Synthesis of Cyclopentenediolates and Cyclopentane-1,2-diones by Carbonylation of Titanacyclobutane Complexes Prepared by Free Radical Alkylation

Charles A. G. Carter,1 Gary L. Casty,2 Jeffrey M. Stryker*
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 Canada
Fax +1 (780) 4928231; E-mail: jeff.stryker@ualberta.ca
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For the creativity, originality, and impact of his research, this manuscript is dedicated to Professor Ryoji Noyori, with deep admiration and respect.

Abstract: The synthesis of titanium cyclopentenediolates by the double carbonylation of titanacyclobutane complexes is reported, a process known as the Bercaw carbonylation. The reaction is general for a range of titanacyclobutanes prepared by free radical alkylation of allyltitanium(III) precursors. Titanacyclobutane formation and carbonylation can be conducted in one pot without the isolation of sensitive intermediates. Subsequent conversion to lithium cyclopentenediolates and cyclopentane-1,2-diones provides access to a range of synthetically valuable organic products.

Key words: carbonylations, titanium, enediolates, metallacyclobutane complexes, cyclopentane-1,2-diones

Radical alkylation of permethyltitanocene η1-allyl and related complexes provides substituted titanacyclobutane complexes by highly regioselective addition to the allyl central carbon.1 To realize the synthetic potential of this general process, the organic chemistry of the titanacyclobutane structural class must be further developed. One of the most interesting reactivity patterns already established for early transition metal dialkyl complexes is the transformation to metallocenediolates by reductive double carbonylation: the Bercaw reaction.2 This reaction has previously been used to convert titanium, zirconium, and hafnium metallacyclobutane complexes to the corresponding metalloenediolates or, after acid hydrolysis, to organic 2-hydroxycyclopentanones.3

Here we report that the Bercaw carbonylation reaction is general for a range of 3-substituted bis(pentamethylcyclopentadienyl)titanacyclobutane complexes, leading to the formation of the corresponding titanocyclopentenediolate complexes cleanly and in high yield. The enediolates can be converted in high yield to lithium cyclopentenediolates by exchange with alkyllithium reagents or oxidized to cyclopentane-1,2-diones by an unexpected triphosgene-induced decomplexation, both unprecedented reaction processes with considerable synthetic potential.

With the exception of unsubstituted complex 1f,6 the titanacyclobutane complexes 1 used in this investigation were prepared by the samarium(II)-mediated radical alkylation of bis(pentamethylcyclopentadienyl)titanium(η1-allyl).6,7 More recently, we have reported that titanacyclobutane complexes 1 can be prepared more convenient-ly and in higher yields using a one-pot procedure starting directly with Cp*2TiCl6 (Equation).6 This alkylation/alkylation protocol avoids the isolation of allyltitanium(III) intermediates and minimizes manipulation of air- and water-sensitive materials.

The crude titanacyclobutane complexes 1 thus obtained can be carbonylated directly without further purification.

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LETTER

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m Cyclopentenediolatesa

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<tr>
<th>Substrate (1)</th>
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*a Reaction conditions: 60 psig CO, pentane, 2h, -78 °C − RT; for a more detailed experimental procedure, see reference 9.
*b Isolated yields after purification.

3 in 43% yield; the metal is recovered in high yield as the dicatonic bis(aquo)permethyltitanocene 4 (Scheme 1). As anticipated, ketoalcohol 3 is formed as the expected mixture of two diastereomers after purification by preparative TLC.15

Scheme 1

Demetallation by acetylation is similarly inefficient, returning the α-acetoxytitanacyclopentane 5 in poor yield after treatment with acetyl chloride/pyridine (Scheme 1).

Two alternative demetallation pathways have been developed to address these deficiencies. Transmetallation to lithium is obtained upon treatment of cyclopentenediolate complexes 2 with two equivalents of methyl lithium at room temperature. As illustrated for complex 2a, the reaction leads to the formation of Cp*₂TiMe₂ and the corresponding lithium enediolate 6, both isolable in high yields (Scheme 2).18 The organic chemistry of lithium enediolates and related acyloin condensation intermediates has been extensively developed, connecting this titanium-mediated manifold to a range of downstream transformations, including simple quenching to α-ketols.19,20

Scheme 2

The conversion of titanocene enediol complexes to organic cyclic carbonates by treatment with phosgene has been reported, a particularly unattractive option for further development. To circumvent the problem of phosgene toxicity, the use of the crystalline phosgene surrogate, bis(trichloromethyl)carbonate (triphosgene), was investigated for the demetallation of permethyltitanocene enediol complexes. Triphosgene, however, unexpectedly mediates a novel oxidative cleavage reaction, converting the enediolates cleanly to 4-substituted cyclopentane-1,2-diones 7, which are isolated as the enol tautomers (Scheme 2). The organometallic fragment is returned largely as Cp*₂TiCl₂, although the mechanism of this transformation has yet to be investigated. Enolic cyclopentane-1,2-diones are well-precedented; both 7a and 7b exhibit spectroscopic properties fully consistent with the assigned structures.22

In combination with the alkylative titanacyclobutane formation, the double carbynoylation of titanacyclobutane complexes thus provides a general method for the preparation of functionalized cyclopentane compounds at either the acyloin or diketone oxidation state. Extension of this process to the synthesis of more highly substituted cyclopentenediolates requires further development of titanium templates that can accommodate the radical alkylation of substituted allyl ligands. Finally, we note that the development of additional pathways for converting substituted titanacyclobutane complexes to synthetically valuable organic products is also under investigation.

Acknowledgement

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References and Notes

(1) Current address: NOVA Research and Technology Centre, NOVA Chemicals Corporation, 2928 16th Street N.E., Calgary, Alberta T2E 7K7 Canada.
(2) Current address: Exxon Research and Engineering, 1545 Route 22 East, Annandale, New Jersey 08801, USA.

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(6) The unsubstituted titanacyclobutane complex II was prepared in 85% isolated yield by the addition of LiEt2BH (1 equiv) to the cationic Ti(IV) complex [Cp*2Ti(ν1-allyl)]BPh4 at –78 °C under an atmosphere of ethylene to inhibit the decomposition of the titanacyclobutane under the reaction conditions (Carter, C. A. G., Ph.D. Dissertation, University of Alberta, 1998). Nucleophilic alkylation of [Cp*2Ti(ν1-allyl)]BPh4 has been previously reported: Tjaden, E. B.; Casty, G. L.; Stryker, J. M. J. Am. Chem. Soc. 1993, 115, 9814.


(9) All products have been completely characterized (IR, 1H and 13C NMR, HRMS). Representative experimental procedure and characterization data for bis(pentamethylyclopentadienyl)titanium(4-isopropylcyclopentene-1,2-diolate) 2a. In a drybox or otherwise under inert atmosphere, a Lab Cret aerosol pressure vessel (Andrews Glass Co.) fitted with Swagelok Quick connects, sampling port, and pressure gauge was charged with 3-isopropyl titanacyclobutane 1a (0.101 g, 0.251 mmol) and pentane (10 mL). The sealed vessel was cooled to –78 °C and pressurized with CO (60 psi gauge pressure). After 0.5 h at low temperature, the cooling bath was removed and the reaction mixture stirred for an additional 2 h. The pressure was released and the solution concentrated under reduced pressure. Cooling to –35 °C yielded complex 2a as a brown powder, pure by spectroscopic analysis (0.095 g, 83%). Characterization data for 2a: IR (pentane cast, cm–1) 2960, 2906, 2838, 1558, 1542, 1490, 1472, 1456, 1436, 1419, 1374, 1261, 1089, 1020, 803, 668; 1H NMR (400 MHz, C6D6): 2.23 (m, 4H, CH2), 1.80 (s, 15H, Cph2), 1.78 (s, 15H, Cph2), 1.56 (m, 1H, CH(CH3)2), 0.92 (d, J = 6.6 Hz, 6H, CH(CH3)3); 13C NMR (100 MHz, C6D6, gated decoupling) 6 147.5 (s, C = C), 121.9 (s, CMe2), 121.0 (s, CMe2), 42.7 (d, J = 123 Hz, C4), 37.1 (d, J = 128 Hz, CH2), 34.3 (d, J = 128 Hz, CHMe2), 20.7 (q, J = 124 Hz, CHMe2). Evaporation of the hexane fraction gave crude product, which was purified by flash chromatography (4:1 hexane/ether) to give 4-allyl-2-hydroxy-2-cyclopentenone 7a as an off-white solid (0.016 g, 95%). Characterization data for 7a: IR (cast, cm–1) 3350, 3082, 2913, 1703, 1648, 1634, 1395, 1198, 1099; 1H NMR (360 MHz, C6D6): 5.27 (s, 1H), 5.01 (s, 1H), 4.94 (t, J = 1.2 Hz, 1H), 4.35 (t, J = 1.2 Hz, 1H), 3.50 (m, 1H, CH2), 3.42 (m, 1H, CH2), 2.53 (m, 1H, CH2), 2.48 (m, 1H, CH2), 2.05 (s, 3H, CH3), 2.00 (s, 3H, CH3), 1.98 (s, 3H, CH3), 1.95 (s, 3H, CH3), 1.94 (s, 3H, CH3), 1.92 (s, 3H, CH3), 1.89 (s, 3H, CH3), 1.88 (s, 3H, CH3), 1.85 (s, 3H, CH3), 1.79 (s, 3H, CH3), 1.78 (s, 3H, CH3), 1.75 (s, 3H, CH3), 1.72 (s, 3H, CH3), 1.70 (s, 3H, CH3), 1.69 (s, 3H, CH3), 1.66 (s, 3H, CH3), 1.62 (s, 3H, CH3), 1.59 (s, 3H, CH3), 1.57 (s, 3H, CH3), 1.55 (s, 3H, CH3), 1.53 (s, 3H, CH3), 1.51 (s, 3H, CH3), 1.49 (s, 3H, CH3), 1.47 (s, 3H, CH3), 1.44 (s, 3H, CH3), 1.42 (s, 3H, CH3), 1.40 (s, 3H, CH3), 1.39 (s, 3H, CH3), 1.37 (s, 3H, CH3), 1.35 (s, 3H, CH3), 1.33 (s, 3H, CH3), 1.31 (s, 3H, CH3), 1.29 (s, 3H, CH3), 1.27 (s, 3H, CH3), 1.25 (s, 3H, CH3), 1.23 (s, 3H, CH3), 1.21 (s, 3H, CH3), 1.19 (s, 3H, CH3), 1.17 (s, 3H, CH3), 1.15 (s, 3H, CH3), 1.13 (s, 3H, CH3), 1.11 (s, 3H, CH3), 0.99 (d, J = 6.6 Hz, 6H, CH(CH3)3).
MHz, CHCl$_3$) $\delta$ 6.51 (d, $J = 2.9$ Hz, 1H, H2), 5.78 (m, 1H, = CH allyl), 5.45 (s, 1H, OH), 5.08 (m, 2H, = CH$_2$ allyl), 2.89 (m, 1H, H4), 2.60 (dd, $J = 19.4, 5.9$ Hz, 1H, H5), 2.25 (m, 2H, CH$_2$ allyl), 2.11 (dd, $J = 19.4, 1.6$ Hz, 1H, H5); $^{13}$C NMR (100 MHz, CHCl$_3$, gated decoupling) $\delta$ 203.1 (s, C = O), 152.5 (s, = COH), 135.1 (d, $J = 154$ Hz, = CH), 132.5 (d, $J = 165$ Hz, = CH), 117.5 (t, $J = 156$ Hz, = CH$_2$), 39.6 (t, $J = 121$ Hz, CH$_2$), 38.3 (t, $J = 132$ Hz, CH$_3$), 34.0 (d, $J = 136$ Hz, C4); HRMS (EI, 40 eV) calcd for C$_8$H$_{10}$O$_2$: 138.06808, found 138.06771.