chloride. In the previous paper\textsuperscript{3}

\begin{align*}
\text{SnCl}_2 + \text{HCl} + \text{CR}_2 &= \text{CR'}\text{COOR'}^\rightarrow \text{Cl}_2\text{SnCR}_2\text{CR'}\text{COOR'}^\rightarrow (1) \\
\text{Sn} + 2\text{HCl} + 2\text{CR}_2 &= \text{CR'}\text{COOR'}^\rightarrow \text{Cl}_2\text{Sn(CR}_2\text{CR'}\text{COOR'})_2 (2)
\end{align*}

\((R, R', \text{and } R'' = \text{H or alkyl}; \text{OR'}^\rightarrow = \text{alkyl, amine or halide group})\)

we reported the synthesis and structure of functionally substituted monoalkyltin trichloride, \(\text{CH}_3\text{OOCCH}_2\text{CH(COOCH}_2\text{)} \)

\(\text{CH}_2\text{SnCl}_2\text{ from the reaction of dimethyl itaconate(\(\text{CH}_3\text{OOCCH}_2\text{C(COOCH}_2\text{)} = \text{CH}_3\)) with SnCl}_2\text{ 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.}

\(\text{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°C (Ref.\textsuperscript{9} 154-155°C)). Anal. Found: C, 22.00; H, 2.84. Calcld. for \(\text{C}_7\text{H}_{18}\text{O}_6\text{Sn}: \text{C}, 21.88; \text{H}, 2.89.\)

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, \(\text{CH}_3\text{OOCCH}_2\text{CH(COOCH}_2\text{)} \)

\(\text{CH}_2\text{SnCl}_2\text{ 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 a, b-unsaturated carbonyl compounds with \(\text{HSnCl}_3\) has been well established.\textsuperscript{9} 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 trichloride 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 preceding results, the reaction of dimethyl itaconate 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.

**Acknowledgement.** We gratefully acknowledge the support of this work by the Ministry of Science and Technology.

**References**

10. \(\text{HSnX}_3\) species \((X = \text{Cl, Br})\) have been isolated as complexes with EtO or amines. The trichlorostannane has been prepared by reaction of \(\text{SnX}_2\) with LiAlH\(_4\) and also by addition of \(\text{SnX}_2\) to a solution of excess \(\text{HX}\) in EtO. See ref. 2 and therein ref. 5 and 6.
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 \([\text{M(CO)}_3(\text{9S3})]\)
\((\text{M}=\text{Cr}, \text{Mo, W}), \text{Crystal Structure of }[\text{W(CO)}_3(\text{9S3})]\)\(\text{(9S3} = \text{1.4.7-Trithiacyclononane)}\)**

Hyun-Joon Kim, Youngkyu Do, Hyo Won Lee, Jong Hwa Jeong, and Youn Soo Sohn

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-650

\(^1\)Department of Chemistry, Chungbuk National University, Cheongju 360-763

\(^2\)Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-971

Received February 21, 1991

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 \(\sigma\)-donor
and n-acid character as well as its strong chelating ability stems from the retention of endonate conformation binding to a trigonal face of a metal. To date most exploratory research on the coordination chemistry of 9S3 has proceeded to determine its scope. The observation of large set of homolecule complexes suggests that 9S3 generally stabilizes a wide variety of lower oxidation states of metal ions and lacks sufficient flexibility to accommodate conformational changes other than a trigonal endonate conformation although examples became realized in the direction of extending the scope of crown thiocarbamate chemistry.

While homolecule complexes are noble and useful, their robustness and the absence of vacant coordination sites may lead to their low reactivity. On the other hand, homolecule 9S3 complexes, which constitute a newly emerging class, contain heteroleptic ligands which are potentially susceptible for further reaction. As part of our efforts to exploit the chemistry of heteroleptic class of crown thiocarbamate, 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)₅(CH₂CN)] and 9S3 in 20 mL of CH₂CN was allowed to react anaerobically at ambient temperature, producing yellow precipitate. The yellow solids were collected, washed with Et₂O and recrystallized from DMF-Et₂O pair, affording analytically pure crystalline [M(CO)₃(9S3)] (1: M = Cr; 2: M = Mo; 3: M = W) 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. Elemental analysis 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. The molecular structure of 3, displayed in Figure 1, reveals that 9S3 and three carbonyl groups are situated facially, approaching the overall symmetry of Cr₃. The WS₅Cr 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 WS₅Cr 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 (R = sp²-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-SR₂ interaction. 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, the lighter congener analogue of 3. This observation is consistent with the expectation that a soft base 9S3 interacts more strongly with the softer acid tungsten.

The structurally characterized Cr₃ molecular symmetric nature of 2 and 3 provides explanation for the vibrational spectral pattern (A₁ and E) of 2 and 3 in the region of ν₃, which and comparison of IR spectra of 1, 2 and 3, in turn, suggest the facial Cr₃Cr₃ coordination geometry of 1 in the solid state. The carbonyl stretching 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, indicating the integrity of [M(CO)₃(9S3)] in solution. The complex ¹H-NMR patterns of 2 and 3 are ascribed to AA'BB' or ABCD coupling of carbonyl protons. On the other hand, for 1, a relatively sharp singlet enables to speculate fluxionality in 1 such as a mercury-ground type rotation of 9S3 with respect to Cr center although no example of 9S3 complex with fluxionality is available to date.

![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).](image)

| Table 1. Spectroscopic Data for [M(CO)₃(9S3)] |  |
| M | IR⁺ | ¹H-NMR +¹C-{¹H}-NMR⁺/ppm |  |
| vₚ/pm |  |
| Cr | 1910,1790 | 2.53 (s) | 31.9 | 232.1 |  |
| Mo | 1915,1796 | 2.55-2.69 | 31.3 | 222.7 |  |
| W | 1905,1788 | (complex) | 32.5 | 216.2 |  |

*KBr, t-DMSO. Relative to TMS. *Coupling due to ¹HSW (I = 1/2, 14.28%) has not been resolved in both NMR spectra.

| Table 2. Comparison of IR Data for a series of [LM₃(CO)₃] |  |
| L | νₚ/pm |  |
| 9S3 | 1915,1796 | This work |  |
| 9N3 | 1850,1740-1700 | 20 |  |
| C₆H₆ | 1896,1936,1921 | 21 |  |
| C₆H₄ | 1901,1796,1746 | 22 |  |
| HBF₄⁻ | 1897,1761 | 23 |  |
| C₂B₁₀H₁₁⁻ | 1908,1876,1741 | 24 |  |
| 12P₃ | 1945,1840 | 25 |  |
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)₆(9S3)] toward oxidative decarboxylation reaction. A relative measure of π-acidity of L in a series of isoelectronic complexes LM(CO)₆ estimated by the comparison of ν₀ in Table 2, suggests the π-acidity decreases in the order C₃H₆, 12P₃, 9S3, C₂B₆H₁₄−, C₆H₆. HBP₅−, and 9N3. With this trend in mind, it is worth noting that in case of L=C₂B₆H₁₄− and C₆H₆, oxidative decarboxylation reactions have been observed. Further studies on the reactivities of 9S3 complexes and the development of heteroleptic crown thioether chemistry are under investigation.

Acknowledgement. This work was in part supported by the Korea Science and Engineering Foundation. YD thanks Yun Am Cultural Foundation.

References
10. (a) Anal. data for 1 (C₆H₄O₂S₂Cr). Calcd (found): C, 34.2 (34.2); H, 3.82 (3.83); (b) Anal. data for 3 (C₆H₄O₂S₂W). Calcd (found): C, 24.1 (24.1); H, 2.70 (2.66); (c) Analysis of 2 was omitted since its synthesis¹¹ and structure¹¹ have been previously reported.
13. Suitable crystals of 3 were grown by diffusing Et₂O/S/W into a DMF solution. Crystallographic data for 3: C₆H₄O₂S₂W, monoclinic, space group P2₁/n, a = 9.134(1), b = 11.060(2), c = 12.619(2), β = 92.74(1)°, V = 1273.3(3) A³, R(Ref) = 0.0310 (0.0335). A parallelepiped yellow crystal (0.21 × 0.25 × 0.41 mm) was sealed in a glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. Diffraction data were collected at ambient temperature using MoKα radiation to a maximum 29 value of 50° with 2θ-2θ scan mode. Data were corrected for Lorentz, polarization and absorption effects. Intensity data for 1791 reflections with 1<3(1) were used for Patterson method and SHELX 76.
15. The 0.01 Å shortening of the average M-S distance in 3 can be counted as significant because the covalent radius of W is longer than Mo by 0.01 Å.
16. The covalent radii for Mo(0) and W(0) are 1.45 and 1.46 Å, respectively: I. S. Butler and J. F. Harrod, Inorganic Chemistry-Principles and Applications. Benjamin/Cumings Pub., p 48 (1989).
17. Chemical shifts (ppm) of free 9S3: 1H-NMR (CDCl₃/d₂-DMF), 3.13/3.07(s); 3¹H-NMR (CD3CN), 3.54.
19. At our hands, only starting complexes have been obtained from the attempted oxidative decarboxylation of [M(CO)₆(9S3)] with elemental sulfur at room temperature. Simultaneous use of Me₂NO proved to be also ineffective.

New Synthesis of Acylferrocene from Ferrocene-carboxaldehyde by Rh(I) Catalyst

Chul-Ho Jun*, Jung-Be Kang, and Jin-Yong Kim

Agency for Defense Development, Taean 300-600

Received February 21, 1991

The C-H bond activation by transition metal complexes has been one of the recent interests in organometallic chemistry.¹ It has been reported that C-H bond activation of the aldime by Rh(I) generated iminoacrylicrhodium(III) hydride complex which inserted mon-oolefin and conjugate dienes to form iminoacrylicrhodium(III) allyl and allyl-substituted η⁵-allyl complexes,² respectively. They were readily reductive-eliminated to give corresponding ketimines, potential precursors for ketone since hydroslysis of them produce ketones. Consequently aldehyde can be easily converted to ketone