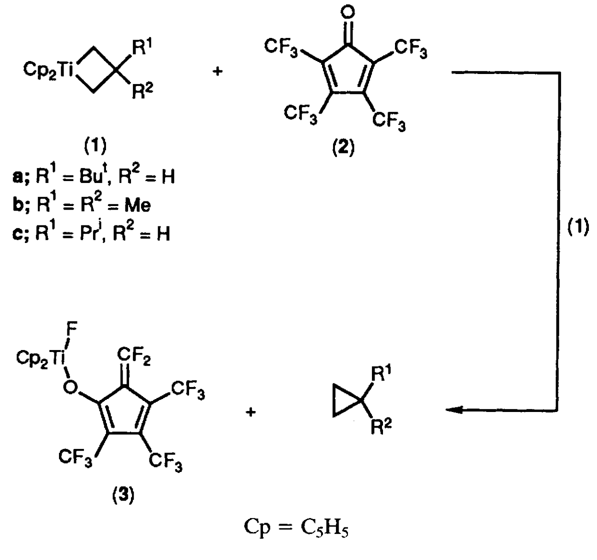
Oxidatively Induced Reductive Elimination. A Novel Titanium Complex resulting from C–F Bond Activation

Mark J. Burk,* Donna L. Staley, and William Tumas*

Contribution No. 5412, Central Research and Development, E.I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, DE 19880, USA

Reaction between bis(cyclopentadienyl)titanacyclobutanes (**1**) and tetrakis(trifluoromethyl)cyclopentadienone (**2**) results in formal reductive elimination of cyclopropanes and activation of an sp^3 C–F bond in (**2**) to afford the novel organometallic product (**3**) (structurally characterized by *X*-ray crystallography).

We have investigated the chemistry of tetrakis(trifluoromethyl)cyclopentadienone (**2**) with particular emphasis on its reactivity with transition metal complexes. Bis(cyclopentadienyl)titanacyclobutanes, (**1**), are well known to undergo a number of synthetically useful reactions with organic substrates including Wittig-like methylenation of carbonyl compounds.[1] Rather than the expected methylene transfer to dienone (**2**), we have found that the d^0 metallacycles (**1**) react rapidly with (**2**) to produce one equivalent of the corresponding cyclopropane and the novel titanium complex (**3**), which has been structurally characterized. The activation of an sp^3 C–F bond in (**2**) *via* an intermediate titanocene–dienone complex appears to be a likely pathway for the formation of (**3**), equation (1). An immediate reaction occurs with a colour change from red to light orange upon mixing the dienone (**2**) and the titanacyclobutanes (**1a**—**c**) in CH_2Cl_2 at −20 °C. Addition of pentane to the reaction mixture afforded the new complex (**3**) as a thermally sensitive orange solid in good yield (80%). The ^{19}F NMR spectrum† of (**3**) exhibited a broad Ti–F resonance at δ +60 ppm as well as three resonances for the CF_3 groups and separate signals for the inequivalent fluorines of a CF_2 unit, indicating the presence of a dienone-derived ligand.



(**1**)

a; $R^1 = Bu^t$, $R^2 = H$
b; $R^1 = R^2 = Me$
c; $R^1 = Pr^i$, $R^2 = H$

(**2**)

(**3**)

$Cp = C_5H_5$

(1)

The structure of (**3**) was established by *X*-ray crystallography‡ (Figure 1). Orange crystals suitable for *X*-ray diffraction were obtained by slow crystallization from CH_2Cl_2/pentane (*ca.* 1:1) at −30 °C. A normal bent metallocene

---

† *Spectral data* for (**3**): NMR (CD_2Cl_2) δ 6.4 (d, J_{HF} 3.4 Hz, Cp); δ_F −56.4 (sept, J_{FF} 12.2 Hz, 3F, CF_3), −54.5 (dq, J_{FF} 30.3, 12.3 Hz, 3F, CF_3), −52.8 (br., 3F, CF_3), −51.5 (dd, −80 °C, J_{FF} 69.5, 60.3 Hz, 1F, CF_2, at 25 °C this resonance is broad), −47.2 (dq, J_{FF} 69.5, 27.0 Hz, 1F, CF_2), 71.8 (br. s, 1F, Ti–F); δ_C 171.7 (d, J_{CF} 11.8 Hz, C–O confirmed by ^{13}C-substitution), 157.8 (dd, J_{CF} 323 Hz, CF_2), 133.6, 123.2 (CF_3), 121.4 (CF_3), 121.0 (CF_3), 119.3 (d, J_{CF} 2.3 Hz, C_5H_5), 108.3, 95.9 (assignments assisted by ^{19}F decoupling); IR (CH_2Cl_2 soln.) 1528 cm^{-1} (C–O stretch confirmed by ^{13}C-substitution).

‡ *Crystal data* for (**3**): monoclinic, $P2_1/n$ (No. 14), $a = 23.639(4)$, $b = 8.289(1)$, $c = 9.838(2)$ Å, $\beta = 99.97(1)°$, $T = -100$ °C, $U = 1898.6$ Å^3, Mo-K_α radiation, $\mu_{calc.} = 5.66\ cm^{-1}$, $D_c = 1.855\ g\ cm^{-3}$, $Z = 4$, $F(000) = 530.19$. The structure was solved by automated Patterson analysis (PHASE) and refined by a full-matrix least-squares procedure to residuals of $R = 0.064$, $R_w = 0.059$, GOF = 1.81 for 2146 unique reflections with $I > 3.0\ \sigma(I)$ and 298 variables. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

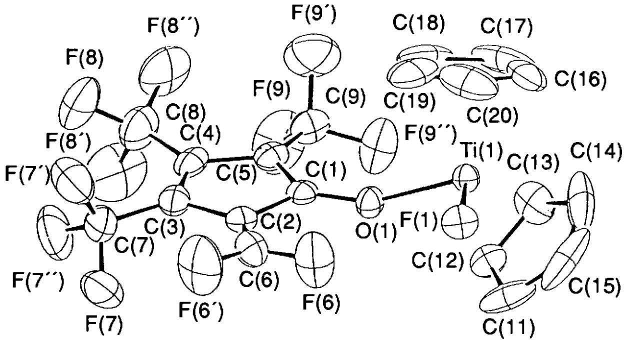
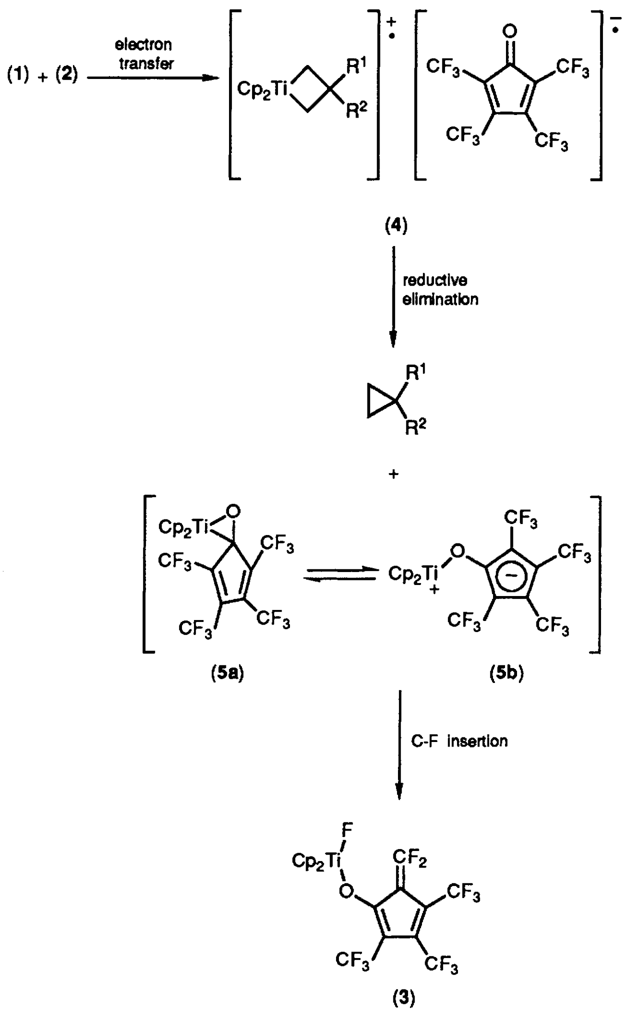


Figure 1. ORTEP drawing of titanium complex (**3**). Selected bond distances (Å) and angles (°) are as follows: Ti(1)–F(1) 1.838(3), Ti(1)–O(1) 1.937(3), C(1)–C(2) 1.471(7), C(2)–C(3) 1.455(7), C(3)–C(4) 1.344(8), C(4)–C(5) 1.473(8), C(5)–C(1) 1.394(7), C(2)–C(6) 1.341(8); F(1)–Ti(1)–O(1) 97.6, Ti(1)–O(1)–C(1) 157.9. Hydrogen atoms are omitted for clarity.



Scheme 1

structure (Cp_2MX_2) ($Cp = C_5H_5$) is observed for (**3**). The two X ligands of (**3**) arise from insertion into a C–F bond of a CF_3 group adjacent to the carbonyl moiety of the dienone (**2**). Interestingly, the dienone is transformed into an oxygen-bound trienolate ligand (alternating single and double bonds) which is essentially planar, presumably due to resonance delocalization throughout the ring. There is no evidence for any interaction between the CF_2 unit and the Ti–F group or the Ti centre in the solid state.

We have found[2] that dienone (**2**) is a potent one-electron oxidant [$E_{\frac{1}{2}}$ 0.38 V vs. standard calomel electrode (SCE)] for various transition metal complexes. Jordan has reported that one-electron oxidants induce fragmentation of d^0 zirconium compounds Cp_2ZrR_2 (R = Me, CH_2Ph) to yield cationic zirconium alkyl complexes.[3] Furthermore, recent work in our laboratory including electrochemical studies has revealed that d^0 metal complexes exhibit a rich redox chemistry.[4] Based on these studies, a plausible mechanism for formation of cyclopropanes and (**3**) from reaction of (**1**) with (**2**) is outlined in Scheme 1. Initial charge transfer between (**1**) and (**2**) would lead to a transient radical ion pair (**4**).§ Subsequent reductive elimination of cyclopropane followed by collapse of the ion pair would produce the intermediate titanocene–dienone complex (**5**). Insertion of Ti into an accessible C–F bond adjacent to the co-ordinated carbonyl group affords the complex (**3**). The absence of insertion into C–F bonds of the β-CF_3 groups of (**2**) suggests prior oxygen co-ordination to the Ti centre, supporting the intermediacy of complex (**5**). Although recent examples of aryl C–F bond activation by transition metal centres have been reported,[5] to our knowledge, complex (**3**) represents the first example of the isolation/characterization of the initial product resulting from activation of an sp^3 C–F bond by a metal centre.

Preliminary investigations suggest that the dienone-mediated oxidation chemistry observed here may prove to be quite general for other d^0 Group IV complexes. For instance, reaction between (**2**) and Cp_2ZrPh_2 affords biphenyl and the Zr analogue of (**3**). Dienone (**2**) appears to be an ideal reagent for studying one-electron oxidation processes involving transition metal complexes since the resulting intermediates can be trapped as stable, soluble adducts of the dienone. Studies aimed at elucidating the scope and mechanistic details of these and related systems are in progress.

We thank J. E. Feaster, B. A. Kurtz, W. Marshall, and L. Lardear for expert technical assistance. In addition, we are grateful to E. Conaway for obtaining NMR spectra, F. Davidson for performing ^{19}F-decoupled ^{13}C NMR experiments, and J. C. Calabrese for assistance in solving and refining the crystal structure of (**3**).

Received, 12th February 1990; Com. 0/00651C

References

1 K. A. Brown-Wensley, S. L. Buchwald, L. Cannizzo, L. Clawson, S. Ho, D. Meinhardt, J. R. Stille, D. Straus, and R. H. Grubbs, *Pure Appl. Chem.*, 1983, **55**, 1733; R. H. Grubbs and W. Tumas, *Science*, 1989, **243**, 907.

2 M. J. Burk, P. Krusic, and M. D. Ward, unpublished results.

3 R. F. Jordan, *J. Chem. Ed.*, 1988, **65**, 285, and references cited therein; R. F. Jordan, R. E. LaPointe, C. S. Bajgur, S. F. Echols, and R. Willett, *J. Am. Chem. Soc.*, 1987, **109**, 4111.

4 M. J. Burk, W. Tumas, M. D. Ward, and D. R. Wheeler, *J. Am. Chem. Soc.*, submitted for publication.

5 T. G. Richmond, C. E. Osterberg, and A. M. Arif, *J. Am. Chem. Soc.*, 1987, **109**, 8091, and references cited therein.

---

§ Currently, it is uncertain whether dienone co-ordination to (**1**) is involved in the formation of (**4**) (*i.e.*, inner sphere *vs.* outer sphere electron-transfer process).