Table III

Rate and Equilibrium Constants for Reaction 5 in Various Solvents at $\mu = 0.100$

Y	Temp, °C	$10^5 k_1$,[a] sec^{-1}	$10^3 k_2'$,[b] M^{-1} sec^{-1}	K_{eq}[c]
Solvent H_2O[d]				
I^-, N_3^-, NO_2^-, SCN^-, SO_3^{2-}	25	130–150	0	>1
$S_2O_3^{2-}$	25	150	5930	>>1
OH^-	25	130	55	...
Solvent CH_3OH				
NO_2^-	25	1.4	0	...
NO_2^-	47	17.2	0	0.8
I^-	47	14.1	0	...
Solvent $(CH_3)_2SO$				
I^-	25	5.4	0	0.06
Cl^-	25	4.8	0	>1
NO_2^-	25	4.5	3.6	...
Br^- [e]	25	8.3	0	17[f]
Solvent CH_3CN				
I^-	47	4.9	0.27	0.3
Cl^-	47	4.5	1.97	>1

[a] As defined in reaction 2. [b] As defined in reaction 4. [c] As defined by eq 6. [d] Data from ref 2 and 3. [e] Reaction of iodo complex with bromide ion. [f] Reciprocal of K_{eq} for reaction of bromo complex with iodide ion.

$k_1(DMSO) = 108k_1(H_2O)$.[9] This behavior was attributed to the relative stability of the Pt–S bond of the DMSO solvento complex over that of the Pt–O bond in the corresponding aquo complex. Although Pd(II) is not as selective as Pt(II), the same order of stability is expected for these soft Lewis acids. The fact that $k_1(H_2O) = 25k_1(DMSO)$ for $Pd(Et_4dien)Br^+$ indicates the effect of steric hindrance in this system; the bulkier DMSO has more difficulty than the smaller H_2O in approaching the palladium.

It is also evident that the reagent-dependent path (eq 4) exists for certain ligands in $(CH_3)_2SO$ and CH_3CN, where it is experimentally nonexistent in CH_3OH and H_2O. Both chloride and iodide ions show this dependence in CH_3CN (although the evidence for iodide ion is marginal) but not in $(CH_3)_2SO$. This may indicate a solvation by CH_3CN of the ethyl groups of Et_4-dien, permitting them to spread out from the palladium, thereby allowing easier entrance of the nucleophile. This solvation of the ethyl groups is less important in $(CH_3)_2SO$, since only nitrite ion shows this rate dependence, and a nitrite dependence in CH_3OH or H_2O was not observed, indicating a solvation effect of much less significance. Thus the better solvating solvents (for the ethyl groups) allow a more "square-planar" behavior for this sterically hindered system in that the two-term law (eq 7) is now followed to a higher degree.

$$\text{rate} = \{k_1 + k_2'[Y]\}[Pd(Et_4dien)Br^+] \qquad (7)$$

These results may also be attributed to the solvation of the reagent ions. Thus in the protonic solvents the solvation energy of the reagent anions is large, making their reactivity small compared with the aprotic systems where the energy of solvation of the reagent anions is small. Extensive studies have been made of solvent effect on substitution reactions of platinum(II) complexes.[10] The results show that the effect of solvent on reagent reactivity is not large and that the order of reactivity is the same in protonic and in aprotic solvents. In spite of this the solvation of reagent anions may be more significant for reactions of Pd(II) which is less discriminating than is Pt(II). Note that changes in solvent have not been found to cause a reversal in the order of nucleophilic strength toward Pt(II) substrates, but for $Pd(Et_4dien)Br^+$ the order of reactivity is $Cl^- > I^-$ for the solvent CH_3CN (Table III).

Furthermore it is seen from the equilibrium constants that the formation of bromo complex over iodo complex is actually favored in CH_3CN and $(CH_3)_2SO$. For water, Hewkin and Poë[11] have estimated that $K_{eq} \cong 10$ for reaction 8, but in CH_3CN and $(CH_3)_2SO$, $K_{eq} < 1$

$$Pd(Et_4dien)Br^+ + I^- \rightleftharpoons Pd(Et_4dien)I^+ + Br^- \qquad (8)$$

(Table III). This reversal in stability may be explained by the ability of the "soft" solvents to solvate the "soft" iodide ion to a greater degree than the somewhat harder bromide ion;[6] on this basis alone, the bromide ion would tend to remain bound, whereas the iodide ion would prefer to remain free in its solvated state.

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Some Reactions of Dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin with Thiols

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Organotin halides are smoothly converted into the corresponding thio derivatives on treatment with thiols in the presence of a base.[1,2] We have found that dichlorobis(dicarbonyl-π-cyclopentadienyl)tin, $[\pi\text{-}C_5H_5Fe(CO)_2]SnCl_2$ (I), reacts under similar conditions with thiophenol and with dithiols by replacement of the Sn–Cl bonds by Sn–S, while the iron–tin bonds remain intact.

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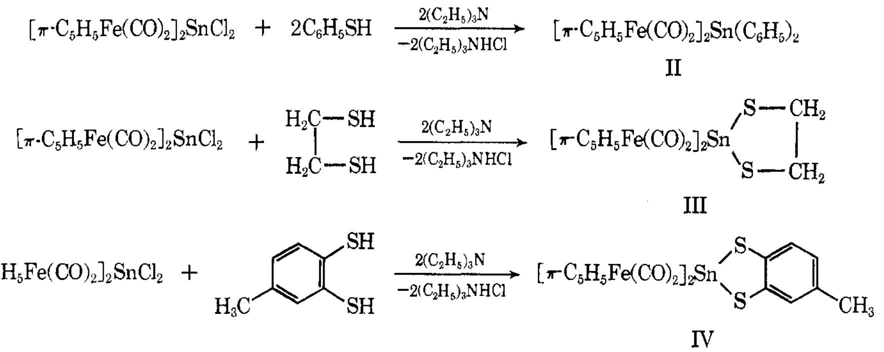

The complexes II–IV appear to be stable in air both in the crystalline state and in solution in organic solvents, although all, especially III, are somewhat sensitive to light.

Very recently similar reactions between ethane-1,2-dithiol and $Cl_2Sn[M(CO)_5]_2$ (where M = Mn, Re) to give tin–sulfur heterocycles have been reported.[3]

Treatment of I with potassium thiocyanate in acetone yields the light-sensitive complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2$-$Sn(NCS)_2$ (V). The infrared spectrum of this compound provides no conclusive evidence for its formulation as an isothiocyanate, as in the regions where characteristic frequencies of the –NCS group fall [2080–2010 cm^{-1} (–C═N str) and 860–780 cm^{-1} (C—S str)][4,5] carbonyl and π-cyclopentadienyl ring vibrations, respectively, also occur. However the absence of absorption in the region of the spectrum characteristic of S-bonded thiocyanate [690–720 cm^{-1} (C—S str)][5] and the fact that the NCS group usually bonds to tin through nitrogen[6] may suggest that the formulation of V as an isothiocyanate is correct.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin was prepared by a standard method.[7] Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany.

Bis(dicarbonyl-π-cyclopentadienyl)bis(phenylthio)tin (II).—A solution of thiophenol (1.1 g, 10 mmol) and triethylamine (1.0 g, 10 mmol) in benzene (50 ml) was added dropwise with stirring to $[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ (2.72 g, 5 mmol) in benzene (50 ml). Immediate precipitation of triethylamine hydrochloride occurred, and the solution turned deep red. The reaction mixture was stirred at room temperature (2 hr), when triethylamine hydrochloride (1.20 g, 94%; mp 250–252°, lit.[8] 254°) was filtered off. Removal of solvent from the filtrate gave a brown oil from which ochre crystals of the product were isolated by dissolving in acetone and precipitating with water; yield 2.90 g (84%); mp 132–134°. *Anal.* Calcd for $C_{26}H_{20}Fe_2O_4S_2Sn$: C, 45.2; H, 2.92; S, 9.3. Found: C, 45.3; H, 2.99; S, 9.1. Infrared spectrum in chloroform: ν_{CO}: 2017 vs, 1994 vs, 1961 s cm^{-1}.

2,2-Bis(dicarbonyl-π-cyclopentadienyliron)-2-stanna-1-3-dithiacyclopentane (III) was prepared similarly. After removal of triethylamine hydrochloride, the filtrate was evaporated to small bulk and petroleum ether (bp 40–60°) was added to precipitate the product, which was obtained as orange-yellow microcrystals (60%); mp 160–160–165° after two recrystallizations from aqueous methanol. *Anal.* Calcd for $C_{16}H_{14}Fe_2O_4S_2Sn$: C, 34.0; H, 2.50; S, 11.4. Found: C, 34.2; H, 2.55; S, 11.2. Infrared spectrum in chloroform: ν_{CO}: 2011 s, 1990 vs, 1965 s cm^{-1}; in cyclohexane; 2015 s, 1997 s, 1991 vs, 1963 s, 1951 s cm^{-1}.

The crude product IV was recrystallized from chloroform–methanol to afford deep orange plates (72%), mp 172–173°. *Anal.* Calcd for $C_{21}H_{16}Fe_2O_4S_2Sn$: C, 40.2; H, 2.57; S, 10.2; Sn, 18.9. Found: C, 40.0; H, 2.46; S, 10.4; Sn, 19.1. Infrared spectrum in chloroform: ν_{CO}: 2018 vs, 1993 s, 1962 s, 1950 sh cm^{-1}; in cyclohexane: 2020 vs, 1990 s, 1968 s, 1950 m cm^{-1}.

Diisothiocyanatobis(dicarbonyl-π-cyclopentadienyliron)tin. (V).—$[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ (1.37 g, 2.5 mmol) and potassium thiocyanate (0.8 g, 8.1 mmol) were heated under reflux in acetone (50 ml) for 2 hr. Potassium chloride (0.29 g, 80%) was filtered off and water (100 ml) was added to the filtrate, when the crude product (1.15 g, 77%) separated. It was twice recrystallized from chloroform–methanol to give orange, light-sensitive needles, mp 197° dec. *Anal.* Calcd for $C_{16}H_{10}Fe_2N_2O_4S_2Sn$: C, 32.6; H, 1.71; Fe, 19.0; S, 10.9. Found: C, 32.6; H, 1.69; Fe, 19.0; S, 11.4. Infrared spectrum in chloroform (broad poorly resolved bands): ν_{CO} and ν_{CN}: 2025 vs, 2008 vs, 1985 s, 1965 sh cm^{-1}.

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Lanthanide Picolinate Chelate Stabilities[1]

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Critical examination of the stability data for lanthanide picolinates reported by Thompson[2] reveals that K_1/K_2 ratios do not coincide with the ratios observed when α-hydroxyisobutyrate and 1-hydroxycyclopentane-1-carboxylate (HCPC) anions bond bidentately to tripositive lanthanide cations[3,4] and that K_2/K_3 ratios are inordinately small in view of the theories of Bjerrum.[5] Previous work by Powell, *et al.*,[4]

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