Inorganica Chimica Acta, *131* (1987) 147–150

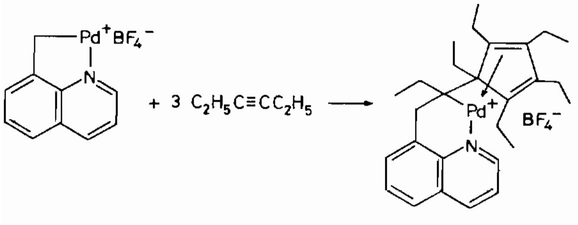
Multiple Alkyne Insertions in Cyclopalladated Complexes. The Crystal and Molecular Structure of $[\eta^2\text{-}(Et_5C_5)C(Et)CH_2(C_9H_6N)Pd(FBF_3)]$

ARNOLD L. RHEINGOLD*, GUANGZHONG WU
and RICHARD F. HECK

Department of Chemistry and the Center for Catalytic Science and Technology, University of Delaware, Newark, Del.19716, U.S.A.

(Received February 12, 1987)

Reactions of covalent cyclopalladated chloride dimer complexes with alkynes proceed via insertion of one or more alkyne units, undergo palladium(0) elimination or rearrangement to other products [1]. We recently reported a general reaction scheme that reveals relationships among all of the various products so far obtained from these reactions [2]. We also found that converting the cyclopalladated dimer complexes to the corresponding ionic tetrafluoroborates significantly activates the complexes allowing reactions with alkynes at room temperature. One of these reactions, that of the tetrafluoroborate of cyclopalladated 8-methylquinoline and 3-hexyne, led to a 20% yield of a triple alkyne insertion product (**I**) reminiscent of a 2-butyne trimerization reported by Maitlis [3].



I

We wish now to disclose the crystal structure of **I** which reveals several unusual features including a coordinatively bound tetrafluoroborate anion.

Experimental

I ($C_{28}H_{38}BF_4NPd$) was prepared as previously described [2] and recrystallized from ether/pentane. A yellow crystal (0.32 × 0.40 × 0.40 mm) was cleaved from a larger specimen and epoxied to a fine glass fiber. Preliminary photographic characterization revealed $2/m$ Laue symmetry, and systematic absences in the diffraction data determined $P2_1/n$ as the unique monoclinic space group: $a = 8.602(2)$, $b = 18.060(3)$, $c = 17.518(3)$ Å, $\beta = 91.39(2)°$, $V = 2720.4(8)$ Å^3, $Z = 4$, μ(Mo Kα) = 7.1 cm^{-1}, $D_c = 1.420$ g cm^{-3}, $T = 292$ K. Of 3837 reflections collected (Nicolet R3m/μ, 2θ(max) = 45°), 2981 systematically present reflections with $F_o \geqslant 3\sigma(F_o)$ were considered observed, corrected for a linear 5% decay in reflection intensity and for Lp effects, but not for absorption. The Pd atom coordinates were obtained from a Patterson synthesis. All non-hydrogen atoms

TABLE I. Atomic Coordinates (× 10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
Pd	1313(1)	2262(1)	3034(1)	35(1)*
N(1)	−459(5)	3062(2)	3122(2)	36(1)*
C(2)	−1280(7)	3216(3)	2494(3)	42(2)*
C(3)	−2404(7)	3756(3)	2440(3)	46(2)*
C(4)	−2727(7)	4174(3)	3067(3)	43(2)*
C(5)	−1912(6)	4029(3)	3757(3)	33(2)*
C(6)	−2199(6)	4433(3)	4428(3)	40(2)*
C(7)	−1402(7)	4279(3)	5085(4)	51(2)*
C(8)	−241(7)	3731(3)	5099(3)	44(2)*
C(9)	120(6)	3328(3)	4464(3)	35(2)*
C(10)	−753(6)	3465(3)	3772(3)	32(2)*
C(11)	1389(6)	2754(3)	4540(3)	37(2)*
C(12)	2576(6)	2750(3)	3896(3)	31(2)*
C(13)	3121(6)	3520(3)	3677(3)	39(2)*
C(14)	3693(7)	4007(3)	4332(4)	54(2)*
C(15)	3881(6)	2141(3)	3938(3)	35(2)*
C(16)	3280(6)	1456(3)	4362(3)	36(2)*
C(17)	2674(6)	968(3)	3860(3)	36(2)*
C(18)	2935(6)	1240(3)	3069(3)	36(2)*
C(19)	3723(6)	1906(3)	3093(3)	41(2)*
C(20)	5504(7)	2377(4)	4212(4)	50(2)*
C(21)	6744(7)	1786(4)	4063(5)	72(3)*
C(22)	3274(8)	1401(4)	5221(3)	49(2)*
C(23)	3557(10)	927(5)	5572(4)	90(4)*
C(24)	1805(7)	271(3)	4017(4)	54(2)*
C(25)	47(8)	371(4)	3950(4)	81(3)*
C(26)	2822(7)	730(3)	2379(4)	50(2)*
C(27)	4229(8)	222(4)	2355(4)	65(3)*
C(28)	4705(7)	2224(3)	2460(4)	53(2)*
C(29)	3845(9)	2600(4)	1793(4)	70(3)*
F(1)	−430(7)	1539(3)	2293(3)	52(2)*
F(2)	−2353(6)	1545(5)	1424(4)	137(5)*
F(3)	−443(11)	726(4)	1342(6)	85(4)*
F(4)	−33(10)	1906(4)	1111(4)	139(5)*
F(1′)	251(9)	1813(5)	1899(6)	77(5)*
F(2′)	−1922(10)	1806(5)	1194(4)	77(4)*
F(3′)	−304(16)	852(6)	1157(7)	85(7)*
F(4′)	−1671(13)	1085(6)	2188(5)	163(9)*
B	−875(6)	1405(3)	1569(3)	64(3)*

[a] Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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*Author to whom correspondence should be addressed.

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TABLE II. Selected Bond Distances and Angles for I

Bond lengths (Å)

Pd–N(1)	2.109(4)	Pd–C(12)	2.039(5)
Pd–C(18)	2.314(5)	Pd–C(19)	2.171(5)
Pd–F(1)	2.355(5)	Pd–F(1′)	2.315(10)
N(1)–C(2)	1.322(7)	N(1)–C(10)	1.380(7)
C(2)–C(3)	1.375(8)	C(3)–C(4)	1.366(8)
C(4)–C(5)	1.407(8)	C(5)–C(6)	1.410(8)
C(5)–C(10)	1.426(7)	C(6)–C(7)	1.355(8)
C(7)–C(8)	1.406(8)	C(8)–C(9)	1.372(8)
C(9)–C(10)	1.431(7)	C(9)–C(11)	1.509(7)
C(11)–C(12)	1.539(7)	C(12)–C(13)	1.519(7)
C(12)–C(15)	1.572(7)	C(13)–C(14)	1.518(8)
C(15)–C(16)	1.539(7)	C(15)–C(19)	1.542(8)
C(15)–C(20)	1.526(8)	C(16)–C(17)	1.341(7)
C(16)–C(22)	1.508(8)	C(17)–C(18)	1.492(8)
C(17)–C(24)	1.493(8)	C(18)–C(19)	1.381(8)
C(18)–C(26)	1.521(8)	C(19)–C(28)	1.524(9)
C(20)–C(21)	1.537(9)	C(22)–C(23)	1.515(10)
C(24)–C(25)	1.524(10)	C(26)–C(27)	1.520(9)
C(28)–C(29)	1.526(9)	F(1′)–B	1.337(10)
F(1)–B	1.336(7)	F(2′)–B	1.319(10)
F(2)–B	1.315(8)	F(3′)–B	1.334(13)
F(3)–B	1.345(9)	F(4′)–B	1.420(12)
F(4)–B	1.419(9)		

Bond angles (°)

N(1)–Pd–C(12)	91.3(2)	N(1)–Pd–C(18)	168.9(2)
C(12)–Pd–C(18)	90.9(2)	N(1)–Pd–C(19)	153.0(2)
C(12)–Pd–C(19)	66.5(2)	C(18)–Pd–C(19)	35.7(2)
N(1)–Pd–F(1)	88.2(2)	C(12)–Pd–F(1)	165.6(2)
C(18)–Pd–F(1)	87.0(2)	C(19)–Pd–F(1)	117.2(2)
N(1)–Pd–F(1′)	91.8(2)	C(12)–Pd–F(1′)	168.4(3)
C(18)–Pd–F(1′)	88.2(2)	C(19)–Pd–F(1′)	107.1(3)
F(1)–Pd–F(1′)	25.8(3)	Pd–N(1)–C(2)	117.1(4)
Pd–N(1)–C(10)	124.6(3)	C(2)–N(1)–C(10)	118.2(4)
N(1)–C(2)–C(3)	124.4(5)	C(2)–C(3)–C(4)	119.6(5)
C(3)–C(4)–C(5)	118.8(5)	C(4)–C(5)–C(6)	121.8(5)
C(4)–C(5)–C(10)	118.8(5)	C(6)–C(5)–C(10)	119.4(5)
C(5)–C(6)–C(7)	120.5(5)	C(6)–C(7)–C(8)	120.2(6)
C(7)–C(8)–C(9)	122.3(5)	C(8)–C(9)–C(10)	118.1(5)
C(8)–C(9)–C(11)	118.1(5)	C(10)–C(9)–C(11)	123.8(5)
N(1)–C(10)–C(5)	120.2(4)	N(1)–C(10)–C(9)	120.4(4)
C(5)–C(10)–C(9)	119.5(5)	C(9)–C(11)–C(12)	115.4(4)
Pd–C(12)–C(11)	101.1(3)	Pd–C(12)–C(13)	111.7(3)
C(11)–C(12)–C(13)	113.3(4)	Pd–C(12)–C(15)	95.7(3)
C(11)–C(12)–C(15)	117.0(4)	C(13)–C(12)–C(15)	115.3(4)
C(12)–C(13)–C(14)	115.8(5)	C(12)–C(15)–C(16)	109.7(4)
C(12)–C(15)–C(19)	95.8(4)	C(16)–C(15)–C(19)	102.6(4)
C(12)–C(15)–C(20)	117.8(4)	C(16)–C(15)–C(20)	112.9(5)
C(19)–C(15)–C(20)	115.9(5)	C(15)–C(16)–C(17)	110.0(5)
C(15)–C(16)–C(22)	122.9(5)	C(17)–C(16)–C(22)	126.9(5)
C(16)–C(17)–C(18)	109.1(5)	C(16)–C(17)–C(24)	128.5(5)
C(18)–C(17)–C(24)	122.4(5)	Pd–C(18)–C(17)	100.6(3)
Pd–C(18)–C(19)	66.5(3)	C(17)–C(18)–C(19)	110.1(5)
Pd–C(18)–C(26)	115.8(4)	C(17)–C(18)–C(26)	122.1(5)
C(19)–C(18)–C(26)	125.0(5)	Pd–C(19)–C(15)	91.5(3)
Pd–C(19)–C(18)	77.8(3)	C(15)–C(19)–C(18)	107.5(5)
Pd–C(19)–C(28)	113.5(4)	C(15)–C(19)–C(28)	123.9(5)

(continued)

TABLE II. *(continued)*

C(18)–C(19)–C(28)	125.9(5)	C(15)–C(20)–C(21)	112.7(5)
C(16)–C(22)–C(23)	115.0(5)	C(17)–C(24)–C(25)	112.7(5)
C(18)–C(26)–C(27)	110.6(5)	C(19)–C(28)–C(29)	117.3(5)
Pd–F(1)–B	141.9(4)	Pd–F(1′)–B	146.1(7)
F(1)–B–F(2)	113.7(5)	F(1)–B–F(3)	111.8(6)
F(2)–B–F(3)	113.0(7)	F(1)–B–F(4)	106.4(5)
F(2)–B–F(4)	105.9(6)	F(3)–B–F(4)	105.4(6)
F(1′)–B–F(2′)	113.0(7)	F(1′)–B–F(3′)	111.9(8)
F(1′)–B–F(4′)	104.7(7)	F(2′)–B–F(3′)	113.5(7)
F(2′)–B–F(4′)	105.6(7)	F(3′)–B–F(4′)	107.4(7)

were refined anisotropically; hydrogen atoms were treated as idealized isotropic contributions. The F atoms of tetrafluoroborate were disordered over two sites (refined occupancies unprimed F atoms, 63(1)%; primed F atoms 37(1)%). At convergence: R_F = 4.32%, R_{wF} = 4.68%, *GOF** = 1.257, Δ/σ = 0.08, $\Delta(\rho)$ = 0.41 e Å^{-3}, and N_o/N_v = 8.4. Table I contains the atom coordinates, and Table II selected bond distances and angles. See also 'Supplementary Material'. All software was part of the SHELXTL (5.1) Library (Nicolet Corp., Madison, Wis.).

Discussion

The insertion of three moles of 3-hexyne to cyclopalladated 8-methylquinoline tetrafluoroborate leads to the formation of **I** containing a 5-substituted pentaethylcyclopentadiene, one double bond of which [C(18)–C(19)] forms an unusual single η^2-olefin bond to palladium. At the 5-position the exocyclic half of an alkyne molecule has formed a σ bond to the formerly Pd-bonded methylene of the 8-methylquinoline residue. The essentially square-planar Pd(II) coordination environment consists of the α carbon of the exocyclic alkyne positioned *trans* to a coordinated BF_4 group, and the quinoline N atom *trans* to the coordinated olefin.

The C(15) to C(19) cyclopentadiene system is planar, maximum deviation 0.016 Å, and the double bonds are localized; the coordinated double bond, C(18)–C(19) 1.381(8) Å, is expectedly somewhat longer than the free double bond, C(16)–C(17) 1.341(7) Å. The Pd–C (olefin) distances are distinctly different: Pd–C(18), 2.314(5) Å and Pd–C(19), 2.171(5) Å; these values are very similar to those found in $C_5Me_5CH(p\text{-tolyl})CH_2Pd(acac)$ (**II**): 2.30(2) and 2.13(2) Å [3]. The Pd–C σ bond distance 2.039(5) Å is similar to the corresponding bond in **II** [2.03(1) Å] [3].

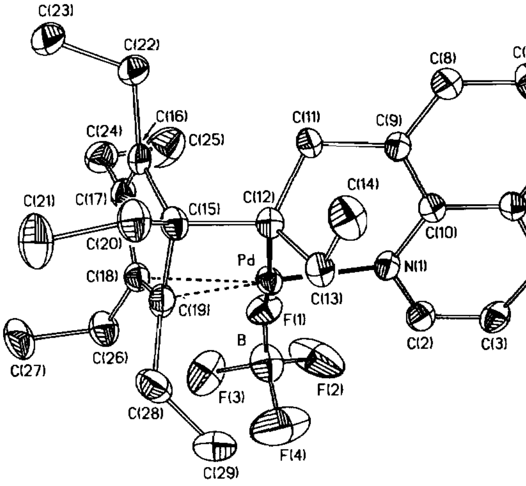

Fig. 1. Molecular structure and labeling scheme for **I** with 40% probability ellipsoids and omission of hydrogen atoms. The F atoms of tetrafluoroborate are disordered; only the majority positions are shown.

We have found no precedent for organometallic compounds of Pd or Pt containing coordinated tetrafluoroborate. Although tetrafluoroborate is disordered with two sets of fluorine atoms in a 63/37 ratio, the two sets are structurally very similar. The majority set, shown in Fig. 1, has a Pd–F distance of 2.355(5) Å; this is considerably longer than the Pd–F distance (2.15 Å) in octahedrally coordinated PdF_2 [4]. The Pd–C(12) and Pd–N(1) distances are normal.

None of the distances or angles in the saturated C(15)–C(12)–C(11)–C(9) chain show evidence of strain in the formation of the six-membered metallacycle.

Supplementary Material

The anisotropic thermal parameters, H-atom parameters and the observed and calculated structure factors have been deposited with the Editor-in-Chief.

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*Goodness of fit.

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