Zerovalent titanium-sulfur complexes. Novel dithiocarbamato derivatives of $Ti(CO)_6$: $[Ti(CO)_4(S_2CNR_2)]^-$

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Experimental for $[KL_n][Ti(CO)_4(S_2CNR_2)]$, L = 15-crown-5, n = 2; 18-crown-6, n = 1; R = Me (**1**), Et (**2**).

$[KL_2]$[**1**], L = 15-crown-5: A solution of $(Me_2NCS_2)_2$ (0.270 g, 1.12 mmol) in pyridine (50 mL, -40 °C) was added to a cold solution of $[KL_2]_2[Ti(CO)_6]$•pyridine, (1.50 g, 1.20 mmol) in pyridine (100 mL, -40 °C). A greenish-brown solution was obtained after 5 h of stirring while slowly warming to 0 °C. Above 0 °C, the solution was bright green. Following filtration, solvent was removed *in vacuo* and the resulting residue was thoroughly washed with thf (-70 °C), isopropanol (-50 °C), (-50 °C) diethyl ether, and then dried *in vacuo*. Recrystallization from THF-Et_2O afforded satisfactorily pure green microcrystals of $[KL_2]$[**1**] (0.18 g, 21% yield, based on the thiuram disulfide). Elemental analysis (%) calcd for $C_{27}H_{46}KNO_{14}S_2Ti$: C 42.68, H 6.10, N 1.84; found: C 42.47, H 6.15, N 2.08. IR (thf): ν(CO) 1925 m, 1785 s cm^{-1}. $^{13}C\{^1H\}$ (75 MHz, $[^2H_5]$pyridine, 20 °C, $SiMe_4$, resonances due to cation omitted): δ 41.1 (CH_3) 206.8 (CS_2), 291.7 (CO) ppm. Attempts to grow suitable single crystals for X-ray analysis were unsuccessful, but dark green blocks of the closely related [K(18-crown-6)][**1**] were grown from helptane-thf at 0 °C. The spectroscopic properties of anion **1** for this salt were identical to those of [K(15-

crown-5)$_2$][**1**]. Details of this structure will be published elsewhere; however, the $Ti(CO)_4S_2$ core structure was essentially identical to that of anion **3**. *Crystal data* for $C_{19}H_{30}KNO_{10}S_2Ti$, M = 583.56, orthorhombic, space group P_{bcn}, a = 33.88(1), b = 8.511(3), c = 19.052(7) Å, $\alpha = \beta = \gamma = 90°$, V = 5494(3) Å^3, T = 173K, Z = 8, μ(Mo-Kα) = 0.663 mm^{-1}, 38486 reflections collected, 4854 unique (R_{int} = 0.0603). Refinement on F^2, final R1 = 0.0388 (for 3492 reflections with $I > 2\sigma(I)$), $wR2$ = 0.0931 (for all data), with GOF on F^2 of 0.982.

[KL_2][**2**]: An entirely analogous reaction of $(Et_2NCS_2)_2$ with $[KL_2]_2[Ti(CO)_6]$ in pyridine afforded, after an identical work-up procedure to that employed above for [KL_2][**1**], satisfactorily pure green microcrystals of [KL_2][**2**] (0.21 g, 24% yield based on the thiuram disulfide). Elemental analysis (%) calcd for $C_{29}H_{50}KNO_{14}S_2Ti$: C 44.21, H 6.40, N 1.78; found: C 44.38, H 6.44, N 2.03. IR (thf): ν(CO) 1924 m, 1785 s cm^{-1}. $^{13}C\{^1H\}$ (75 MHz, [$^2H_5$]pyridine, 20 °C, $SiMe_4$, resonances due to cation omitted): δ 12.8 (CH_3), 45.8 (CH_2), 206.5 (CS_2), 291.5 (CO) ppm. Dark green plates, suitable for X-ray analysis, were grown from heptane-thf at 0 °C. Although the X-ray analysis confirmed the nature of the salt, severe disorder of the 15-crown-5 units of three independent cations led to an unacceptably high R value for the structure solution, the details of which will not be published. Nevertheless, the three independent anions, were well-resolved and had essentially the same trigonal prismatic $Ti(CO)_4S_2$ cores as present in **1** and **3**.

Table S1. Dihedral Angles Between Selected Least-Squares Planes in Anion **3**.

defining planes	dihedral angle, deg
S_1TiS_2: O_1TiO_2	136[a]
S_1TiS_2: O_3TiO_4	136[a]
O_1TiO_2: O_3TiO_4	92
S_1TiS_2: $O_1O_2O_3O_4$	89[b]
S_1TiS_2: O_1TiO_3	44[c]
S_1TiS_2: O_2TiO_4	45[c]

[a] angles are larger than that of an ideal trigonal prism (120°), presumably due to repulsions of dtc and CO ligands.
[b] ideal trigonal prism, angle = 90°
[c] ideal trigonal prism, angle = 45° (see fig. S1 below)

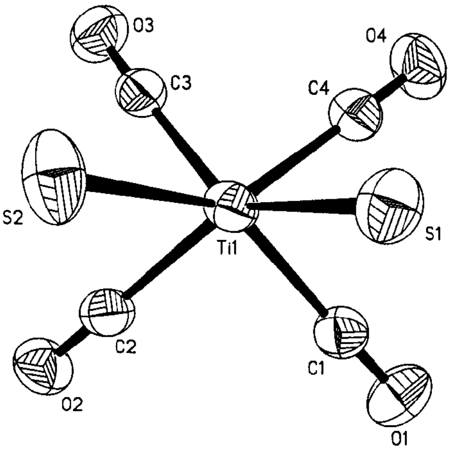

Fig. S1. Molecular structure of anion **3** viewed approximately down the TiS_1S_2 plane, with the carbamato group, CNC_5H_{10}, omitted for clarity, to emphasize the trigonal prismatic geometry about titanium. See Table S1 for corresponding dihedral angle data and Figure 1 for selected interatomic data.