

Oxidation State Control of the Reactivity of a Transition Metal–Carbon Double Bond. Synthesis, X-Ray Crystal Structure, and Reactions of the Zerovalent Difluorocarbene Complex $[\text{Ru}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$

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Reaction of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ with $[\text{Cd}(\text{CF}_3)_2(\text{MeOCH}_2\text{CH}_2\text{OMe})]$ produces the zerovalent CF_2 -complex, $[\text{Ru}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$; X-ray crystal structure determination reveals very distorted trigonal bipyramidal geometry and an $\text{Ru}=\text{C}$ distance of 1.83(1) Å, and reactions indicate that when compared with an Ru^{II} CF_2 -complex, the CF_2 -ligand in the zerovalent compound has greatly reduced reactivity towards nucleophiles and in fact reacts with the electrophiles HCl and Ag^+ giving $[\text{Ru}(\text{CF}_2\text{H})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{CF}_2\text{Ag}(\text{H}_2\text{O}))(\text{CO})_2(\text{PPh}_3)_2]^+$, respectively.

Studies of the chemical behaviour of transition metal carbene complexes, $\text{L}_n\text{M}=\text{CXY}$, have led to the recognition of two apparently distinct types of reactivity. Complexes of early transition metals show ylide-type reactivity, *i.e.* the carbene centre is nucleophilic, *e.g.* $[\text{Ta}(=\text{CH}_2)(\text{Me})\text{cp}_2]$ ($\text{cp} = \text{C}_5\text{H}_5$),¹ while most complexes of later transition elements exhibit electrophilic carbene centres, *e.g.* $[\text{Fe}(=\text{CH}_2)(\text{CO})_2\text{cp}_2]^+$ (this compound is stable only as a Lewis base adduct, *e.g.* $[\text{Fe}(\text{CH}_2\text{-SMe}_2)(\text{CO})_2\text{cp}_2]^+$).² The electrophilicity is clearly enhanced

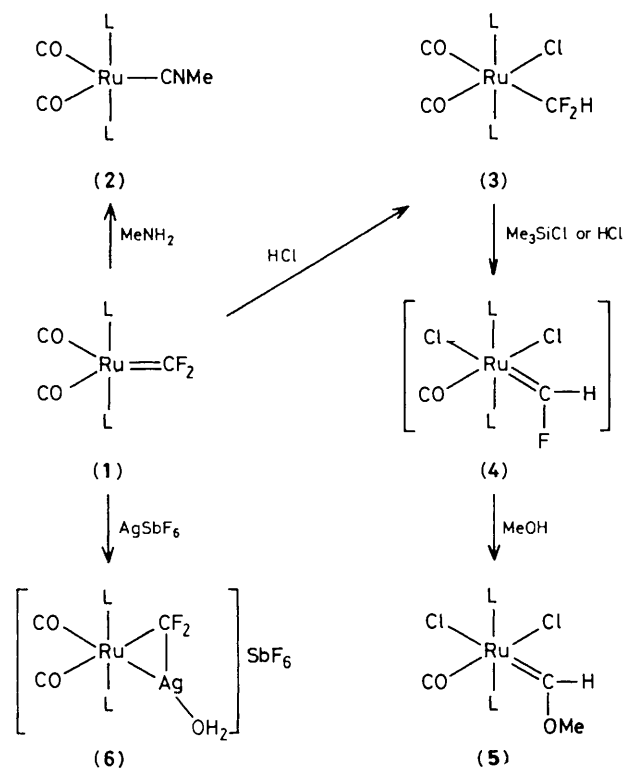
when the complex bears an overall positive charge. However, the observed reactivity is not necessarily a reflection of the real charge distribution and both Mulliken population analysis^{3,4} and e.s.c.a. measurements⁵ indicate that the carbene centres are often more negative than the carbon atoms of other accompanying ligands, *e.g.* CO , in these molecules. The direction of nucleophile addition can then be explained in terms of frontier orbital control of these reactions.^{4,6}

The effect upon carbene reactivity of changes in oxidation

state of the metal is not readily observed because few complexes are known with the same carbene ligand bound to a metal in two different oxidation states. We have recently described the ruthenium(II) CF_2 -complex, $[\text{RuCl}_2(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2]^7$ and in this particular environment the CF_2 -ligand exhibits the expected electrophilic properties and readily undergoes substitution reactions with a variety of nucleophiles [equation (1)].



In this communication we report (i) the synthesis of a zerovalent CF_2 -complex, $[\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$, (ii) an *X*-ray crystal structure determination of this molecule, and (iii)



Scheme 1. Reactions of $[\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{L} = \text{PPh}_3$).

a demonstration that the CF_2 -ligand in this zerovalent complex has greatly reduced reactivity towards nucleophiles and instead reacts with electrophiles such as H^+ , Ag^+ , and Au^+ .

Reaction between $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2]^8$ and $[\text{Hg}(\text{CF}_3)_2]$ gives the simple oxidative-addition product, $[\text{Ru}(\text{CF}_3)(\text{HgCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$, the structure of which has been confirmed crystallographically.⁷ When $[\text{Cd}(\text{CF}_3)_2(\text{MeOCH}_2\text{CH}_2\text{OMe})]^9$ is used instead of $[\text{Hg}(\text{CF}_3)_2]$ the product is $[\text{Ru}(\text{CF}_3)(\text{CdCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$, but here the weaker $\text{Ru}-\text{Cd}$ bond allows an elimination reaction forming the zerovalent CF_2 -complex. Pale-yellow, air-stable crystals of (1) suitable for *X*-ray analysis were grown from $\text{C}_6\text{H}_6-\text{C}_6\text{H}_{12}$.

Crystal data for (1): $\text{C}_{39}\text{H}_{30}\text{F}_2\text{O}_2\text{P}_2\text{Ru}-\text{C}_6\text{H}_6$, $M = 809.8$, monoclinic, space group $P2_1/c$, $a = 17.927(2)$, $b = 12.390(3)$, $c = 18.726(2)$ Å, $\beta = 102.84(1)^\circ$, $U = 4055(2)$ Å³, $Z = 4$, $D_c = 1.326$ g cm⁻³, $\mu(\text{Mo}-K_\alpha) = 5.05$ cm⁻¹. R is presently 0.088 (phenyl carbon atoms assigned isotropic temperature factors, hydrogen atoms not yet included) for 2590 observed reflections [$I > 3\sigma(I)$, $\text{Mo}-K_\alpha$ radiation, $\theta_{\text{max}} = 21^\circ$] corrected for

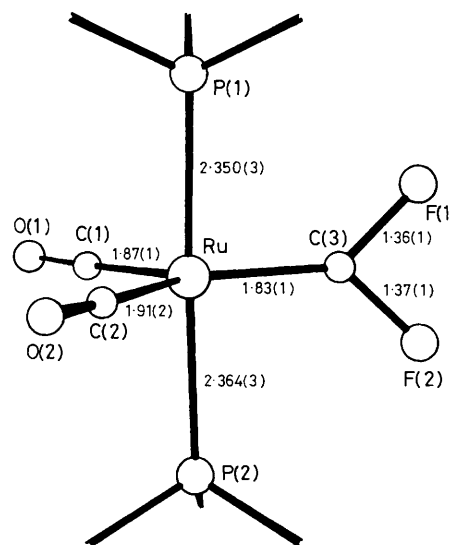


Figure 1. Molecular structure of $[\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (phenyl rings omitted for clarity). Bond lengths are given in Å. Important angles are: $\text{C}(2)-\text{Ru}-\text{C}(2)$ $109.5(6)$, $\text{C}(1)-\text{Ru}-\text{C}(2)$ $116.1(6)$, $\text{C}(2)-\text{Ru}-\text{C}(3)$ $134.4(6)$, $\text{F}(1)-\text{C}(3)-\text{F}(2)$ $88.7(9)$, $\text{Ru}-\text{C}(3)-\text{F}(1)$ $136.6(8)$, and $\text{Ru}-\text{C}(3)-\text{F}(2)$ $134.5(8)^\circ$.

Table 1. I.r. data (in cm^{-1})^a for ruthenium complexes.^b

Complex	$\nu(\text{CO})$	$\nu(\text{CF})$
$[\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (1)	1983, 1910	1083, 980
$[\text{Ru}(\text{CNMe})(\text{CO})_2(\text{PPh}_3)_2]$ (2)	1900, 1855	—
$[\text{Ru}(\text{CF}_2\text{H})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ (3)	2059, 2042, 1999, 1979 ^c	980, 944, 928, 911
$[\text{RuCl}_2(\text{CHOMe})(\text{CO})(\text{PPh}_3)_2]$ (5)	1989	—
$[\text{Ru}(\text{CF}_2\text{Au})(\text{CO})_2(\text{PPh}_3)_2]$	2029, 1985	1057, 1000, 978, 968
$[\text{Ru}(\text{CF}_2\text{Ag}\{\text{H}_2\text{O}\})(\text{CO})_2(\text{PPh}_3)_2]^+$ (6)	2018, 1943	1094, 1019

^a Nujol mulls. ^b All compounds have satisfactory elemental analyses. ^c Solid-state splitting. $\nu(\text{CO})$ measured in CH_2Cl_2 solution at 2035, 1995 cm^{-1} .

absorption and isotropic decay (10%), Enraf-Nonius CAD4 diffractometer.†

The structure shown in Figure 1 reveals a Ru-CF₂ distance significantly shorter than the Ru-CO distances. There is no obvious reason for the marked asymmetry of the angular arrangement of the equatorial ligands. The CF₂-ligand lies perpendicular to the equatorial plane where maximum π -overlap with Ru-orbitals would occur. The structure of [Os(=CH₂)-Cl(NO)(PPh₃)₂] also has CH₂ lying perpendicular to the equatorial plane.¹⁰ This geometry of the CF₂-attachment suggests this ligand is functioning as a very good π -acceptor ligand and this is evident also from the i.r. data presented in Table 1. The ν (CO) values for (1) are higher than those for [Ru(CO)₂(CS)(PPh₃)₂] and [Ru(CO)₂(CSe)(PPh₃)₂]¹¹ where both CS and CSe are recognized as excellent π -accepting ligands.

Complex (1) can be recrystallized from wet solvents and also from alcohols without reaction. This contrasts with [RuCl₂(CF₂)(CO)(PPh₃)₂] where the reactivity of the CF₂-ligand is such that this molecule can be prepared only in rigorously-dried solvents. Complex (1) was inert towards PhLi but did react slowly with MeNH₂ to give [Ru(CNMe)(CO)₂(PPh₃)₂], (2). Reaction with AgSbF₆ gives the bridging CF₂-complex, [Ru(CF₂Ag{H₂O})(CO)₂(PPh₃)₂]SbF₆, (6), (see Scheme 1) and a related Au^I complex, [Ru(CF₂AuI)(CO)₂(PPh₃)₂], results from reaction with the conveniently soluble Au^I salt, Et₄NAuI₂. The structure of these complexes is

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

probably similar to that found for [Os(CH₂AuI)Cl(NO)(PPh₃)₂].¹⁰ Complex (1) reacts instantly with HCl forming the difluoromethyl-complex, [Ru(CF₂H)Cl(CO)₂(PPh₃)₂], (3). Fluoride can be abstracted from (3) with either HCl or Me₃SiCl forming the CFH-complex, [RuCl₂(CFH)(CO)(PPh₃)₂], (4). This has not been isolated but trapped through reaction with methanol as the stable compound, [RuCl₂(CHOMe)(CO)(PPh₃)₂], (5).

The synthesis of low-valent CF₂-complexes using [Cd(CF₃)₂(MeOCH₂CH₂OMe)] appears to be of wide applicability and we have prepared and are studying [Os(=CF₂)(CO)₂(PPh₃)₂], [Ru(=CF₂)Cl(NO)(PPh₃)₂], and [Os(=CF₂)Cl(NO)(PPh₃)₂].

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References

- 1 R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98.
- 2 S. Brandt and P. Helquist, *J. Am. Chem. Soc.*, 1979, **101**, 6473.
- 3 T. F. Block and R. F. Fenske, *J. Organomet. Chem.*, 1977, **139**, 235.
- 4 H. Nakatsuji, J. Ushio, S. Han, and T. Yonezawa, *J. Am. Chem. Soc.*, 1983, **105**, 426.
- 5 W. B. Perry, T. F. Schaaf, W. L. Jolly, L. J. Todd, and D. L. Cronin, *Inorg. Chem.*, 1974, **13**, 2038.
- 6 N. M. Kostić and R. F. Fenske, *Organometallics*, 1982, **1**, 974.
- 7 G. R. Clark, S. V. Hoskins, and W. R. Roper, *J. Organomet. Chem.*, 1982, **234**, C9.
- 8 B. E. Cavit, K. R. Grundy, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1972, 60; K. R. Grundy, *Inorg. Chim. Acta*, 1981, **53**, L225.
- 9 L. J. Krause and J. A. Morrison, *J. Am. Chem. Soc.*, 1981, **103**, 2995.
- 10 A. F. Hill, W. R. Roper, J. M. Waters, and A. H. Wright, submitted to *J. Am. Chem. Soc.*
- 11 A. F. Hill, S. V. Hoskins, and W. R. Roper, unpublished work.