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Fluorocarbyne complexes *via* electrophilic fluorination of carbido ligands†

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The new fluorocarbynes $[M(\equiv CF)(CO)_2(Tp^*)]$ ($M = Mo, W$; $Tp^* =$ tris(dimethylpyrazolyl)borate) arise from electrophilic fluorination of the lithiocarbynes $[M(\equiv CLi)(CO)_2(Tp^*)]$ with $FN(SO_2Ph)_2$. The reactions of $[W(\equiv CF)(CO)_2(Tp^*)]$ with $[AuCl(SMe_2)]$ and $PhICl_2$ afford the first μ_2 -fluorocarbyne complex $[WAu(\mu-CF)Cl(CO)_2(Tp^*)]$ and the first high oxidation state fluorocarbyne $[W(\equiv CF)Cl_2(Tp^*)]$, respectively.

Introduction

Isolable terminal fluorocarbyne complexes remain exceedingly rare,¹ being limited to those reported by Hughes² and Ozerov³ (Scheme 1). In both cases, access exploits the enhanced nucleofugacity of fluorine bound to a carbon α -to a transition metal.⁴

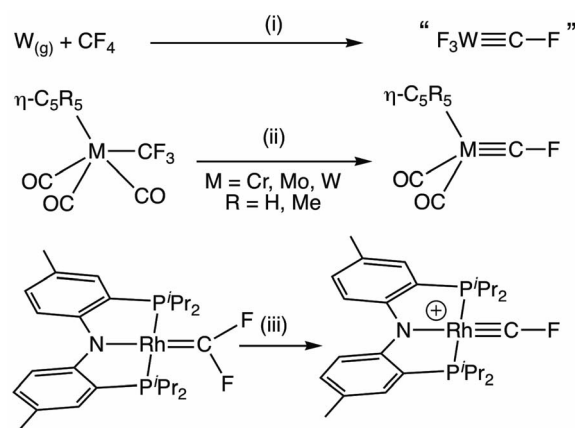
Beyond the addition of cobalt carbonyl to $[Mo(\equiv CF)(CO)_2(\eta^5-C_5Me_5)]$ to afford a μ_3 -fluorocarbyne capped cluster $[MoCo_2(\mu_3-CF)(CO)_8(\eta^5-C_5Me_5)]$,^{2a} no subsequent reactivity of fluorocarbyne ligands has been reported. This is in marked contrast to the heavier halocarbynes $[M(\equiv CX)(CO)_2(Tp^*)]$ ($M = Mo, W$; $X = Cl, Br$; $Tp^* =$ hydrotris(dimethylpyrazolyl)borate),⁵ the synthetic utility of which has been convincingly demonstrated.^{6–9} This utility centres on nucleophilic substitution of the halogen that may be spontaneous^{6–9} or palladium-mediated,¹⁰ the latter *via* the intermediacy of μ -carbido complexes $[MPd(\mu-C)Br(CO)_2(PPh_3)_2(Tp^*)]$.¹¹ Alternatively, lithium/halogen exchange with ^tBuLi affords, *in situ*, the lithiocarbynes $[M(\equiv CLi)(CO)_2(Tp^*)]$ ($M = Mo, W$) that allow the introduction of carbyne substituents in electrophilic form.^{9,12} This latter approach has allowed the synthesis of carbyne ligands that bear substituents based on boron and all the elements of groups 14–16 as well as a range of transition metals.^{11,12}

Missing from the otherwise complete series of molybdenum and tungsten halocarbyne complexes are the lightest members $[M(\equiv CF)(CO)_2(Tp^*)]$ ($M = W$ **1a**, Mo **2a**) that might be seen as analogues of Hughes' fluorocarbynes $[M(\equiv CF)(CO)_2(\eta^5-C_5R_5)]$. These are not available *via* Lalor's original halocarbyne synthesis due to a range of very specific factors peculiar to that system,^{5b} thereby preventing a complete comparative analysis

beyond computational interrogation of the hypothetical complexes $[M(\equiv CX)(CO)_2(Tp^*)]$ ($X = F, Cl, Br, I$; $Tp^* =$ hydrotris(pyrazolyl)borate).¹³ Herein, we now describe (i) the synthesis of the low-valent fluorocarbyne complexes **1a** and **2a** *via* a novel strategy; (ii) the reaction of **1a** to afford the first example of a μ_2 -fluorocarbyne complex **3**; (iii) oxidation to afford the first isolable¹ high-valent fluorocarbyne complex $[W(\equiv CF)Cl_2(Tp^*)]$ (**4**).

Results and discussion

In the absence of the requisite but yet to be described complexes $[M(CF_3)(CO)_3(Tp^*)]$, Hughes' fluorocarbyne synthetic strategy *via* 2-electron reduction of trifluoromethyl complexes (Scheme 1) is not applicable. Although thermodynamically feasible, bromide substitution of, *e.g.*, $[W(\equiv CBr)(CO)_2(Tp^*)]$ (**1c**) by fluoride ($[^tBu_4N]F$ or AgF) fails under the conditions we have so far explored. We therefore turned to an alternative strategy employing the lithiocarbyne $[W(\equiv CLi)(CO)_2(Tp^*)]$ originally

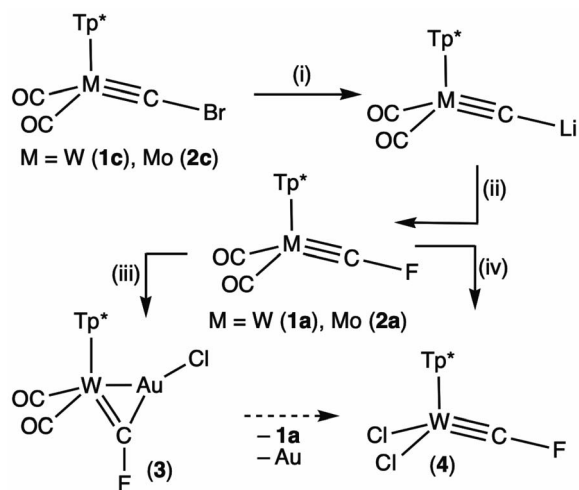


Scheme 1 Synthesis of fluorocarbyne complexes *via* fluoride abstraction from CF_4 , trifluoromethyl and difluorocarbene ligands. (i) $Ar_{(s)}, 8K^{\cdot 1}$ (ii) $2K^{\cdot 8}, -2F^{\cdot}, -CO^{\cdot 2}$ (iii) $[H(SiEt_3)_2][HCB_{11}Cl_{11}], -Et_3SiF^{\cdot 3}$

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Scheme 2 Synthesis of fluorocarbyne complexes via electrophilic fluorination of lithiocarbynes. (i) $n\text{-BuLi}$, $-n\text{-BuBr}$. (ii) $\text{F-N(SO}_2\text{Ph)}_2$. (iii) $[\text{AuCl(SMe}_2)]$. (iv) PhICl_2 .

described by Templeton,¹⁴ but now more conveniently accessible via a simple lithium/halogen exchange reaction of **1c** with $n\text{-BuLi}$ (THF, $-78\text{ }^\circ\text{C}$, Scheme 2).^{10a,12} Templeton has previously accessed the iodocarbyne $[\text{W}(\equiv\text{C-I})(\text{CO})_2(\text{Tp}^*)]$ (**1d**)^{5b} via iodination of $[\text{W}(\equiv\text{C-Cl})(\text{CO})_2(\text{Tp}^*)]$.¹⁴ We therefore considered whether such a strategy might also afford fluorocarbyne complexes.

Treating the lithiocarbyne $[\text{W}(\equiv\text{C-Cl})(\text{CO})_2(\text{Tp}^*)]$, generated *in situ*, with an electrophilic source of fluorine, viz. $\text{FN(SO}_2\text{Ph)}_2$,¹⁵ affords the new fluorocarbyne complex $[\text{W}(\equiv\text{C-F})(\text{CO})_2(\text{Tp}^*)]$ (**1a**, 59%). Similar treatment of $[\text{Mo}(\equiv\text{C-Br})(\text{CO})_2(\text{Tp}^*)]$ (**2c**) affords the molybdenum analogue $[\text{Mo}(\equiv\text{C-F})(\text{CO})_2(\text{Tp}^*)]$ (**2a**, 77%, Scheme 2).

In addition to spectroscopic and electrochemical data (Table 1) **1a** was characterised crystallographically to confirm connectivity, however detailed geometric analysis is precluded by positional disorder of isosteric CO and CF ligands (one contributor shown in Fig. 1 inset), as also recognised for Hughes' complexes $[\text{M}(\equiv\text{C-F})(\text{CO})_2(\eta^5\text{-C}_5\text{R}_5)]$ (M/R = Mo/Me, W/

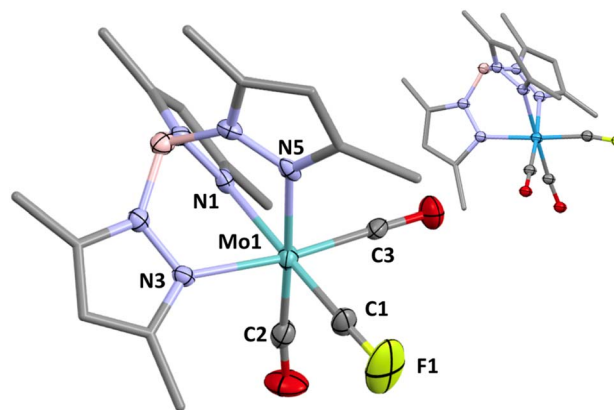


Fig. 1 Molecular structure of $[\text{Mo}(\equiv\text{C-F})(\text{CO})_2(\text{Tp}^*)]$ (**2a**) in a crystal (50% displacement ellipsoids, pyrazolyl groups simplified). Selected bond lengths (Å) and angles ($^\circ$): Mo1–N1 2.247(5), Mo1–N3 2.221(5), Mo1–N5 2.210(5), Mo1–C1 1.886(7), Mo1–C2 1.938(8), Mo1–C3 1.959(7), F1–C1 1.214(8), F1–C1–Mo1 168.4(7), C1–Mo1–N3 100.3(3), C1–Mo1–N5 98.2(3). Inset = less precise structural model for **1a** (positional disorder of CF and CO ligands, one contributor shown).

Me, W/H).² Accordingly, and not surprisingly, crystals of **1a** were found to be essentially isomorphous with those of the radical $[\text{W}(\text{CO})_3(\text{Tp}^*)]$.¹⁶ Crystals of the molybdenum complex **2a**, however, led to a precise structural model free of disorder, geometric data for which indicate that the CF ligand exerts a pronounced *trans* influence on the unique pyrazolyl donor that is reproduced in the computationally optimised geometries of **1a**, **2a** and the simpler model complex $[\text{W}(\equiv\text{C-F})(\text{CO})_2(\text{Tp})]$ (see ESI†). It is a useful feature of the Tp^* ligand that in contrast to cyclopentadienyls for which analogies are entertained, the more clearly octahedral geometry allows both structural and computational interrogation of bonding and implications, e.g., the *trans* influence. Comparative data for F–C(sp) bonds are surprisingly limited to Hughes' (in all but one case disordered) fluorocarbynes^{2,3} and the unique fluoroethynyl complex $[\text{Ru}(\text{C}\equiv\text{C-F})(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)]$ (C–F = 1.324(4) Å).^{15a} Amongst the spectroscopic data of interest, the carbyne gives rise to a doublet resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{C}} = 200.8$

Table 1 Data for the complexes $[\text{M}(\equiv\text{C-R})(\text{CO})_2(\text{Tp}^*)]$ (M = W, Mo)

M	R	ν_{CO}^a cm^{-1}	k_{CO}^b N cm^{-1}	δ_{WC}^c ppm	$^1J_{\text{WC}}$ Hz	E^{0d} V
W	F (1a)	1988, 1888	15.15	200.8	275	0.795
W	Cl (1b)	1991, 1902	15.29	205.7	259	0.830
W	Br (1c)	1994, 1905	15.33	198.0	254	0.820
W	I (1d) ¹⁴	1992, 1907	15.33	183.2	n.r.	—
Mo	F (2a)	2002, 1910	15.44	193.5	—	0.865
Mo	Cl (2b)	2005, 1921	15.54	208.7	—	0.825
Mo	Br (2c)	2008, 1924	15.59	202.5	—	0.830
Mo	I (2d) ^{5b}	2009, 1927	15.62	n.r.	—	—
W	H ¹⁴	1986, 1891	15.16	280.6	192	n.r.
W	CH ₃ (ref. 7d and 17)	1968, 1867	14.86	289.3	n.r.	+0.510
W	Ph ¹⁸	1969, 1876	14.91	277.9	187	n.r.
W	C≡C ^t Bu ^{10c,19}	1977, 1886	15.05	250.6	199	+0.761

^a Measured in CH_2Cl_2 . ^b k_{CK} = Cotton–Kraihanzel CO force constant. ^c Measured in CDCl_3 . ^d Relative to ferrocene ($E_{1/2} = 0.460\text{ V}$ cf. $\text{Ag/Ag}^+ = 0$), measured in CH_2Cl_2 with 1.0 M $[\text{N}^t\text{Bu}_4][\text{PF}_6]$ at 100 mV s^{-1} ; see ESI for cyclic and square-wave voltammograms. n.r. = not reported.

showing coupling to both ^{19}F ($^1J_{\text{CF}} = 528$ Hz) and ^{183}W ($^1J_{\text{CW}} = 274.6$ Hz) nuclei, the latter being somewhat larger than typically found for other carbyne complexes of pseudo-octahedral tungsten.^{5c} The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum comprises a single resonance ($\delta_{\text{F}} = 45.5$) straddled by a doublet due to the ^{183}W isotopomer ($^2J_{\text{WF}} = 111.1$ Hz).

With the complete series of halocarbynes now in hand, a host of physico-chemical data is available to benchmark the nature of the fluorocarbyne ligand against other halocarbynes and more conventional carbyne ligands in the complexes $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{Tp}^*)]$ (R = F, Cl, Br, I, H, $^{14}\text{CH}_3$, ^{17}Ph , $^{18}\text{C}\equiv\text{CPh}$,¹⁹ Table 1) and to validate recent predictions based on the model complexes $[\text{Mo}(\equiv\text{CX})(\text{CO})_2(\text{Tp})]$ (X = F, Cl, Br, I).¹³

Descending group 17 for the halocarbyne series, the metal centre becomes marginally more electron-poor and less π -basic (increase in ν_{CO} and k_{CO}). In the absence of **1a** it might seem that the carbyne ^{13}C resonance moves to higher frequency down group 17 showing a normal halogen dependence arising from relativistic spin-orbit coupling.²⁰ The non-conforming position of **1a** in the series therefore most likely reflects a competing inverse halogen effect arising from paramagnetic shielding due to magnetic coupling of occupied and unoccupied orbitals, *e.g.*, $\sigma^*(\text{C-F})$ and $\pi^*(\text{WC})$. The oxidation potential is remarkably insensitive to the nature of the halogen, as might be expected from computational studies on the hypothetical series $[\text{Mo}(\equiv\text{CX})(\text{CO})_2(\text{Tp})]$ that show the energy of the metal-based HOMO (orthogonal to the C-X vector) to be essentially invariant.

Whilst μ_3 -fluorocarbyne complexes are well-known^{2a,21} there are no previous examples of doubly bridging fluorocarbyne ligands. The addition of the 'AuCl' fragment to terminal carbyne complexes has on numerous occasions been shown to afford heterobimetallic μ_2 -carbynes²² including the recent isolation of bromo- and chlorocarbyne examples.¹³ Accordingly, the reaction of **1a** with $[\text{AuCl}(\text{SMe}_2)]$ was investigated and found to afford the μ_2 -fluorocarbyne complex $[\text{WAu}(\mu\text{-CF})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$

(**3**). The resonance for the fluorocarbyne carbon appears at $\delta_{\text{C}} = 236.6$, to higher frequency of the precursor and displays a reduced coupling to tungsten-183 ($^1J_{\text{CW}} = 143.8$ Hz) and fluorine-19 nuclei ($^1J_{\text{CF}} = 454$ Hz), consistent with a decrease in *s*-character for the sp^2 vs. sp carbon hybridisation and the increase in W-C bond length (1.876(6) Å). The molecular structure (Fig. 2) reveals that the fluorocarbyne ligand adopts an unsymmetrical semi-bridging mode (W1-C1-F1 = 148.7(6)°), as is commonly encountered for carbyne (and carbonyl) ligands bridging between tungsten and d^{10} metal centres. Therein, the carbyne may be viewed as a Z-type σ -acceptor ligand, *i.e.*, donation from gold(i) to a π -hole on the carbonyl ligand. Similar geometric features are reproduced upon geometry optimisation ($\omega\text{B97X-D/6-31G}^*/\text{LANL2DZ}$, see ESI†) of the model complex $[\text{WAu}(\mu\text{-CF})\text{Cl}(\text{CO})_2(\text{Tp})]$ (**3'**: W=C = 1.893 Å; Au-C = 2.042 Å, W-Au = 2.829 Å, W-C-Au = 91.8° W-C-F = 149.7°) for which Löwdin bond orders (WC = 1.80, AuC = 0.72) suggest that a dimetallacyclopropene description is useful.

The complex **3** is unstable in solution, gradually depositing elemental gold (accompanied by some reformation of **1a**) to provide a new purple species identified as the high-valent fluorocarbyne complex $[\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp}^*)]$ (**4**). Once recognised as such, complex **4** could be more expediently and directly prepared from **1a** and iodobenzene dichloride. Key spectroscopic features of note for **4** include a resonance for the carbyne carbon ($\delta_{\text{C}} = 224.9$) that is moved to higher frequency of that for **1a**, with a similar $^1J_{\text{CF}}$ coupling (512.8 Hz) but augmented $^1J_{\text{WC}}$ coupling (316 Hz). The $^2J_{\text{WF}}$ coupling (105.1 Hz) observed in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum is similar to that observed for **1a**. Taken together, these suggest retention of octahedral geometry at tungsten and *sp*-hybridisation at the carbyne carbon. Oxidative interconversion of 'Fischer' and 'Schrock' classes of carbyne is well established²³ but in this case is gratifying in that **4** represents a connection between the exotic matrix-isolated 'Schrock-type' carbynes $\text{X}_3\text{M}\equiv\text{CF}$ (X = F, Cl)¹ and tractable low-valent compounds such as **1a**, **2a** and Hughes' $[\text{M}(\equiv\text{CF})(\text{CO})_2(\eta^5\text{-C}_5\text{R}_5)]$ (M = Cr, Mo, W; R = H, Me). For simplicity, the frontier molecular orbitals of interest for the model complexes $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp})]$ (**1a'**) and $[\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp})]$ (**4'**) are shown in Fig. 3 (those for the full and sterically congested molecules **1a** and **4** are provided in the ESI† alongside those for the matrix molecules $\text{X}_3\text{W}\equiv\text{CF}$, X = F, Cl, calculated at the same level of theory). In the case of **1a**, the HOMO is primarily associated with metal carbonyl back-donation (' d_{xy} ' taking '*z*' as the W...F vector), explaining why the oxidation potentials (Table 1) are rather insensitive to changes in the carbyne substituent. The HOMO - 1 and HOMO - 2 comprise the two orthogonal π -components of the $\text{W}\equiv\text{C}$ multiple bond for **1a'**. For **4'**, the manifold of frontier orbitals is rather similar with the notable exception that the ' d_{xy} ' orbital is now vacant and available for nucleophilic attack. This leaves the near degenerate pair of WC π -bonding orbitals as the highest in energy, as is also the case for the Schrock-type molecules $\text{X}_3\text{W}\equiv\text{CF}$. Notably, for **1a'**, while the LUMO has both metal and carbyne-carbon character, the real complex **1a** is not especially susceptible to hydrolysis (*cf.* difluorocarbene complexes), easily surviving chromatographic purification without any identifiable formation of the

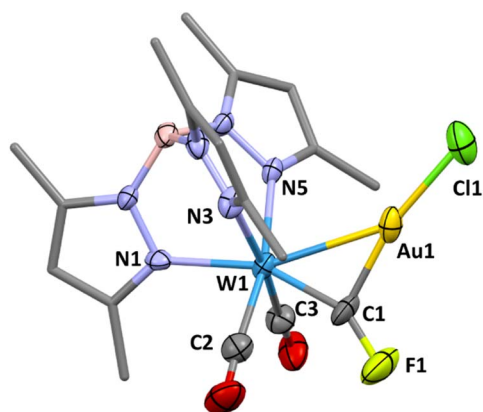


Fig. 2 Molecular structure of $[\text{WAu}(\mu\text{-CF})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (**3**) in a crystal (50% displacement ellipsoids, pyrazolyl groups simplified). Selected bond lengths (Å) and angles (°): Au1-W1 2.7974(4), Au1-Cl1 2.268(2), Au1-C1 2.007(8), W1-C1 1.876(6), F1-C1 1.318(7), Cl1-Au1-W1 150.49(6), C1-Au1-W1 42.08(18), C1-Au1-Cl1 167.42(19), W1-C1-Au1 92.1(3), F1-C1-Au1 119.2(5), F1-C1-W1 148.7(6).



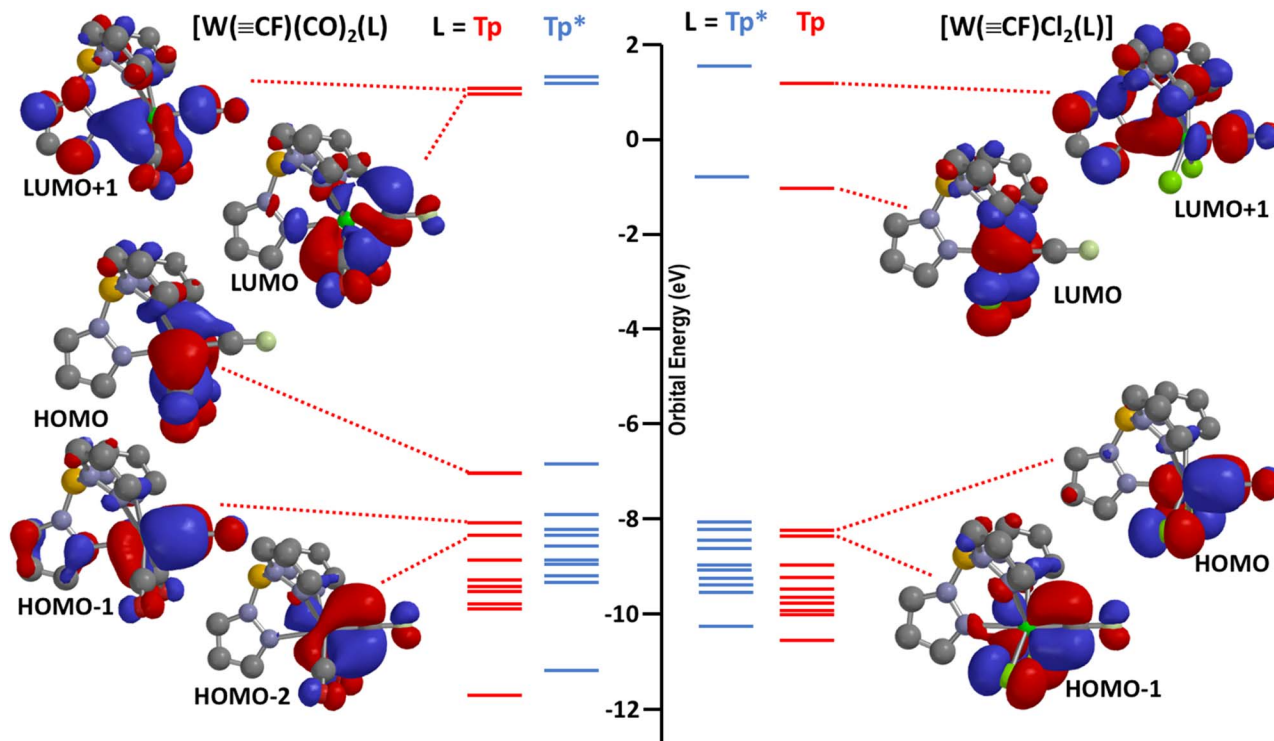


Fig. 3 Frontier orbitals (ω B97X-D/6-31G*/LANL2DZ/gas phase) of interest for the complexes $[W(\equiv CF)(CO)_2(L)]$ and $[W(\equiv CF)Cl_2(L)]$ ($L = Tp$, red, Tp^* blue).

anticipated hydrolysis product $[WH(CO)_3(Tp^*)]$. The situation for the high-valent **4'** is intriguing in that, by analogy with chloro- and bromo-carbynes, nucleophilic substitution of the fluoride would seem plausible. Furthermore, oxidation state has been shown to profoundly enhance the susceptibility of difluorocarbene ligands towards nucleophilic attack, as demonstrated for the zero- and divalent ruthenium complexes $[Ru^0(=CF_2)(CO)_2(PPh_3)_2]$ ²⁴ *cf.* $[Ru^{II}Cl_2(=CF_2)(CO)(PPh_3)_2]$, respectively.²⁵ High-valent Schrock-type carbyne complexes of the form $[W(\equiv CR)_X_2(Tp')]$ ($X = Cl, Br; Tp' = Tp, Tp^*$)^{23c,26} are generally prone to hydrolysis *via* nucleophilic attack (H_2O/HO^-) at the metal to provide $[W(=CHR)Cl(=O)(Tp')]$. It is therefore noteworthy and somewhat surprising that complex **4** is comparatively robust, air stable and not readily hydrolysed.

In conclusion, electrophilic fluorination of carbido ligands provides a viable route to fluorocarbyne complexes, building upon previous examples of the iodination of terminal carbido ligands^{14,27} and the chlorination or bromination of bridging μ_2 -carbido complexes.²⁸ The 'Fischer-type' fluorocarbyne $[W(\equiv CF)(CO)_2(Tp^*)]$ may be oxidised to a rare example^{23d} of a high oxidation state halocarbyne $[W(\equiv CF)Cl_2(Tp^*)]$ that is best viewed as a 'Schrock-type' carbyne.

Experimental

General experimental details and instrumentation, synthetic methods, spectroscopic data, selected spectra, Cartesian coordinates and computational details are provided in the accompanying ESI.†

Data availability

The datasets supporting this article have been uploaded as part of the ESI.† Crystallographic data have been deposited at the CCDC under 2226627 and 2226628 and can be obtained from <http://ccdc.cam.ac.uk>.

Author contributions

RAM was responsible for the design and execution of the experimental research, the acquisition and critical analysis of the characterising data. AFH was responsible for funding acquisition, project conceptualisation and administration, validation and compilation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 Though not isolable, infrared spectroscopic evidence has been presented for the generation *inter alia* of complexes of the form $F_3M\equiv CF$ ($M = Cr, Mo, W$) in argon matrices:



- (a) J. T. Lyon and L. Andrews, *Inorg. Chem.*, 2006, **45**, 9858–9863; (b) J. T. Lyon, H.-G. Cho and L. Andrews, *Organometallics*, 2007, **26**, 6373–6387; (c) H.-G. Cho and L. Andrews, *Organometallics*, 2010, **29**, 2211–2222.
- 2 (a) H. Huang, R. P. Hughes, C. R. Landis and A. L. Rheingold, *J. Am. Chem. Soc.*, 2006, **128**, 7454–7455; (b) H. Huang, R. P. Hughes and A. L. Rheingold, *Dalton Trans.*, 2011, **40**, 47–55.
- 3 C. J. Pell, Y. Zhu, R. Huacuja, D. E. Herbert, R. P. Hughes and O. V. Ozerov, *Chem. Sci.*, 2017, **8**, 3178–3186.
- 4 (a) D. L. Reger and M. D. Dukes, *J. Organomet. Chem.*, 1978, **153**, 67–72; (b) G. R. Clark, S. V. Hoskins and W. R. Roper, *J. Organomet. Chem.*, 1982, **234**, C9–C12; (c) A. M. Crespi and D. F. Shriver, *Organometallics*, 1985, **4**, 1830–1835; (d) S. Anderson, A. F. Hill, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 266–267; (e) R. P. Hughes, R. B. Laritchev, J. Yuan, J. A. Golen, A. N. Rucker and A. L. Rheingold, *J. Am. Chem. Soc.*, 2005, **127**, 15020–15021; (f) P. J. Brothers and W. R. Roper, *Chem. Rev.*, 1988, **88**, 1293–1326; (g) D. J. Harrison, A. L. Daniels, I. Korobkov and R. T. Baker, *Organometallics*, 2015, **34**(24), 5683–5686.
- 5 (a) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 457–459; (b) F. J. Lalor, T. J. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez and B. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1995, 1709–1726; (c) L. M. Caldwell, *Adv. Organomet. Chem.*, 2008, **56**, 1–94.
- 6 (a) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75–77; (b) S. Chaona, F. J. Lalor, G. Ferguson and M. M. Hunt, *J. Chem. Soc., Chem. Commun.*, 1988, 1606–1608; (c) F. J. Lalor and S. A. O'Neill, *J. Organomet. Chem.*, 2003, **684**, 249–265.
- 7 (a) M. Etienne, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1991, **113**, 2324–2325; (b) G. M. Jamison, P. S. White and J. L. Templeton, *Organometallics*, 1991, **10**, 1954–1959; (c) B. E. Woodworth and J. L. Templeton, *J. Am. Chem. Soc.*, 1996, **118**, 7418–7419; (d) B. E. Woodworth, D. S. Frohnepfel, P. S. White and J. L. Templeton, *Organometallics*, 1998, **17**, 1655–1662; (e) K. C. Stone, P. S. White and J. L. Templeton, *J. Organomet. Chem.*, 2003, **684**, 13–19; (f) K. C. Stone, G. M. Jamison, P. S. White and J. L. Templeton, *Organometallics*, 2003, **22**, 3083–3095; (g) K. C. Stone, G. M. Jamison, P. S. White and J. L. Templeton, *Inorg. Chim. Acta*, 2002, **330**, 161–172; (h) A. E. Enriquez and J. L. Templeton, *Organometallics*, 2002, **21**, 852–863.
- 8 (a) L. Weber, I. Schumann, T. Schmidt, H.-G. Stammler and B. Neumann, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1759–1764; (b) L. Weber, I. Schumann, H.-G. Stammler and B. Neumann, *Chem. Ber.*, 1994, **127**, 1349–1353; (c) L. Weber, I. Schumann, M. H. Scheffer, H.-G. Stammler and B. Neumann, *Z. Naturforsch., B: J. Chem. Sci.*, 1997, **52**, 655–662; (d) L. Weber, G. Dembeck, R. Boese and D. Bläser, *Chem. Ber.*, 1997, **130**, 1305–1308; (e) L. Weber, G. Dembeck, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 1998, 579–582; (f) L. Weber, G. Dembeck, H.-G. Stammler, B. Neumann, M. Schmidtman and A. Müller, *Organometallics*, 1998, **17**, 5254–5259; (g) L. Weber, G. Dembeck, P. Lönneke, H.-G. Stammler and B. Neumann, *Organometallics*, 2001, **20**, 2288–2293; (h) L. Weber, G. Dembeck, R. Boese and D. Bläser, *Organometallics*, 1999, **18**, 4603–4607.
- 9 (a) B. J. Frogley, A. F. Hill and C. S. Onn, *Dalton Trans.*, 2019, **48**, 11715–11723; (b) B. J. Frogley, T. L. Genet, A. F. Hill, C. S. Onn and S. Chee, *Dalton Trans.*, 2019, **48**, 7632–7643; (c) L. M. Caldwell, A. F. Hill, A. D. Rae and A. C. Willis, *Organometallics*, 2009, **27**, 341–345.
- 10 (a) M. I. Bruce, M. L. Cole, M. Gaudio, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2006, **691**, 4601–4614; (b) R. L. Cordiner, P. A. Gugger, A. F. Hill and A. C. Willis, *Organometallics*, 2009, **28**, 6632–6635; (c) R. A. Manzano and A. F. Hill, *Dalton Trans.*, 2019, **48**, 6596–6610; (d) L. K. Burt, R. L. Cordiner, A. F. Hill, R. A. Manzano and J. Wagler, *Chem. Commun.*, 2020, **56**, 5673–5676; (e) A. L. Colebatch and A. F. Hill, *J. Am. Chem. Soc.*, 2014, **136**, 17442–17445; (f) B. J. Frogley and A. F. Hill, *Chem.–Eur. J.*, 2020, **26**, 12125–12128; (g) A. F. Hill and R. A. Manzano, *Angew. Chem., Int. Ed.*, 2019, **58**, 15354–15357; (h) A. F. Hill and R. A. Manzano, *Angew. Chem., Int. Ed.*, 2019, **58**, 7357–7360.
- 11 L. K. Burt and A. F. Hill, *Dalton Trans.*, 2020, **49**, 8143–8161.
- 12 (a) R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 5177–5179; (b) B. J. Frogley, A. F. Hill, R. Shang, M. Sharma and A. C. Willis, *Chem.–Eur. J.*, 2020, **26**, 8819–8827; (c) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 2126–2129; (d) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2019, **55**, 12400–12403; (e) A. L. Colebatch, B. J. Frogley, A. F. Hill and C. S. Onn, *Chem.–Eur. J.*, 2021, **27**, 5322–5343; (f) B. J. Frogley, A. F. Hill and L. J. Watson, *Chem.–Eur. J.*, 2020, **26**, 12706–12716.
- 13 (a) L. K. Burt and A. F. Hill, *Dalton Trans.*, 2022, **51**, 12080–12099. For further computational studies of fluorocarbyne complexes see ref. 1 and 2 and ; (b) X. Gong, X. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, *Dalton Trans.*, 2010, **39**, 5242–5253; (c) X.-M. Liu, C.-Y. Wang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, *Chem.–Eur. J.*, 2009, **15**, 5520–5530.
- 14 A. E. Enriquez, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 2001, **123**, 4992–5002.
- 15 Selected applications of FN(SO₂Ph)₂ in organometallic contexts: (a) L. M. Hall, D. P. Tew, N. E. Pridmore, A. C. Whitwood, J. M. Lynam and J. M. Slattery, *Angew. Chem., Int. Ed.*, 2017, **56**, 7551–7556; (b) K. Sünkel, S. Weigand, A. Hoffmann, S. Blomeyer, C. G. Reuter, Y. V. Vishnevskiy and N. W. Mitzel, *J. Am. Chem. Soc.*, 2015, **137**, 126–129; (c) G. E. Herberich, U. Englert and T. Wirth, *Eur. J. Inorg. Chem.*, 2005, 4924–4935.
- 16 (a) M. B. Hursthouse, B. Piggott and M. Harman, *CSD Communication*, CCDC 216027, ASIFUD, 2003; (b) C. C. Philipp, P. S. White and J. L. Templeton, *Inorg. Chem.*, 1992, **31**, 3825–3830.
- 17 D. S. Frohnepfel, B. E. Woodward, H. H. Thorp and J. L. Templeton, *J. Phys. Chem. A*, 1998, **102**, 5665–5669.



- 18 K. C. Stone, G. M. Jamison, P. S. White and J. L. Templeton, *Inorg. Chim. Acta*, 2002, **330**, 161–172.
- 19 (a) B. Schwenzler, J. Schleu, N. Burzlaff, C. Karl and H. Fischer, *J. Organomet. Chem.*, 2002, **641**, 134–141; (b) A. F. Hill and R. A. Manzano, *Adv. Organomet. Chem.*, 2019, **72**, 103–171.
- 20 (a) J. Autschbach, in *High Resolution Nuclear Magnetic Resonance Parameters for Understanding Molecules and their Electronic Structure, Vol. 3 of Science & Technology of Atomic, Molecular, Condensed Matter & Biological Systems*, ed. R. H. Contreras, Elsevier, Amsterdam, 2013, pp. 69–117; (b) R. V. Viesser, L. C. Ducati, C. F. Tormena and J. Autschbach, *Phys. Chem. Chem. Phys.*, 2018, **20**, 11247–11259.
- 21 (a) D. Lentz, I. Brudgam and H. Hartl, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 119–120; (b) W. Schulze, H. Hartl and K. Seppelt, *J. Organomet. Chem.*, 1987, **319**, 77–85; (c) D. Lentz and H. Michael, *Chem. Ber.*, 1988, **121**, 1413–1416; (d) R. Vilar, S. E. Lawrence, D. M. P. Mingos and D. J. Williams, *Chem. Commun.*, 1997, 285–286; (e) D. Lentz and H. Michael-Schulz, *Inorg. Chem.*, 1990, **29**, 4396–4401.
- 22 (a) G. R. Clark, C. M. Cochrane, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1980, **199**, C35–C38; (b) G. A. Carriedo, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597–1603; (c) G. A. Carriedo, V. Riera, G. Sánchez and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1988, 1957–1962; (d) C. E. Strasser, S. Cronje and H. G. Raubenheimer, *New J. Chem.*, 2010, **34**, 458–469; (e) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, 2017, **46**, 4355–4365; (f) B. J. Frogley, A. F. Hill and C. S. Onn, *Dalton Trans.*, 2019, **48**, 11715–11723; (g) B. J. Frogley, A. F. Hill and L. J. Watson, *Chem. Commun.*, 2019, **55**, 14450–14453; (h) B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2020, **49**, 12390–12400; (i) X. Zhou, Y. Li, Y. Shao, Y. Hua, H. Zhang, Y.-M. Lin and H. Xia, *Organometallics*, 2018, **37**, 1788–1794.
- 23 (a) A. Mayr and G. A. McDermott, *J. Am. Chem. Soc.*, 1986, **108**, 548–549; (b) A. C. Filippou, C. Wagner, E. O. Fischer and C. Vliikl, *J. Organomet. Chem.*, 1992, **438**, C15–C22; (c) S. Anderson, D. J. Cook, A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, *Organometallics*, 2004, **23**, 2552–2557; (d) A. F. Hill and R. Y. Kong, *Chem. Commun.*, 2017, **53**, 759–762.
- 24 G. R. Clark, S. V. Hoskins, T. C. Jones and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1983, 719–721.
- 25 G. R. Clark, S. V. Hoskins and W. R. Roper, *J. Organomet. Chem.*, 1982, **234**, C9–C12.
- 26 (a) A. R. Delaney, B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2019, **48**, 13674–13684; (b) A. C. Filippou, P. Hofmann, P. Kiprof, H. R. Schmidt and C. Wagner, *J. Organomet. Chem.*, 1993, **459**, 233–247; (c) J. C. Jeffery, J. A. McCleverty, M. D. Mortimer and M. D. Ward, *Polyhedron*, 1994, **13**, 353–356; (d) S. Ahn and A. Mayr, *J. Am. Chem. Soc.*, 1996, **118**, 7408–7409.
- 27 A. Reinholdt, T. Vosch, A. Jos and J. Bendix, *Angew. Chem., Int. Ed.*, 2016, **55**, 12484–12487.
- 28 (a) H. J. Barnett and A. F. Hill, *Chem. Commun.*, 2020, **56**, 7738–7740; (b) H. J. Barnett and A. F. Hill, *Chem. Commun.*, 2019, **55**, 1734–1737.

