Metal Carbonyl Chemistry. Part XXII.[1] Some Reactions of the Anions $[M(CO)_2(PPh_3)_2]^-$ (M = Rhodium or Iridium) with Fluoro-olefins and Hexafluorobut-2-yne

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Perfluorocyclohexene and perfluorocyclobutene react with the anions $[M(CO)_2(PPh_3)_2]^-$ (M = Rh or Ir) to afford the complexes $[\overline{(CF_2)_4\cdot CF{:}C}\cdot M(CO)_2(PPh_3)_2]$ and $[\overline{(CF_2)_2\cdot CF{:}C}\cdot M(CO)_2(PPh_3)_2]$ respectively. Reaction of the rhodium anion with $CF_2{:}CFCl$ similarly gives $[(CF_2{:}CF)Rh(CO)_2(PPh_3)_2]$ whereas the iridium anion does not react. The preparations are also described of the compounds $[\{CF_3\cdot CH{:}C(CF_3)\}M(CO)_2(PPh_3)_2]$ by reaction of these anions with hexafluorobut-2-yne in tetrahydrofuran.

CARBONYLMETAL ANIONS which behave as strong nucleophiles, such as $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ or $[Re(CO)_5]^-$, are known to give perfluorovinyl metal complexes with fluoro-olefins, whereas weakly nucleophilic anions do not react.[2-6] Recent work has shown that the anions $[M(CO)_2(PPh_3)_2]^-$ (M = Rh or Ir) are quite strong nucleophiles capable of displacing F^- from fluoroaromatic compounds,[1,7] the nucleophilic strength of the rhodium anion being comparable to that of $[Re(CO)_5]^-$.[1] It was of interest, therefore, to investigate the reactions of the rhodium and iridium anions with fluoro-olefins as a route to new perfluorovinyl transition-metal complexes.

Reaction of the Anions with Fluoro-olefins and Hexafluorobut-2-yne.—Perfluorocyclohexene and perfluorocyclobutene react with the anions $[M(CO)_2(PPh_3)_2]^-$ (M = Rh or Ir) at room temperature in tetrahydrofuran under an atmosphere of carbon monoxide to afford the complexes (Ia) and (Ib) and (IIa) and (IIb) respectively. The yields for the rhodium complexes [(Ia) 41 and (IIa) 52%] are considerably higher than those for the corresponding iridium complexes [(Ib) 29 and (IIb) 21%], in accordance with the higher nucleophilic strength of the rhodium anion.[1] The compounds are all yellow crystalline solids which are thermally stable up to >160 °C, and appear to be indefinitely stable in air in the solid state, and stable in air for 10—20 h in solution at room temperature. They are only moderately soluble in most common organic solvents. The i.r. spectra * show only one strong band in the metal

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* Detailed i.r. and ^{19}F n.m.r. spectra for compounds (Ia, b), (IIa, b), (III), and (IVa, b) are deposited as a Supplementary publication (SUP No. 21373; 4 pp); see Notices to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue, for details of this Scheme.

[1] Part XXI, B. L. Booth, R. N. Haszeldine, and I. Perkins, *J.C.S. Dalton*, preceding paper.

[2] W. R. Cullen, *Fluorine Chem. Rev.*, 1969, **3**, 73.

[3] P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5830.

[4] M. I. Bruce, P. W. Jolly, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1602.

[5] D. J. Cooke, M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1771.

[6] B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J. Organometallic Chem.*, 1968, **11**, 5.

[7] B. L. Booth, R. N. Haszeldine, and I. Perkins, *J. Chem. Soc.* (*A*), 1971, 927.

carbonyl region indicative of a trigonal bipyramid structure with *trans*-diaxial CO ligands. The spectrum of (IIb) shows two additional weak bands which may be due to another isomer; attempts to purify this compound by repeated t.l.c. and recrystallisation were unsuccessful. The cyclohexenyl complexes both show a weak ν(C=C) band at 1 644 cm^{-1}, and the medium-strong ν(C–F) bands in the region 940—1 280 cm^{-1} are in good agreement with those observed for similar compounds.[3] The olefinic stretching vibrations for the cyclobutenyl complexes are at lower frequency (1 616—1 620 cm^{-1}), and again there is a good correlation with the spectra of previously reported compounds of this type.[3] The ^{19}F n.m.r. spectra of the cyclohexenyl derivatives show five well-separated bands having the assignments shown, whereas the cyclobutenyl complexes show the expected three bands, the band at lowest field being assigned to the allylic F atoms adjacent to the metal.[3]

While the rhodium anion reacts with chlorotrifluoroethylene at room temperature to give a 44% yield of the vinyl complex (III) after 6 h, the iridium anion failed to react under similar conditions and the only product isolated was $[IrH(CO)_2(PPh_3)_2]$ in 31% yield. It is assumed that the hydride arises from the unchanged anion by proton abstraction either from the tetrahydrofuran solvent or from water on the chromatography column used during work-up. Compound (III) is thermally stable up to *ca.* 180 °C, and is stable in air for several months in the solid state, and for several hours in solution. Its i.r. spectrum shows a medium band at 1 688 cm^{-1} for ν(C=C) and additional bands at 1 220 (=CF_2 asym. stretch), 1 090m (=CF stretch), and 958 cm^{-1} (=CF_2 sym. stretch). The ^{19}F n.m.r. spectrum shows the expected three bands of equal intensity having assignments in accordance with those reported for similar complexes.[3,4] The compound is not very soluble in $CHCl_3$ and a weak spectrum only was obtained. Although the coupling observed agreed approximately with those recorded for similar compounds accurate coupling constants could not be measured.

These results not only emphasise that the rhodium anion is the stronger nucleophile, but also suggest that cycloaliphatic fluoro-olefins are more susceptible to nucleophilic attack than $CF_2{:}CFCl$. It is well established[8] that the order of reactivity of cycloaliphatic fluoro-olefins towards nucleophilic attack is:

$$\overline{CF_2{\cdot}CF_2{\cdot}CF{:}CF} > \overline{CF_2{\cdot}(CF_2)_2{\cdot}CF{:}CF} > \overline{CF_2{\cdot}(CF_2)_3{\cdot}CF{:}CF}$$

It is also known[9] that the order of reactivity of aliphatic fluoro-olefins is:

$$CF_2{:}C(CF_3)_2 > CF_3{\cdot}CF{:}CF_2 > CF_2{:}CF_2 > CF_2{:}CFCl$$

There appears, however, to be little information as to the correlation between the cycloaliphatic series and the aliphatic series. Our results suggest that, in general, the cycloaliphatic olefins are more reactive than the aliphatic olefins, and some support for this view comes from some previously reported observations on the reactions of $[Mn(CO)_5]^-$ with fluoro-olefins. The latter anion, which is known to react readily with perfluorocyclohexene and perfluorocyclobutene to give high yields of the corresponding vinyl complexes, reacts only slowly with $CF_3{\cdot}CF{:}CF_2$,[3] and does not react at all with C_2F_4 under similar conditions. It should be stressed that all these reactions were carried out in the same solvent under almost identical conditions. Assuming that the rate-limiting step is similar in each of these reactions this suggests an order of reactivity of

$$\overline{CF_2{\cdot}CF_2{\cdot}CF{:}CF} > \overline{CF_2{\cdot}(CF_2)_3{\cdot}CF{:}CF} > CF_3{\cdot}CF{:}CF_2 > CF_2{:}CF_2$$

in some agreement with our observations. The reaction of $[Mn(CO)_5]^-$ with $CF_2{:}CFCl$ is rather anomalous in that the reported product formed in low yield is $[(CHFCl{\cdot}CF_2)Mn(CO)_5]$ rather than a vinyl derivative.[4] It has been suggested[4] that this product arises by initial formation of the carbanion $[(\bar{C}FCl{\cdot}CF_2)Mn(CO)_5]$, which then abstracts a proton from the tetrahydrofuran solvent, but it is difficult to reconcile this explanation with the facts that under very similar conditions $[Mn(CO)_5]^-$ does not react with C_2F_4 nor, in our own investigations, does $[Ir(CO)_2(PPh_3)_2]^-$, which is a stronger nucleophile than the manganese ion, react with $CF_2{:}CFCl$.

Previous work has shown[10,11] that the anions $[Re(CO)_5]^-$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ react with hexafluorobut-2-yne to afford the allenyl complexes $[\{(CF_2{:}C{:}C(CF_3)\}M]$ [where M = $Re(CO)_5$ or $(\pi\text{-}C_5H_5)Fe(CO)_2$] in 8—13% yields. A low yield of the compound $[(CO)_5Re\{C(CF_3){:}C(CF_3){\cdot}CF_2{\cdot}CH{:}C(CF_3)\}Re(CO)_5]$ (10%) was also isolated from the reaction with the rhenium ion, but no other organometallic compounds were detected. In an attempt to obtain perfluoroallene complexes of rhodium and iridium the reactions between hexafluorobut-2-yne and the anions $[M(CO)_2(PPh_3)_2]^-$ (M = Rh or Ir) have been investigated. Rather surprisingly these reactions carried out under similar conditions to those described previously gave the vinyl complexes (IVa) and (IVb) in 52 and 8% yields respectively. The compound $[\{Rh(CO)_2(PPh_3)_2\}_2]$[12,13] was also isolated in 31% yield from the reaction of the rhodium anion, while $[IrH(CO)_2(PPh_3)_2]$ (17%) was obtained from the iridium anion reaction. A careful examination of the product mixtures from these reactions failed to reveal any perfluoro-

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[9] R. D. Chambers and R. H. Mobbs, *Adv. in Fluorine Chem.*, 1965, **4**, 50.

[10] M. Green, N. Mayne, and F. G. A. Stone, *Chem. Comm.*, 1966, 755.

[11] R. J. Goodfellow, M. Green, N. Mayne, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 177.

[12] D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2660.

[13] B. L. Booth, M. J. Else, R. Fields, and R. N. Haszeldine, *J. Organometallic Chem.*, 1971, **27**, 119.

allene complexes. The i.r. spectra of the compounds (IVa) and (IVb) show only one band in the metal carbonyl region in agreement with a structure having ***trans***-diaxial CO groups and a weak ν(C=C) absorption in the region of 1 601—1 621 cm^{-1}, in contrast to the strong band at *ca.* 1 990 cm^{-1} expected for an allenic compound.[11] The ^{19}F n.m.r. spectrum shows two bands of equal intensity as expected for the assigned structures, but, unfortunately, the low solubility of the compounds and the complexity of the bands prevented calculation of coupling constants. The ^{1}H n.m.r. spectrum as a 20% solution in $CDCl_3$ shows a broad band at τ 4.28 [compound (IVa)] and at τ 4.0 [compound (IVb)] for the vinylic proton, but again coupling constants could not be determined and the stereochemistry of these complexes could not be decided.

The formation of *cis*-vinyl metal compounds rather than allenyl complexes has been noted previously for the reactions between $[Re(CO)_5]^-$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ and 3,3,3-trifluoropropyne, and between the iron anion and pentafluorophenylacetylene.[14]* It has been proposed that these reactions occur by a concerted mechanism, whereby as the nucleophile attacks the developing ***trans***-carbanion centre abstracts a proton, probably from the strongly acidic fluoroacetylene. Such a proton source is not, of course, available in the reactions of the rhodium and iridium anions described above, and for a similar mechanism to operate the proton must come from the solvent. Whilst this is a possibility, it is difficult to appreciate why it apparently does not also occur during the reactions of hexafluorobut-2-yne and the anions $[Re(CO)_5]^-$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ in the same solvent.

Another possible explanation for the difference between the reactions of $CF_3{\cdot}C{\vdots}C{\cdot}CF_3$ with the iron and rhenium anions and those of the rhodium and iridium anions may be that for the latter anions the rate of nucleophilic attack on the acetylene is slow compared with the rate of formation of $[HM(CO)_2(PPh_3)_2]$ (M = Ir or Rh) by abstraction of a proton from the solvent. In the case of the rhodium anion reaction any hydride formed would almost certainly decompose to some appreciable extent to give one of the observed products $[\{Rh(CO)_2(PPh_3)_2\}_2]$ under the reaction conditions.[12] An attempt to react $CF_3{\cdot}C{\vdots}C{\cdot}CF_3$ with $[\{Rh(CO)_2(PPh_3)_2\}_2]$ in benzene under an atmosphere of hydrogen, that is, conditions which favour the formation of $[HRh(CO)_2(PPh_3)_2]$,[12] failed to give any trace of compound (IVa). However, similar insertion reactions of hexafluorobut-2-yne with the hydrides $[MH(CO)(PPh_3)_3]$ (M = Rh [15] or Ir [16]) to give the *cis*-alkenylmetal complexes *cis*-$[\{CF_3{\cdot}CH{:}C(CF_3)\}Rh(CO)(PPh_3)_2]$ and *cis*-$[\{CF_3{\cdot}CH{:}C(CF_3)\}Ir(CO)(PPh_3)_3]$, respectively, have been reported recently.

EXPERIMENTAL

I.r. spectra were determined either on a Perkin-Elmer model 257 or a model 621 spectrometer. ^{19}F N.m.r. spectra were determined on a R 20A Hitachi–Perkin-Elmer instrument using trifluoroacetic acid as an external reference; proton n.m.r. spectra were measured on a Varian HA 100 instrument. Chromatographic separations were carried out on Florisil. The anions were prepared as reported elsewhere,[1] and all reactions were carried out under an atmosphere of carbon monoxide.

Reactions of $[Rh(CO)_2(PPh_3)_2]^-$.—(a) *With perfluorocyclohexene.* The anion (1.6 g, 2.4 mmol) and perfluorocyclohexene (1.0 g, 3.8 mmol) in tetrahydrofuran (50 ml) were stirred at room temperature for 18 h. Removal of the solvent and chromatography of the residue (10% diethyl ether–light petroleum eluant), gave pale yellow crystals of *dicarbonylperfluorocyclohexenylbis(triphenylphosphine)rhodium* (Ia) (0.9 g, 0.97 mmol, 41%), m.p. 169—170 °C, which were recrystallised from a 1 : 1 mixture of light petroleum and n-hexane (Found: C, 57.1; H, 3.4; P, 7.0; F, 18.1%; *M*, 923. $C_{44}H_{30}F_9O_2P_2Rh$ requires C, 57.0; H, 3.2; P, 6.7; F, 18.5%; *M*, 926).

(b) *With perfluorocyclobutene.* A solution of the anion (1.6 g, 2.4 mmol) in tetrahydrofuran (50 ml) was slowly added to perfluorocyclobutene (1.0 g, 6.2 mmol) in tetrahydrofuran (30 ml) at −40° C. The reaction mixture was stirred at this temperature for 1 h and at room temperature for a further 6 h. Filtration and chromatography of the yellow solution (elution with a 50% mixture of diethyl ether–dichloromethane) gave *dicarbonylperfluorocyclobutenylbis(triphenylphosphine)rhodium* (IIa) (1.0 g, 1.2 mmol, 52%) as yellow crystals, m.p. 170—172 °C (with decomp.), which were recrystallised from diethyl ether (Found: C, 61.3; H, 3.8; F, 11.4. $C_{42}H_{30}F_5O_2P_2Rh$ requires C, 61.0; H, 3.6; F, 11.5%).

(c) *With chlorotrifluoroethylene.* The anion (1.6 g, 2.4 mmol) and chlorotrifluoroethylene (1.0 g, 8.6 mmol) in tetrahydrofuran (30 ml) were stirred at −22 °C for 3 h, and then at room temperature for a further 5 h. Filtration of the solution followed by chromatography (diethyl ether eluant) gave *dicarbonylperfluorovinylbis(triphenylphosphine)rhodium* (III) (0.8 g, 1.04 mmol, 44%) as yellow crystals, m.p. 182—183 °C, after recrystallisation from a 5 : 1 mixture of light petroleum–acetone (Found: C, 63.2; H, 4.2; F, 7.1%; *M*, 758. $C_{40}H_{30}F_3O_2P_2Rh$ requires C, 62.8; H, 3.9; F, 7.4%; *M*, 764).

(d) *With perfluorobut-2-yne.* A solution of the anion (1.6 g, 2.4 mmol) in tetrahydrofuran (50 ml) was added dropwise to perfluorobut-2-yne (0.6 g, 3.7 mmol) in tetrahydrofuran (50 ml) at −44 °C, and the mixture was stirred for 1 h at −44 °C and for a further 5 h at room temperature. Filtration gave μ-dicarbonyl-bis[carbonylbis(triphenylphosphine)rhodium] (0.5 g, 0.37 mmol, 31%) which was identified by i.r. spectroscopy. Chromatography of the filtrate using a 1 : 1 mixture of light petroleum–diethyl ether as eluant gave yellow crystals of *dicarbonyl*-1,1,1,4,4,4-*hexafluorobut*-2-*en*-2-*ylbis(triphenylphosphine)rhodium* (IVa) (0.7 g, 0.83 mmol, 52%), m.p. 179—180 °C (Found: C, 59.8; H, 4.0; F, 13.4. $C_{41}H_{31}F_6O_2P_2Rh$ requires C, 59.6; H, 3.7; F, 13.5%).

Reaction of $[Ir(CO)_2(PPh_3)_2]^-$.—(a) *With perfluorocyclohexene.* When the anion (1.59 g, 2.05 mmol) and perfluorocyclohexene (1.0 g, 3.8 mmol) in tetrahydrofuran (50 ml)

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* A Referee has drawn our attention to these as possibly analogous reactions.

[14] M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 895.

[15] B. L. Booth and A. D. Lloyd, *J. Organometallic Chem.*, 1972, **35**, 195.

[16] W. H. Baddley and G. B. Tupper, *J. Organometallic Chem.*, 1974, **67**, C16.

were stirred at room temperature for 18 h yellow crystals of *dicarbonylperfluorocyclohexenylbis(triphenylphosphine)iridium* (Ib) (0.6 g, 0.6 mmol, 29%), m.p. 209 °C, were obtained after chromatography (20% light petroleum–diethyl ether eluant), and recrystallisation from a 2 : 1 mixture of light petroleum–diethyl ether (Found: C, 52.2; H, 3.0; F, 17.1. $C_{44}H_{30}F_9IrO_2P_2$ requires C, 52.0; H, 3.0; F, 16.9%).

(b) *With perfluorocyclobutene.* A solution of the sodium salt (1.59 g, 2.05 mmol) in tetrahydrofuran (50 ml) was slowly added to perfluorocyclobutene (1.0 g, 6.2 mmol) in tetrahydrofuran (30 ml) at −40 °C, and the mixture was stirred at this temperature for 1 h and for a further 6 h at room temperature. Filtration and chromatography of the filtrate using a 1 : 1 mixture of light petroleum–diethyl ether as eluant gave *dicarbonylperfluorocyclobutenylbis(triphenylphosphine)iridium* (IIb) (0.41 g, 0.44 mmol, 21%) as yellow crystals, m.p. 174 °C, after recrystallisation from a 1 : 1 light petroleum–diethyl ether mixture (Found: C, 54.8; H, 3.5; F, 10.4. $C_{42}H_{30}F_5IrO_2P_2$ requires C, 55.1; H, 3.3; F, 10.4%).

(c) *With perfluorobut-2-yne.* A solution of the anion (1.59 g, 2.05 mmol) in tetrahydrofuran (50 ml) was added to perfluorobut-2-yne (1.0 g, 6.2 mmol) in tetrahydrofuran (30 ml) at −44 °C and the mixture was stirred at this temperature for 1 h and at room temperature for a further 5 h. After filtration, the filtrate was chromatographed using a 20% mixture of light petroleum–diethyl ether as eluant, followed by recrystallisation from the same solvent mixture, to give *dicarbonyl-1,1,1,4,4,4-hexafluorobut-2-en-2-ylbis(triphenylphosphine)iridium* (IVb) (0.15 g, 0.16 mmol, 8%) as yellow crystals, m.p. 219—220 °C (with decomp.) (Found: C, 54.2; H, 3.6; F, 12.4. $C_{42}H_{31}F_6IrO_2P_2$ requires C, 53.9; H, 3.3; F, 12.2%). Further elution with diethyl ether gave pale yellow needles of dicarbonylhydridobis(triphenylphosphine)iridium (0.2 g, 0.3 mmol, 17%), m.p. 134 °C (reported[17] 135—136 °C), which was identified by i.r. spectroscopy.

Attempted Reaction of $[HRh(CO)_2(PPh_3)_2]$ *with Hexafluorobut-2-yne.*—Hydrogen was bubbled through a suspension of μ-dicarbonyl-bis[carbonylbis(triphenylphosphine)-rhodium] (1.6 g, 1.2 mmol) in benzene (40 ml) at room temperature until the solution turned deep red; this indicated that formation of the hydride had occurred.[17] Hexafluorobut-2-yne (0.8 g, 5.0 mmol) was added and the mixture was stirred for 5 h under an atmosphere of hydrogen. Chromatography of the product mixture gave only recovered rhodium carbonyl (0.66 g, 41%), and examination of the residue by i.r. and ^{19}F n.m.r. spectroscopy showed no evidence for any fluorine-containing compounds.

[4/1972 *Received, 26th September,* 1974]

[17] G. Yagupsky and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 725.