A Novel Unsaturated (Alkyne)titanium(II) Complex (η^5-C_5H_5)(η^5-C_5Me_5)Ti(Ph–C≡C–Ph) and its Coupling Reaction with Carbon Dioxide

Bernard Demerseman, Roger Mahé, and Pierre H. Dixneuf

Laboratoire de Chimie de Coordination Organique (ERA CNRS 477), Université de Rennes, 35042 Rennes Cédex, France

The titanium derivatives CpCp'TiX_2 (Cp = η^5-C_5H_5; Cp' = η^5-C_5Me_5; X = Me, Ph, or CO) have been synthesized and the reaction of CpCp'Ti$(CO)_2$ with diphenylacetylene and trimethylphosphine affords the unsaturated (alkyne)titanium(II) complex CpCp'Ti(C_2Ph_2) which readily adds carbon dioxide to give the metallacyclic compound CpCp'Ti–C(Ph)=C(Ph)-C(=O)O *via* carbon-carbon bond formation.

Unsaturated titanium(II) intermediates are expected to promote the reduction of substrates[1,2] and unstable species arising from the precursor $Cp_2Ti(CO)_2$ (Cp = η^5-C_5H_5) have been shown to be useful for the reduction of carbon dioxide[2] or alkynes,[3] and the use of C_5Me_5 groups in Cp'_2TiCl_2 (Cp' = η^5-C_5Me_5) has allowed the isolation of highly reactive species such as [Cp'_2Ti],[1] $(Cp'_2Ti)_2N_2$,[1] or $Cp'_2Ti(C_2H_4)$.[4] In the course of our studies on the activation of alkynes[3] we have studied the mixed-ring CpCp'TiX_2 systems and we now report the isolation and characterisation of the formally 16 electron species CpCp'Ti(Ph–C≡C–Ph) and its reactivity towards carbon dioxide.

In an attempt to find a convenient, large scale route to the precursor CpCp'TiCl_2,[5] obtained previously from Cp'TiCl_3, the reaction of Cp'Li with CpTiCl_2 in tetrahydrofuran (THF) at room temperature followed by reoxidation with HCl and extraction with $CHCl_3$ led us to isolate purple needles of (**1**)† in 50% yield.

The displacement of the chloride groups of (**1**) was easily performed by treatment with PhLi or MeLi in diethyl ether whereupon the orange-red complex (**2**)† (60%) and the

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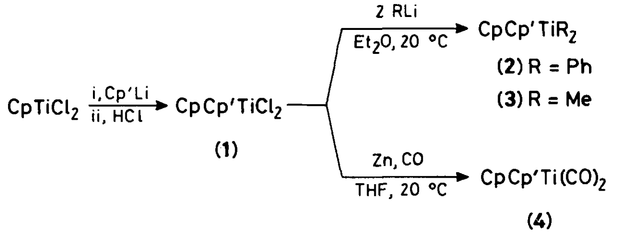
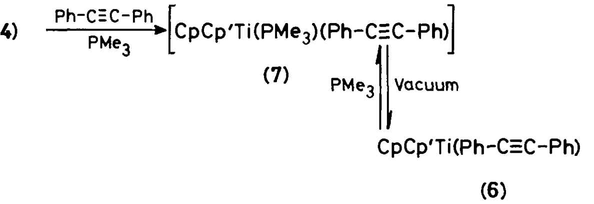
† Satisfactory elemental analyses have been obtained.





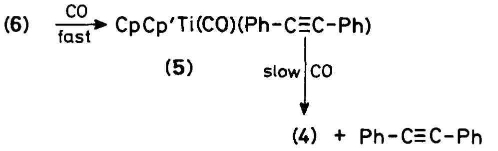
(1)

orange compound (3)† (90%) were obtained respectively [^{1}H n.m.r. (CD_2Cl_2) δ (2) 6.83 (Ph), 5.89 (Cp), 1.73 (Cp'); (3) 5.94 (Cp), 1.88 (Cp'), −0.47 (Me)]. The stability of (3) is noteworthy: whereas Cp_2TiMe_2 is unstable in the solid state[6] and Cp'_2TiMe_2 loses one equivalent of methane in refluxing toluene,[1] complex (3) is air stable at room temperature for several months and was unchanged after two days in refluxing toluene.

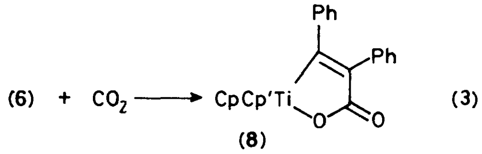
The almost quantitative formation of the red-brown air-sensitive dicarbonyltitanium(II) complex (4)† [85%, ν_{CO}(hexane) 1956, 1875 cm^{-1}] was obtained by reduction of (1) with Zn powder under a carbon monoxide atmosphere in a similar way[7,8] to $Cp_2Ti(CO)_2$ and $Cp'_2Ti(CO)_2$. In these reactions the isolation of the dicarbonyltitanium(II) complex has been significantly improved by the convenient elimination of the resulting $ZnCl_2$ as a precipitate of $ZnCl_2 \cdot 6\,NH_3$ when the reaction solution was stirred under an ammonia atmosphere. As a reflection of the formal electron density at the titanium centre, the carbonyl i.r. absorption frequencies of (4) are intermediary between those of $Cp_2Ti(CO)_2$ (1979, 1897 cm^{-1})[8] and those of $Cp'_2Ti(CO)_2$ (1930, 1850 cm^{-1}).[1] Relevant to this higher electron donating effect of the Cp' ligand, the displacement of one carbonyl of (4) by PMe_3 was not observed in refluxing heptane whereas this reaction occurs readily using $Cp_2Ti(CO)_2$ in hexane.[8]

By contrast, compound (4) reacts with diphenylacetylene to give (6), but only in the presence of PMe_3 which forms the intermediate adduct (7), equation (1). When (4) was treated with one equivalent of diphenylacetylene in refluxing hexane the formation of the intermediate (5) (ν_{CO} 1980 cm^{-1}) took place but no product could be isolated. However, when complex (4) was heated with one equivalent of diphenylacetylene and 2—3 equivalents of PMe_3, after evaporation of volatile products and crystallization of the residue in hexane, red-brown crystals of (6) were isolated in 60% yield. Under similar conditions, $Cp_2Ti(CO)_2$ gave the yellow, stable $Cp_2Ti(PMe_3)(Ph\text{–}C{\equiv}C\text{–}Ph)$.[3] However, elemental analysis shows that (6) retains less than 0.1 PMe_3 per Ti. These observations suggest the formation of the intermediate (7) which loses the labile PMe_3 ligand under vacuum.

The isolation of complex (6) points out the novelty of the behaviour of (4). Whereas $Cp_2Ti(CO)_2$ with diphenylacetylene gives $Cp_2Ti(CO)(Ph\text{–}C{\equiv}C\text{–}Ph)$ which decomposes at room temperature to form the metallacyclopentadienyl complex[9] $Cp_2\overline{Ti\text{–}C(Ph){=}C(Ph)\text{–}C(Ph){=}C}(Ph)$, no evidence of formation of such a metallocyclic compound has been obtained starting from (4) or (6). $Cp_2Ti(Ph\text{–}C{\equiv}C\text{–}Ph)$ was believed to exist in solution[10] and $Cp'_2Ti(Me\text{–}C{\equiv}C\text{–}Me)$ has been mentioned[4] but these suggested intermediates require in their syntheses strong reducing agents compared to those in the transformation (1) → (4) → (6).



(2)



(3)

Compound (6) is further characterized by its reaction with carbon monoxide shown in equation (2). Complex (6) in hexane reacts with carbon monoxide (1 atm, room temp.) to afford within a few minutes complex (5) as shown by i.r. [ν_{CO} 1980 cm^{-1}, as expected from ν_{CO} 1995 cm^{-1} for the parent compound $Cp_2Ti(CO)(Ph\text{–}C{\equiv}C\text{–}Ph)$[9]] and then the intermediate (5) slowly disappears to generate after two hours the precuror (4) (1956, 1875 cm^{-1}). These reactions also illustrate the reversibility of the transformation (4)→(6).

The activation of carbon dioxide, to form a carbon–carbon bond, requires an electron rich metal centre[11,12] and the unsaturated electron rich complex (6) in hexane reacts smoothly with CO_2 under atmospheric pressure. After one hour a red air-stable precipitate was separated from the black solution and identified as complex (8) [equation (3)], a Ti^{IV} adduct of CO_2 and (6). Complex (8)† decomposes only above 250 °C [43%, i.r. (Nujol) 1640vs cm^{-1} (CO_2); ^{1}H n.m.r. δ (CD_2Cl_2) 7.17(Ph), 6.42 (Cp), 1.73 (Cp')]. The structure of the adduct (8) is also supported by the well known tendency of titanium to form stable Ti–O bonds. The transformation (6)→(8) supports the proposal of a Cp_2Ti(benzyne) intermediate in the reaction of Cp_2TiPh_2 with carbon dioxide[13] under more drastic conditions.

Interestingly, the addition of carbon monoxide to the black residual solution afforded additional complex (8) (11%) with concomitant formation of (4). On the basis of the ability of carbon monoxide to induce dismutation reactions of Ti^{III} complexes,[7,14,15] we suggest the formation of a binuclear Ti^{III} complex such as (9), resulting formally from the reaction of (8) with (6), and able to lead by dismutation with CO to the Ti^{IV} complex (8) and Ti^{II} compound (4). To support this hypothesis, as PMe_3 is able to co-ordinate the titanium atom of (6) and consequently to prevent the formation of the intermediate (9), complex (6) was treated with CO_2 in the presence of more than one equivalent of PMe_3 in hexane and gave complex (8) in 60% yield. No further reaction with carbon monoxide was observed in this case. Moreover, the lability of the Ti–PMe_3 bond does not hinder the reaction of (6) with CO_2 whereas no reaction was observed with CO_2 and $Cp_2Ti(PMe_3)$-$(Ph\text{–}C{\equiv}C\text{–}Ph)$ which has a strong enough Ti–PMe_3 bond to allow isolation.[3]

$$[CpCp'Ti^{III}\text{–}C(Ph){=}C(Ph)\text{–}CO_2\text{–}Ti^{III}Cp'Cp]$$

(9)

These reactions with CO_2 indicate that besides the required electron density at the metal centre, the unsaturated coordination of the metal atom plays a major role in the coupling reaction of an unsaturated substrate with carbon dioxide.

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