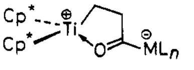
acyldirhenium carbonyl complex determined by a single-crystal X-ray analysis.[12] Thus, the complex has a novel zwitterionic structure, in which the positive charge is on the titanium moiety while the negative charge is delocalized over the rhenium carbonyl residue. The acyl ligand is cis to the Re–Re 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 ^1H 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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Acknowledgment. The authors thank Ministry of Education, Science and Culture, Japan, for grants in support of this work (No. 61540388 and No. 61470047).

Supplementary Material Available: ^1H 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; ^1H 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_5Me_5), 12.05 (J_{CH} = 127 Hz, C_5Me_5), 28.05 [J_{CH} = 126 Hz, C(7) or C(8)], 29.46 (J_{CH} = 129 Hz, CMe_3), 30.53 (J_{CH} = 126 Hz, CMe_3), 58.21 (CMe_3), 62.00 (CMe_3), 68.41 [J_{CH} = 127 Hz, C(7) or C(8)], 116.30 ($2C_5Me_5$), 191.34 (J_{CW} = 122 Hz), 202.95 (J_{CW} = 129 Hz) (relative intensity 1.0, 4.4, CO), 207.90 ($CNCMe_3$), 224.78 ($CNCMe_3$), 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 $[AlR_3]_n\cdot CE$[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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(1) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, **1984**; Vol. 1, pp 375–405.

(2) Robinson, G. H.; Bott, S. G.; Elgamal, H.; Hunter, W. E.; Atwood, J. L. *J. Inclusion Phenom.* **1985**, *3*, 65.

(3) Robinson, G. H.; Atwood, J. L.; Elgamal, H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* **1984**, *2*, 367.

(4) Atwood, J. L.; Hrncir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* **1982**, *1*, 1021.

(5) Prinz, H.; Bott, S. G.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2113.

(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.

(7) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495.

(8) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(9) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(10) Patai, S., Ed. *Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogs*; Wiley: New York, **1980**, Part 1, Supplement E.

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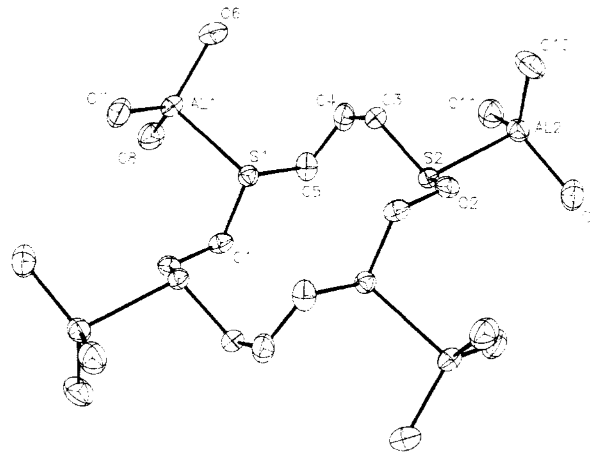

Figure 1. Structure of $[Al(CH_3)_3]_4[14]aneS_4$.

complexes with transition metals underscores the significance of these ligands. The sulfur macrocycle $[14]aneS_4$ was a logical ligand to examine as it has been shown to form stable complexes with $Ni(BF_4)_2$[12] and $Cu(ClO_4)_2$[13] as well as with Co(III) and Rh(III) ions.[14] Reaction of $Al(CH_3)_3$ with $[14]aneS_4$ in toluene yields colorless, rectangular, extremely air-sensitive crystals of $[Al(CH_3)_3]_4[14]aneS_4$ in nearly quantitative yield.[15] The X-ray crystal structure of the title compound is shown in Figure 1.

The title compound crystallizes in the triclinic space group $P\bar{1}$ with cell constants a = 8.032 (5) Å, b = 10.330 (4) Å, c = 11.205 (4) 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 reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.028$ (R_w = 0.029). Anisotropic thermal parameters were used for all atoms. The hydrogen atoms were refined. The details of data collection and refinement are as given in Holton et al.[16] The reaction product represents the first reported group IIIA (group 13)[17] metal alkyl–thiacrown ether complex. The compound resides on a crystallographic center of symmetry; all four sulfur atoms lie in the same plane.

The nonbonding distances between the sulfur atoms range from 4.287 Å for S(1)···S(1)′ to 6.260 Å for S(2)···S(2)′ (S(1)′ and S(2)′ are related to S(1) and S(2) through the center of symmetry). The S–C distances average 1.816 Å. The independent Al–S distances of 2.512 (2) and 2.531 (2) Å are worthy of note. The literature reveals, to the best of our knowledge, only two other organometallic compounds containing Al–S bonds that have been characterized by X-ray diffraction methods,[18] namely, $[(CH_3)_2AlSCH_3]_n$[19] with an Al–S distance of 2.348 (2) Å and $K[Al_2(CH_3)_6SCN]$[20] with an Al–S distance of 2.489 (2) Å. Thus, the Al–S distances in the title compound must be considered among the longest reported. The fact that sulfur carries a negative charge in CH_3S^- and SCN^- does not have a substantial effect on the Al–C bond distances in the adjacent $Al(CH_3)_3$ units. The average Al–C bond distance in the title compound of 1.954 (6) Å falls between the mean Al–C distances of 1.944 (7) and 1.962 (5) Å for $[(CH_3)_2AlSCH_3]_n$ and $K[Al_2(CH_3)_6SCN]$, respectively.

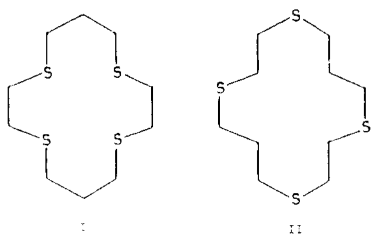

Figure 2. Illustration of the endo (I) and exo (II) conformations of $[14]aneS_4$.

The sulfur macrocycle $[14]aneS_4$ is interesting in itself in that the flexibility of the macrocycle, the size of the metal ion, and competing ligands (anions) determine the complexation mode of the macrocycle. With $Hg(ClO_4)_2 \cdot xH_2O$[21] the macrocycle assumes an endo-type conformation (Figure 2, I) as the metal is coordinated by all four sulfur atoms as well as by one H_2O adduct. The exo conformation (Figure 2, II) is observed with $HgCl_2$[20] as each pair of sulfur atoms coordinates to one $HgCl_2$ unit. In $[(NbCl_5)]_2[14]aneS_4$[22,23] the two $NbCl_5$ units are bridged by the ligand while it is in the exo conformation. The ligand is in the exo conformation in the title compound (Figure 1). It should be noted, however, that X-ray crystal structures of the uncomplexed ligand have revealed it to exist in both endo and exo conformations.[24]

The title compound is critically important as we explore the potential use of macrocycles other than crown ethers in organoaluminum chemistry in general and liquid clathrates specifically. The fact that $Al(CH_3)_3$ formed a stable compound with a metal ion complexing macrocycle is a strong indication that liquid clathrates will be accessible via those metal ions that the particular macrocycle coordinates.[2-4] Studies are currently underway in our laboratory using $[Al(nCH_3)_3]_4[14]aneS_4$ to catalyze the formation of liquid clathrates based on late-transition-metal ions.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554) and to J.L.A. We thank Duane C. Hrncir

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(12) Davis, P. H.; White, L. K.; Belford, R. L. *Inorg. Chem.* **1975**, *14*, 1753.

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(14) Travis, K.; Busch, D. H. *Inorg. Chem.* **1974**, *13*, 2591.

(15) Inside a glovebox (Vacuum Atmospheres Dri-Lab HE-43), a reaction tube was charged with $[14]aneS_4$ (Aldrich Chemical Co.) (1.86 mmol), toluene (20 mL), and trimethylaluminum (Aldrich Chemical Co.) (7.44 mmol). The macrocycle was completely insoluble in toluene. The reaction tube was removed from the glovebox and heated in an oil bath (60 °C). The reaction mixture was transferred to a 150-mL Schlenk flask (via cannula) and solvent reduced in vacuo. Upon cooling, X-ray quality crystals resulted. The product was obtained in quantitative yield. ^1H NMR (C_6D_6): δ 2.25 (s, 8 H, SCH_2CH_2S), 2.10 (t, 8 H, $SCH_2CH_2CH_2S$), 1.36 (quintet, 4 H, $SCH_2CH_2CH_2S$), -0.38 (s, 36 H, $AlCH_3$). $^{13}C\{^1H\}$ NMR: δ 31.82, 31.28 ($[14]aneS_4$), -7.97 ($AlCH_3$).

(16) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(17) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated. Groups IA and IIA thus become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(18) There have been, however, organometallic compounds containing Al–S bonds whose structures have been reported where gas-phase electron diffraction was used. The molecular structure of $[(CH_3)_2AlSCH_3]_2$ was reported (Haaland, A.; Stokkeland, O.; Weidlein, J. *J. Organomet. Chem.* **1975**, *94*, 353) as having a Al–S distance of 2.370 (3) Å, while the molecular structure of $(CH_3)_3AlS(CH_3)_2$ was reported (Fernholt, L.; Haaland, A.; Hargittai, M.; Seip, R.; Weidlein, J. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 529) as having a Al–S distance of 2.55 (2) Å. The latter compound has a comparable Al–S distance to the title compound.

(19) Brauer, D. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 5462.

(20) Shakir, R.; Zaworotko, M. J.; Atwood, J. L. *J. Organomet. Chem.* **1979**, *171*, 9.

(21) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1978**, 394.

(22) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 942.

(23) DeSimone, R. E.; Glick, M. D. *J. Coord. Chem.* **1976**, *5*, 181.

(24) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 762.

for assistance with NMR experiments.

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (8 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Characterization of a Stable (η^3-Indenyl)iron Metalate, (η^3-C_9H_7)$Fe(CO)_3^-$. A Role for η^3-η^5 Indenyl Ligand Tautomerization during Alkyl-CO Insertion Reactions

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Received December 12, 1986

Summary: The (η^5-indenyl)iron metalate (η^5-In)$Fe(CO)_2^-Na^+$ irreversibly associates carbon monoxide in THF solution and affords the stable CO adduct (η^3-In)$Fe(CO)_3^-Na^+$, which was isolated (77% yield) as its $(Ph_3P)_2N^+$ salt, **4**-PPN$^+$. A single-crystal X-ray diffraction study established the η^3-indenyl coordination: the dihedral fold angle, between planes defined by the η^3-carbons and by the In benzenoid ring, is 22°. In solution, IR and ^{1}H and ^{13}C NMR spectral studies demonstrated that the η^3-indenyl structure endures: its $^{13}C\{^1H\}$ NMR spectrum, for example, exhibits a 29 ppm downfield shift for the ipso C3a,C7a carbons (vs. those on Na^+In^-). Methylating **4**-PPN$^+$ with CH_3I cleanly affords mixtures of (η^5-In)$(CO)_2FeCOCH_3$ and $In(CO)_2FeCH_3$. The yield of the former increases with CO pressure (to 42% at 5.3 atm). Arguments are presented for intermediacy of (η^3-In)$(CO)_3FeCH_3$ in this reaction and for the η^3-to-η^5 indenyl ligand tautomerization driving the alkyl-CO migratory insertion.

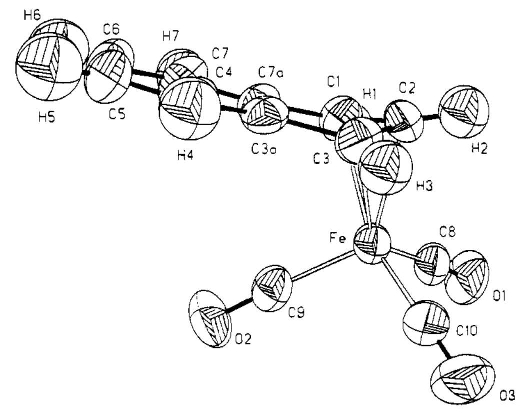
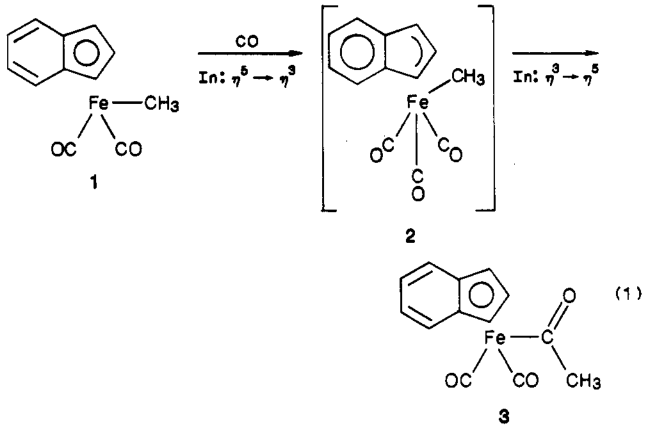


Figure 1. ORTEP plot of 4. Selected structural parameters: Fe–C1, 2.183 (5) Å; Fe–C2, 1.996 (5) Å; Fe–C3, 2.192 (5) Å; Fe–C3a, 2.885 (6) Å; Fe–C7a, 2.869 (7) Å; C1–C2, 1.416 (7) Å; C2–C3, 1.407 (7) Å; C3–C3a, 1.456 (7) Å; C3a–C7a, 1.397 (6) Å; C1–C7a, 1.469 (7) Å; Fe–C8, 1.742 (5) Å; Fe–C9, 1.779 (5) Å; Fe–C10, 1.752 (6) Å; C8–Fe–C10, 93.3 (2)°; C8–Fe–C9, 108.4 (2)°; C9–Fe–C10, 103.2 (2)°.

The η^5-indenyl ligand (In), serving as a replacement for its η^5-cyclopentadienyl (Cp) counterpart, provides a means of promoting associative reactions at the metal center.[1] Reversible slippage of the metal across the five-membered ring[2] thus can form a more reactive η^3-indenyl tautomer that has both benzenoid resonance stablization and an accesible coordination site.[3] Structural studies on a number of η^5-In complexes indeed indicate a minor "slip-fold" distortion already favoring a metal shift away from the indenyl central carbon–carbon bond.[2b,4] Three other coordinatively saturated compounds having η^3-In coordination have been structurally characterized.[5,6] In previous studies, we observed that substituting an η^5-In for η^5-Cp on iron alkyl complexes greatly facilitates their carbonylation (eq 1),[7a] which was attributed to the In ligand promoting an associative reaction (e.g., giving **2**). We now



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