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The Preparation of $((C_6H_5)_3P)_2Pt[n^2-(-C=C(CF_2)_2)_3]$ and $(C_6H_5)_3\underset{+}{P}-C=C(CF_2)_2C=COCF_2CO$

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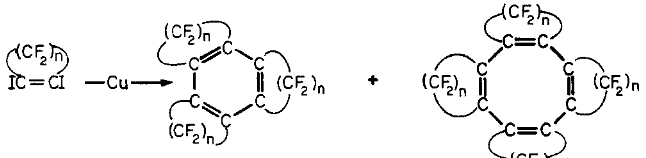
SUMMARY

The title compounds are prepared by reacting tetrakistriphenylphosphine·platinum(0) with perfluorobenzo[1,2:3,4:5,6]tricyclobutene, and triphenylphosphine with 2,2'-dichloro(perfluorobicyclobuten-1-yl).

Coupling of 1,2-diiodoperfluorocycloalkenes with copper affords a number of interesting trimers, 1 and tetramers 2, [1,2].



1a n=2
1b n=3

2a n=2
2b n=3

Both 1a and 2a are planar molecules [3-5], the latter unexpectedly so, and all should have very interesting chemical properties.

The trimer 1a reacts with tetrakistriphenylphosphineplatinum in benzene solution to displace two moles of phosphine as evidenced by the analytical data for the resulting yellow solid. The structure as determined by X-ray techniques [6] is shown in 3. The coordination around the

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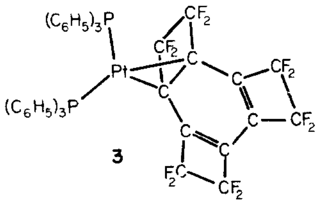
platinum is almost planar and the η^2-bonding of 1a results in a bending back of the $(CF_2)_2$ group of the coordinated cyclobutene group. The angle between the 6-membered ring and the 4-membered one is 51°. If this structure is preserved in solution the ^{19}F n.m.r. spectrum would be expected to be quite complicated and indeed it is so. Moreover the spectrum is essentially temperature invariant from -60°C to +95°C.



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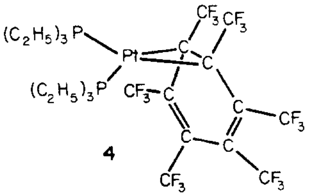


4

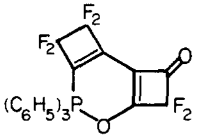
A similar molecule 4 can be obtained from hexakistrifluoromethyl benzene [7,8]. It is bound by an η^2-moiety with concomitant localization of the other two double bonds as in 3. However, the n.m.r. spectrum of 4 shows one ^{19}F resonance at 30°C and a limiting spectrum is not reached on cooling to -90°C. Thus there is an easy path for metal migration around the ring [7].

The trimer 1a is aromatic in the sense that the bond lengths in the 6-membered ring are equal [3,4]. However, fluxionality in 3 would probably result in considerable bond reorganization including a localization of double bonds between the four membered rings. Arguments can be made in favor of contributions from structures with such exocyclic double bonds to the ground state of 1a. However, the determined structure offers littl support. Binding through the localized double bonds of such a cannonical form would result in considerable strain in the ligand.

It should be pointed out that $Rh(\eta^5-C_5H_5)$ $(\eta^4-C_6(CF_3)_6)$ is rigid at 30°C [9] but nickel derivatives of the type $Ni((C_6H_5)_3P)_2(\eta^4-C_6(CF_3)_6)$ are fluxional even at -90°C [10].

Although the displacement reaction to prepare 3 was successful, similar reactions involving tetrakistriphenylphosphineplatinum and a number of fluorocarbon derivatives produced very complex mixtures of products. One source of the problem was found to be a facile reaction of the displaced triphenylphosphine with the unreacted fluorocarbon. Consequently, some of these side reactions have been studied in isolation. Thus when triphenylphosphine and 2,2'-dichloro(perfluorobicyclobuten-1-yl) are mixed in ether or benzene an immediate reaction accompanied by dramatic color changes occurs. However, the products defied characterization apart from triphenylphosphine oxide.

In the belief that unstable phosphonium compounds or ylids are initially produced, the reactions were carried out in acetic acid in an attempt to trap a product. The ultimately successful conditions are given in the experimental section. (Triphenylarsine does not react under identical conditions). The analytical and spectroscopic data suggest that the product could be either the zwitter ion 6 or the heterocycle 5, and the work of Birum and Matthews [11] offers a precedent for a cyclic structure like 5.



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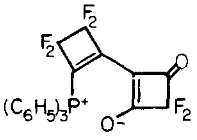

6

The ^{19}F spectrum of the product indicates a $\underset{|}{C}F_2$-$\underset{|}{C}F_2$ $\underset{|}{C}O$-$\underset{|}{C}F_2$ sequence and the ^{31}P spectrum which is actually an overlapping triplet of triplets (J(P,F) = 14 and 7Hz) shows that the phosphorus atom is attached to the ring with the $\underset{|}{C}F_2$-$\underset{|}{C}F_2$ moiety.

The X-ray structure [12] is conclusively that of 6 with the negative charge being extensively delocalized over the whole fluorocarbon group. Thus the structure is analogous to that proposed for the product obtained in a similar way from the reaction of pyridine and 2,2'-dichloro(perfluorobicyclobuten-1-yl) [13].

EXPERIMENTAL

Reaction of 1a with tetrakistriphenylphosphineplatinum(0)

The platinum complex (1.24g, 1 mmol) and 1a (0.37g, 1 mmol) were dissolved in benzene (10 mL) and sealed in a Carius tube. The solution turned dark red after 24h at room temperature. The solvent was removed and the solid residue was dissolved in a minimum amount of dichloromethane and chromatographed on a Florisil column. Elution with dichloromethane gave a yellow band. Removal of solvent afforded bright yellow crystal of the product (0.7g) $((C_6H_5)_3P)_2Pt[\eta^2\text{-}(\text{-}C{=}C(CF_2)_2)_3]$ (n.c.) m.p. 210°. Anal. Calcd. for $C_{48}H_{30}F_{12}P_2Pt$: C, 52.8, H, 2.8. Found: C, 53.1, H, 2.9. Spectral data included: ^1H n.m.r., 7.2 (multiplet broad). ^{19}F n.m.r., broad multiplets at - 85.9 and -107.8 ppm. The former shows Pt, F coupling.

Reaction of triphenylphosphine with 2,2'-dichloro(perfluorobicyclobuten-1-yl)

Into a 15 mL Schlenk tube was added a small magnetic bar, 8.9 mL of glacial acetic acid, 0.2 mL H_2O and 0.35 g (1.10 mmol) of 2,2'-dichloro(perfluorobicyclobuten-1-yl). The solution was vacuum degassed then purged with nitrogen. Triphenylphosphine (0.43g, 1.65 mmol) was rapidly added to give a bright yellow solution which turned to a clear light red solution within a few minutes. After 24h at room temperature the stirred reaction mixture was filled with a white precipitate. All solvents were removed under vacuum and the light yellow solid residue was extracted repeatedly with ether to remove 0.025g of unreacted triphenylphosphine and triphenylphosphine oxide. The yellow solid was then recrystallized once from $CHCl_3$ then from mixture of $CHCl_3/CH_2Cl_2$ to give 0.50g (91%) of pale yellow flat crystals of $(C_6H_5)_3\underset{+}{P}\text{-}C{=}C(CF_2)_2C{=}C\underset{-}{O}CF_2CO$ (mp, 277.5-279.0 sl. dec.) Anal. Calcd. for $C_{26}H_{15}O_2F_6P.CHCl_3$: C, 52.01%; H, 2.58%. Found C, 52.71%; H, 2.42%. (n.c.)

The purified product submitted to high resolution mass spectrum analysis gave the molecular ion 504.0716 (52.78%) corresponding to $C_{26}H_{15}O_2F_6P$ and a base peak at 475.0689 (100%) corresponding to the loss of CHO from the molecular ion. Other spectral data included: ^{19}F n.m.r., multiplets at -101.97 (2F) and -112.51 ppm (2F) and a singlet at -120.67 ppm; ^{31}P n.m.r., septet +9.83 ppm (H_3PO_4 int standard).

ACKNOWLEDGMENTS

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