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SHORT COMMUNICATIONS

Me_2ESiMe_3 (E = As, N, P) Compounds—Efficient Reagents for Replacement of the Fluorine Atom by Me_2E Group in the Complex $[(\eta^6\text{-1-F-3,5-}Me_2C_6H_3)(\eta^5\text{-}C_5EtMe_4)Rh](CF_3SO_3)_2$

L. I. Goryunov[1], **J. Grobe**[2], and **V. D. Shteingarts**[1]

[1] Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences
pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: shtein@nioch.nsc.ru

[2] Institut für anorganische und analytische Chemie der Westfälischen Wilhelm-Universität,
Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany
e-mail: grobe@uni-muenster.de

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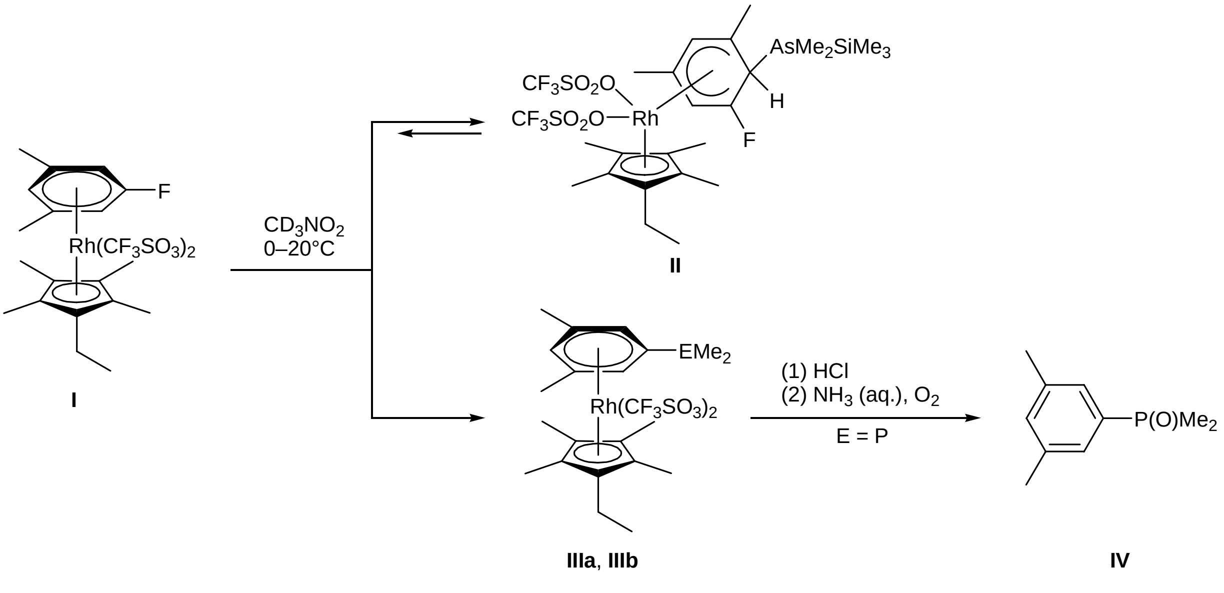
Reagents like Me_3SiEMe_2 (E = As, N, P) were successfully used to introduce Me_2E groups into polyfluorinated aromatic compounds via replacement of one or two fluorine atoms [1, 2]. While studying the possibility for analogous substitution in fluoroarenes activated by π-coordination with an electron-acceptor metal-complex fragment [3, 4] we have found that complex **I** readily reacts with Me_3SiEMe_2 compounds according to Scheme 1, as follows from the ^1H, ^{19}F, and ^{31}P NMR spectra of the reaction mixtures.

In the reaction with dimethyl(trimethylsilyl)arsine, complex **I** is completely converted in 5 min into an equimolar mixture of two compounds, which were identified by NMR spectroscopy as [2–6-η-2-fluoro-*exo*-1-dimethyl(trimethylsilyl)arsino-4,6-dimethylcyclohexadienyl](η^5-ethyltetramethylcyclopentadienyl)rhodium(III) bis(trifluoromethanesulfonate) (**II**) and (η^6-1-dimethylarsino-3,5-dimethylbenzene)(η^5-ethyltetramethylcyclopentadienyl)rhodium(III) bis(trifluoromethanesulfonate) (**IIIa**). The cyclohexadienyl

Scheme 1.



I, E = As, N, P; **III**, E = As (**a**), N (**b**).

ligand in complex **II** gives rise to the following signals in the ^{1}H NMR spectrum, δ, ppm (*J*, Hz)**:** 5.47 d (1H, 3-H, $^3J_{HF}$ = 8.0), 5.00 s (1H, 5-H), 4.07 d (1H, *endo*-1-H, $^3J_{HF}$ = 13.0). The spectral pattern is analogous to that reported for the complexes $[(\eta^5\text{-}C_6H_6PR_3)(\eta^5\text{-}C_5EtMe_4)Rh](BF_4)_2$ (R = *n*-Bu, Me, Ph) [5]. In the ^{19}F NMR spectrum a broadened singlet was observed at δ_F –137.3 ppm (1F). After 20 min, the above signals disappeared, and the intensity of signals belonging to $FSiMe_3$ and π-complex **IIIa** increased. Compound **IIIa** was isolated from the mixture in 93% yield.

The reaction of complex **I** with Me_2NSiMe_3 was complete in 5 min. The product was (η^6-1-dimethylamino-3,5-dimethylbenzene)(η^5-ethyltetramethylcyclopentadienyl)rhodium(III) bis(trifluoromethylsulfonate) (**IIIb**), which was isolated in 89% yield.

In the reaction of complex **I** with Me_2PSiMe_3, the fluorine atom was replaced also quickly (in 2 min) by dimethylphosphino group. However, a mixture of complexes was obtained, presumably due to fast rearrangement of primary product like **III** (E = P). From the reaction mixture we isolated 41% of dimethyl(3,5-dimethylphenyl)phosphine oxide (**IV**).

Our results demonstrate prospects in extending studies on the application of Me_2ESiMe_3 compounds (E = As, P, N) as reagents for replacement of halogen atoms in π-complexes of haloarenes with transition metals by Me_2E group. These groups can serve as additional coordination centers which could give rise (or modify) catalytic and other useful properties of the resulting compounds.

(η^6-1-Fluoro-3,5-dimethylbenzene)(η^5-ethyltetramethylcyclopentadienyl)rhodium(III) bis(trifluoromethanesulfonate) (I). To a solution of 3.01 g (4.8 mmol) of $[(C_5EtMe_4)RhCl_2]_2$ and 1.90 g (15.3 mmol) of 1-fluoro-3,5-dimethylbenzene in 10 ml of nitromethane we added 4.95 g (19.3 mmol) of $AgCF_3SO_3$, and the mixture was stirred for 30 min under argon. The precipitate of AgCl was filtered off and washed with 5 ml of nitromethane. The filtrate was combined with the washings and diluted with 20 ml of diethyl ether. The yellow crystals were filtered off and purified by reprecipitation from nitromethane with ether. Yield 4.90 g (78%), colorless crystals. ^{1}H NMR spectrum (CD_3NO_2), δ, ppm: 7.55 d (2H, CH, J_{HF} = 5.8 Hz), 7.21 s (1H, CH), 2.63 q (2H, CH_2, *J* = 7.8 Hz), 2.60 s (6H, CH_3), 2.24 s (6H, CH_3), 2.23 s (6H, CH_3), 1.17 t (3H, CH_3, *J* = 7.8 Hz). ^{19}F NMR spectrum, δ_F, ppm: –117.3 m (1F, CF), –79.0 s (6F, CF_3SO_3). Found, %: C 36.52; H 3.75. $C_{21}H_{26}F_7O_6RhS_2$. Calculated, %: C 37.40, H 3.89.

Complex (IIIa). A reactor was charged with 0.202 g (0.30 mmol) of complex **I**, and 0.059 g (0.33 mmol) of $Me_3SiAsMe_2$ and 0.5 ml of CD_3NO_2 were condensed thereto under reduced pressure (0.05 mm) on cooling with liquid nitrogen. The mixture was allowed to warm up to 0–20°C, stirred for 0.5 h, and treated with 7 ml of diethyl ether. The precipitate was filtered off, washed with 2 ml of methylene chloride and 2 ml of diethyl ether, and dried under reduced pressure. Yellow crystals. Yield 0.211 g (93%). ^{1}H NMR spectrum (CD_3NO_2), δ, ppm: 7.21 s (2H, CH), 7.09 s (1H, CH), 2.48 s (6H, CH_3), 2.47 q (2H, CH_2, *J* = 7.5 Hz), 2.11 br.s (12H, CH_3), 1.45 s (6H, CH_3), 1.12 t (3H, CH_3, *J* = 7.5 Hz). Found, %: C 35.55; H 3.93. $C_{23}H_{32}AsF_6O_6RhS_2$. Calculated, %: C 36.33, H 4.24.

Complex (IIIb) was synthesized in a similar way from 0.202 g (0.30 mmol) of compound **I** and 0.039 g (0.33 mmol) of Me_3SiNMe_2. Yield 0.187 g (89%). ^{1}H NMR spectrum (CD_3NO_2), δ, ppm: 6.84 s (1H, CH), 6.81 s (2H, CH), 3.38 s (6H, CH_3), 2.64 q (2H, CH_2, *J* = 7.6 Hz), 2.47 s (6H, CH_3), 2.19 s (6H, CH_3), 2.20 s (6H, CH_3), 1.13 t (3H, CH_3, *J* = 7.6 Hz). Found, %: C 38.98; H 4.60; N 2.04. $C_{23}H_{32}F_6NO_6RhS_2$. Calculated, %: C 39.49, H 4.61; N 2.00.

Dimethyl(3,5-dimethylphenyl)phosphine oxide (IV). Excess hydrochloric acid was added to the mixture obtained as described above from 0.202 g (0.30 mmol) of compound **I** and 0.044 g (0.33 mmol) of Me_3SiPMe_2. The resulting mixture was stirred for 12 h, neutralized with ammonia, and heated at 50°C in a vacuum (0.06 mm) to remove volatile components. The residue was sublimed at 70°C, subjected to thin-layer chromatography on Silufol UV-254 plates (using diethyl ether as eluent), and sublimed again. Yield 0.022 g (41%), mp 93–94°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.29 d (2H, CH, $^3J_{HP}$ = 11.8 Hz), 7.11 s (1H, CH), 2.32 s (6H, CH_3), 1.67 d (6H, CH_3, $^2J_{HP}$ = 12.8 Hz). ^{31}P–{^{1}H} NMR spectrum: δ_P 34.4 ppm, s. Found, *m*/*z*: M^+ 182.0867. $C_{10}H_{15}OP$. Calculated: *M* 182.0861.

The NMR spectra were recorded on a Bruker AC 200 instrument at 200.13 (^{1}H), 188.31 (^{19}F), and 81.02 MHz (^{31}P) using CD_3NO_2 (δ 4.29 ppm) or $CDCl_3$ (δ 7.25 ppm) as solvent. Trichlorofluoromethane and 85% H_3PO_4 were used as external references for ^{19}F and ^{31}P, respectively. The mass spectra were obtained on a Varian MAT 212 spectrometer.

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