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Synthesis and characterization of titanium tetraisocyanide complexes, [CpTi(CNXyl)$_4$E], E = I, SnPh$_3$, and SnMe$_3$ ☆

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Dedicated to the memory of Professor F. Albert Cotton, for his wonderful support of and contributions to fundamental research in inorganic and organometallic chemistry.

Abstract

Oxidation of [CpTi(CO)$_4$]$^-$ by I$_2$, Ph$_3$SnCl, and Me$_3$SnCl in the presence of four equivalents of CNXyl, Xyl = 2,6-dimethylphenyl, affords unprecedented titanium tetraisocyanide complexes, [CpTi(CNXyl)$_4$E], E = I, SnPh$_3$, SnMe$_3$. These have been isolated and characterized by spectroscopic methods as well as single-crystal X-ray crystallography. A by-product of the iodine reaction was the Ti(III) complex, [CpTi(CNXyl)$_2$I$_2$], which was also characterized by X-ray crystallography.
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1. Introduction

Isocyanide complexes of metals date back to 1856, when Meyer, and later Gautier, obtained silver monoisocyanide complexes, of the composition Ag(CN)(CNR), by the treatment of silver cyanide with alkyl iodides [2]. Subsequently, numerous di- and poly-isocyanide complexes have been reported for most transition metals [3,4], but relatively little progress in this area has been achieved for the group 4 elements. For example, no poly-isocyanide complexes of Ti, Zr, or Hf are known, nor have any isocyanide complexes containing these elements in zero- or lower-valent states been described in the scientific literature. In view of recent progress in the synthesis of novel group 5 isocyanide complexes, including [V(CNXyl)$_6$]^0 [5], [Ta(CNXyl)$_7$]$^+$ and [Nb(CNXyl)$_6$]$^-$ [6], Xyl = 2,6-dimethylphenyl, extension of this research to the group 4 elements was of interest. Mono- and di-isocyanide

complexes of these metals have been reported previously, including CpTi(CNR)$_2$Cl$_2$, R = C$_6$H$_{11}$ [7], Xyl [8]; Cp$_2$Ti-(CNXyl)Cl [9], Cp$_2$M(CO)(CNR), M = Ti, Zr, Hf, R = *t*-Bu; M = Ti, Zr, R = Xyl [10a], Cp$_2$M(CNXyl)$_2$, M = Ti, Zr [10b], *cis*-TiCl$_4$(CN-*t*-Bu)$_2$ [11], [TiCl$_4$(CNXyl)]$_2$ [12], and *trans*-[Ti(TPP)(CN-*t*-Bu)$_2$], TPP = *meso*-tetra-*p*-tolylporphyrin [13]. In this article, we describe the first titanium tetraisocyanide complexes, [CpTi(CNXyl)$_4$E], E = I, SnPh$_3$, SnMe$_3$.

2. Experimental

2.1. General information

All reactions were carried out under an argon atmosphere with a double manifold vacuum line that has been previously described [14]. See a prior paper for a discussion of general procedures and the purification of solvents [15]. [Et$_4$N][CpTi(CO)$_4$] was prepared according to the literature procedure [16]. All other reagents were obtained from commercial sources and freed of dioxygen and moisture by standard methods [17] before use.

2.2. Synthesis of [CpTi(CNXyl)₄I] (1)

Cold toluene (100 mL, −78 °C) was added to a solid mixture of [Et₄N][CpTi(CO)₄] (1.00 g, 2.82 mmol) and CNXyl (1.50 g, 11.4 mmol). A solution of I_2 (0.716 g, 2.82 mmol) in toluene (60 mL, 20 °C) was then added via cannula with stirring. The mixture immediately turned brown and began evolving carbon monoxide (*Caution*: carbon monoxide is a very toxic gas, so this procedure and similar ones described below, must be carried out in a well-ventilated hood). It was then stirred overnight while slowly warming to room temperature and after 48 h, the reaction mixture was royal purple. Following filtration, the solvent was removed under vacuum to afford an air-sensitive dark purple solid. Excess CNXyl was removed by sublimation (20 °C, 0.1 torr). The compound was recrystallized from toluene to afford satisfactorily pure dark purple microcrystals of **1** (2.013 g, 94%), m.p. 120–122 °C (dec). Elemental Anal. Calc. for $C_{41}H_{41}IN_4Ti$: C, 64.16; H, 5.38. Found: C, 64.60; H, 5.23%. IR (toluene), $v(CN)$: 2035 vs, 1996 w cm^{-1}. ^{1}H NMR (500 MHz, C₆D₆, 25 °C): δ 2.42 (s, 24 H, o-CH_3), 5.50 (s, 5H, C_5H_5), 6.68 (m, 12 H, m and p-H). ^{13}C{^{1}H} NMR (125 MHz, C₆D₆, 24 °C): δ 19.9 (s, o-CH_3), 95.8 (s, C_5H_5), 127.1, 128.9, 129.7, 133.8 (s, phenyl carbons), 197.9 (s, CNXyl).

X-ray quality single-crystals of **1** · 1/2 (pentane) were grown as dichroic plates, i.e., purple by reflected light and green by transmitted light, from a pentane-layered THF solution at 20 °C after several days under an argon atmosphere. The formula unit contains 0.5 pentane solvent molecules, disordered over an inversion center.

2.3. Synthesis of [CpTi(CNXyl)₂I₂] (2)

Treatment of **1** (0.167 g, 0.218 mmol) with I_2 (0.028 g, 0.11 mmol) in cold toluene (40 mL, −65 °C), followed by warming to room temperature, with constant stirring, over a period of about 5 h, resulted in an apple-green solution. The solution was filtered and the solvent removed under vacuum, giving a bright green solid. However, attempts to separate the product from free CNXyl invariably resulted in partial to nearly complete decomposition to give a brownish solution, from which only small amounts of brownish-green impure solid **2** was obtained. An IR spectrum of impure **2** in THF or toluene showed a weak broad absorption centered at about 2156 cm^{-1}, due to product, along with an intense band due to free CNXyl, $v(CN)$: 2116 cm^{-1} in THF. However, X-ray quality single-crystals of **2** were grown as green plates from a pentane layered-THF solution at room temperature and provided unambiguous evidence for the presence of this substance in the reaction mixture. The IR spectrum of single-crystals of **2** in solution were identical to those shown above.

2.4. Synthesis of [CpTi(CNXyl)₄(SnPh₃)] (3)

A slurry of bright red [Et₄N][CpTi(CO)₄] (0.500 g, 1.4 mmol) in cold toluene (20 mL, −70 °C) was treated sequentially with cold (−70 °C) colorless solutions of Ph₃SnCl (0.571 g, 1.4 mmol) and CNXyl (0.744 g, 5.7 mmol) in toluene (30 mL and 20 mL, respectively) with vigorous stirring. On warming the reaction mixture slowly to room temperature over a period of about 10 h, it gradually changed from bright red to bright purple. After stirring for five days under ambient conditions, the mixture was filtered and solvent was removed under vacuum from the filtrate. Free CNXyl was separated by sublimation. The product was then recrystallized from toluene to provide satisfactorily pure deep purple **3** (0.606 g 44%), m.p. 147–149 °C (dec). Elemental Anal. Calc. for $C_{59}H_{56}N_4SnTi$: C, 71.75; H, 5.71. Found: C, 71.13; H, 5.46%. IR (THF), $v(CN)$: 2005 sh, 1977 vs cm^{-1}; IR (toluene), $v(CN)$: 2005 sh, 1976 vs cm^{-1}. ^{1}H NMR (500 MHz, C₆D₆, 25 °C): δ 2.15 (s, 24 H, o-CH_3), 5.93 (s, with satellites, $J_{Sn-H} = 11.5$ Hz, 5H, C₅H₅), 6.7–6.9 (m, m- and p-H in SnPh₃, CNXyl), 7.85 (dd with satellites, $^3J_{H-H} = 8$ Hz, $^4J_{H-H} = 1.5$ Hz, $J_{Sn-H} = 31.8$ Hz, o-H in SnPh₃). ^{13}C{^{1}H} NMR (75 MHz, C₆D₆, 25 °C): δ 19.6 (s, o-CH_3), 95.5 (s, C₅H₅), 126.5, 127.0, 128.3, 133.3 (s, phenyl in CNXyl), 127.6 (s with satellites, $J_{Sn-C} = 22$ Hz, o- or m-C in SnPh₃), 130.0 (s with satellites, $J_{Sn-C} = 14$ Hz, p-C in SnPh₃), 139.1 (s with satellites, $J_{Sn-C} = 30$ Hz, m or o-C in SnPh₃), 153.5 (s with satellites, $J_{Sn-C} = 48$ Hz, i-C in SnPh₃), 214.1 (s, CNXyl) ppm. ^{119}Sn NMR (112 MHz, CDCl₃, 25 °C, SnMe₄ ref): δ −69.0 s ppm. X-ray quality single-crystals of **3** were grown as purple blocks from a pentane-layered concentrated toluene solution at 20 °C over a four month period.

2.5. Synthesis of [CpTi(CNXyl)₄(SnMe₃)] (4)

By the same procedure employed to prepare **3**, toluene suspensions or solutions of [Et₄N][CpTi(CO)₄] (0.500 g, 1.4 mmol), Me₃SnCl (0.279 g, 1.4 mmol), and CNXyl (0.744 g, 5.7 mmol) were combined at −70 °C. After warming to room temperature and stirring for 5 days, the solution was deep purple. Following filtration and purification as described for **3**, satisfactorily pure black (or intensely deep purple) microcrystals of **4** were obtained (0.339 g, 31%), m.p. 133–135 °C (dec). Elemental Anal. Calc. for $C_{44}H_{50}N_4SnTi$: C, 65.94; H, 6.29. Found: C, 66.62; H, 6.84%. IR (THF), $v(CN)$: 2005 sh, 1969 vs cm^{-1}; IR (toluene), $v(CN)$: 2005 sh, 1969 vs cm^{-1}. ^{1}H NMR (300 MHz, C₆D₆, 25 °C): δ 0.42 (s with satellites, $J_{Sn-H} = 29$ Hz, 9H, SnMe_3) 2.37 (s, 24H, o-CH_3), 5.37 (s with satellites, $J_{Sn-H} = 11.4$ Hz, 5H, C₅H₅), 6.79 (m, 12 H, m- and p-H) ppm. ^{13}C{^{1}H} NMR (75 MHz, C₆D₆, 25 °C): δ −1.8 (s with satellites, $J_{Sn-C} = 45$ Hz, SnMe_3), 19.7 (s, o-CH_3), 94.4 (s, C₅H₅), 126.8, 128.5, 130.3, 132.5 (s, phenyl CNXyl), 222.2 (s, CNXyl) ppm. ^{119}Sn{^{1}H} NMR (186 MHz, C₆D₆, 25 °C, SnMe₄ ref): δ −17.4 (s) ppm. X-ray quality single-crystals of **4** were grown as black blocks from a pentane-layered concentrated diethyl ether solution at −20 °C over a period of several weeks.

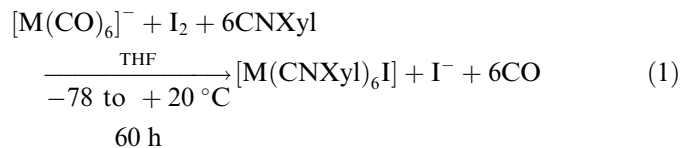## 2.6. X-ray crystallographic analyses of (1)–(4)

Crystallographic data for compounds **1**–**4** are summarized in Table 1. Procedures for the growth of X-ray quality crystals are described under their syntheses. A selected crystal was coated with viscous oil and attached to a glass fiber under an inert atmosphere and mounted on a Siemens SMART Platform CCD diffractometer for data collection (Mo Kα radiation, graphite monochromer). The intensity data were integrated using SAINT [18] and corrected for absorption and decay using SADABS [19]. Structures were solved by direct methods using SHELXL-97 software [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Molecular structures and selected interatomic data for **1**–**4** will be shown and discussed in the following section.

3. Results and discussion

3.1. Syntheses of 1–4

Recently we reported on the oxidation of the hexacarbonylmetalates (1-) of niobium and tantalum by I_2, followed by the addition of a slight excess, seven equivalents, of 2,6-dimethylphenyl isocyanide, CNXyl, to afford 70–80% isolated yields of the monovalent metal complexes, $[M(CNXyl)_6I]$, M = Nb, Ta [6], which represented the first fully substituted isocyanide derivatives of the unknown $[M(CO)_6I]$ for these elements:

$$[M(CO)_6]^- + I_2 + 6CNXyl$$

$$\xrightarrow[\substack{-78 \text{ to } +20\,°C \\ 60\text{ h}}]{\text{THF}} [M(CNXyl)_6I] + I^- + 6CO \qquad (1)$$

We were surprised that the CNXyl ligand was able to replace all carbonyls in view of prior reports that similar reactions only gave mixed isocyanide carbonyl complexes, such as $[Nb(CO)_2(CNXyl)_4I]$ and $[Ta(CO)_3[(CN-t-Bu)_3I]$ [21].

Our attention then turned to the possibility of extending this research to the group 4 elements, because, as mentioned in the introduction, many opportunities for exciting new discoveries exist in this poorly explored area of titanium, zirconium and hafnium chemistry, particularly in low-valent systems. Herein we describe some new results involving the first carbonyltitanate complex, $[CpTi(CO)_4]^-$, originally reported in 1986 [22].

Table 1
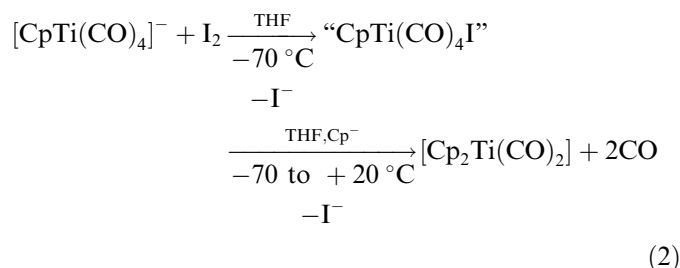Crystal data, data collection, and solution refinement for **1**–**4**

Compound	1	2	3	4
Empirical formula	$C_{43.5}H_{47}IN_4Ti$	$C_{23}H_{23}I_2N_2Ti$	$C_{59}H_{59}N_4SnTi$	$C_{44}H_{50}N_4SnTi$
Formula weight	800.65	629.13	987.67	801.47
Crystal color, habit	Purple/green plate	Green, plate	Purple, block	Black, block
Crystal size (mm)	$0.41 \times 0.31 \times 0.18$	$0.47 \times 0.38 \times 0.14$	$0.40 \times 0.40 \times 0.30$	$0.45 \times 0.45 \times 0.35$
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.287(1)	8.1280(9)	15.703(3)	14.643(3)
b (Å)	16.460(2)	8.4359(9)	17.301(3)	16.108(3)
c (Å)	21.816(2)	17.586(2)	18.432(3)	20.490(6)
α (°)	90	99.646(2)	86.133(7)	106.251(4)
β (°)	93.843(2)	93.812(2)	89.420(6)	103.020(4)
γ (°)	90	96.739(2)	87.057(7)	108.970(3)
V (Å)³	4044.0(7)	1176.0(2)	4990(1)	4113(2)
Z	4	2	4	4
ρ_{calc} (Mg m^{-3})	1.315	1.777	1.315	1.294
μ(Mo Kα) (nm^{-1})	1.009	3.000	0.702	0.835
Temperature (K)	173(2)	173(2)	173(2)	173(2)
θ Range (°)	1.55–27.53	2.47–27.52	1.18–27.51	1.10–25.09
Index ranges	$-14 \leqslant h \leqslant 14$, $-21 \leqslant k \leqslant 21$, $-28 \leqslant l \leqslant 28$	$-10 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 10$, $-22 \leqslant l \leqslant 22$	$-20 \leqslant h \leqslant 20$, $-22 \leqslant k \leqslant 22$, $-23 \leqslant l \leqslant 23$	$-17 \leqslant h \leqslant 17$, $-19 \leqslant h \leqslant 19$, $-24 \leqslant l \leqslant 24$
Reflections collected	46276	13546	59051	39090
Unique reflections	9287	5313	22661	14498
R_{int}^a	0.0377	0.0340	0.0220	0.0445
Data/restraints/parameters	9287/31/469	5313/0/254	22661/0/1171	14498/21/934
Reflections with $I > 2\sigma(I)$	7714	4789	19959	13056
R_1^b; wR_2^c ($I > 2\sigma(I)$)	0.0300; 0.0770	0.0287; 0.0742	0.0344; 0.0762	0.0598; 0.1507
R_1; wR_2 (all data)	0.0406; 0.0832	0.0328; 0.0766	0.0425; 0.0786	0.0672; 0.1562
Goodness-of-fit on F^2	1.028	1.019	1.133	1.085
Largest difference peak/hole (e Å^{-3})	0.995/−0.331	1.187/−0.917	0.858/−0.446	3.057/−1.733

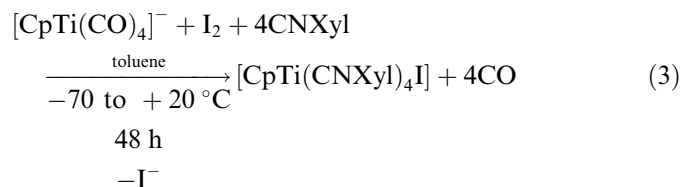[a] $R_{int} = \sum |F_o^2 - \langle F_c^2 \rangle| / \sum |F_o^2|$.
[b] $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.
[c] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum (w(F_o^2)^2) \right]^{1/2}$.

Prior work showed that treatment of $[CpTi(CO)_4]^-$ with I_2 at $-70\,°C$ in THF or CH_2Cl_2 produced solutions of an exceedingly unstable deep red substance. This species was tentatively identified as "$CpTi(CO)_4I$" [16], on the basis of its reaction with $Na^+C_5H_5^-$, which gave small amounts of the prototypical titanium carbonyl complex $[Cp_2Ti(CO)_2]$ [23]:

$$[CpTi(CO)_4]^- + I_2 \xrightarrow[-70\,°C]{\text{THF}} \text{``}CpTi(CO)_4I\text{''}$$
$$-I^-$$
$$\xrightarrow[-70 \text{ to } +20\,°C]{\text{THF,Cp}^-} [Cp_2Ti(CO)_2] + 2CO$$
$$-I^-$$
$$(2)$$
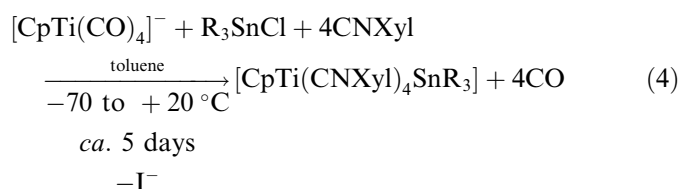
To obtain more evidence for the existence of the presumed precursor, $[CpTi(CO)_4I]$, an analogous iodination of $[CpTi(CO)_4]^-$ was carried out in the presence of slightly more than four equivalents of CNXyl. Also, the reaction was conducted in toluene, rather than THF or CH_2Cl_2, previously employed in related reactions [16]. The latter two solvents gave very poor conversion to product, likely due to the instability of intermediates in these solutions. Because $[Et_4N][CpTi(CO)_4]$ is essentially insoluble in toluene, the reaction proceeded slowly and required about 2 days to achieve optimum results and provided about 90% isolated yields of dark purple $[CpTi(CNXyl)_4I]$, **1**:

$$[CpTi(CO)_4]^- + I_2 + 4CNXyl$$
$$\xrightarrow[-70 \text{ to } +20\,°C]{\text{toluene}} [CpTi(CNXyl)_4I] + 4CO$$
$$48 \text{ h}$$
$$-I^-$$
$$(3)$$

The product is of interest as a completely substituted isocyanide complex of the unknown $[CpTi(CO)_4I]$, and its formation lends credence to the premise that the carbonyl iodide complex is a thermally unstable precursor in this reaction. A green by-product, obtained in small amounts from this reaction, was the Ti(III) complex $CpTi(CNXyl)_2I_2$, **2**, an iodo-analog of the previously known and also green $CpTi(CNXyl)_2Cl_2$ [8]. Compound **2** was also obtained by the reaction of **1** with 0.5 equivalent of I_2. However, attempts to obtain acceptably pure bulk samples of **2** from this reaction were unsuccessful due to its apparent instability in THF or toluene. Spectral and single-crystal X-ray crystallographic structural data for **1** and **2** will be presented and discussed below.

Reactions of $[CpTi(CO)_4]^-$ with the organotin electrophiles, R_3SnCl, R = Ph, Me, also provided thermally unstable products proposed to have the corresponding formulas $[CpTi(CO)_4SnR_3]$. IR and NMR spectral data for the triphenylstannyl adduct have been previously reported [16]. Both of these formally Ti(II) complexes are believed to be unstable due to the lability of their CO groups and on this basis it was anticipated that they would be stabilized

by exchange of one or more CO groups by better σ-donor ligands, such as isocyanides. Thus, when a slight excess of CNXyl was added to an initial mixture of $[Et_4N]$-$[CpTi(CO)_4]$ and R_3SnCl, R = Ph, Me, in toluene, under the same conditions employed in the synthesis of **1**, see above, the corresponding mixed tin–titanium complexes, $[CpTi(CNXyl)_4SnR_3]$, R = Ph, **3**, and Me, **4**, were obtained as thermally stable dark purple and nearly black microcrystals. Isolated yields of **3** and **4** were appreciably lower, *ca.* 30–40%, than those for **1** mainly due to the much greater solubility of these species in hydrocarbon solvents and subsequent difficulty in their separation from uncoordinated CNXyl:

$$[CpTi(CO)_4]^- + R_3SnCl + 4CNXyl$$
$$\xrightarrow[-70 \text{ to } +20\,°C]{\text{toluene}} [CpTi(CNXyl)_4SnR_3] + 4CO \qquad (4)$$
$$ca. \ 5 \text{ days}$$
$$-I^-$$

Spectral and X-ray data for **3** and **4** will be discussed below.

3.2. Characterizations of 1–4

Selected spectral data for the coordinated isocyanide groups in **1–4** are shown in Table 2. IR spectra for $[CpTi(CNXyl)_4E]$, E = I, **1**; $SnPh_3$, **3**; $SnMe_4$, **4**, in the isocyanide $v(CN)$ region show one intense (and broad peak), suggestive of pseudo-octahedral structures of the general formula *trans*-$LL'M(CNR)_4$, where the η^5-C_5H_5 groups are approximately opposite to the iodo or triorganotin units, in accord with the molecular structures for these species observed in the solid state, see below. Qualitatively similar IR spectra in the $v(CO)$ region were previously reported for the related $[Cp^*Ti(CO)_4E]$ complexes, E = I, $SnPh_3$, and $AuPPh_3$, and analogous structures were proposed for these carbonyls on this basis [16]. As expected, the $v(CN)$ positions of the most intense peak for $[CpTi(CNXyl)_4E]$ decrease in the order $E = I > SnPh_3 > SnMe_3$, which is just the opposite of the relative donor abilities of these substituents. It is noteworthy that the $v(CN)$ values are well below that for free CNXyl, 2116 cm^{-1}, which indicates that the isocyanide groups in **1**, **3**, and **4** are functioning as net acceptor ligands in these formally Ti(II) electron rich complexes. In contrast, the infrared spectrum of $[CpTi(CNXyl)_2I_2]$, **2**, a formal Ti(III) complex, shows a single broad $v(CN)$ absorption at

Table 2
Selected IR and NMR data for **1–4** and CNXyl in toluene

Compound	$v(CN)$ (cm^{-1})	^{13}C $\delta(CN)$ (ppm)
1	2035 br vs, 1996 w	197.9
2	2156 br vs	–
3	2005 sh, 1976 br vs	214.1
4	2005 sh, 1969 br vs	222.2
CNXyl	2116 vs	165.4

2156 cm^{-1}, which is 40 cm^{-1} above that of the free ligand. Notably, the previously reported chloro-analog of **2**, [CpTi(CNXyl)$_2$Cl$_2$], which was not structurally characterized, is also a green substance and shows a single intense v(CN) band at 2160 cm^{-1} [18]. IR data for **2** and the chloro-analog indicate that the isocyanide ligands in these much less electron rich Ti(III) complexes function primarily as donor ligands. These IR spectral changes for **1–4** are entirely consistent qualitatively with expectations based on the classic Chatt–Dewar–Duncanson model for back-bonding [24]. However, the IR v(CN) peaks for **1**, **3**, and **4** are much broader than corresponding peaks for the [Cp*Ti(CO)$_4$E] complexes, due to the non-linearity of the M-CNR units, which effectively decreases the symmetries of isocyanide complexes compared to carbonyl analogs. Cotton and Zingales first reported on this phenomenon nearly 50 years ago [25]. A recent example involved comparison of IR spectra of [Ta(CNXyl)$_6$]$^-$ and [Ta(CO)$_6$]$^-$ [6]. Prominent shoulders observed in the IR v(CN) spectral region for **3** and **4**, but not **1**, suggests that the bulky character of the R$_3$Sn groups in the former two complexes, also contributes to further reduction in the local symmetry of the titanium. A similar bifurcation of the IR v(CN) band envelope in THF solution was recently reported for *trans*-[Fe(CNXyl)$_4$(SnPh$_3$)$_2$], which contains a Fe(CN)$_4$Sn$_2$ core structure of nearly D_{4h} symmetry in the solid state [26].

^{1}H and ^{13}C NMR spectra of diamagnetic **1**, **3**, and **4** are summarized in Section 2 under the respective compounds and show normal resonances and positions for the Cp and aliphatic/aromatic portions of the coordinated CNXyl ligands. In addition, unexceptional ^{1}H, ^{13}C and ^{119}Sn NMR spectra for the Ph$_3$Sn and Me$_3$Sn ligands in **3** and **4**, respectively, were observed. In Table 2, the ligated isocyanide carbon ^{13}C NMR resonances are collected for the new complexes, along with that of free CNXyl in toluene. They show the expected trend, i.e., the isocyanide δ_C values become more positive as the transition metal center becomes more electron rich [27]. Thus, these results are consistent with the IR v(CN) data for [CpTi(CNXyl)$_4$E], where the relative donor ability of the substituents increase in the order E = I < SnPh$_3$ < SnMe$_3$.

Single-crystal X-ray structural characterizations were carried out to confirm the formulations of **1–4** and to provide interatomic data for these unusual compounds. Molecular structures of the iodo complexes, **1** and **2** are shown in Figs. 1 and 2, respectively. Structural features and interatomic data, which are common to **1–4** will be summarized and discussed below and compared to previously reported structures of related organotitanium complexes. However, the Ti–I distances in **1**, 3.0541(6) Å, and **2**, (av) 2.76(2) Å, are quite different and warrant separate consideration. The latter value is normal and statistically identical to the corresponding distances reported for [Cp$_2$TiI$_2$], 2.7690(7) [28] and [Cp$_2^‡$TiI], 2.759(2), where Cp‡ = C$_5$Me$_4$H [29]. In contrast the Ti–I distance in **1** is about 0.15 Å longer than the previous "record" value observed in the Ti(II) complex, Cs[TiI$_3$], 2.8992(7) Å [30].
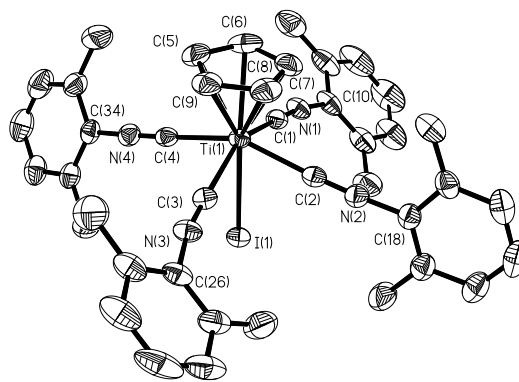

Fig. 1. Molecular structure of **1**. Thermal ellipsoids are set at the 50% probability level, with hydrogens omitted for clarity. Selected distances (Å) and angles (°): Ti–C(1) 2.137(3), Ti–C(2) 2.122(3), Ti–C(3) 2.144(3), Ti–C(4) 2.149(3), Ti–C(5) 2.427(3), Ti–C(6) 2.384(3), Ti–C(7) 2.326(3), Ti–C(8) 2.333(3), Ti–C(9) 2.391(3), Ti–I 3.0541(6), C(1)–N(1) 1.162(4), C(2)–N(2) 1.171(4), C(3)–N(3) 1.167(4), C(4)–N(4) 1.165(4), Cp(centroid)–Ti–I 179.6.
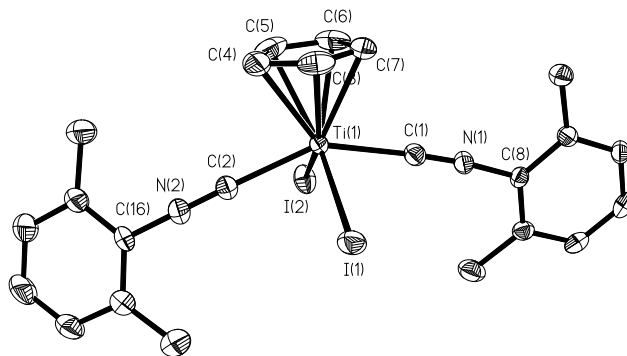

Fig. 2. Molecular structure of **2**. Thermal ellipsoids are set at the 50% probability level, with hydrogens omitted for clarity. Selected distances (Å) and angles (°): Ti–C(1) 2.180(3), Ti–C(2) 2.185(3), Ti–C(3) 2.360(3), Ti–C(4) 2.351(3), Ti–C(5) 2.334(3), Ti–C(6) 2.324, Ti–C(7) 2.344(3), Ti–I(1) 2.7454(5), Ti–I(2) 2.7699(6), C(1)–N(1) 1.155(3), C(2)–N(2) 1.153(4), I(1)–Ti–I(2) 115.19(2), av Cp(centroid)–Ti–C 106.4, av Cp(centroid)–Ti–I 122.7.

The latter has a K[NiCl$_3$] lattice-type [31] containing polymeric [Ti(μ-I)$_3$]$_n^{n-}$ units with bridging Ti–I bonds, which are longer than terminal Ti–I bonds in similar environments. For example, in [{TiI$_2$(PMe$_3$)$_2$}$_2$(μ-I)$_2$], which contains six-coordinate Ti(III), the average Ti–I (terminal) and Ti–I (bridging) distances are 2.69(1) and 2.86(2) Å, respectively [32]. It is also noteworthy that the Ti–I distance in **1** is about 0.4 Å longer than the sum of standard covalent radii of titanium and iodine, 2.65 Å [33].

Undoubtedly the anomalously long Ti–I distance in **1** is due to the presence of the four bulky xylylisocyanide groups, which, along with the η^5-Cp group, provide a very crowded environment about the eight-coordinate titanium center. Although **1** behaves as a non-electrolyte, for example, it is soluble in saturated and unsaturated hydrocarbons and its IR spectra are nearly identical in THF and toluene, available data do not rule out the possibility that the Ti–I interaction in **1** is predominantly electrostatic, in which

case it would contain a 16 electron cation, [CpTi(CN-Xyl)$_4$]$^+$, tightly ion-paired to I$^-$. In this regard, attempts to obtain bona fide salts containing this cation, such as [CpTi(CNXyl)$_4$][B(C$_6$F$_5$)$_4$] will be of interest in shedding more light on the constitution of **1**.

The molecular structures of **3** and **4** are extremely similar and the one for **3** is shown in Fig. 3. Both structures are similar to that of **1** and are fully compatible with the solution IR and NMR data previously discussed for these species. The Ti–Sn distances in [CpTi(CNXyl)$_4$E], E = SnPh$_3$, 2.9839(6), and SnMe$_3$, 2.949(1) Å, are longer than values for prior compounds containing Ti–Sn bonds, but not anomalously long, as in the case of the Ti–I bond in **1**. For example, Ti–Sn distances in previously known triorganotin–titanium complexes range from 2.83(2) Å in [Ti(CO)$_5$(SnPh$_3$)$_2$]$^{2-}$ [34] to 2.921(1) Å in [Ti(CO)$_6$(SnR$_3$)]$^-$, R = cyclohexyl, [35], where the latter is only 0.03 Å shorter than that observed in **4**. Also, in contrast to **1**, for which structural and spectroscopic data were inconclusive in determining the nature of the Ti–I bond, NMR data indicate that the corresponding Ti–Sn bonds in **3** and **4** are predominantly covalent in character. Thus, the ^{119}Sn NMR spectra for **3** and **4** show sharp resonances at −69.0 and −17.4 ppm, respectively, which are significantly downfield of the corresponding values for salts of the stannyl anions, e.g., [Ph$_3$SnLi], −110 ppm [36], and [Me$_3$SnLi], −183 ppm [37]. On this basis, there is no doubt that **3** and **4** contain long, but otherwise unexceptional, titanium–tin bonds.

Table 3 shows interatomic data for structural units that are common to **1–4**. The only Ti(III) complex in this study, **2**, has an overall four-legged "piano stool" geometry (Fig. 2) that is related to ones previously observed for [CpTi(CO)$_4$]$^-$ [22] and [CpTi(PMe$_3$)$_2$Cl$_2$] [8]. The Ti–Cp(centroid) value of 2.021(1) Å for **2** lies within the range of values reported for mono(cyclopentadienyl)titanium compounds, i.e., 2.01 Å in the Ti(IV) complex,

Table 3
Selected average interatomic distances (Å) and angles (°) for **1–4**

	1	**2**	**3**	**4**[c]
Ti–C(CNR)	2.14(1)	2.183(3)	2.115(4)	2.10(1)
Ti–C(Cp)	2.37(4)	2.34(2)	2.37(4)	2.36(2)
Ti–Cp(centroid)	2.047(1)	2.021(1)	2.048(1)	2.035(3)
C–N (CNR)[a]	1.166(4)	1.154(4)	1.170(3)	1.18(1)
Ti–C–N	176(2)	174(3)	173(1)	176(1)
C–N–C	172(4)	174(2)	173(2)	167(5)
cis-C–Ti–C[a]	86(3)	–	75(2)	72(4)
trans-C–Ti–C[a]	150.8(3)	147.0(1)	149.8(6)	142.4(8)
C–Ti–X[b]	75.5(3)	81(2)	75(2)	72(4)

[a] For ligated C of isocyanides.
[b] For ligated C of isocyanides, X = I (**1**, **2**) or Sn (**3**, **4**).
[c] Cp(centroid)–Ti–Sn 174.4°.

[CpTiCl$_3$] [38] to 2.049 Å in the Ti(0) complex [CpTi(CO)$_4$]$^-$ [22]. Corresponding Ti–Cp(centroid) distances for **1**, **3** and **4** are somewhat longer than that of **2**, likely owing to both the higher coordination number (eight versus seven) and lower oxidation state (II versus III) of the titanium atoms in the former complexes. Interatomic data for the isocyanide groups in **1–4** are qualitatively in accord with expectations based on IR and NMR (for **1**, **3**, and **4**) spectra discussed previously. Thus, the longest average Ti–C(isocyanide) and shortest ligated carbon C–N distances of 2.183(3) and 1.154(4) Å, respectively, were observed for **2** which had the highest IR ν(CN) value among these complexes, in accord with the Chatt–Dewar–Dunson model for back-bonding [24]. Also of interest is comparison of **2** with the d^0 Ti(IV) complex, [Ti(CNXyl)Cl$_4$]$_2$, which has corresponding Ti–C and C–N distances of 2.235(2) and 1.147(8) Å, respectively, and an IR ν(CN) absorption at 2200 cm^{-1} [11], a value well above that of **2** or free CNXyl (Table 2). If the isocyanide is functioning essentially as a pure donor ligand in the Ti(IV) complex, it is evident that some degree of Ti to π*(CNXyl) back-bonding is present in **2**, in accord with both spectral and structural data. Other data shown in Table 3 provide more details on the molecular structures of **1–4**, but these are largely unexceptional and will not be discussed herein.

4. Conclusion

Oxidation of [CpTi(CO)$_4$]$^-$ by I$_2$, Ph$_3$SnCl and Me$_3$SnCl in the presence of CNXyl afford new eight-coordinate Ti(II) complexes of the general formula [CpTi(CN-Xyl)$_4$E], E = I, SnPh$_3$, SnMe$_3$. Spectroscopic and X-ray structural studies indicate that discrete coordinated isocyanides are present in these unprecedented examples of titanium tetraisocyanide complexes. Extensions of this study to alkyl isocyanides, the heavier group 4 elements, and analogous oxidations of [Cp*Ti(CO)$_4$]$^-$ [16] in the presence of CNXyl will be of significance to determine whether related group 4 isocyanide complexes are possible. Use of Cp* instead of Cp in the titanium chemistry is of particular interest because of a prior study by Teuben and co-workers which showed that the reaction of the
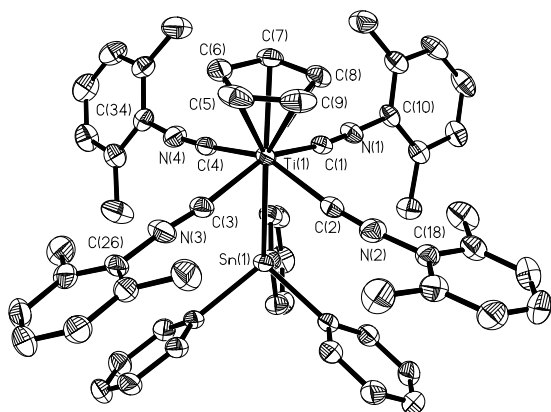

Fig. 3. Molecular structure of **3**. Thermal ellipsoids are set at the 50% probability level, with hydrogens omitted for clarity. Selected distances (Å) and angles (°): Ti–C(1) 2.121(2), Ti–C(2) 2.113(2), Ti–C(3) 2.113(2), Ti–C(4) 2.112(2), Ti–C(5) 2.426(2), Ti–C(6) 2.378(2), Ti–C(7) 2.327(2), Ti–C(8) 2.336(2), Ti–C(9) 2.393(2), Ti–Sn 2.9839(6), C(1)–N(1) 1.170(3), C(2)–N(2), 1.169(3), C(3)–N(3) 1.168(3), C(1)–N(4) 1.172(3), Cp(centroid)–Ti–Sn 176.8.

quite labile diene complex ([Cp*Ti(diene)Cl], diene = 2, 3-dimethyl-1,3-butadiene), with CNXyl afforded a reductively coupled isocyanide complex, [(Cp*TiCl)$_2$(µ-{N(Xyl)-C}$_2$)] [39], instead of one containing discrete isocyanide ligands, as in the case of **1**. In particular, did the reductive coupling of CNXyl in Teuben's system arise due to the presence of the diene, the Cp* group, both ligands simultaneously, or other factors?

Acknowledgements

Appendix A. Supplementary material

CCDC 661872, 661873, 661874 and 661875 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.047.

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