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Preliminary communication

FLUORODICYCLOOCTENERHODIUM(I), A VERSATILE RHODIUM COMPLEX

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Summary

$[RhF(C_8H_{14})_2]_n$ has been prepared and used in the synthesis of $RhF(PPh_3)_3$ and of other halo-, phosphine-, carbonyl- and/or dinitrogen-containing rhodium(I) complexes.

Rhodium(I)—olefin complexes are used as starting materials [1, 2] for the preparation of a great variety of rhodium compounds, both by nucleophilic (Lewis base) displacement [3] and by oxidative displacement of the olefin [4]. Monoolefins are superior to diolefins as the latter cannot always be displaced e.g. by tertiary phosphines [5]. In preparative rhodium chemistry, metathesis of a chloro ligand is interesting, but often difficult to realise, but this metathesis problem has been overcome by the use of the easily displacable fluoro ligand in $RhF(CO)(PPh_3)_2$ [6]. This complex, the only previously known fluororhodium compound, was prepared from $RhCl(CO)(PPh_3)_2$ and AgF.

We now report the preparation of a novel fluoro-olefin complex of rhodium(I), $[RhF(C_8H_{14})_2]_n$ (I) (C_8H_{14} = cyclooctene), which is easy to handle, and which, by the presence of good leaving ligands, is particularly useful for synthetic purposes. A few examples of its use are given.

$[RhF(C_8H_{14})_2]_n$ is synthesized under nitrogen by stirring 1.0 g (3 mmol) $[RhCl(C_8H_{14})_2]_2$ (prepared according to ref. 1) and 0.8 g (6.3 mmol) AgF (Fa. Merck) in acetone in the dark for 2½ h. The black precipitate is collected on a filter, and extracted with 100 ml benzene. The solution is filtered over Hyflo and concentrated at reduced pressure, and hexane is added. The yellow precipitate is filtered off and dried under vacuum. Yield 60—75%, analysis: Found: C, 52.68; H, 7.98; Cl, 0.52; F, 5.41. $C_{16}H_{28}FRh$ calcd.: C, 56.14; H, 8.24; Cl, 0.00; F, 5.55%. Apparently the compound is contaminated with a few percent of the $AgF \cdot AgCl$ double salt [7], which does not interfere much in its reactions. I can be stored in air for over a month at room temperature, and longer in the cold. It probably has

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a dimeric fluoro-bridged structure*. The chlorine metathesis of $[RhCl(C_8H_{14})_2]_2$ with $AgNO_3$ and $Ag(CH_3COO)$ led to less complete displacement of Cl, and the formed cyclooctene complexes were less stable than I.

The reaction of phosphines, CO, N_2 and sodium halides with I have been studied. $RhF(PPh_3)_3$ (II) was isolated from the reaction of I with PPh_3 in benzene by precipitation with hexane. Analyses: Found: C, 70.09; H, 5.24; calcd.: C, 70.19; H, 5.20%. The compound must be stored under nitrogen; in air $OPPh_3$ is slowly formed. As a hydrogenation catalyst (cyclohexene in benzene, 25°C, P_H 100 cmHg, $[c_0]$ 4×10^{-3} mol/l) II is initially slightly more active than $RhCl(PPh_3)_3$ [8], but its activity falls within 25 minutes to about 15%. (It is noteworthy that an attempted synthesis of II from $RhCl(PPh_3)_3$ and AgF failed [9]). Treatment of II with CO leads to $RhF(CO)(PPh_3)_2$; similarly, treatment of I with PCy_3 (Cy = cyclohexyl) and CO results in $RhF(CO)(PCy_3)_2$. Analysis: Found: C, 60.62; H, 9.14; calcd. C, 62.52; H, 9.36%. ν(Rh—F) 470, ν(CO) 1936 and δ(RhCO) 606 cm^{-1}.

Reaction of I in benzene with an aqueous solution of NaBr gives an orange benzene layer presumably containing $[RhBr(C_8H_{14})_2]_n$, which is too unstable to isolate. Freshly prepared in solution, it has been used to synthesize $RhBr(PPh_3)_2(CO)$. Addition of NaI in water to a benzene solution of I leads to immediate decomposition of (it is assumed) $[RhI(C_8H_{14})_2]_n$. If first phosphine and then a sodium halide is added to I, both olefin displacement and fluorine metathesis can be readily achieved, and in this way $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ have been prepared. The best demonstration of the versatility of I is the one-step synthesis of $RhX(PCy_3)_2(N_2)$ (X = Br, I) from I, PCy_3, NaX and molecular nitrogen. Full details of these reactions will be reported later. Dinotrogen coordination by a rhodium(I) complex is known for the reaction of $RhCl(PCy_3)_2$ with N_2 [10].

The thermal stability of $[RhF(C_8H_{14})_2]_n$ is consistent with the stability order often found for Group VIIIb and VIIIc halo-olefin complexes [11], e.g. Cl > Br > I. If chelating ligands are included, the order of stability of $[RhX(C_8H_{14})_2]_n$ complexes is: F > Cl > Et_2NCS_2 [4] > CH_3COO ~ NO_3 > Br (> I).

It is clear that $[RhF(C_8H_{14})_2]_n$ is a useful starting material for the synthesis of novel fluororhodium(I) complexes, and more generally for rhodium compounds containing a variety of anionic ligands in cases when direct chlorine replacement may fail.

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*Such a structure was recently found for $[CoF(C_5H_8N_2)_3(BF_4)]_2$ [12].

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