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Facile Cyclotrimerization of $CF_3C{\equiv}CH$ and $CF_3C{\equiv}CCF_3$ with Bimetallic Rhodium Catalysts.

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Abstract: Complexes with the formulation $[\{Rh(\mu\text{-}SR_F)(C_8H_{12})\}_2]$ (R_F= C_6F_5 **1**, C_6F_4H-*p* **2** and C_6H_4F-*p* **3**) have been used as catalyst precursors for the cyclotrimerization of $CF_3C{\equiv}CH$ and $CF_3C{\equiv}CCF_3$ at room temperature and under atmospheric pressure. Copyright © 1996 Elsevier Science Ltd

The introduction of fluorinated substituents into an aromatic ring is known as a complex nonselective process.[1, 2] Hexafluorobut-2-yne, the most extensively investigated example of these systems,[3] forms a cyclic trimer; however, severe conditions are usually required, for instance, temperatures around 375°C.[4] Recent studies in the field[5] have reported cyclotrimerization of perfluoroalkylacetylenes and perfluoro-oxaalkylacetylenes under a variety of severe conditions.

In the present work we have studied the cyclotrimerization of perfluoroalkylacetylenes ($CF_3C{\equiv}CH$ and $CF_3C{\equiv}CCF_3$) for the synthesis of hexakis(trifluoromethyl)benzene, $C_6(CF_3)_6$ and 1,3,5tris(trifluoromethyl)-benzene, 1,3,5-$C_6H_3(CF_3)_3$ in nearly quantitative yields under significantly milder conditions.

The basic experimental strategy was the use of transition metal complexes of the type $[\{Rh(\mu\text{-}SR_F)(C_8H_{12})\}_2]$ (R_F= C_6F_5 **1**, C_6F_4H-*p* **2** or C_6H_4F-*p* **3**).[6, 7] Recently these compounds have been described as promoters of acetylene polymerization reactions by Ogawa *et al.*[8]

Results and Discussion.[9]

Cyclotrimerization of 1,1,1-trifluoropropyne and 1,1,1,4,4,4-hexafluorobut-2-yne.

The reaction of benzene solutions of $[\{Rh(\mu\text{-}SC_6F_5)(COD)\}_2]$ **1**, $[\{Rh(\mu\text{-}SC_6F_4H\text{-}4)(COD)\}_2]$ **2** or $[\{Rh(\mu\text{-}SC_6H_4F\text{-}4)(COD)\}_2]$ **3** with gaseous 1,1,1-trifluoropropyne or 1,1,1,4,4,4-hexafluorobut-2-yne causes an immediate darkening of the reddish solutions and the formation of 1,3,5-$C_6H_3(CF_3)_3$ or $C_6(CF_3)_6$, respectively. The starting rhodium complexes were recovered unchanged in all cases. The course as well as the products from these reactions seem to be independent of the initial concentration of the fluorinated acetylene, and the conversion to both trimers are continuous as long as acetylenes are fed into the reactor. Yields of several grams of the trimers have been obtained from 1 to 2 hours of reaction. Results are summarized in Table 1.

Table 1. Cyclization Yields.

Catalyst	Yield of $C_6(CF_3)_6$*	Yield of 1,3,5-$C_6H_3(CF_3)_3$*
[{Rh(μ-SC_6F_5)(COD)}$_2$] **1**	96	91
[{Rh(μ-SC_6F_4H-*p*)(COD)}$_2$] **2**	92	90
[{Rh(μ-SC_6H_4F-*p*)(COD)}$_2$] **3**	88	87

*Defined as acetylene conversion to trimer by unit of time. All results determined at room temperature (20°C), in benzene solutions, reaction time 1h.

In all cases the reaction is too fast to be followed to any significative extent by ^{19}F-NMR spectroscopy at room temperature. No intermediate products have been detected even when the reaction has been conducted at -40°C.

Mass spectra of both 1,3,5-$C_6H_3(CF_3)_3$ and $C_6(CF_3)_6$ show the expected parent ions and the successive loss of H, CF_3 and ring rupture reported previously.

Electronic variations have practically no consequences on the catalytic process. The cyclotrimerization reactions are essentially equivalent, and only minor changes in their velocities can be observed. Thus, velocities, measured as the time required to obtain equal yields follow the order: $C_6F_5 > C_6F_4H$-p $> C_6H_4F$-p.

Acknowledgments

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9) In a typical experiment, the rhodium catalyst (**1**, **2** or **3**) (0.018 mmol) was dissolved in 20 cm^{-3} of different distilled solvents in a range of polarities, namely: benzene, toluene and acetone. 1,1,1,4,4,4-hexafluorobut-2-yne or 1,1,1-trifluoropropyne were admitted continuously to the stirred reaction mixture for 5 min. at room temperature and atmospheric pressure. After the evaporation of the solvent, the catalysts were separated from the white trimer either by sublimation (at 100°C, 0.1 mm Hg) or by chromatography in silica gel, eluting with hexane-ethyl acetate (5:1) (v/v). Both trimers were identified by direct comparison with authentic samples prepared as reported before.[4,5]

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