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Preliminary communication

ADDITION OF HEXAFLUORO-2-BUTYNE TO PALLADIUM(II) β-DIKETONATO RINGS: THE CRYSTAL STRUCTURE OF THE ADDUCT $Pd(Acac)_2(C_4F_6)_2$

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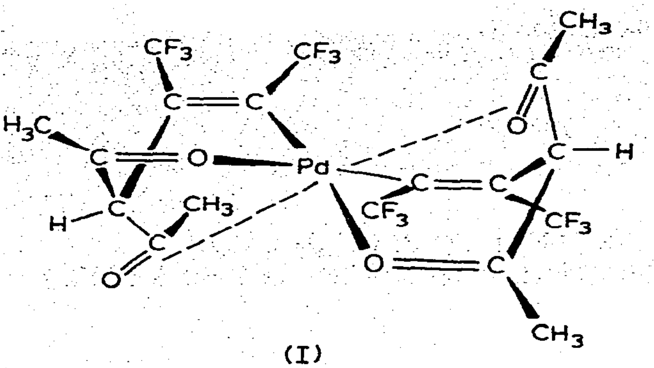
Summary

A crystal structure analysis shows that hexafluoro-2-butyne reacts with bis(acetylacetonato)palladium(II) to give $Pd[O{=}C(Me)CH(COMe)C(CF_3){=}C(CF_3)]_2$ in which the hexafluoro-2-butyne links the γ-CH of the β-diketonato ligands to the palladium. Other palladium(II) β-diketonato systems behave similarly.

Hexafluoro-2-butyne readily adds 1/4 to certain rhodium(I)-β-diketonato ring systems [1, 2]. Further studies now reveal that d^8 palladium(II) β-diketonato complexes undergo a similar addition reaction.

Hexafluoro-2-butyne reacts with bis(acetylacetonato)palladium(II) in benzene solution at 60°C to give cream crystals of an air-stable product $Pd(Acac)_2(C_4F_6)_2$ (I). The IR spectrum of (I) shows strong C=O absorptions at 1713, 1674 cm^{-1} and a weak C=C absorption at 1598 cm^{-1}. The ^{19}F NMR spectrum of (I) in benzene solution contains two quartets at −11.5 and −3.4 ppm (relative to benzotrifluoride) which may be assigned to the α- and β-CF_3 groups respectively of a vinylic system $Pd{-}C(C^{\alpha}F_3){=}C(C^{\beta}F_3)$, $J(F{-}F)$ 16Hz. The ^1H NMR spectrum of (I) in methylene chloride exhibits a single broad line in the methyl region at room temperature, which resolves to two signals (τ 7.33, 7.60) at −28 °C. An X-ray crystal structure determination reveals that (I) has the structure shown in Fig. 1.

Crystals of (I), $C_{18}H_{14}F_{12}O_4Pd$ (mol.wt. 628.7) are monoclinic, space group $P2_1/n$, with a 9.512, b 23.29, c 11.30Å, β 114.9°, U 2271Å^3, $Z = 4$. The intensities of reflexions with $\sin\theta/\lambda < 0.7$Å^{-1} were measured with an automated Stoe Weissenberg diffractometer using Mo-K_α radiation and a graphite monochromator. After correcting the data for Lorentz, polarisation and absorption effects, the structure was solved by conventional heavy atom methods. Block-diagonal least squares refinement of parameters, using anisotropic temperature factors for all non-hydrogen atoms, for the 4302 significant ($I \geqslant 3\sigma(I)$) reflexions converged with $R = 0.058$.



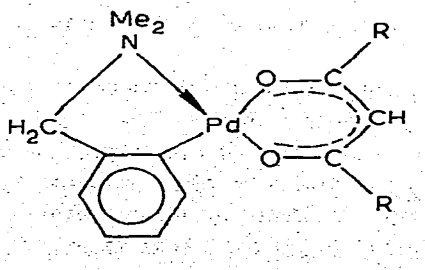
(I)

Fig. 1.

The palladium atom is essentially four-coordinate with two Pd—C bonds, averaging 1.993 ± 0.01 Å, and two Pd—O bonds, averaging 2.114 ± 0.01 Å, in a *cis*-square-planar arrangement. There is a slight tetrahedral distortion with the coordinating atoms lying alternately ± 0.09 Å from the mean plane. The second carbonyl groups of each β-diketone fragment occupy the remaining positions of a distorted octahedron, but at distances (Pd—C: 3.30, 3.28; Pd—O: 3.23, 3.43Å, in a sideways-on, or "π-bonding" orientation) which imply that any interaction must be very weak. This result contrasts with the structure of the 1/4 addition product of C_4F_6 with a Rh(Acac) ring [1], where both carbonyl groups of the β-diketone system are equally bound to the metal atom.

The proximity of the non-bonded carbonyl groups to the palladium atom suggests a possible mechanism for the facile process whereby the methyl groups of the Acac group become equivalent in the ^{1}H NMR spectrum. Initially the non-bonded carbonyl groups rotate to shorten the Pd—O distance forming an octahedral intermediate. A trigonal twist about the palladium atom followed by reversal of the initial process produces an equivalent structure with the methyl groups interchanged.

Reactions leading to similar addition products also occur with other β-diketonato complexes (II). Thus hexafluoro-2-butyne reacts with (IIa) and (IIb) to give the products (IIIa) and (IIIb) respectively, formulated from spectroscopic data. The ^{1}H NMR spectrum of (IIIa) exhibits a broad resonance between τ 7.2 - 7.7 for the methyl resonances of the NMe_2 and Acac groups. At -6°C the resonance splits into four signals at τ 7.22, 7.75 (NMe_2) and 7.43,



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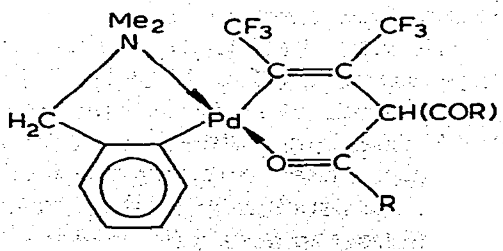
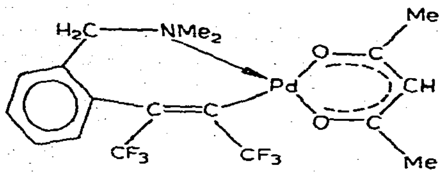
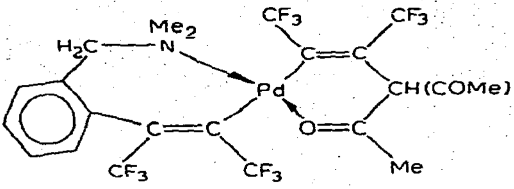
(IIb) R = t-Bu



(IIIa) R = Me
(IIIb) R = t-Bu



(IV)



(V)

7.63 (Acac). This behaviour is similar to that observed in (I) but in addition the *N,N*-dimethylbenzylamine ligand is also fluxional. In the reaction with (IIa), two further products (IV) and (V) can be isolated.

Acknowledgement

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References

1 D.M. Barlex, J.A. Evans, R.D.W. Kemmitt and D.R. Russell, Chem. Commun., (1971) 331.
2 D.M. Barlex, A.C. Jarvis, R.D.W. Kemmitt and B.Y. Kimura, J. Chem. Soc. Dalton Trans., (1972) 2549.