and decachlorobis(cyclopentadienyl) (**8**). (Very little HgI_2 is produced.) Vacuum sublimation of **3d** proceeds readily at 120°, but the sublimate consists mainly of **8** and $HgCl_2$, with very little starting material

$$C_5Cl_5HgCl\text{–}HgCl_2 \longrightarrow [C_5Cl_5\cdot + HgCl\cdot + HgCl_2] \longrightarrow (C_5Cl_5)_2 + Hg_2Cl_2 + HgCl_2$$

being recovered. The sublimation residue consists mainly of Hg_2Cl_2. Similarly, attempted sublimation of **5** at 135° leaves a brown solid residue. The sublimate consists of C_6H_5HgCl, $(C_6H_5)_2Hg$, and **8**.

These products suggest the intermediacy of the $C_5Cl_5\cdot$ and $RHg\cdot$ radicals, in contrast to reactions of CCl_3HgX mercurials, which yield dichlorocarbene. Attempts were made to detect the analogous carbene, tetrachlorocyclopentadienylidene, which has been produced by the photolysis of tetrachlorodiazocyclopentadiene.[34] Stirring of **3a** in cyclohexene for 1 week, either with or without uv irradiation, produced a mixture which contained only **8**, **6**, and inorganic salts.

The mass spectrum of **3a** illustrates the easy rupture of the C–Hg bond. The lowest *m/e* component of the parent peak, at *m/e* 470, is not due to C_5Cl_5HgCl, as the odd-mass contributions of ^{199}Hg and ^{201}Hg are absent. Its *m/e* pattern is assignable to $C_{10}Cl_{10}^+$. The base peak at *m/e* 237 is assignable to $C_5{}^{35}Cl_4{}^{37}Cl^+$; the other intense peak, at *m/e* 202, is mainly due to $^{202}Hg^+$. Only a few very weak peaks could be observed which were due to species containing both mercury and carbon. These data suggest formation and dimerization of $C_5Cl_5\cdot$ radicals prior to electron impact.

Only one solid mercurial has been observed to be air-sensitive: **2e** deteriorates in air to give a yellow powder whose ir spectrum suggests a structure such as $(C_5Cl_5Hg)_2O$. Solutions of **2** oxidize slowly.

The mercurials are readily decomposed by chloride ion, displacing **1**, which then decomposes to give blue and green solutions. This salt-like property of C_5Cl_5HgX compounds is found in other mercurials with highly electronegative organic groups.[35] For this reason the preparation of **3a** requires careful rinsing of

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(33) We have not attempted to assign the high-energy 220-nm band in the uv spectra of 2–5, since it resembles bands found in many plausible models and could be an overlay of several of them.

(34) E. T. McBee, J. A. Bosoms, and G. J. Morton, *J. Org. Chem.*, **31**, 768 (1966).

(35) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I. 3rd ed, Methuen, London, 1968, p 166.

the $ClHgOCH_3$ precipitate with methanol: if the NaCl or LiCl by-product is not removed, it will cause part of the product to decompose. This also (in part) explains the ineffectiveness of the reaction of LiC_5Cl_5 or NaC_5Cl_5 with $HgCl_2$ or C_6H_5HgCl in producing **2–5**.

Attempts to use C_5Cl_5 mercurials in the preparation of perchlorometallocenes, analogous to the use of $(C_5H_5)_2Hg$ as a mild reagent in the preparation of ferrocene,[32] met with no success. The reaction of **2** or **3a** with $(Et_4N)_2FeCl_2Br_2$ in dichloromethane solution produced **6**, **8**, and Et_4NFeCl_4. This reaction, followed by low-temperature ir, showed **6** growing in as **2** decreased. No spectral evidence for perchloroferrocene could be seen, but green colors produced when the reaction mixture was warmed suggest the possible intermediacy of the anion, **1**.

Similarly, the reaction of black α-CoI_2 with **2** in dichloromethane gave high yields of **8**, mercury metal, and yellow β-CoI_2. Other reactions of **2** and **3a** have been discussed in a previous paper.[2]

Reaction of 3 mol of **3a** with $SbCl_3$ in dichloromethane resulted in slow precipitation of $HgCl_2$ and Sb_2O_3. Work-up of the solution afforded very pure **6**. Hence decomposition probably proceeded by hydrolysis rather than *via* the radical **7**.

Attempts to apply the synthetic routes used here to organotin chemistry failed. The reaction of bis(tributyltin) oxide with **6** in pentane at 0° produced considerable decomposition to blue and green tars and **8**, **6**, and $(C_4H_9)_3SnCl$.

From the experiments described above, the reactions of the pentachlorocyclopentadienylmercurials are apparently dominated by two tendencies: (1) the easy displacement of the weakly basic, poorly nucleophilic, and unstable anion **1** by ligands such as chloride or even coordinating solvents; and (2) the easy rupture of the C–Hg bond to give the relatively stable radical **7**. Synthesis of other σ-bonded organometallic derivatives of **1** may be limited to the more electronegative metals which will not readily give metal cations and the **1** anion, and which cannot oxidize the σ-bonded C_5Cl_5 group.

Experimental Section

General. All solvents were dried and distilled prior to use. Most analyses were performed by Schwarzkopf Microanalytical Labs, Inc., Woodside, N. Y. (Table I). Ir spectra were recorded of mineral oil mulls between CsI or CsBr plates. Solution spectra were obtained in CCl_4, $CHBr_3$, and C_6H_6 solution using 1.0-mm matched CsI cells. A Perkin-Elmer IR-457 spectrophotometer was used. Uv spectra were recorded on a Cary 14 recording spectrophotometer using 10.0- and 1.0-mm matched quartz cells. Solid-state spectra were of mineral oil mulls between NaCl or quartz plates. Reflectance due to solid particles was recorded in the visible region, then extrapolated into the ultraviolet region and subtracted. Nqr spectra were recorded on a Decca Radar NQR spectrometer using Zeeman modulation, then rerecorded using frequency modulation and sideband suppression. Proton nmr spectra were recorded on a Varian A-60A spectrometer while ^{13}C spectra were recorded on a Varian XL-100-15 spectrometer provided with a Fourier transform accessory. Mass spectra were recorded on a MA-902 high-resolution mass spectrometer at 70 eV.

Preparation of Bis(pentachlorocyclopentadienyl)mercury (2). Method A. $Tl^+C_5Cl_5^-$ (1a, 20 mmol) was prepared as described previously.[2] The low-temperature apparatus was cooled to −78°, the underside of the frit pressurized with N_2, and 20 ml of purified THF, precooled to −78°, was added to the top of the frit to dissolve 1a. A solution of 10.0 mmol of $HgCl_2$ in 20 ml of THF was slowly added to the top of the frit. TlCl precipitated immediately. After stirring for 15 min, the solution was filtered. (The receiver[2] was replaced by a pot to pot distillation apparatus.) The THF was removed at −15° leaving behind white **2e**. Enough pentane was added to redissolve **2e** at room temperature and the pentane solution cooled to −15°. Large colorless crystals of **2e** were obtained. Since **2e** was unstable to air oxidation, it was not analyzed; however, THF was detected by nmr spectroscopy.

Method B. In a 500-ml three-necked flask provided with a mechanical stirrer, nitrogen inlet, and powder addition funnel was placed 200 ml of 1.0 *M* LiOMe in methanol. Solid mercuric acetate (0.10 mol) was slowly added with stirring and the stirring continued for 1 hr. The insoluble solid obtained was filtered under nitrogen, washed with 200 ml of anhydrous methanol and 30 ml of anhydrous ether, and aspirated dry to yield 23.94 g (91%) of "$Hg(OCH_3)_2$," a yellow powder which rapidly turned orange (and inactive) in air.

Under nitrogen, the "$Hg(OCH_3)_2$" was stirred in 50 ml of dry *n*-hexane at −10°. A solution of 38.13 g (0.16 mol) of **6** in 65 ml of hexane was slowly added with stirring and the stirring continued for 1 hr. The slurry was filtered into 25 ml of *n*-heptane and the solid extracted with 2 × 40-ml portions of ether to remove 3.0 g of mercury. The ether extract and the hydrocarbon solutions were combined and the solvents removed under reduced pressure to afford 35.2 g (65%) of **2** which was found to be a mixture of small colorless crystals of **2a** and large octahedral yellow crystals of **2b**.

Pentachlorocyclopentadienylmercuric Chloride (3). Method A. In a 500-ml three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and addition funnel was placed 27.2 g (0.10 mol) of $HgCl_2$ and 100 ml of absolute methanol. The slurry was stirred and 100 ml of 1.0 *M* LiOMe in methanol was slowly added. Stirring was continued overnight and the white creamy precipitate that was formed was filtered under nitrogen, washed with 400 ml of anhydrous methanol and then with small amounts of anhydrous ether, and aspirated dry. The yield of air sensitive "$ClHgOCH_3$" was 24.4 g (88%).

The solid obtained above was stirred to a paste under nitrogen with 50 ml of *n*-hexane, cooled to 0°, and treated with a solution of 20.9 g (0.090 mol) of **6** in 25 ml of *n*-hexane. The slurry was stirred for 2 hr at 0° and filtered under nitrogen to afford 35.3 g of crude **3a**. A second crop of 1.2 g of **3a** was obtained by concentration of the mother liquor; combined yield, 87%.

Crude **3a** obtained above was dissolved in 125 ml of dichloromethane, filtered, and diluted with 20 ml of *n*-heptane. The solution was concentrated under reduced pressure to afford 29.9 g of **3a** as yellowish crystals. If the dichloromethane solution was filtered directly into *n*-heptane cream colored **3c** was obtained. **3c** may be redissolved and the solution concentrated to give mixtures of **3a** and **3c**, but in a short time these mixtures revert entirely to **3c**.

Method B (3c). To a slurry of 2.7 g (10 mmol) of mercuric chloride in 50 ml of dry benzene was added 6.8 g (10 mmol) of **2**. The slurry was stirred under nitrogen at room temperature. All of the mercuric chloride went into solution in about 1 hr and a cream-colored precipitate formed. The slurry was stirred for an additional hour. Benzene was removed at room temperature under aspirator vacuum. The solid was diluted with 20 ml of hexane and filtered and washed on the filter with two 10-ml portions of hexane. The yield of **3c** was 9.8 g (93%): mass spectrum *m/e* (rel intensity), formula: 474 (5), $C_{10}Cl_{10}^+$; 439 (1), $HgC_5Cl_5^+$; 404 (18), $C_{10}Cl_8^+$; 332 (8), $C_{10}Cl_6^+$; 316 (2), $HgC_3Cl_2^+$; 272 (20), $HgCl_2^+$; 262 (3), $C_{10}Cl_4^+$; 237 (100), $C_5Cl_5^+$; 202 (65), Hg^+ or others; 167 (27), $C_5Cl_3^+$; 141 (24), $C_3Cl_3^+$; 130 (18), $C_5Cl_2^+$.

Pentachlorocyclopentadienylmercuric Bromide (4). To a filtered solution of 3.40 g (5.0 mmol) of **2** in 30 ml of bromobenzene, stirred in a cold-water bath, was added slowly a solution of 1.80 g (5.0 mmol) of $HgBr_2$ in 30 ml of refluxing bromobenzene. The reaction mixture was filtered and solvent was pumped off at 25°. Cream-colored crystals formed. A second crop was obtained by cooling to −30°, and a third by diluting the mother liquor with excess pentane (yield about 60%). The compound was stored at 0°.

Adduct with $HgBr_2$ (4a). The above procedure was followed using 3.96 g (11.0 mmol) of $HgBr_2$. After half the $HgBr_2$ had been added, each further addition precipitated lemon-yellow crystals o **4a**. A second crop was obtained from the cooled mother liquor Total yield was 4.07 g (93%).

Phenyl(pentachlorocyclopentadienyl)mercury (5). In a 100-m flask provided with a magnetic stirrer and nitrogen inlet was placed 15.0 mmol of "phenylmercuric hydroxide," 15.0 mmol of **6**, 3 m of 2,2-dimethoxypropane, and 35 ml of hexane; the mixture wa stirred at 0° for 2.5 hr and 1 hr at 25°. The precipitated solid wa filtered; an additional crop was obtained by evaporation of th mother liquor. Recrystallization from 1:8 ether–pentane afforded large colorless crystals of **5** in 34% yield. The compound was stored at −15°; nmr (CDCl$_3$–TMS) τ 2.61–2.84 (multiplet).

Ether Adducts. Compounds **2**–**4** were dissolved in a minimum amount of the appropriate ether. Several volumes of heptane were added and the solution was filtered. The filtrate was cooled to −20°. Large colorless crystals (which tend to take on an orange surface coloration) were obtained. The adducts were stored at −20°.

Analyses of the ether adducts were performed by pumping on weighed air-dried samples until they reached constant weight. The analytical results for **3f** are high due to loss of the mercurial by sublimation during pumping.

Compound **2d** was pumped for 2 days before reaching constant weight. Ir of the residue revealed it to be **2a**. Grinding of this opaque white residue in cyclohexane caused it to turn yellow; the ir spectrum of this mull showed the predominant presence of **2b**. Apparently **2d** must have a structure closely related to that of unstable **2a**, which is unable to convert rapidly to the more stable **2b** in the solid state. Solution ir spectra reveal that **2** in solution consists of a mixture of **2a** and **2b** in an approximate 1:1 ratio.

Photolysis of 3a. A solution of 1.0 g of **3a** in 40 ml of dry cyclohexene was irradiated with a medium-pressure mercury lamp for 60 hr through Pyrex. The solution was filtered and the solvent removed under reduced pressure: the oily residue was chromatographed on silica gel. Compounds **6** and **8** were eluted by hexane. Traces of an unidentified carbonyl compound was eluted with benzene. No product with an ir absorption at 1012 cm^{-1}, characteristic of a spiroadduct,[34] could be isolated.

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Additions to Bicyclic Olefins. VI. Stereochemistry of the Oxymercuration–Demercuration of Norbornene, 7,7-Dimethylnorbornene, and Related Olefins[1,2]

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Abstract: The oxymercuration–demercuration of norbornene, 7,7-dimethylnorbornene, and related olefins reveals the stereochemical and regioselective effects of methyl substituents in this bicyclic system. The reaction of these norbornene derivatives with mercuric acetate in aqueous tetrahydrofuran is essentially quantitative, addition of both moieties proceeding predominantly exo. Reduction of the oxymercurial with sodium borohydride produces the corresponding norbornanol derivative essentially exclusively exo (>99.8%). Consequently, in this reaction the presence of the bulky 7,7-dimethyl substituents fails to prevent exo addition. 2-Methylnorbornene undergoes rapid transformation into 2-methyl-*exo*-norbornanol. Oxymercuration–demercuration of 1-methylnorbornene and bornylene provides roughly equal amounts of the 2- and 3-exo alcohols, indicating no significant directive influence of the 1-methyl substituent. The additional observation that the intermediate kinetic mercurial adduct has the cis-exo structure by pmr in both the norbornyl and 7,7-dimethylnorbornyl derivatives lends doubt to the existence of a cyclic symmetrical mercurinium ion as a significant intermediate in the oxymercuration reaction.

Based on the results realized in the reduction of ketones by complex metal hydrides, it has been argued that the 7,7-dimethyl substituents in the norbornyl system will make exo addition so difficult that all electrophilic additions, in the absence of the intervention of a "special effect," σ-bridging, would go preferentially endo.[4,5] However, very little is known about the relative steric requirements for the reaction of complex metal hydrides with ketones and the steric requirements of other reactions with the norbornyl moiety. Consequently, such an argument rests largely upon untested assumptions and should not be accepted without more definitive data.[6] Indeed, there are presently known several instances in which there is a strong preference for exo substitution in both the norbornyl and 7,7-dimethylnorbornyl systems for reactions which do not involve cationic intermediates.[7]

It is now well recognized that all reactions of the norbornane system reveal a strong preference for exo attack and exo substitution, attributed to the greater steric influence of the endo-5,6-hydrogen atoms as compared to that of the syn-7-hydrogen atom.[7] The steric requirements of a *syn*-7-methyl group must be considerably larger than those of the syn-7-hydrogen atom. Consequently, a systematic study of additions to norbornene, 7,7-dimethylnorbornene, and related olefins was undertaken in order to evaluate the relative importance of the endo-5,6-hydrogen atoms *vs.* the *syn*-7-methyl group in controlling the stereochemistry of additions to the norbornyl system. In previous papers it was established that exo additions to the norbornyl system which go through cyclic transition states or intermediates, such as hydroboration,[7,8] epoxidation,[9] silver nitrate complexation,[7] addition of ni-

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(1) Solvomercuration–Demercuration. V.

(2) A preliminary account of a portion of this study has appeared earlier: H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **89**, 1525 (1967).

(3) Graduate research assistant on Grants G 19878 and GP 6492X supported by the National Science Foundation.

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