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

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Oxidation of $[Ti(CO)_6]^{2-}$ by thiuram disulfides, $(R_2NCS_2)_2$, affords the first isolable mononuclear six-coordinate titanium(0) carbonyls, $[Ti(CO)_4(S_2CNR_2)]^-$, which have unusual trigonal prismatic geometries and chemical and spectral properties that are remarkably similar to those of the 18-electron and seven-coordinate anion $[Ti(CO)_4(\eta^5\text{-}C_5H_5)]^-$.

Metal carbonyl chemistry is well-developed for most d-block elements,[2] but for titanium, particularly in the absence of cyclopentadienyl or other dienyl ligands, it remains rather poorly explored.[3] Thus, despite the rich history of metal carbonyls with sulfur-containing ligands,[4] none have been described for titanium, or the heavier group 4 elements. We report herein on the synthesis, isolation and characterization of the initial examples: dithiocarbamatocarbonyltitanates(1−), $[Ti(CO)_4(S_2CNR_2)]^-$, for R = Me (**1**), Et (**2**) and C_5H_{10} or pentamethylene (**3**). These species are of additional interest because they are unprecedented examples of isolable mononuclear six-coordinate Ti(0) carbonyls and possess some unusual properties (see below). The only previously reported compound of this type is the exceedingly unstable 16-electron $Ti(CO)_6$, which reportedly decomposes at about 40 K in a CO/inert gas matrix.[5] All prior isolable and well-established mononuclear Ti(0) carbonyls have been 18-electron seven-coordinate complexes, such as $[Ti(CO)_4(\eta^5\text{-}C_5H_5)]^-$ (**4**),[6] $[Ti(CO)_5(SnPh_3)_2]^{2-}$,[7] and $[Ti(CO)_6(AuPEt_3)]^-$.[8]

These initial examples of zerovalent titanium dithiocarbamates[9] were prepared by the oxidation of dark red $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$[10] with thiuram disulfides, $(R_2NCS_2)_2$, in tetrahydrofuran, thf. Satisfactorily pure green microcrystals of composition $[K(15\text{-crown-}5)_2][Ti(CO)_4(S_2CNR_2)]$, were thereby obtained in about 20–30% isolated yields for **1** and **2**. Difficulties in separating these materials from the potassium dithiocarbamate byproducts led to the relatively low yields, Scheme 1, (see ESI§). Similar reactions of dipentamethylenethiuram disulfide, $(C_5H_{10}NCS_2)_2$, gave an analogous titanate product, **3**, but it could not be separated completely from the byproduct, $[C_5H_{10}NCS_2]^-$. However, a pure bis(triphenylphosphine)iminium or PPN salt of **3** was readily obtained by mixing $[PPN][Ti(CO)_4(\eta^3\text{-}BH_4)]$, where the latter anion is an exceptionally labile titanium carbonyl,[11] with $K[C_5H_{10}NCS_2]$ in thf. Poor solubility of the byproduct, KBH_4, facilitated the purification of **3**, which was isolated as a green PPN salt in 58% yield, Scheme 2.¶

$$[Ti(CO)_6]^{2-} + (R_2NCS_2)_2 \xrightarrow[-60\text{ to }0\ ^\circ C]{thf} [Ti(CO)_4(S_2CNR_2)]^- + [R_2NCS_2]^-$$

$$(R = Me, Et, \tfrac{1}{2}\,(CH_2)_5)$$

Scheme 1

Spectroscopic properties of **1–3** were independent of cation and entirely consistent with the proposed formulations. IR spectra in the carbonyl stretching frequency region showed essentially identical two band patterns in thf, ν(CO) 1925m, 1785s cm^{-1}, which were nearly superimposable on corresponding spectra in thf observed for **4**, ν(CO) 1921m, 1775s cm^{-1}.[6] ^{13}C NMR spectra of **1–3** had single very downfield carbonyl carbon resonances at about 292 ppm in pyridine or thf (see ESI§), which were close to the position reported for **4**, in dmso, δ_C = 289 ppm.[6] In contrast, normal 18-electron *cis*-disubstituted octahedral carbonyl complexes, such as $[Mo(CO)_4(S_2CNEt_2)]^-$,[12] have strikingly different IR spectra in the ν(CO) region, showing generally four major peaks, and a ^{13}C NMR spectrum consisting of two different carbonyl carbon resonances of equal intensity.

Despite the formal 16-electron natures of **1–3**, they showed no tendency to combine with CO, PMe_3 or PPh_3 in thf or neat pyridine at room temperature.[13] In this respect, they resemble the 18-electron titanate **4**, but are significantly less reactive than the previously known formally unsaturated dithiocarbamato carbonyls, $M(CO)_2(S_2CNR_2)_2$, M = Mo, W; R = alkyl. Unlike **3**, the latter species are CO carriers and readily add a variety of donors to afford isolable seven-coordinate complexes, $M(CO)_2L(S_2CNR_2)_2$, L = CO, PPh_3, pyridine, and related ligands.[14]

Single-crystal X-ray analyses of **1** and **3** were carried out to confirm their formulations. Unlike all previously reported mononuclear six-coordinate zerovalent metal complexes, they exhibited nearly trigonal prismatic geometry about the metals (Fig. 1)‖. Because their $Ti(CO)_4S_2$ core structures are almost identical, only the molecular structure of **3** will be described herein (See ESI§ for **1**).[15] The asymmetric unit contains a normal PPN cation, well separated from anion **3**. To emphasize the unusual character of **3**,

$$[PPN][Ti(CO)_4(BH_4)] + K[C_5H_{10}NCS_2] \xrightarrow{thf} [PPN][Ti(CO)_4(S_2CNC_5H_{10})] + KBH_4$$

$$PPN = N(PPh_3)_2;\ C_5H_{10} = (CH_2)_5$$

Scheme 2

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§ Electronic supplementary information (ESI) available: Experimental procedures and characterizations of compounds **1**, **2** and X-ray crystal data for **3**. See DOI: 10.1039/b700808b

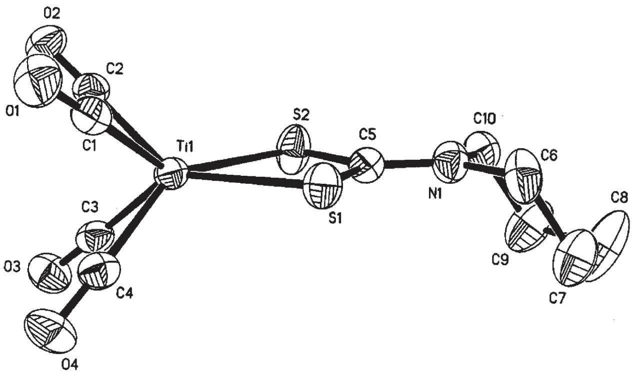

Fig. 1 Molecular structure of **3**; cation is not shown. Thermal ellipsoids are set at the 50% probability level, with hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–C(1) 2.018(2), Ti–C(2) 2.021(2), Ti–C(3) 1.996(2), Ti–C(4) 1.996(2), Ti–S(1) 2.5258(6), Ti–S(2) 2.5313(6), S(1)–C(5) 1.726(2), S(2)–C(5) 1.726(2), N(1)–C(5) 1.324(3), C(1)–O(1) 1.160(2), C(2)–O(2) 1.161(2), C(3)–O(3) 1.169(2), C(4)–O(4) 1.169(2); S(1)–Ti–S(2) 70.44(2), S(1)–C(5)–S(2) 115.3(1), av Ti–C–O 178(1).

salient features of its structure will be compared to those of the conventional 18-electron W(0) complex, $[W(CO)_4(S_2CNC_5H_{10})]^-$, **5**, which has an identical ligand set.[12] Whereas anion **5** contains a normal $M(CO)_4$ core structure appropriate for a *cis*-octahedral fragment, the corresponding unit in **3** has a strikingly different square pyramidal geometry, resulting in four equivalent carbonyl groups. Remarkably, the $Ti(CO)_4$ group in **3** is nearly superimposable on that of the seven-coordinate complex **4**.[16] This feature helps to explain why the IR and NMR spectra of **3** are so similar to those of **4**, but very different from those of **5**, in the carbonyl region. Only minor structural deviations are present in the essentially planar bidentate dithiocarbamato, or dtc, S_2CN units in **3** and **5**. For example, the average C–S distance in **3**, 1.726(2) Å, is slightly longer than that in **5**, 1.707(7) Å.[17] More important are differences in the metal–sulfur distances in the two anions, where the average M–S distance in **3**, 2.529(3) Å,[18] is nearly 0.06 Å shorter than the corresponding distance in **5**, 2.586(2) Å.[12] These data indicate that the metal–sulfur interactions in **3** are significantly stronger than those in **5**, particularly because the atomic radius of titanium is about 0.06 Å larger than that of tungsten.[19] Indeed, the spectral, chemical and structural properties of **1–3** strongly suggest that the dtc ligands function as both σ- and π-donors and thereby become electronically equivalent to the η^5-cyclopentadienyl group in **4**. On this basis, **1–3** should be regarded as 18 electron complexes, and are strikingly robust examples of transition metal compounds in which "π-stabilized unsaturation" plays a key role in defining their physicochemical properties.[20] Structural properties of **1–3** are also in accord with independent theoretical analyses by Templeton and Ward[21] and Kubacek and Hoffmann[22] on closely related six-coordinate low-spin d^4 complexes, including $Mo(CO)_2(S_2CNPr^i_2)_2$. Like **1–3**, the latter species has a nearly trigonal prismatic geometry, and both studies showed that optimization of cooperative π-donor (SR)–π-acceptor (CO) interactions with the metal centers was achieved in this unusual coordination environment.

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Notes and references

¶ Satisfactory elemental analyses (C, H, N) were obtained for all new compounds. [PPN[[**3**]: A solution of $K[S_2CNC_5H_{10}]$ (0.281 mmol) in thf (20 mL, 0 °C), prepared *in situ* from a potassium naphthalene reduction of the thiuram disulfide, was added to a red solution of $[PPN][Ti(CO)_4(BH_4)]$[11] (0.193 g, 0.271 mmol) in thf (10 mL, 0 °C). The resulting green solution was stirred at 0 °C for 1 h, filtered, and evaporated *in vacuo*. Purification was effected by washing the residue with diethyl ether, pentane, and then drying *in vacuo* to afford a satisfactorily pure deep green solid (0.139 g, 58% yield). IR (thf): ν(CO) 1925m, 1785s cm^{-1}. $^{13}C\{^1H\}$ (75 MHz, $[^2H_8]$thf, 20 °C, $SiMe_4$, resonances due to PPN omitted, labeling of C as per Fig. 1): δ 25.2 ($C_{7,9}$ or C_8), 26.6 (C_8 or $C_{7,9}$), 49.4 ($C_{6,10}$), 205.3 (C_5), 293.0 (CO). Green needles for the X-ray crystal study were grown from a diethyl ether–thf layered solution at −30 °C.

‖ *Crystal data* for [PPN][**3**]: $C_{46}H_{40}N_2O_4P_2S_2Ti$, $M = 858.76$, monoclinic, space group $P2_1/n$, $a = 9.8175(8)$, $b = 22.0718(17)$, $c = 19.6526(16)$ Å, $V = 4257.6(6)$ Å^3, $T = 173$ K, $Z = 4$, μ(Mo-Kα) = 0.420 mm^{-1}, 49057 reflections collected, 9768 unique ($R_{int} = 0.0357$). Refinement on F^2, final $R1 = 0.0413$ (for 7916 reflections with $I > 2\sigma(I)$). $wR2 = 0.0928$ (for all data). CCDC 637410. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700808b

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13 Thus, in these cases no significant change in the spectra of **1–3** were observed. Interestingly, below −10 °C solutions of **1** in neat pyridine changed from green to brown, but IR and NMR spectra remained nearly unchanged indicating the interaction of **1** with the solvent was quite weak. On warming above −10 °C the original color reappeared. Carbonyl exchange and related reactions with **1–3** will be described elsewhere.

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16 For example, average Ti–C and C–O distances in **3**, 2.01(1) and 1.165(5) Å, respectively, are statistically identical to corresponding values in **4**, 1.994(6) and 1.164(6), respectively. Also, the average *cis* and *trans* C–Ti–C angles of the $Ti(CO)_4$ units in **3** (*cis* 71(2); *trans* 110(1)°) and **4** (*cis*, 72(2); *trans*, 113(2)°) are essentially the same[6].

17 The N–C distance in **3**, 1.324(3) Å, is marginally shorter than the corresponding distance in **5**, 1.335(9) Å[12].

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