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Synthesis and characterization of titanium tetraisocyanide complexes, $[CpTi(CNXyl)_4E]$, 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_3SnCl, and Me_3SnCl in the presence of four equivalents of CNXyl, Xyl = 2,6-dimethylphenyl, affords unprecedented titanium tetraisocyanide complexes, $[CpTi(CNXyl)_4E]$, 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, $[CpTi(CNXyl)_2I_2]$, which was also characterized by X-ray crystallography.

Keywords: Titanium; Isocyanides; Tin; X-ray structure

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 $CpTi(CNR)_2Cl_2$, R = C_6H_{11} [7], Xyl [8]; $Cp_2Ti(CNXyl)Cl$ [9], $Cp_2M(CO)(CNR)$, M = Ti, Zr, Hf, R = *t*-Bu; M = Ti, Zr, R = Xyl [10a], $Cp_2M(CNXyl)_2$, M = Ti, Zr [10b], *cis*-$TiCl_4(CN\text{-}t\text{-}Bu)_2$ [11], $[TiCl_4(CNXyl)]_2$ [12], and *trans*-$[Ti(TPP)(CN\text{-}t\text{-}Bu)_2]$, TPP = *meso*-tetra-*p*-tolylporphyrin [13]. In this article, we describe the first titanium tetraisocyanide complexes, $[CpTi(CNXyl)_4E]$, 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]. $[Et_4N][CpTi(CO)_4]$ 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.

☆ Highly Reduced Organometallics, Part 64. For Part 63, see Ref. [1].

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2.2. Synthesis of [CpTi(CNXyl)$_4$I] (1)

Cold toluene (100 mL, −78 °C) was added to a solid mixture of [Et_4N][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), ν(CN): 2035 vs, 1996 w cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 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, C_6D_6, 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, *C*NXyl).

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)$_2$I$_2$] (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, ν(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)$_4$(SnPh$_3$)] (3)

A slurry of bright red [Et_4N][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 Ph_3SnCl (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), ν(CN): 2005 sh, 1977 vs cm^{-1}; IR (toluene), ν(CN): 2005 sh, 1976 vs cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 2.15 (s, 24 H, *o*-CH_3), 5.93 (s, with satellites, $J_{Sn-H} = 11.5$ Hz, 5H, C_5H_5), 6.7–6.9 (m, *m*- and *p*-H in $SnPh_3$, 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 $SnPh_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ 19.6 (s, *o*-*C*H_3), 95.5 (s, *C*$_5H_5$), 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 $SnPh_3$), 130.0 (s with satellites, $J_{Sn-C} = 14$ Hz, *p*-C in $SnPh_3$), 139.1 (s with satellites, $J_{Sn-C} = 30$ Hz, *m* or *o*-C in $SnPh_3$), 153.5 (s with satellites, $J_{Sn-C} = 48$ Hz, *i*-C in $SnPh_3$), 214.1 (s, *C*NXyl) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 25 °C, $SnMe_4$ 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)$_4$(SnMe$_3$)] (4)

By the same procedure employed to prepare **3**, toluene suspensions or solutions of [Et_4N][CpTi(CO)$_4$] (0.500 g, 1.4 mmol), Me_3SnCl (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), ν(CN): 2005 sh, 1969 vs cm^{-1}; IR (toluene), ν(CN): 2005 sh, 1969 vs cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.42 (s with satellites, $J_{Sn-H} = 29$ Hz, 9H, Sn*Me*$_3$) 2.37 (s, 24H, *o*-CH_3), 5.37 (s with satellites, $J_{Sn-H} = 11.4$ Hz, 5H, C_5*H*$_5$), 6.79 (m, 12 H, *m*- and *p*-*H*) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ −1.8 (s with satellites, $J_{Sn-C} = 45$ Hz, Sn*Me*$_3$), 19.7 (s, *o*-*C*H_3), 94.4 (s, *C*$_5H_5$), 126.8, 128.5, 130.3, 132.5 (s, phenyl CNXyl), 222.2 (s, *C*NXyl) ppm. ^{119}Sn{^{1}H} NMR (186 MHz, C_6D_6, 25 °C, $SnMe_4$ 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.