Notes

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Alkyne Insertion into the Pd–C Bond of a Metallacycle Stabilized by a Weak O→Pd Bond Leading to an Unusual (η^2-Aryl)→Pd Interaction.[1] Molecular Structure of $[NC_9H_6CH_2C(CF_3){=}C(CF_3)]Pd[C(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6)OCH_3]$

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Complexes containing cyclopalladated amines have been shown to be useful starting materials for the selective syntheses of carbon–carbon bonds and, in some cases, carbon–nitrogen bonds.[3,4] These compounds react with a great variety of electrophilic or nucleophilic reagents, our contribution in this field being mainly concentrated on the reactivity of their Pd–C bonds toward internal alkynes.[4b,5] We have already shown that these reactions can occur in different ways depending on the nature of the cyclopalladated ligands. During these studies we came to the conclusion that, prior to insertion, the alkyne should be linked to Pd within its coordination plane after one N→Pd bond has been broken.[5] We have recently synthesized new cyclopalladated compounds with the 1-methoxynaphth-8-yl chelate (MXN) in which the intramolecular O→Pd bond has been shown to be rather labile.[6] We though therefore that the Pd–C bonds of these complexes should display an enhanced reactivity when compared to those of the corresponding compounds in which the donor atom is nitrogen, and we have indeed already reported that a large variety of reagents readily react with bis(1-methoxynaphth-8-yl)palladium(II) to afford new pathways to carbon–carbon bond formation.[7] We report here that, as anticipated, compounds of type **1** react readily with hexafluorobut-2-yne (Hfb), leading to organometallic compounds via insertion of the alkyne into the Pd–C bonds. These new complexes have an unprecedented geometry.

Experimental Section

The reaction conditions and physical measurements were performed as described in a previous paper.[5] The starting compounds **1a–c** were prepared by published methods.[6] NMR data are summarized in Table I.

Syntheses. $[NC_9H_6CH_2C(CF_3){=}C(CF_3)]Pd[(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6)OCH_3]$ **(2a).** Hexafluorobut-2-yne (2.5 mmol) was condensed in vacuo at −196 °C in a Schlenk tube containing a solution of compound **1a** (0.405 g, 1 mmol) in toluene (30 mL). As soon as the temperature of the solution reached 20 °C, it turned red. The solvent was then removed in vacuo; the residue was washed with pentane (30 mL) and dissolved in toluene (20 mL). Addition of pentane to this solution afforded compound **2a** as white crystals after 24 h at −20 °C (0.120 g, 14%). Crystals suitable for the X-ray structure determination were obtained from a CH_2Cl_2–pentane solution.

Anal. Calcd for $C_{29}H_{17}F_{12}NOPd$: C, 47.71; H, 2.33; N, 1.92. Found: C, 48.08; H, 2.33; N, 1.97.

$[NC_{13}H_8C(CF_3){=}C(CF_3)]Pd[C(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6)OCH_3]$ **(2b) and** $[NMe_2C_{10}H_6C(CF_3){=}C(CF_3)]Pd[C(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6)OCH_3]$ **(2c).** The procedure used for the syntheses of **2b** and **2c** followed that used for **2a**, starting from **1b** and **1c**, respectively. Compounds **2b** and **2c** were obtained as white and yellow crystals in 51% and 8% yields, respectively.

Anal. Calcd for $C_{32}H_{17}F_{12}NOPd$ (**2b**): C, 50.16; H, 2.22; N, 1.83. Found: C, 50.18; H, 2.87; N, 2.43.

Anal. Calcd for $C_{31}H_{21}F_{12}NOPd$ (**2c**): C, 49.11; H, 2.27; N, 1.84. Found: C, 49.78; H, 2.79; N, 1.81.

$[NMe_2C_{10}H_6C(CF_3){=}C(CF_3)]COPd[C(CF_3){=}C(CF_3)(\eta^2\text{-}C_{10}H_6)OCH_3]$ **(3).** Carbon monoxide was bubbled through a solution of compound **2c** (0.120 g, 0.16 mmol) in toluene (15 mL). The solution immediately turned lemon yellow, and some metallic palladium was formed. The solution was then stirred for 3 h and filtered, and pentane (20 mL) was added to the filtrate. After 24 h at −78 °C yellow crystals of **3** were obtained (0.057 g, 46%). In the solid state at room temperature **3** lost its CO over a period of 10 days to afford **2c** quantitatively.

Anal. Calcd for $C_{32}H_{21}F_{12}NO_2Pd$ (**3**): C, 48.89; H, 2.67; N, 1.78. Found: C, 48.70; H, 2.60; N, 1.80. IR ν(CO) (KBr, pellet): 2130 cm^{-1}.

X-ray Structure Determination. Crystals of compound **2a** are monoclinic, space group $P2_1/n$, $Z = 4$, with cell constants $a = 11.715$ (1) Å, $b = 20.473$ (7) Å, $c = 11.453$ (1) Å, $\beta = 93.28$ (1)°, $V = 2742.4$ (7) Å^3, μ(Cu Kα) = 65.9 cm^{-1}, and $d_{calcd} = 1.76$ g cm^{-3}. A total of 4810 intensities were measured on a Nonius CAD4 diffractometer employing graphite-monochromated Cu Kα radiation ($2.5 < \theta < 65°$; h −13 to 13, k 0–24, l 0–13; crystal dimensions 0.15 × 0.2 × 0.2 mm). A total of 987 intensities were below the $2.5\sigma(I)$ level and were treated as unobserved. The structure was solved by means of the heavy-atom method. After isotropic block-diagonal least-squares refinement, an empirical absorption correction was applied[8] and the refinement was continued anisotropically. A difference Fourier synthesis indicated the H atoms but in addition showed disorder for the group C(8)F(10)F(11)F(12); F(11) is split and F(10) and F(12) are elongated. No attempts to fit a model to the disorder were made. After the H atoms were introduced with isotropic temperature parameters, continued refinement converged to $R = 0.042$ ($R_w = 0.066$). The anomalous dispersion of Pd was taken into account, and a weighting scheme, $w = 1/(7.1 + F_o + 0.07F_o^2)$, was applied. The calculations were carried out with XRAY76.[9] The scattering factors and the dispersion correction were taken from ref 10 and 11, respectively.

Results and Discussion

Treating toluene solutions of **1a–c** with an excess of Hfb led to almost instantaneous reactions at room temperature, affording compounds **2a–c**, respectively, in moderate to good yields. The rather low yield of these compounds in the case of the reactions with **1a** and **1c** can be explained by the fact that other organometallic products are formed during the reaction but their syntheses and purification were only slightly reproducible. Therefore we do not describe them in this paper. They seemed however to contain, in both cases, only one Hfb per Pd atom

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[1] Reactivity of Cyclopalladated Compounds. 14. Part 13: see ref 3.

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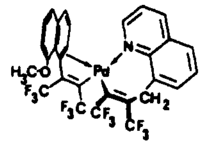
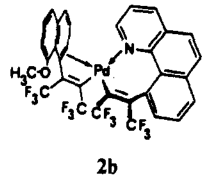
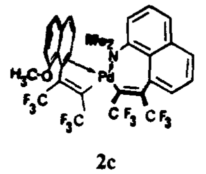
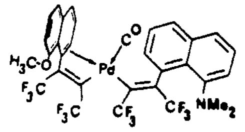
Table I. NMR Data for Compounds **2** and **3**

compds	^{1}H NMR[a]					^{19}F NMR[b] CF$_3$
	H24[c]	H25	H26	OCH$_3$	others	
 **2a**	7.23	6.51	7.10	4.07	8.09 (H17) 6.85 (H16) 6.04 (H15) 6.33, 4.18 (dd, CH$_2$ of 8-mq, $^2J_{HH}$ = 14.8)	52.35 (m, $^5J_{FF}$ = 12.5, $^6J_{FF}$ = 5.5) 54.24 (m, $^5J_{FF}$ = 10.3, $^6J_{FF}$ = 5.5) 60.05 (q, $^5J_{FF}$ = 12.5) 63.16 (q, $^5J_{FF}$ = 10.3)
 **2b**	6.84	5.50	6.23	4.04	6.47 (H ortho to the N of the Bhq ring)	53.22 (m,br) 57.57[d] (m,br) 64.42 (q, $^5J_{FF}$ = 10.3)
 **2c**	*e*	6.47	6.26	3.96	2.41 (NCH$_3$) 1.52 (NCH$_3$)	52.04 (m, $^5J_{FF}$ = 13, $^6J_{FF}$ = 6) 55.86 (q, $^5J_{FF}$ = 13) 56.40 (m, $^5J_{FF}$ = 11.2, $^6J_{FF}$ = 6) 63.09 (q, $^5J_{FF}$ = 11.2)
 **3**	6.70	6.42	6.00	3.96	2.73 (NCH$_3$) 2.70 (NCH$_3$)	*f*

[a] In CDCl$_3$ at 20 °C. δ relative to internal Me$_4$Si; J in Hz. [b] In CDCl$_3$ at 20 °C. Chemical shifts positive upfield relative to external CFCl$_3$. [c] The numbering of the protons follows that indicated in Figure 1. [d] This signal corresponds to two CF$_3$ groups. [e] Not observed. [f] Not recorded.

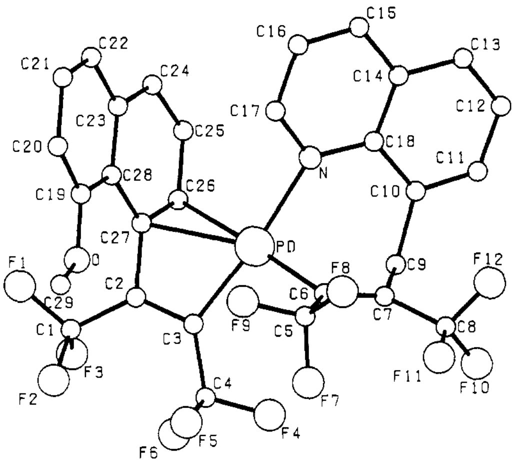
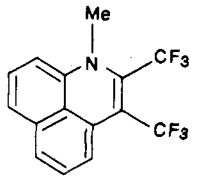


Figure 1. Pluto drawing of compound **2a**.

instead of two in compounds **2** (see later). We have determined moreover that the reaction between **1a** and Hfb occured with decomposition since about 60% of the methoxynaphthyl unit was recovered as an organic dimer (MXN)$_2$[7] via a coupling reaction of two palladated MXN units. This rapid reaction of compounds **1** toward Hfb is in marked contrast to what has been described earlier with bicyclic compounds in which both three-electron-donor chelates had a nitrogen as the donor atom.[5] In these latter cases the reaction was complete only after ca. 4–24 h. Thus, the introduction of one labile O→Pd bond has had a dramatic effect, as far as the kinetics are concerned, upon the reactivity of both metal–carbon σ bonds of compounds **1**.

Compounds **2** display the usual spectroscopic features of related bicyclic compounds in which two alkyne molecules have been inserted into their Pd–C bonds.[5] The ^{19}F NMR spectra for instance are particularly diagnostic of the structure invoked: the CF$_3$ groups are inequivalent, leading to a $^5J_{FF}$ value (ca. 12 Hz) that is characteristic of such a grouping cis-positioned on an alkene unit. It is moreover possible to detect for **2b** and **2c** another coupling constant of ca. 6 Hz, which most likely should involve the two CF$_3$ groups located at the two carbon atoms bonded to the Pd. This coupling constant should therefore be of a $^6J_{FF}$ type. The ^{1}H NMR spectra of compound **2c** show unambiguously that the nitrogen atom of the dimethylnaphthylamine ligand(Dman) is bound to palladium since two well-separated signals are found for the NMe$_2$ unit. This diastereotopicity is obviously due to the nonplanarity of the seven-membered ring that resulted from the insertion of one Hfb molecule into the Pd–C bond of the palladated Dman in **1c**. This is, by the way, the first time that we have been able to isolate an organometallic intermediate by reaction of an Hfb molecule with a "Pd(Dman)" unit: all attempts made previously[4b,5] always led to the formation of an heterocyclic product by formation of a N–C bond and partial demethylation of the nitrogen atom.



In all three compounds of type **2** the chemical shifts of the methoxy group of the methoxynaphthyl unit (ca 4.0 ppm) are close to what was found in parent compounds where the oxygen atom is noncoordinated to Pd.[6] This would leave the palladium atom with only three σ-bonded atoms, and therefore an X-ray structure determination has been carried out on compound **2a** in order to determine how this metal can cope with this rather unusual situation.

An ORTEP view of the molecular structure of **2a** is shown in Figure 1 together with its numbering system. Atomic coordinates are given in Table II. Bond distances and angles are given in Table III.

This structure clearly shows that the insertion of one Hfb molecule has indeed taken place in each Pd–C bond of **1a**. This results in the formation of a seven-membered palladacyclic ring with the 8-mq ligand whose geometry has already been described

Table II. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for Compound **2a**

atom	*x*	*y*	*z*	U_{eq}, Å^2
Pd	0.03877 (3)	0.13463 (2)	0.18961 (3)	0.0297 (2)
C1	−0.2764 (5)	0.0545 (3)	0.0855 (5)	0.046 (3)
C2	−0.1643 (4)	0.0855 (2)	0.1256 (4)	0.032 (2)
C3	−0.0661 (4)	0.0588 (2)	0.1589 (4)	0.031 (2)
C4	−0.0461 (4)	−0.0131 (2)	0.1706 (4)	0.038 (3)
C5	0.1253 (5)	0.0665 (3)	0.4096 (5)	0.052 (3)
C6	0.1581 (4)	0.0880 (2)	0.2900 (4)	0.036 (2)
C7	0.2617 (4)	0.0849 (2)	0.2482 (5)	0.040 (3)
C8	0.3671 (5)	0.0548 (3)	0.3068 (6)	0.053 (3)
C9	0.2812 (4)	0.1160 (3)	0.1303 (5)	0.040 (3)
C10	0.3162 (4)	0.1876 (3)	0.1425 (4)	0.040 (3)
C11	0.4216 (5)	0.2071 (3)	0.1100 (6)	0.058 (4)
C12	0.4631 (6)	0.2708 (4)	0.1214 (7)	0.066 (4)
C13	0.3982 (6)	0.3170 (3)	0.1693 (6)	0.063 (4)
C14	0.2883 (5)	0.3007 (3)	0.2063 (5)	0.050 (3)
C15	0.2203 (6)	0.3479 (3)	0.2595 (6)	0.060 (4)
C16	0.1156 (6)	0.3309 (3)	0.2947 (7)	0.069 (4)
C17	0.0774 (5)	0.2678 (3)	0.2747 (6)	0.052 (3)
C18	0.2450 (4)	0.2363 (2)	0.1902 (4)	0.039 (3)
C19	−0.2583 (4)	0.1869 (3)	0.2929 (4)	0.044 (3)
C20	−0.2962 (6)	0.2339 (4)	0.3667 (5)	0.061 (4)
C21	−0.2870 (7)	0.3006 (3)	0.3382 (6)	0.071 (4)
C22	−0.2389 (6)	0.3197 (3)	0.2410 (6)	0.066 (4)
C23	−0.1940 (5)	0.2726 (3)	0.1630 (5)	0.049 (3)
C24	−0.1343 (6)	0.2928 (3)	0.0663 (6)	0.058 (4)
C25	−0.0829 (5)	0.2481 (3)	−0.0035 (5)	0.053 (3)
C26	−0.0924 (4)	0.1809 (3)	0.0219 (5)	0.042 (3)
C27	−0.1550 (4)	0.1580 (2)	0.1131 (4)	0.033 (2)
C28	−0.2059 (4)	0.2053 (2)	0.1892 (4)	0.038 (3)
C29	−0.2936 (6)	0.0980 (4)	0.4233 (6)	0.069 (4)
N	0.1353 (3)	0.2215 (2)	0.2229 (4)	0.037 (2)
O	−0.2662 (4)	0.1224 (2)	0.3116 (4)	0.056 (2)
F1	−0.3634 (3)	0.0970 (2)	0.0828 (4)	0.066 (2)
F2	−0.3066 (3)	0.0050 (2)	0.1542 (4)	0.070 (2)
F3	−0.2748 (3)	0.0307 (2)	−0.0221 (3)	0.065 (2)
F4	0.0631 (3)	−0.0301 (2)	0.1646 (4)	0.063 (2)
F5	−0.0794 (4)	−0.0375 (2)	0.2705 (3)	0.066 (2)
F6	−0.1005 (3)	−0.0489 (2)	0.0854 (3)	0.064 (2)
F7	0.1299 (5)	0.0014 (2)	0.4226 (4)	0.100 (3)
F8	0.1894 (5)	0.0902 (3)	0.4947 (3)	0.129 (4)
F9	0.0189 (4)	0.0801 (3)	0.4289 (4)	0.106 (4)
F10	0.4192 (7)	0.0186 (4)	0.2439 (7)	0.195 (7)
F11	0.3546 (5)	0.0230 (6)	0.3979 (9)	0.255 (9)
F12	0.4426 (5)	0.0971 (3)	0.3370 (8)	0.164 (6)

Table III. Selected Bond Lengths (Å) and Angles (deg) for Compound **2a**

Pd–C3	1.998 (3)	C6–C7	1.331 (5)
Pd–C6	2.001 (3)	C7–C9	1.522 (5)
Pd–C26	2.571 (4)	C9–C10	1.526 (5)
Pd–C27	2.433 (3)	C10–C18	1.428 (5)
Pd–N	2.130 (3)	C18–N	1.392 (5)
C2–C3	1.311 (4)	C26–C27	1.392 (5)
C2–C27	1.496 (5)		
C3–Pd–C6	97.6 (2)	Pd–C6–C7	115.9 (3)
C3–Pd–C26	79.6 (2)	C6–C7–C9	119.0 (4)
C3–Pd–C27	62.5 (2)	C7–C9–C10	111.9 (4)
C6–Pd–C26	166.7 (1)	C9–C10–C18	123.1 (4)
C3–Pd–N	174.1 (1)	C28–C19–O	115.6 (4)
C6–Pd–N	87.1 (2)	C2–C27–C28	124.7 (3)
C26–Pd–N	96.6 (2)	Pd–N–C28	128.5 (2)
C27–Pd–N	112.0 (2)	C19–O–C29	120.6 (4)
C3–C2–C27	112.0 (4)		
Pd–C3–C2	104.3 (3)		

for a related compound.[5] On the other hand the insertion of Hfb into the Pd–C bond of the Pd(MXN) unit in **1a** led to a completely different bonding scheme between the new ligand and the Pd atom. As the ^{1}H NMR spectra suggested, the oxygen atom of the methoxy group is not interacting with Pd(Pd$\cdots$O > 3.5 Å). C26 and C27 are found at 2.571 (4) and 2.433 (3) Å, respectively, from the Pd atom; the angle between the C26–C27 vector and the coordination plane of Pd, defined by Pd, N, C6, and C3, is 31°. Since C26 and C27 are roughly located at the fourth coordination site of Pd, it is reasonable to assume that there must be a bonding interaction between the naphthyl ring, through the C26–C27 double bond, and the Pd atom although the Pd–C26 and Pd–C27 bond distances are rather large for a conventional carbon–carbon double-bond π bonded to such a metal.[12]

Such an interaction has never been described before between an aryl ring and a Pd(II) atom although it has been postulated by Parshall as being a likely intermediate in the CH activation reaction of an arene by this metal.[13]

It is clear from the ^{1}H NMR spectrum of compound **2c** that this η^2-naphthyl to Pd interaction causes a significative upfield shift of the corresponding aromatic protons. Compounds **2c** can reversibly bind one molecule of carbon monoxide, affording compounds **3**. The ^{1}H NMR spectrum of this compound reveals that the NMe$_2$ grouping is no longer diastereotopic and hence the CO must have displaced this unit rather than the η^2-naphthyl$\rightarrow$Pd bond. The ortho, meta, and para protons of the part of the naphthyl group interacting with Pd are clearly found at higher frequency as compared with those of compound **1c**. This upfield shift is likely to be due to the presence of the Pd atom. The shielding effect that Pd causes upon the chemical shifts of the naphthyl protons is much less obvious in the case of compounds **2a** and **2b** because of the shielding effect that the naphthyl and the quinolyl rings exert on each other. For compound **2a**, for instance, H17 resonates at 6.04 ppm, i.e. at 2.5–3.0 ppm higher that in any related compound containing the 8-mq chelate.[4b,5,6] This can be explained by the fact that this proton is located at 2.71 Å above the plane of the naphthyl ring, and therefore it experiences the shielding of this ring. A similar trend is found for compound **2b**, the proton ortho to the nitrogen being found also at an unusually high frequency.

Registry No. **1a**, 87370-34-1; **1b**, 87370-35-2; **1c**, 87370-36-3; **2a**, 106905-48-0; **2b**, 106905-49-1; **2c**, 106905-50-4; **3**, 106928-94-3; hexafluorobut-2-yne, 692-50-2.

Supplementary Material Available: An ORTEP stereoview of compound **2a** and Tables S1 and S2, listing the derived hydrogen positions and thermal parameters (3 pages); Table S3, listing calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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Electron Diffraction Reinvestigation of the Molecular Structure of Calcium Dihalides

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The present investigation of the molecular structure of calcium dihalides is a natural extension of our studies on first-row transition-metal dihalides (see Ref 2 and references therein). The alkaline-earth-metal dihalides themselves are also the subject of much recent structural interest. Qualitative models of bonding and structure,[3,4] empirical correlations,[4,5] semiempirical

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