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PRELIMINARY COMMUNICATION

BIS(TRIFLUOROMETHYL)METHYLENE INSERTION INTO THE PALLADIUM–CHLORINE BOND

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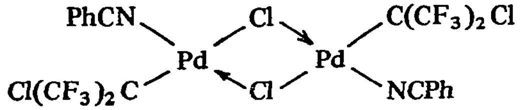
Recent studies[1] have shown that the reaction of bis(trifluoromethyl)diazomethane with transition metal complexes can lead to the insertion of the $(CF_3)_2C$ group into metal–hydrogen and into metal–metal bonds. Some of these reactions may involve reaction of the electrophilic carbene, bis(trifluoromethyl)methylene and, as such, are of considerable interest. Here we report on the insertion of $(CF_3)_2C$ into a metal–chlorine bond. In a recent communication[2] on the reaction of $CNCHN_2$ with $[Ph_3PPdCl_2]_2$ it was suggested that cyanomethylene insertion into the Pd–Cl bond occurs. However, the polymeric nature of the product limited structural studies.

A solution of bis(benzonitrile)palladium dichloride in methylene chloride reacts at room temperature with $(CF_3)_2CN_2$ to form the complexes (I) and (II). The yellow crystalline complex (I), m.p. 170° (dec.) (Found: C, 35.0; H, 1.5; F, 32.4; N, 4.2. $C_{20}H_{10}N_2F_{12}Cl_2Pd$ calcd.: C, 35.1; H, 1.5; F, 32.8; N, 4.1%) showed a sharp singlet ^{19}F NMR resonance at 62.3 ppm (rel. to CCl_3F 0.0 ppm), and no Pd–Cl bands in the infrared spectrum in the range 600–200 cm^{-1}. Thus (I) may be assigned the illustrated structure, and is formed by insertion of $(CF_3)_2C$ into both Pd–Cl bonds of $(C_6H_5CN)_2PdCl_2$.

$(PhCN)_2Pd[C(CF_3)_2Cl]_2$

(I)



(II)

The orange crystalline complex (II), m.p. 140° (dec.) (Found: C, 28.3; H, 1.2; Cl, 16.9; N, 3.4; mol.wt. 810 ($CHCl_3$). $C_{20}H_{10}Cl_4F_{12}N_2Pd_2$ calcd.: C, 28.0; H, 1.2; Cl, 16.6; N, 3.3%; mol.wt. 860) had a sharp ^{19}F NMR resonance at 62.9 ppm, and may be depicted as a binuclear chloride bridged system. Benzonitrile is readily displaced from both complexes by a variety of ligands.

The stability of (I) and (II), which contain a carbon to palladium σ-bond and no stabilizing π-acceptor ligands, illustrates the stabilizing influence of the electronegative trifluoromethyl groups.

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