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The effect of titanium alkoxides in the synthesis of heterobimetallic complexes by titanocene(III) alkoxide-induced metal–metal bond cleavage of metal carbonyl dimers

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Abstract

A series of titanocene(III) alkoxides $L_2Ti(III)OR$ where L = Cp, R = Et(**1b**), ^{t}Bu(**1a**), 2,6-$Me_2C_6H_3$(**1c**), 2,6-^{t}Bu_2-4-Me–C_6H_2(**1d**), or L = Cp*, R = Me(**2e**), ^{t}Bu(**2a**), Ph(**2f**) was synthesized and subjected to reaction with $[CpM(CO)_3]_2$ [M = Mo, W], $[CpRu(CO)_2]_2$, and $Co_2(CO)_8$. The Ti(III) precursors **1a**, **1c**, **2a**, **2e**, and **2f** reacted with $[CpM(CO)_3]_2$ [M = Mo, W] to form heterobimetallic complexes $L_2Ti(OR)(\mu\text{-}OC)(CO)_2MCp$ [M = Mo, W], of which Ti and M are linked by an isocarbonyl bridge. Reactions of these Ti(III) complexes with $Co_2(CO)_8$ resulted in formation of Ti–Co_1 heterobimetallic complexes, $Cp^*_2Ti(O^tBu)(\mu\text{-}OC)Co(CO)_3$ from **2a**, **2e**, or **2f**, or Ti–Co_3 tetrametallic complexes, $Cp_2Ti(O^tBu)(\mu\text{-}OC)Co_3(CO)_9$ from **1a**, **1b**, or **1c**. The products were characterized by NMR, IR, and X-ray crystallography. Reaction mechanisms were proposed from these results, in particular, from steric/electronic effects of titanium alkoxides.

Keywords: Heterobimetallic complexes; Ti(III) alkoxides; Ti(III) complex; Dinuclear metal carbonyls

1. Introduction

Heterobimetallic complexes have received considerable attention from organometallic chemists in terms of potential cooperative effects by two metals in the complex leading to activation of organic molecules in homogeneous catalysis [1]. In typical examples, their catalysis has been investigated in hydroformylation [2–5], carbonylation [6], hydrogenation/isomerization [7], asymmetric synthesis [8–11], olefin methathesis [12], enol ester formation [13], and olefin polymerization [14]. In our previous papers, we have reported unique access to heterobimetallic complexes by reactions of titanocene *t*-butoxides, $Cp_2Ti(O^tBu)$ (Cp = η^5-C_5H_5; **1a**) and $Cp^*_2Ti(O^tBu)$ (Cp* = η^5-C_5Me_5; **2a**), with certain metal carbonyl dimers, $[CpM(CO)_3]_2$ [M = Mo, W], $[CpRu(CO)_2]_2$, and $Co_2(CO)_8$ [15]. Heterobimetallic complexes, in which two organometallic units are linked by an isocarbonyl bridge, $Cp_2Ti(O^tBu)(\mu\text{-}OC)$-$(CO)_2MCp$ [M = Mo (**3a-Mo**), W (**3a-W**)] and their Cp^*_2Ti-homologues [M = Mo (**4a-Mo**), W (**4a-W**)], were prepared from **1a** or **2a** with $[CpM(CO)_3]_2$, whereas a Ti–Ru complex having a Ti–Ru direct bond, $Cp_2Ti(O^tBu)Ru(CO)_2Cp$ (**5a**), was formed by photo-assisted reaction of **1a** with $[Cp_2Ru(CO)_2]_2$ [15a]. Two Ti–Co complexes, $Cp_2Ti(O^tBu)(\mu\text{-}OC)Co(CO)_3$ (**6a**) and $Cp^*_2Ti(O^tBu)(\mu\text{-}OC)Co(CO)_3$ (**7a**) were obtained by treatment of **1a** or **1b** with $Co_2(CO)_8$; **6a** readily reacted with $Co_2(CO)_8$ existing in the reaction medium to result in formation of $Cp_2Ti(O^tBu)(\mu\text{-}OC)Co_3(CO)_9$ (**8a**) [15b].

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A unique feature of these reactions is that the titanocene(III) *t*-butoxides are good reagents to cleave the metal–metal bond of metal carbonyl dimers, presumably via electron transfer from Ti(III) to the metal dimer, and the metal–metal bond cleavage leads to change of the oxidation state of titanium from III to IV and formation of heterobimetallic complexes. Although formation of anionic organometallic compounds is often seen in reactions of metal-carbonyl dimers with alkali metals or mercury by way of the metal–metal bond fission [16], it is rare that titanium(III) complexes act as reducing reagents. On the other hand, a number of heterobimetallic complexes which have an organotitanium moiety and a metal carbonyl fragment in the molecule have been synthesized and characterized; however, they are commonly synthesized from Ti(IV) precursors [1e,17–21]. In typical examples, treatment of Cp_2TiCl_2 with Li$[Co_3(CO)_{10}]$ gives $Cp_2Ti[(\mu\text{-}OC)Co_3(CO)_9]_2$ and LiCl [17], whereas reaction of Cp_2TiMe_2 with $CpMo(CO)_3H$ affords $Cp_2TiMe(\mu\text{-}OC)(CO)_2MoCp$ via methane elimination [18]. The closest example to the $Cp_2Ti(O^tBu)$-induced heterobimetalic formation is a brief comment from a research group of Moïse, in which reaction of Cp_2TiCl with $Co_2(CO)_8$ slowly produced $Cp_2TiCl(\mu\text{-}OC)Co_3(CO)_9$ [22]. We reexamined the reaction of Cp_2TiCl with $Co_2(CO)_8$ and compared its reaction rate with the reaction of **1a** with $Co_2(CO)_8$ under similar conditions; The reaction of Cp_2TiCl was approximately 150 times slower than that of **1a**. This clearly demonstrates the special reactivity of titanocene *t*-butoxides for the heterobimetallic formation, and prompted us to compare their reactivity with other titanocene(III) alkoxides. In this paper, we wish to report our studies and findings on this *t*-butoxide effect, in which a series of titanocene(III) alkoxides shown in Fig. 1 were synthesized and systematically reacted with metal carbonyl dimers as shown in Scheme 1. The results showed that two factors, steric circumstance around the titanium center and monomeric or dimeric structure of the titanocene(III) alkoxides, proved to be important.

2. Results and discussion

2.1. Preparation and characterization of titanocene(III) alkoxides

It is known that Cp_2TiCl exists as a chloro-bridged dimer, $Cp_2Ti(\mu\text{-}Cl)_2TiCp_2$ [23]. In sharp contrast, the molecular structure of Cp_2TiO^tBu (**1a**) revealed a monomeric structure as reported previously [15a]. In several other titanocene(III) alkoxides synthesized and characterized, whether the complex is monomeric or dimeric depends on the steric bulkiness of the ligands around the titanium center [24,25]. In fact, a titanocene(III) complex with a small alkoxide ligand such as Cp_2TiOEt (**1b**) is dimeric [24], whereas a sterically bulky titanium alkoxide like $Cp_2Ti[O(2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2)]$ (**1d**) exists as a monomer [25]. Since the bulky pentamethylcyclopentadienyl group prevents the dimerization of $Cp^*_2Ti(OR)$, **2a**, **2e**, and **2f** are monomeric regardless of the steric bulkiness of the alkoxide [26].

We are interested in a new complex, $Cp_2Ti[O(2,6\text{-}Me_2C_6H_3)]$ (**1c**) which has a phenoxide of medium size, and possibly has both monomeric and dimeric structures. Preparation of **1c** was made by treatment of Cp_2TiCl with $Li[O(2,6\text{-}Me_2C_6H_3)]$ in THF at room temperature for 12 h. Purification of the reaction mixture by sublimation gave **1c** as red violet crystals in 67% yield; these were paramagnetic and showed an ESR signal at $g = 1.98$ in a 1×10^{-5} M toluene solution. The molecular structure of **1c** was determined by crystallography, and the ORTEP view is illustrated in Fig. 2. Similar to the structure of **1a**, **1c** is monomeric, and two Cp and one alkoxide are bound to the titanium center. There are interesting differences in the Ti–O–C bond angle and the bond distances of the Ti–O and O–C bonds in **1c** from those in **1a**: the Ti–O–C angle of **1c** [144.2 (2)°] is smaller than that of **1a** [175 (1)°]. The Ti–O bond of **1c** [1.895 (2) Å] is longer than that of **1a** [1.810 (3) Å], whereas the O–C bond of **1c** [1.343 (4) Å] is shorter than that of **1a** [1.411 (5) Å]. The reason for these significant

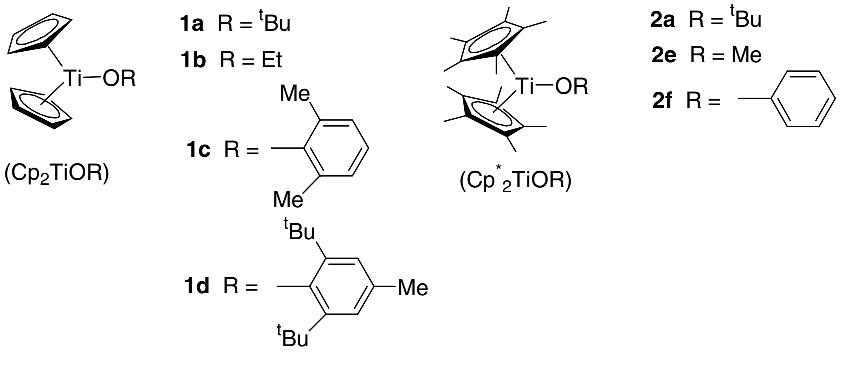

Fig. 1. Titanocene(III) alkoxides.