

Synthesis and Reactivity of Titanium/Cobalt Complexes with Ti-O-C-Co Bridges

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Reactions between titanium metallocene dicarbonyls and dicobalt octacarbonyl were investigated and found to give a variety of Ti/Co complexes depending on the reaction conditions. Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in nondonor solvents led to the formation of the known $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$ via a novel redox/cluster-building process. However, reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in tetrahydrofuran led to the formation of the ionic compound $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$. A mechanism in which isocarbonyl bridge formation is required to build the cluster compounds is proposed. Reaction between $\text{Cp}^*\text{Ti}(\text{CO})_2$ (Cp^* = pentamethylcyclopentadienyl) and $\text{Co}_2(\text{CO})_8$ yields the Ti(IV) isocarbonyl-bridged complex $\text{Cp}^*\text{Ti}[\text{OCCo}(\text{CO})_3]_2$ from toluene but gives the paramagnetic Ti(III) dimer $[\text{Cp}^*\text{TiOCCo}(\text{CO})_3]_2$ from hexane solution. Reactions of the above Ti/Co complexes with triphenylphosphine induce inner-sphere electron transfer from Co to Ti to take place via the isocarbonyl bridge.

Introduction

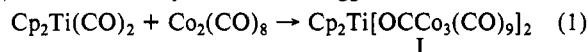
The study of reactions combining transition-metal group IV complexes (as well as lanthanide compounds) with metal carbonyl compounds later in the transition series has yielded a wealth of complexes with unusual structures.² In many cases, the dominant feature in the structures obtained is the presence of M-O-C-M' bridges, a bonding mode to which we will refer as isocarbonyl bridges. In previous reports we discussed the syntheses, molecular structures, and reaction chemistry of complexes containing both titanium and molybdenum that are held together by these isocarbonyl bridges.^{2a,j} Our synthetic route to these Ti/Mo compounds exemplifies the underlying concept of our synthetic strategy for obtaining early/late transition metal combinations: the reaction of a low-valent group IV metal complex with a reactive later transition-metal dimer.

We turned our attention to applying this strategy to the synthesis of early/late metal compounds utilizing cobalt carbonyl as the later transition-metal complex. This approach led both to the synthesis of some known compounds through novel redox routes and to the synthesis of some new and unusual Ti/Co complexes. This paper discusses the results of our synthetic program to make Ti/Co combination materials and some reactions that show the importance of electron transfer mediated by the isocarbonyl bridge in the chemistry of these Ti/Co complexes.

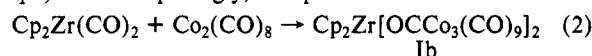
Results

We found that the general concept for forming early/late metal complexes that we applied in our Ti/Mo work, i.e. the reaction of a low-valent group IV metal complex with a reactive metal dimer, served us well in the case of the reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$. However, we found the chemistry to be quite complex and highly dependent on such factors as the nature of the solvent and the substitution on the cyclopentadienyl rings on the titanium. Each of these effects will be discussed in turn in the following subsections.

Reaction between $\text{Cp}_2\text{M}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Hexane. When $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ are combined in hexane, a black, crystalline material, I, precipitates from solution within minutes (eq 1). All of the analytical evidence suggests that I is the known³



bis[(oxymethylidene)tricobalt nonacarbonyl] complex $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$ (Figure 1). A similar complex is formed with $\text{Cp}_2\text{Zr}(\text{CO})_2$. Reaction between $\text{Cp}_2\text{Zr}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in hexane yields black crystals of the known³ $\text{Cp}_2\text{Zr}[\text{OCCo}_3(\text{CO})_9]_2$ (Ib, eq 2). Not surprisingly, the spectral features for this com-



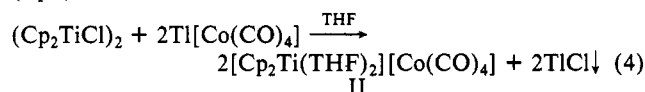
pound are identical with those for the titanium analogue.

Attempts were made to intercept the noncluster intermediate in this reaction by varying stoichiometry and reaction conditions in hydrocarbon solvents, but it appears that cluster formation is a very favorable process and only I was formed in these reactions. However, when reactions were carried out in the donor solvent, tetrahydrofuran (THF), the reaction takes a different course.

Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in THF. Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and 1 equiv of $\text{Co}_2(\text{CO})_8$ in THF leads to the formation of a material quite different from I (eq 3). In this $\text{Cp}_2\text{Ti}(\text{CO})_2 + \text{Co}_2(\text{CO})_8 \rightarrow [\text{Cp}_2\text{Ti}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$ (3)

II

case, the new complex, II, is blue-green and paramagnetic. The infrared spectrum of II in THF displays a single, broad absorption at 1890 cm^{-1} , a feature that is diagnostic of free $\text{Co}(\text{CO})_4^-$. Elemental analysis and spectral data led us to formulate II as the ionic complex $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$.⁴ Given this formulation, we also were able to come up with an alternate synthesis of II via the reaction between $(\text{Cp}_2\text{TiCl})_2$ and $\text{Co}(\text{CO})_4^-$ in THF (eq 4).



Reaction between $\text{Cp}^*\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$. A slow reaction takes place between $\text{Cp}^*\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in hexane leading to the precipitation of a green, insoluble Ti(III) complex, III (eq 5). (A more rapid reaction yielding the same product takes place $\text{Cp}^*\text{Ti}(\text{CO})_2 + \text{Co}_2(\text{CO})_8 \rightarrow [\text{Cp}^*\text{Ti}(\text{OC})\text{Co}(\text{CO})_3]_2 \downarrow$ (5)

III

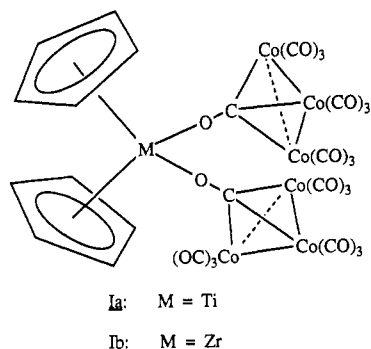
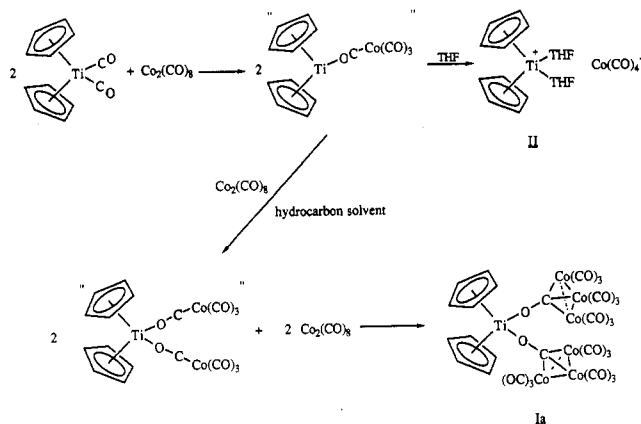
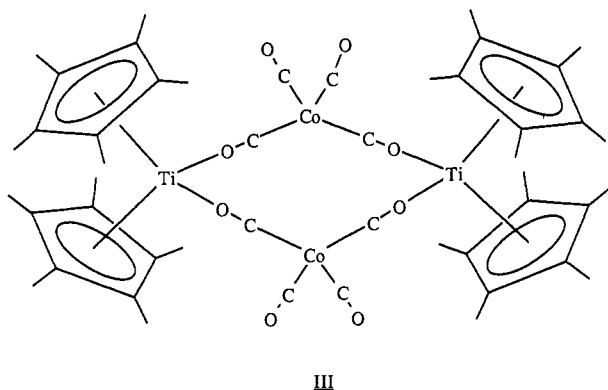
with the more reactive $\text{Cp}^*\text{Ti}(\text{H}_2\text{C}=\text{CH}_2)$ complex). The infrared spectrum of III, obtained from a mull, displayed bands at 2020, 1942, and 1835 cm^{-1} . When III is dissolved in toluene, an

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(2) (a) Gambarotta, S.; Stella, S.; Floriani, C.; Chiese-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 254 (Ti/Co). (b) Osborne, J. H.; Rheingold, A. L.; Troglor, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 6292 (V/V). (c) de Boer, E. J.; de With, J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1666 (Ti/Mo). (d) Boncella, J. M.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 809 (Yb/Co). (e) Pasynskii, A. A.; Eremenko, I. L.; Suleimanov, G. Z.; Nuriev, Yu. A.; Beletskaya, I. P.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *266*, 45 (La/Mo). (f) Sartain, W. J.; Selegue, J. P. *Organometallics* **1984**, *3*, 1922 (Zr/Mo). (g) Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A.; Zentz, S. *Organometallics* **1984**, *3*, 334 (Ti/Mo). (h) Martin, J.; Moise, C. *J. Organomet. Chem.* **1982**, *232*, C55 (V/Mo). (i) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360 (Zr/Mo). (j) Merola, J. S.; Gentile, R. A.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1982**, *1*, 1731 (Ti/Mo). (k) Berry, D. H.; Bercaw, J. E.; Viricitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4713 (Zr/Fe and Zr/Mo). (l) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985 (Yb/Co). (m) Hamilton, D. M.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255 (Ti/Mo).

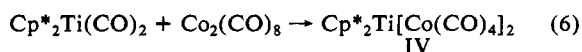
(3) Stutte, B.; Bätzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603.

(4) We also had occasion to carry out the single-crystal X-ray structure determination of II, which confirmed this assignment. This structure shows some unusual features in the $\text{Cp}_2\text{Ti}(\text{THF})_2^+$ fragment that are discussed in a separate paper: Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A. Submitted for publication in *Inorg. Chim. Acta*.

Figure 1. Structure of $\text{Cp}_2\text{M}[\text{OCCo}_3(\text{CO})_9]_2$.Figure 2. Pathways for $\text{Cp}_2\text{Ti}(\text{CO})_2/\text{Co}_2(\text{CO})_8$ reactions.Figure 3. Structure of $[\text{Cp}^*_2\text{TiOCCo}(\text{CO})_3]_2$.

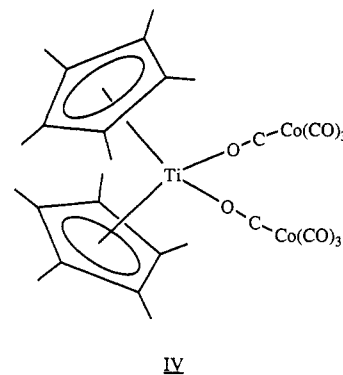
irreversible chemical reaction takes place to convert III to a new diamagnetic compound whose identification is discussed below. The elemental analysis of III suggested the formulation $\text{Cp}^*_2\text{Ti-Co}(\text{CO})_4$. The crystal structure of this material was rather poor due to poor crystal quality,⁵ but it was able to show connectivity and confirm our proposed structure as a dimer, $[\text{Cp}^*_2\text{TiOCCo}(\text{CO})_3]_2$, shown in Figure 3.

When $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ are allowed to react in *toluene* at room temperature, there is no precipitate formed and evaporation of the solution allows us to isolate a material, IV, whose elemental analysis and spectroscopic data would indicate it to be the Ti(IV) complex $\text{Cp}^*_2\text{Ti}[\text{Co}(\text{CO})_4]_2$ (eq 6). The



infrared spectrum of IV displays bands at 2050 and 1850 cm^{-1} , and the ^1H NMR spectrum indicates that it is diamagnetic with

(5) The crystal structure determination of $[\text{Cp}^*_2\text{TiOCCo}(\text{CO})_3]_2$ was attempted by Dr. C. S. Day of Crystallitics Corp., Lincoln, NE. The crystals were extremely thin, and a high-quality data set could not be obtained (lowest *R* value was 13%). However, the available results did show the connectivity for the molecule as shown in Figure 3.

Figure 4. Proposed structure of $\text{Cp}^*_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$.

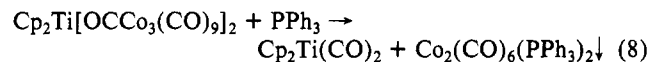
a single resonance at δ 1.67 due to the ring methyl groups. Infrared data would suggest that the Ti and Co are linked by an isocarbonyl bridge, leading us to postulate the structure shown in Figure 4. With IV in hand, we could go back and determine that the material we obtain when III is dissolved in toluene is actually IV.

Reactions of Ti/Co Complexes. Having isolated several unique mixed-metal complexes incorporating both titanium and cobalt, we turned our attention to the reaction chemistry of these complexes. Particularly, we were interested in taking advantage of the unique Ti-O-C-Co interactions that we found in exploring reactions of carbon monoxide. The most reduced carbon monoxide is found in the Ti/Co cluster compound $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$. Although this compound was reported previously, nothing was known about its reaction chemistry so we decided to examine this complex further. An attempt was made to react I with molecular hydrogen in the hopes of generating methanol or a metal alkoxide via hydrogenolysis of the Co-bridge CO bond. We found that heating I in toluene under 1 atm of hydrogen resulted in the formation of $\text{CpCo}(\text{CO})_2$ as the only isolable organometallic complex in addition to much insoluble material. GLC analysis of the reaction mixture failed to detect the presence of methanol or any methanol-derived products. We found that hydrogen is not necessary for this transformation, which occurs simply on heating I to refluxing toluene temperatures (eq 7). This transfer

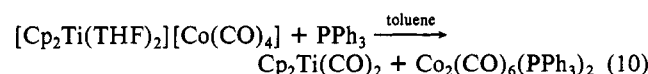
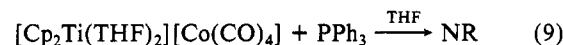


of cyclopentadienyl from titanium to cobalt is a fairly efficient process: we isolated a 64% yield of $\text{CpCo}(\text{CO})_2$ based on the number of moles of Cp available in the system.

We uncovered a remarkable reaction between I and triphenylphosphine (PPh_3). When I is allowed to react with PPh_3 in toluene, $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$ precipitates from solution leaving behind $\text{Cp}_2\text{Ti}(\text{CO})_2$ (eq 8). Moreover, there appears to be no



reaction between $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$ and PPh_3 in THF solution, but a rapid reaction occurs at room temperature in toluene solution to yield $\text{Cp}_2\text{Ti}(\text{CO})_2 + \text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$ (eq 9 and 10).



Discussion

We have been interested in redox reactions between low-valent group 4 metallocene complexes and other "later" transition-metal carbonyls and have reported on reactions between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $[\text{CpMo}(\text{CO})_2]_2$.^{2a,j} We have now extended our work to the reactions between $\text{Cp}_2\text{M}(\text{CO})_2$ compounds and $\text{Co}_2(\text{CO})_8$. We found that the products observed in these reactions were varied and highly dependent on the solvent in which the reaction takes place. In the case of both $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Cp}_2\text{Zr}(\text{CO})_2$, a facile

reaction occurs in hydrocarbon solvents (hexane, toluene) to yield the known $\text{Cp}_2\text{M}[\text{OCCo}(\text{CO})_3]_2$ compounds (Ia, M = Ti; Ib, M = Zr). These complexes were prepared previously by Schmid and co-workers via the nucleophilic displacement of chloride in the reaction between Cp_2MCl_2 and the preformed cluster nucleophile $\text{Li}[\text{Co}_3(\text{CO})_{10}]$.³ In our work, starting from $\text{Cp}_2\text{M}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$, the cluster complexes are formed via redox reaction between Ti and Co to form isocarbonyl-bridged compounds followed by a cluster-building process. The cluster formation is rapid and essentially quantitative. Attempts to intercept the reaction in the early stages and isolate noncluster compounds by using low Co/Ti ratios failed: I and unreacted $\text{Cp}_2\text{Ti}(\text{CO})_2$ were the only products observed from such reactions.

Our ability to intercept a noncluster compound only by carrying out the reaction in THF indicates the importance of the Ti—O—C—Co interaction for cluster building. Our current belief in how these complexes are formed is depicted in Figure 2.⁶ Possibly, the first step is a reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ to form the Ti(III) species $\text{Cp}_2\text{Ti}(\text{OC})\text{Co}(\text{CO})_3$. In nondonor solvents, this material reacts rapidly with additional $\text{Co}_2(\text{CO})_8$ to form $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$. While we did not observe these complexes for the Cp_2Ti reactions, credence for their possible intermediacy comes from our isolation of analogous compounds in the Cp^*Ti system (see below) and by analogy to the Ti/Mo system.^{2a,j} Structural data for $\text{M—O—C—M}'$ complexes would indicate that Ti—O—C—M bonds are polarized toward the canonical form $\text{Ti—O—C}\equiv\text{M}'$ with a formal metal-carbon triple bond. $\text{Co}_2(\text{CO})_8$ is known to react with carbon-carbon and carbon-metal triple bonds to form carbon-cobalt clusters. So, in the last steps of the reaction, $\text{Co}_2(\text{CO})_8$ reacts with what may be thought of as a cobalt-carbon triple bond in the Ti—O—C \equiv Co linkage resulting in the formation of the observed cluster compounds.⁸ When the reaction is carried out in THF solvent, the two metallic fragments in $\text{Cp}_2\text{Ti}(\text{OC})\text{Co}(\text{CO})_3$ are separated into discrete ions, with THF coordinating to titanium. This ion separation and THF coordination seems to have two effects. First, it appears that THF coordination stabilizes the Ti(III) state, so there is no further oxidation by $\text{Co}_2(\text{CO})_8$ to form a Ti(IV) complex. Second, since there is no longer an isocarbonyl bridge, there is no further reaction of the $\text{Co}(\text{CO})_4^-$ fragment with $\text{Co}_2(\text{CO})_8$ to form the clusters.

Our results are in many ways similar to those of Fachinetti in his studies involving the synthesis of $\text{M—O—CCo}(\text{CO})_3$ complexes where M is an alkali-metal ion.⁹ Only in the poorly coordinating ether solvent di-*n*-butyl ether did Fachinetti observe reaction between $\text{LiCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$ to form $\text{Li—O—CCo}(\text{CO})_3$. The presence of even 3% THF in his mixtures prevented the cluster formation from taking place. In addition, no cluster formation took place when M = Na, a poorer Lewis acid. In our case, the Ti cation is needed to coordinate to one CO of $\text{Co}(\text{CO})_4^-$ to polarize the CO bond for the cluster-building process, a role taken up by the Li^+ in Fachinetti's work.

Although II exists as discrete ions in THF solution, its infrared spectrum in toluene shows a new feature at 1750 cm^{-1} . We take this as an indication that an equilibrium is obtained in the non-donor solvent and that $\text{Cp}_2\text{Ti}(\text{THF})(\text{OC})\text{Co}(\text{CO})_3$, the cobalt

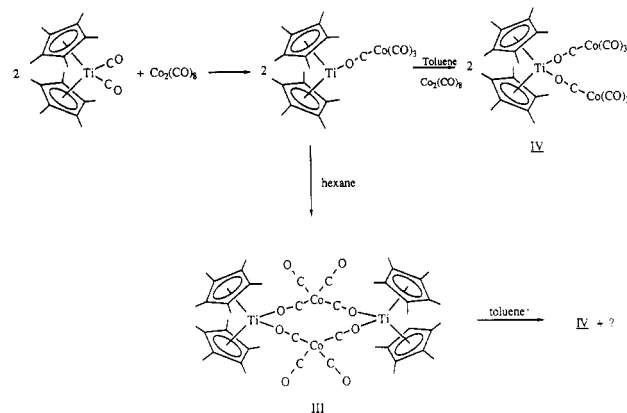


Figure 5. Pathways for $\text{Cp}^*_2\text{Ti}(\text{CO})_2/\text{Co}_2(\text{CO})_8$ reactions.

analogue to a previously isolated molybdenum complex, is the species in toluene solutions (eq 11). Addition of THF to such $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]^- \rightleftharpoons \text{Cp}_2\text{Ti}(\text{THF})\text{OCCo}(\text{CO})_3 + \text{THF}$ (11)

a toluene solution drives the equilibrium back to the ionic species resulting in the precipitation of II from solution. Attempts to isolate the isocarbonyl-bridged material were unsuccessful. The nature of the solution species and whether or not the Ti—O—C—Co interaction is occurring will be important when we later discuss the reactions of II with PPh_3 .

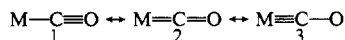
We also examined the reactions of pentamethylcyclopentadienyl (Cp^*) complexes of Ti. It is generally observed that substitution of Cp^* for Cp results in the stabilization of complexes of higher oxidation states and produces compounds with increased solubility. The formation of III in the reaction between $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ is quite surprising in light of our previous results in the molybdenum system. While $\text{Cp}_2\text{Ti}(\text{CO})_2$ reacted with $\text{CpMo}(\text{CO})_2\equiv\text{Mo}(\text{CO})_2\text{Cp}$ to yield a Ti(III) complex, the reaction of $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ with the same molybdenum dimer resulted in the formation of a Ti(IV) complex,^{2i,10} a result not unexpected in light of the increased electron density on a Cp^*_2Ti center and the stabilization of the higher oxidation state. Moreover, results described above show that even the unsubstituted $\text{Cp}_2\text{Ti}(\text{CO})_2$ with $\text{Co}_2(\text{CO})_8$ yields a Ti(IV) product, again not a surprising result, since $\text{Co}_2(\text{CO})_8$ is a better oxidizing agent than $\text{CpMo}(\text{CO})_2\equiv\text{Mo}(\text{CO})_2\text{Cp}$ (or, more correctly, $\text{CpMo}(\text{CO})_3-\text{Mo}(\text{CO})_3\text{Cp}$). Therefore, we would predict that reaction between $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ would yield a Ti(IV) product, but that is not what we observe from hexane solution. Apparently, III is the product from the first steps in the reaction that is trapped only because of its complete insolubility in hexane solution. If the reaction is carried out in toluene, all species remain soluble, and the observed product is the expected Ti(IV) compound, IV. Further, when III is dissolved in toluene, it is unstable with respect to disproportionation, forming IV and, presumably, a Ti(II) compound that we have not isolated. These transformations are summarized in Figure 5.

The isolation of $[\text{Cp}^*_2\text{Ti}(\text{OC})\text{Co}(\text{CO})_3]$ and $\text{Cp}^*_2\text{Ti}[\text{Co}(\text{CO})_4]_2$ supports the speculation that analogous (but more reactive) compounds may be involved in the Cp_2Ti system. We have seen no evidence for Co_3 cluster formation in the Cp^* system, a point that we ascribe to unfavorable steric constraints. An examination of a model of III shows clearly that the ring methyl groups protrude over the Ti—O—C bonds, blocking any further reaction at those sites. From examination of a model of $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$ it is obvious that the clusters already impose severe steric problems in the unsubstituted compound, so it is unlikely that clusters will form in the methyl-substituted compounds.

The chemistry of the various Ti/Co compounds provides some intriguing information on the reaction pathways available to this class of compounds. Our inability to induce the hydrogenolysis

(6) A suggestion that similar reactions may take place with Cp_2V was made in: Martin, J.; Moise, C. J. *Organomet. Chem.* **1982**, 232, C55.

(7) For all of the structurally characterized isocarbonyl-bridged complexes, there is a significant lengthening of the C—O bond in the bridge compared to those normal terminal CO's along with a significant decrease in the M—C bond length. This suggests that for system of tautomers



form 3 makes a significant contribution to the overall bonding picture for the isocarbonyl.²

(8) This is also similar in many respects to a previous discussion by Nicholas where he envisions H^+ coordinating to CO to form a hydroxycarbyne, which initiates a cluster-building process: Nicholas, K. M. *Organometallics* **1982**, 1, 1713.

(9) (a) Fachinetti, G. J. *Chem. Soc., Chem. Commun.* **1979**, 396. (b) Adams, H. N.; Fachinetti, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1980**, 19, 404.

(10) The analogous Zr complex was reported by Bercaw and co-workers from the dinitrogen complex of Cp^*_2Zr and $[\text{CpMo}(\text{CO})_3]_2$.^{1k}

of the quadruply bridging CO in I was disappointing, with the only observable reaction being the Cp transfer depicted in eq 7. We know nothing of the possible mechanism for the transformation shown in eq 7 nor do we know the identity of other products from this reaction, but such a Cp transfer has been observed before in the reaction between Cp_2TiCl_2 and TiCl_4 , which yields CpTiCl_3 .¹¹

While $\text{Co}_3(\text{CO})_{10}^-$ clusters are unusual ligands, they bear a similarity to alkoxides in terms of their bonding to Ti: the Ti-O bonds in I are short, indicative of strong Ti-O bonds.¹² In the reaction with PPh_3 , the oxidation state of the titanium in I has been reduced from +4 to +2. That this occurs simply on the addition of PPh_3 suggests that the complex is delicately balanced on the +2/+4 edge. We speculate that addition of PPh_3 initially results in substitution of PPh_3 for a CO on the $\text{Co}_3(\text{CO})_9$ cluster. This causes the cluster unit to become more electron rich, and an internal redox reaction then takes place with the electrons moving from the cluster over the Ti-O-C-Co₃ bridge. That we are able to effect Ti-O bond cleavage in this system is unusual, given the oxophilic nature of titanium. To our knowledge, this is the first example of reversal of Ti-O bond formation in a group IV metal system and of such a mild reduction of Ti from +4 to +2.

The accessibility of internal redox reaction pathways for these Ti/Co complexes is also manifested in reactions of the noncluster complex II. The free tetracarbonylcobaltate anion, $\text{Co}(\text{CO})_4^-$, is inert with respect to substitution by ligands such as PPh_3 under mild conditions.¹³ Thus, there is no reaction between $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4^-]$ and PPh_3 in THF solution, where the anion exists as free $\text{Co}(\text{CO})_4^-$. However, when the same reaction is carried out in toluene where infrared evidence indicates a Ti-O-C-Co bond formed, there is a rapid transformation that leads to the production of $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$. We presume that the first step in the reaction is the substitution of PPh_3 for a CO ligand on the cobalt. That this reaction takes place at all indicates a strong electronic communication between the Cp_2Ti^+ moiety and the $\text{Co}(\text{CO})_4^-$ fragment via the isocarbonyl bridge. The Ti-O-C-Co bridge is not merely acting as a "tight ion pair", but there is also further electronic interaction between the Ti and Co. Trogler et al. have discussed the bonding that takes place in $\text{Cp}^*_2\text{V}(\text{OC})\text{V}(\text{CO})_5$ and, while their results show that the primary interaction is electrostatic, calculations suggest that a π -donation from $\text{V}(\text{CO})_6^-$ to Cp^*_2V^+ through the isocarbonyl bridge results in a net π -bond interaction.^{2b} Such an interaction may account for the higher reactivity of $\text{Co}(\text{CO})_4^-$ bound to Cp_2Ti^+ : some degree of π -donation to Ti results in a lowering of electron density on Co, and its substitution behavior is more like that of Co^0 . An alternate explanation could well be that the complex responsible for this reaction actually contains a Ti-Co bond.¹⁴ However, on the basis of our experience with Ti/Mo and Ti/Co compounds, we believe that Ti-Co bond formation in these metallocene systems is unlikely.

The substitution of PPh_3 for one CO on Co results in an electron-rich Co center, and an electron transfers through the isocarbonyl bridge from Co to Ti. The Ti(II) species then reacts with the CO liberated in the substitution reaction to form the observed $\text{Cp}_2\text{Ti}(\text{CO})_2$, and the $\text{Co}(\text{CO})_3(\text{PPh}_3)$ dimerizes to $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$. These reactions appear to be further examples of inner-sphere electron-transfer reactions occurring via isocarbonyl bridges, a phenomenon first reported by Trogler, Basolo, and co-workers.¹⁵

Conclusions

We have seen that reactions between low-valent titanium and zirconium dicyclopentadienyl compounds and dicobalt octacarbonyl are quite complex and are influenced by the substitution on the cyclopentadienyl rings and on the solvent used for the reaction. As has been observed previously with these metal carbonyl/group IV transition-metal combinations, formation of isocarbonyl bridges is an important contributor to the chemistry. In the case of sterically unhindered systems, once isocarbonyl bridge formation takes place, a cluster-building process can then occur to yield $\text{M-O-C-Co}_3(\text{CO})_9$ complexes. For sterically hindered systems, the cluster building cannot take place and stops at $\text{M-O-C-Co}(\text{CO})_3$ species. We have also established that inner-sphere electron transfer through M-O-C-M' bridges appears to be an important feature of these isocarbonyl compounds. This indicates that the observation of such inner-sphere electron transfer first made by Basolo, Trogler, and co-workers for a vanadium carbonyl system¹⁵ may be a general feature for such isocarbonyl-bridged complexes.

Experimental Section

All experiments were carried out under an atmosphere of nitrogen either in a Vacuum-Atmospheres glovebox or in standard Schlenkware. The following materials were all purchased from Strem Chemicals: Cp_2TiCl_2 , $\text{Cp}^*_2\text{TiCl}_2$, Cp^*H , $\text{Co}_2(\text{CO})_8$, Ti, and Cp_2ZrCl_2 . The following materials were synthesized by using literature procedures: $(\text{Cp}_2\text{TiCl})_2$,¹⁶ $\text{Cp}_2\text{Ti}(\text{CO})_2$,¹⁷ $\text{Cp}_2\text{Zr}(\text{CO})_2$,¹⁸ $\text{Cp}^*_2\text{Ti}(\text{H}_2\text{C}=\text{CH}_2)$,¹⁹ and $\text{Ti}[\text{Co}(\text{CO})_4]$.²⁰ Tetrahydrofuran was dried over sodium/benzophenone and distilled before use. All other solvents were of reagent grade and were thoroughly deoxygenated before use. ¹H NMR spectra were obtained on a Varian EM360 NMR spectrometer, and infrared spectra were recorded on a Perkin-Elmer 783 infrared spectrophotometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Hexane (6/1 Co/Ti). $\text{Cp}_2\text{Ti}(\text{CO})_2$, 1.0 g (4.26 mmol), was dissolved in 125 mL of *n*-hexane and the solution filtered to remove any insoluble impurities. Also, 4.38 g (12.8 mmol) of $\text{Co}_2(\text{CO})_8$ was dissolved in 125 mL of hexane and the solution filtered. The two solutions were combined and stirred magnetically for 10 min, and the resulting solution was allowed to stand undisturbed. Black crystals began to form within minutes, and the reaction was allowed to proceed overnight. The black, crystalline product was filtered out, washed with hexane, and dried to yield 4.2 g (3.85 mmol, 90% yield) of $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$, identified on the basis of the following information. Anal. Found (calcd for $\text{C}_{30}\text{H}_{10}\text{TiCo}_6\text{O}_{20}$): C, 31.99 (33.0); H, 1.10 (0.92); Ti, 5.01 (4.39); Co, 31.99 (32.38). IR (toluene): terminal ν_{CO} = 2100 (m), 2050 (s), 2040 (s), 2035 (s), 2000 cm^{-1} (m); bridging ν_{CO} = 1375, 1333 cm^{-1} . NMR (C_6D_6): δ 6.17 (s, Cp protons) ppm. These analytical data are consistent with those of the previous report of this compound.³

Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Hexane (1/1 Co/Ti). $\text{Cp}_2\text{Ti}(\text{CO})_2$, 0.5 g (2.14 mmol), was dissolved in 50 mL of hexane and the solution filtered. To this solution was added a filtered hexane solution containing 0.37 g (1.07 mmol) of $\text{Co}_2(\text{CO})_8$. From this reaction mixture, 0.12 g (0.19 mmol) of $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$ precipitated. This represents a 54% yield based on cobalt, the limiting reagent. The infrared spectrum of the filtrate showed weak bands due to $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$ and unreacted $\text{Cp}_2\text{Ti}(\text{CO})_2$, with no bands present for $\text{Co}_2(\text{CO})_8$.

Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Toluene. In a series of experiments, $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ were allowed to react in toluene with monitoring by infrared spectroscopy. In cases where a deficiency of $\text{Co}_2(\text{CO})_8$ was used (Co/Ti < 6), only infrared bands for $\text{Cp}_2\text{Ti}[\text{OCCo}_3(\text{CO})_9]_2$ and unreacted $\text{Cp}_2\text{Ti}(\text{CO})_2$ were present.

Reaction between $\text{Cp}_2\text{Zr}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Hexane. $\text{Cp}_2\text{Zr}(\text{CO})_2$, 0.5 g (1.8 mmol), and $\text{Co}_2(\text{CO})_8$, 0.92 g (2.7 mmol), were combined in 50 mL of hexane, and the solution was stirred at room temperature. After about 2 h, only a small amount of precipitate had formed. Evap-

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oration of some of the hexane and cooling led to the precipitation of purple crystals. These were filtered to yield 0.7 g (0.57 mmol, 63% yield based on Co) of $\text{Cp}_2\text{Zr}[\text{OCCo}(\text{CO})_3]_2$ identified by comparison of its NMR and IR spectra with those previously published.³

Reaction between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in THF. $\text{Cp}_2\text{Ti}(\text{CO})_2$, 0.50 g (2.14 mmol), was dissolved in 50 mL of THF. $\text{Co}_2(\text{CO})_8$, 0.36 g (1.07 mmol), was added as a solid to the above solution, and gas evolution was noted by foaming of the reaction mixture. Infrared analysis of the reaction mixture indicated, in addition to bands due to $\text{Co}_2(\text{CO})_8$, a very strong absorption at 1890 cm^{-1} , indicative of the $\text{Co}(\text{CO})_4^-$ species. The solution was stirred at room temperature for 3 h. Pentane was slowly added to the reaction mixture to precipitate 0.65 g (1.32 mmol, 62% yield) of a blue-green crystalline solid identified as $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$ on the basis of the following information. IR (THF solution): 1890 cm^{-1} . IR (toluene solution): 2010, 1915, 1750 cm^{-1} . Due to the lability of the THF molecules, a satisfactory elemental analysis could not be obtained. However, the single-crystal X-ray structure did confirm the composition.⁴

Reaction between $(\text{Cp}_2\text{TiCl})_2$ and $\text{TiCo}(\text{CO})_4$. $(\text{Cp}_2\text{TiCl})_2$, 1.0 g (2.34 mmol), was dissolved in 75 mL of THF, and the $\text{TiCo}(\text{CO})_4$ (1.76 g, 4.68 mmol) was added as a solid. The reaction mixture was stirred at room temperature for 18 h, at the end of which time there was a white precipitate of TiCl_4 . The mixture was filtered, and the blue-green filtrate was diluted with pentane to precipitate 1.5 g (3.03 mmol, 65%) of a blue-green crystalline solid identical in all respects with the material synthesized from $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ described above.

Reaction between $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Hexane. $\text{Cp}^*_2\text{Ti}(\text{CO})_2$, 0.5 g (1.34 mmol), was dissolved in 50 mL of hexane and the solution filtered to remove any insoluble material. Likewise, $\text{Co}_2(\text{CO})_8$, 0.46 g (1.34 mmol) was dissolved in 50 mL of hexane and the solution filtered. The two solutions were combined, stirred, and then allowed to stand undisturbed. After about 1 h, crystal formation was evident. After 18 h, the mixture was filtered and 0.31 g of a green, crystalline solid was isolated. After 48 h, an additional 0.24 g of product was isolated. The total yield was 0.55 g (1.12 mmol, 83% yield) of $[\text{Cp}^*_2\text{TiOCCo}(\text{CO})_3]_2$, identified on the basis of the following data. Anal. Found (calcd for $\text{C}_{24}\text{H}_{30}\text{CoO}_4\text{Ti}$): C, 58.3 (58.9); H, 5.81 (6.19); Ti, 9.97 (9.79); Co, 11.87 (12.04). IR (ν_{CO} , Nujol mull): 2020 (m), 1942 (s), $1835\text{ (m cm}^{-1})$. An attempt was made to obtain the X-ray crystal structure of this complex.⁵ Due to poor crystal quality the structure was not able to be refined completely, but the dimeric nature of this complex was confirmed.

Reaction between $\text{Cp}^*_2\text{Ti}(\text{H}_2\text{C}=\text{CH}_2)$ and $\text{Co}_2(\text{CO})_8$ in Hexane. $\text{Cp}^*_2\text{Ti}(\text{H}_2\text{C}=\text{CH}_2)$, 0.20 g (0.59 mmol), was dissolved in 50 mL of

hexane. $\text{Co}_2(\text{CO})_8$, 0.20 g (0.58 mmol), was added to the solution. A green precipitate formed immediately. The precipitate was filtered out, washed with hexane, and dried to yield 0.22 g (0.45 mmol, 78% yield) of $[\text{Cp}^*_2\text{TiOCCo}(\text{CO})_3]_2$, identical with the material formed by using $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ as starting material.

Reaction between $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ in Toluene. $\text{Cp}^*_2\text{Ti}(\text{CO})_2$, 0.5 g (1.34 mmol), was dissolved in 50 mL of toluene. To the above solution was added, 0.23 g (0.67 mmol) of $\text{Co}_2(\text{CO})_8$ as a solid. An infrared spectrum of the reaction solution at this point indicated that all of the $\text{Co}_2(\text{CO})_8$ had been consumed with a significant portion of the $\text{Cp}^*_2\text{Ti}(\text{CO})_2$ remaining, so an additional 0.23 g of $\text{Co}_2(\text{CO})_8$ was added. The reaction mixture was stirred for 18 h. The solvent was removed under reduced pressure, and the residue was washed with hexane, leaving 0.66 g (1.0 mmol, 75% yield) of $\text{Cp}^*_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$, identified on the basis of the following information. Anal. Found (calcd for $\text{C}_{28}\text{H}_{30}\text{Co}_2\text{O}_8\text{Ti}$): C, 51.33 (50.92); H, 4.41 (4.59); Co, 17.40 (17.85); Ti, 7.71 (7.25). IR (ν_{CO} , Nujol mull): 2050 (s), $1850\text{ (m cm}^{-1})$. $^1\text{H NMR}$ (C_6D_6): δ 1.67 ppm.

Thermolysis of $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$. $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$, 1.0 g (0.9 mmol), was dissolved in 50 mL of xylene, and the solution was heated to reflux for 4 h. The reaction mixture was cooled, and the xylene was removed at reduced pressure. The residue was extracted with hexane, and the hexane was removed to yield 0.21 g of a dark red oil, identified as $\text{CpCo}(\text{CO})_2$ by comparison of its IR and NMR spectra with those of an authentic sample. Based on the number of available Cp rings in the system, this represents a 64% yield of $\text{CpCo}(\text{CO})_2$. The hexane-insoluble material was not characterized.

Reaction between $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$ and PPh_3 in Toluene. $[\text{Cp}_2\text{Ti}(\text{THF})_2][\text{Co}(\text{CO})_4]$, 0.5 g (1.01 mmol), was dissolved in 60 mL of toluene. To this solution was added 0.34 g (1.34 mmol) of PPh_3 as a solid. The solution immediately changed from green to red-brown, and after 10 min, a red-brown precipitate had formed. The mixture was allowed to stir for 3 h, and then it was filtered to collect 0.26 g (0.32 mmol, 64% yield based on Co) of $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$, identified by comparison of its IR spectrum with that of authentic material. An infrared spectrum of the filtrate showed only absorptions due to $\text{Cp}_2\text{Ti}(\text{CO})_2$.

Reaction between $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$ and PPh_3 . $\text{Cp}_2\text{Ti}[\text{OCCo}(\text{CO})_3]_2$, 0.30 g (0.33 mmol), was dissolved in 50 mL of toluene. To this solution was added, 0.5 g (1.9 mmol) of PPh_3 as a solid. After a few minutes, a red-brown solid precipitated from solution. This solid was collected, washed with hexane, and dried to yield 0.65 g (0.8 mmol, 81% yield based on Co) of $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$. Infrared analysis of the solution showed only the presence of $\text{Cp}_2\text{Ti}(\text{CO})_2$.

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Multinuclear NMR Studies of Molybdenum and Tungsten Carbonyl Isocyanide Complexes¹

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$\text{M}(\text{CO})_{6-n}(\text{CNR})_n$ ($n = 0-6$) complexes ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = 2,6\text{-dimethylphenyl}, \text{tert-butyl}, \text{cyclohexyl}, \text{isopropyl}$) have been synthesized. Depending on the R group of the isocyanide ligand, four or six carbonyl groups in $\text{M}(\text{CO})_6$ can be replaced. The NMR properties of the atoms in these complexes have been studied. The metal centers, observed by ^{95}Mo or ^{183}W NMR, show increased deshielding with the substitution of carbonyl ligands by isocyanide ligands. ^{95}Mo NMR serves as an excellent tool for the identification of mixtures of these compounds and was useful to monitor the reactions. The nitrogen in the isocyanide ligand, observed by ^{14}N NMR spectroscopy, gets more deshielded when the isocyanide is coordinated to the metal center, but with further substitution, the nitrogen becomes more shielded again. The ^{14}N chemical shift of an isocyanide ligand trans to a carbonyl ligand differs slightly from the chemical shift of an isocyanide ligand trans to another isocyanide ligand in the tetrasubstituted complex. The ^{13}C NMR signal of the CNR carbon becomes more deshielded with an increasing number of isocyanides present in the complex. CNR carbons trans to carbonyl groups are more shielded than CNR carbons trans to isocyanides. With the successive substitution of carbonyl groups by isocyanides, the electronic absorption bands in the UV-vis region shift toward longer wavelengths; i.e., the color of the compounds changes from white to orange-red.

Introduction

A number of papers have been published containing ^{13}C ,^{2,3} ^{14}N ,^{4,5} or ^{17}O ⁵ NMR data on molybdenum(0) and tungsten(0)

carbonyl isocyanide complexes. The data available so far are limited to mono- to trisubstituted complexes, and no NMR data for the metal nuclei in these complexes have been published.

Albers and co-workers^{6,7} discovered a convenient route to

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