JOM 24163PC

Preliminary Communication

The regiospecific reaction of diphenylacetylene with bis(cyclopentadienyl)-(*o*-fluorobenzyne)titanium. The crystal structure of the $Cr(CO)_3$ derivative of 1,1-bis(cyclopentadienyl)-2,3-diphenyl-7-fluorotitanole

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(Received March 18, 1993; in revised form September 7, 1993)

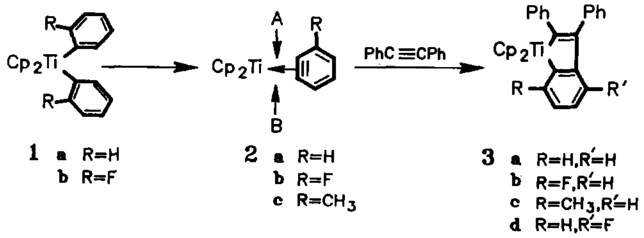
Abstract

Diphenylacetylene reacts with the pyrolysis product of bis(cyclopentadienyl)-bis(*o*-fluorophenyl)titanium to afford predominantly one isomer of the expected titanole. The crystal structure of the $Cr(CO)_3$ derivative **4** of the titanole shows that the fluorine is in the 7-position indicating that attack of the acetylene on the benzyne intermediate occurs along the less sterically hindered path. Compound **4**: monoclinic, *Cc*, $a = 7.983(2)$ Å, $b = 19.602(4)$ Å, $c = 16.834(4)$ Å, $\beta = 91.59(2)°$. $R_f = 0.052$ from 1069 observed reflections.

The thermal decomposition reactions of $(\eta\text{-}C_5H_5)_2Ti(aryl)_2$ compounds such as **1a** are known to proceed via intramolecular hydrogen abstraction processes. If the abstraction takes place from one of the aryl groups, the result is the elimination of one arene and the formation of a titanium aryne fragment such as **2a** (Scheme 1) [1,2]. The reactive intermediate has been characterized by its trapping reactions with, for example, N_2, CO_2, olefins, and acetylenes. In the case of diphenylacetylene, metallacycles such as **3a** are formed the structures of which have been established by independent synthesis [3].

In an earlier study [4] of the reactions of **1b** with diphenylacetylene the insertion product was isolated in high yield, and there was a preponderance of one isomer as judged by the ^{19}F NMR spectrum. Thus the reaction took place almost exclusively along path A or B (Scheme 1). The structure **3d** resulting from attack along path A (A attack) was assigned to the product even though the results of Rausch and Mintz [5] indicate that **2c**, one of the intermediates in the thermolysis of $Cp_2Ti(m\text{-}C_6H_4CH_3)_2$, reacts with diphenylacetylene with exclusive formation of **3c** via B attack. Crystals of the fluorinated product were unsuitable for an X-ray study and the normal ^1H spectrum of **3b**/**3d** gives little structural information since all the aryl resonances are overlapped: the 2D-SUPER-COSY spectrum reveals that, as expected, the fluorinated ring is the one metallated by titanium. Verification of the proposed structure thus depended on the preparation of a suitable derivative. This has now been done and the correct structure of the major product is **3b** in line with attack along path **B** which shows lower steric hinderance in accordance with earlier postulates [3]. The same phenomenon has been noted by Buchwald and his coworkers [2] in the course of related studies on zirconium derivatives and we have recently become aware of closely related work on titanium by the same group [6].

The reaction product **3b**/**3d** was derivatized by reacting it with $(CH_3CN)_3Cr(CO)_3$ (Scheme 2). Two green products are formed and the predominant one can be isolated by using column chromatography. The ^1H NMR spectrum of this product establishes that the



Scheme 1.

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* Dedicated to Professor M.F. Lappert in the occasion of his 65th birthday.

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0022-328X/93/$6.00

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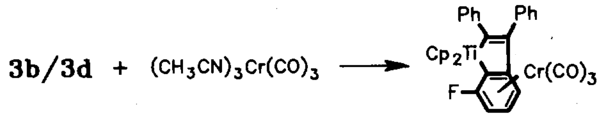

4

Scheme 2.

$Cr(CO)_3$ moiety is bound to the fluorinated ring since the resonances in this ring are shifted up field by ~ 1.5 ppm. (The Cp resonances are inequivalent and the chemical shift difference is 0.12 ppm.) However, the distinction between **3b** and **3d** cannot be made with certainty. Fortunately the isolated product is crystalline and its structure is shown in Fig. 1. The chromium moiety is bound to the fluorinated arene ring that was originally present in **2b**. This ring has a fluorine substituent on C(5) which can only arise if the diphenylacetylene attacks **2b** along path B, indicating a strong steric discrimination in the insertion process. The basic structure of **4** is similar to those of other arenechromium tricarbonyl derivatives. The conformation of the $Cr(CO)_3$ moiety is almost eclipsed as is usually found in substituted arene derivatives: the nearly *syn*-eclipsing of the electronegative fluorine substuent may be unusual [7]. The Cr–C(4) and Cr–C(9) distances, av. 2.29 Å, seem to be longer than the other Cr–ring carbon distances, av. 2.22 Å, but the data are not good enough to make this more than a possibility even though this trend is commonly found in $Cr(CO)_3$ derivatives of fused polycyclic hydrocarbons [7].

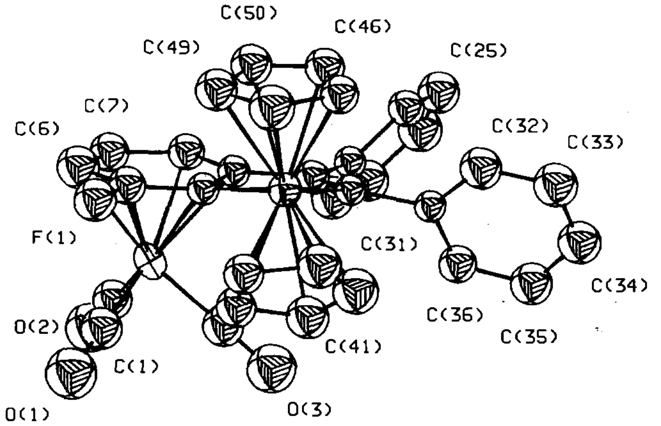

Fig. 1. SNOOPI plot of compound **4**. Selected bond distances (Å) angles (°) are as follows: Cr–C(1) 1.777(20); Cr–C(2), 1.812(18); Cr–C(3), 1.799(18); Cr–C(4), 2.298(14); Cr–C(5), 2.197(16); Cr–C(9), 2.279(14); Ti–C(4), 2.175(14); Ti–C(11), 2.173(13); Ti–C(41), 2.378(20); Ti–C(46), 2.352(17); C(5)–F, 1.385(17). C(2)–Cr–C(1), 88.3(8); C(3)–Cr–C(1), 88.7(8); C(3)–Cr–C(2), 85.0(8); C(11)–Ti–C(4), 76.8(5); C(5)–C(4)–Ti(1), 131.3(10); C(9)–C(4)–Ti, 112.3(9).

1. Experimental details

All procedures were carried out on a standard vacuum line by using Schlenk apparatus and an argon atmosphere. Solvents were predried and distilled prior to use. Column chromatography was carried out by using a neutral alumina (Grade 1) support. ^1H NMR data were obtained by using a Brüker WH-400 instrument. Mass spectral data were acquired by using a Kratos MS-50 spectrometer. Compounds **3b/3d** and $(CH_3CN)_3Cr(CO)_3$ were prepared according to the literature procedures [4].

1.1. Preparation of 4

A suspension of $(CH_3CN)_3Cr(CO)_3$ (1.0 g, 3.9 mmol (excess)) and **3b/3d** (0.45 g, 0.1 mmol) in diethyl ether (20 ml) and THF (20 ml) was stirred for 24 h at room temperature. The reaction progress was monitored by using tlc (aluminum backed Kieselgel plates (Merck)). Four colored bands were observed and are listed in the order of decreasing R_f value: (a) green, (b) deep green, (c) yellow, (d) brown/red (**3b/3d**), the reaction mixture was left until no starting material remained. The products were isolated, by using column chromatography as follows: the yellow band was eluted with diethyl ether to give, on solvent removal, excess unreacted metal carbonyl; the deep green band, which was also eluted by diethyl ether yielded **4** after crystallization (diethyl ether/hexane) as a deep green powder (yield 60–70% based on **3b/3d**. The minor green band eluted by using diethyl ether/CH_2Cl_2, but no attempt was made to identify it. Recrystallization of a small quantity of **4** from a concentrated CH_2Cl_2 solution layered with n-hexane gave crystalline **4**.

4: Mass spectrum (120°C) m/e (relative intensity): 587 (7.02); 586 (13.71), M^+; 504 (16.78); 503 (38.91); 502 (81.64); 501 (14.28); 500 (14.53); 450 (10.75); 449 (6.27); 448 (14.50); 428 (10.05); 427 (3.62); 426 (5.40); 366 (10.80); 365 (13.25); 364 (8.13); 326 (11.62); 325 (10.81); 324 (29.87); 323 (7.23); 322 (13.78); 305 (9.12); 304 (13.34); 303 (20.59); 254 (15.21); 253 (37.80); 252 (69.19); 251 (21.19); 250 (25.75); 249 (20.92); 248 (60.29); 178 (52.45); 132 (33.57); 117 (24.34); 113 (20.89); 52 (100.00).

Parent ion M^+ isotope pattern (measured mass, formula, standard deviation, relative intensity): 452.1261, $C_{30}H_{23}F^{50}Ti$, 0.2, 11.11; 451.1295, $C_{30}H_{23}F^{49}Ti$, 3.3, 33.26; 450.1261, $C_{30}H_{23}F^{48}Ti$, −0.2, 86.14; 449.1177, $C_{30}H_{22}F^{48}Ti$, −0.8, 43.76;

TABLE 1. Crystallographic and experimental data

Crystal data	
Formula	$C_{33}H_{23}CrTiOF$
Molecular weight	586.44
Crystal system	Monoclinic
Space group	Cc
a Å	7.983(2)
b, Å	19.602(4)
c, Å	16.834(4)
β, °	91.59(2)
V, Å^3	2603.5
Z	4
μ (Mo Kα), mm^{-1}	0.750
D_{calc}, Mg m^{-3}	1.496
Data collection and refinement	
Crystal dimensions, mm	0.04×0.25×0.36
Temperature, K	295
Radiation	Mo Kα = 0.71069 Å
Transmission factors	0.8404–0.9706
Scan mode	Coupled ω–2θ
Scan speed range, ° min^{-1}	0.87–5.49
Scan width, °	$0.75 + 0.35 \tan \theta$
Theta limits, °	$0 < 2\theta \leq 47$
Data collection range	$h, k, \pm l$
Unique reflections	1932
Observed reflections ($I \geq 2\sigma(I)$)	1069
Number of variables	173
R_f [a]	0.052
R_{wf} [b]	0.056
Goodness of fit [c]	1.095

[a] $R_f = \Sigma \| F_o | - F_c \| / \Sigma | F_o |$. [b] $R_{wf} = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma F_o^2]^{1/2}$.
[c] G.O.F. $= [\Sigma w(| F_o | - | F_c |)^2 / (\text{No. of degrees of freedom})]^{1/2}$.

$C_{30}H_{21}F^{48}Ti$, 1.4, 100.00; 447.1104, $C_{30}H_{21}F^{47}Ti$, −4.1, 17.70; 446.1046, $C_{30}H_{20}F^{47}Ti$, −2.0, 26.38.

^{1}H NMR: δ ($CHCl_3$) 400 MHz: 4.37 (dd, 1); 5.02 (dd, 1); 5.36 (dt, 1, $J_{F-H} = 4.8$ Hz); 6.52 (s, 5); 6.53 (s, 5); 6.55–6.60 (m, 2); 6.80–7.10 (m's, 8).

1.2. X-ray structure determination for 4

A suitable crystal was selected and transferred to an Enraf-Nonius CAD4F diffractometer equipped with graphite monochromated Mo Kα radiation. The unit cell was obtained from the accurate setting angles of 25 reflections ($4 < 2\theta < 24°$). Two standard reflections measured every 5400 s showed some variation with time (1.46%) and the data was scaled with a five point smoothing curve. A total of 1998 reflections were collected of which 1069 were considered to be observed ($I \geq 2\sigma(I)$). The data were corrected for Lorentz polarization and for absorption effects by Gaussian integration [8]. Pertinent crystallographic and experimental parameters are given in Table 1.

The structure was solved by heavy atom methods, and refined by full-matrix least-squares. The majority of the hydrogen atoms were found in difference Fourier maps but it was decided to geometrically place these atoms. An attempt was made to determine the absolute structure of the compound using a Rogers polarity parameter (η) [9] which gave inconclusive results = 0.469(311) but weakly favored the structure that had been chosen. The variables included in the final cycles of refinement were scale, polarity, positional and anisotropic thermal parameters for the two metal atoms, positional parameters and isotropic thermal parameters for the remaining non hydrogen atoms, and similar hydrogen atoms were allowed to have equivalent isotropic temperature factors.

The final residuals were $R = 0.052$, and $R_W = 0.056$, and the goodness of fit was 1.095. Refinement was by full-matrix least-squares minimizing the function

TABLE 2. Atomic coordinates and U_{eq} or U_{iso} (Å^2) (×10^4) with e.s.d.'s in parentheses for the non-hydrogen atoms in $CrTiC_{33}H_{23}O_3F$

Atom	x	y	z	U_{eq} / U_{iso}
Cr(1)	4986(8)	9214(1)	5031(2)	410
Ti(1)	4198(7)	11239(1)	4215(2)	356
F(1)	4201(12)	9685(5)	3205(5)	619(27)
O(1)	1726(19)	8664(7)	4404(8)	908(43)
O(2)	5386(17)	7949(7)	5997(8)	820(40)
O(3)	3134(17)	9737(7)	6426(7)	828(39)
C(1)	3045(23)	8869(9)	4653(11)	597(46)
C(2)	5274(21)	8442(9)	5611(10)	535(44)
C(3)	3875(22)	9524(9)	5877(10)	585(46)
C(4)	5291(17)	10227(7)	4363(8)	353(36)
C(5)	5322(20)	9667(8)	3852(9)	487(41)
C(6)	6388(23)	9098(9)	3895(10)	622(49)
C(7)	7520(20)	9076(8)	4538(10)	522(45)
C(8)	7647(19)	9624(8)	5089(9)	455(41)
C(9)	6521(17)	10199(7)	5013(7)	355(35)
C(10)	6464(17)	10764(8)	5566(7)	384(34)
C(11)	5433(16)	11291(7)	5383(7)	324(32)
C(21)	7652(17)	10772(7)	6277(8)	341(31)
C(22)	7768(24)	10242(9)	6818(10)	621(47)
C(23)	8933(21)	10261(9)	7472(10)	583(46)
C(24)	9946(24)	10806(10)	7581(11)	669(50)
C(25)	9876(21)	11339(10)	7055(10)	596(48)
C(26)	8747(19)	11342(8)	6417(9)	440(40)
C(31)	5129(18)	11852(7)	5956(8)	341(35)
C(32)	5360(23)	12533(9)	5792(10)	598(46)
C(33)	5052(24)	13042(9)	6342(10)	660(51)
C(34)	4424(22)	12883(10)	7048(10)	637(52)
C(35)	4083(22)	12225(9)	7222(10)	607(50)
C(36)	4489(19)	11711(8)	6691(9)	489(42)
C(41)	1716(24)	11661(10)	4814(11)	728(57)
C(42)	1476(23)	11721(10)	4021(11)	677(54)
C(43)	1473(21)	11067(8)	3684(10)	556(47)
C(44)	1677(21)	10602(8)	4309(10)	553(47)
C(45)	1877(23)	10975(9)	5041(11)	630(50)
C(46)	6618(20)	11888(8)	3939(10)	526(44)
C(47)	5200(20)	12244(8)	3616(9)	508(43)
C(48)	4530(24)	11838(10)	3002(11)	715(55)
C(49)	5495(21)	11239(9)	2957(10)	613(46)
C(50)	6764(21)	11301(9)	3528(9)	577(45)

$\Sigma w(|F_o| - |F_c|)^2$, where w was calculated from a three term Chebyshev series so that $w = [0.4117\ t_0(x) + 0.4076 t_1(x) + 0.2515 t_2(x)]^{-1}$, where $x = F_o - F_{\max}$ [10]. The refinement was considered complete when the ratio of all shifts to e.s.d.'s was less than 0.1. The highest peak in the final difference map was 0.33(4) e Å^{-3} and was situated 0.864 Å from O(1). Complex neutral atom scattering factors were taken from the *International Tables for Crystallography* [11]. Calculations were carried out on a Microvax II computer with use of the NRC VAX Crystal Structure System [12] and the CRYSTALS suite of programs [13]. Positional parameters are given in Table 2: the origin was fixed by restraining separately the sum of all x and z shifts to be zero (reducing off-diagonal terms). A view of 4 is given in Fig. 1 [14] and selected bond distances and angles are listed in its caption. Anisotropic thermal parameters, hydrogen atoms coordinates, the remaining molecular dimensions and tables of calculated and observed structure factors are available as supplementary material from the authors.

Acknowledgments

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial assistance.

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