Journal of Organometallic Chemistry, 234 (1982) C9—C12
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

DIFLUOROCARBENE COMPLEXES OF RUTHENIUM DERIVED FROM TRIFLUOROMETHYL COMPOUNDS. $RuCl_2(CF_2)(CO)(PPh_3)_2$, $RuCl_2(CFNMe_2)(CO)(PPh_3)_2$, $RuCl_2(CFOMe)(CO)(PPh_3)_2$ AND THE STRUCTURE OF $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$

G.R. CLARK, S.V. HOSKINS and W.R. ROPER*

Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received May 4th, 1982)

Summary

$Ru(CO)_3(PPh_3)_2$ or $Ru(CO)_2(PPh_3)_3$ with $Hg(CF_3)_2$ gives $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$. X-ray crystal structure determination reveals an octahedral geometry and the average C—F distance in the CF_3 group which is Ru-bound is 0.1 Å longer than in the CF_3 group Hg-bound. This and other Ru—CF_3 complexes such as $Ru(CF_3)Cl(CO)_2(PPh_3)_2$ react with aqueous acids converting the CF_3 group to a CO group. Difluorocarbene complexes are implicated in these reactions and a crystalline example of such a compound is $RuCl_2(CF_2)(CO)(PPh_3)_2$ derived from $Ru(CF_3)Cl(CO)(MeCN)(PPh_3)_2$ and dry HCl gas in benzene solution. $RuCl_2(CF_2)(CO)(PPh_3)_2$ is readily hydrolysed to $RuCl_2(CO)_2(PPh_3)_2$, while Me_2NH gives $RuCl_2(CFNMe_2)(CO)(PPh_3)_2$, MeOH gives $RuCl_2(CFOMe)(CO)(PPh_3)_2$, and ethanediol gives $RuCl_2(\overline{COCH_2CH_2O})(CO)(PPh_3)_2$.

The successful characterisation of stable dichlorocarbene complexes of ruthenium and osmium, $RuCl_2(CCl_2)(CO)(PPh_3)_2$ [1] and $OsCl_2(CCl_2)(CO)(PPh_3)_2$ [2], suggested the possibility of isolating crystalline complexes containing transition metal-bound difluorocarbene, e.g., $RuCl_2(CF_2)(CO)(PPh_3)_2$. The tetraphenylporphyrin-iron system which provides the molecules $Fe(TPP)(CX_2)$ for $CX_2 = CCl_2$, CBr_2, CFCl, and CFBr does not yield a pure crystalline material for $Fe(TPP)(CF_2)$ although such a species was detected spectroscopically [3]. Another report describes $[CpMo(CF_2)(CO)_3]^+$ detected by ^{19}F and ^{13}C NMR spectroscopy, but not isolated as a solid, from the reaction of $CpMo(CF_3)(CO)_3$ with SbF_5 in liquid SO_2 [4].

We have approached the synthesis of $RuCl_2(CF_2)(CO)(PPh_3)_2$ by first introducing a trifluoromethyl group into a ruthenium(II) complex and

0022-328X/82/0000—0000/$02.75

attempting, either through F^- abstraction, or through fluoride migration to metal, conversion to a difluorocarbene complex. We have found H^+ to be a suitable reagent for F^- abstraction.

Introduction of a CF_3 group was achieved by reaction between $Hg(CF_3)_2$ and either $Ru(CO)_2(PPh_3)_3$ [5] or $Ru(CO)_3(PPh_3)_2$ [6] to give $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$. An X-ray crystal structure determination was performed on this molecule because it provides a unique opportunity to make an internal comparison of the dimensions of a CF_3 transition metal-bound and a CF_3 main group-bound. The crystals form as colourless needles in the monoclinic space group $P2_1/c$ with 4 molecules in a unit cell of dimensions a 13.983(2), b 19.424(2), c 15.876(3) Å, β 118.03(1)°. Intensity data were collected on an automatic diffractometer using Mo-K_α-radiation. The structure was solved by conventional methods and is being refined by least-squares techniques. The residual, R, is presently 0.041 (phenyl rings assigned isotropic temperature factors, other atoms anisotropic) for 2654 observed reflections. The structure is shown in Fig. 1 along with important dimensions. As expected the average C—F distance for the Ru—CF_3 group is almost 0.1 Å longer than the average C—F distance for the Hg—CF_3 group. This bond weakening is reflected in the chemistry to be described.

The ruthenium—mercury bond is conveniently cleaved by Cl_2 in a quantitative reaction yielding $Ru(CF_3)Cl(CO)_2(PPh_3)_2$. Further reaction chemistry should be followed in Scheme 1. The high ν(CO) values for $Ru(CF_3)Cl(CO)_2(PPh_3)_2$ (see Table 1) point to the lability of a carbonyl ligand and indeed dissolution in acetonitrile leads to $Ru(CF_3)Cl(CO)(MeCN)(PPh_3)_2$. The three trifluoromethyl derivatives above react with aqueous perchloric acid in a quantitative conversion of the CF_3 group to a CO, i.e. to form $[Ru(HgCF_3)(CO)_3$-

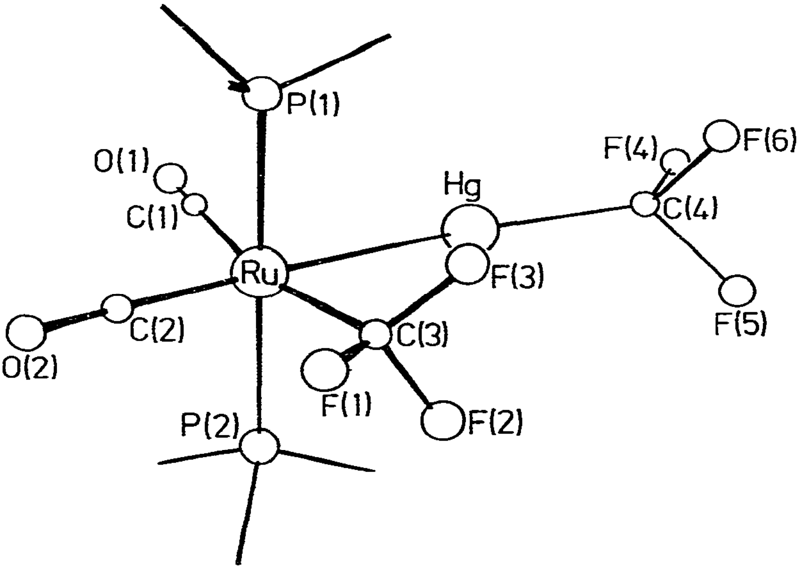
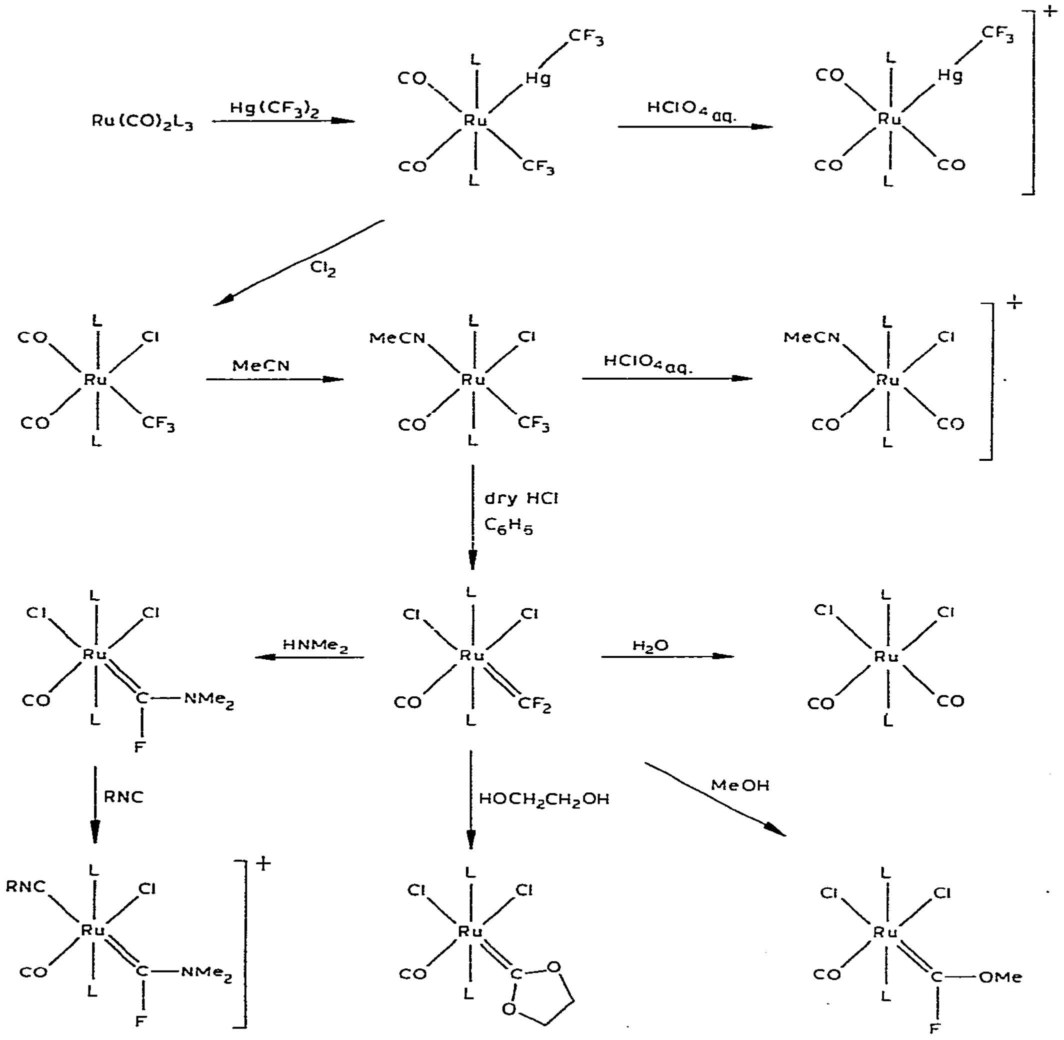


Fig. 1. Molecular structure of $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ with phenyl groups omitted for clarity. Important geometrical parameters are: Ru—Hg 2.628(1), Ru—C(3) 2.084(13), Ru—C(1) 2.038(16), Ru—C(2) 1.948(15), C(3)—F 1.38(1) (average), C(4)—F 1.29(1) Å (average); $<$ Ru—Hg—C(4) 173.0(4)°.



Scheme 1. Synthesis and reactions of $RuCl_2(CF_2)(CO)L_2$ (L = PPh_3)

$(PPh_3)_2]^+$, $[RuCl(CO)_3(PPh_3)_2]^+$ and $[RuCl(CO)_2(MeCN)(PPh_3)_2]^+$, respectively. This remarkable reactivity of a metal-bound CF_3 group suggests the intermediacy of a CF_2-complex which is rapidly hydrolysed to CO, viz.:

$$L_nRuCF_3 \xrightarrow{H^+} L_nRu{=}CF_2]^+ \xrightarrow{H_2O} L_nRuCO]^+$$

We have trapped $RuCl_2(CF_2)(CO)(PPh_3)_2$ by reaction of $Ru(CF_3)Cl(CO)(MeCN)(PPh_3)_2$ with dry HCl gas in dry benzene. This complex forms colourless crystals, is extremely moisture-sensitive, and exhibits ν(C—F) IR activity at 1210 and 1155 cm^{-1}, a position almost 200 cm^{-1} higher than the precursor CF_3 complex (see Table 1).

TABLE 1

IR[a] AND ^{1}H NMR DATA FOR TRIFLUOROMETHYL- AND FLUOROCARBENE-RUTHENIUM DERIVATIVES

Compound[b]	ν(CO) (cm^{-1})	ν(CF) (cm^{-1})	Other bands (cm^{-1})	Chemical shifts (τ)[c]
$Ru(CF_3)(HgCF_3)(CO)_2L_2$	2018,1963	1102,1051,1012 960		
$Ru(CF_3)Cl(CO)_2L_2$	2061 ,2005	1073,1006,990 980,974,965		
$Ru(CF_3)Cl(CO)(MeCN)L_2$	1950	1060,985,963 958	2320,2280 ν(CN)	
$[Ru(HgCF_3)(CO)_3L_2]^+$	2093,2043 2022	1108,1057		
$[RuCl(CO)_2(MeCN)L_2]^+$	2069,2012			
$RuCl_2(CF_2)(CO)L_2$	2035,2014[d]	1210,1184 1155m,1138m		
$RuCl_2(CFNMe_2)(CO)L_2$	1979	1026 m	1572 ν(CN)	7.27d, ^4J(F—H) 2 Hz, $N(CH_3)_2$ 7.90d, ^4J(F—H) 5 Hz, $N(CH_3)_2$
$[RuCl(CFNMe_2)(CO)(CNR)L_2]^{+}$[e]	2003	1038 m	2163,1501 ν(CN)	7.10d, ^4J(F—H) 2 Hz, $N(CH_3)_2$ 7.32d, ^4J(F—H) 5 Hz, $N(CH_3)_2$
$RuCl_2(CFOMe)(CO)L_2$	1973	1060 m	1310,1281 ν(CO)	7.10 3H—OCH_3
$RuCl_2(\overline{COCH_2CH_2O})(CO)L_2$	1970		1228 ν(CO)	

[a] Measured as Nujol mulls; all bands strong unless indicated otherwise. [b] L = PPh_3, satisfactory elemental analyses obtained for all compounds, cations as perchlorate salts. [c] In $CDCl_3$ solution. [d] Solid-state splitting [e] R = *p*-tolyl.

A selection of the simple reactions of $RuCl_2(CF_2)(CO)(PPh_3)_2$ is given in Scheme 1. Water produces $RuCl_2(CO)_2(PPh_3)_2$, ethanediol the dioxolanylidene complex, $RuCl_2(\overline{COCH_2CH_2O})(CO)(PPh_3)_2$ and methanol the fluoromethoxy carbene complex, $RuCl_2(CFOMe)(CO)(PPh_3)_3$. Dimethylamine gives the fluoro dimethylamino carbene complex, $RuCl_2(CFNMe_2)(CO)(PPh_3)_2$. The ^{1}H NMR spectra of this compound and the derived cation show long-range coupling of the NMe_2 groups to fluorine (see Table 1). Related complexes, $CH_3C_5H_4Mn(CFNEt_2)(CO)_2$ and $C_5H_5Mn(CFPh)(CO)_2$ have been described from addition of F^- to cationic carbyne complexes [7].

We thank the N.Z. Universities Grants Committee for grants towards instrumental facilities and Johnson Matthey for a generous loan of ruthenium.

References

1 W.R. Roper and A.H. Wright, J. Organometal. Chem., 233 (1982) C59.
2 G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Amer. Chem. Soc., 102 (1980) 1206.
3 D. Mansuy, Pure Appl. Chem., 52 (1980) 681.
4 D.L. Reger and M.D. Dukes, J. Organometal. Chem., 153 (1978) 67.
5 B.E. Cavit, K.R. Grundy and W.R. Roper, J. Chem. Soc. Chem. Commun., (1972) 60.
6 J.P. Collman and W.R. Roper, J. Amer. Chem. Soc., 87 (1965) 4008.
7 E.O. Fischer, W. Kleine and F.R. Kreissl, Angew. Chem. Internat. Edn., 15 (1976) 616; E.O. Fischer, W. Kleine, W. Schambeck and U. Schubert, Z. Naturforsch. B. 36 (1981) 1575.