

Fluoroalkynes

International Edition: DOI: 10.1002/anie.201702401 German Edition: DOI: 10.1002/ange.201702401

A Structurally Characterized Fluoroalkyne

Lewis M. Hall, David P. Tew, Natalie E. Pridmore, Adrian C. Whitwood, Jason M. Lynam,* and John M. Slattery*

In memory of Roger Mawby 1939-2017

Abstract: The facile synthesis of a stable and isolable compound with a fluoroalkynyl group, $M-C\equiv CF$, is reported. Reaction of $[Ru(C\equiv CH)(\eta^5-C_5Me_5)(dppe)]$ with an electrophilic fluorinating agent (NFSI) results in the formation of the fluorovinylidene complex $[Ru(=C=CHF)(\eta^5-C_5Me_5)(dppe)]$ - $[N(SO_2Ph)_2]$. Subsequent deprotonation with $LiN(SiMe_3)_2$ affords the fluoroalkynyl complex $[Ru(C\equiv CF)(\eta^5-C_5Me_5)-(dppe)]$. In marked contrast to the rare and highly reactive examples of fluoroalkynes that have been reported previously, this compound can be readily isolated and structurally characterized. This has allowed the structure and bonding in the CCF motif to be explored. Further electrophilic fluorination of this species yields the difluorovinylidene complex $[Ru(C=CF_2)(\eta^5-C_5Me_5)(dppe)][N(SO_2Ph)_2]$.

Despite numerous examples of $C(sp^3)$ -F and $C(sp^2)$ -F bonds in chemistry, which play a hugely important role in materials, medicinal and agrochemical applications^[1] there are few examples of compounds containing C(sp)-F bonds. Those that have been reported are often highly reactive and, in marked contrast to fluoroalkanes, fluoroalkenes and fluoroaromatic compounds, fluoroalkynes readily undergo oligomerization reactions. For example, FC=CF is unstable at temperatures above -196°C^[2] and 'BuC=CF undergoes cyclotrimerization below 0°C.^[3] Fluoroalkynes having perfluoroalkyl groups, however, appear to have greater stability.^[4] Recent calculations indicate that the source of this high reactivity is a dimerization processes to (initially) give a diradical.^[5] In the case of fluorinated alkynes, the transition state for dimerization is at low energy compared to the alkynes and the resulting diradical is thermodynamically more stable than the starting compounds. In contrast, for the non-fluorinated analogues, the barrier to dimerization is much higher and the resulting diradicals are thermodynami-

[*]	L. M. Hall, Dr. N. E. Pridmore, Dr. A. C. Whitwood, Dr. J. M. Lynam,
	Dr. J. M. Slattery
	Department of Chemistry
	The University of York
	Heslington, York, YO10 5DD (UK)
	E-mail: jason.lynam@york.ac.uk
	john.slattery@york.ac.uk
	Dr. D. P. Tew
	School of Chemistry
	University of Bristol
	Cantock's Close, Bristol, BS8 1TS (UK)
	Supporting information and the ORCID identification number(s) for
Ā	the author(s) of this article can be found under:

https://doi.org/10.1002/anie.201702401.

Angew. Chem. Int. Ed. 2017, 56, 1–7

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

cally unstable. As fluorinated alkynes, RC=CF, are rare and demonstrably unstable they have not been studied or utilized extensively. Herein we report the synthesis of a stable, isolable fluoroalkynyl complex that allows 1) a detailed characterization of the RC=CF motif, where R in this case is a metal-containing fragment, and 2) a preliminary study of the reactivity of the fluoroalkynyl ligand.

We recently described how the electrophilic fluorination of alkenyl-containing^[6] and alkynyl-containing^[7] ligands within the coordination sphere of ruthenium^[8] may lead to the rapid and selective formation of new fluorinated ligands, including rare examples of fluorovinylidenes (Scheme 1 a).



Scheme 1. a) synthesis of fluorinated vinylidenes and b) proposed synthetic strategy.

This occurs via the novel outer-sphere electrophilic fluorination (OSEF) mechanism. Extension of this synthetic methodology promised to allow access to previously unexplored fluorinated alkynyl complexes, Scheme 1b. The proposed route involved electrophilic fluorination of a hydrogen-substituted alkynyl complex MC=CH to give the cationic vinylidene complex [M=C=CHF]⁺ and subsequent deprotonation to give the desired fluorinated alkynyl MC=CF. It was anticipated that the metal center and ancillary ligands would provide protection of the fluorinated alkyne functionality, inhibiting the facile dimerization pathway in the organic analogues. Herein we describe the successful implementation of this strategy and characterization of a rare example of a molecule with a stable C=CF group.

Reaction of $[\text{Ru}(C=CH)(\eta^5-C_5Me_5)(dppe)]$ (1), with NFSI in toluene solution at -78 °C followed by warming to room temperature resulted in selective fluorination at the coordinated alkynyl ligand and formation of $[\text{Ru}(\eta^5-C_5Me_5)(=C=CHF)(dppe)][N(SO_2Ph)_2]$, 2[N(SO_2Ph)_2], Scheme 2. The for-

Communications





Scheme 2. i_1 + NFSI, toluene, $-78 \,^{\circ}C \rightarrow RT$; i_1 + LiN(SiMe₃)₂, $-HN(SiMe_3)_2$, $-Li[N(SO_2Ph)_2]$, THF, $-78 \,^{\circ}C \rightarrow RT$. Structures of the 2⁺ cation and 3 are shown with thermal ellipsoids at 50% probability and hydrogen atoms [except H(4A) and H(4B)] are omitted for clarity. In the 2⁺ cation the hydrogen and fluorine atoms of the vinylidene are disordered over two positions.

mation of the vinylidene ligand was confirmed by the observation of resonances at $\delta = 362.8$ (d, ${}^{3}J_{CF} = 43.5$ Hz) and 173.9 (d, ${}^{1}J_{CF} = 236.2$ Hz) ppm in the ${}^{13}C{}^{1}H$ NMR spectrum and doublets at $\delta = 7.32$ and -235.8 ppm in the ${}^{1}H$ and ${}^{19}F$ NMR spectra, respectively (${}^{2}J_{FH} = 80.2$ Hz). Salt metathesis with NaPF₆ resulted in the formation of **2**[PF₆] which was structurally characterized by single crystal X-ray diffraction,^[9] confirming the assignments of the NMR spectra.

Conversion of $2[N(SO_2Ph)_2]$ into the desired alkynyl complex $[Ru(C=CF)(\eta^5-C_5Me_5)(dppe)]$ (3), was achieved by deprotonation with LiN(SiMe_3)₂ in THF solution at -78 °C followed by warming to room temperature. The presence of the alkynyl group in 3 was confirmed by a band in the IR spectrum at 2148 cm⁻¹, resonances at $\delta = 185.6$ and 111.4 (d, ${}^{1}J_{CF} = 332.2$ Hz) ppm in the ${}^{13}C{}^{1}H{}$ NMR spectrum, and a triplet resonance at $\delta = -189.4$ (t, ${}^{4}J_{FP} = 4.8$ Hz) ppm in the ${}^{19}F$ NMR spectrum. The structure of 3 was confirmed by single-crystal X-ray diffraction, which unambiguously showed the presence of the fluorinated alkynyl ligand.

Complex 3 proved to be stable for extended periods in both solution and the solid state. The 1H and $^{31}P\{^1H\}$ NMR

spectra of a C_6D_6 solution of **3** were essentially unchanged over a period of four months at room temperature and, although some new resonances of low intensity appeared in the ¹⁹F NMR spectrum over this time, the long-term stability of a fluoroalkyne in a condensed phase is without precedent.^[10] The spectroscopic parameters for **3** are more closely related to fluorinated alkynes such as FC=CF than to the fluorocarbyne complexes $[Mo(\eta^5-C_5Me_5)(CO)_2(\equiv CF)]^{[11]}$ and $[(PNP)Rh \equiv CF][CHB_{11}Cl_{11}]^{[12]}$ which are to our knowledge the only other structurally characterized examples of a C(sp)-F bond (PNP = $\{2^{-i}Pr_2P-4-Me-C_6H_4\}_2N^{-}$). For example, **3** shows a resonance in the ¹⁹F NMR spectrum at $\delta_F = -189.4$ $({}^{1}J_{CF} = 332.2 \text{ Hz})$ ppm and the corresponding resonance in FC=CF is at $\delta_F = -261.3$ (¹ $J_{CF} = 287.3$ Hz) ppm, but [Mo(η^5 - $C_5Me_5)(CO)_2(\equiv CF)$] ($\delta_F = 78.15$ (${}^1J_{CF} = 556$ Hz) ppm) and $[(PNP)Rh \equiv CF][CHB_{11}Cl_{11}] (\delta_F = 66.2 (^1J_{CF} = 470 \text{ Hz}) \text{ ppm})$ show a marked difference. Furthermore, a comparison between the spectroscopic and structural parameters for fluorinated and non-fluorinated alkynes (Table 1) shows that the presence of fluorine substituents shortens the C=C bond and there is a commensurate blue shift in the C=C stretch in

Compound	C≡C [Å]	C—F [Å]	C-H [Å]	Ru—C [Å]	ν C≡C [cm ⁻¹]	ν C–H or C–F $[cm^{-1}]$
НС≡СН	1.2084 ^[14]		1.0570 ^[14]	_	1974 ^[15]	3374 and 3287 ^[15]
	1.208		1.076		2085	3525 and 3421
FC=CH	1.198(3) ^[16]	1.279(5) ^[16]	1.053(5) ^[16]	-	2240 ^[17]	3358 1057, 586 and 583 ^[17]
	1.204	1.271	1.074		2357	3450, 1119 and 651
FC==CF ^[18]	1.197(3)	1.276(2)		_	2437	1349 and 794
	1.195	1.278			2591	1419 and 820
[Ru]−C≡CH ^[19] 1	1.202(3)		-	2.015(2)	1925	3269
	1.230		1.075	2.000	2056	3489
[Ru]−C≡CF 3	1.187(4)	1.324(4)		2.036(3)	2148	1068
	1.224	1.295		2.017	2307	1115

Table 1: Structural comparisons between fluorinated and non-fluorinated alkyne/ alkynyl compounds.^[a]

[a] Unscaled, calculated values at the (RI)-pbe0/def-SV(P) level in italics.

www.angewandte.org

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers!

the vibrational spectra. Although the crystallographically determined $C \equiv C$ bond lengths in the alkynyl groups of **1** and **3** are statistically indistinguishable, the $C \equiv C$ stretch of the alkynyl ligand exhibits the same blue shift on fluorination observed in the alkyne analogues. These data support the suggestion that the compound is best viewed as containing a fluorinated alkynyl ligand and that the C–F bond in **3** is closely related to the fluoroalkynes.

To assess whether the stability of **3** arises from a thermodynamic stabilization of the C–F bond, the bond dissociation energies (BDEs) for a range of C–H and C–F bonds with sp, sp^2 , and sp^3 hybridization have been calculated (see Supporting Information for methodology and calibration).^[13] The resulting data are shown graphically in Figure 1, in which the



Figure 1. Plot of calculated C–F bond dissociation energy versus calculated C–H bond dissociation energy. The dotted line represents a 1:1 relationship between the parameters. Insert shows expansion between $510-560 \text{ kJ mol}^{-1}$.

dotted line represents a 1:1 relationship between C–H and C– F BDEs. Systems with sp²- and sp³-hybridized bonds appear above the line, indicating that, as expected, the C–F bonds in these systems are stronger than the corresponding C–H bonds. However, the same trend in relative BDEs is not predicted for compounds containing C=CH and C=CF groups: in these cases, the calculated BDE for the C–H and C–F bonds are essentially identical. This is also true for compounds **1** and **3**.

The similarity between the spectroscopic parameters and C–F BDE of **3** and compounds RC=CF presumably indicates that the enhanced stability of the ruthenium-substituted compound is not thermodynamic in nature. This is supported by additional calculations which demonstrate that the putative diradical arising from the dimerization of **3** (Scheme 3) is thermodynamically more stable ($\Delta G_{298} = -18 \text{ kJ mol}^{-1}$) than two molecules of **3**. The corresponding dimerization of **1** is thermodynamically disfavored ($\Delta G_{298} = +131 \text{ kJ mol}^{-1}$), mirroring the behavior of alkynes RC=CF and RC=CH.^[5] We therefore suggest that the presence of the bulky dppe and Cp* ligands kinetically stabilize the C=CF linkage by inhibiting the intermolecular dimerization and oligomerization reac-



$R_1 = R_2 = H$	∆G ₂₉₈ = +128 kJ mol ⁻¹
$R_1 = F R_2 = H$	∆G ₂₉₈ = +14 kJ mol ⁻¹
$R_1 = R_2 = F$	∆G ₂₉₈ = -86 kJ mol ⁻¹
$R_1 = Ru(\eta^5 - C_5 H_5)(dppe) R_2 = H(1)$	∆G ₂₉₈ = +131 kJ mol ⁻¹
$R_1 = Ru(\eta^5 - C_5 H_5)(dppe) R_2 = F(3)$	∆G ₂₉₈ = -18 kJ mol ⁻¹

(b)



Scheme 3. a) DFT-calculated ((RI-)PBE0-D3/def2-TZVPP//(RI-)BP86/ SV(P) level in CH₂Cl₂ (ϵ = 8.93) using the COSMO model) energies for alkynes and their corresponding diradical dimerization products. The data for R₁ = R₂ = H and R₁ = F and R₂ = H show good agreement with those previously reported.^[5] b) Calculated structure of the diradical arising from the dimerization of **3**.

tions observed in the metal-free analogues. This is supported by preliminary mechanistic investigations, which showed that ΔG_{298}^{\pm} for dimerization of the sterically less encumbered model complex [Ru(C=CF)(η^5 -C₅Me₅)(PH₂C₂H₄PH₂)] is + 80 kJ mol⁻¹, similar to that for the dimerization of FC=CF (+ 68 kJ mol⁻¹). However, potential energy surface scans (at the PBE0/def2-TZVPP//BP86/SV(P) level) suggest that when the full dppe ligands are included, this creates a sterically more crowded transition state for dimerization of **3**, with an electronic energy barrier around 50 kJ mol⁻¹ higher in energy than the model system.

To rationalize the structural and spectroscopic changes observed upon the introduction of fluorine into alkynyl systems, the electronic structures of FC=CF, HC=CF, HC= CH, [Ru(η^5 -C₅H₅)(PH₃)₂(C=CF)], and [Ru(η^5 -C₅H₅)(PH₃)₂-(C=CH)] were optimized using explicitly correlated Brueckner coupled cluster theory (BCCD(T)-F12).^[20] Brueckner orbitals (BOs) derived from these calculations were qualitatively similar to the Kohn–Sham orbitals obtained from a treatment of FC=CF, HC=CF, HC=CH, [Ru(η^5 -C₅H₅)-(PPh₃)₂(C=CF)], and [Ru(η^5 -C₅H₅)(PPh₃)₂(C=CH)] at the (RI)-PBE0/def2-TZVPP level, although the energies obtained from the BOs were closer to those expected on the basis of photoelectron spectroscopy giving confidence that the resulting wavefunctions were effectively modeling the electronic structure of the molecules (Figure 2).



Communications

Angewandte International Edition Chemie



Figure 2. Brueckner orbitals for FC=CF, HC=CF, HC=CH, $[Ru(\eta^{5}-C_{5}H_{5})(PH_{3})_{2}(C=CH)]$, and $[Ru(\eta^{5}-C_{5}H_{5})(PH_{3})_{2}(C=CF)]$. Energies are in electron-volts.

An examination of the frontier orbitals provides an explanation for some of the observed changes on incorporation of fluorine into sp-hybridized systems. For example, the highest occupied orbital in all instances has C–C π -bonding character, but is C–F π -antibonding. This interaction is therefore expected to weaken C–F bonding, in a similar way that the occupancy of the doubly degenerate π^* orbitals in F₂ weakens the F–F bond. This provides a ready explanation for the weaker-than-expected C–F bond in sp-hybridized systems. In FC=CF there are a total of 12 electrons involved in π bonding (orbitals 10–15). Of these, eight are involved in C–C π -bonding interactions (orbitals 10, 11, 14, and 15) whereas those in orbitals 12 and 13 are C–C

 π antibonding. A net C-C π -bond order of two might be predicted on this basis; however, as the orbitals 12 and 13 are largely based on fluorine, their effect on decreasing the C-C bond order is expected to be small, which may explain the shortening of the C=C bond on fluorine incorporation.

Inspection of the orbitals for $[Ru(\eta^5-C_5H_5)(PH_3)_2(C\equiv CF)]$ and $[Ru(\eta^5-C_5H_5)(PH_3)_2(C\equiv CH)]$ revealed that the C–F interactions within the alkynyl moiety showed broadly the same features (notably orbitals 52–54, which correspond to a set of three 4d orbitals with antibonding interactions with the CCF π system and display the same antibonding C–F interactions as the FCCF frontier orbitals), although the decreased symmetry results in a breaking of the degeneracy of

www.angewandte.org

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers!



the π system. This, coupled with the mirroring of the analogous spectroscopic parameters with FC=CF reinforces the notion that **3** is best viewed as a ruthenium-substituted fluorinated alkyne.

The ready availability of **3** offered the opportunity to explore the reactivity of the MC=CF group and, specifically, to incorporate a second fluorine atom into the complex and form a difluorinated vinylidene ligand. Free vinylidenes are at a much higher energy than the corresponding alkynes and it is only in the coordination sphere of some metals where this is reversed.^[21] The lowest difference in energy between the alkyne/vinylidene pair is for the difluorovinylidene and difluoroacetylene pair (ca. 130 kJ mol⁻¹).^[21,22] Furthermore the isomerization of difluorovinylidene to difluoroacetylene has a much more substantial barrier (ca. 136 kJ mol⁻¹) than the hydrogen-containing analogues, which is believed to be due to the antiaromatic transition state for fluorine migration and the commensurate requirement to cleave a C-F bond.^[22c] As a consequence of this high barrier to isomerization to its parent alkyne, difluorovinylidene can be observed in low temperature matrices.^[23] Curiously, this stability has not resulted in an extensive chemistry of difluorovinylidene as a ligand, indeed the only examples are in dimeric complexes prepared through defluorination reactions.^[24]

Using OSEF methodology,^[6,7] the fluoroalkynyl ligand in **3** may be readily converted into a difluorovinylidene. Reaction of **3** with NFSI in THF at -78 °C resulted in formation of [Ru(η^5 -C₅Me₅)(=C=CF₂)(dppe)][N(SO₂Ph)₂], (4[N-(SO₂Ph)₂]), Scheme 4, which was characterized in the same manner as **2**[N(SO₂Ph)₂] and **3**, Scheme 2. Resonances at δ -134.0 (s) ppm in the ¹⁹F NMR spectrum and at δ 366.7 (t, ³J_{CF}=22.5 Hz) and δ 231.3 (t, ¹J_{CF}=277.6 Hz) ppm in the ¹³C{¹H} NMR spectrum of **4**[N(SO₂Ph)₂] are again consistent with the presence of the difluorinated vinylidene ligand. The structure of **4**[PF₆] was also confirmed by single-crystal X-ray diffraction (Scheme 4).



Scheme 4. i) + NFSI, THF, $-78 \,^{\circ}$ C \rightarrow RT. Structure of the 4⁺ cation shown with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.

Angew. Chem. Int. Ed. 2017, 56, 1-7

C 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.angewandte.org

These are not the final page numbers!

In conclusion, it has been demonstrated that the versatile nature of OSEF may be used to prepare a novel fluorinesubstituted alkynyl ligand which acts as model for more reactive non-metal-substituted compounds. Detailed insight into the structure of fluorinated alkynes has been obtained and the ready preparation of this compound has demonstrated that it may be used for further organometallic chemistry.

Acknowledgements

We are grateful to the University of York (PhD studentships to LMH and NEP) and EPSRC (grants EP/H011455 and EP/ K031589/1) for funding. DPT thanks the Royal Society for a University Research Fellowship. Fruitful discussions with Professors Robin Perutz, Youichi Ishii and Odile Eisenstein are also gratefully acknowledged.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkynes \cdot alkynyls \cdot electrophilic fluorination \cdot fluorine \cdot vinylidenes

- a) J.-P. Bégué, D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, Wiley, Hoboken, **2008**; b) M. Hird, *Chem. Soc. Rev.* **2007**, *36*, 2070–2095; c) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; d) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev.* **2014**, *114*, 2432–2506.
- [2] H. Bürger, S. Sommer, J. Chem. Soc. Chem. Commun. 1991, 456–458.
- [3] Z.-K. Yao, Z.-X. Yu, J. Am. Chem. Soc. 2011, 133, 10864–10877.
- [4] R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine, K. Mullen, D. R. Taylor, *Tetrahedron Lett.* **1968**, *9*, 3909–3910.
- [5] S. Fabig, G. Haberhauer, R. Gleiter, J. Am. Chem. Soc. 2015, 137, 1833–1843.
- [6] L. M. Milner, N. E. Pridmore, A. C. Whitwood, J. M. Lynam, J. M. Slattery, J. Am. Chem. Soc. 2015, 137, 10753–10759.
- [7] L. M. Milner, L. M. Hall, N. E. Pridmore, M. K. Skeats, A. C. Whitwood, J. M. Lynam, J. M. Slattery, *Dalton Trans.* 2016, 45, 1717–1726.
- [8] L. M. Hall, J. M. Lynam, L. M. Milner, J. M. Slattery, UK Patent GB1421598.2, 2014.
- [9] Complex 2-PF₆ co-crystallized as two forms, one green with no solvent of crystallization and one orange as a CH_2Cl_2 solvate. Only the bond metrics for the green form are discussed in the manuscript. Crystal data and CIFs for all compounds (including both solvates) are provided in the Supporting Information. CCDC 1535738–1535741, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [10] Perfluoromethylacetylene has been reported to undergo no change in the gas phase at 25 °C at 10 cmHg over one month or at



20°C at 1.25 atm over four days, however, it undergoes polymerization at higher pressures. $^{[4]}$

- [11] H. Huang, R. P. Hughes, C. R. Landis, A. L. Rheingold, J. Am. Chem. Soc. 2006, 128, 7454–7455.
- [12] C. J. Pell, Y. Zhu, R. Huacuja, D. E. Herbert, R. P. Hughes, O. V. Ozerov, *Chem. Sci.* **2017**, *8*, 3178–3186.
- [13] For related studies in which a similar methodology has been used to assess changes in M-C and H-C bonding on fluorination see a) E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* 2011, 44, 333-348; b) M. E. Evans, C. L. Burke, S. Yaibuathes, E. Clot, O. Eisenstein, W. D. Jones, *J. Am. Chem. Soc.* 2009, *131*, 13464-13473.
- [14] J. Overend, Trans. Faraday Soc. 1960, 56, 310-314.
- [15] G. Herzberg, Molecular spectra and molecular structure II, Infrared and Raman spectra of polyatomic molecules, 2nd ed., Van Nostrand Reinhold, New York, **1945**, p. 180.
- [16] http://cccbdb.nist.gov/ accessed 03.03.2017.
- [17] L. Andrews, G. L. Johnson, B. J. Kelsall, J. Phys. Chem. 1982, 86, 3374–3380.
- [18] J. Breidung, T. Hansen, W. Thiel, J. Mol. Spectrosc. 1996, 179, 73-78.

- [19] M. I. Bruce, B. G. Ellis, P. J. Low, B. W. Skelton, A. H. White, Organometallics 2003, 22, 3184–3198.
- [20] D. P. Tew, J. Chem. Phys. 2016, 145, 074103.
- [21] O. J. S. Pickup, I. Khazal, E. J. Smith, A. C. Whitwood, J. M. Lynam, K. Bolaky, T. C. King, B. W. Rawe, N. Fey, Organometallics 2014, 33, 1751–1761.
- [22] a) M. J. Frisch, R. Krishnan, J. A. Pople, P. v. R. Schleyer, *Chem. Phys. Lett.* **1981**, *81*, 421–423; b) J. Breidung, W. Thiel, *J. Mol. Spectrosc.* **2001**, *205*, 28–37; c) Z.-H. Loh, R. W. Field, *J. Chem. Phys.* **2003**, *118*, 4037–4044.
- [23] J. Breidung, H. Bürger, C. Kötting, R. Kopitzky, W. Sander, M. Senzlober, W. Thiel, H. Willner, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1983–1985; *Angew. Chem.* **1997**, *109*, 2072–2075.
- [24] a) W. Schulze, K. Seppelt, *Inorg. Chem.* 1988, 27, 3872-3873;
 b) D. J. Anderson, R. McDonald, M. Cowie, *Angew. Chem. Int. Ed.* 2007, 46, 3741-3744; *Angew. Chem.* 2007, 119, 3815-3818;
 c) M. E. Slaney, M. J. Ferguson, R. McDonald, M. Cowie, *Organometallics* 2012, 31, 1384-1396.

Manuscript received: March 6, 2017 Final Article published:





Communications



L. M. Hall, D. P. Tew, N. E. Pridmore, A. C. Whitwood, J. M. Lynam,* J. M. Slattery* ______

A Structurally Characterized Fluoroalkyne



Kinetic stabilisation by {Cp*Ru(dppe)}

Fancy a fluorine? In contrast to other fluorinated alkynes, structurally characterized $\{M-C=CF\}$ exhibits considerable long-term stability. Structural, spectroscopic and computational analyses reveal that this longevity is underpinned by kinetic stabilization by a half-sandwich ruthenium substituent. Subsequent fluorination provides facile access to a rare example of a difluorovinylidene complex.