Fluorovinyl Derivatives of Transition Metals

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ALTHOUGH numerous perfluoro-alkyl and -aryl transition-metal compounds have been reported, very few related fluorovinyl derivatives have been described.[1] We now report two reactions which unexpectedly lead to transition-metal–vinyl compounds in excellent yield.

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[1] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **15b**, 763.

(*a*) We have studied the reaction of trifluoroethylene with *trans*-bis(triethylphosphine)hydridochloroplatinum(II) in cyclohexane at 120°. The principal involatile product (40% yield), obtained as a white crystalline solid by crystallisation from petroleum, was bis(triethylphosphine)chloro(1,2-difluorovinyl)platinum(II)* $[(C_2H_5)_3P]_2PtCl(CF{=}CFH)$. This constitution was confirmed, and also the presence of both the *cis*- and *trans*-olefinic isomers established, by a study of the infrared and proton magnetic resonance spectra. The former showed absorption bands at 1635 and 1680 (C=C stretch), and 910, 1010, 1035, 1080, and 1100 cm.$^{-1}$ (C–F stretch) in addition to bands associated with the phosphine. The proton resonance spectrum, in addition to the signals of the ethyl protons, consisted basically of two quartets, centred about τ 4·46 and 2·42 respectively, with respect to tetramethylsilane, the coupling constants being those expected for the protons of *cis*- and *trans*-MFC=CFH groups respectively. The components of each quartet were of equal intensity, and each showed a secondary splitting to a triplet, presumably due to coupling to platinum-195. The volatile reaction product was silicon tetrafluoride, itself presumably a secondary product from hydrogen fluoride. An ethylplatinum compound has previously been prepared from the reaction of ethylene with *trans*-bis(triethylphosphine)hydridochloroplatinum(II),[2] and several compounds, such as $HCF_2{\cdot}CF_2Mn(CO)_5$, have been obtained from fluoro-olefins and rhenium or manganese pentacarbonyl hydrides.[3] We are currently investigating the reactions of fluoro-olefins with other phosphine–transition-metal hydrides, in order to examine the mechanism for the elimination of hydrogen fluoride which leads to the vinyl compound, rather than to a fluoroalkyl derivative.

(*b*) Recently, we described[4] the formation of the compound $(CH_3)_3SnC_2F_4Mn(CO)_5$, formed by addition of tetrafluoroethylene to $(CH_3)_3SnMn(CO)_5$. Surprisingly, we have now found that when trifluoroethylene reacted with $(CH_3)_3SnMn(CO)_5$, the corresponding derivative, $(CH_3)_3SnC_2F_3\,HMn(CO)_5$, was not obtained. The reaction was performed in pentane at 65° under ultraviolet irradiation for 4 hr. A large yield of trimethyltin fluoride resulted, as well as two almost colourless crystalline solids which were separated by liquid chromatography followed by sublimation. These were identified as the *cis*- and *trans*-isomers of 1,2-difluorovinylmanganese pentacarbonyl, $CHF{=}CFMn(CO)_5$.* The isomers were characterised spectroscopically. This *cis*-isomer shows infrared absorption bands at 1630 cm.$^{-1}$ (C=C stretch), and 1297, 1045, and 968 cm.$^{-1}$ (C–F stretch) in addition to the peaks associated with the $Mn(CO)_5$ group. The proton magnetic resonance spectrum consisted of a quartet centred at τ4·43 with respect to tetramethylsilane, the four components being of equal intensity. The infrared spectrum of the *trans*-isomer showed absorption at 1670 cm.$^{-1}$ (C=C stretch), 1272, 1088, and 1010 cm.$^{-1}$ (C–F stretch) in addition to the expected absorptions of the $Mn(CO)_5$ group. The proton resonance spectrum was again a quartet centred at τ2·53 with respect to tetramethylsilane; the proton–fluorine coupling constants of the *cis*- and *trans*-isomers are in excellent agreement with those of the isomers of *trans*-$[(C_2H_5)_3P]_2PtCl(CF{=}CFH)$, and also of the isomers of $(CH_3)_3SnCF{=}CFH$.[5] At this stage we have investigated the fluorine-19 magnetic resonance spectrum of only *cis*-$(CFH{=}CF)Mn(CO)_5$ and the results are in full agreement with the assigned configuration, thus further supporting the suggested configurations of the platinum and tin difluorovinyl compounds.

The factors which lead to the vinylmanganese carbonyl rather than the compound $(CH_3)_3SnC_2F_3\,HMn(CO)_5$ are currently being studied.

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* These formulations were supported by elemental analyses and molecular weight determinations.

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

[3] P. M. Treichel and F. G. A. Stone, *Adv. Organometallic Chem.*, 1964, **1**, 143.

[4] H. C. Clark and J. H. Tsai, *Chem. Comm.*, 1965, 111.

[5] A. D. Beveridge and H. C. Clark, unpublished results.