Scheme IV

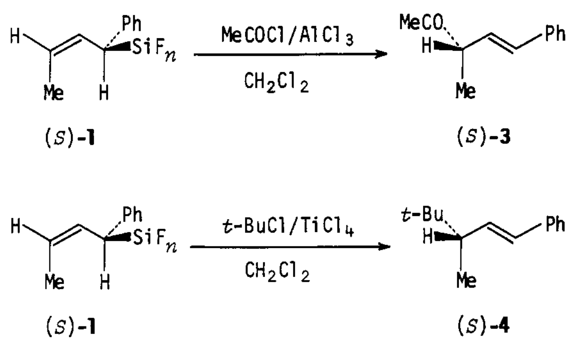

Table I. Electrophilic Reaction of the Allylfluorosilanes

entry	allylsilane (% ee)	electrophile	reaction time, min	yield,[a] %	product, (% ee)[b]
1	(*S*)-**1c** (26)	MeCOCl/$AlCl_3$[c]	20	88	(*S*)-**3** (24)
2		*t*-BuCl/$TiCl_4$[d]	1	73	(*S*)-**4** (29)
3	(*S*)-**1b** (26)	MeCOCl/$AlCl_3$	60	30	(*S*)-**3** (14)
4		*t*-BuCl/$TiCl_4$	3	59	(*S*)-**4** (29)
5	(*S*)-**1a** (37)	MeCOCl/$AlCl_3$	60	10	(*S*)-**3** (<5)
6		*t*-BuCl/$TiCl_4$	5	0	
7[e]	(*R*)-**2** (24)	MeCOCl/$AlCl_3$	5	74	(*R*)-**3** (19)
8[e]		*t*-BuCl/$TiCl_4$	1	75	(*R*)-**4** (27)

[a] Isolated yield by preparative TLC. [b] Determined by optical rotation data for **4** and by ^1H NMR analysis in the presence of $Eu(dcm)_3$ for **3**. The maximum rotations of (*S*)-**3** and (*S*)-**4** are $[\alpha]^{20}_D$ +289° (*c* 0.25, CCl_4) and −65° (*c* 1.0, CCl_4), respectively.[3a] [c] To a mixture of allylsilane and $AlCl_3$ (1.1 equiv) in dichloromethane was added MeCOCl (1.1 equiv) at −78 °C. The mixture was stirred at the same temperature for the given minutes and hydrolyzed with water. [d] To a solution of allylsilane and *tert*-BuCl (1.1 equiv) in dichloromethane was added $TiCl_4$ (1.1 equiv) at −78 °C. [e] These results have been reported previously in ref 3a.

benzene) 37% ee) and its methyldifluorosilyl analogue (*S*)-**1b**[7] ($[\alpha]_D^{20}$ +32.6° (*c* 2.95, benzene), 26% ee), were prepared by palladium- ($PdCl_2$[(*R*)-(*S*)-PPFA[8]]) catalyzed asymmetric hydrosilylation of 1-phenyl-1,3-butadiene[9] with trichlorosilane or methyldichlorosilane followed by fluorination[10] of the resulting allylchlorosilanes with $CuF_2 \cdot 2H_2O$ in ether (Scheme III). The enantiomeric purity and configuration of the allylsilanes **1a** and **1b** were determined by methylation of the allylchlorosilanes to give the known allyl(trimethyl)silane (*S*)-**2**.[3a] (*S*)-Allyl(dimethylfluoro)silane **1c**[11] ($[\alpha]_D^{20}$ +25.1° (*c* 2.77, benzene), 26% ee) was obtained by selective monomethylation of difluorosilane **1b**.

The optically active allylfluorosilanes were subjected to electrophilic substitution with MeCOCl/$AlCl_3$ and *t*-BuCl/$TiCl_4$ (Scheme IV). The results are summarized in Table I, which also contains data obtained[3a] in the reaction of allyl(trimethyl)silane **2** for comparison. The acetylation of dimethylfluorosilane (*S*)-**1c** in dichloromethane at −78 °C for 20 min gave (*E*)-3-acetyl-1-phenyl-1-butene (**3**) with *S* configuration of 24% ee in 88% yield (entry 1), and the *tert*-butylation gave a 73% yield of the (*E*)-olefin **4** of *S* configuration (29% ee) (entry 2). These results indicate that the electrophiles attacked the double bond of **1c** anti with respect to the leaving dimethylfluorosilyl group and the stereoselectivity and reactivity of **1c** are quite similar to those of the allyl(trimethyl)silane **2** (entries 7 and 8).[3a] Anti stereochemistry was also observed in the S_E' reactions of methyldifluorosilane (*S*)-**1b**, though the chemical yields are rather low in both acetylation and *tert*-butylation and a significant loss of the enantiomeric purity was observed in the acetylation (entries 3 and 4). The trifluorosilane **1a** underwent electrophilic reactions with difficulty. Thus, the acetylation gave a low yield of the almost racemic product **3** that was contaminated with 15% of the *Z* isomer, and the S_E' product was not formed at all in the *tert*-butylation (entries 5 and 6).

The results obtained above indicate that σ–π conjugative interaction between the carbon–silicon bond and the olefin π system,[12] which increases the electron density on the olefin and is responsible for the anti S_E' reaction, is pronounced in dimethylfluorosilane **1c** as well as in the trimethylsilyl analogue. The σ–π conjugation is less important in the methyldifluorosilane and is not a factor in the trifluorosilane. This order seems to be consistent with the electronic nature of fluorosilyl groups (SiF_nR_{3-n}).

Acknowledgment. We thank the Yamada Science Foundation for partial financial support of this work and Shin-etsu Chemical Industry Co., Ltd., for a gift of chlorosilanes. We are grateful to Professor Barry M. Trost, University of Wisconsin, for valuable discussions.

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(6) **1a**: ^1H NMR ($CDCl_3$) δ 1.719 (d, *J* = 5.4 Hz, 3 H), 3.759 (d, *J*. = 8.7 Hz, 1 H), 5.59–5.79 (m, 2 H) 7.15–7.36 (m, 5 H).

(7) Reaction of 1-phenylbutadiene with $HSiMeCl_2$ in the presence of 0.01 mol % of $PdCl_2$[(*R*)-(*S*)-PPFA] at 80 °C for 14 h gave 72% yield of (*S*)-(*Z*)-MeCH=CHCH($SiMeCl_2$)Ph regio- and stereoselectively. **1b**: ^1H NMR ($CDCl_3$) δ 0.279 (t, *J* = 6.1 Hz, 3 H), 1.699 (md, *J* = 6.6 Hz, 3 H), 3.554 (td, *J* = 3.4, 10.4 Hz, 1 H), 5.677 (ddq, *J* = 0.9, 6.6, 10.6 Hz, 1 H), 5.758 (qt, *J* = 1.6, 10.6 Hz, 1 H), 7.17–7.33 (m, 5 H).

(8) (*R*)-(*S*)-PPFA stands for (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine.

(9) Hayashi, T.; Kabeta, K. *Tetrahedron Lett.* **1985**, *26*, 3023.

(10) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983.

(11) Treatment of **1b** with 1 equiv of $MeMgBr/Et_2O$ at 0 °C for 10 min followed by bulb-to-bulb distillation gave 89% yield of the monomethylated product. **1c**: ^1H NMR ($CDCl_3$) δ 0.162 and 0.178 (a pair of d, *J* = 7.2 Hz, 6 H), 1.677 (ddd, *J* = 0.4, 1.8, 6.8 Hz, 3 H), 3.443 (dd, *J* = 4.9, 11.1 Hz, 1 H) 5.599 (ddq, *J* = 1.0, 10.7, 6.8 Hz, 1 H) 5.814 (qt, *J* = 1.8, 10.9 Hz, 1 H), 7.11–7.29 (m, 5 H).

(12) (a) Weidner, U.; Schweig, A. *Angew. Chem.* **1972**, *84*, 167. (b) Weidner, U.; Schweig, A. *J. Organomet. Chem.* **1972**, *39*, 261.

Reaction of $(\eta^5\text{-}C_5Me_5)_2\overline{TiOC[{=}Re(CO)_4Re(CO)_5]CH_2CH_2}$ with *tert*-Butyl Isocyanide: Molecular Structure of a New Zwitterionic Complex Involving (η^2-Imidoyl)titanium and Acyldirhenium Carbonyl Moieties

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Received August 13, 1986

Summary: Reaction of $(\eta^5\text{-}C_5Me_5)_2\overline{TiOC[{=}Re(CO)_4Re(CO)_5]CH_2CH_2}$ (**1a**) and *tert*-butyl isocyanide results in the

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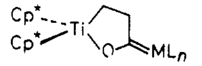
[‡] Kumamoto University.

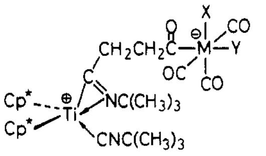
formation of the 1:2 adduct 2 whose molecular structure has been elucidated by X-ray crystallography, revealing that it has a novel zwitterionic structure possessing (η^2-imidoyl)titanium cation and anionic acyldirhenium carbonyl moieties linked by a two-methylene bridge. The controlled experiments show that 2 is produced by a thermal rearrangement of the initially formed complex 3 in which acyl ligand is trans to the Re–Re bond. The tungsten derivative 1b also gives the corresponding tungsten analogue of 2.

Chemistry of carbene–metal complexes has been the subject of considerable current interest.[2] We have previously described the synthesis and characterization of new cyclic titanoxycarbene–metal carbonyl complexes 1 [Cp* = η^5-C_5Me_5; ML_n = $Re_2(CO)_9$, $W(CO)_5$, etc.].[3] We now report the molecular structures of the novel complexes obtained by the reactions of 1 with *tert*-butyl isocyanide.



1a, $ML_n = Re_2(CO)_9$
1b, $ML_n = W(CO)_5$

Treatment of an orange-red solution of 1a in toluene with excess *tert*-butyl isocyanide under argon at -35 °C and then at room temperature led to the formation of a pale yellow solution. The yellow crystalline material precipitated at -80 °C was separated from the supernatant liquid to give air-sensitive complex 2 in 81% yield.[4,5] The molecular structure of 2 has been established by single-crystal X-ray diffraction methods,[6] which is shown in Figure 1. Titanium atom has a distorted tetrahedron geometry defined by two η^5-C_5Me_5, isocyanide, and η^2-imidoyl ligands.[7,8] The Ti-C(6) bond distance of 2.14 (3) Å represents a normal Ti-C(sp^2) single-bond distance,[9] suggesting a smaller contribution from the carbene resonance form, as has been pointed out for the (η^2-imidoyl)zirconium complex.[8b] Titanium atom is coordinated with only three anionic ligands but has a closed 18-electron-valence shell. This might be the reason for the observed stability of 2.[10] The η^1-acyl coordination on rhenium is reflected in the values of the O(1)–C(9) and Re(1)–C(9) distances and the Re(1)–C(9)–O(1) angle of 1.20 (3) Å, 2.27 (2) Å, and 127.4 (17)°, respectively.[11] To our knowledge this provides the first structural data for anionic



2, M = Re, X = $Re(CO)_5$, Y = CO
3, M = Re, X = CO, Y = $Re(CO)_5$
4, M = W, X = Y = CO

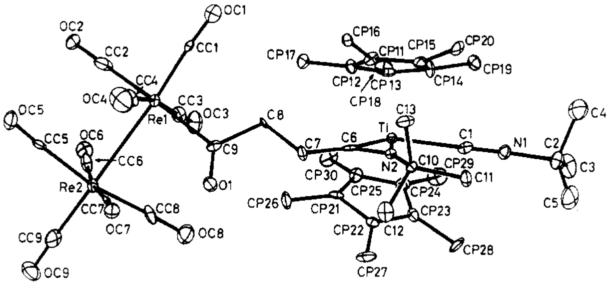


Figure 1. Molecular structure of the complex 2, with all hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (deg); Ti–C(1) = 2.17 (2), Ti–C(6) = 2.14 (3), Ti–N(2) = 2.17 (2), N(2)–C(6) = 1.26 (3), C(6)–C(7) = 1.51 (3), C(7)–C(8) = 1.52 (3), C(8)–C(9) = 1.57 (3), O(1)–C(9) = 1.20 (3), Re(1)–C(9) = 2.27 (2), Re(1)–Re(2) = 3.060 (2), Ti–O(1) = 5.96 (2), Ti–Re(1) = 7.056 (4), O(1)–Re(1) = 3.15 (2); Ti–C(6)–N(2) = 74.1 (15), Ti–N(2)–C(6) = 72.1 (14), Ti–C(6)–C(7) = 155.0 (16), C(1)–Ti–C(6) = 117.4 (9), N(2)–Ti–C(6) = 33.9 (7), C(1)–Ti–N(2) = 83.6 (9), N(2)–C(6)–C(7) = 130.8 (22), C(6)–C(7)–C(8) = 116.0 (21), C(7)–C(8)–C(9) = 113.2 (21), C(8)–C(9)–O(1) = 119.4 (20), Re(1)–C(9)–O(1) = 127.4 (17), Re(1)–C(9)–C(8) = 113.3 (16), Re(2)–Re(1)–C(9) = 91.7 (6).

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(1) Research student at IMS from Kumamoto University (April 1985–March 1986).

(2) Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K. Eds.; *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

(3) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145.

(4) Satisfactory elemental analyses were obtained for **2** and **3**. Complex **2** crystallizes with 1 equiv of toluene.

(5) NMR spectra were recorded on a JEOL GX400 spectrometer in THF-d_8 using solvent absorptions at δ_H 3.62 and δ_C 68.00 as internal standards, unless otherwise stated. **2**: mp 119–122 °C dec; ^{1}H NMR (22 °C) δ 1.50 (s, CMe_3), 1.80 (s, CMe_3), 1.87 (s, $2C_5Me_5$), 3.29–3.33 (m), 3.44–3.48 (m) [C(7)H_2 and C(8)H_2]; ^{13}C NMR (–30 °C) δ 13.34 (J_{CH} = 125 Hz, $2C_5\mathit{Me}_5$), 30.42 (J_{CH} = 129 Hz, $C\mathit{Me}_3$), 31.15 [J_{CH} = 127 Hz, C(7) or C(8)], 31.97 (J_{CH} = 127 Hz, $C\mathit{Me}_3$), 60.29 ($\mathit{C}Me_3$), 63.84 ($\mathit{C}Me_3$), 118.36 ($2\mathit{C}_5Me_5$), 189.81, 195.76, 197.49, 200.22 (relative intensity 1.0, 2.4, 2.7, 4.9, CO), 205.45 ($\mathit{C}NCMe_3$), 226.91 ($\mathit{C}NCMe_3$), 250.70 [C(9)]. The signals due to C(8) or C(7) and the solvent THF are considered to overlap at 68.00 ppm. When ^{13}C NMR was measured in CD_2Cl_2, signals due to C(7) and C(8) were observed at δ 29.59 (J_{CH} = 127 Hz) and 66.16 (J_{CH} = 127 Hz) (the solvent absorption at δ 53.60 was used as internal standard). IR (KBr): ν 2162 (m, N≡C), 2084 (m), 2008 (s), 1973 (vs), 1955 (sh), 1932 (s), 1918 (s), 1876 (s) (CO), 1650 (m, tentatively assigned to acyl), 1586 (m, C=N) cm^{-1}. **3**: mp 124–126 °C dec; ^{1}H NMR (–50 °C) δ 1.54 (s, CMe_3), 1.81 (s, CMe_3), 1.89 (s, $2C_5Me_5$), 3.45–3.49 (m), 3.58–3.60 (m) [C(7)H_2 and C(8)H_2]; ^{13}C NMR (–50 °C) δ 13.34 (J_{CH} = 127 Hz, $2C_5\mathit{Me}_5$), 30.34 (J_{CH} = 129 Hz, $C\mathit{Me}_3$), 31.84 (J_{CH} = 129 Hz, $C\mathit{Me}_3$), 31.24 (J_{CH} = 127 Hz), 72.49 (J_{CH} = 129 Hz) [C(7) and C(8)], 60.30 ($\mathit{C}Me_3$), 63.80 ($\mathit{C}Me_3$), 118.29 ($2\mathit{C}_5Me_5$), 191.43, 203.21, 203.65 (relative intensity 1.0, 7.8, 5.6, CO), 205.52 ($\mathit{C}NCMe_3$), 226.89 ($\mathit{C}NCMe_3$), 235.60 [C(9)]; IR (KBr) ν 2162 (m, N≡C), 2085 (m), 1960 (vs), 1935 (sh), 1883 (s) (CO), 1648 (vw, tentatively assigned to acyl), 1565 (w, C=N) cm^{-1}.

(6) Crystal data for **2**: $C_{42}H_{52}O_{10}N_2Re_2Ti \cdot C_7H_8$; M_r 1257.32; monoclinic, space group $P2_1/n$; a = 14.964 (2) Å, b = 26.207 (4) Å, c = 14.719 (3) Å; β = 100.30 (1)°; U = 5679.3 (16) Å^3; Z = 4; D_{calcd} = 1.471 g cm^{-3}; graphite-monochromated (Mo $K\alpha$) radiation; μ(Mo $K\alpha$) = 46.881 cm^{-1}; crystal size 0.10 × 0.15 × 0.45 mm. A suitable crystal grown from a mixture of hexane-toluene at 4 °C was sealed in a thin-walled glass capillary under argon and mounted on a Rigaku AFC-5 diffractometer. Data were collected at -120 °C in the range 2° < 2θ < 55°. The structure was solved by Patterson method and refined by block diagonal least squares using 4852 observed reflections with $|F_o| > 3\sigma(F_o)$. Refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and with isotropic thermal parameters for hydrogen atoms to give final R = 0.068 (R_w = 0.089).

(7) For imidoylzirconium complexes, see: (a) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35. (b) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450. (c) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(8) The crystal structures of some (η^2-imidoyl)metal complexes have been determined. (a) Ti(III): Van Bolhuis, F.; de Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299. (b) Zr(IV): Bristow, G. S.; Lappert, M. F.; Atwood, J. L.; Hunter, W. E., unpublished results. See: Cardin, D. J.; Lappert, M. F.; Raston, C. L. Eds.; *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Ltd: Chichester, 1986, Chapters 8 and 10. (c) Mo(II): Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41. (d) Ru(II): Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27. (e) U(IV): Zanella, P.; Paolucci, G.; Rossetto, G.; Benetollo, F.; Polo, A.; Fischer, R. D.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1985**, 96.

(9) Atwood, J. L; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

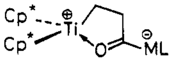
(10) Recently formation of such type of products has been reported for the reaction of cationic alkylbis(cyclopentadienyl)titanium and *tert*-butyl isocyanide: Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610.

(11) For the structural data of a rhenaacetylacetonate anion, see: Lenhert, P. G.; Lukehart, C. M.; Sotiropoulos, P. D.; Srinivasan, K. *Inorg. Chem.* **1984**, *23*, 1807.

acyldirhenium carbonyl complex determined by a single-crystal X-ray analysis.[12] Thus, the complex has a novel zwitterionic structure, in which the positive charge is on the titanium moiety while the negative charge is delocalized over the rhenium carbonyl residue. The acyl ligand is cis to the Re–Re bond which contrasts with the starting complex **1a** where the carbenic carbon is trans to the Re–Re bond.[3] The spectral data of **2** are consistent with the above structure.[5,13]

It should be noted when the above reaction was carried out at −55 °C for 4 h, and then the volatile material was removed in vacuo below −30 °C, another 1:2 complex, **3**,[4,5] a stereoisomer of **2**, could be obtained as yellow crystals in 77% yield. This compound in THF-d_8 gradually isomerized to **2** even at −10 °C, as monitored by ^{1}H NMR spectroscopy. The half-life of **2** in THF at 0 °C is 41 min. These findings indicate that the formation of the cis isomer **2** proceeds sequentially via the trans isomer **3**. It is not clear at present whether the rearrangement proceeds by way of an intermediate possessing an alkyl–rhenium bond formed by alkyl migration.[14]

Similar reaction of **1b** with *tert*-butyl isocyanide afforded the corresponding tungsten carbonyl complex **4**, whose structure is based on spectroscopic data.[15] The above results suggest that these reactions will be general for the cyclic titanoxycarbene–metal carbonyl complexes of type **1**. Since titanium has strong oxophilic nature, dissociation of oxygen ligand from titanium is rather unusual. This may be a consequence of the unique molecular structure of the starting complex **1** that has a long Ti–O bond and considerably shorter C(3)–O bond length than that of a usual C–O single bond, indicating an important contribution from the dipolar resonance structure **5**.[3]



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Supplementary Material Available: ^{1}H NMR spectra for **2**–**4**, a stereoview of **2**, a table of elemental analyses for **2**–**4**, and tables of atomic positions, thermal parameters, and selected bond lengths and angles for **2** (17 pages); a listing of structure factors for **2** (24 pages). Ordering information is given on any current masthead page.

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(12) Et_4N^+ *cis*-$(CO)_9Re_2CHO^-$ and Li^+ *cis*-$(CO)_9Re_2CHO^-$ have been prepared and characterized spectroscopically: Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. Gladysz, J. A.; Tam, W. *Ibid.* **1978**, *100*, 2545.

(13) The complex $(\eta^5\text{-}C_5H_5)_2Ti[C_6H_5CN\text{-}2,6\text{-}(CH_3)_2C_6H_3]$ shows an IR absorption at 1573 cm^{-1} assigned to ν(C═N).[8a] For (η^2–imidoyl)-zirconocene complexes, IR absorptions due to ν(C═N) have been observed in the region 1520–1578 cm^{-1} and ^{13}C NMR resonances due to imidoyl carbon at 233–246 ppm.[7a]

(14) Such type of isomerization has been proposed for *cis*-acetylbenozyltetracarbonylrhenate(I): Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723. Casey, C. P.; Baltusis, L. M. *Ibid.* **1982**, *104*, 6347.

(15) **4**: mp 66–70 °C dec; ^{1}H NMR (−50 °C) δ 1.52 (s, CMe_3), 1.81 (s, CMe_3), 1.87 (s, $2C_5Me_5$), 3.35–3.39 (m), 3.45–3.48 (m) [$C(7)H_2$ and $C(8)H_2$]; ^{13}C NMR (CD_2Cl_2, −45 °C) δ 12.00 (J_{CH} = 127 Hz, $C_5\mathit{Me}_5$), 12.05 (J_{CH} = 127 Hz, $C_5\mathit{Me}_5$), 28.05 [J_{CH} = 126 Hz, C(7) or C(8)], 29.46 (J_{CH} = 129 Hz, $C\mathit{Me}_3$), 30.53 (J_{CH} = 126 Hz, $C\mathit{Me}_3$), 58.21 ($\mathit{C}Me_3$), 62.00 ($\mathit{C}Me_3$), 68.41 [J_{CH} = 127 Hz, C(7) or C(8)], 116.30 ($2\mathit{C}_5Me_5$), 191.34 (J_{CW} = 122 Hz), 202.95 (J_{CW} = 129 Hz) (relative intensity 1.0, 4.4, CO), 207.90 ($\mathit{C}NCMe_3$), 224.78 ($\mathit{C}NCMe_3$), 274.53 [J_{CW} = 88 Hz, C(9)]; IR (KBr) ν 2162 (m, N≡C), 2041 (m), 1986 (w), 1947 (w), 1894 (s), 1874 (sh) (CO), 1642 (w, tentatively assigned to acyl), 1553 (w, C═N) cm^{-1}. Anal. Calcd for $C_{38}H_{52}N_2O_6TiW$: C, 52.79; H, 6.06; N, 3.24. Found: C, 51.26; H, 5.69; N, 2.98.

Reaction of Trimethylaluminum with Thiacrown Ethers. Crystal and Molecular Structure of $[Al(CH_3)_3]_4[14]aneS_4$

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Summary: Reaction of an excess of trimethylaluminum with 1,4,8,11-tetrathiacyclotetradecane, $[14]aneS_4$, in toluene affords the crystalline complex $[Al(CH_3)_3]_4[14]aneS_4$. The title compound belongs to the triclinic space group $P\bar{1}$ with a = 8.032 (5) Å, b = 10.330 (4) Å, c = 11.205 (3) Å, α = 95.24 (3)°, β = 94.85 (5)°, γ = 105.46 (5)°, and D_{calcd} = 1.04 g cm^{-3} for Z = 1. Least-squares refinement based on 1639 observed reflection led to a final R value of 0.028 (R_w = 0.029). The Al–S distances average 2.522 Å.

We have previously reported that aluminum alkyl–crown ether complexes serve as catalysts in the two-phase effect (liquid clathrate phenomenon).[1] These $[AlR_3]_n$·CE[2-4] complexes (CE = crown ether) enabled us to extend our examination of metal ions that exhibited liquid clathrate behavior beyond alkali metals to early-transition metals.[5] So as to afford liquid clathrates based on late-transition-metal ions, we sought to examine macrocyclic ligands capable of forming complexes with such ions. We chose the sulfur-based crown ether 1,4,8,11-tetrathiacyclotetradecane (hereafter $[14]aneS_4$)[6] to initiate these studies. Although the development of thiacrown ether chemistry has not paralleled that of crown ethers,[7-11] their ability to form

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(6) Following IUPAC rules, as noted above, the name of this macrocycle would be 1,4,8,11-tetrathiacyclotetradecane. Ochrymowycz et al. (Ochrymowycz, L. A.; Mak, C. P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079) suggested S_4-ethano-propano[14] or S_4-e-pr[14], thus denoting a 14-membered ring containing four sulfur atoms separated by alternating ethano and propano fragments. Glick et al.[13] used the trivial name of 14-ane-S_4 for the same macrocycle. Busch and Travis[14] used the abbreviation TTP for this macrocycle. In their studies of 1,4,7,10,13,16-hexathiacyclooctadecane, the sulfur analogue of 18-crown-6, Cooper et al. (Hintsa, E. J.; Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 3738) used the trivial name hexathia-18-crown-6. In following with this example, we have chosen to use in our laboratory the trivial name of tetrathia-14-crown-4 for 1,4,8,11-tetrathiacyclotetradecane, thus denoting a 14-membered crown ether containing four sulfur atoms. Herein, however, we have used the designation $[14]aneS_4$ used by Glick et al. (Virginia, B. P.; Diaddario, L. L.; Dockal, E. R.; Corfield, P. W.; Ceccarelli, C.; Glick, M. D.; Ochymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661) where the brackets signify a macrocyclic ligand, "ane" implies saturation, and S_4 signifies four sulfur atoms.

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