chloride. In the previous paper[9]

$$SnCl_2+HCl+CR_2=CR'COOR''\rightarrow Cl_3SnCR_2CR'_2COOR'' \quad (1)$$

$$Sn+2HCl+2CR_2=CR'COOR''\rightarrow Cl_2Sn(CR_2CR'_2COOR'')_2 \quad (2)$$

(R, R', and R''=H or alkyl; OR''=alkyl, amine or halide group)

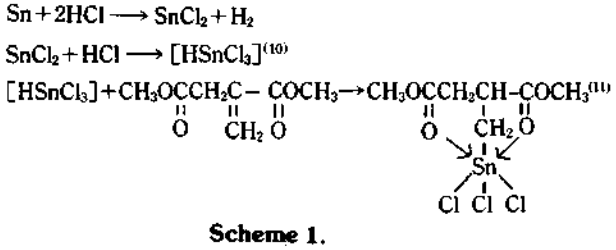
we reported the synthesis and structure of functionally substituted monoalkyltin trichloride, $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ from the reaction of dimethyl itaconate($CH_3OOCCH_2C(COOCH_3)=CH_2$) with $SnCl_2$ and HCl gas. Recently, further study on this compound system is under way. With view to expanding this chemistry, the present paper describes the result of the reaction of dimethyl itaconate with metallic tin and gaseous hydrogen chloride.

Sn (29.67 g, 250 mmol) and dimethyl itaconate (79.08 g, 500 mmol) in 200 *ml* of ethylene glycol dimethyl ether (or diethyl ether) were placed in a 500 *ml* three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet tube. Through the stirred suspension was bubbled for 5 hours anhydrous hydrogen chloride (27.37 g, 750 mmol) at room temperature. The solvent was removed, and the residue was washed with cold ethyl ether to produce a white crystalline solid in 92% (based on tin consumed) yield. The solid product was recrystallized from dichloromethane-petroleum ether solvent mixture (1:1) resulting in colorless crystals (mp. 154-155℃ (Ref.[9] 154-155℃)). Anal. Found: C, 22.00; H, 2.84. Calcd. for $C_7H_{11}O_4Cl_3Sn$: C, 21.88; H, 2.89.

As is seen in the above experimental result, the reaction of dimethyl itaconate with metallic tin in the presence of gaseous hydrogen chloride produces the monoalkyltin trichloride, $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ instead of the dialkyltin dichloride. The reaction seems to proceed in the following general Scheme 1.

At the beginning stage of the above reaction, formation of a large amount of stannous chloride could easily be identified, but the quantity of the stannous chloride was diminished as the reaction proceeded. The reaction of α, β-unsaturated carbonyl compounds with $[HSnCl_3]$ has been well established.[2] We also carried out the equimolar reaction of metallic tin with dimethyl itaconate. However, only monoalkyltin trichloride was formed irrespective of the mole ratio. Thus the formation of monoalkyltin trichlorde in the reaction system is intrinsic and is not the result of a particular synthetic strategy. Why the reaction affords only monoalkyltin trichloride, rather than dialkyltin dichloride is not clear. There is a temptation to invoke the steric hindrance of dimethyl itaconate.

In conclusion, unlike the precedented results, the reaction of dimethyl itaconate either with stannous chloride or with metallic tin in the presence of hydrogen chloride affords the same product: the reaction is the first example that only monoalkyltin trihalide is specifically prepared irrespective of the synthetic route.



Scheme 1.

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11. One carbonyl group involved in the six-membered chelate is released from the tin atom in solution, so that the tin atom is pentacoordinate in solution in contrast to hexacoordinate in the solid state as pointed out in ref. 9.

Heteroleptic Crown Thioether Complexes: Synthesis and Characterization of $[M(CO)_3(9S3)]$ (M=Cr, Mo, W). Crystal Structure of $[W(CO)_3(9S3)]$(9S3=1,4,7-Trithiacyclononane)

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A nine-membered crown thioether 1,4,7-trithiacyclononane (9S3), among others, has been employed in the development of crown thioether chemistry owing to its unique σ-donor

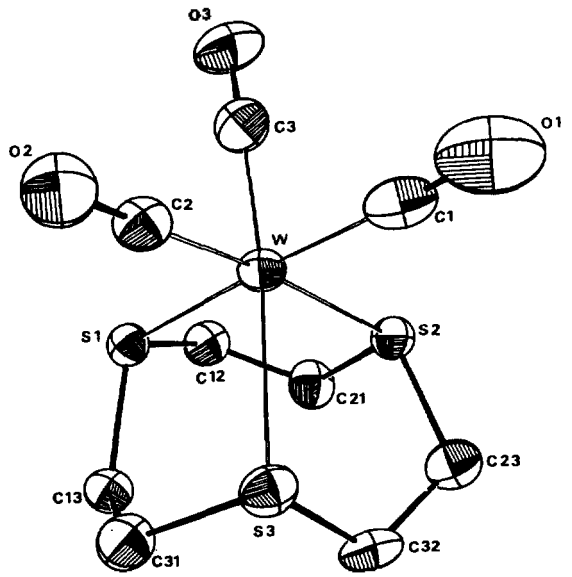

Figure 1. ORTEP plot of $[W(CO)_3(9S3)]$ (**3**), showing thermal ellipsoids at 50% probability level. All methylene hydrogen atoms are omitted for clarity. Selected average distances (Å) and angles (deg) with calculated standard deviation in parentheses: W-S, 2.509(7); W-C (carbonyl carbon), 1.957(7); carbonyl C-O, 1.161(7); S-W-S, 82.6(1); C-W-C (carbonyl carbon atoms), 89.9(16); S-W-C (*trans*), 172.7(11); two sets of S-W-C (*cis*): 90.3(12), 97.3(12).

and π-acid character as well as its strong chelating ability stemmed from the retention of endodentate conformation on binding to a trigonal face of a metal.[1-3] To date most exploratory research on the coordination chemistry of 9S3 has proceeded to determine its scope. The observation[3] of large set of homoleptic complexes suggests that 9S3 generally stabilizes a wide variety of lower oxidation states of metal ions and lacks sufficient flexibility to accommodate conformations other than a trigonal endodentate conformation although examples[4,5] became realized in the direction of extending the scope of crown thioether chemistry.

While homoleptic complexes are noble and useful, their robustness and the absence of vacant coordination sites may lead to their low reactivity.[6] On the other hand, heteroleptic 9S3 complexes, which constitute a newly emerging class,[3,5-7] contain heteroleptic ligands which are potentially susceptible for further reaction. As part of our efforts to exploit the chemistry of heteroleptic class of crown thioether, the group 6 metal carbonyl complexes of 9S3, $[M(CO)_3(9S3)]$ (M=Cr, Mo, W), were synthesized and characterized, brief accounts of which are reported herein.

An equimolar (0.3 mmol) reaction mixture of $[M(CO)_3(CH_3CN)_3]$[8] and 9S3[9] in 20 m*l* of CH_3CN was allowed to react anaerobically at ambient temperature, producing yellow precipitate. The yellow solids were collected, washed with Et_2O and recrystallized from DMF-Et_2O pair, affording analytically pure crystalline $[M(CO)_3(9S3)]$ (**1**: M=Cr; **2**: M=Mo; **3**: M=W)[10] in the yields of 30, 40 and 32% for **1**, **2** and **3**, respectively. The composition and crystal structure of **3** were established by single-crystal X-ray analysis.[13] Elemental analysis[10a] of **1** and the comparison of spectroscopic data for **1**, **2** and **3**, *vide infra*, indicate that the compound of the lightest congener, **1**, has the same structural core as its heavier analogues.

Table 1. Spectroscopic Data for $[M(CO)_3(9S3)]$

	M	IR[a]	^{1}H-NMR[b]	^{13}C-{^{1}H}-NMR[b]/ppm[c]	
		ν_{CO}/cm^{-1}	ppm[c]	9S3	CO
1	Cr	1910,1790	2.53 (s)	31.9	232.1
2	Mo	1915,1796	2.55-2.69 (complex)	31.3	222.7
3	W[d]	1905,1788	2.55-2.68 (complex)	32.6	216.2

[a]KBr. [b]d_6-DMSO. [c]Relative to TMS. [d]Coupling due to ^{183}W (I=1/2, 14.28%) has not been resolved in both NMR spectra.

Table 2. Comparison of IR Data for a series of $[LMo(CO)_3]$

L	ν_{CO}, cm^{-1}	Ref.
9S3	1915,1796	This work
9N3	1850,1740-1700	20
C_6H_6	1969,1936,1921	21
$C_5H_5^-$	1901,1796,1746	22
$HBPz_3^-$	1897,1761	23
$C_2B_9H_{11}^{2-}$	1909,1876,1741	24
12P3	1945,1840	25

The molecular structure of **3**, displayed in Figure 1, reveals that 9S3 and three carbonyl groups are situated facially, approaching the overall symmetry of C_3. The WS_3C_3 coordination sphere deviates from the regular octahedral geometry. Constriction of the S-W-S bond angles (average 82.6°), a measure of the extent of distortion in WS_3C_3 coordination geometry, does not lead to corresponding dilation of carbonyl trigonal face as indicated by the average C-W-C (carbonyl carbon atoms) bond angle of 89.9°. The structure of **3** provides rare example of the W-SR_2 (R=sp^3-C) bonding distance whose average value of 2.509(7) Å in **3** is shorter by *ca* 0.06 Å than those in previously reported compounds with W-SR_2 interaction.[14] It is also interesting to note that the average W-S distance in **3** is shorter than the average Mo-S distance of 2.520(15) Å in **2**,[11] the lighter congener analogue of **3**.[15] This observation is consistent with the expectation that a soft base 9S3 interacts more strongly with the softer acid tungsten.[16]

The structurally characterized C_3 molecular symmetric nature of **2**[11] and **3** provides explanation for the vibrational spectral pattern (A_1 and E) of **2** and **3** in the region of ν_{CO}, which and comparison of IR spectra of **1**, **2** and **3**, in turn, suggest the facial CrS_3C_3 coordination geometry of **1** in the solid state. The carbonyl streching frequencies for **1**, **2** and **3** are listed in Table 1 along with other spectroscopic data. Upon dissolution in DMSO, no liberation of 9S3 is observed in all three compounds,[17] indicating the integrity of $[M(CO)_3(9S3)]$ in solution. The complex ^{1}H-NMR patterns of **2** and **3** are ascribed to AA′ BB′ or ABCD coupling of methylene protons. On the other hand, for **1**, a relatively sharp singlet enables to speculate fluxionality in **1** such as a merry-go-round type rotation of 9S3 with respect to Cr center although no example of 9S3 complex with fluxionality is available to date.[18]

As stated earlier in this report, the unique σ-base and π-acid character of 9S3 might be attributed to the stability of $[M(CO)_3(9S3)]$ toward oxidative decarbonylation reaction.[19] A relative measure of π-acidity of L in a series of isoelectronic complexes $LM(CO)_3$, estimated by the comparison of ν_{co} in Table 2, suggests the π-acidity decreases in the order C_6H_6, 12P3, 9S3, $C_2B_9H_{11}^{2-}$, $C_5H_5^-$, $HBPz_3^-$, and 9N3. With this trend in mind, it is worth noting that in case of $L=C_2B_9H_{11}^{2-}$[24] and $C_5H_5^-$,[26] oxidative decarbonylation reactions have been observed. Further studies on the reactivities of three 9S3 complexes and the development of heteroleptic crown thioether chemistry are under investigation.

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New Synthesis of Acylferrocene from Ferrocenecarboxaldehyde by Rh(I) Catalyst

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The C-H bond activation by transition metal complexes has been one of the recent interests in organometallic chemistry.[1] It has ben reported that C-H bond activation of the aldimine by Rh(I) generated iminoacylrhodium(III) hydride complex which inserted mono-olefin and conjugate dienes to form iminoacylrhodium(III) alkyl[2] and alkyl-substituted η^3-allyl complexes,[3] respectively. They were readily reductive-eliminated to give corresponding ketimines, potential precursors for ketone since hydrolysis of them produce ketones. Consequently aldehyde can be easily converted to ketone